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VISCOSITY OF ELECTROLYTES AND RELATED PROPERTIES

BY R. H. STOKES AND R. MILLS

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INTRODUCTION

THE International Encyclopedia of Physical Chemistry and Chemical Physics is a comprehensive and modern account of all aspects of the domain of science between chemistry and physics, and is written primarily for the graduate and research worker. The Editors-in-Chief, Professor E. A. GUGGENHEIM, Professor J. E. MAYER and Professor F. C. TOMPKINS, have grouped the subject matter in some twenty groups (General Topics), each having its own editor. The complete work consists of about one hundred volumes, each volume being restricted to around two hundred pages and having a large measure of independence. Particular importance has been given to the exposition of the fundamental bases of each topic and to the development of the theoretical aspects; experimental details of an essentially practical nature are not emphasized although the theoretical background of techniques and procedures is fully developed.

The Encyclopedia is written throughout in English and the recommendations of the International Union of Pure and Applied Chemistry on notation and cognate matters in physical chemistry are adopted. Abbreviations for names of journals are in accordance with *The World List of Scientific Periodicals.*

CONTENTS

CHAPTER 1

HYDRODYNAMICS OF VISCOUS LIQUIDS

HYDRODYNAMICS, the study of fluids in motion, is an important branch of applied mathematics with applications in innumerable fields from water-supply to cosmology. The main early development of the subject took place in the eighteenth century, and is particularly associated with the names of Daniel Bernoulli, d'Alembert, Euler and Lagrange. These workers dealt with the so-called perfect fluids, those showing no internal friction or viscosity. Such fluids are characterized by the property that the stress across any element of surface in the fluid is wholly normal to that surface; there is no tangential component of stress. From this property it follows that the only way in which the fluid can gain or lose energy other than kinetic energy is by compression or expansion; a shearing motion in which one portion of liquid moves tangentially with respect to an adjacent portion is unopposed. Though such fluids may seem to a physical chemist a mathematical abstraction of little practical interest, the theory of their motions is actually of great value; in aerodynamics, for example, it is found that except for a relatively thin boundary-layer near a moving solid surface, the air can be treated as an inviscid fluid.

Already in the seventeenth century the genius of Newton had dealt with some problems of motion in a resisting medium, in the second book of the *Principia*. A liquid in which the viscosity is independent of the rate of shear (i.e. the frictional resistance is directly proportional to the velocity of the shearing motion) is fittingly known today as a Newtonian liquid. The main development of the theory of viscous fluids, however, was made in the nineteenth century, chiefly by Navier and Stokes.

The new feature of the theory, when viscosity is considered, is the introduction of tangential stresses across every element of surface. In Newtonian fluids, the component stresses are proportional to the corresponding velocity-gradients, and the constant of proportionality is called the *viscosity* of the fluid. It is impracticable to develop the theory in a short volume, and the interested reader is referred to the standard treatises of Lamb[1] and of Milne-Thomson.[2] Here we can do no more than give the fundamental equations of the hydrodynamics of viscous fluids and state without proof the results which are of importance in the theory of electrolyte solutions.

The motion of the fluid at the point $P(x, y, z)$ is characterized by a velocity vector $\mathbf{q}$ having components u, v, w in the directions of x, y and z respectively. The fluid at this point is also subject to an external force $\mathbf{F}$ per unit mass, with components X, Y, Z; its density is ρ, the pressure is p, and its viscosity is η. We assume that η and ρ are constants, i.e. that the viscosity is independent of the direction and rate of shear, and that the fluid is incompressible. The latter assumption is justifiable in all applications with which we shall be concerned; the former applies only to Newtonian liquids and may fail for solutions of long-chain molecules or ions such as polyelectrolytes. In these, the molecules tend to line up along the direction of shear, to an extent which increases as the rate of shear increases, and the formulae given below will apply only at infinitesimally small rates of shear.

Incompressible fluids satisfy the equation

$$\operatorname{div} \mathbf{q} \equiv \nabla \cdot \mathbf{q} \equiv \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0. \tag{1.1}$$

Subject to this simplification, the differential equations of motion of a viscous liquid may be written:

$$\rho\left(\frac{\partial \mathbf{q}}{\partial t} + \mathbf{q} \cdot \nabla \mathbf{q}\right) = \rho \mathbf{F} - \nabla p + \eta \nabla^2 \mathbf{q} \tag{1.2}$$

where $\mathbf{q} \cdot \nabla \mathbf{q}$ and $\nabla^2 \mathbf{q}$ are dyadic products and ∇p denotes the gradient of the pressure. In terms of the Cartesian components (2) becomes

$$\rho\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z}\right) = \rho X - \frac{\partial p}{\partial x} + \eta \nabla^2 u \tag{1.3a}$$

$$\rho\left(\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} + w\frac{\partial v}{\partial z}\right) = \rho Y - \frac{\partial p}{\partial y} + \eta \nabla^2 v \tag{1.3b}$$

$$\rho\left(\frac{\partial w}{\partial t} + u\frac{\partial w}{\partial x} + v\frac{\partial w}{\partial y} + w\frac{\partial w}{\partial z}\right) = \rho Z - \frac{\partial p}{\partial z} + \eta \nabla^2 w \tag{1.3c}$$

where $\nabla^2 u = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}$.

These are the Navier–Stokes equations for an incompressible viscous fluid. By virtue of the terms $u(\partial u/\partial x)$, etc., on the left they are non-linear in the velocities, and hence few exact solutions exist. For sufficiently low velocities, these quadratic terms can be ignored, but this statement requires a definition of the term "sufficiently low" to make it meaningful. The relative importance of the quadratic terms can be estimated for particular cases by considering the *Reynolds number*

$$\mathrm{Re} = ua\rho/\eta \tag{1.4}$$

where u is a velocity of the order of those occurring in the problem, and a is a typical linear dimension which is relevant, such as the diameter of a tube through which liquid flows, or the radius of a sphere moving in a liquid. The Reynolds number is a dimensionless quantity, since viscosity has dimensions $\mathrm{ML^{-1}\,T^{-1}}$. As a rough approximation we may take it that the quadratic terms are negligible when the Reynolds number does not exceed 1000.

Particular interest for our purposes centres on the value of the Reynolds number for the motion of an ion in typical conductance or diffusion processes. Under a gradient of 1 volt $\mathrm{cm^{-1}}$, an ion of equivalent conductivity 100 $\mathrm{cm^2\,ohm^{-1}\,equiv^{-1}}$ moves with a velocity $u_0 \approx 10^{-3}\ \mathrm{cm\ s^{-1}}$. Its radius is a few Ångstroms, and the viscosity of most solvents is a few hundredths of a poise. Hence $\mathrm{Re} \approx 10^{-9}$ so that we need have no qualms about ignoring the quadratic terms in the velocity. Whether we can justifiably apply the equations for a hydrodynamic continuum to phenomena at the molecular level is of course another matter.

In problems of steady flow, where $\partial \mathbf{q}/\partial t = 0$, the general equations for an incompressible liquid at small Reynolds numbers become:

$$\rho X = \frac{\partial p}{\partial x} - \eta\nabla^2 u \tag{1.5a}$$

$$\rho Y = \frac{\partial p}{\partial y} - \eta\nabla^2 v \tag{1.5b}$$

$$\rho Z = \frac{\partial p}{\partial z} - \eta\nabla^2 w, \tag{1.5c}$$

and in the absence of external forces, simply:

$$\frac{\partial p}{\partial x} = \eta \nabla^2 u \tag{1.6a}$$

$$\frac{\partial p}{\partial y} = \eta \nabla^2 v \tag{1.6b}$$

$$\frac{\partial p}{\partial z} = \eta \nabla^2 w. \tag{1.6c}$$

These differential equations must of course be supplemented by appropriate boundary-conditions to give solutions to particular problems. In nearly all cases, the chief boundary condition is taken to be that the velocity vanishes at any fixed solid surface. This is obviously true for the normal component of the velocity (unless the surface leaks), but the assumption that there is no tangential component of velocity relative to any solid surface is peculiar to the theory of viscous liquids: it is usually called the hypothesis of no slip. It appears to be fully justified by experiment in all macroscopic problems: even coating the surface of a capillary tube with a water-repellent silicone film makes no difference to the flow-rate. It is however possible that "slip" may occur at the surface of a simple spherical ion, if again we can validly think of an ion in hydrodynamic terms. Another common boundary-condition is that the velocity should vanish at infinite distance from a given disturbance in a liquid otherwise at rest.

In the remainder of this chapter we give, without proof, a number of solutions of the equations of motion of viscous fluids for cases which are of importance for the theory of electrolyte solutions and finally a formal definition of terms.

(*a*) Laminar flow through a circular cylindrical tube under pressure

$$\frac{V}{t} = \frac{\pi(p_0 - p_1)R^4}{8\eta l} \tag{1.7}$$

$$v = \frac{(p_0 - p_1)(R^2 - r^2)}{4\eta l} \tag{1.8}$$

where: p_0, p_1 are the pressures at the two ends of the tube,
l is the length of the tube,
r is the radial distance from the axis,

R is the radius of the tube,
v is the velocity of the liquid at distance r from the axis,
V is the volume flowing through the tube in time t,
η is the viscosity.

Equation (7), due to Poiseuille[3] and Hagenbach[4], is the fundamental equation of the capillary-tube type of viscometer (see Chapter 2). Equation (8) shows that the velocity-profile is parabolic, the velocity being zero at the walls and a maximum in the centre.

(*b*) For a tube of elliptical cross-section with semi-axes a, b

$$\frac{V}{t} = \frac{\pi(p_0 - p_1)a^3b^3}{4\eta l(a^2 + b^2)} \tag{1.9}$$

$$v = \frac{p_0 - p_1}{2\eta l}\,\frac{a^2b^2}{a^2 + b^2}\left(1 - \frac{x^2}{a^2} - \frac{y^2}{b^2}\right) \tag{1.10}$$

where v is the velocity at a point given by (x, y) in Cartesian axes based on the axis as origin, with the x and y axes coinciding with the major and minor axes of the ellipse, and other symbols are as in (*a*) above.

(*c*) For a liquid between two coaxial cylinders, one rotating and the other fixed, provided the flow-lines are all circular:

$$T = 4\pi\eta\,\frac{R_1^2R_2^2}{R_1^2 - R_2^2}\,\omega_0 \tag{1.11}$$

where: R_1 and R_2 are the radii of the inner and outer cylinders
ω_0 is the angular velocity of the moving cylinder
T is the couple exerted on the fixed cylinder, per unit length measured along the axis, by the viscous drag of the moving liquid.

The angular velocity of the liquid at distance r from the axis, if R_1 refers to the stationary cylinder is[1]

$$\omega = \omega_0(R_1^2 - R_2^2)\left(\frac{1}{r^2} - \frac{1}{R_1^2}\right). \tag{1.12}$$

(*d*) For a sphere moving at low Reynolds numbers through a liquid, if the liquid does not slip at the surface of the sphere, the force due to the viscous resistance is[5]

$$F = 6\pi\eta a v \tag{1.13}$$

where: v is the velocity
a is the radius of the sphere.

If the liquid can slip at the surface of the sphere, with a coefficient of friction β, the force becomes

$$F = 6\pi\eta a v \frac{2\eta + \beta a}{3\eta + \beta a}, \tag{1.14}$$

so that for frictionless slip at the surface the force is[1]

$$F = 4\pi\eta a v. \tag{1.15}$$

(*e*) For an ellipsoid of semi-axes a, b, c under conditions of no slip at the surface, moving with velocity v parallel to the semi-axis a, the force is[1]

$$F = 6\pi\eta R v \tag{1.16}$$

where

$$R = \frac{8}{3}\frac{abc}{\chi_0 + \alpha_0 a^2} \tag{1.17}$$

and

$$\chi_0 = abc\int_0^\infty \frac{\partial\lambda}{[(a^2+\lambda)(b^2+\lambda)(c^2+\lambda)]^{\frac{1}{2}}} \tag{1.18}$$

$$\alpha_0 = abc\int_0^\infty \frac{\partial\lambda}{(a^2+\lambda)[(a^2+\lambda)(b^2+\lambda)(c^2+\lambda)]^{\frac{1}{2}}}. \tag{1.19}$$

(*f*) For an ellipsoid of revolution, with semi-axes a, b, moving with random orientation to its direction of motion, the mean frictional resistance is that of a sphere of the same volume, multiplied by the factor f/f_0 given by [6,7]

$$\frac{f}{f_0} = \frac{\sqrt{1 - \dfrac{a^2}{b^2}}}{\left(\dfrac{a}{b}\right)^{2/3} \ln \dfrac{1 + \sqrt{1 - a^2/b^2}}{a/b}} \tag{1.20}$$

where a denotes the minor and b the major semi-axis.

(*g*) For an ellipsoid of revolution, where $2a$ denotes the axis of revolution, and $2b$ the equatorial axis, the frictional force for motion with velocity v parallel to the axis of revolution is:[8]

$$F = 8\pi\eta bv \left[1 + \frac{\alpha^2}{\alpha^2 - 1}\frac{\cosh^{-1}\alpha}{\sqrt{\alpha^2 - 1}} - \frac{\alpha}{\alpha^2 - 1}\right]^{-1} \text{if } a > b \quad (1.21)$$

where $\alpha = \dfrac{a}{b}$, or

$$F = 8\pi\eta bv \left[1 + \frac{\alpha^2}{\alpha^2 - 1}\frac{\tan^{-1}\dfrac{\sqrt{1-\alpha^2}}{\alpha}}{\sqrt{1-\alpha^2}} - \frac{\alpha}{\alpha^2 - 1}\right] \text{if } a < b. \quad (1.22)$$

(*h*) The average viscosity of a dilute suspension of rigid spherical particles, randomly distributed, is[9]

$$\eta/\eta^{\circ} = 1 + 2{\cdot}5\phi \quad (1.23)$$

where: η is the average viscosity of the suspension
η^0 is viscosity of the liquid in the absence of the spheres
ϕ is the fraction of the total volume occupied by the spheres.

Definitions

Absolute Viscosity

The absolute viscosity has in effect been defined on page 2 and this definition used in the derivation of the Navier–Stokes equations (2) and (3). For clarity we now define it and associated quantities in a more formal manner.

For laminar flow in a Newtonian fluid, the absolute viscosity can be defined simply as the force per unit area required to maintain unit difference in velocity between two parallel layers of the fluid which are unit distance apart. It may be written

$$\eta = \frac{\tau}{\dfrac{\partial u}{\partial y}}, \quad (1.24a)$$

or

$$\tau = \eta \frac{\partial u}{\partial y}, \quad (1.24b)$$

where η is the absolute viscosity, τ is the force per unit area or shear stress and $\partial u/\partial y$ is the velocity gradient normal to the planes of flow. Because η appears as a proportionality factor between the shear stress and velocity gradient, it is usually termed the coefficient of viscosity.

From (24*a*) it will be seen that the dimensions of absolute viscosity are $ML^{-1}T^{-1}$ which in c.g.s. units will be g cm^{-1} s^{-1}. To recognize Poiseuille's pioneer contributions to experimental viscometry the corresponding unit is termed the poise. Thus a poise (P) is equivalent to 1 g cm^{-1} s^{-1}. In practice the centipoise (cP) = 0·01 P is commonly used, the absolute viscosity of water at 20°C being approximately 1 cP.

Kinematic Viscosity

Kinematic viscosity is defined as the ratio of absolute viscosity to density

$$\nu = \frac{\eta}{\rho} \tag{1.25}$$

where ν is the kinematic viscosity. The dimensions in this case are L^2T^{-1} which in c.g.s. units is $cm^2 s^{-1}$. The unit 1 $cm^2 s^{-1}$ is called the stokes but 0·01 stokes or the centistokes is the common practical unit.

Relative Viscosity

The relative viscosity is the ratio of the viscosity of a solution to that of the pure solvent under the same conditions.

$$\eta_{\mathrm{rel}} = \eta/\eta^0. \tag{1.26}$$

Specific Viscosity

The specific viscosity is the ratio of the difference between the solution and solvent viscosities to the solvent viscosity.

$$\eta_{\mathrm{sp}} = \frac{\eta - \eta^0}{\eta^0} = \eta_{\mathrm{rel}} - 1. \tag{1.27}$$

Fluidity

The fluidity, ϕ, is defined as the reciprocal of the absolute viscosity.

$$\phi = 1/\eta. \tag{1.28}$$

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

THE measurement of such properties as conductance and transport numbers in electrolytes involves techniques which are specifically associated with these systems, but in the case of viscosity this is not so. Viscometry has been extensively studied and developed for all types of liquids with perhaps the greatest emphasis on petroleum hydrocarbons. It is obviously not within the scope of this book to present a full review of all techniques. It is proposed instead to describe two viscometers which seem to be best adapted for electrolyte studies, and this description will be preceded by an account of the principles governing their use.

Almost invariably, viscometers used for measurements on liquid electrolytes have been of the capillary type. Measurements with these viscometers depend for their interpretation on a relationship between the rate of flow of liquids under an applied pressure and the dimensions of the capillary tubes through which they are forced. Such a relationship arose from the work of Poiseuille[1] and Hagenbach[2] and has been formulated in Chapter 1 as

$$\frac{V}{t} = \frac{\pi(p_0 - p_1)R^4}{8\eta l} \tag{1.7}$$

or

$$\eta = \frac{\pi R^4(p_0 - p_1)t}{8Vl} \tag{2.1}$$

where V is the volume of liquid flowing through the tube in time t, p_0, p_1 are the pressures at the two ends, R is its radius and l its length.

The derivation of (1), which is known as Poiseuille's Law, assumes adherence to the following conditions[3] during flow through the capillary:

(*a*) The flow is everywhere parallel to the axis of the tube.

(*b*) The flow is steady, initial disturbances due to accelerations from rest having been damped out.

(*c*) There is no slip at the walls of the tube.

(*d*) The fluid is incompressible.

(*e*) The fluid will flow when subjected to the smallest shearing force, the viscous resistance being proportional to the velocity gradient.

These requirements influence the design of capillary viscometers and departures from them necessitate the introduction of correction factors.

Condition (*a*) implies that the flow through the capillary must be laminar. In the flow of liquids through uniform tubes, turbulence is expected to arise when the Reynolds number exceeds about 2000. Capillary viscometers are therefore designed to operate well below this region, normally in a range where the Reynolds number is less than 300.

Condition (*b*) cannot be realized in those portions of the capillary adjacent to its entrance and exit and therefore leads to the necessity for important end corrections. The most significant of these is the kinetic energy or Hagenbach correction. The effect arises when the applied pressure is not solely dissipated by viscous forces, some being used to accelerate the liquid in the entrance reservoir from rest to the velocity distribution characteristic of the liquid when obeying Poiseuille's Law. The correction can therefore be expressed as a decrement in the pressure. Except at very low rates of flow, when there may be a compensating effect at the exit of the capillary, this extra kinetic energy is dissipated as heat in the exit reservoir. The correction is therefore dependent on the flow rate and becomes negligible at very low values. Its calculation is given in detail by Barr[3] and leads to the expression:

$$p^{\text{eff}} = (p_0 - p_1) - \frac{m\rho V^2}{\pi^2 R^4 t^2} \tag{2.2}$$

where p^{eff} is the pressure actually used in overcoming viscous forces, ρ is the density, and m is a numerical coefficient (≈ 1) introduced to take account of the particular shape of the capillary ends.

It is evident from (*b*) that p^{eff} is the pressure that should be used in (1) and substitution gives

$$\eta = \frac{\pi R^4 (p_0 - p_1) t}{8Vl} - \frac{m\rho V}{8\pi l t}. \tag{2.3}$$

The last term in (3) is referred to as the "kinetic energy term". The correction will be further discussed in relation to the viscometers described below.

A lesser correction related to Condition (*a*), known as the 'Couette correction', is usually included in the basic capillary equation (3). It relates to the viscous energy used in the formation of streamlines at entrance and exit and is expressed as an increase λ in the effective length of the capillary. (3) can thereby be modified to

$$\eta = \frac{\pi R^4(p_0 - p_1)t}{8V(l + \lambda)} - \frac{m\rho V}{8\pi(l + \lambda)t}. \tag{2.4}$$

Capillary viscometers can be broadly grouped as under:

(*A*) Viscometers for absolute viscosity measurements.

(*B*) Viscometers for relative viscosity measurements
  (i) Applied pressure viscometers
  (ii) Kinematic viscometers.

The instruments in section (*A*) are normally only used for the establishment of primary standards and require very accurate control of applied pressure as well as precise knowledge of the capillary dimensions.

Type (*B*) viscometers are those in which measurements are made relative to a primary standard liquid (obtained with Type (*A*)) or to derived secondary standards. Variable pressure instruments under subsection *B*(i) typified by the Bingham viscometer use an externally applied pressure to force standard and test liquids through their capillaries. The second class, *B*(ii), as exemplified by the Ostwald viscometer, utilizes the head of the liquid itself to furnish the pressure differential across the capillary. The inherent simplicity of these latter kinematic viscometers accounts for their almost universal use in electrolyte studies.

Two kinematic instruments which have been used for precise measurements in electrolytes are shown in Figs. 1 and 2. Both types claim descent from the simple Ostwald viscometer. The basic operation in these instruments is to load the bulbs above the capillary with the test liquid and then allow flow through the capillary to proceed whilst accurately measuring the period of the passage of the meniscus between the two etched marks. The Ubbelohde viscometer described here[4] differs from the Cannon–Fenske[5] viscometer in the provision of a suspended level at the junction of the capillary and bulb *C*. This feature, which is obtained by opening tap 2 to the atmosphere, ensures that the liquid issuing from the capillary adheres as a film to the walls of bulb *C*. It is claimed that this device eliminates loading and surface tension errors (see later discussion).

The Ostwald type of viscometer is also most favoured in measurements with molten salts. The only essential differences in these systems are the provision of materials resistant to high temperatures and the measurement of time of flow by the breaking of an electrical circuit in place of visual observation. For very reactive melts, however, the oscillating crucible method is considered more suitable.[6] In this technique, a crucible containing the molten electrolyte is caused to oscillate

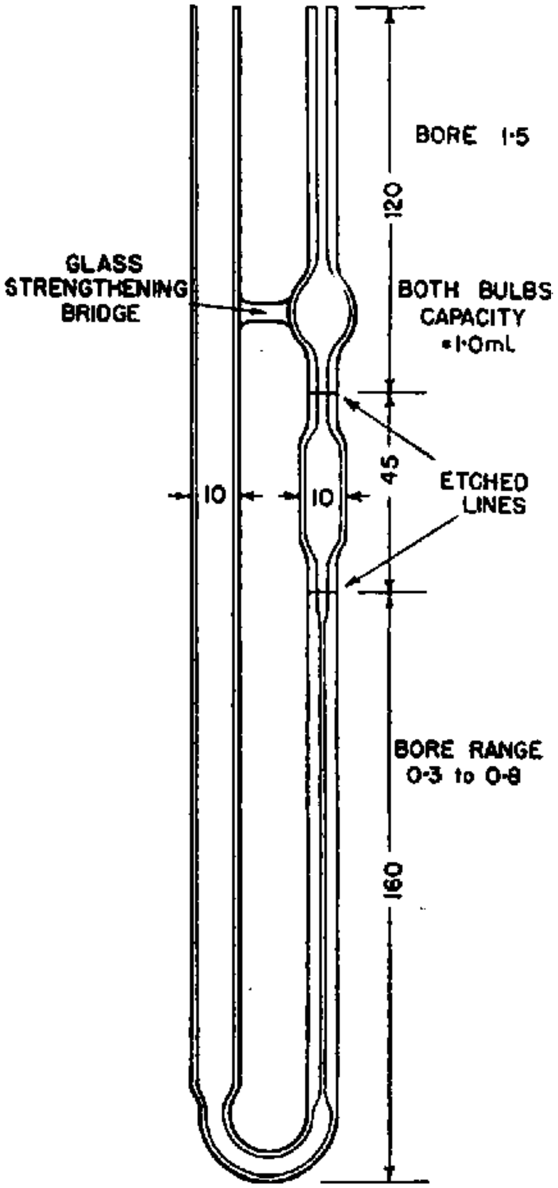

FIG. 2.1. Viscometer designed by Cannon and Fenske (1938). Dimensions in millimetres. (Reproduced with permission from *Industr. Engng. Chem. Anal. Ed.*)

and the logarithmic decrements of the oscillations are measured. By using equations developed by Andrade[7] the viscosity can then be calculated. In principle the method can give absolute viscosities but the computations are difficult and in practice it is normally used for relative measurements, apparatus constants being determined by calibration with liquids of known viscosity.

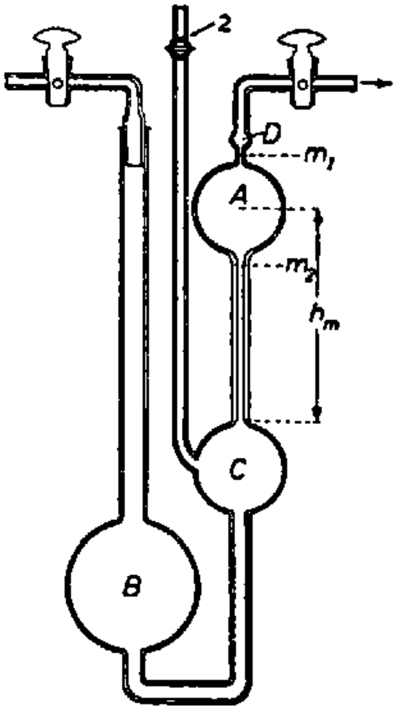

FIG. 2.2. Ubbelohde viscometer after Kaminsky. (Reproduced with permission from *Zeit. phys. Chem.* (N.F.).)

For viscosity measurements in kinematic instruments, the pressure term $p_0 - p_1$ in (4) is replaced by the term $h_m g\rho$ so that

$$\eta = \frac{\pi R^4 h_m g\rho t}{8V(l + \lambda)} - \frac{m\rho V}{8\pi(l + \lambda)t} \tag{2.5}$$

where h_m is the mean height of the liquid column (see Fig. 2) and g is the acceleration due to gravity. Measurements with kinematic viscometers therefore usually have to be associated with accurate determinations of density.

From inspection of (5) it is seen that the kinetic energy correction can be reduced most easily by decreasing the rate of flow and having a small efflux volume. The time of flow for a given instrument can be increased by decreasing the radius of the capillary but there is a practical limit to this course because the presence of dust and fibres will cause non-reproducibility in very fine bores. The compromise usually adopted in measurements with electrolytes is to employ capillary radii in the range 0·03 to 0·08 cm.

Efflux volumes are best held in the range 1 to 20 ml. Kaminsky's viscometer[4], as illustrated in Fig. 2, has an efflux volume of 505 ml.

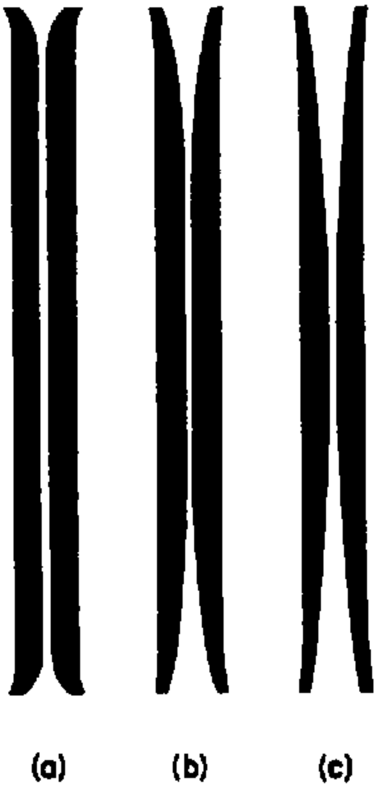

FIG. 2.3. Shapes of capillaries in viscometers after Caw and Wylie.
(a) Conventional
(b) Long flared with parallel centre section
(c) Overlapping long flares.
(Reproduced with permission of authors).

Although this volume seems unnecessarily large, it may be noted that he used the instrument for comparing the viscosities of very dilute electrolyte solutions with those of pure water at various temperatures. Efflux times were very similar so that in this particular case the kinetic energy correction would still retain a reasonable value.

A recent development which seems to be of considerable importance in the field of viscosity measurement is the construction of viscometers in which there is no significant kinetic energy correction. Caw and Wylie[8] have recently reported on the design, construction and testing of viscometers of this type. The main feature in these instruments is the provision of long flared capillaries, the shapes of which are illustrated in Fig. 3.

For practical purposes, Equation (5) is usually written in the form

$$\nu = Ct - B/t \tag{2.6}$$

where ν is the kinematic viscosity, $C = \dfrac{\pi R^4 h_m g}{8\nu(l + \lambda)}$ and $B = \dfrac{mV}{8\pi(l + \lambda)}$. C and B are regarded as instrumental constants although in the case of B this is true only over limited ranges of flows because in general m varies with Reynolds number. Caw and Wylie[8] have proposed a viscosity-flow equation for flared capillary viscometers of the form

$$\nu = Ct - K/t^n \tag{2.7}$$

where K is an instrumental constant. For the Reynolds numbers usually encountered in viscosity measurements $n = 4$. From (7) it is obvious that with such instruments, for normal rates of flow the second term will be negligible and (5) can be written in the form

$$\frac{\nu}{\nu_0} = \frac{t}{t_0} \tag{2.8}$$

where ν_0, t_0 and ν, t refer to the calibrating and test liquid respectively.

If a conventional viscometer is being used and the kinetic energy correction has to be allowed for then (6) must be used. When two or more liquids are available whose kinematic viscosities are accurately known, then the apparatus constants can be determined from the relationships

$$\frac{\nu_1}{\nu_2} = \left(\frac{Ct_1 - B/t_1}{Ct_2 - B/t_2}\right) \tag{2.9}$$

or

$$\frac{\nu_1}{\nu_2} = \frac{t_1}{t_2}\left(\frac{1 - D/t_1^2}{1 - D/t_2^2}\right) \tag{2.10}$$

where

$$D = B/C = \frac{mV^2}{\pi^2 R^4 h_m g}$$

and subscripts 1 and 2 refer to the two calibrating liquids.

Expanding (10) in terms of D/t_2^2, neglecting terms higher than second order, we have for small values of D/t_2^2.

$$\frac{\nu_1}{\nu_2} = \frac{t_1}{t_2}\left[1 + D\left(\frac{1}{t_2^2} - \frac{1}{t_1^2}\right) + D^2\left(\frac{1}{t_2^4} - \frac{1}{t_2^2\, t_1^2}\right)\right]. \tag{2.11}$$

Thus for measurements with times of flow within the range from t_1 to t_2, the correction factor in square brackets can be used. It will be noted that the Couette correction λ (see eq. 6) has been eliminated.

A somewhat better and more accurate procedure is to measure the efflux times of several calibration solutions and then plot ν/t against $1/t^2$. Interpolation on the resulting curve gives the kinematic viscosity directly. A typical curve of this type is given in Fig. 4 below:

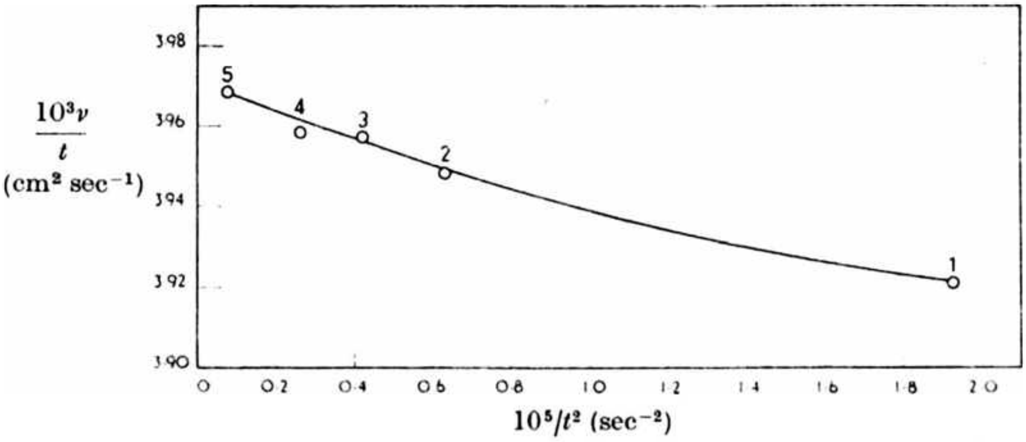

FIG. 2.4. Calibration curve at 25°C for viscometer
(1) Water; (2) 20% Sucrose; (3) 25% Sucrose;
(4) 30% Sucrose; (5) 40% Sucrose

Still another procedure can be used if only one calibrating liquid is available. For this case (1) can be used with subscript 1 referring to the test liquid and 2 to the calibrating one. The value of D in the correction term has now to be computed for a particular instrument and therefore the coefficient m needs to be known. Its value tends to zero for low rates of flow but in the range Re = 50 to 400 is close to unity and can be considered to be constant. For capillaries with fairly square-cut ends, m can be allotted a value of 1.12. For gradually tapered orifices a value of $\sim$0·6 has been generally preferred but the recent work of Caw and Wylie[8] shows that 1·25 is more correct. For a more detailed discussion of m values, the reader is referred to Barr[3] and to Swindells, Hardy and Cottington.[9] This uncertainty in the value of m and its variation with Reynolds number is, however, a limitation on the accuracy of this method of applying the kinetic energy correction.

Kaminsky[4], using the latter procedure, has calculated the extent of the correction for the viscosities of sodium sulphate solutions both from his own work and from the data of Glass and Madgin[10] who did not apply the correction. The values are given in Table 1 below. Water has been used as the calibrating fluid in both cases.

TABLE 2.1

C'/m/l.	T/°C	D/s^2	t/s	t_0/s	Correction factor
0·001	22°	$4{\cdot}02 \times 10^{5(a)}$	3301·74	3299·50	1·00006
0·14	22°	$4{\cdot}02 \times 10^{5(a)}$	3427·02	3300·25	1·00275
2·0	25°	$4{\cdot}55 \times 10^{3(b)}$	1838·5	900·4	1·00429
2·0	40°	$4{\cdot}55 \times 10^{3(b)}$	1288·6	663·6	1·00767

(a) Kaminsky's viscometer
(b) Glass and Madgin's viscometer.

These figures are given to illustrate that in conventional viscometers this correction cannot be neglected in precise measurements, particularly where there is a large difference between flow rates. Many authors have stated that their viscometers had been designed to give negligible kinetic energy corrections but in numerous cases their reported measurements have covered a wide range of viscosities where it is doubtful if this assumption is correct. Future experimenters in the field of electrolyte viscosity would be well advised to study Caw and Wylie's paper and investigate the use of flared capillaries.

Surface Tension Correction

An error due to surface tension may arise from the adhesion of liquid to the walls of the bulbs immediately above the capillary and in the exit reservoirs. This has the effect of altering the hydrostatic pressure head of the liquid. In relative measurements its magnitude will be dependent on the difference in surface tensions of the calibrating and test liquids. The surface tensions of aqueous solutions of electrolytes change very little with concentration, for example the value for a 2 M sodium chloride solution at 25°C is only 5% higher than that of pure water. Since the correction is small it can be safely neglected in these systems. However, if non-aqueous solutions are being calibrated against water, it must be taken into account; for example the surface tension of ethyl alcohol is less than a third of that of water.

Both viscometers described above have been designed to minimize the effect of surface tension. In the Cannon–Fenske instrument the bore of the receiving tube is of the same bore as the fiducial bulb (see Fig. 1). Any loss of hydrostatic pressure in the latter is therefore compensated for by the corresponding gain in the former. The Ubbelohde viscometer is reputed to eliminate the surface tension effect by the provision of the suspended level at the top of *C* which is so designed as to compensate for the forces operating in bulb *A*. However, Peter and Wagner[11] have recently made a detailed study of this effect in various viscometers. In the course of this work, they examined the error which would be caused by its neglect in Ubbelohde and Ostwald viscometers if water and propanol, which have widely differing surface tensions, were used as calibrating and test liquids. The error computed for the Ubbelohde instrument was 0·17% and that for the Ostwald 0·13% so that the above claim in respect of the former is open to question. It should be noted that the normal Ostwald viscometer has a wide receiving bulb and that the Cannon–Fenske type shown in Fig. 1 should be somewhat better. An alternative procedure to making a surface tension correction is to use the non-aqueous solvent as a calibrating liquid in cases where its viscosity is accurately known.

Experimental Errors

It is not within the scope of this book to detail experimental procedure, but brief mention will be made of the errors associated with loading, alignment and temperature control.

The Cannon–Fenske viscometer needs to have very precise loading. Any differences in the volume of liquid discharging through the instrument will be reflected in the mean driving fluid head h_m. In the Ubbelohde viscometer, however, the loading error is practically eliminated since the mean head is not dependent on the liquid in the lower reservoir but terminates at the junction of the capillary with bulb *C* (see Figs. 1 and 2).

Cannon and Fenske[5] have shown that a change from angle *A* to

$A + \mathrm{d}A$ in the alignment of the vertical capillary axis produces a change in the liquid head of

$$1 - \cos(A + \mathrm{d}A)/\cos A.$$

A deviation of 2·5° will therefore produce an inaccuracy of 0·1% in the measured viscosity.

Temperature control to better than a hundredth of a degree is needed in precise work. This is necessary because a change of 0·01°C causes approximately a 0·02% change in the viscosity of water.

Calibrating Standards

The primary standard on which all relative viscosity measurements are based is pure water at 20°C. Appropriate secondary standards which have been calibrated against this primary one are used for a particular viscosity range which is under examination.

The accepted value for the viscosity of water at 20°C is 1·0020 cP.[12] This figure has been recommended for international adoption by the International Organisation for Standardisation and has been accepted by such institutes as the National Bureau of Standards, U.S.A., the National Physical Laboratory, England, and the Physikalisch Technischen Bundesanstalt, Germany. This standard value was reported by Swindells, Coe and Godfrey[12] at the U.S. National Bureau of Standards. In a project lasting more than a decade, very accurate measurements were made of the transit of water through capillary tubes under an applied pressure. Stringent precautions were taken to select capillaries of even bore, to measure their dimensions accurately and to have precisely controlled pressures and temperature. A valuable independent confirmation of the validity of the above figure has been obtained recently by Roscoe and Bainbridge[13] who used an oscillating disc method to report a value for water at 20°C of 1·0025 ± 0·0005 cP.

Secondary standards commonly used in electrolyte studies are the viscosities of pure water and of sucrose solutions over a range of temperatures. Values for water are tabulated in Robinson and Stokes[14] and for both water and sucrose solutions in the *Handbook of Chemistry and Physics*.[15] It should be noted that if the tabulation being used lists the data of Bingham and Jackson[16] then a correction factor is needed. The values of these authors are based on the older value for the absolute viscosity of water at 20°C of 1·005. A correction factor of 1002/1005 or 0·9970 should therefore be used. Condensed tables for calibrating liquids are also given in Appendix 1.

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CHAPTER 3

LONG-RANGE ELECTROSTATIC INTERACTION

AT THE beginning of the century, Grüneisen[1] measured the viscosities of many electrolyte solutions down to very low concentrations and observed an effect which has since been named after him. He found, in these dilute solutions, that the viscosities are not approximately linear with the concentration as in higher ranges but instead show a characteristic curvature. This curvature is always negative and therefore the viscosity initially increases irrespective of whether, at higher concentrations, the solute increases or decreases the viscosity relative to the pure solvent. In 1929, Jones and Dole[2] gave a quantitative formulation of the effect with their empirical equation

$$\frac{\eta}{\eta^0} = 1 + Ac^{\frac{1}{2}} + Bc \tag{3.1}$$

where A and B are constants. The second term on the right-hand side was ascribed to the Grüneisen Effect and is the one with which we shall be concerned in this chapter.

In 1929, the interionic attraction theory as developed by Debye and Hückel[3] was gaining acceptance and Jones and Dole correctly surmised that the dependence on the square root of the concentration arose from long-range coulomb forces between the ions. In the same year Falkenhagen *et al.*[4,5,6] initiated the theoretical calculation of the constant A using the equilibrium theory as a starting point. In the first instance, the development was applied only to simple electrolytes whose constituent ions were of similar mobilities but later extended to the case where they differed. Then in 1932, Onsager and Fuoss[7] published a comprehensive paper on the theory of irreversible processes in electrolytes in which general equations were developed to describe viscosity, conduction and diffusion in dilute solutions. These general equations were then specialized for each of the three processes. Their development for the viscosity case gave final equations for systems containing more than two species of ions whereas Falkenhagen's treatment was only carried through for simple electrolytes.

It is not proposed to give a detailed account of the theory for which the original literature can be consulted. The development presented here follows that of Onsager and Fuoss as it leads to the more general case of multicomponent systems. It will be assumed that the reader is familiar with the Debye–Hückel equilibrium theory.

The overall physical model upon which the calculations are based can be pictured very simply. At equilibrium, in a dilute electrolyte solution, each ion will possess on a time-average a spherically symmetrical atmosphere of ions of opposite charge. When a linear velocity gradient is imposed on such a solution as in a capillary viscosity measurement, these ionic atmospheres will be distorted from their spherically symmetrical distribution by the associated shearing forces. Interionic attraction and thermal movements will tend to restore the more stable equilibrium distribution and since there is a finite time of relaxation for this process, an ellipsoidal distribution results and persists. The restoring force can be thought of as an addition to the shearing force necessary to maintain flow and therefore as an independent increment to the viscosity of the solvent (or more strictly to a solution of equivalent concentration of uncharged solute). A diagrammatic representation of this model for the two-dimensional case is given in Fig. 1.

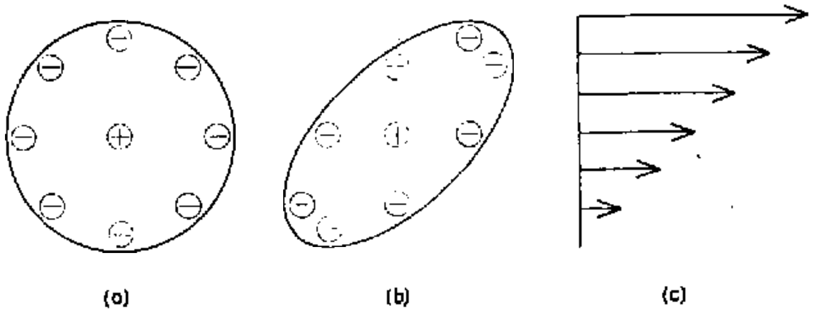

FIG. 3.1. Two-dimensional diagrammatic representation of charge distribution in electrolyte solution.
(a) Equilibrium condition
(b) Sheared condition
(c) Direction of linear velocity gradient.

Accepting this picture, the first requirement in developing the theory is to calculate the altered distribution functions and associated potentials resulting from the perturbing force. In the equilibrium theory the ion and ion atmosphere potentials were computed from differential equations which were formulated by combining the potential around a central ion calculated by the Boltzmann principle and the charge density distribution from the Poisson equation. In irreversible processes however, in the equivalent calculation, the equation of continuity replaces the Boltzmann principle and the charge density distribution is computed for the external perturbations superimposed on the static values. The Boltzmann principle is of course indirectly involved as it is implicit in the calculation of the equilibrium potential.

As a starting point we reproduce Fig. 2 from Onsager and Fuoss.[7]

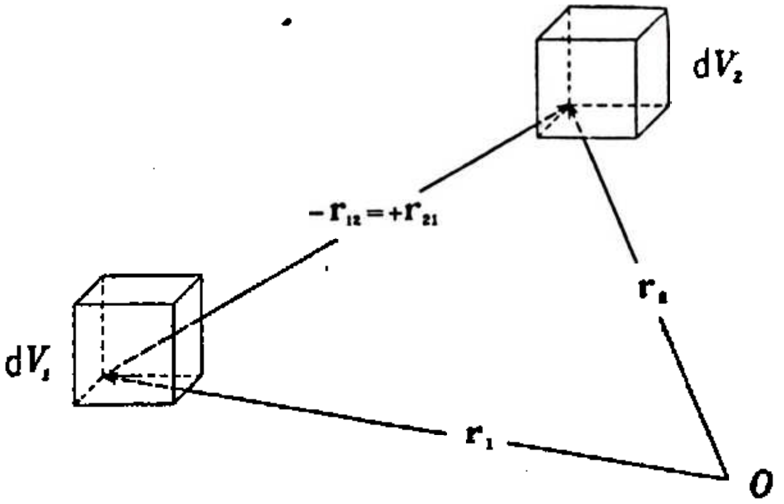

Fig. 3.2. Volume elements vectorially related to an arbitrary origin O. (Reproduced with permission from *Physical Chemistry of Electrolytic Solutions*.)

In this diagram, dV_1 and dV_2 are small elements of volume located by the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Distribution functions of the type f_{ji} can be defined by the relation

$$f_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_j n_{ji}(\mathbf{r}_1, \mathbf{r}_{21}) = n_i n_{ij}(\mathbf{r}_2, \mathbf{r}_{12}) = f_{ij}(\mathbf{r}_1, \mathbf{r}_2) \qquad (3.3)$$

where n_i and n_j are the numbers of ions per ml. The function f_{ji} therefore gives the time average distribution of i ions in the neighbourhood of a j ion. In the equilibrium case it will be recalled that the distribution f^0_{ji} is centrosymmetric so that vectorial representation is not required. It is given by the Debye–Hückel theory as

$$f^0_{ji} = n_j n_i \left(1 - \frac{e_j e_i}{\varepsilon kT} \frac{\exp -\kappa r}{r}\right). \qquad (3.4)$$

If a velocity gradient is imposed on a system previously at equilibrium the resultant distribution function, f_{ji}, now contains an asymmetric term, f'_{ji}, and may be written in the form

$$f_{ji} = f'_{ji}(\mathbf{r}_1, \mathbf{r}_{12}) + f^0_{ji}(r). \tag{3.5}$$

The potential on the ions, being related to the distribution, will also contain a perturbation term

$$\psi_j = \psi'_j(\mathbf{r}_1, \mathbf{r}_{21}) + \psi^0_j(r) \tag{3.6}$$

where

$$\psi^0_j(r) = \frac{e_j}{\varepsilon}\frac{\exp - \kappa r}{r}, \tag{3.7}$$

hence the two asymmetric terms in (5) and (6) can be related by the Poisson equation as below

$$\nabla \cdot \nabla \psi'_j = -\frac{4\pi}{\varepsilon}\sum_i \frac{f'_{ji}e_i}{n_j}. \tag{3.8}$$

We now turn to the equation of continuity to describe the behaviour of the ions in volume elements $\mathrm{d}V_1$ and $\mathrm{d}V_2$, in hydrodynamic terms. Laminar viscous flow is a steady state process implying that the ionic density distribution is independent of time. The equation of continuity in this case takes the form

$$\nabla_1 \cdot (f_{ij}\mathbf{v}_{ij}) + \nabla_2 \cdot (f_{ji}\mathbf{v}_{ji}) = 0 \tag{3.9}$$

where subscripts 1 and 2 refer respectively to differentiation with respect to the components of $\mathbf{r}_1$ and $\mathbf{r}_2$. $\mathbf{v}_{ij}$ is the velocity of a j ion in the vicinity of an i ion.

During viscous flow the three factors governing the ionic velocities are (*a*) bulk flow of the solution, (*b*) electrical interaction, and (*c*) thermal motion. The velocities can therefore be expressed in the form

$$\mathbf{v}_{ji} = \mathbf{V}(\mathbf{r}_2) + \omega_i(\mathrm{K}_{ji} - kT\,\nabla_2 \ln f_{ji}) \tag{3.10}$$

where $\mathbf{V}(\mathbf{r}_2)$ is the bulk velocity at the point located by $\mathbf{r}_2$, K_{ji} the electrical force acting on ion i in the vicinity of ion j, $\omega_i kT\nabla_2 \ln f_{ji}$ the average diffusion velocity and ω_i is the mobility of ion i. K_{ji} is the electrical force arising from the asymmetric distortion of the ionic atmosphere, i.e.

$$\mathrm{K}_{ji} = -e_i\nabla_2\psi_i(0) - e_i\nabla_2\psi_j(\mathbf{r}_1, \mathbf{r}_{21}). \tag{3.11}$$

Equations (5), (6), (10) and (11) can now be substituted into (9), with a number of simplifying approximations to get the equation of continuity specialized for viscous flow

$$(\mathbf{V}(\mathbf{r}_2)\cdot\nabla_2 f^0_{ji}) + (\mathbf{V}(\mathbf{r}_1)\cdot\nabla_1 f^0_{ij}) - e_i\omega_i n_i n_j \nabla_2\cdot\nabla_2\psi'_j - e_j\omega_j n_i n_j \nabla_1\cdot\nabla_1\psi'_i - \omega_i kT\nabla_2\cdot\nabla_2 f'_{ji} - \omega_j kT \nabla_1\cdot\nabla_1 f'_{ij} = 0. \quad (3.12)$$

Equation (12) is converted into a suitable form for mathematical treatment by substituting the perturbed potentials ψ_j' for the distribution functions f'_{ji} through use of the Poisson equation. In turn ψ_j' is replaced by a more specialized potential function ξ_j, and the equation of continuity now has the form

$$(\nabla\cdot\nabla)^2\xi_j(r) - \frac{4\pi}{\varepsilon kT}\sum_{i=1}^{s}\frac{n_i e_i^2\omega_i}{\omega_i+\omega_j}\nabla\cdot\nabla\xi_j(r) - \frac{4\pi}{\varepsilon kT}\sum_{i=1}^{s}\frac{e_i e_j\omega_j n_i}{\omega_i+\omega_j}\nabla\cdot\nabla\xi_i(r) = \frac{4\pi}{(\varepsilon kT)^2}\frac{\exp -\kappa r}{\kappa}\sum_{i=1}^{s}\frac{n_i e_i^2 e_j}{\omega_i+\omega_j}. \quad (3.13)$$

Onsager and Fuoss, using the methods of matrix algebra gave solutions for the differential equation system (13) in terms of $\xi_j(0)$. Their general solution is in matrix notation and given by their equation (3.5.16).[7] For an electrolyte dissociating into two kinds of ions, the solution is

$$\nabla\cdot\nabla\xi_j(0) = \frac{\kappa e_j}{2\varepsilon kT}\left\{\frac{\bar{P}}{4\kappa^2} - \left(P_j - \frac{\bar{P}^2}{\bar{P}}\right)\frac{(1-\sqrt{q^*})1}{(1+\sqrt{q^*})\kappa^2}\right\} \quad (3.14)$$

where

$$\bar{P} = \frac{n_1e_1^2/\omega_1 + n_2e_2^2/\omega_2}{n_1e_1^2 + n_2e_2^2} \quad (3.15)$$

$$\bar{P}^2 = \frac{n_1e_1^2/\omega_1^2 + n_2e_2^2/\omega_2^2}{n_1e_1^2 + n_2e_2^2} \quad (3.16)$$

$$q^* = \frac{n_1e_1^2\omega_1 + n_2e_2^2\omega_2}{(n_1e_1^2 + n_2e_2^2)(\omega_1+\omega_2)}. \quad (3.17)$$

The final step in the development is to relate the perturbed potential function ξ_j to the actual ionic viscosity increment η^*. To do this we return to the consideration of stress relationships in an electrolyte solution in which viscous flow is occurring. As implied in the introductory paragraphs, two factors contribute to force transfer in such flow. The first is friction between solvent molecules and the second is relative motion between ions and solvent, the latter giving rise to the ionic viscosity increment.

Before developing equations to describe the second of these two factors, a few words should be said about the force transfer process itself. Onsager and Fuoss[7] by considering the generalized stress–viscosity relationship with regard to the equations of motion for an incompressible fluid, conclude that the ionic viscosity increment can be treated as an addition to the volume force. They also discuss the mechanism of force transfer and on their model, consider that in the case of a constant velocity gradient the transfer of force between ions and solvent must take place along the boundaries of the system. Falkenhagen[4] on the other hand assumed in his treatment that this force transfer occurred in the interior of the solution. However, the practical consequences of the divergence of approach to this problem do not appear important insofar as the final equations for simple electrolytes as derived from each are identical.

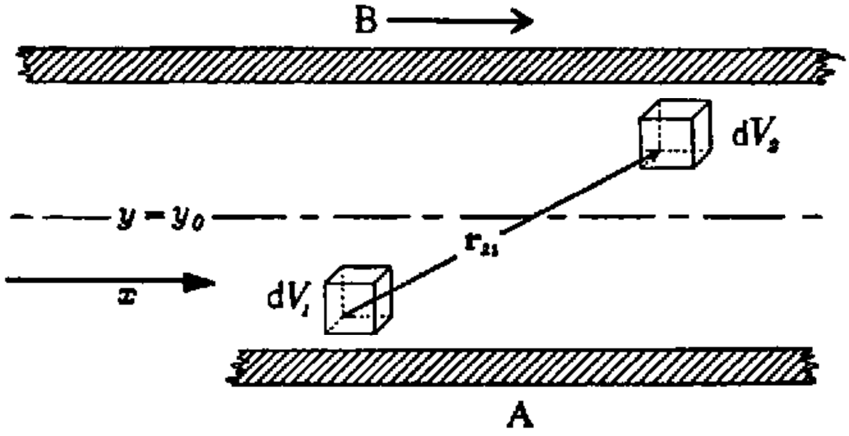

FIG. 3.3. Diagram for computation of stress. (Reproduced with permission from *Physical Chemistry of Electrolytic Solutions*.)

As a basis for development of the equations describing the ionic viscosity increment, we reproduce from Onsager and Fuoss' paper, the diagram given by Fig. 3.

An electrolyte is pictured as confined between planes A and B. Laminar flow in the x direction and a constant velocity gradient in the y direction are assumed.

From the definition of the viscosity coefficient we have

$$S_{xy} = \eta \frac{\partial v_x}{\partial y} \tag{3.18}$$

where S_{xy} is the total stress per unit area over the xy plane and $\partial v_x/\partial y$ is the velocity gradient. If we assume that this stress is additively compounded of friction between solvent molecules and the interaction of electrostatic forces between the ions, then

$$S_{xy} = S^0_{xy} + S^*_{xy} \tag{3.19}$$

where

$$S^0_{xy} = \eta^0 \frac{\partial v_x}{\partial y} \tag{3.20a}$$

and

$$S^*_{xy} = \eta^* \frac{\partial v_x}{\partial y} \tag{3.20b}$$

where the superscripts 0 and * refer to the solvent–solvent and ionic interaction respectively. It is the computation of the stress S^*_{xy} which is now necessary.

In Fig. 3, we locate a plane $y = y_0$ and investigate the transfer of electrostatic force S^*_{xy} across unit area of this plane. This stress must obviously be restricted to ions whose co-ordinates obey the restriction

$$y_1 < y_0 < y_2.$$

The mutual forces between the ions in the two volume elements $\mathrm{d}V_1$ and $\mathrm{d}V_2$ can be calculated in the following manner. The force transferred from a j ion in $\mathrm{d}V_1$ to the ions in $\mathrm{d}V_2$ is

$$\frac{e_j}{\varepsilon} \sum_i e_i n_{ji}(\mathbf{r}_{21}) \mathrm{d}V_2 \frac{\mathbf{r}_{21}}{r^3}$$

since the coulomb force between any two ions is

$$\frac{e_j e_i}{\varepsilon} \frac{\mathbf{r}_{21}}{r^3}.$$

The total interaction between all pairs of ions in the two volume elements is then

$$-\sum_{ji} \frac{e_i e_j}{\varepsilon} f_{ij}(\mathbf{r}_{12}) \mathrm{d}V_1 \mathrm{d}V_2 \frac{\mathbf{r}_{21}}{r^3}.$$

Integrating over all volume elements satisfying the above restriction, we obtain

$$S^*_{xy} = -\tfrac{1}{2}\iiint_{-\infty}^{+\infty} \frac{xy}{r^3} \sum_{ji} \frac{e_j e_i}{\varepsilon} f_{ji}(\mathrm{r})\mathrm{d}V. \tag{3.21}$$

Eliminating f_{ji} by the potential function ξ_j, through the Poisson equation and completing the integration we get

$$S^*_{xy} = \frac{1}{15}\frac{\partial v_x}{\partial y} \sum_j n_j e_j \ \nabla \cdot \nabla \xi_j(0) \tag{3.22}$$

whence

$$\eta^* = \frac{1}{15} \sum_j n_j e_j \nabla \cdot \nabla \xi_j(0). \tag{3.23}$$

We can now substitute the previously obtained solution for $\xi_j(0)$ in (23). The general equations for η^* in matrix notation are (3.7.1) and (3.7.2) in Onsager and Fuoss' paper.[7] For binary electrolytes substitution of (14) in (23) gives

$$\eta^* = \frac{\kappa}{480\pi}\left\{\bar{P} + 4\left(\frac{\bar{P}^2}{\bar{P}} - \bar{P}\right)\frac{(1 - \sqrt{q^*})}{(1 + \sqrt{q^*})}\right\}. \tag{3.24}$$

The first term in the brackets gives the viscosity increment in terms of ionic strength and mobilities and is usually the dominant one. The second term is a correcting one involving the second power of the difference between the mobilities.

Thus when $\omega_1 = \omega_2$ the correction term vanishes and we get

$$\eta^* = \frac{\kappa}{480\pi\omega} \tag{3.25}$$

a result first obtained by Falkenhagen and Dole[4] for a simple electrolyte in the case where the ions have similar mobilities.

Falkenhagen and Kelbg[8] and Pitts[9] have attempted to extend the range of equations of type (25) and (24) respectively by including a parameter a related to ion size. It will be recalled that the theory so far has considered the ions only as point charges. The analogous modification in conductivity theory has extended the range of the comparable limiting equations significantly.

The former authors obtain the approximate equation

$$\eta^* = \frac{e^2}{60\varepsilon kT\omega}\frac{n}{\kappa}\,r(\kappa a) \tag{3.26}$$

where

$$r(\kappa a) = \frac{1 + 15/4g(\kappa a)}{1 + \kappa a}, \tag{3.27}$$

and

$$g(\kappa a) = \frac{1}{60}\,\kappa a - \frac{7}{60}\,(\kappa a)^2 - \frac{1}{40}\,(\kappa a)^3 + \frac{1}{40}\,(\kappa a)^4. \tag{3.28}$$

As shown in Fig. 4, comparison of experimental data with this equation shows that the modification extends its range of validity a negligible amount. Pitts made more extensive computations based on the inclusion of the parameter a and found that his final theoretical expressions were not only of the wrong sign but predicted the wrong concentration dependence, when compared with experiment. With reference to Fig. 4 it is obvious why this kind of modification has no significant effect. The absolute magnitude of the electrostatic increment to the viscosity is small. For example, the contribution from ionic interaction in a 0·1 N solution of KCl at 25°C amounts to only 0·14% of

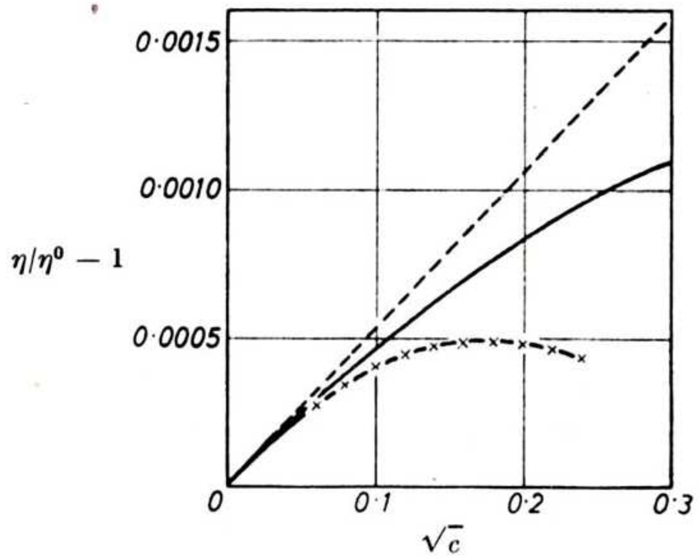

FIG. 3.4. Viscosity of KCl at 25° after Falkenhagen.
– – – – – – – – – limiting curve
× × × × × × × × × Experimental values
———————— eq. (6)
(Reproduced with permission from *Modern Aspects of Electrochemistry*, No. 2.)

the total viscosity. On the other hand the viscosity increase from ion-solvent interaction represented by the Bc term in equation (1) is quite large. Small changes in the $A\sqrt{c}$ term are quickly swamped out, therefore.

TABLE 3.1

Values of Coefficient A for Single Electrolytes

Salt	T°C	A (exp.)	A (theor.)	Ref.	A (exp.)	A (theor.)	Ref.
		Aqueous solutions			*Non-aqueous solutions*		
NaCl	12·5	0·0058	0·0058	(1)			
	15	0·0058	0·0059	(1)			
	25	0·0062	0·0060	(1)			
	35	0·0065	0·0062	(1)			
	42·5	0·0071	0·0064	(1)			
Li_2SO_4	15·1	0·0160	0·0160	(1)			
	20	0·0165	0·0164	(1)			
	25	0·0167	0·0166	(1)			
	30	0·0169	0·0168	(1)			
	42·5	0·0173	0·0172	(1)			
KCl	25	0·0052	0·0050	(2)	0·0151	0·0173	(6)
$KBrO_3$	25	0·0058	0·0058	(3)	(Methanol)		
KI	25				0·0159	0·0158	(6)
KNO_3	25	0·0050	0·0052	(3)	(Methanol)		
NH_4Cl	25	0·0052	0·0050	(4)	0·0183	0·0165	(6)
$MgSO_4$	25	0·0230	0·0228	(2)	(Methanol)		
NaI	25				0·027	0·0255	(7)
$K_4Fe(CN)_6$	25	0·03695	0·03690	(5)	(Ethanol)		

1. KAMINSKY, *Z. phys. Chem.*, 1956, **8**, 173.
2. KAMINSKY, *Z. phys. Chem.*, 1957, **12**, 206.
3. JONES AND TALLEY, *J. Amer. chem. Soc.*, 1933, **55**, 624.
4. KAMINSKY, *Z. phys. Chem.*, 1955, **5**, 154.
5. JONES AND STAUFFER, *J. Amer. chem. Soc.*, 1936, **58**, 2558; ASMUS, *Z. Elektrochem.*, 1940, **46**, 596.
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7. COX AND WOLFENDEN, *Proc. roy. Soc.*, 1934, **A 145**, 475.

The constant A may be evaluated from experimental data by plotting a suitable form of eq. (1). Such plots are illustrated in Chapter 4. Many tests have been made of the validity of the limiting equations, mainly for simple electrolytes but in one or two cases for electrolytes with three species of ions. The recent precise viscosity measurements of Kaminsky[10,11] have enabled good tests to be made of A for both different salts and for the same salt at different temperatures.

Representative tabulations of theoretical and observed values of A are given in Tables 1 and 2.

The agreement in aqueous solutions is generally good and the validity of the equations at low concentrations can be regarded as established. For non-aqueous solutions, the agreement is fair but much more precise data are needed for adequate testing in these cases.

TABLE 3.2

Values of Coefficient A for Aqueous Electrolyte Mixtures at 25°.

Mixture	Composition mole % $CuSO_4$	A (exp.)	A (theor.)
$CuSO_4 + KCl$	82·3	0·0077	0·00753
	64·8	0·0070	0·00709
	47·9	0·0067	0·00650
	21·0	0·0052	0·00521
$CuSO_4 + H_2SO_4$	84·3	0·0071	0·00702
	72·9	0·0064	0·00639
	56·8	0·0055	0·00557
	43·4	0·0049	0·00492

Reference: ASMUS, *Ann. Phys., Lpz.*, 1939, **36**, 166.

In view of the swamping effect of the Bc term mentioned above there seems little point in trying to elaborate the simple electrostatic theory to apply it to higher concentrations. The theory of long-range interionic contributions to the viscosity of electrolytes is therefore virtually a closed chapter.

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CHAPTER 4

THE *B*-COEFFICIENT

IN Chapter 3, the viscosity increment in very dilute electrolyte solutions, due to long-range interionic forces, was discussed. Experimental evidence indicates that this effect can explain the behaviour of concentration–viscosity curves up to about 0·002 M. It was pointed out also that elaboration of the dilute solution theory to include a parameter for the finite size of the ions, fails to extend the range of the equations significantly.

At concentrations above about 0·002 M, a marked linear variation of viscosity with concentration is shown by strong electrolytes, extending to 0·1 M and higher in aqueous solutions and to somewhat lower concentrations in some non-aqueous systems. The existence of this linear dependence was first given quantitative significance by the formulation of the empirical Jones–Dole equation,[1] which was introduced in the previous chapter. It is usually expressed in the form:

$$\eta/\eta^0 = 1 + A\sqrt{c} + Bc \tag{4.1}$$

where A is the positive, computable constant discussed in Chapter 3. B is an empirical constant which can be either positive or negative, and its qualitative correlation with other solution properties forms the subject matter of this chapter.

The applicability of this equation to electrolyte systems is well illustrated in Fig. 1 where addition of the ordinates of the $A\sqrt{c}$ and Bc curves gives the central curve which fits the experimental data within its stated error up to about 0·05 M.

In the concentration region from 0·002 to 0·1 M with which we are concerned in this chapter, interest therefore centres on the coefficient B. This coefficient can be obtained from experimental data by rearranging (1) and plotting $(\eta/\eta^0 - 1)/\sqrt{c}$ against $\sqrt{c}$ as in Fig. 2. The slope of the resulting straight line gives the value of B directly, and the intercept should agree with the theoretical value of the coefficient A.

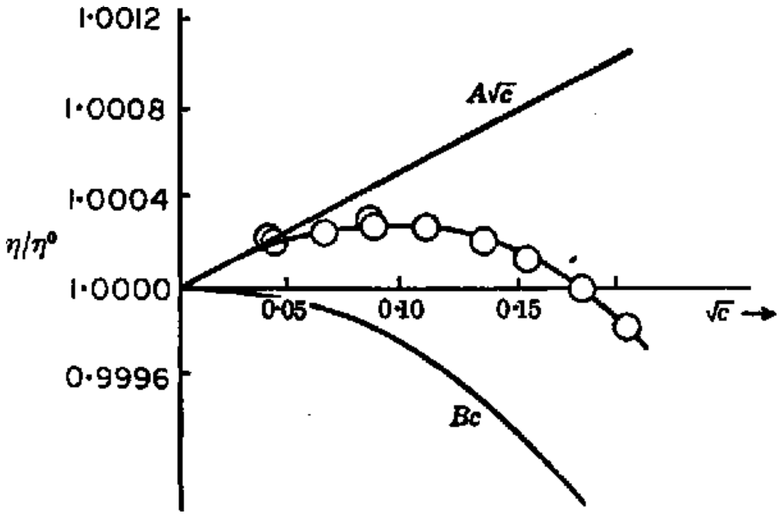

FIG. 4.1. Relative viscosity of aqueous solutions of KCl at 18°C. ○, Experimental data. (Reproduced with permission from *Ionic Processes in Solution*, by Gurney, Copyright 1953. McGraw-Hill Book Company.)

A representative selection of B-coefficients for various salts is given in Tables 1 and 2. Examination of these tables allows two important deductions to be made.

The first of these relates to the effect of change of solvent. Negative

TABLE 4.1

B-coefficients of Salts in Aqueous Solution at 25°C

	Cl^-	Br^-	I^-	SO_4^{2-}	Picrate$^-$
Li^+	0·143	0·106	0·0810	0·508	0·451
Na^+	0·0793		0·018	0·390	
K^+	−0·0140	−0·048	−0·0755	0·1937	
Rb^+	−0·037	−0·061	−0·099		
Cs^+	−0·052		−0·114		
NH_4^+	−0·0144	−0·037	−0·08		
Mg^{+2}	0·3712			0·5937	
La^{+3}	0·5672				
$N(C_2H_5)_4^+$		0·343			0·743

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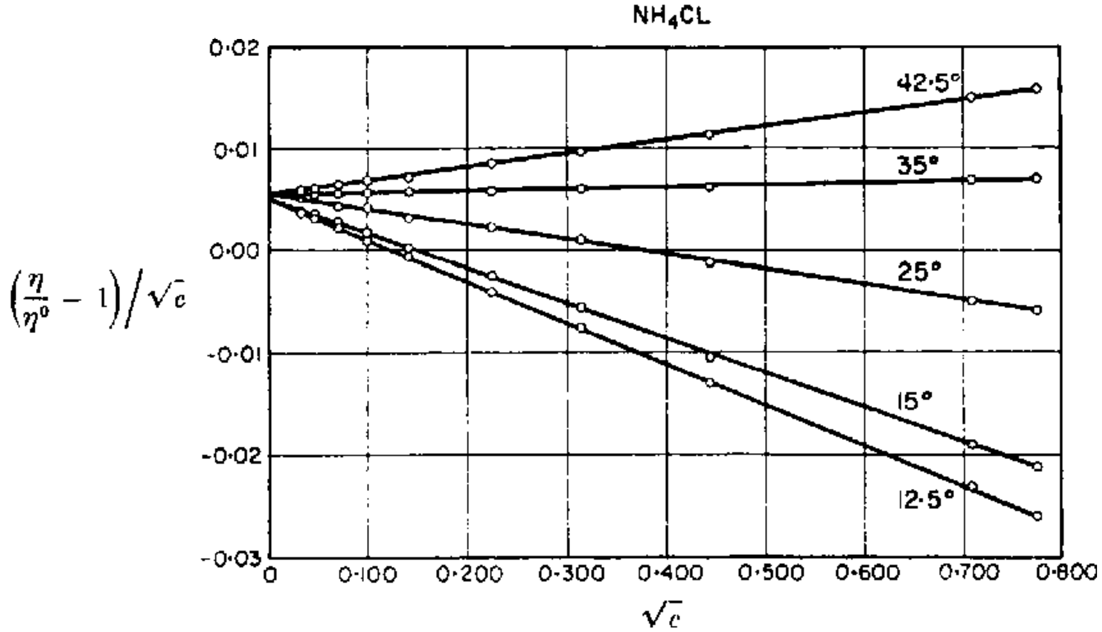

FIG. 4.2. Plot of equation $\eta/\eta^0 - 1/\sqrt{c} = A + B\sqrt{c}$ for NH_4Cl at various temperatures after Kaminsky. (Reproduced with permission from *Zeit. phys. Chem.* (N.F.).)

B-coefficients are confined to highly associated solvents, with water as the prime example, at fairly low temperatures. This type of coefficient is therefore probably related to the disturbance of the structure which is present in such liquids. The *B* values also vary widely for different

TABLE 4.2

B-coefficients of Salts in Various Solvents

	CH_3OH (25°C)	C_2H_5OH (25°C)	H_2SO_4 (25°C)	0% CH_3OH 100% H_2O (35°C)	40% CH_3OH 60% H_2O (35°C)	50% CH_3OH 50% H_2O (35°C)
KCl	0·7635[a]			0·01	0·02	0·06[b]
KBr	0·7396					
KI	0·6747					
NH_4Cl	0·6610					
NaI		1·15[c]				
NH_4HSO_4			−0·1[d]			
$NaHSO_4$			+0·8			
$KHSO_4$			+1·0			
$Ba(HSO_4)_2$			+4·4			

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[a] JONES AND FORNWALT, *J. Amer. chem. Soc.*, 1935, **57**, 2041.
[b] SINGH, DAS AND PATNAIK, *J. Indian chem. Soc.*, 1957, **34**, 494.
[c] COX AND WOLFENDEN, *Proc. roy. Soc.*, 1934, **A 145**, 475.
[d] GILLESPIE, *Rev. roy. Austral. chem. Inst.*, 1959, **9**, 1.

solvents and show progressive change in mixed solvents. The viewpoint is generally accepted that B-coefficients are a manifestation of ion–solvent interaction and this is of course supported by the linearity of the Bc term in the concentration.

The second important deduction concerns the evidence for the additivity of ionic contributions. For example, the B values for pairs of salts with the same anion but different cations have constant differences. Additivity is therefore adduced to the separate ions and most correlations with other solution properties are made in terms of ionic B-coefficients.

The division of B-coefficients into individual ionic values is a rather arbitrary process, there being no quantity analogous to transport numbers as used in mobility assignments. Gurney[2] has computed ionic B-coefficients in aqueous solutions by equating the contributions made by K^+ and Cl^- ions to the B-coefficient of KCl at 25°C. Kaminsky[3] has extended this treatment to the temperature range 15–45°C. These assignments are based on the fact that the B-coefficient for KCl is very small and that the mobilities of K^+ and Cl^- are very similar over the above range of temperatures, which implies that their effect on the water structure is also comparable. Nightingale[4] has recently criticized this division on the basis that from mobility considerations alone, other salts would be more suitable such as RbCl or CsCl. However, if the two factors, low overall effect and equivalence of mobilities are taken into account, KCl appears to be the best choice. Further, the close correlations that have been obtained with thermodynamic properties, to be described later, confirm the KCl division as a good approximation.

At this juncture it should be mentioned that a somewhat analogous treatment for the increments of fluidity in electrolytes was suggested by Bingham.[5] For solutions of concentration 1 N, he divided the increments of fluidity of the electrolyte above that of the pure solvent into ionic contributions again by equating the contributions of K^+ and Cl^- ions. The fluidity increments for various ions were then calculated and found to be additive when tested with observed values for single salts and mixtures. Implicit in this treatment is the neglect of the $A\sqrt{c}$ term, which is justifiable at these concentrations. This type of formulation is purely empirical and has not been extended to give information on ion–solvent interaction as has its B-coefficient counterpart.

Generally, in non-aqueous and mixed solvent systems no division into ionic B values has been attempted. An important exception is the case where sulphuric acid is the solvent and salts of the type $M.HSO_4$ are the solute. In these systems Gillespie[6] has assigned the total salt *B* coefficient to the cation involved. The very reasonable assumption is made that anions of the type HSO_4^- being of the same size and character as the solvent molecules will have very little disturbing effect on the solution structure.

Tables of ionic *B*-coefficients values and graphs of the temperature dependence of the *B* values for representative ions are given below.

TABLE 4.3

Ionic B-coefficients in Aqueous Solutions

T °C	Li^+	Na^+	K^+	Cs^+	Mg^{+2}	La^{+3}
15	0·1615	0·0860	−0·0200		0·4091	
25	0·1495	0·0863	−0·0070	−0·045	0·3852	0·588
35	0·1385	0·0851	+0·0049		0·3625	
42·5	0·1310	0·0861	+0·0121		0·3472	
T °C	Cl^-	Br^-	I^-	SO_4^{2-}	Picrate	NH_4^+
15	−0·0200			0·1899		−0·0137
25	−0·0070	−0·032	−0·0685	0·2085	(18°) 0·434	−0·0074
35	+0·0049		−0·0536	0·2277		−0·0027
42·5	+0·0121			0·2399		+0·0018
T °C	$N(CH_3)_4^+$	$N(C_2H_5)_4^+$	$N(C_3H_7)_4^+$	$N(C_4H_9)_4^+$		
20	0·1223	0·3999				
25	0·1175	0·3807	1·092	1·396		
30	0·1158	0·3636				
42·5	0·1143	0·3520				

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No general theory has yet been developed for the *B*-coefficient but important qualitative explanations have been advanced in terms of ion-solvent interaction. These interpretations are more significant if given for individual *B*-ion values and certain facts and regularities that can be obtained from the above tables form a basis for discussion. They can be placed in isothermal and temperature-dependent divisions.

TABLE 4.4

Ionic B-coefficients in Sulphuric Acid and Water at 25°C

Solvent	H_3O^+	NH_4^+	K^+	Na^+	Li^+	Ba^{+2}
H_2SO_4	−0·4	−0·1	+0·2	+0·8	+1·0	+4·4
H_2O	+0·07	−0·01	−0·007	+0·09	+0·15	+0·22

Reference

GILLESPIE, *Rev. Roy. Austral. Chem. Inst.*, 1959, 9, 1.

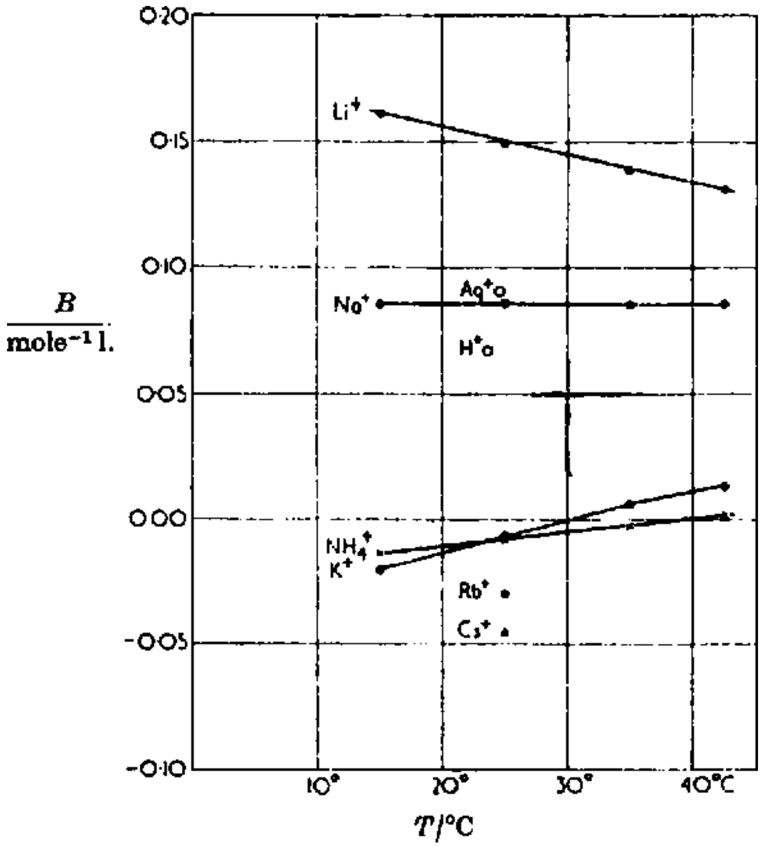

FIG. 4.3. Temperature dependence of ionic *B*-coefficients for a series of cations after Kaminsky. (Reproduced with permission from *Disc. Faraday Soc.*)

Isothermal Characteristics

It will be observed (Tables 3 and 4) that within a group of the Periodic Table, a regular sequence of values occurs from the ion of smallest crystal radius to the largest. The smallest ions increase viscosity the most in such a sequence and large monatomic ions the least. Further, at certain temperatures the latter ions decrease the viscosity and the B values are negative. Large molecular ions such as the tetra-alkyl-ammonium ions and picrate ion have large positive values, however. The higher the charge on an ion also the greater the B value. Lastly, ammonium ion has a B value close to zero both in water and sulphuric acid.

Temperature Dependence

Referring to Table 3 and Fig. 3, it will be observed that as the temperature increases small B values increase, negative ionic B values becoming positive. The temperature coefficient of the B values $(\partial B/\partial T)$ also shows a regular transition down a group of the Periodic Table. In the alkali metal group, for instance, Li^+ ion has a negative coefficient, Na^+ is close to zero and K^+ has a positive coefficient.

A number of different approaches have been made to explain these regularities and all are based on the postulate that there exists around an ion, a region of modified solvent differing from the bulk in structure and properties. Gurney's[2] cosphere, Frank and Wen's[7] A, B and C zones and Nightingale's[4] hydrated radius are recent reflections of this idea.

In order to give an overall picture of these interpretations, we propose to use an analysis of our own which embodies many of the ideas from the above approaches and that presented by Kaminsky.[3] It also emphasises that the observed viscosity changes result from *competition* between various effects occurring in the ionic neighbourhood.

We equate the viscosity of a dilute electrolyte solution to that of the solvent plus the contributions from four other sources in the following manner

$$\eta = \eta^0 + \eta^* + \eta^E + \eta^A + \eta^D \tag{4.2}$$

here η^* is the positive increment in viscosity caused by coulombic interaction which has been described in Chapter 2. η^E is the viscosity increment arising from the size and shape of an ion, which is closely related to the Einstein effect (see Chapter 5). It will always be positive and normally increases with increasing ion size.

η^A is the increment due to the alignment or orientation of polar molecules by the ionic field. Since the freedom of movement of these molecules is restricted this generally results in a "stiffening" of the solution and the increment will again be positive.

η^D is the viscosity change associated with distortion of the solvent structure leading to greater fluidity. This distortion can be thought of as due to competing forces from the solvent structure in the bulk and from the ionic field and/or the oriented molecules associated with the ion. It will cause a decrement in the viscosity and will be negative in our representation.

If (2) is substituted into the Jones–Dole equation (1) we have

$$\eta^* + \eta^E + \eta^A + \eta^D = \eta^0 (A\sqrt{c} + Bc). \tag{4.3}$$

Eliminating the ionic interaction contributions from both sides;

$$\eta^E + \eta^A + \eta^D = \eta^0 Bc. \tag{4.4}$$

Therefore, at a given concentration the B-coefficient can be interpreted in terms of a competition between these specialized viscosity effects.

Small and highly charged cations such as Li^+ and Mg^{++} strongly orient water molecules and in fact are believed to have a primary sheath of firmly-attached molecules which moves with them as a kinetic entity. η^E will therefore be large because the ion plus its primary sheath can be visualized as a single particle. It is also probable that at room temperature water molecules beyond this inner layer are oriented to some extent, giving a positive η^A. The sum of $\eta^E + \eta^A$ will far outweigh the decrement due to η^D. It may be remarked here that η^D is thought to be small for these ions, because the fixed outward-pointing hydrogen atoms fit reasonably well into the tetrahedral water structure. In this class of ions then $\eta^E + \eta^A \gg \eta^D$ and B is fairly large and positive.

At the other end of the scale, ions of the greatest crystal radius (within a group) such as Cs^+ or I^- have small surface charge densities and have only a weak orienting effect in the first layer. η^E would be equivalent to that for the bare ion and so very small while η^A is also small. There is, however, considerable distortion in the immediate neighbourhood of the ion due to competition between the ionic field and the bulk structure so that η^D is now large. In this class $\eta^E + \eta^A < \eta^D$ and B is negative.

Ions intermediate in size between these two extremes such as K^+ and Cl^- as would be expected, have a close balance of viscous forces in their vicinity, i.e. $\eta^E + \eta^A \approx \eta^D$ so that B is close to zero. Ammonium ion falls into this class also both in aqueous and in sulphuric acid solutions. It is thought that its tetrahedral configuration allows it to fit into the structure of these liquids with a minimum of disturbance. It would also have little polarizing power so that all the effects are small and its B-coefficient is close to zero over a considerable range of temperatures. In many other respects, e.g. mobility, this ion also closely resembles K^+.

Large molecular ions such as the tetra-alkyl-ammonium ions would be expected to have large η^E values because of their size. Orienting and distorting effects would be small so that $\eta^E + \eta^A \gg \eta^D$ and again B is positive and large. It may be remarked here that Frank[7,8] introduces a further effect to account for the high viscosities of solutions of these ions. He suggests that the "ice-like" structure of the water at a distance from these ions is increased by their presence. If this effect is real, it will in our view be additional to those already invoked in the above description.

Ionic B-coefficients in sulphuric acid are also interpretable in terms of local viscosities. These coefficients are however much larger in this solvent than in water (see Table 3) and Gillespie[6] attributes this in part to the larger size of the solvent molecules. In our interpretation this would lead to large η^E values (for solvated ions) and η^A effects would also be greater.

With regard to the temperature dependence of B values, we first have to explain the change from negative to positive B values with increasing temperature. Ions with negative B values (Cs^+ or I^-) have a large η^D or distortion term at lower temperatures. With increasing temperature η^D will decrease because there will be less competition between the ionic field and the reduced solvent structures. η^E will remain fairly constant and η^A will decrease fairly slowly so that eventually $\eta^E + \eta^A > \eta^D$ and B will be positive. Nightingale[4] also suggests that hydration may increase as the water structure is broken down but it is arguable that the increased thermal motion would counteract this tendency. It may be added that there is no thermodynamic evidence to support increased hydration.

The negative temperature coefficient of B for small and highly charged ions must also be explained. Kaminsky[3] had made the suggestion that this may be related to the fact that oriented water molecules in the secondary layer will be less rigidly held due to increased thermal motion. This will give a significant decrease in η^A. However, in spite of this decrease the sum of $\eta^E + \eta^A$ will still be larger than η^D for the reasons given in the preceding paragraph.

Explanations similar in principle to those given above have been used to explain the experimental data obtained from many other properties of electrolyte solutions. Two of special interest to the viscosity case are the temperature coefficient of ionic mobility and the ionic entropy.

Ions of large crystal radius such as Cs^+ or I^- have the smallest temperature coefficients of mobility and small ions like Li^+ have the largest. This can be qualitatively explained in the following way. In the preceding section the view has been advanced that around large unhydrated ions there is considerable distortion and the fluidity is enhanced (η^D is large) whilst with small hydrated ions this effect is minimal. With increasing temperature the solvent structure is broken down and the fluidity is increased. The mobility of an ion to a first approximation is dependent on the fluidity of the medium in its immediate surroundings. In the large ion case, this temperature-induced fluidity will obviously have less effect *relatively* than in the case of small ions. Consequently, the temperature coefficient of the mobility will be less for the former type. Since ionic B values have been interpreted in terms of the same kind of phenomena, we might

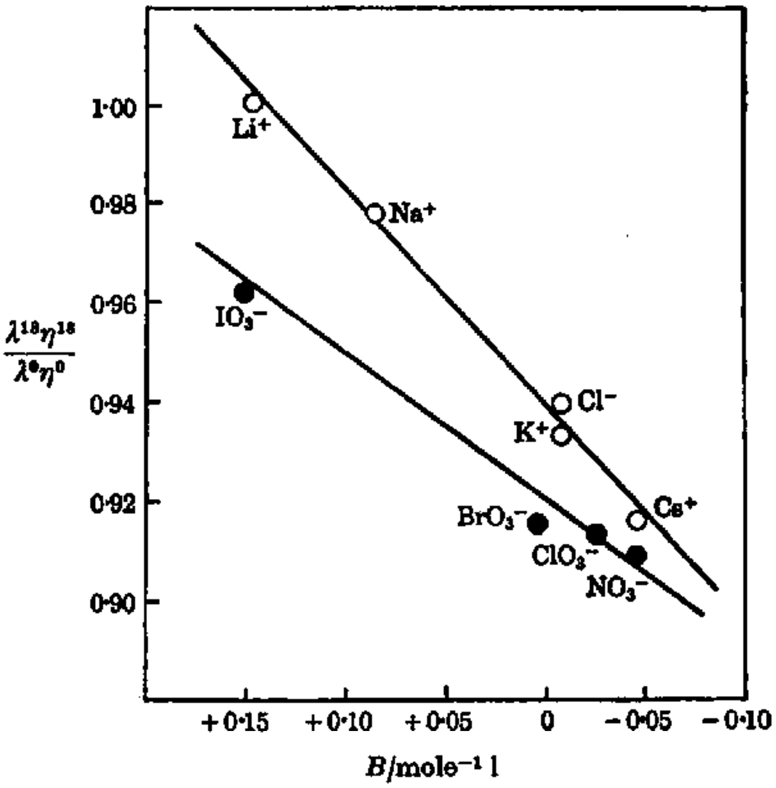

FIG. 4.4. Values of $\lambda^{18}\eta^{18}/\lambda^0\eta^0$ plotted against ionic B-coefficients after Gurney. (Reproduced with permission from *Ionic Processes in Solution*. Copyright 1953. McGraw-Hill Book Company.)

expect a fairly close relation between those two properties. Gurney[2] has demonstrated this relationship by plotting ionic B-coefficients against the ratios of mobility–viscosity products at two temperatures. These ratios are simply related to the temperature coefficients of mobilities but are a more sensitive variable. The plots are linear as shown in Fig. 4.

TABLE 4.5

Entropy of Solution Values for Salts at 25°C

Solvent	Solute	$\Delta S^0 - S^*$ cal deg^{-1} mole^{-1}	B
H_2O	KI	+9·4	−0·105
H_2O	KCl	+2·1	−0·014
H_2O	NaCl	−5·7	+0·0787
H_2O	NaOH	−18·3	+0·21
CH_3OH	KCl	−30·5	+0·7635
CH_3OH	KBr	−26·8	+0·7396

S^* is the 'cratic' part of the entropy which for water at 25° ≈ 16 cal deg^{-1} mole^{-1} and for methanol ≈ 14 cal deg^{-1} mole^{-1}.

In the case of the entropy correlation, somewhat similar considerations apply. Part of the entropy of an ion in solution can be thought of as due to the degree of disorder around the ion so that like the B-coefficient its value will be affected by ion–solvent interaction. Gurney[2] has convincingly demonstrated two aspects of this relationship.

In the first instance, the B-coefficients for various salts both in aqueous and non-aqueous solution change in a predictable manner with the molar entropy of solution values, as shown in Table 4.5 above. The molar entropy of solution ΔS^0 may be defined as the difference between the molar entropy of the crystal and the partial molal entropy of the solute in a hypothetical ideal 1 M solution.

It will be observed in this table, that a positive entropy change is accompanied by a negative B-coefficient and vice versa. Also that large entropy changes as in methanol are related to correspondingly large B-coefficients. The entropy of solution, ΔS^0, has been corrected for its "cratic" contribution which is non-specific and related only to the concentration of ions in the solutions. Obviously, the section of the entropy change that is of interest is that which is dependent on the interaction of specific ions and their surroundings.

Secondly, ionic B values show a linear relationship with the partial molar ionic entropies, at least for various categories of ions. Gurney[2] obtains a single linear plot between these properties for all monatomic ions by equating the entropy of the hydrogen ion ($\bar{S}^0_{\mathrm{H}^+}$) to $-5{\cdot}5$ cal mole^{-1} deg^{-1}.

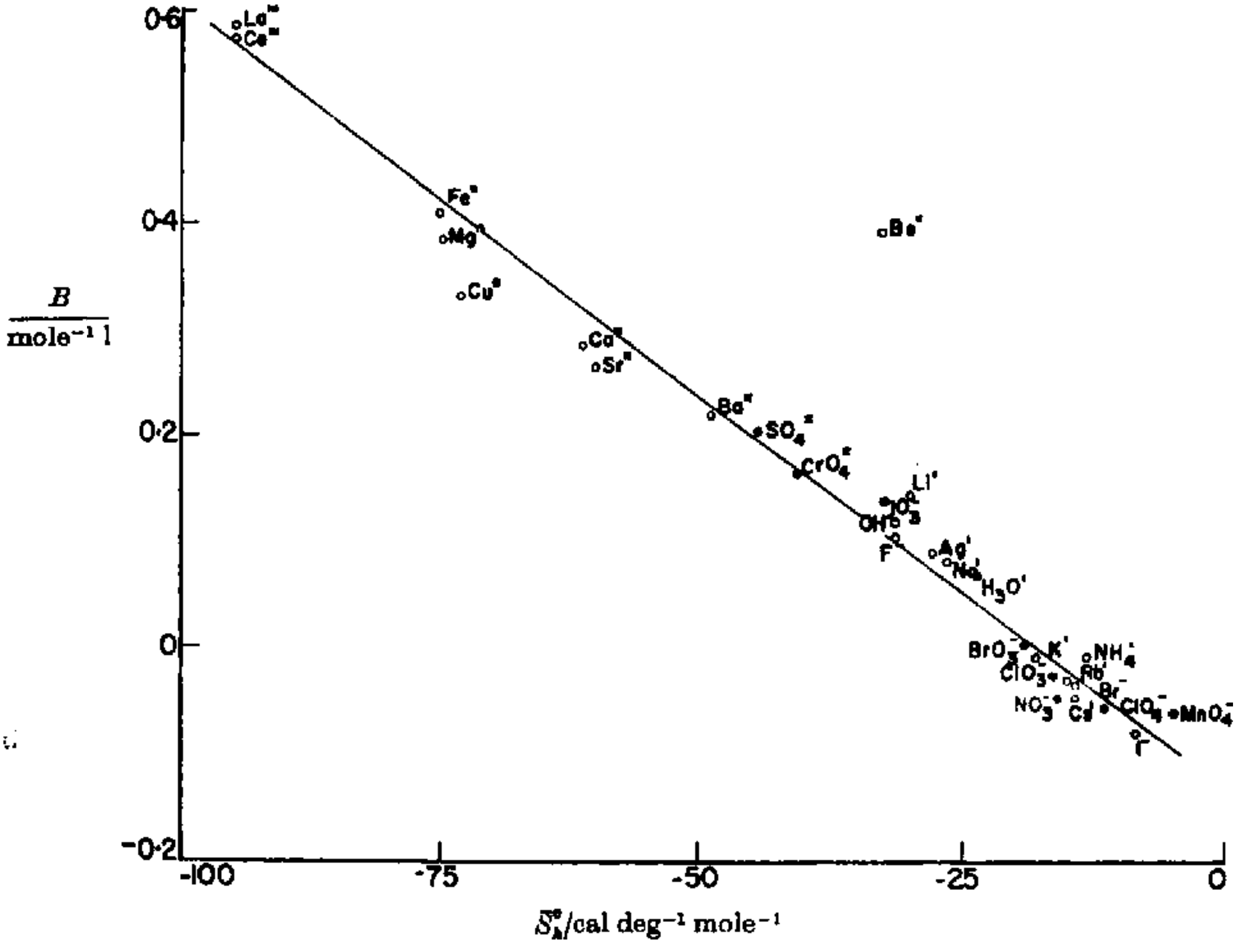

FIG. 4.5. Ionic B-coefficients plotted against partial molar entropies of hydration at 25°. (Reproduced with permission from *J. phys. Chem.*)

A further more sensitive entropy variable is the partial molar entropy of hydration, $\bar{S}^0_{\mathrm{h}}$ which is related to the entropy of solution in the following manner:

$$\bar{S}^0_{\mathrm{h}} = \bar{S}^0_{\mathrm{aq}} - \bar{S}^0_{\mathrm{g}} \tag{4.5}$$

where

$$\bar{S}^0_{\mathrm{aq}} = \bar{S}^0_{\mathrm{ref}} + \Delta S^0 \tag{4.6}$$

and $\bar{S}^0_{\mathrm{g}}$ is the calculated sum of the translational and rotational entropies of the gaseous ions. Asmus[9] used the entropy of hydration to correlate ionic B values and recently Nightingale[4] has shown that a single linear relationship can be obtained with it for both monatomic and polyatomic ions, as in Fig. 5.

Interesting as these various correlations are, it should be emphasized that they are, as yet, qualitative in nature and a quantitative theory for the B-coefficient still awaits development.

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CHAPTER 5

SHAPE AND SIZE EFFECTS

A SUSPENSION of rigid particles in a continuous medium will have a higher viscosity than the medium alone, because of interference by the particles with the stream-lines of the flow pattern. An effect of this kind will be expected in electrolyte solutions containing ions large relative to the solvent molecules; it is therefore particularly likely to contribute to the viscosity of solutions containing strongly hydrated ions such as Li^+, Mg^{++}, La^{+++}.

The first hydrodynamic treatment of this problem was given by Einstein,[1] and dealt with the case of rigid spheres suspended in a continuum. His result, restricted to the case of small volume fractions of spherical particles, is

$$\eta/\eta^0 = 1 + 2{\cdot}5\phi \tag{5.1}$$

where η is the viscosity of the suspension, η^0 that of the medium, and ϕ the volume-fraction occupied by the particles. Later treatments have elaborated on this in two ways: First, departures from spherical shape were shown to increase the coefficient 2·5.[2,3,4,5] For reasons of mathematical convenience the shapes considered have usually been ellipsoids of revolution. The early calculations assumed that the particles would be oriented with the longer axis parallel to the direction of shear in the liquid, but Simha[4] recognized that at the rates of shear normally prevailing the orientation would be effectively randomized by the Brownian motion. His results may be expressed by

$$\eta/\eta^0 - 1 = a_1\phi \tag{5.2}$$

where a_1 is a complicated function of the axial ratio but does not depend on the absolute size of the particles, provided they are large compared to the solvent molecules. The coefficient a_1 has a minimum value of 2·5 (the Einstein value) for spheres, and its variation with axial ratio is shown in Fig. 1. The increase for highly elongated particles is of great importance in connection with the viscosity of polyelectrolytes and other macromolecules, but is not particularly relevant to the simple electrolytes discussed in this volume.

Other refinements of the original Einstein treatment have attempted to deal with higher concentrations of the particles, where the flow-patterns around neighbouring particles can no longer be treated as independent. The result obtained by Vand,[6] for spherical particles, is

$$\ln \frac{\eta}{\eta^0} = \frac{2{\cdot}5\phi}{1 - Q\phi} \tag{5.3}$$

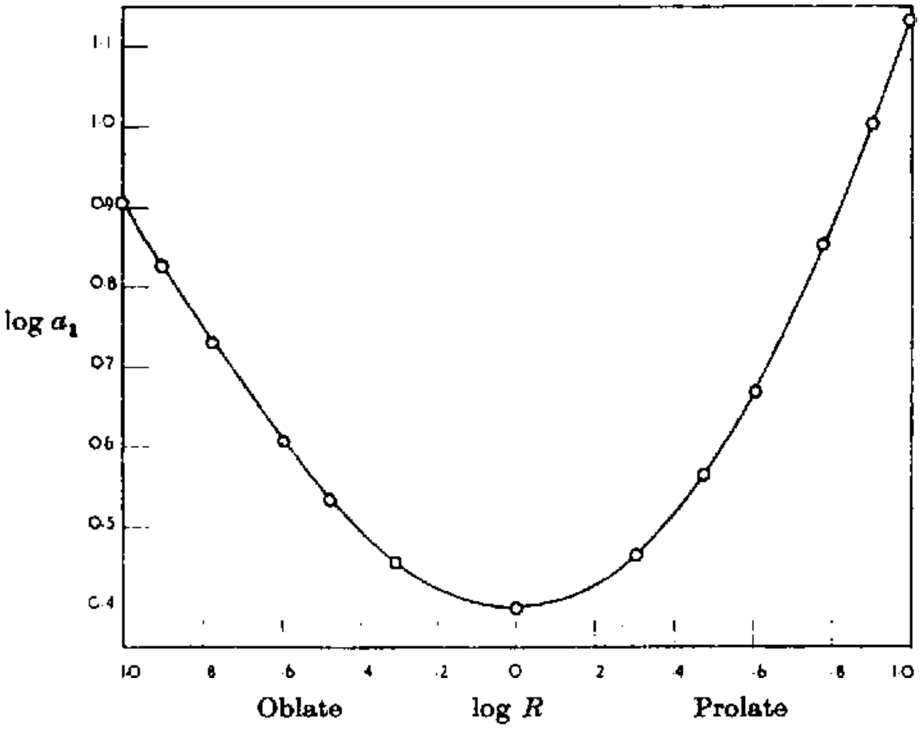

FIG. 5.1. Variation with axial ratio of coefficient a_1 from eq. (2).

where Q is an interaction coefficient which has been evaluated only approximately. This equation reduces to (1) for small volume fractions, and the logarithmic form provides a theoretical justification of the empirical Arrhenius equation

$$\ln(\eta/\eta^0) = kc. \tag{5.4}$$

In eqs. (1–3) the volume fraction ϕ must be taken to include the volume of any solvent immobilized on the surface of the particle. The validity of eq. (1) has been established experimentally[7] for suspensions of small polystyrene latex spheres (radius ~1300 Å), for which the additional volume of any water held on the surface would be negligible. Where the volume of attached solvent is a significant part of the whole, the volume fraction ϕ may be expressed by

$$\phi = cV_{\text{h}} \tag{5.5}$$

where c is the concentration (in moles l.^{-1}) and V_{h} is the molar volume of the solute *including* attached solvent (in l. mole^{-1}). It would also be reasonable to suppose that an equation of the same form as (3) would hold for higher concentrations of non-spherical particles, with the coefficient 2·5 replaced by the appropriate value a_1 of equation (2). We thus obtain

$$\ln \frac{\eta}{\eta^0} = \frac{ac}{1 - bc} \tag{5.6}$$

with $a = a_1 V_{\text{h}}$, $b = QV_{\text{h}}$.

Before considering the applicability of eq. (6) to electrolyte solutions, we should see whether it adequately describes the viscosity of non-electrolytes with fairly large rigid molecules. The sucrose molecule can be approximately regarded as an oblate[7] ellipsoid of axial ratio 0·5. For this shape, Simha's equations give $a_1 = 2{\cdot}85$. The viscosity of aqueous solutions at 25°C obeys the equation

$$\ln \frac{\eta}{\eta^0} = \frac{0{\cdot}875c}{1 - 0{\cdot}231c} \tag{5.7}$$

giving $V_{\text{h}} = 0{\cdot}875/2{\cdot}85 = 0{\cdot}307\ \text{l. mole}^{-1}$.

The apparent molar volume of sucrose in solution, based on the anhydrous molecular weight, is $0{\cdot}212\ \text{l. mole}^{-1}$. The difference between this value and V_{h} may be attributed to the presence of about five firmly attached water molecules per sucrose molecule, a figure which is quite consistent with the thermodynamic behaviour of sucrose solutions at 25°.

The smaller but more nearly spherical molecule of pentaerythritol, $C(CH_2OH)_4$, gives by a similar calculation a hydrated molar volume of $136\ \text{ml mole}^{-1}$ at 25° compared with $102\ \text{ml mole}^{-1}$ for the apparent molar volume based on the anhydrous molecular weight, implying about two molecules of water of hydration. For glucose the corresponding figure is four molecules of water, and for mannitol (treated as a prolate ellipsoid of axial ratio 2·5 : 1) it is two molecules of water. The eminently reasonable nature of these results suggests that it would be worthwhile to apply this method of calculation to the viscosities of electrolytes having hydrated ions of large effective size, in particular to polyvalent monatomic cations, for which spherical shape can safely be assumed. Equation (1) becomes

$$2{\cdot}5\phi = A\sqrt{c} + Bc \tag{5.8}$$

In Chapter 3 it was pointed out that the $A\sqrt{c}$ term is very small in comparison with Bc. It can safely be neglected then and since also $\phi = c\overline{V}_i$ we obtain

$$2{\cdot}5\overline{V}_i = B. \tag{5.9}$$

Therefore if the viscosities of large ions have a large contribution from the Einstein effect we would expect B to be approximately linear with $\overline{V}_i$.

The tetra-alkyl ammonium ions form a natural starting-point for examining the relation between the B-coefficient and the sizes of ions. For the ion $N(CH_3)_4^+$ the average radius can be calculated from crystal lattice dimensions as 2·67 Å; spheres of this radius would give according to eq. (9) a B-coefficient of 0·120, which compares well with the values of Hückel and Schaaf quoted in Table 3 (0·123 at 20°C to 0·114 at 42·5°C). For the ion $N(C_2H_5)_4^+$ the crystal radius is approximately 3·5 Å, but models with the ethyl groups fully extended show a radius of nearer 4 Å. The B values obtained by Hückel and Schaaf for this ion correspond, via eq. (9), to spheres of radius 3·8–4·0 Å. For $N(C_3H_7)_4^+$ and $N(C_4H_9)_4^+$ the B values suggest that in solution the alkyl chains are extended, with water molecules more or less immobilized in the spaces between them, but a quantitative check of the Einstein relation eq. (9) is scarcely possible, since these ions do not approximate well to spherical shape. Such difficulties would not arise with hydrated monatomic cations, which are likely to be very nearly spherical. Thus for Mg^{++} and La^{+++} at 25° the B-coefficients, interpreted wholly in terms of the Einstein effect, suggest molar volumes of 154 and 235 ml mole^{-1} for the respective hydrated ions. These volumes correspond to spheres of radii 3·94 and 4·53 Å respectively, values which are in reasonable agreement with those estimated from the ionic mobilities by Stokes' Law, viz. 3·46 and 3·95 Å. (It should be noted that Stokes' Law is known to lead to somewhat low values of radii when applied to particles as small as ions.)

Fuoss and Tuan[9] measured the partial volumes and viscosities of a number of tetra-alkyl-ammonium salts in acetonitrile. For the ions $N(C_4H_9)_4^+$, $NH(C_4H_9)_3^+$, $N(C_3H_7)_4^+$ and $B(C_6H_6)_4^-$ they found quantitative agreement between the ionic radii calculated from the molar volume and from the viscosity data, assuming behaviour in accordance with Einstein's relationship. For smaller ions, however, the viscosity data indicated larger radii than did the molar volumes; the difference was especially marked for the halide ions, and could well be due to solvation. "Structure-breaking" effects are probably absent in this solvent.

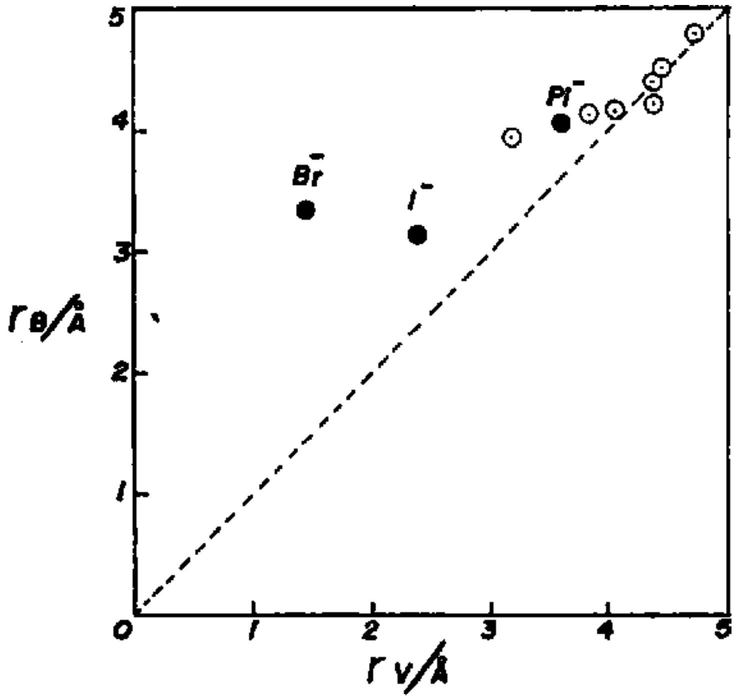

FIG. 5.2. Ionic radii of NR_4^+ salts in acetonitrile.
r_B = radius calculated from B-coefficient by eq. (9).
r_v = radius calculated from apparent molar volume.
Data from Tuan and Fuoss[9].

When it is desired to represent the viscosity at concentrations above a few tenths molar, eq. (6) is frequently superior to linear or quadratic expressions for η/η^0, and the value of a for electrolytes is generally not greatly different from the B-coefficient found from more dilute solutions. Thus the viscosities of lithium chloride at 25°C are fitted up to several molar by $a = 0{\cdot}135$, $b = 0{\cdot}0079$; the B-coefficient for lithium chloride is $0{\cdot}143$.

It may be concluded that large ions, whether they owe their size to solvation or to their intrinsic size, affect the viscosity mainly through the obstruction of streamlines, and that the effect can be calculated with reasonable accuracy by Einstein's equation (5.1) provided that the true volume-fraction of the ions in the solution can be ascertained.

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CHAPTER 6

THE MOBILITIES OF IONS IN RELATION TO VISCOSITY

QUITE early in the study of electrolytic conductance a correlation was noted between the mobilities of ions and the fluidity of the medium in which they moved. This is especially evident in the increase of conductance with temperature in a given solvent, which often parallels the increase in fluidity. Arrhenius,[1] followed later by Green,[2] noted a reduction in conductance upon the addition of sucrose which increases the viscosity. Walden,[3] as a result mainly of studies of the conductance of tetra-ethyl-ammonium picrate, proposed Walden's rule that the product of the limiting conductance and the solvent viscosity should be constant for all temperatures and solvents for a given electrolyte: $\Lambda^0\eta^0 = \text{constant}$.

This rule is fairly reliable for large organic ions in various single solvents, e.g., the product $\lambda^0\eta^0$ for tetra-ethyl-ammonium ion was found to be $0{\cdot}294 \pm 0{\cdot}001$ (λ in cm^2 ohm^{-1} equiv.$^{-1}$, η in poise) for water, methanol, ethanol, acetone, furfural acetonitrile and pyridine as solvents at 25°C, and in several of these solvents at other temperatures. More recently, however, Fuoss *et al.*[4] have shown that the rule is less exact for mixtures of polar and non-polar solvents. The electrolyte tetra-butyl-ammonium tetraphenyl boride, for example, in spite of the large size of its ions, shows a variation of the Walden product from 0·411 in pure acetonitrile to 0·386 in a mixture of 5% acetonitrile with 95% carbon tetrachloride; and the Walden product for tetra-methyl-ammonium picrate in methanol–water mixtures rises from 0·57 in water to 0·67 in 60% methanol, then falls again to 0·59 in pure methanol.

For small ions such as K^+ or Cl^- the Walden product may show variations of two- or three-fold in different solvents. In many cases the mobilities in water are anomalously high compared with other solvents, e.g., for potassium, sodium and iodide ions the Walden products in water are about twice the values in methanol or ethanol. This effect is in the wrong direction to be explained by solvation, and we are forced to conclude that for such ions the simple hydrodynamic picture is untenable.

Recently, Boyd[5] and Zwanzig[6] have examined theoretically an additional "viscous" force which should arise when an ion moves through a polar solvent, owing to the rotation of solvent dipoles and the subsequent relaxation to random orientation as the ion moves away. Boyd obtained for this dielectric retarding force on a univalent ion

$$F_D = -\frac{4}{9}\frac{e^2\tau}{\varepsilon_s r^3}\mathbf{v} \tag{6.1}$$

where e denotes the electronic charge, τ the dipole relaxation time, ε_s the static dielectric constant, and r the radius of the ion, and $\mathbf{v}$ is the velocity of the ion. Zwanzig's result, for the case of a single relaxation-time τ, is

$$F_D = -\frac{2e^2\tau}{3r^3}\frac{\varepsilon_s - \varepsilon_\infty}{\varepsilon_s^2}\mathbf{v} \tag{6.2}$$

where ε_∞ is the dielectric constant for infinite frequency and the other symbols are the same as in Boyd's equation. When ε_s is large compared with ε_∞, his result reduces to 3/2 times that of Boyd.

In contrast to the ordinary viscous force, this 'dielectric force' is proportional to $1/r^3$ instead of r; it should therefore be relatively most important for small ions. If we insert the numerical values for water in Zwanzig's formula, and compare with the Stokes' Law viscous force F_s, we find

$$r = 2\text{Å},\ F_D/F_s = 0{\cdot}56$$
$$r = 5\text{Å},\ F_D/F_s = 0{\cdot}014.$$

Remembering that F_D should be *additional* to F_s, it is difficult to understand why the mobilities of small ions in water are in fact greater than Stokes' Law predicts. A possible explanation is that the bulk viscosity of water used in the Stokes' Law calculation already contains a component due to the energy dissipation caused by the rotation of dipoles in each others' fields as one layer of water moves in shear with respect to another. Boyd's and Zwanzig's calculations do however go a long way towards providing an explanation of the effects observed by Fuoss *et al.*[4] on ion mobilities in mixed polar and non-polar solvents.

Prue and Sherrington[7] have made a detailed study of ion mobilities in dimethylformamide as solvent, and have compared their results with those in a number of solvents of similar polarity ($\varepsilon = 32$ to 47). In general the anion radii determined from Stokes' Law are fairly close to the crystal radii. These figures clearly suggest that the halide ions are "bare" in DMF, DMA and DMSO, and perhaps that they are slightly solvated in methanol. The very low values in water are the more remarkable in that the water molecule is by far the smallest among these solvents, and one would therefore expect a *better* approximation to the hydrodynamic conditions for Stokes' Law to hold in water than in the other solvents.

Solvent	"Stokes' radius" of ion (Å) Cl^-	Br^-	I^-	ClO_4^-
DMF	1·9	1·9	2·0	2·0
DMSO	—	1·7	1·7	1·7
DMA	—	2·1	2·1	2·1
Methanol	2·9	2·7	2·4	2·1
Water	1·2	1·2	1·2	1·4
Crystal radius	1·81	1·95	2·16	2·4

DMF = Dimethylformamide
DMSO = Dimethylsulphoxide
DMA = Dimethylacetamide

One is bound to conclude that the halide ions and perchlorate and nitrate ions, in some way destroy the water "structure" in their vicinity so that they are in effect moving through a less viscous medium. Such an effect has already been invoked in Chapter 4 to explain negative B-coefficients. With the majority of cations (exceptions being Rb^+, Cs^+) the Stokes' Law radii in water are greater than or equal to the crystal radii; the same was found to be true for the other solvents in the work of Prue and Sherrington referred to above. The cations, being smaller, are apparently able to retain a firmly-held layer of solvent during their motion.

It was also mentioned in Chapter 4 that the temperature-dependence of ionic mobilities in a given solvent shows important correlations with the viscosity. Large ions such as the tetra-alkyl-ammonium ions exhibit near-constancy of the product $\lambda^0\eta^0$, as do polyvalent cations, which are also effectively large because of solvation. The group which show impossibly low Stokes' radii in water, viz; Cl^-, Br^-, I^-, NO_3^-, ClO_4^-

and the larger alkali-metal ions, show a quite different temperature dependence: the $\lambda^0\eta^0$ product falls appreciably with increasing temperature. In other words, as the temperature is raised their deviation from Stokes' Law behaviour becomes less pronounced. This is consistent with the idea that they exert a structure-breaking effect, for at high temperatures the structure is already largely destroyed by thermal agitation and the ions are in a more 'normal' type of liquid environment.

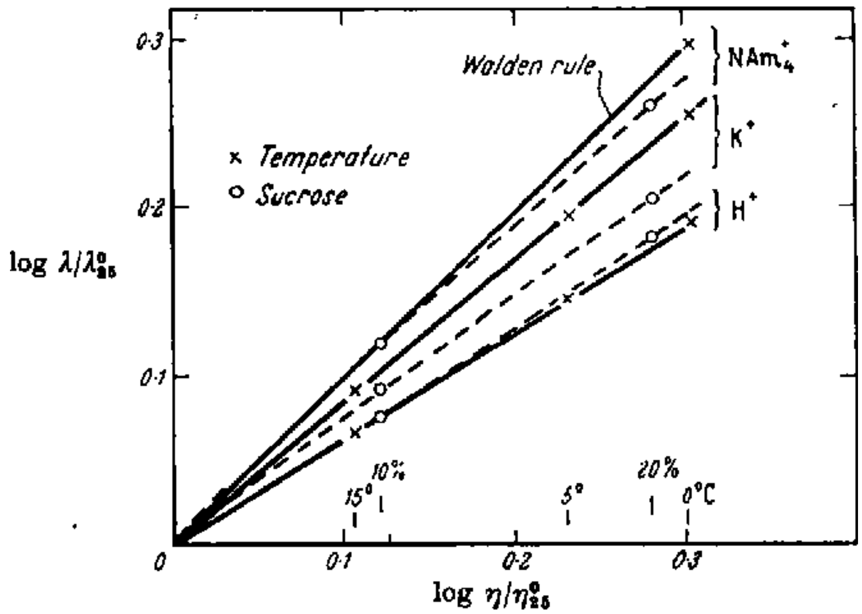

FIG. 6.1. Effects on various ions of viscosity increases caused by:
(a) addition of sucrose, ○
(b) lowering of temperatures, ×.

Ion Mobilities in Aqueous Solutions Containing Added Non-electrolytes

Non-electrolytes such as sugars increase the viscosity of water and decrease the mobility of ions in the solution. It is tempting to regard these two phenomena as cause and effect, but this is an over-simplification. To facilitate thinking about this problem it is convenient to consider the change in the 'friction' experienced by the moving ion as a result of the presence of the non-electrolyte; and to avoid complications due to interionic forces, we should evaluate this change in friction from the ion mobilities at infinite dilution. The relative friction f may be defined as

$$f = \lambda_w^0/\lambda_s^0 \tag{6.3}$$

where λ_w^0 is the mobility of the ion at infinite dilution in water, and λ_s^0 the corresponding value in the non-electrolyte solution.

For ions behaving in accordance with Stokes' Law (or Walden's rule) we should expect

$$f = \eta/\eta_0. \tag{6.4}$$

In practice (Fig. 1), we find that in solutions of sugars and similar substances there is a clear correlation between the relative viscosity and the friction experienced by the ion, but only the largest ions approach the Walden's rule prediction. There is a marked dependence on the size (or mobility) of the ion considered, the hydrogen ion being the least affected. The general pattern resembles that found when a similar graph of frictional ratio against viscosity for water at different temperatures is prepared. The inadequacy of the viscosity as a guide to ion mobility is clearly brought out by the case of 'Ficoll' solutions. This substance is a high polymer prepared by condensation of sucrose molecules; its average molecular weight is about 10^5, and it is supposed to consist of approximately spherical molecules. Though its viscosity at a given weight percentage in water is many times higher than that of a sucrose solution, its effect on the mobilities of ions is no greater than that of the same weight percentage of sucrose.[8] Presumably the polymer has a sponge-like structure with a good deal of water immobilized within it; this would explain the high viscosity, and yet permit relatively small ions to move through the polymer particles without experiencing a resistance much different from that in a sucrose solution. A somewhat similar phenomenon is seen in the relatively high mobilities of ions in gels of agar or gelatin, where the viscosity is effectively infinite. Arrhenius,[9] for example, showed that the conductivities of sodium chloride and zinc sulphate in 4·2% gelatin were only about 20% lower than in water, and were not discontinuous at the gelling temperature of 24°C. These special cases are however not especially relevant to the main problem: molecules of sucrose or mannitol are certainly not permeable to ions.

An alternative point of view is, instead of looking for direct correlations between the viscosity and the ion mobility, to regard the non-electrolyte molecules as obstructions in the path of the ions. This idea was first developed quantitatively by Fricke[10] in 1924; he found good agreement between the measured conductivity of blood and that calculated for a conducting medium (with the conductivity of the cell-free plasma) containing insulating spheroidal obstructions with the known shape of blood-cells; this agreement extended over a wide range of concentration of blood-cells relative to plasma. Other workers have treated the problem, or the mathematically equivalent one of the effective dielectric constant of a medium containing suspended particles of a different dielectric constant, and there is general agreement that for low concentrations of spherical particles the result is

$$\kappa_{\mathrm{sp}}/\kappa_{\mathrm{sp}}^0 = 1 - 3\phi/2, \tag{6.5}$$

where κ_{sp}^0 is the specific conductance of the medium in the absence of the obstructions, κ_{sp} is the observed specific conductance, and ϕ is the volume-fraction of the obstructing particles. In comparing this formula with experimental *equivalent* conductances of electrolytes at the same concentration in the presence and absence of added non-electrolytes, it must be remembered that κ_{sp}^0 refers to the solution *outside* the non-electrolyte molecules, whereas the electrolyte concentration used in calculating the equivalent conductance is conventionally based on the total volume of solution. Allowance for this effect leads to the conclusion[11] that for an electrolyte solution at a fixed low concentration c calculated on the total volume basis, the equivalent conductance Λ_s^0 in the presence of the non-electrolyte should be related to Λ_w^0, the value in the absence of the non-electrolyte, by

$$\Lambda_s^0/\Lambda_w^0 = 1 - \phi/2. \tag{6.6}$$

Comparing this with Einstein's eq. (1) for the viscosity of a solution containing suspended spherical particles

$$\eta/\eta^0 = 1 + 5\phi/2 \tag{5.1}$$

we see that the relative fall of conductance should be only one-fifth of the relative increase in viscosity. This is a limiting result which should be true only for the case where the ions and the solvent molecules are negligibly small compared with the obstructing non-electrolyte molecules. No practical case yet studied has approached these conditions but it is noteworthy that the ratio Λ_s^0/Λ_w^0 is found to lie between the limits $1 - \phi/2$ and $1 - 5\phi/2$, the latter being the value for simultaneous validity of Stokes' Law for the ionic motion and Einstein's equation for the viscosity.

An important question for the theory of electrolytic conductance is: when an electrolyte is dissolved, the viscosity of the solution is changed; to what extent does this change of viscosity affect the mobilities of the ions of the electrolyte which themselves have brought about this change? We recall that the relative viscosity of the solution is of the form:

$$\eta_{\text{rel}} = 1 + A\sqrt{c} + Bc. \tag{4.1}$$

In this equation, the square-root term arises from coulomb interactions between the ions as those in one layer move in shear past those in adjacent layers; the term $A\sqrt{c}$ represents the long-range electrostatic contribution to the retarding force on the ions in such motion. In the theory of conductance, such forces are also explicitly dealt with, giving rise to the electrophoretic and relaxation terms of the theory; it is therefore not appropriate to allow for them again as a purely viscous drag. This term should therefore be ignored in estimating the effect of the solution viscosity on the conductance. However, the square-root term is usually small compared with the linear term Bc at concentrations where the viscosity-change is substantial, so that the linear term needs more careful consideration. Unfortunately, the concentrations at which viscosity changes exceed a small fraction of one percent are usually higher than the upper limit of reliability of the mathematical treatment of the relaxation and electrophoretic effects on ionic mobility, so that it is not easy to separate purely viscous effects from other deviations from the theoretical formulae for the mobility. However, by comparing the conductance curves of salts like lithium chloride which show a marked increase of viscosity with those of others like potassium chloride where the viscosity-change is small, it becomes evident that the viscosity is in fact "felt" by the moving ions. Falkenhagen *et al.*,[12,13] Wishaw and Stokes,[14] and Campbell *et al.*,[15–20] have used the measured relative viscosity of the solution as a correcting factor in equations of the form

$$\Lambda = \Lambda'\eta^0/\eta \tag{6.7}$$

where Λ' is the equivalent conductance calculated from Onsager's equation with appropriate modifications to account for the effects of finite ion size. Fuoss *et al.*,[21] in their extremely detailed recent treatments of electrolytic conductance have also introduced a factor representing the effect of solution viscosity, based on the Einstein expression for a suspension of spherical particles. There is some evidence, particularly that derived from studies[22] of the mobilities of ions in solutions of non-electrolytes, which suggest that (7) represents an over-correction in the case of ordinary small ions; the correction factor should perhaps be more nearly $(\eta^0/\eta)^{0\cdot7}$. Closely related to the conductance are diffusion phenomena in electrolyte solutions, and here too the solution viscosity must be considered when dealing with concentrations above a few hundredth molar. The ordinary diffusion of an electrolyte down a concentration-gradient is an extremely complex process, involving simultaneous motion of the ions in one direction and solvent in the other, as well as the often marked non-ideality of the gradient of chemical potential. Even for non-electrolyte solutions there is as yet no completely successful theoretical treatment of these effects. The process of tracer-diffusion is however somewhat more amenable to theoretical treatment.

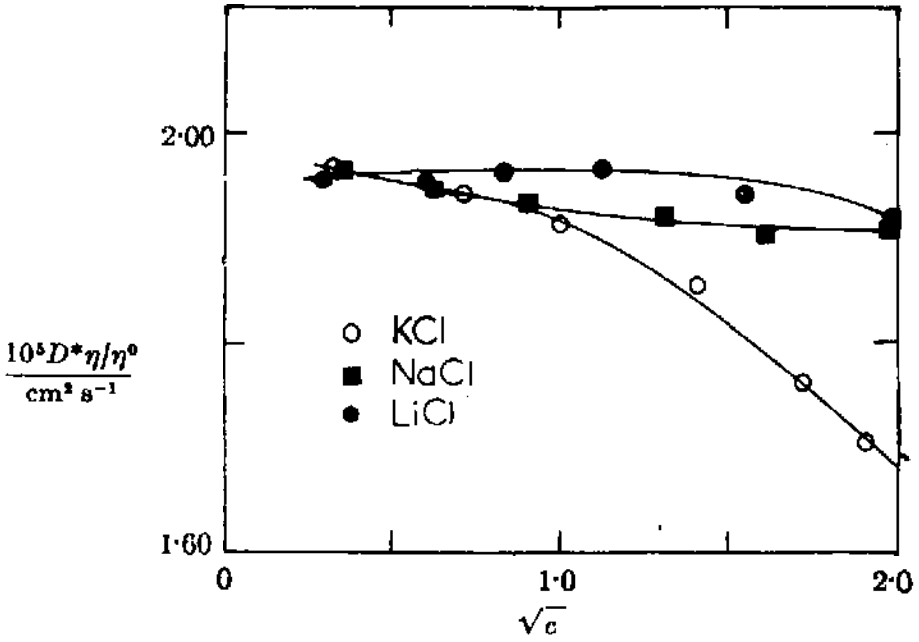

FIG. 6.3. Plot of iodide tracer diffusion data (from Fig. 2) multiplied by relative viscosity showing effect of viscosity correction.

In tracer-diffusion we are concerned with the diffusional motion of one species of ion which is present at vanishingly low concentrations in an otherwise uniform supporting electrolyte. The diffusing ion may be an isotopic variety of one of those of the supporting electrolyte, or an ion of different chemical species. The diffusion of iodide ion in alkali chloride solutions has been rather fully studied,[23] and leads to some useful conclusions about the effect of viscosity on diffusion. Figure 2 shows the variation in the tracer-diffusion coefficient of I^- with alkali chloride concentration, and Fig. 3 shows the product $D^*\eta/\eta^0$. The marked differences between the curves for different electrolytes are greatly reduced by the introduction of the viscosity "correction", but the order of the curves is reversed. This is further

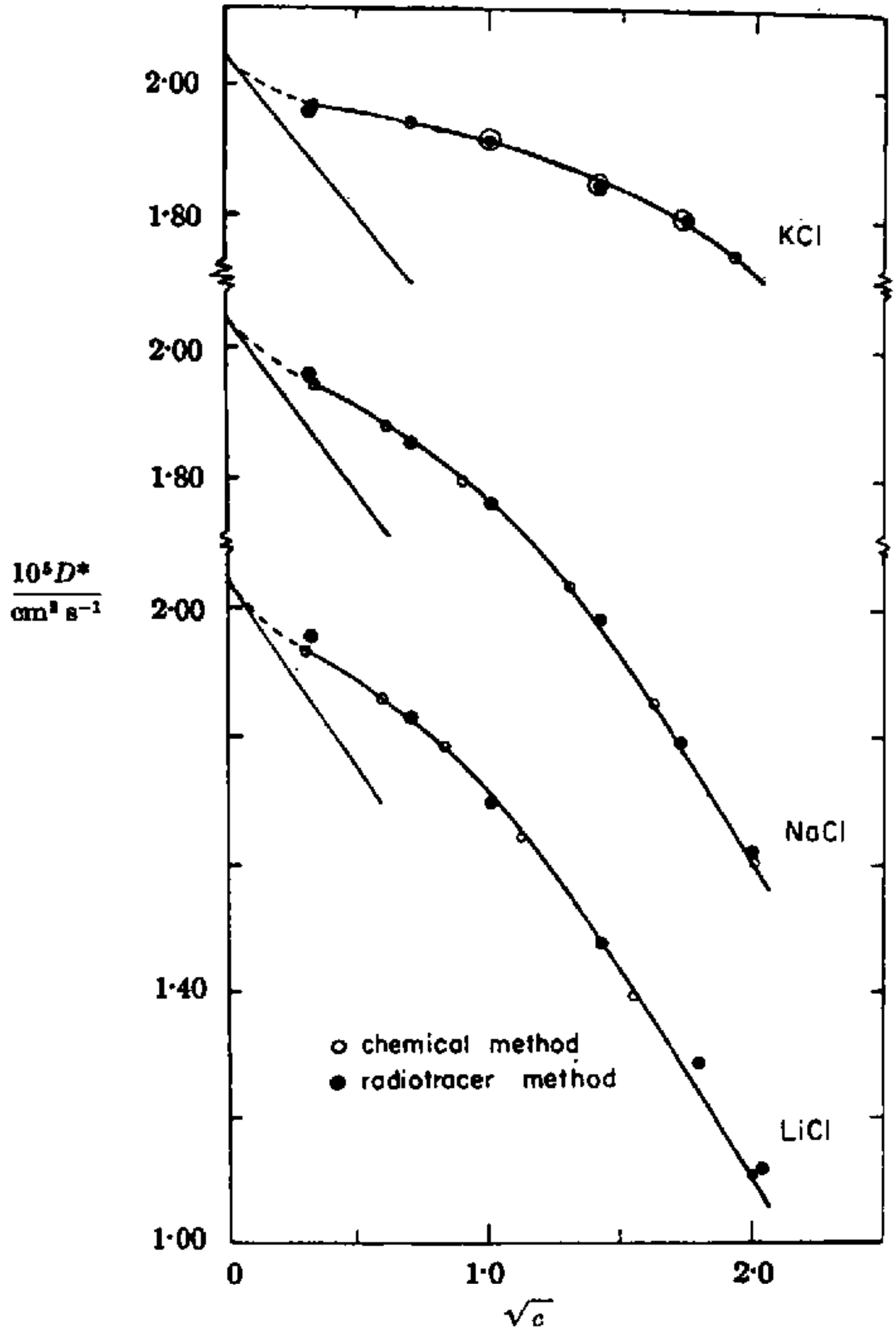

FIG. 6.2. Tracer-diffusion coefficients of iodide ion in aqueous alkali chloride solutions at 25°C. After Stokes, Woolf and Mill.

evidence that the first power of the relative viscosity *over-corrects* the mobility of small ions. The curves are brought even close together by a correction factor $(\eta/\eta^0)^{0\cdot7}$, which also accounts fairly well for the limiting equivalent conductances of iodide ion in solutions containing added non-electrolytes.

A question that is often raised regarding the relation of viscosity to other transport processes such as diffusion and conduction, concerns the Curie principle. According to this principle macroscopic causes always have fewer elements of symmetry than the effects they produce. In our context this means that fluxes and forces of different tensorial character do not couple and since the forces causing viscous flow are tensorial and those producing conduction and diffusion are vectorial, we should expect no direct relationship. The principle is well discussed by de Groot.[24] Nevertheless, there are obvious empirical correlations between the two types of processes and since such relationships are useful, we should have no qualms about employing or extending them.

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CHAPTER 7

CONCENTRATED SOLUTIONS AND MOLTEN SALTS

In Chapters 3 and 4 it was pointed out that the electrostatic theory was applicable in aqueous electrolyte solutions up to about 0·002 M and that description of viscosity in terms of B-coefficients extended in general to about 0·1 M. In this chapter we shall be concerned with solutions in the range 1 M to saturation and also with molten salts.

The property usually studied in this concentrated region is the temperature dependence of the viscosity. In pure liquids and in molten salts such dependence has been represented in the great majority of cases by a semi-empirical equation, attributed to Andrade[1] which is

$$\eta = A \exp b/T \tag{7.1}$$

where A and b are constants.

If viscous flow is treated as a rate process then (1) can be expressed as an Arrhenius-type equation of the form

$$\eta = A \exp E_{\text{vis}}/RT \tag{7.2}$$

where E_{vis} is the experimental energy of activation. Equation (2) can be differentiated to give

$$E_{\text{vis}} = R\partial \ln \eta/\partial \left(\frac{1}{T}\right) \tag{7.3}$$

and E_{vis} is therefore determined from a plot of ln η against $1/T$.

A more sophisticated type of equation containing this exponential dependence has been developed by Eyring *et al.*[2] from rate process theory and has now come into common use for interpreting effects in the concentration region under review. The Eyring rate process approach to viscous flow is widely known and no detailed exposition is needed here. In essence the model treats the liquid as a lattice with a certain proportion of the lattice points consisting of holes. Molecules or ions are visualized as being able to make a jump from one lattice position into a hole at an adjoining point. In so doing the molecules pass through an activated or transition state to which various thermodynamic quantities are related. At equilibrium the potential barriers to movement are equal in all directions but when a shearing force is imposed on a liquid, molecules moving in the direction of shear will be given an extra energy increment, so that net movement is produced.

The final equation from the Eyring approach is

$$\eta = (hN/V) \exp \Delta G^*/RT \tag{7.4}$$

$$= (hN/V) \exp (\Delta H^*/RT - \Delta S^*/R) \tag{7.5}$$

where h is Planck's constant, V the molar volume, N the Avogadro number, ΔG^*, ΔH^* and ΔS^*, the free energy, heat and entropy of activation respectively. If V and ΔS^* are taken as constant, (5) reduces to

$$\eta = A \exp \frac{\Delta H^*}{RT} \tag{7.6}$$

which is essentially of the same form as (2) so that E_{vis} can be equated to ΔH^* in this instance.

As mentioned in the second paragraph, these equations were derived for pure non-associated liquids and within this class, good agreement with experiment is obtained in a large number of cases. In associated liquids such as water or alcohols, viscous flow involves distortion of structure in addition to normal molecular friction. Extra energy is therefore needed to promote flow in structured liquids and it is termed 'structural activation energy'.

The amount of structure in an electrolyte solution where the solvent is an associated liquid will in general depend on both temperature and concentration. Temperature will affect the structure through the amount of thermal movement. Concentration alters structural characteristics by reason of ion–solvent interaction; the extent of alteration will depend on the types of ions present and their average separation. For both effects it can be seen that the magnitude of the entropy change over a range of temperature or concentration will be dependent on the amount of structure present. The assumption that ΔS^* is constant is not necessarily valid and (5) may not then reduce to (2).

Concentrated Solutions

In view of the effect of structure just described, electrolytes in associated solvents might not be expected to obey the simple linear law. Nevertheless, many electrolyte systems of this type do show linearity in their log η vs. $1/T$ plots. Dawson, Hagstrom and Sears[3] have shown that solutions of LiBr in methanol–acetone mixtures obey the Andrade type equation up to concentrations of 2 M and Kotorlenko, Golik and Kovneristaya[4] report comparable results for LiCl in alcohol mixtures. In dilute aqueous solutions linearity is not in general observed and in concentrated solutions there are conflicting results. For example Miller and Doran[5] report that their viscosity data for NaSCN, $NaClO_4$ and NaI in the range 2–10 M do not have the linearity implied by (1). Gopal[6] states that potassium salts in supersaturated solutions follow Andrade's equation although $MgSO_4$ and $KCOOCH_3$ do not. Again, Suryanarayana and Venkatesen[7] show that KCl, NaCl, KNO_3, $CuSO_4$ and $ZnSO_4$ have the requisite linear dependence from 1 M to saturation.

If the last-mentioned agreement is real a possible explanation may be given in terms of a model for aqueous electrolytes recently proposed by Satoh.[8] The normal water structure in concentrated solutions ($>$ 1 M) is considered to be broken down due to interaction between ionic hydration shells. The ions can then be pictured as embedded in a different solvent from that in the dilute range. Such solutions could then conform to the simple Andrade-type equation. In view of the conflicting experimental evidence in concentrated solutions however, such concepts must remain rather conjectural.

Recently, there have been attempts to use the Eyring equations (4) and (5) to calculate entropies of activation in concentrated electrolyte solutions both for salts as a function of concentration and for a series of ions at the same concentration. The aim of such studies is to gain information on ion–solvent interaction in this region in an analogous manner to the use of B-coefficients in dilute solution.

Miller and Doran[5] in their study measured the viscosities of concentrated aqueous solutions of NaSCN, $NaClO_4$, NaI and LiCl over a range of temperatures. As mentioned previously plots of the logarithm of the viscosities of these solutions against $1/T$ are not linear. Nevertheless, they are sufficiently close to calculate an approximate value of E_{vis} for the range. If E_{vis} is equated to ΔH^* and ΔG^* is calculated from another form of (4), i.e.

$$\Delta G^* = RT \ln \frac{\eta V}{hN} \tag{7.6}$$

then ΔS^* can be obtained from (5). A representative selection of these data is given in Table 1.

It will be observed that at concentrations around 2 M the value of ΔS^* is less than that of water indicating the added salt has an initial structure-breaking effect. At really high concentrations (> 8 M) the entropy values rise sharply and this rise can be interpreted in terms of the appearance of local order. From partial molal entropy values for both water and the various salts in their concentrated solutions, Miller and Doran infer that in the case of NaSCN, $NaClO_4$ and NaI this order is of the type found in molten salts where a high degree of local order may extend over several ionic diameters. In the case of LiCl however, the order suggested by the high ΔS^* values is, on the evidence available, most likely related to the hydration of the Li^+ ion.

TABLE 7.1

Free Energy, Heat and Entropy of Activation for Viscous Flow

	c m l^{-1}	ΔG^* kcal $mole^{-1}$	ΔH^* kcal $mole^{-1}$	ΔS^* cal deg^{-1} $mole^{-1}$
Water		2·17	3·89	5·7
NaSCN	2	2·27	3·63	4·5
	7	2·88	4·44	5·2
	9	3·30	5·70	7·9
	10	3·55	8·18	15·3
$NaClO_4$	2	2·26	3·54	4·2
	7	2·97	4·68	5·6
	9	3·45	8·70	17·3
	9·5	3·59	9·85	20·7
NaI	2	2·22	3·40	3·9
	6	2·59	3·90	4·3
	8	2·92	4·42	5·0
LiCl	10·75	3·38	4·68	4·3
	13	3·72	8·50	15·7

An alternative method of approach was adopted by Nightingale and Benck[9] who calculated ΔS^* values of both salts and ions in aqueous solutions at 25°C. As above, ΔG^* values were calculated from (6). To obtain a value for E_{vis}, the Jones–Dole equation (4.1) was substituted for η in (3) with neglect of the small electrostatic term giving

$$E_{\text{vis}} = R\,\frac{\mathrm{d}\ln \eta^0}{\mathrm{d}(1/T)} + \frac{1}{1 + Bc} \times \frac{\mathrm{d}(1 + Bc)}{\mathrm{d}(1/T)}. \tag{7.7}$$

Using B-coefficient values obtainable in the literature, E_{vis} was calculated for various salts and equated to ΔH^*. ΔS^* values for these salts were thus obtained and then divided into ionic ΔS^* contributions in an analogous manner to that used for B-coefficients. In general the hydrated or order-producing ions with positive B-coefficients have positive activation energies, whereas structure-breaking ions with negative coefficients have negative activation energies. In part this is a reflection of the B-values used in the calculation so adds little new information. Certain marginally hydrated ions such as Ba^{++}, IO_3^- and SO_4^{-2}, however, have positive B-coefficients and negative activation energies. This is probably due to their having positive dB/dT values and these authors suggest that there may be increased hydration at higher temperatures. As mentioned in Chapter 4 the reality of this effect is very arguable.

An exponential relation showing the concentration dependence of the viscosity in concentrated electrolytes also deserves mention in this chapter. This is an empirical equation proposed by Suryanarayana and Venkatesen[7]

$$\eta = \eta^0 \exp(BC_p) \tag{7.8}$$

where B is a constant which is considered to be related to specific properties of the solute and C_p is the ratio of the mole fraction of the solute at any given concentration to that at saturation at the same temperature. The equation has been extensively tested on many systems by the above workers. They propose that the internal pressure of the solution is the fundamental property which determines the viscosity and other transport processes in solutions. At this stage it is difficult to evaluate the significance of this correlation.

Molten Salts

Molten salts in the respect that they are of uniform composition and resemble pure liquids might be expected to obey (2) and in fact it is found to be valid for a large number of systems. Figure 1 for melts of the alkali carbonates illustrates the typical linear plots obtained. In such studies the activation energies for viscous flow, E_{vis} have been determined using (3) and being independent of temperature serve as a very useful standard of comparison between various salts.

Since no theory comparable to the interionic attraction theory for dilute solutions of electrolytes exists for molten salts, their viscosity data can only be used to make comparisons of a qualitative nature. Nevertheless information on such properties as transport mechanisms and states of aggregation can be inferred from such data. For a detailed discussion on these qualitative theories, review articles such as that by Harrap and Heymann[10] should be consulted. To illustrate the manner in which viscosity measurements can be used to gain information, we have selected a recent precise study on the alkali metal carbonates by Janz and Saegusa.[11]

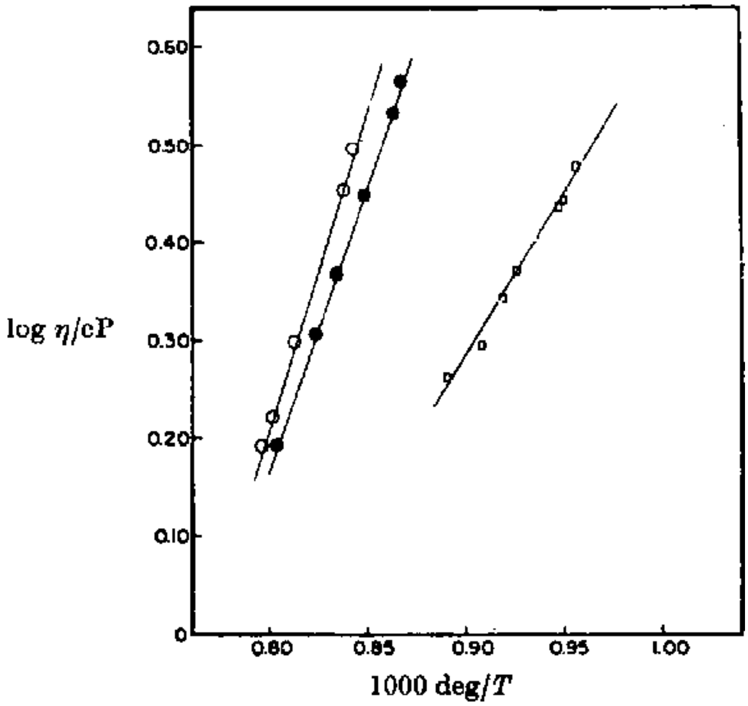

FIG. 7.1. Plot of the logarithm of the viscosity against the reciprocal of the absolute temperature for the molten salt systems:
○, Na_2CO_3, ●, K_2CO_3, □, Li_2CO_3
(Reproduced with permission from *J. electrochem. Soc.*)

In the first instance the measured activation energies for viscous flow and conductance in such melts show considerable differences and this is true of most molten salt systems. In Table 2, we reproduce the E_{vis} and E_{Λ} data of the above workers.

Examination of this table shows that there is evidently no simple relationship between conductance and viscosity of the type described in Chapter 6 and that the activation energies for viscous flow are greater than those for conductance. The explanation offered for this effect is that in conductance the smaller or more mobile ion can carry most of the current whereas in viscous flow both ions are involved due to electrical neutrality requirements. On the Eyring model larger holes would need to be created to accommodate the anions and since the energy of hole formation may account for a large part of the activation energy, this would lead to an increased E_{vis}. This is supported by the fact that the E_{vis} values for the carbonate melts have very high values compared with the chloride ones, reflecting the larger size of the carbonate ion.

TABLE 7.2

Comparison of Activation Energies of Electrical Conduction and Viscous Flow

Salt	m.p. °C	E_Λ kcal mole^{-1}	E_{vis} kcal mole^{-1}	$\frac{E_{\text{vis}}}{E_\Lambda}$
LiCl	610	2·06	5·6	2·7
NaCl	808	2·92	12·2	4·2
KCl	772	3·36	7·6	2·3
Li_2CO_3	726	4·40	16·9	3·8
Na_2CO_3	858	4·18	25·7	6·1
K_2CO_3	899	4·65	29·1	6·3

Janz and Saegusa also use the Eyring equation (5) to calculate values for ΔS^*, E_{vis} being equated to ΔH^*. Values of ΔS^* for Li_2CO_3, Na_2CO_3 and K_2CO_3 are 3·8, 9·9 and 11·9 cal deg^{-1} mole^{-1} respectively. These are of comparable magnitude suggesting a common type of transport process and the positive values, characteristic of association, give support to the postulate that paired ions of the type $[M^+CO_3^=]^-$ are formed. The existence of such pairs has been independently proposed from conductance and X-ray studies.

In concluding this chapter, it is of interest that somewhat similar methods for the interpretation of viscosity measurements are being used for both concentrated electrolyte solutions and molten salts. In recent years, a number of people have expressed the view that any theoretical treatment of concentrated solutions would best be approached from the molten salt region and not from dilute solution theory. The studies described here tend to reinforce this view.

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LIST OF APPENDICES

EXPLANATORY NOTES ON APPENDICES

Appendix 1 lists viscosity and density data which are commonly used for the calibration of viscometers.

Appendices 2 and 3 contain the relative viscosities of many electrolytes in aqueous and non-aqueous solutions. As the International Critical Tables list viscosity data up to about 1929, this compilation is confined to studies in the period 1929–1963. The tabulation has also been condensed in the following manner. For solutions more dilute than about 0·1 M, we have given equations of the Jones–Dole type where these reproduce the data to 0·1% or better. The accuracy of fit to these equations is indicated by listing the average deviation (δ) in the 'Remarks' column.

Electrolytes are listed alphabetically by the name (not the symbol) of the cation throughout Appendix 2. In Appendix 2.2, the solvents are listed in alphabetical order and in each solvent the electrolytes are listed as above. In Appendix 2.3, mixed solvents are listed by the solvent which comes first alphabetically. Concentrations are expressed wherever possible by the molarity denoted by c (moles of electrolyte per litre of solution). In certain cases, however, the molality denoted by m (moles of electrolyte per 1000 grams of solvent) has been retained for convenience of tabulation where comparisons are made over a wide range of temperature. Relative viscosities (viscosity of solution/viscosity of solvent at same temperature and pressure) are, with one or two exceptions, used throughout Appendix 2.

For Appendix 3, an explanatory note regarding listing and concentration units precedes the tabulation.

APPENDICES

APPENDIX 1.1

Viscosity and Density of Water over Temperature Range 0–100°C

Temp. °C	Density g ml^{-1}	Viscosity cP	Remarks	Ref.
0	0·99987	1·787	Viscosities reported in Landolt–Börnstein are on average 0·2% higher in range 0–20°C and 0·2% lower in range 20–100°C. However, the data in this table obtained from more recent work are probably more reliable	(1), (2), (3), (4)
5	0·99999	1·516		
10	0·99973	1·306		
15	0·99913	1·138		
18	0·99862	1·053		
20	0·99823	1·002		
25	0·99707	0·8903		
30	0·99568	0·7975		
35	0·99406	0·7194		
38	0·99299	0·6783		
40	0·99224	0·6531		
45	0·99024	0·5963		
50	0·98807	0·5467		
55	0·98573	0·5044		
60	0·98324	0·4666		
65	0·98059	0·4342		
70	0·97781	0·4049		
75	0·97489	0·3788		
80	0·97183	0·3554		
85	0·96865	0·3345		
90	0·96534	0·3156		
95	0·96192	0·2985		
100	0·95838	0·2829		

1. Swindells, Coe and Godfrey, *J. res. Nat. Bur. Stand.*, 1952, **48**, 1.
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APPENDIX 1.2

Viscosity and Density of Aqueous Sucrose Solutions from 15 to 25°C

°C	Composition wt. % in vacuum	Density g ml^{-1}	Viscosity cP	Remarks	Ref.
15	20	1·08233	2·254	The viscosity data are based on measurements made at the National Bureau Standards Washington, U.S.A. and are considered to be accurate to about 0·1%	(1) viscosity (2) density
	30	1·12863	3·757		
	40	1·17837	7·463		
	50	1·23173	19·53		
	60	1·28884	79·49		
	70	1·34976	746·9		
20	20	1·08096	1·945		
	30	1·12698	3·187		
	40	1·17645	6·167		
	50	1·22957	15·43		
	60	1·28646	58·49		
	70	1·34717	481·6		
25	20	1·07940	1·695		
	30	1·12517	2·735		
	40	1·17439	5·164		
	50	1·22732	12·40		
	60	1·28399	44·03		
	70	1·34452	321·6		

1. *Handbook of Chemistry and Physics*, 43rd ed. 1961–62, p. 2226.
2. TIMMERMANS, *Physico-Chemical Constants of Binary Systems*, Interscience, N.Y., 1960, Vol. 4.

APPENDIX 1.3

Viscosities and Densities of some Common Electrolytic Solvents
(Temperatures 25°C unless otherwise stated)

Solvent	Density g ml^{-1}	Viscosity cP	Ref.
Water	0·99707	0·8903	(1), (2), (3), (4)
Acetone	0·7850	0·3031	
Acetonitrile	0·7768	0·343	
Ammonia (−34°C)	0·6826	0·2550	
Benzene	0·8737	0·6010	
o-Dichlorobenzene	1·3003	1·95	
1:1 Dichloroethane	1·1667	0·465	
1:2 Dichloroethane	1·2453	0·785	
Dimethylacetamide	0·9366	0·916	
Dimethylformamide	0·9443	0·796	
Dimethylpropionamide	0·9205	0·932	
Dimethylsulphoxide	1·0958	1·95	
Dioxan	1·0269	1·192	
Ethanol	0·7851	1·075	
Ethylenediamine	0·8922	1·54	
Formamide	1·1292	3·292	
Glycerol	1·2583	942	
Hydrogen cyanide (18°C)	0·6900	0·205	
Hydrogen peroxide (20°C)	1·4489	1·24	
Methanol	0·7868	0·5429	
N-Methylacetamide (40°C)	0·9420	3·011	
N-Methylbutyramide (30°C)	0·9068	7·450	
N-Methylformamide	0·9976	1·65	
N-Methylpropionamide (30°C)	0·9269	4·554	
Nitrobenzene	1·1986	1·819	
n-Propanol	0·7995	1·924	
Pyridine	0·9779	0·8798	
Sulphuric acid	1·8255	24·47	

1. Timmermans, *Physiochemical Constants of Pure Organic Compounds*, Elsevier, 1950.
2. Weissberger and Proskauer, *Organic Solvents*, Interscience Publishers Inc., New York, 1955.
3. Kraus and collaborators.
4. Walden and collaborators.

The values given in this appendix were mostly selected from the above references, and have been, where considered necessary, adjusted to the currently accepted value for the viscosity of water at 20°C, 1·002 cP.

APPENDIX 2.1

Relative Viscosity of Aqueous Electrolyte Solutions

AMMONIUM BROMIDE—NH_4Br

Temp. °C	c	η/η^0	Remarks	Ref.
35	0·0005 to 0·25	$1 + 0{\cdot}0051\sqrt{c} + 0{\cdot}0032c$	$\delta < 0{\cdot}01\%$	(1)

1. DAS, *J. Ind. Chem. Soc.*, 1954, **31**, 170.

Tetramethyl—AMMONIUM BROMIDE—$N(CH_3)_4Br$

m	η/η^0			Remarks	Ref.
	20°C	25°C	30°C		
0·0005137	1·0000	1·0002	1·0004	Ref. (1) quotes for Jones–Dole eq. $A_{20} = 0{\cdot}0062$ $A_{25} = 0{\cdot}0066$ $A_{30} = 0{\cdot}0064$ $B_{20} = 0{\cdot}0627$ $B_{25} = 0{\cdot}1014$ $B_{30} = 0{\cdot}137$ but accuracy of fit not given	(1)
0·0009992	1·0003	1·0003	1·0005		
0·002997	1·0007	1·0007	1·0009		
0·009939	1·0012	1·0017	1·0021		
0·01685	1·0018	1·0026	1·0033		
0·03384	1·0033	1·0046	1·0059		
0·06015	1·0053	1·0076	1·0099		
0·1013	1·0082	1·0122	1·0161		
0·4065		1·0434			
1·043		1·1060			

1. NIGHTINGALE, *J. phys. Chem.*, 1962, **66**, 894.

Tetraethyl—AMMONIUM BROMIDE—$N(C_2H_5)_4Br$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00418 to 0·03542	$1 + 0{\cdot}0082\sqrt{c} + 0{\cdot}343c$	$\delta \sim 0{\cdot}01\%$	(1)

1. LAURENCE and WOLFENDEN, *J. chem. Soc.*, 1934, 1144.

AMMONIUM CHLORIDE—NH_4Cl

Temp. °C	c	η/η^0	Remarks	Ref.
12·5	0·001 to 0·60078	$1 + 0{\cdot}0049\sqrt{c} - 0{\cdot}0395c$	$\delta < 0{\cdot}01\%$	(1)
15	0·001 to 0·60055	$1 + 0{\cdot}00498\sqrt{c} - 0{\cdot}0337c$	$\delta < 0{\cdot}01\%$	(1)
25	0·00099 to 0·59930	$1 + 0{\cdot}0052\sqrt{c} - 0{\cdot}0144c$	$\delta < 0{\cdot}01\%$ Values from Ref. (2) to 0·2 M are on average 0·01% higher	(1) (2)
35	0·00099 to 0·59729	$1 + 0{\cdot}0052\sqrt{c} + 0{\cdot}0022c$	$\delta < 0{\cdot}01\%$ Values from Ref. (3) to 0·25 M agree to ± 0·01%	(1) (3)
42·5	0·00099 to 0·5958	$1 + 0{\cdot}0053\sqrt{c} + 0{\cdot}0139c$	$\delta < 0{\cdot}01\%$	(1)

1. KAMINSKY, *Z. phys. Chem.* (N.F.), 1955, **5**, 154.
2. JONES and TALLEY, *J. Amer. chem. Soc.*, 1933, **55**, 624.
3. DAS, *J. Ind. Chem. Soc.*, 1954, **31**, 170.

Tetramethyl—AMMONIUM IODIDE—$N(CH_3)_4I$

Temp. °C	c	η/η^0	Remarks	Ref.
12·5	0·001 to 0·10012	$1 + 0{\cdot}0059\sqrt{c}$ $+ 0{\cdot}0319c$	$\delta < 0{\cdot}01\%$	(1)
20	0·001 to 0·1	$1 + 0{\cdot}0060\sqrt{c}$ $0{\cdot}0423c$	$\delta < 0{\cdot}01\%$	(1)
25	0·001 to 0·09988	$1 + 0{\cdot}0062\sqrt{c}$ $+ 0{\cdot}0490c$	$\delta < 0{\cdot}01\%$	(1)
30	0·001 to 0·09974	$1 + 0{\cdot}0063\sqrt{c}$ $+ 0{\cdot}0564c$	$\delta < 0{\cdot}01\%$	(1)
35	0·00099 to 0·09958	$1 + 0{\cdot}0064\sqrt{c}$ $+ 0{\cdot}0616c$	$\delta < 0{\cdot}01\%$	(1)
42·5	0·00099 to 0·0993	$1 + 0{\cdot}0065\sqrt{c}$ $+ 0{\cdot}0678c$	$\delta < 0{\cdot}01\%$	(1)

1. HÜCKEL and SCHAAF, *Z. phys. Chem.* (N.F.), 1959, **21**, 326.

Tetraethyl—AMMONIUM IODIDE—$N(C_2H_5)_4I$

Temp. °C	c	η/η^0	Remarks	Ref.
12·5	0·001 to 0·06508	$1 + 0{\cdot}0070\sqrt{c} + 0{\cdot}3311c$	$\delta < 0{\cdot}01\%$	(1)
20	0·001 to 0·065	$1 + 0{\cdot}0070\sqrt{c} + 0{\cdot}3189c$	$\delta < 0{\cdot}01\%$	(1)
25	0·001 to 0·09988	$1 + 0{\cdot}0072\sqrt{c} + 0{\cdot}3122c$	$\delta < 0{\cdot}01\%$	(1)
30	0·001 to 0·09974	$1 + 0{\cdot}0071\sqrt{c} + 0{\cdot}3042c$	$\delta < 0{\cdot}01\%$	(1)
35	0·001 to 0·07469	$1 + 0{\cdot}0072\sqrt{c} + 0{\cdot}3006c$	$\delta < 0{\cdot}01\%$	(1)
40	0·00099 to 0·07455	$1 + 0{\cdot}0075\sqrt{c} + 0{\cdot}3033c$	$\delta < 0{\cdot}01\%$	(1)

1. HÜCKEL and SCHAAF, *Z. phys. Chem.* (N.F.), 1959, **21**, 326.

AMMONIUM NITRATE—NH_4NO_3

Temp. °C and Ref.	c	η/η^0	Temp. °C and Ref.	c	η/η^0
25 (1)	0·009893	0·999	25 (1)	0·10001	0·995
	0·020033	0·998		0·15363	0·993
	0·029175	0·998		0·20090	0·990
	0·039970	0·997		0·30230	0·986
	0·047956	0·996		0·39993	0·982
	0·050005	0·998		0·49647	0·977
	0·059997	0·996		0·59710	0·975
	0·070046	0·997		0·69976	0·973
	0·079920	0·996		0·79943	0·968
	0·089968	0·996		0·90237	0·967

AMMONIUM NITRATE—NH_4NO_3—(*continued*)

Temp. °C and Ref.	c	η/η^0	Temp. °C and Ref.	c	η/η^0
25 (1)	0·99976	0·963	35 (2)	3·9749	1·0619
	1·0261	0·9699		5·5065	1·1714
	1·7009	0·9619		7·1318	1·3550
	1·9184	0·9616		7·6705	1·4352
	2·4611	0·9664		9·4086	1·8003
	3·9940	1·0115		10·749	2·2434
	5·5346	1·1059		11·95 (Sat.)	2·8923
	7·1685	1·2719	95 (3)	0·1940	1·016
	7·7100	1·3476		0·9963	1·054
	9·4584	1·6901		1·525	1·076
	10·8027	2·1139		2·576	1·142
	11·08 (Sat.)	2·2442		3·600	1·217
35 (2)	0·009864	0·999		4·221	1·296
	0·019972	0·999		6·632′	1·555
	0·029087	0·999		7·95	1·777
	0·039851	0·998		8·74	1·913
	0·047808	0·997		10·12	2·381
	0·049851	0·998		11·13	2·705
	0·059813	0·998		13·31	3·89
	0·069828	0·998		14·81	4·29
	0·079673	0·997	180 (4)	0·0891	1·011
	0·089684	0·997		0·987	1·093
	0·099691	0·998		1·920	1·168
	0·15315	0·996		2·973	1·268
	0·20026	0·995		4·125	1·395
	0·30130	0·992		5·127	1·524
	0·39859	0·992		6·211	1·715
	0·49478	0·988		7·029	1·862
	0·59498	0·987		7·851	2·055
	0·69727	0·987		8·534	2·237
	0·79655	0·984		9·165	2·307
	0·89905	0·984		10·67	2·819
	0·99578	0·982		12·16	3·34
	1·0234	0·9896		13·88	3·98
	1·6940	0·9889		15·01	4·65
	1·9104	0·9914		Fused Salt	10·1
	2·4505	1·0024			

1. CAMPBELL and FRIESEN, *Canad. chem. J.*, 1959, **37**, 1288.
2. CAMPBELL, GRAY and KARTZMARK, *Canad. chem. J.*, 1953, **31**, 617.
3. CAMPBELL and KARTZMARK, *Canad. chem. J.*, 1952, **30**, 128.
4. CAMPBELL and DEBUS, *Canad. chem. J.*, 1955, **33**, 1730.

Tetraethyl—AMMONIUM PICRATE—$N(C_2H_5)_4\ C_6H_2O_7N_3$.

Temp. °C	c	η/η^0	Remarks	Ref.
18	0·000622 to 0·00504	$1 + 0{\cdot}0108\sqrt{c} + 0{\cdot}748c$	$\delta \sim 0{\cdot}01\%$	(1)
25°	0·00397	1·00344	$1 + 0{\cdot}0106\sqrt{c} + 0{\cdot}743\,c$ reproduces data at these concentrations to $\sim 0{\cdot}01\%$	(2)
	0·00970	1·00826		
	0·02007	1·01649		

1. Cox and Wolfenden, *Proc. roy. Soc.*, 1934, **A 145**, 475.
2. Laurence and Wolfenden, *J. chem. Soc.*, 1934, 1144.

BARIUM CHLORIDE—$BaCl_2$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·005 to 0·1	$1 + 0{\cdot}0201\sqrt{c} + 0.207c$	$\delta \sim 0{\cdot}03\%$	(1)
	0·25	1·0644		
	0·4972	1·1289		
	0·9913	1·2805		
35	0·0015 to 0·05	$1 + 0{\cdot}018\sqrt{c} + 0{\cdot}285c$	$\delta \sim 0{\cdot}03\%$	(2)
	0·1	1·0307		
	0·2	1·0577		
	0·3	1·0863		
	0·4	1·1140		

1. Jones and Dole, *J. Amer. chem. Soc.*, 1929, **51**, 2950.
2. Chacravarti and Prasad, *Trans. Faraday Soc.*, 1939, **35**, 1466.

BERYLLIUM SULPHATE—$BeSO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
15	0·00055 to 0·10021	$1 + 0{\cdot}0246\sqrt{c} + 0{\cdot}6234c$	$\delta < 0{\cdot}01\%$	(1)
20	0·00059 to 0·10012	$1 + 0{\cdot}0249\sqrt{c} + 0{\cdot}6134c$	$\delta < 0{\cdot}01\%$	(1)
25	0·00059 to 0·1	$1 + 0{\cdot}0251\sqrt{c} + 0{\cdot}6008c$	$\delta < 0{\cdot}01\%$	(1)
30	0·00059 to 0·09985	$1 + 0{\cdot}0251\sqrt{c} + 0{\cdot}5873c$	$\delta < 0{\cdot}01\%$	(1)
35	0·00059 to 0·09969	$1 + 0{\cdot}0253\sqrt{c} + 0{\cdot}5721c$	$\delta < 0{\cdot}01\%$	(1)
42·5	0·00059 to 0·09941	$1 + 0{\cdot}0256\sqrt{c} + 0{\cdot}5504c$	$\delta < 0{\cdot}01\%$	(1)

1. KAMINSKY, *Z. phys. Chem.* (N.F.), 1957, **12**, 206.

CADMIUM CHLORIDE—$CdCl_2$

Temp. °C	c	η/η^0	Remarks	Ref.
35	0·0006 to 0·108	$1 + 0{\cdot}013\sqrt{c} + 0{\cdot}131c$	$\delta \sim 0{\cdot}03\%$	(1)
	0·2140	1·0331		
	0·321	1·0483		
	0·428	1·0637		
	0·535	1·0776		
	0·642	1·0925		
	0·739	1·1080		
	0·844	1·1226		
	0·950	1·1398		
	1·070	1·1532		

1. CHAKRAVARTI and PRASAD, *J. Ind. chem. Soc.*, 1938, **15**, 479.

CADMIUM SULPHATE—$CdSO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·000069 to 0·008176	$1 + 0{\cdot}0232\sqrt{c} + 0{\cdot}45c$	$\delta \sim 0{\cdot}02\%$	(1)

1. ASMUS, *Ann. Phys., Lpz.*, 1939, **35**, 1.

CAESIUM—See CESIUM

CALCIUM FERRICYANIDE—$Ca_3[Fe(CN)_6]_2$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0000604 to 0·007585	$1 + 0{\cdot}0467\sqrt{c} + 1{\cdot}30c$	$\delta \sim 0{\cdot}03\%$	(1)

1. ASMUS, *Ann. Phys., Lpz.*, 1939, **35**, 1.

CALCIUM FERROCYANIDE—$Ca_2Fe(CN)_6$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0000729 to 0·006337	$1 + 0{\cdot}0495\sqrt{c} + 0{\cdot}98c$	$\delta \sim 0{\cdot}02\%$	(1)

1. ASMUS, *Ann. Phys., Lpz.*, 1939, **35**, 1.

CERIC SULPHATE—$Ce(SO_4)_2$

Temp. °C	c	η/η^0	Remarks	Ref.
20	0·00175 0·0088 0·0439 0·2261	1·0045 1·0090 1·0337 1·1737	Error of measurements quoted as ~ 0·1%	(1)

1. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

CEROUS CHLORIDE—$CeCl_3$

Temp. °C	c	η/η^0	Remarks	Ref.
15	0·001 to 0·29027	$1 + 0{\cdot}0303\sqrt{c} + 0{\cdot}524c + 0{\cdot}110c^2 + 0{\cdot}22c^3$	$\delta < 0{\cdot}01\%$	(1)
18	0·001 to 0·29009	$1 + 0{\cdot}0306\sqrt{c} + 0{\cdot}536c + 0{\cdot}111c^2 + 0{\cdot}18c^3$	$\delta < 0{\cdot}01\%$	(1)
25	0·00099 to 0·28951	$1 + 0{\cdot}0310\sqrt{c} + 0{\cdot}555c + 0{\cdot}112c^2 + 0{\cdot}11c^3$	$\delta < 0{\cdot}01\%$	(1)
35	0·00099 to 0·28851	$1 + 0{\cdot}0315\sqrt{c} + 0{\cdot}572c + 0{\cdot}111c^2 + 0{\cdot}04c^3$	$\delta < 0{\cdot}01\%$	(1)
42·5	0·00099 to 0·28757	$1 + 0{\cdot}0321\sqrt{c} + 0{\cdot}579c + 0{\cdot}119c^2 + 0{\cdot}03c^3$	$\delta < 0{\cdot}01\%$	(1)

1. KAMINSKY, *Z. phys. Chem.* (N.F.), 1956, **8**, 173.

CEROUS NITRATE—$Ce(NO_3)_3$

Temp. °C	c	η/η^0	Remarks	Ref.
20	0·0007	1·0037	Error of measurements quoted as ~0·1%	(1)
	0·0033	1·0058		
	0·033	1·0203		
	0·167	1·0848		
	0·333	1·1742		
	0·667	1·4008		

1. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

CESIUM CHLORIDE—CsCl

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·5975	0·980	—	(1)
	1·509	0·964		
	2·267	0·956		
	3·088	0·977		
	4·058	1·010		

1. SATOH and HAYASHI, *Bull. chem. Soc. Japan*, 1961, **34**, 1260.

CESIUM FORMATE—CsOOCH

Temp. °C	c	η/η^0	Remarks	Ref.
50·5	0·7496	1·0730	—	(1)
	1·784	1·1989		
	2·808	1·3421		
	3·989	1·5599		
	5·819	2·0500		
	6·834	2·4555		
	8·203	3·3199		
	9·605	4·7935		

1. RICE and KRAUS, *Proc. nat. Acad. Sci. Wash.*, 1953, **39**, 802.

CESIUM IODIDE—CsI

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·0002 to 0·200017	$1 + 0{\cdot}0025\sqrt{c} - 0{\cdot}242c$	$\delta < 0{\cdot}05\%$	(1)
	0·285023	0·93480		
	0·385037	0·91467		
	0·496900	0·89346		
	0·750096	0·85166		
	1·00007	0·81561		
	1·43997	0·76524		
25	0·000199 to 0·199281	$1 + 0{\cdot}0039\sqrt{c} - 0{\cdot}118c$	$\delta < 0{\cdot}04\%$	(1)
	0·283884	0·96897		
	0·383349	0·95866		
	0·494697	0·94799		
	0·745855	0·92616		
	0·993688	0·90726		
	1·42912	0·88080		
	1·99969	0·85818		

1. JONES and FORNWALT, *J. Amer. chem. Soc.*, 1936, **58**, 619.

CESIUM NITRATE—$CsNO_3$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0005 to 0·02	$1 + 0{\cdot}0043\sqrt{c} - 0{\cdot}092c$	$\delta < 0{\cdot}01\%$	(1)

1. JONES and TALLEY, *J. Amer. chem. Soc.*, 1933, **55**, 624.

Chromic Sulphate—$Cr_2(SO_4)_3$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0000673 to 0·01009	$1 + 0{\cdot}0495\sqrt{c} + 0{\cdot}89c$	$\delta \sim 0{\cdot}05\%$	(1)

1. Asmus, *Ann. Phys., Lpz.*, 1939, **35**, 1.

Cobaltous Chloride—$CoCl_2$

Temp. °C	c	η/η^0	Remarks	Ref.
35	0·001 to 0·075	$1 + 0{\cdot}016\sqrt{c} + 0{\cdot}370c$	$\delta \sim 0{\cdot}02\%$	(1)
	0·1	1·0438		
	0·125	1·0529		
	0·15	1·0641		
	0·2	1·0828		
	0·25	1·1026		

1. Chacravarti and Prasad, *Trans. Faraday Soc.*, 1939, **35**, 1466.

Copper Sulphate—$CuSO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·000341 to 0·009238	$1 + 0{\cdot}0230\sqrt{c} + 0{\cdot}540c$	$\delta < 0{\cdot}01\%$ For higher concentrations see next table	(1)

1. Asmus, *Ann. Phys., Lpz.*, 1939, **35**, 1.

Copper Sulphate—$CuSO_4$ *(continued)*

m	η/η^0							Ref.
	30°C	35°C	40°C	45°C	50°C	55°C	60°C	
0·0992	1·042	1·047	1·047	1·039	1·042	1·039	1·034	(1)
0·1965	1·070	1·078	1·084	1·080	1·082	1·070	1·076	
0·2921	1·131	1·124	1·119	1·110	1·113	1·108	1·099	
0·3862	1·182	1·172	1·163	1·152	1·149	1·140	1·131	
0·4785	1·246	1·225	1·207	1·195	1·191	1·180	1·169	
0·5693	1·288	1·273	1·259	1·242	1·239	1·223	1·210	
0·6586	1·326	1·318	1·305	1·289	1·282	1·266	1·251	
0·7463	1·403	1·385	1·362	1·339	1·330	1·311	1·293	
0·8326	1·485	1·442	1·417	1·389	1·382	1·355	1·331	
0·9175	1·539	1·502	1·467	1·436	1·418	1·398	1·368	
1·0010	1·602	1·555	1·520	1·490	1·468	1·437	1·411	
1·0830	1·675	1·619	1·580	1·542	1·519	1·480	1·457	
1·1640	1·738	1·687	1·640	1·592	1·565	1·530	1·502	
1·2440	1·827	1·760	1·708	1·656	1·628	1·582	1·552	
1·3210	1·908	1·830	1·771	1·717	1·690	1·641	1·600	
1·3980	2·009	1·914	1·850	1·786	1·753	1·702	1·654	
1·5100	2·162							
1·6500		2·217						
1·8000			2·266					
1·9500				2·246				
2·1200					2·296			
2·3000						2·360		
2·4900							2·394	

1. Suryanarayana and Alamelu, *Bull. chem. Soc. Japan*, 1959, **32**, 333.

FERROUS CHLORIDE—$FeCl_2$

Temp. °C	c	η/η^0	Remarks	Ref.
15·5	0·00099 to 0·29773	$1 + 0{\cdot}0150\sqrt{c} + 0{\cdot}399c$	$\delta < 0{\cdot}01\%$	(1)
18	0·00099 to 0·29750	$1 + 0{\cdot}0151\sqrt{c} + 0{\cdot}399c$	$\delta < 0{\cdot}01\%$	(1)
25	0·00099 to 0·29696	$1 + 0{\cdot}0164\sqrt{c} + 0{\cdot}402c + 0{\cdot}006c^2$	$\delta < 0{\cdot}01\%$	(1)
30	0·00099 to 0·29649	$1 + 0{\cdot}0166\sqrt{c} + 0{\cdot}402c + 0{\cdot}005c^2$	$\delta < 0{\cdot}01\%$	(1)
35	0·00098 to 0·29596	$1 + 0{\cdot}0172\sqrt{c} + 0{\cdot}405c + 0{\cdot}012c^2$	$\delta < 0{\cdot}01\%$	(1)
40	0·00098 to 0·29539	$1 + 0{\cdot}0178\sqrt{c} + 0{\cdot}413c + 0{\cdot}019c^2$	$\delta < 0{\cdot}01\%$	(1)

1. KAMINSKY, *Z. phys. Chem.* (N.F.), 1956, **8**, 173.

HYDROGEN CHLORIDE (Hydrochloric Acid)—HCl

Temp. °C	c	η/η^0	Remarks	Ref.
12·5	0·00083 to 0·1428	$1 + 0{\cdot}0019\sqrt{c} + 0{\cdot}0465c$	$\delta < 0{\cdot}01\%$	(1)
20	0·00083 to 0·1426	$1 + 0{\cdot}0021\sqrt{c} + 0{\cdot}0575c$	$\delta < 0{\cdot}01\%$	(1)
25	0·00083 to 0·1424	$1 + 0{\cdot}0021\sqrt{c} + 0{\cdot}0648c$	$\delta < 0{\cdot}01\%$	(1)
30	0·00083 to 0·1422	$1 + 0{\cdot}0022\sqrt{c} + 0{\cdot}0699c$	$\delta < 0{\cdot}01\%$	(1)
35	0·00083 to 0·1420	$1 + 0{\cdot}0023\sqrt{c} + 0{\cdot}0760c$	$\delta < 0{\cdot}01\%$	(1)
42·5	0·00083 to 0·1416	$1 + 0{\cdot}0025\sqrt{c} + 0{\cdot}0837c$	$\delta < 0{\cdot}01\%$	(1)

1. HÜCKEL and SCHAAF, *Z. phys. Chem.* (N.F.), 1959, **21**, 326.

HYDROGEN NITRATE (Nitric Acid)—HNO_3

Temp. °C	c	η/η^0	Remarks	Ref.
18	0·00994	1·00027	—	(1)
	0·01035	1·00029		
	0·02060	1·00040		
	0·04078	1·00067		
	0·04245	1·00083		
	0·06058	1·00102		
	0·10146	1·00149		
	0·444	1·00561		
	1·110	1·01878		
20	0·00574	1·0029	Average error of measurements quoted as ±0·1%	(2)
	0·0115	1·0027		
	0·02	1·0034		
	0·116	1·0044		
	0·579	1·0123		
	1·450	1·0306		
	2·900	1·0926		
	5·806	1·3145		
35	0·00994	1·00056		(1)
	0·04078	1·00198		
	0·04234	1·00187		
	0·08615	1·00391		
	0·10146	1·00430		
	0·560	1·0222		
	1·120	1·0476		

1. JOY and WOLFENDEN, *Proc. roy. Soc.*, 1931, **A 134**, 413.
2. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

HYDROGEN SULPHATE (Sulphuric Acid)—H_2SO_4

Temp. °C	c	η/η^0	Remarks	Ref.
20	0·0025	1·0038	Average error of measurements quoted as ±0·1%	(1)
	0·005	1·0046		
	0·05	1·0141		
	1·5	1·0996		
	1·981	1·1971		

1. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

LANTHANUM CHLORIDE—$LaCl_3$

Temp. °C	c	η/η^0	Remarks	Ref.
0	0.00025 to 0·1	$1 + 0{\cdot}0278\sqrt{c} + {\cdot}4744c$	$\delta < 0{\cdot}01\%$	(1)
	0·25	1·13849		
	0·5	1·30258		
	1·0	1·77023		
18	0·000217 to 0·00607	$1 + 0{\cdot}037\sqrt{c} + 0{\cdot}516c$	$\delta < 0{\cdot}01\%$	(2)
25	0·00025 to 0·1	$1 + 0{\cdot}0304\sqrt{c} + 0{\cdot}5672c$	$\delta < 0{\cdot}01\%$	(1)
	0·25	1·16314		
	0·5	1·34913		
	1·0	1·84945		

1. JONES and STAUFFER, *J. Amer. chem. Soc.*, 1940, **62**, 335.
2. COX and WOLFENDEN, *Proc. roy. Soc.*, 1934, **A 145**, 475.

LANTHANUM NITRATE—$La(NO_3)_3$

Temp. °C	c	η/η^0	Remarks	Ref.
20	0·0017	1·0043	Average error of measurements quoted as ±0·1%	(1)
	0·0034	1·0059		
	0·0388	1·0239		
	0·169	1·0962		
	1·423	1·2627		
	3·077	1·8399		

1. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

LITHIUM ACETATE—$LiOCOCH_3$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0111 to 0·09393	$1 + 0{\cdot}0066\sqrt{c}$ $+ 0{\cdot}397c$	$\delta \sim 0{\cdot}01\%$	(1)

1. LAURENCE and WOLFENDEN, *J. chem. Soc.*, 1934, 1144.

LITHIUM BROMIDE—LiBr

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00843 to 0·07181	$1 + 0{\cdot}0079\sqrt{c}$ $+ 0{\cdot}106c$	$\delta < 0{\cdot}01\%$	(1)
27	0·597	1·065		(2)
	1·055	1·104		
	1·505	1·147		
	1·968	1·199		
	2·441	1·250		
	2·897	1·320		
	3·376	1·380		
	3·802	1·441		
	4·265	1·516		
	4·728	1·654		

1. LAURENCE and WOLFENDEN, *J. chem. Soc.*, 1934, 1144.
2. SATOH and HAYASHI, *Bull. chem. Soc. Japan*, 1961, **34**, 1260.

LITHIUM CHLORATE—$LiClO_3$

Temp. °C	*c*	η/η^0	Ref.	Temp. °C	*c*	η/η^0	Ref.
25	0·02188	1·002	(1)	131·8	0·1131	1·013	(1)
	0·1002	1·015			0·5321	1·047	
	0·5121	1·067			1·169	1·110	
	0·8532	1·110			1·729	1·165	
	1·247	1·169			2·374	1·257	
	1·640	1·229			3·066	1·323	
	2·113	1·316			3·794	1·408	
	2·928	1·472			4·589	1·519	
	3·115	1·508			5·548	1·686	
	3·742	1·642			6·572	1·903	
	4·549	1·895			8·165	2·364	
	4·908	2·019			9·345	2·838	
	5·157	2·115			11·40	4·263	
	6·199	2·594			12·64	5·477	
	7·185	3·140			14·65	8·836	
	7·762	3·585			17·42	17·48	
	8·047	3·838			20·46	43·38	
	8·947	5·170			23·11	113·0	
	10·19	6·894					
	11·49	10·29					
	12·80	16·37					
	13·93	24·53					
	14·27	28·38					
	16·15	66·26					
	17·95	166·5					
	19·03	334·0					

1. CAMPBELL and PATERSON, *Canad. chem. J.*, 1958, **36**, 1004.

LITHIUM CHLORIDE—LiCl

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00707 to 0·21855	$1 + 0{\cdot}0064\sqrt{c} + 0{\cdot}139c$	$\delta \sim 0{\cdot}01\%$	(1)
	0·2227	1·0342	Data from Refs. (1) and (2) agree to ±0·1% in overlapping range. Data from (3) not included as it differs from (2) by 0–3%.	(2), (3)
	0·4407	1·0661		
	0·7205	1·1075		
	0·8885	1·1332		
	1·396	1·2194		
	1·739	1·2761		
	2·499	1·4274		
	3·095	1·5461		
	3·442	1·6240		
	3·899	1·7391		

1. LAURENCE and WOLFENDEN, *J. chem. Soc.*, 1934, 1144.
2. NICKELS and ALLMAND, *J. phys. Chem.*, 1937, **41**, 861.
3. SATOH and HAYASHI, *Bull. chem. Soc. Japan*, 1961, **34**, 1260.

LITHIUM IODATE—$LiIO_3$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00297 to 0·09018	$1 + 0{\cdot}0079\sqrt{c} + 0{\cdot}299c$	$\delta \sim 0{\cdot}01\%$	(1)

1. LAURENCE and WOLFENDEN, *J. chem. Soc.*, 1934, 1144.

LITHIUM IODIDE—LiI

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00986 to 0·07475	$1 + 0{\cdot}0042\sqrt{c} + 0{\cdot}081c$	$\delta < 0{\cdot}01\%$	(1)

1. LAURENCE and WOLFENDEN, *J. chem. Soc.*, 1934, 1144.

LITHIUM NITRATE—$LiNO_3$

Temp. °C	c	η/η^0	Ref.	Temp. °C	c	η/η^0	Ref.
25	0·010572	1.000	(1)	35	0·010540	1·000	(1)
	0·021061	0·999			0·020996	1·002	
	0·029775	1·004			0·029683	1·003	
	0·038848	1·005			0·038729	1·006	
	0·059158	1·007			0·058975	1·008	
	0·069872	1·009			0·069654	1·010	
	0·076234	1·008			0·075999	1.008	
	0·091701	1·011			0·091418	1·012	
	0·10111	1·011			0·10079	1·014	
	0·14980	1·017			0·14929	1·020	
	0·19937	1·022			0·19874	1·024	
	0·29918	1·043			0·29821	1·044	
	0·39900	1·042			0·39769	1·045	
	0·45941	1·050			0·45787	1·055	
	0·58142	1·060			0·57945	1·066	
	0·71135	1·075			0·70889	1·081	
	0·81640	1·087			0·81351	1·094	
	0·91191	1·098			0·90862	1·106	
	1·00464	1·114			1·0010	1·117	
	1·885	1·221	(2)	110	0·0972	1·010	(2)
	2·740	1·351			0·4936	1·053	
	2·957	1·390			0·9177	1·094	
	3·456	1·490			1·802	1·185	
	3·698	1·534			2·634	1·276	
	4·857	1·826			3·198	1·346	
	5·337	1·984			4·252	1·516	
	5·703	2·122			5·459	1·739	
	6·916	1·637			7·109	2·197	
	7·427	1·914			8·411	2·658	
	8·726	3·849			9·237	3·097	
	9·124	4·218			11·06	4·481	
	9·135	4·236			12·31	5·48	
	9·986	5·142			14·36	7·92	
	11·50	7·987					
	13·55	14·88					

1. CAMPBELL and FRIESEN, *Canad. chem. J.*, 1959, **37**, 1288.
2. CAMPBELL, DEBUS and KARTZMARK, *Canad. chem. J.*, 1955, **33**, 1508.

Lithium Picrate—$LiC_6H_2O_7N_3$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00419 to 0·03572	$1 + 0{\cdot}0091\sqrt{c}$ $+ 0{\cdot}451c$	$\delta \sim 0{\cdot}01\%$	(1)

1. Laurence and Wolfenden, *J. chem. Soc.*, 1934, 1144.

Lithium Sulphate—Li_2SO_4

Temp. °C	c	η/η^0	Remarks	Ref.
15·1	0·00085 to 0·17348	$1 + 0{\cdot}0160\sqrt{c}$ $+ 0{\cdot}5120c$ $+ 0{\cdot}071c^2$	$\delta \sim 0{\cdot}01\%$	(1)
20	0·00084 to 0·17332	$1 + 0{\cdot}0165\sqrt{c}$ $+ 0{\cdot}5096c$ $+ 0{\cdot}067c^2$	$\delta < 0{\cdot}01\%$	(1)
25	0·00084 to 0·17309	$1 + 0{\cdot}0167\sqrt{c}$ $+ 0{\cdot}5076c$ $+ 0{\cdot}064c^2$	$\delta < 0{\cdot}01\%$	(1)
30	0·00084 to 0·17278	$1 + 0{\cdot}0169\sqrt{c}$ $+ 0{\cdot}5058c$ $+ 0{\cdot}066c^2$	$\delta < 0{\cdot}01\%$	(1)
35	0·00084 to 0·17250	$1 + 0{\cdot}0170\sqrt{c}$ $+ 0{\cdot}5048c$ $+ 0{\cdot}062c^2$	$\delta < 0{\cdot}01\%$	(1)
42·5	0·00084 to 0·171999	$1 + 0{\cdot}0173\sqrt{c}$ $+ 0{\cdot}5020c$ $+ 0{\cdot}060c^2$	$\delta < 0{\cdot}01\%$	(1)

1. Kaminsky, *Z. phys. Chem.* (N.F.), 1956, 8, 173.

MAGNESIUM CHLORIDE—$MgCl_2$

Temp. °C	c	η/η^0	Remarks	Ref.
15	0·0025 to 0·16014	$1 + 0{\cdot}0158\sqrt{c} + 0{\cdot}3690c$	$\delta < 0{\cdot}01\%$	(1)
20	0·0025 to 0·16	$1 + 0{\cdot}0161\sqrt{c} + 0{\cdot}3699c$	$\delta < 0{\cdot}01\%$	(1)
25	0·0025 to 0·1598	$1 + 0{\cdot}0165\sqrt{c} + 0{\cdot}3712c$	$\delta < 0{\cdot}01\%$	(1)
30	0·00249 to 0·15958	$1 + 0{\cdot}0169\sqrt{c} + 0{\cdot}3717c$	$\delta < 0{\cdot}01\%$	(1)
35	0·00249 to 0·09862	$1 + 0{\cdot}0172\sqrt{c} + 0{\cdot}3723c$	$\delta < 0{\cdot}01\%$	(1), (2)
	0·125	1·0522	Values from Ref. (2) agree with those from (1) to $\pm \sim 0{\cdot}1\%$ in the overlapping region.	(2)
	0·15	1·0620		
	0·175	1·0725		
	0·2	1·0827		
	0·225	1·0921		
	0·25	1·1023		
	0·3	1·1225		
	0·4	1·1651		
42·5	0·00248 to 0·15888	$1 + 0{\cdot}0175\sqrt{c} + 0{\cdot}3714c$	$\delta < 0{\cdot}01\%$	(1)

1. KAMINSKY, *Z. phys. Chem.* (N.F.), 1957, **12**, 206.
2. CHACRAVARTI and PRASAD, *Trans. Faraday Soc.*, 1939, **35**, 1466.

MAGNESIUM SULPHATE—$MgSO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
15	0·0005 to 0·20045	$1 + 0{\cdot}0226\sqrt{c} + 0{\cdot}5980c + 0{\cdot}05c^2$	$\delta < 0{\cdot}01\%$	(1)
18	0·0005 to 0·20036	$1 + 0{\cdot}0227\sqrt{c} + 0{\cdot}5966c + 0{\cdot}04c^2$	$\delta < 0{\cdot}01\%$	(1)
25	0·0005 to 0·2	$1 + 0{\cdot}0230\sqrt{c} + 0{\cdot}5937c + 0{\cdot}02c^2$	$\delta < 0{\cdot}01\%$ Values from Ref. (2) agree with those of (1) within $\pm \sim 0{\cdot}03\%$.	(1), (2)
30	0·0005 to 0·19966	$1 + 0{\cdot}0232\sqrt{c} + 0{\cdot}5918c + 0{\cdot}02c^2$	$\delta < 0{\cdot}01\%$	(1)
35	0·0005 to 0·19927	$1 + 0{\cdot}0234\sqrt{c} + 0{\cdot}5902c + 0{\cdot}01c^2$	$\delta < 0{\cdot}01\%$	(1)
42·5	0·00049 to 0·19864	$1 + 0{\cdot}0237\sqrt{c} + 0{\cdot}5871c + 0{\cdot}01c^2$	$\delta < 0{\cdot}01\%$	(1)

1. KAMINSKY, *Z. phys. Chem.* (N.F.), 1957, **12**, 206.
2. ASMUS, *Ann. Phys., Lpz.*, 1939, **35**, 1.

MANGANOUS SULPHATE—$MnSO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0000676 to 0·014318	$1 + 0{\cdot}0231\sqrt{c} + 0{\cdot}470c$	$\delta \sim 0{\cdot}05\%$	(1)

1. ASMUS, *Ann. Phys., Lpz.*, 1939, **35**, 1.

NEODYMIUM NITRATE—$Nd(NO_3)_3$

Temp. °C	c	η/η^0	Remarks	Ref.
20	0·004	1·0041	Error of measurements quoted as $\sim \pm 0{\cdot}1\%$.	(1)
	0·02	1·0077		
	0·1	1·0233		
	1·0	1·1964		

1. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

NICKEL CHLORIDE—$NiCl_2$

Temp. °C	c	η/η^0	Remarks	Ref.
35	0·001 to 0·075	$1 + 0{\cdot}028\sqrt{c} + 0{\cdot}316c$	$\delta \sim 0{\cdot}03\%$	(1)
	0·01	1·0431		
	0·125	1·0536		
	0·2	1·0833		

1. CHACRAVARTI and PRASAD, *Trans. Faraday Soc.*, 1939, **35**, 1466.

Nickel Sulphate—NiSO$_4$

m	η/η^0							Ref.
	30°C	35°C	40°C	45°C	50°C	55°C	60°C	
0·1547	1·1145	1·0696	1·0857	1·0788	1·0847	1·0795	1·0667	(1)
0·3032	1·1989	1·1437	1·1606	1·1368	1·1416	1·1406	1·1237	
0·4366	1·2966	1·2260	1·2332	1·2031	1·2089	1·2040	1·1815	
0·5917	1·3918	1·3155	1·3343	1·2846	1·2804	1·2682	1·2495	
0·7042	1·4947	1·3942	1·4006	1·3537	1·3647	1·3404	1·3105	
0·8337	1·5975	1·4915	1·4820	1·4280	1·4339	1·4100	1·3781	
0·9526	1·7179	1·5833	1·5832	1·5140	1·5037	1·4901	1·4608	
1·0840	1·8483	1·7000	1·6812	1·6116	1·5881	1·5739	1·5289	
1·2190	1·9649	1·8085	1·7746	1·7173	1·6914	1·6475	1·6162	
1·3130	2·0940	1·9322	1·9109	1·8145	1·7917	1·7494	1·6970	
1·5250	2·3749	2·2143	2·1651	2·0325	2·0011	1·9447	1·8723	
1·7340	2·7060	2·5410	2·4330	2·3092	2·2297	2·1768	2·0724	
1·9510	2·9216	2·6925	2·5892	2·4635	2·3706	2·2780	2·1496	
2·2100	3·1486	2·8941	2·8219	2·6379	2·5206	2·4564	2·2910	
2·477	3·4006	3·1846	3·0057	2·8274	2·7072	2·5773	2·4689	

1. Alamelu and Suryanarayana, *Acta chim. Acad. Sci. Hung.*, 1959, **20**, 339.

Potassium Acetate—KOCOCH$_3$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00932 to 0·06296	$1 + 0{\cdot}0038\sqrt{c} + 0{\cdot}238c$	$\delta \sim 0{\cdot}01\%$	(1)

1. Laurence and Wolfenden, *J. chem. Soc.*, 1934, 1144.

POTASSIUM BROMATE—$KBrO_3$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·002001 to 0·099999	$1 + 0{\cdot}0058\sqrt{c}$ $- 0{\cdot}0008c$	$\delta < 0{\cdot}01\%$	(1)

1. JONES and TALLEY, *J. Amer. Chem. Soc.*, 1933, **55**, 624.

POTASSIUM BROMIDE—KBr

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·00025 to 0·5	$1 + 0{\cdot}0045\sqrt{c}$ $- 0{\cdot}1546c$ $+ 0{\cdot}04244c^2$	$\delta < 0{\cdot}01\%$	(1)
	1·0	0·88866		
	2·0	0·82882		
	3·0	0·80341		
	3·75	0·80234		
21	0·4315	0·983		(2)
	0·8439	0·967		
	1·271	0·953		
	1·692	0·942		
	2·104	0·943		
	2·524	0·937		
	2·942	0·947		
	3·379	0·954		
	3·802	0·966		
	4·206	0·986		
25	0·001 to 2·00309	$1 + 0{\cdot}00474\sqrt{c}$ $- 0{\cdot}0490c$ $+ 0{\cdot}01221c^2$	$\delta < 0{\cdot}01\%$	(3)
	3·030933	0·96953		
	3·749274	0·99177		

1. JONES and STAUFFER, *J. Amer. chem. Soc.*, 1940, **62**, 335.
2. SATOH and HAYASHI, *Bull. chem. Soc. Japan*, 1961, **34**, 1260.
3. JONES and TALLEY, *J. Amer. chem. Soc.*, 1933, **55**, 4124.

Potassium Chlorate—$KClO_3$

Temp. °C	c	η/η^0	Remarks	Ref.
18	0·00124	1·00014		(1)
	0·00490	1·00005		
	0·01	0·99993		
	0·02	0·99957		
	0·04	0·99875		
	0·0625	0·99786		
	0·125	0·99526		
	0·25	0·99086		
	0·4	0·98711		
25	0·002001 to 0·1	$1 + 0{\cdot}0050\sqrt{c} - 0{\cdot}0309c$	$\delta < 0{\cdot}01\%$	(2)
35	0·00238	1·00018		(1)
	0·00442	1·00029		
	0·00869	1·00045		
	0·02	1·00061		
	0·04	1·00079		
	0·1	1·00114		
	0·16	1·00146		
	0·25	1·00175		
	0·4	1·00328		

1. Joy and Wolfenden, *Proc. roy. Soc.*, 1931, A **134**, 413.
2. Jones and Talley, *J. Amer. chem. Soc.*, 1933, **55**, 624.

POTASSIUM CHLORIDE—KCl

Temp. °C	c	η/η^0	Remarks	Ref.
12·5	0·001 to 0·50079	$1 + 0{\cdot}0050\sqrt{c} - 0{\cdot}0471c + 0{\cdot}003c^2$	$\delta < 0{\cdot}01\%$	(1)
15	0·001 to 0·50052	$1 + 0{\cdot}0051\sqrt{c} - 0{\cdot}0401c + 0{\cdot}003c^2$	$\delta < 0{\cdot}01\%$	(1)
18	0·00198 to 0·10033	$1 + 0{\cdot}0051\sqrt{c} - 0{\cdot}0310c$	$\delta \sim 0{\cdot}01\%$	(2)
	0·25	0·99496		
	0·5	0·98979		
	1·0	0·9823		
20	0·001 to 0·5	$1 + 0{\cdot}0052\sqrt{c} - 0{\cdot}0271c + 0{\cdot}005c^2$	$\delta < 0{\cdot}01\%$	(1)
25	0·001 to 0·49933	$1 + 0{\cdot}0052\sqrt{c} - 0{\cdot}0140c + 0{\cdot}001c^2$	$\delta < 0{\cdot}01\%$ In range 0·001 to 0·1 M both (3) and (4) agree with (1) to within 0·01%. Values of (3) and (4) agree in the overlapping range 0·5 to 3·0 to ∼ 0·01%.	(1), (3) (4)
	0·498450	0·99760		(3)
	0·5	0·9976		(4)
	0·999718	0·99702		(3)
	1·0	0·9972		(4)
	1·5	1·0004		
	2·0	1·0074		
	2·01151	1·00773		(3)
	2·5	1·0184		(4)
	2·962076	1·03211		(3)
	3·0	1·0334		(4)
	3·5	1·0521		
	4·0	1·0755		
30	0·001 to 0·49856	$1 + 0{\cdot}0054\sqrt{c} - 0{\cdot}0020c + 0{\cdot}001c^2$	$\delta < 0{\cdot}01\%$	(1), (5)
35	0·00099 to 0·49770	$1 + 0{\cdot}0055\sqrt{c} + 0{\cdot}0098c$	$\delta < 0{\cdot}01\%$ Values of (2) agree to $< \pm 0{\cdot}1\%$ with (1) in dilute range.	(1), (5) (2)
	0·5	1·0078	Values of (2) and (5) at ∼1 M agree within ± 0·1%. Data of (5) reported in next table.	(2)
	0·75	1·0112		
	1·0	1·0154		
42·5	0·00099 to 0·49630	$1 + 0{\cdot}0055\sqrt{c} + 0{\cdot}0242c$	$\delta < 0{\cdot}01\%$	(1)

POTASSIUM CHLORIDE—KCl (*continued*)

Temp. °C	c	η/η^0	Remarks	Ref.
50	0·1	1·0045	Data from (5) reported in next table.	(4), (5)
	0·3	1·0118		
	0·5	1·0193		
	1·0	1·0381		
	1·5	1·0584		
	2·0	1·0822		
	2·5	1·1094		
	3·0	1·1394		
	3·5	1·1720		
	4·0	1·2093		

1. KAMINSKY, *Z. phys. Chem.*, 1957, **12**, 206.
2. JOY and WOLFENDEN, *Proc. roy. Soc.*, 1931, A **134**, 413.
3. JONES and TALLEY, *J. Amer. chem. Soc.*, 1933, **55**, 624, 4124
4. CHAMBERS, Thesis, University of Western Australia, Perth, W.A.
5. SURYANARAYANA and VENKATESEN, *Bull. Chem. Soc. Japan*, 1958, **31**, 442.

POTASSIUM CHLORIDE—KCl (*continued*)

m	η/η^0						Ref.
	30°C	35°C	40°C	45°C	50°C	55°C	
1·00	1·010	1·014	1·018	1·024	1·034	1·039	(5)
1·50	1·021	1·020	1·039	1·046	1·059	1·059	
2·00	1·028	1·022	1·044	1·058	1·076	1·081	
2·50	1·035	1·049	1·074	1·086	1·104	1·114	
3·00	1·046	1·060	1·089	1·104	1·122	1·135	
3·50	1·064	1·077	1·105	1·125	1·147	1·161	
4·00	1·079	1·103	1·130	1·148	1·173	1·188	
4·50	1·093	1·119	1·148	1·170	1·195	1·214	
4·963	1·145						
5·164		1·159					
5·365			1·199				
5·540				1·238			
5·714					1·271		
5·902						1·308	

5. SURYANARAYANA and VENKATESEN, *Bull. chem. Soc. Japan*, 1958, **31**, 442.

POTASSIUM CHROMATE—K_2CrO_4

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·0005 to 0·05	$1 + 0{\cdot}01104\sqrt{c} - 0{\cdot}0179c$	$\delta < 0{\cdot}01\%$	(1)
	0·1	1·00223		
	0·2	1·00496		
	0·5	1·0249		
	1·0	1·0913		
	2·0	1·3343		
	2·5	1·5224		
25	0·0005 to 0·1	$1 + 0{\cdot}013305\sqrt{c} + 0{\cdot}1521c$	$\delta < 0{\cdot}01\%$	(1)
	0·2	1·03732		
	0·5	1·09446		
	1·0	1·2094		
	2·0	1·53204		
	2·5	1·7584		

1. **Jones** and **Colvin**, *J. Amer. chem. Soc.*, 1940, **62**, 338.

POTASSIUM FERRICYANIDE—$K_3Fe(CN)_6$

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·000333 to 0·033333	$1 + 0{\cdot}02113\sqrt{c} - 0{\cdot}1701c$	$\delta < 0{\cdot}01\%$	(1)
	0·098143	0·99224		
	0·167383	0·98820		
	0·33538	0·98891		
	0·66667	1·03289		
25	0·000333 to 0·033333	$1 + 0{\cdot}0244\sqrt{c} + 0{\cdot}1141c$	$\delta < 0{\cdot}01\%$	(1)
	0·097772	1·01939		
	0·16667	1·03164		
	0·33349	1·06682		
	0·66604	1·17067		
	0·9996	1·33648		
	1·1677	1·44964		

1. **Jones** and **Christian**, *J. Amer. chem. Soc.*, 1944, **66**, 1017.

Potassium Ferrocyanide—$K_4Fe(CN)_6$

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·0002 to 0·2	$1 + 0\cdot03508\sqrt{c} + 0\cdot02123c + 0\cdot4778c^2$	$\delta < 0\cdot01\%$	(1)
25	0·0002 to 0·1	$1 + 0\cdot03695\sqrt{c} + 0\cdot366c$	$\delta < 0\cdot01\%$	(1)
	0·2	1·09414		
	0·5	1·26347		

1. Jones and Stauffer, *J. Amer. chem. Soc.*, 1936, **58**, 2558.

Potassium Fluoride—KF

Temp. °C	c	η/η^0	Remarks	Ref.
26	0·525	1·067		(1)
	1·034	1·135		
	1·564	1·218		
	2·081	1·291		
	2·582	1·382		
	3·107	1·474		
	3·619	1·588		
	4·149	1·701		
	4·661	1·816		
	5·220	1·944		
	6·032	2·194		
	6·445	2·320		

1. Satoh and Hayashi, *Bull. chem. Soc. Japan*, 1961, **34**, 1260.

POTASSIUM FORMATE—KOOCH

Temp. °C	c	η/η^0	Remarks	Ref.
50·5	1·516	1·146		(1)
	3·125	1·339		
	4·199	1·519		
	6·090	1·887		
	8·224	2·685		
	10·38	4·067		
	12·26	6·245		
	13·95	9·493		
	15·64	15·091		

1. RICE and KRAUS, *Proc. nat. Acad. Sci. Wash.*, 1953, **39**, 802.

POTASSIUM IODATE—KIO_3

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·00505 to 0·04458	$1 + 0{\cdot}0066\sqrt{c} + 0{\cdot}132c$	$\delta \sim 0{\cdot}1\%$	(1)

1. LAURENCE and WOLFENDEN, *J. chem. Soc.*, 1934, 1144.

POTASSIUM IODIDE—KI

Temp. °C	c	η/η^0	Remarks	Ref.
18	0·00275 to 0·20009	$1 + 0{\cdot}0045\sqrt{c} - 0{\cdot}105c$	$\delta < 0{\cdot}01\%$	(1)
20	0·00275 to 0·2	$1 + 0{\cdot}0045\sqrt{c} - 0{\cdot}0920c$	$\delta < 0{\cdot}01\%$	(1)
21	0·610	0·964		(2)
	1·208	0·931		
	1·817	0·904		
	2·426	0·919		
	3·015	0·925		
	3·626	0·943		
	4·831	1·022		
	6·039	1·152		
25	0·00275 to 0·19974	$1 + 0{\cdot}0047\sqrt{c} - 0{\cdot}0755c$	$\delta < 0{\cdot}01\%$ Values of (3) are ~ 0·1% lower than (1)	(1) (3), (4)
	0·3	0·9799	Data of (4) and (1) agree within 0·01% at 0·1 M.	(4)
	0·5	0·9661		
	1·0	0·9373		
	1·5	0·9186		
	2·0	0·9083		
	2·5	0·9057		
	3·0	0·9112		
	3·5	0·9243		
	4·0	0·9442		
	4·5	0·9752		
	5·0	1·0154		
	5·5	1·0644		
	6·0	1·1318		
30	0·00275 to 0·19947	$1 + 0{\cdot}0052\sqrt{c} - 0{\cdot}0604c$	$\delta < 0{\cdot}01\%$	(1)
35	0·00274 to 0·19947	$1 + 0{\cdot}0052\sqrt{c} - 0{\cdot}485c$	$\delta < 0{\cdot}01\%$	(1)
40	0·00273 to 0·19875	$1 + 0{\cdot}0054\sqrt{c} - 0{\cdot}0390c$	$\delta < 0{\cdot}01\%$	(1)
50	0·1	0·9987		
	0·3	0·9944		(4)
	0·5	0·9910		
	1·0	0·9860		
	1·5	0·9858		

Potassium Iodide—KI (*continued*)

Temp. °C	c	η/η^0	Remarks	Ref.
50	2·0	0·9926		(4)
	2·5	1·0050		
	3·0	1·0249		
	3·5	1·0534		
	4·0	1·0878		
	4·5	1·1362		
	5·0	1·1924		
	5·5	1·2596		
	6·0	1·3514		

1. Kaminsky, *Z. phys. Chem.*, 1955, **5**, 154.
2. Satoh and Hayashi, *Bull. chem. Soc. Japan*, 1961, **34**, 1260.
3. Laurence and Wolfenden, *J. chem. Soc.*, 1934, 1144.
4. Chambers, Thesis, University of Western Australia, Perth, W.A., 1956.

Potassium Nitrate—KNO_3

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·001 to 0·1	$1 + 0{\cdot}0050\sqrt{c} - 0{\cdot}0531c$	$\delta < 0{\cdot}01\%$	(1)

1. Jones and Talley, *J. Amer. chem. Soc.*, 1933, **55**, 624.

POTASSIUM PERMANGANATE—$KMnO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·000511 to 0·100314	$1 + 0{\cdot}0058\sqrt{c} - 0{\cdot}179c$	$\delta \sim 0{\cdot}01\%$	(1)
	0·125493	0·98047		
	0·150518	0·97625		
	0·180744	0·97221		
25	0·000509 to 0·099961	$1 + 0{\cdot}0047\sqrt{c} - 0{\cdot}066c$	$\delta \sim 0{\cdot}01\%$	(1)
	0·125028	0·99388		
	0·149938	0·99261		
	0·180015	0·99127		
	0·250256	0·98868		
	0·351500	0·98483		
	0·450368	0·98165		

1. JONES and FORNWALT, *J. Amer. chem. Soc.*, 1936, **58**, 619.

POTASSIUM SULPHATE—K_2SO_4

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·0005 to 0·05	$1 + 0{\cdot}01216\sqrt{c} + 0{\cdot}0339c$	$\delta < 0{\cdot}01\%$	(1)
	0·1	1·00787		
	0·2	1·01606		
	0·3	1·03020		
12·5	0·0025 to 0·09015	$1 + 0{\cdot}013\sqrt{c} + 0{\cdot}1372c + 0{\cdot}04c^2$	$\delta < 0{\cdot}01\%$	(2)

POTASSIUM SULPHATE—K_2SO_4 (*continued*)

Temp. °C	c	η/η^0	Remarks	Ref.
15	0·0025 to 0·09011	$1 + 0{\cdot}0130\sqrt{c} + 0{\cdot}1473c + 0{\cdot}038c^2$	$\delta < 0{\cdot}01\%$	(2)
20	0·0025 to 0·09	$1 + 0{\cdot}0133\sqrt{c} + 0{\cdot}1705c + 0{\cdot}035c^2$	$\delta < 0{\cdot}01\%$	(2)
25	0·0005 to 0·1	$1 + 0{\cdot}01406\sqrt{c} + 0{\cdot}1935c$	$\delta < 0{\cdot}01\%$ Data from (2) agrees with (1) in range to 0·1 M to better than ± 0·01%.	(1) (2)
	0·2	1·04535		(1)
	0·3	1·06760		
	0·5	1·11470		
30	0·00249 to 0·08976	$1 + 0{\cdot}0136\sqrt{c} + 0{\cdot}2145c + 0{\cdot}028c^2$	$\delta < 0{\cdot}01\%$	(2)
35	0·00249 to 0·08961	$1 + 0{\cdot}0139\sqrt{c} + 0{\cdot}2362c + 0{\cdot}010c^2$	$\delta < 0{\cdot}01\%$	(2)
42·5	0·00248 to 0·08936	$1 + 0{\cdot}0141\sqrt{c} + 0{\cdot}2640c$	$\delta < 0{\cdot}01\%$	(2)

1. JONES and COLVIN, *J. Amer. chem. Soc.*, 1940, **62**, 338.
2. KAMINSKY, *Z. phys. Chem.*, 1957 (N.F.), **12**, 206.

PRASEODYMIUM NITRATE—$Pr(NO_3)_3$

Temp. °C	c	η/η^0	Remarks	Ref.
20	0·0013	1·0044	Error of measurements quoted as ~ 0·1%	(1)
	0·0067	1·0084		
	0·033	1·0228		
	0·333	1·1945		

1. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

Rubidium Nitrate—RbNO$_3$

Temp. °C	c	η/η^0	Remarks	Ref.
18	0·00199	1·00002		(1)
	0·00495	0·99981		
	0·01	0·99936		
	0·02	0·99845		
	0·05	0·99583		
	0·1	0·99157	(1) and (2) agree to ~ 0·02% at this concentration (0·1 M).	(2)
	0·14641	0·98770		
	0·18870	0·98386		
	0·25762	0·97846		
	0·49800	0·96278		
	0·76984	0·94826		
	0·98051	0·94100		
	1·09699	0·93740		
	1·4566	0·93128		
	1·8391	0·9306		
	2·1799	0·9338		
25·01	0·09306	0·99422		
	0·14616	0·99100		(2)
	0·18838	0·98850		
	0·25716	0·98490		
	0·49702	0·97383		
	0·76815	0·96308		
	0·97821	0·95877		
	1·09434	0·95629		
	1·4528	0·95421		
	1·8341	0·95715		
	2·1735	0·96394		
35	0·00259	1·00016		(1)
	0·00775	1·00013		
	0·02204	0·99981		
	0·03846	0·99932		
	0·1	0·99699		
	0·25	0·9927		
	0·5	0·9857		
	1·0	0·9800		

1. Joy and Wolfenden, *Proc. roy. Soc.*, 1931, A **134**, 413.
2. Smith, Wolfenden and Hartley, *J. chem. Soc.*, 1931, 403.

SAMARIUM NITRATE—$Sm(NO_3)_3$

Temp. °C	c	η/η^0	Remarks	Ref.
20	0·0014	1·0040	Error in measurements quoted as ± 0·1%.	(1)
	0·0072	1·0079		
	0·072	1·0416		
	0·36	1·2017		

1. TOLLERT, *Z. phys. Chem.*, 1939, **A 184**, 165.

SILVER NITRATE—$AgNO_3$

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·001 to 0·5	$1 + 0{\cdot}00515\sqrt{c} - 0{\cdot}03656c + 0{\cdot}049844c^2$	$\delta < 0{\cdot}01\%$	(1)
	1·0	1·01373		
	2·0	1·08445		
	3·0	1·19439		
	4·0	1·33998		
	5·0	1·52342		
25	0·002 to 2·0	$1 + 0{\cdot}0063\sqrt{c} + 0{\cdot}043805c + 0{\cdot}017845c^2$	$\delta < 0{\cdot}01\%$ Data from (2) are 0·1% lower than (1) at 0·1 and 0·6% at 1 M.	(1) (2), (3)
	3·0	1·29888	(1) and (3) agree to better than 0·1% over range 1·0–5·0 M.	(1)
	3·0458	1·3063		(3)
	3·8399	1·4343		
	4·0	1·46261		(1)
	4·2526	1·5081		(3)
	5·0	1·66264		(1)
	5·2027	1·7071		(3)
	6·1730	1·9479		
	7·6996	2·4366		
	9·62 (Sat.)	3·3781		

Silver Nitrate—$AgNO_3$ *(continued)*

Temp. °C	c	η/η^0	Remarks	Ref.
35	0·010127	1·002		(2)
	0·019335	1·003		
	0·029369	1·004		
	0·039873	1·004		
	0·049507	1·005		
	0·058136	1·005		
	0·068130	1·007		
	0·079763	1·007		
	0·089681	1·008		
	0·10032	1·008		
	0·14867	1·011		
	0·19734	1·016		
	0·29899	1·022		
	0·39842	1·029		
	0·55080	1·037		
	0·59314	1·038		
	0·69679	1·050		
	0·78873	1·058		
	0·89180	1·066		
	0·99713	1·076		
	1·4023	1·1259		(3)
	1·7757	1·1656		
	3·0322	1·3322		
	3·8230	1·4675		
	4·2306	1·5393		
	5·1064	1·7238		
	5·1784	1·7421		
	6·1438	1·9851		
	7·6633	2·4723		
	10·90 (Sat.)	4·201		
95	0·0534	0·9928		(4)
	1·220	1·122		
	2·189	1·263		
	2·967	1·425		
	4·829	1·797		
	6·591	2·280		
	8·830	3·107		
	9·906	3·590		
	11·876	4·262		

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1. Jones and Colvin, *J. Amer. chem. Soc.*, 1940, **62**, 338.
2. Campbell and Friesen, *Canad. chem J.*, 1959, **37**, 1288.
3. Campbell, Gray and Kartzmark, *Canad. chem. J.*, 1953, **31**, 617.
4. Campbell and Kartzmark, *Canad. chem. J.*, 1952, **30**, 128.

SODIUM BROMIDE—NaBr

Temp. °C	c	η/η^0	Ref.	Temp. °C	c	η/η^0	Ref.
25	0·1	1·0062	(1)	50	0·1	1·0098	(1)
	0·3	1·0175			0·3	1·0267	
	0·5	1·0290			0·5	1·0440	
	1·0	1·0623			1·0	1·0907	
	1·5	1·1035			1·5	1·1424	
	2·0	1·1538			2·0	1·2018	
	2·5	1·2138			2·5	1·2685	
	3·0	1·2835			3·0	1·3447	
	3·5	1·3658			3·5	1·4320	
	4·0	1·4620			4·0	1·5314	
	4·5	1·5756			4·5	1·6460	
	5·0	1·7120			5·0	1·7775	
	5·5	1·8729			5·5	1·9290	
	6·0	2·0625			6·0	2·1028	
	6·5	2·2903			6·5	2·3052	
	7·0	2·5596			7·0	2·5372	

1. CHAMBERS, Thesis, University of Western Australia, Perth, W.A., 1956.

SODIUM CHLORIDE—NaCl

Temp. °C	c	η/η^0	Remarks	Ref.
0	0·002 to 0·2	$1 + 0·00448\sqrt{c} + 0·02438c$	$\delta < 0·01\%$	(1)
	0·5	1·01895		
	1·0	1·04858		
	2·0	1·14534		
12·5	0·001 to 0·50034	$1 + 0·0058\sqrt{c} + 0·0616c + 0·0088c^2$	$\delta < 0·01\%$	(2)
15	0·001 to 0·50025	$1 + 0·0058\sqrt{c} + 0·0660c + 0·0086c^2$	$\delta < 0·01\%$	(2)
25	0·001 to 0·5	$1 + 0·0062\sqrt{c} + 0·0793c + 0·008c^2$	$\delta < 0·01\%$ In range 0·002 to 0·5 M (1), (2) and (3) agree to ~ 0·01%.	(2) (2) (1), (3)
	1·0	1·09582	(1) and (3) also agree to ± 0·01% from 0·5 to 2 M.	(1)
	1·5	1·1528		(3)
	2·0	1·2186		(1)
	2·5	1·2913		(3)
	3·0	1·3788		
	3·5	1·4722		
	4·0	1·5797		
	4·5	1·7150		
	5·0	1·8581		
35	0·00099 to 0·49985	$1 + 0·0065\sqrt{c} + 0·0901c + 0·0071c^2$	$\delta < 0·01\%$	(2)
42·5	0·00099 to 0·49983	$1 + 0·0071\sqrt{c} + 0·0982c + 0·0058c^2$	$\delta < 0·01\%$	(2)
50	0·1	1·0129		(3)
	0·3	1·0355		
	0·5	1·0580		
	1·0	1·1184		
	1·5	1·1836		
	2·0	1·2555		
	2·5	1·3348		
	3·0	1·4234		
	3·5	1·5190		
	4·0	1·6266		
	4·5	1·7495		
	5·0	1·8866		

Sodium Chloride—NaCl (*continued*)

m	η/η^0						Ref.
	30°C	35°C	40°C	45°C	50°C	55°C	
1·00	1·107	1·092	1·104	1·106	1·113	1·113	(4)
1·50	1·152	1·145	1·157	1·161	1·167	1·170	
2·00	1·212	1·207	1·224	1·224	1·235	1·236	
2·50	1·284	1·277	1·290	1·293	1·303	1·308	
3·00	1·356	1·354	1·373	1·372	1·380	1·381	
3·50	1·434	1·420	1·439	1·443	1·449	1·450	
4·00	1·522	1·506	1·531	1·522	1·531	1·533	
4·50	1·614	1·603	1·615	1·619	1·621	1·625	
5·00	1·709	1·715	1·726	1·731	1·729	1·725	

1. Jones and Christian, *J. Amer. chem. Soc.*, 1937, **59**, 484.
2. Kaminsky, *Z. phys. Chem.* (N.F.), 1956, **8**, 173.
3. Chambers, Thesis, University of Western Australia, Perth, W.A., 1956.
4. Suryanarayana and Venkatesen, *Trans. Faraday Soc.*, 1958, **54**, 1709.

Sodium Ferrocyanide—$Na_4[Fe(CN)_6]$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·000293 to 0·011911	$1 + 0{\cdot}0405\sqrt{c} + 0{\cdot}805c$	$\delta \sim 0{\cdot}01\%$	(1)

1. Asmus, *Z. Electrochem.*, 1940, **46**, 596.

Sodium Fluoride—NaF

m	η/η^0			Ref.
	20°C	25°C	30°C	
0·000568		1·0003		(1)
0·00103	1·0000	1·0004	1·0021	
0·003686		1·0011		
0·01022	1·0034	1·0026	1·0078	
0·01696		1·0040		
0·03436	1·0093	1·0076	1·0118	
0·06228		1·0131		
0·1014	1·0230	1·0206	1·0223	
0·4103		1·0896		
0·9622		1·2104		

1. Nightingale and Benck, *J. phys. Chem.*, 1959, **63**, 1777.

Sodium Hydroxide—NaOH

Temp. °C	c	η/η^0	Remarks	Ref.
12·5	0·00083 to 0·1428	$1 + 0{\cdot}0035\sqrt{c} + 0{\cdot}1917c$	$\delta < 0{\cdot}01\%$	(1)
18	0·00083 to 0·1426	$1 + 0{\cdot}0035\sqrt{c} + 0{\cdot}1984c$	$\delta < 0{\cdot}01\%$	(1)
25	0·00083 to 0·1425	$1 + 0{\cdot}0036\sqrt{c} + 0{\cdot}2051c$	$\delta < 0{\cdot}01\%$	(1)
30	0·00083 to 0·1422	$1 + 0{\cdot}0037\sqrt{c} + 0{\cdot}2097c$	$\delta < 0{\cdot}01\%$	(1)
35	0·00083 to 0·1420	$1 + 0{\cdot}0037\sqrt{c} + 0{\cdot}2132c$	$\delta < 0{\cdot}01\%$	(1)
42·5	0·00082 to 0·1416	$1 + 0{\cdot}0038\sqrt{c} + 0{\cdot}2188c$	$\delta < 0{\cdot}01\%$	(1)

1. Hückel and Schaaf, *Z. phys. Chem.* (N.F.), 1959, **21**, 326.

SODIUM IODIDE—NaI

Temp. °C	c	η/η^0	Remarks	Ref.
23	0·499	1·022		(1)
	0·998	1·042		
	1·487	1·055		
	1·982	1·094		
	2·470	1·127		
	2·963	1·212		
	3·457	1·247		
	3·951	1·371		
	4·450	1·447		
	4·937	1·596		

1. SATOH and HAYASHI, *Bull. chem. Soc. Japan*, 1961, **34**, 1260.

Viscosity data for sodium iodide up to saturation at 0°, 30°, and 50°C (1), are contained in Document No. 4773, obtainable from the American Documentation Institute, Library of Congress, Washington 25, D.C., U.S.A.

1. MILLER and DORAN, *J. phys. Chem.*, 1956, **60**, 184.

SODIUM NITRATE—$NaNO_3$

m	η/η^0						Ref.
	30°C	35°C	40°C	45°C	50°C	55°C	
1·00	1·050	1·073	1·082	1·086	1·094	1·102	(1)
2·00	1·137	1·185	1·200	1·205	1·218	1·224	
3·00	1·264	1·282	1·300	1·307	1·319	1·345	
4·00	1·409	1·431	1·446	1·454	1·466	1·476	
5·00	1·568	1·605	1·624	1·629	1·643	1·650	
6·00	1·748	1·788	1·802	1·804	1·817	1·824	
7·00	1·954	1·996	2·016	2·005	2·007	2·002	
8·00	2·164	2·215	2·224	2·218	2·222	2·228	
9·00	2·419	2·467	2·469	2·458	2·453	2·454	
11·31	3·022						
11·81		3·204					
12·32			3·361				
12·83				3·500			
13·34					3·634		
13·90						3·718	

1. SURYANARAYANA and VENKATESEN, *Acta chim. Acad. Sci. Hung.*, 1958, **16**, 149.

SODIUM PERCHLORATE—$NaClO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0008987 to 0·1	$1 + 0{\cdot}0068\sqrt{c} + 0{\cdot}03c$	$\delta \sim 0{\cdot}01\%$	(1)
	0·3948	1·0101		
	1·0008	1·049		
	1·9975	1·150		

1. Nightingale, *J. phys. Chem.*, 1959, **63**, 742.

Viscosity data for sodium perchlorate up to saturation at 0°, 30°, and 50°C (1), are contained in Document No. 4773, obtainable from the American Documentation Institute, Library of Congress, Washington 25, D.C., U.S.A.

1. Miller and Doran, *J. phys. Chem.*, 1956, **60**, 184.

SODIUM PERIODATE—$NaIO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·000506 to 0·0968	$1 + 0{\cdot}0072\sqrt{c} + 0{\cdot}0216c$	$\delta \sim 0{\cdot}05\%$	(1)

1. Nightingale and Benck, *J. phys. Chem.*, 1959, **63**, 1777.

SODIUM SULPHATE—Na_2SO_4

Temp. °C	c	η/η^0	Remarks	Ref.
15	0·001 to 0·14016	$1 + 0{\cdot}0148\sqrt{c} + 0{\cdot}361c + 0{\cdot}045c^2$	$\delta < 0{\cdot}01\%$	(1)
22	0·001 to 0·14	$1 + 0{\cdot}0152\sqrt{c} + 0{\cdot}375c + 0{\cdot}034c^2$	$\delta < 0{\cdot}01\%$	(1)
25	0·0005 to 0·07125	$1 + 0{\cdot}0153\sqrt{c} + 0{\cdot}382c$	$\delta \sim 0{\cdot}01\%$	(2)
30	0·00099 to 0·13976	$1 + 0{\cdot}0155\sqrt{c} + 0{\cdot}390c + 0{\cdot}026c^2$	$\delta < 0{\cdot}01\%$	(1)
40	0·00099 to 0·13922	$1 + 0{\cdot}0159\sqrt{c} + 0{\cdot}409c + 0{\cdot}020c^2$	$\delta < 0{\cdot}01\%$	(1)

m	η/η^0										Ref.
	25°C	27°C	29°C	31°C	32°C	33°C	34°C	36°C	38°C	40°C	
0·01783	1·0079	1·0079	1·0080	1·0083	1·0083	1·0085	1·0085	1·0088	1·0092	1·0096	(2)
0·07156	1·0313	1·0316	1·0318	1·0321	1·0323	1·0326	1·0329	1·0335	1·0342	1·0348	
0·14437	1·0626	1·0630	1·0634	1·0636	1·0641	1·0644	1·0647	1·0654	1·0663	1·0673	
0·29296	1·1296	1·1301	1·1307	1·1312	1·1315	1·1318	1·1321	1·1328	1·1335	1·1348	
0·44938	1·2062	1·2064	1·2066	1·2070	1·2073	1·2074	1·2077	1·2081	1·2087	1·2091	
0·61247	1·2943	1·2945	1·2947	1·2949	1·2950	1·2951	1·2953	1·2956	1·2957	1·2960	
0·78607	1·3944	1·3938	1·3933	1·3928	1·3925	1·3923	1·3920	1·3917	1·3918	1·3910	
0·95279	1·5106	1·5086	1·5069	1·5054	1·5047	1·5041	1·5037	1·5026	1·5020	1·5014	
1·34412	1·8095	1·8024	1·7939	1·7870	1·7848	1·7826	1·7804	1·7776	1·7748	1·7715	
1·55108	1·9779	1·9691	1·9626	1·9558	1·9527	1·9501	1·9474	1·9423	1·9377	1·9333	
1·77155	2·2155	2·1945	2·1788	2·1632	2·1568	2·1514	2·1473	2·1386	2·1321	2·1271	
2·00111	2·4844	2·4498	2·4272	2·4060	2·3985	2·3913	2·3830	2·3730	2·3615	2·3550	
2·24276		2·7459	2·7113	2·6831	2·6710	2·6601	2·6507	2·6337	2·6219	2·6120	
2·50123			3·0671	3·0352	3·0202	3·0045	2·9928	2·9653	2·9439	2·9228	
3·01142				3·8792	3·8391						
3·27607						4·3193	4·2850	4·2240	4·1706	4·1399	

1. KAMINSKY, *Z. phys. Chem.* (N.F.), 1955, 5, 154.
2. GLASS and MADGIN, *J. chem. Soc.*, 1934, 1124.

SODIUM THIOCYANATE—NaSCN

Viscosity data for sodium thiocyanate up to saturation at 0°, 30°, and 50°C (1), are contained in Document No. 4773, obtainable from the American Documentation Institute, Library of Congress, Washington 25, D.C., U.S.A.

1. MILLER and DORAN, *J. phys. Chem.*, 1956, **60**, 184.

ZINC SULPHATE—$ZnSO_4$

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·000306 to 0·008742	$1 + 0{\cdot}0229\sqrt{c} + 0{\cdot}534c$	$\delta \sim 0{\cdot}01\%$	(1)

1. ASMUS, *Ann. Phys., Lpz.*, 1939, **5**, 1.

ZINC SULPHIDE—$ZnSO_4$ (*continued*)

m	η/η^0							Ref.
	30°	35°	40°	45°	50°	55°	60°	
0·2266	1·114	1·105	1·101	1·093	1·097	1·087	1·067	(2)
0·4562	1·243	1·230	1·215	1·223	1·201	1·187	1·173	
0·6428	1·362	1·340	1·316	1·299	1·293	1·275	1·259	
0·8347	1·493	1·464	1·433	1·406	1·396	1·369	1·350	
1·016	1·651	1·573	1·572	1·520	1·517	1·484	1·459	
1·19	1·821	1·719	1·712	1·661	1·633	1·592	1·559	
1·48	2·159	2·024	1·987	1·948	1·877	1·813	1·763	
1·77	2·661	2·362	2·295	2·188	2·169	2·078	2·034	
2·06	3·159	2·902	2·796	2·641	2·537	2·417	2·321	
2·35	4·952	3·490	3·344	3·149	2·998	2·774	2·685	
2·64	4·779	4·338	4·103	3·817	3·607	3·341	3·183	
2·93	5·942	5·327	5·019	4·623	4·317	4·015	3·843	
3·22	7·400	6·578	6·140	5·667	5·248	4·837	4·483	
3·51	9·176	8·134	7·542	6·872	6·323	5·803	5·394	
3·823	11·129							
4·1		12·043						
4·345			13·121					
4·53				13·473				
4·711					14·222			
4·971						14·802		
5·207							15.328	

2. SURYANARAYANA and ALAMELU, *Acta. chim. Acad. Sci., Hung.*, 1959, **20**, 91.

APPENDIX 2.2

Relative Viscosity of Electrolytes in Non-aqueous Solutions

SOLVENT—ACETONE

LITHIUM CHLORIDE—LiCl

Temp. °C	*c*	η/η^0	Remarks	Ref.
18	0·00431	1·0027		(1)
	0·00863	1·0055		
	0·03429	1·0211		
	0·07771	1·0435		
	0·1368	1·0711		
	0·2739	1·1454		
25	0·00854	1·0052		
	0·03395	1·0193		
	0·07694	1·0421		
	0·13545	1·0685		
	0·2712	1·1402		

1. HOOD and HOHLFELDER, *J. phys. Chem.*, 1934, **38**, 979.

SOLVENT—ETHANOL

LITHIUM NITRATE—$LiNO_3$

Temp. °C	*c*	η/η^0	Remarks	Ref.
25	0·2503	1·276	Measurements also made by (1) in C_2H_5OH/H_2O mixtures. See Appendix 2.3.	(1)
	0·5321	1·591		
	0·9916	2·209		
	1·567	3·215		
	2·121	4·365		
	2·593	5·617		
	3·206	7·51		

1. CAMPBELL and DEBUS, *Canad. chem. J.*, 1956, **34**, 1232.

Sodium Iodide—NaI

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0007 to 0·009	$1 + 0{\cdot}027\sqrt{c} + 1{\cdot}15c$	$\delta \sim 0{\cdot}03\%$	(1)
	0·01396	1·01755		
	0·1680	1·02079		

1. Cox and Wolfenden, *Proc. roy. Soc.*, 1934, A 145, 475.

Solvent—Glycerol

Potassium Iodide—KI

Temp. °C	c	η/η^0	Ref.	Temp. °C	c	η/η^0	Ref.
25	0·1045	0·9934	(1)	50	0·1031	0·9961	(1)
	0·1970	0·9824			0·1946	0·9868	
	0·2675	0·9728			0·2641	0·9796	
	0·3647	0·9586			0·3601	0·9700	
	0·4926	0·9403			0·4866	0·9566	
	0·6653	0·9168			0·6570	0·9404	
	0·7899	0·9013			0·7800	0·9293	
	0·9812	0·8779			0·9690	0·9119	
	1·2976	0·8425			1·2819	0·8873	
	1·4740	0·8262			1·4560	0·8758	
	1·7438	0·8071			1·7224	0·8611	
	2·1770	0·7876			2·1516	0·8464	
30	0·1042	0·9936	(1)	60	0·1026	0·9964	(1)
	0·1965	0·9837			0·1936	0·9888	
	0·2667	0·9739			0·2627	0·9830	
	0·3638	0·9603			0·3583	0·9747	
	0·4913	0·9433			0·4841	0·9641	
	0·6635	0·9211			0·6537	0·9505	
	0·7879	0·9065			0·7762	0·9418	
	0·9784	0·8839			0·9641	0·9293	
	1·2943	0·8510			1·2754	0·9065	
	1·4703	0·8364			1·4488	0·8970	
	1·7393	0·8170			1·7143	0·8850	
	2·1716	0·7978			2·1412	0·8725	

Potassium Iodide—KI (*continued*)

Temp. °C	c	η/η^0	Ref.	Temp. °C	c	η/η^0	Ref.
40	0·1037	0·9944	(1)	70	0·1021	0·9972	(1)
	0·1955	0·9850			0·1926	0·9914	
	0·2654	0·9767			0·2614	0·9865	
	0·3620	0·9648			0·3565	0·9800	
	0·4890	0·9490			0·4814	0·9721	
	0·6603	0·9304			0·6504	0·9616	
	0·7840	0·9176			0·7722	0·9550	
	0·9737	0·8985			0·9592	0·9445	
	1·2881	0·8688			1·2691	0·9265	
	1·4632	0·8554			1·4417	0·9195	
	1·7309	0·8375			1·7058	0·9100	
	2·1620	0·8224			2·1309	0·9000	

1. Briscoe and Rinehart, *J. phys. Chem.*, 1942, **46**, 387.

Solvent—Methanol

Ammonium Chloride—NH_4Cl

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0005015 to 0·0099441	$1 + 0{\cdot}0183\sqrt{c} \mp 0{\cdot}6610c$	$\delta < 0{\cdot}01\%$	(1)
	0·0149778	1·01166		
	0·0200046	1·01476		
	0·0300215	1·02102		
	0·0400008	1·02707		
	0·0499413	1·03298		
	0·0700415	1·04386		
	0·100215	1·05990		
	0·199413	1·10932		
	0·351163	1·18134		

1. Jones and Fornwalt, *J. Amer. chem. Soc.*, 1935, **57**, 2041.

POTASSIUM BROMIDE—KBr

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0004104 to 0·0100141	$1 + 0{\cdot}0142\sqrt{c} + 0{\cdot}7396c$	$\delta < 0{\cdot}01\%$	(1)
	0·0149908	1·01257		
	0·0300121	1·02265		
	0·0500105	1·03548		
	0·0800065	1·05363		
	0·100011	1·06527		
	0·118905	1·07649		

1. JONES and FORNWALT, *J. Amer. chem. Soc.*, 1935, **57**, 2041.

POTASSIUM CHLORIDE—KCl

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0004786 to 0·0099940	$1 + 0{\cdot}0151\sqrt{c} + 0{\cdot}7635c$	$\delta < 0{\cdot}01\%$	(1)
	0·0199816	1·01676		
	0·0299878	1·02376		
	0·0350097	1·02716		
	0·0400159	1·03055		

1. JONES and FORNWALT, *J. Amer. chem. Soc.*, 1935, **57**, 2041.

Potassium Iodide—KI

Temp. °C	c	η/η^0	Remarks	Ref.
25	0·0002504 to 0·0100232	$1 + 0{\cdot}0159\sqrt{c} + 0{\cdot}6747c$	$\delta < 0{\cdot}01\%$ Over concentration range 0·05 to 0·6 M, (1) and (2) agree to $\sim \pm 0{\cdot}3\%$.	(1) (2)
	0·0271490	1·01962		
	0·0499222	1·03316		
	0·0752514	1·04752		
	0·100245	1·06107		
	0·199325	1·11215		
	0·348769	1·18420		
	0·501918	1·25651		
	0·603193	1·30385		
30	0·0503	1·0332		(2)
	0·0979	1·0596		
	0·1979	1·1100		
	0·3460	1·1781		
	0·5010	1·2482		
	0·6023	1·2945		
	0·7452	1·3608		
35	0·0501	1·0328		(2)
	0·0973	1·0586		
	0·1967	1·1080		
	0·3441	1·1750		
	0·4982	1·2437		
	0·5992	1·2895		
	0·7442	1·3544		
40	0·0497	1·0325		(2)
	0·0968	1·0579		
	0·1956	1·1066		
	0·3421	1·1726		
	0·4955	1·2403		
	0·5958	1·2858		
	0·7403	1·3496		
45	0·0494	1·0323		(2)
	0·0962	1·0574		
	0·1945	1·1057		
	0·3401	1·1710		
	0·4926	1·2382		
	0·5925	1·2830		
	0·7365	1·3461		

POTASSIUM IODIDE—KI (*continued*)

Temp. °C	c	η/η^0	Remarks	Ref.
50	0·0491	1·0320		(2)
	0·0956	1·0570		
	0·1933	1·1051		
	0·3381	1·1699		
	0·4898	1·2363		
	0·5893	1·2803		
	0·7322	1·3433		

1. JONES and FORNWALT, *J. Amer. chem. Soc.*, 1935, **57**, 2041.
2. BRISCOE and RINEHART, *J. phys. Chem.*, 1942, **46**, 387.

ZINC HALIDES

Viscosity data for zinc halides in methanol from −50 to 20°C(1) are contained in Document No. 3257 which can be obtained from the American Documentation Institute, Library of Congress, Washington, D.C., U.S.A.

1. DAWSON, ZIMMERMAN, SWEENEY and DINGA, *J. Amer. chem. Soc.*, 1951, **73**, 4326.

SOLVENT—NITROBENZENE

Tetraethyl—AMMONIUM PICRATE—$N(C_2H_5)_4C_6H_2O_7N_3$

Temp. °C	c	η/η^0	Remarks	Ref.
18	0·000537 to 0·00790	$1 + 0{\cdot}0129\sqrt{c} + 1{\cdot}039c$	$\delta < 0{\cdot}01\%$	(1)

1. COX and WOLFENDEN, *Proc. roy. Soc.*, 1934, **A 145**, 475.

SOLVENT—SULPHURIC ACID

AMMONIUM HYDROGEN SULPHATE—NH_4HSO_4

Temp. °C	m	d^{25}_{4}	η/η^0	Remarks	Ref.
25	0·0964	1·8306	1·0033	Viscosity of sulphuric acid at 25° used for calculation of η/η^0 is 24·54 cp.	(1)
	0·3741	1·8323	0·9747		
	0·6556	1·8348	0·9751		
	0·9245	1·8391	0·9951		
	1·3000	1·8437	1·0130		

1. GILLESPIE and WASIF, *J. chem. Soc.*, 1953, 215.

BARIUM HYDROGEN SULPHATE—$Ba(HSO_4)_2$

Temp. °C	m	d^{25}_{4}	η/η^0	Remarks	Ref.
25	0·0650	1·8475	1·1589		(1)
	0·1122	1·8612	1·2771		
	0·1997	1·8871	1·5281		
	0·3917	1·9382	2·2233		
	0·4486	1·9530	2·4735		
	0·7901	2·0361	4·6822		

1. GILLESPIE and WASIF, *J. chem. Soc.*, 1953, 215.

LITHIUM HYDROGEN SULPHATE—$LiHSO_4$

Temp. °C	m	d^{25}_{4}	η/η^0	Remarks	Ref.
25	0·2491	1·8310	1·1438		(1)
	0·5712	1·8455	1·3341		
	0·6331	1·8484	1·3765		
	1·127	1·8660	1·7449		

1. GILLESPIE and WASIF, *J. chem. Soc.*, 1953, 215.

POTASSIUM HYDROGEN SULPHATE—$KHSO_4$

Temp. °C	m	d^{25}_4	η/η^0	Remarks	Ref.
25	0·2526	1·8446	1·0281		(1)
	0·4633	1·8578	1·0652		
	0·5291	1·8622	1·0958		
	0·8084	1·8780	1·1532		
	1·199	1·8993	1·3011		
	1·776	1·9276	1·5827		

1. GILLESPIE and WASIF, *J. chem. Soc.*, 1953, 215.

SODIUM HYDROGEN SULPHATE—$NaHSO_4$

Temp. °C	m	d^{25}_4	η/η^0	Remarks	Ref.
25	0·2755	1·8437	1·1202		(1)
	0·4392	1·8531	1·2001		
	0·6968	1·8665	1·3733		
	0·9108	1·8784	1·4633		
	1·365	1·8994	1·8007		
	1·454	1·9064	1·8798		

1. GILLESPIE and WASIF, *J. chem. Soc.*, 1953, 215.

STRONTIUM HYDROGEN SULPHATE—$Sr(HSO_4)_2$

Temp. °C	m	d^{25}_4	η/η^0	Remarks	Ref.
25	0·0616	1·8416	1·1487		(1)
	0·2266	1·8767	1·6222		
	0·3250	1·8980	1·9845		
	0·5366	1·9382	3·0102		
	0·7568	1·9775	4·6740		
	0·8404	1·9920	5·6112		

1. GILLESPIE and WASIF, *J. chem. Soc.*, 1953, 215.

APPENDIX 2.3

Relative Viscosity of Electrolytes in Mixed Solvents

SOLVENT—ACETONE/METHANOL

LITHIUM BROMIDE—LiBr

Viscosity data for lithium bromide in 50/50 wt.% acetone/methanol from 20–50°C (1) can be obtained from the Department of Chemistry, University of Kentucky, Lexington, Ky., U.S.A.

1. DAWSON, HAGSTROM and SEARS, *J. electrochem. Soc.*, 1955, **102**, 341.

SOLVENT—ACETONE/WATER

BARIUM ACETATE—$Ba(OCOCH_3)_2$

Temp. °C	c	η/η^0 for various wt. percentages of acetone					Ref.
		0	8·5	21·2	30·8	40·9	
25	0·125	1·0930	1·0969	1·1039	1·1025	1·0983	(1)
	0·25	1·1349	1·2015	1·2018	1·2047	1·2094	
	0·375	1·2876	1·3127	1·3145	1·3192	1·3307	
	0·5	1·4053	1·4467	1·4524	1·4515	1·4513	
	0·75	1·6777	1·7297	1·7438			
	1·0	2·0163	2·1097	2·1112			

1. PADOVA, *J. chem. Phys.*, 1963, **38**, 2635.

MAGNESIUM ACETATE—$Mg(OCOCH_3)_2$

Temp. °C	c	η/η^0 for various wt. percentages of acetone						Ref.
		0	8·5	21·2	30·8	40·9	52·0	
25	0·125	1·1131	1·1279	1·1248	1·1096	1·1186	1·1090	(1)
	0·25	1·2323	1·2641	1·2510	1·2411	1·2453	1·2470	
	0·375	1·3754	1·4096	1·3912	1·3892	1·3779	1·4077	
	0·5	1·5305	1·5918	1·5624	1·5650	1·5383	1·6176	
	0·75	1·9196	1·9963	1·9699	1·9974			
	1·0	2·4184	2·5503	2·5240	2·6163			

1. PADOVA, *J. chem. Phys.*, 1963, **38**, 2635.

MAGNESIUM SULPHATE—$MgSO_4$

Temp. °C	c	η/η^0 for various wt. percentages of acetone			Ref.
		0	8·5	21·2	
25	0·125	1·0789	1·0702	1·0956	(1)
	0·25	1·1661	1·1543	1·1928	
	0·375	1·2598	1·2629	1·3068	
	0·5	1·3690	1·3750	1·4684	
	0·75	1·6205	1·6526	1·9224	
	1·0	1·9504	2·0601		

1. PADOVA, *J. chem. Phys.*, 1963, 38, 2635.

MANGANOUS CHLORIDE—$MnCl_2$

Temp. °C	c	η/η^0 for various wt. percentages of acetone						Ref.
		0	8·5	21·2	30·8	40·9	52·0	
25	0·25	1·0989	1·0934	1·1089	1·1358	1·1422	1·1602	(1)
	0·5	1·2072	1·1984	1·2378	1·2731	1·3111	1·3453	
	1·0	1·4445	1·4394	1·5301	1·6394			
	1·5	1·7383	1·7295	1·8997	2·1368			
	2·0	2·0844	2·0938	2·400				
	2·5	2·500	2·5421	3·139				

1. PADOVA, *J. chem. Phys.*, 1963, **38**, 2635.

POTASSIUM ACETATE—$KOCOCH_3$

Temp. °C	c	η/η^0 for various wt. percentages of acetone						Ref.
		0	8·5	21·2	30·8	40·9	52·0	
25	0·125	1·0290	1·0337	1·0229	1·0366	1·0373	1·0263	(1)
	0·25	1·0580	1·0579	1·0478	1·0598	1·0680	1·0624	
	0·375	1·0860	1·0862	1·0782	1·0852	1·0931	1·0803	
	0·5	1·1152	1·1162	1·1011	1·1125	1·1254	1·1438	
	0·75	1·1740	1·1749	1·1610	1·1788	1·1988	1·2031	
	1·0	1·2330	1·2484	1·2274	1·2457	1·2705		

1. PADOVA, *J. chem. Phys.*, 1963, **38**, 2635.

SODIUM ACETATE—$NaOCOCH_3$

Temp. °C	c	η/η^0 for various wt. percentages of acetone						Ref.
		0	8·5	21·2	30·8	40·0	52·0	
25	0·125	1·0432	1·0412	1·0434	1·0463	1·0475	1·0497	(1)
	0·25	1·0859	1·0831	1·0764	1·0903	1·0951	1·1004	
	0·375	1·1299	1·1213	1·1224	1·1368	1·1430	1·1509	
	0·5	1·1756	1·1719	1·1642	1·1806	1·1913	1·1966	
	0·75	1·2732	1·2562	1·2545	1·2832	1·2850		
	1·0	1·3753	1·3720	1·3485	1·4050	1·3999		

1. PADVOA, *J. chem. Phys.*, 1963, **38**, 2635.

SODIUM SULPHATE—Na_2SO_4

Temp. °C	c	η/η^0 for various wt. percentages of acetone			Ref.
		0	8·5	21·2	
25	0·125	1·0491	1·0521	1·0533	(1)
	0·25	1·1042	1·1080	1·1152	
	0·375	1·1669	1·1612	1·1741	
	0·5	1·2290	1·2313	1·2739	
	0·75	1·3704	1·4150		

1. PADOVA, *J. chem. Phys.*, 1963, **38**, 2635.

SOLVENT—DIOXANE/WATER

BARIUM BROMIDE—$BaBr_2$

Temp. °C	c	η/η^0 for various wt. percentages of dioxane			Ref.
		10	20	30	
35	0·001 to 0·1	$1 + 0{\cdot}0113\sqrt{c} + 0{\cdot}284c^{0{\cdot}9}$	$1 + 0{\cdot}0122\sqrt{c} + 0{\cdot}440c^{0{\cdot}95}$	$1 + 0{\cdot}0131\sqrt{c} + 0{\cdot}675c^{0{\cdot}95}$	(1)
			$\delta \sim 0{\cdot}05\%$		

1. DAS and PATNAIK, *J. Ind. chem. Soc.*, 1962, **39**, 13.

BARIUM CHLORIDE—$BaCl_2$

Temp. °C	c	η/η^0 for various wt. percentages of dioxane			Ref.
		10	20	30	
35	0·001 to 0·1	$1 + 0{\cdot}0225\sqrt{c} + 0{\cdot}230c$	$1 + 0{\cdot}0231\sqrt{c} + 0{\cdot}405c^{0{\cdot}96}$	$1 + 0{\cdot}0241\sqrt{c} + 0{\cdot}648c^{1{\cdot}04}$	(1)
			$\delta \sim 0{\cdot}05\%$		

1. DAS and PATNAIK, *J. Ind. chem. Soc.*, 1962, **39**, 13.

Potassium Chloride—KCl

Temp. °C	c	η/η^0 for various wt. percentages of dioxane					Ref.
		10	20	30	40	50	
35	0·0010	1·0001	1·0003	1·0003	1·0004	1·0004	(1)
	0·0025	1·0002	1·0003	1·0006	1·0006	1·0006	
	0·0050	1·0004	1·0006	1·0009	1·0009	1·0009	
	0·0075	1·0007	1·0010	1·0014	1·0014	1·0011	
	0·0100	1·0008	1·0011	1·0017	1·0017	1·0020	
	0·0250	1·0016	1·0021	1·0029	1·0039	1·0045	
	0·0500	1·0025	1·0037	1·0048	1·0066	1·0088	
	0·0750	1·0032	1·0049	1·0071	1·0093	1·0120	
	0·1000	1·0041	1·0061	1·0080	1·0119	1·0151	

1. Acharya, Das and Patnaik, *J. Ind. chem. Soc.*, 1957, **34**, 56.

Sodium Chloride—NaCl

Temp. °C	c	η/η^0 for various wt. percentages of dioxane					Ref.
		10	c	20	c	30	
35	0·0290	1·0031	0·0215	1·0036	0·02	1·0045	(1)
	0·0347	1·0042	0·037	1·0057	0·0353	1·0075	
	0·0487	1·0060	0·0517	1·0076	0·0411	1·0087	
	0·0532	1·0063	0·0645	1·0092	0·0496	1·0097	
	0·0612	1·0075	0·0722	1·0101	0·0537	1·0108	
	0·075	1·0083	0·0893	1·0125	0·0626	1·0118	
	0·0831	1·0093	0·0966	1·0138	0·0679	1·0134	
	0·0878	1·0102	0·1012	1·0141	0·0793	1·0162	
	0·985	1·0109	0·1120	1·0150	0·0934	1·0181	
	0·1175	1·0130	0·1248	1·0166	0·1068	1·0199	

1. Das, *J. Ind. chem. Soc.*, 1959, **36**, 613.

Solvent—Ethanol/Water

Barium Acetate—Ba(OCOCH$_3$)$_2$

Temp. °C	c	η/η^0 for some weight percentages C$_2$H$_5$OH					Ref.
		0	8·5	18·5	29·5	40·4	
25	0·125	1·0930	1·0858	1·0733	1·0808	1·0794	(1)
	0·25	1·1349	1·1860	1·1434	1·1622	1·1651	
	0·375	1·2876	1·2893	1·2182	1·2486	1·2557	
	0·5	1·4053	1·4033	1·3162	1·3597	1·3534	
	0·75	1·6777	1·6511	1·5472			
	1·0	2·0163	2·0027	1·8509			

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1. Padova, *J. chem. Phys.*, 1963, **38**, 2635.

Lithium Nitrate—LiNO$_3$

Temp. °C	c	30 wt. % C$_2$H$_5$OH	c	70 wt. % C$_2$H$_5$OH	Ref.
25	0·1891	1·001	0·01132	1·004	(1)
	0·04256	1·002	0·02484	1·009	
	0·08623	1·004	0·08582	1·029	
	0·5231	1·033	0·1271	1·043	
	1·059	1·073	0·2419	1·073	
	1·769	1·128	0·5502	1·160	
	2·259	1·187	0·8324	1·250	
	2·985	1·288	1·263	1·386	
	3·951	1·472	1·740	1·579	
	4·561	1·613	2·379	1·875	
	4·680	1·665	2·785	2·108	
	5·643	1·968	3·510	2·610	
	6·639	2·445	4·324	3·359	
	7·850	3·226	5·034	4·194	
	9·188	4·450	6·012	5·723	
	10·48	6·48			
	10·62	6·77			

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1. Campbell and Debus, *Canad. chem. J.*, 1956, **34**, 1232.

MAGNESIUM ACETATE—$Mg(OCOCH_3)_2$

Temp. °C	c	η/η^0 for various weight percentages C_2H_5OH									Ref.
		0	8·5	18·5	29·5	40·4	52·0	60·2	70·3	79·8	
25	0·125	1·1131	1·1030	1·1123	1·1214	1·1176	1·1140	1·1246	1·1289	1·1577	(1)
	0·25	1·2323	1·2232	1·2411	1·2563	1·2382	1·2392	1·2521	1·2799	1·3175	
	0·375	1·3754	1·3615	1·3761	1·3943	1·3904	1·3850	1·4165	1·4590	1·5147	
	0·5	1·5305	1·5143	1·5315	1·5496	1·5476	1·5607	1·5995	1·6598	1·7498	
	0·75	1·9196	1·8855	1·9234	1·9220	1·9248	2·0102	2·0726	2·1758		
	1·0	2·4184	2·3617	2·4762	2·3587	2·4606	2·6050	2·7345	2·9189		

1. PADOVA, *J. chem. Phys.*, 1963, **38**, 2635.

MAGNESIUM SULPHATE—$MgSO_4$

Temp. °C	c	η/η^0 for various wt. percentages C_2H_5OH				Ref.
		0	8·5	18·5	29·5	
25	0·125	1·0789	1·0705	1·0816	1·0916	(1)
	0·25	1·1661	1·1639	1·1749	1·1954	
	0·375	1·2598	1·2606	1·2770	1·3122	
	0·5	1·3690	1·3593	1·4051	1·4303	
	0·75	1·6205	1·6302	1·6835		
	1·0	1·9504	2·0102			

1. PADOVA, *J. chem. Phys.*, 1963, **38**, 2635.

Manganous Chloride—$MnCl_2$

Temp. °C	c	η/η^0 for various wt. percentages C_2H_5OH				Ref.
		0	8·5	18·5	29·5	
25	0·125	1·0989	1·0859	1·0955	1·1060	(1)
	0·5	1·2072	1·1841	1·1994	1·2167	
	1·0	1·4445	1·3990	1·4330	1·4630	
	1·5	1·7383	1·6704	1·7124	1·7886	
	2·0	2·0844	2·0020	2·0480	2·2440	
	2·5	2·500	2·4182	2·4314		
	3·0	3·023				

1. Padova, *J. chem. Phys.*, 1963, **38**, 2635.

Potassium Acetate—$KCOOCH_3$

Temp. °C	c	η/η^0 for various weight percentages C_2H_5OH											Ref.
		0	8·5	18·5	29·5	40·4	52·0	60·2	70·3	79·8	89·9	99·6	
25	0·125	1·0290	1·0193	1·0124	1·0105	1·0255	1·0182	1·0331	1·0393	1·0492	1·0666	1·0976	(1)
	0·25	1·0580	1·0378	1·0336	1·0330	1·0430	1·0340	1·0563	1·0738	1·0882	1·1200	1·1827	
	0·375	1·0860	1·0572	1·0548	1·0416	1·0613	1·0565	1·0822	1·1039	1·1273	1·1796	1·2538	
	0·5	1·1152	1·0862	1·0761	1·0519	1·0824	1·0831	1·1021	1·1447	1·1690	1·2576	1·3543	
	0·75	1·1740	1·1316	1·1107	1·0966	1·1176	1·1253	1·1636	1·2052	1·2543	1·3810	1·5413	
	1·0	1·2330	1·1674	1·1480	1·1246	1·1570	1·1703	1·2280	1·2673	1·3392	1·5103	1·7480	

1. Padova, *J. chem. Phys.*, 1963, **38**, 2635.

Sodium Sulphate—Na_2SO_4

Temp. °C	c	η/η^0 for various percentages of C_2H_5OH			Ref.
		0	8·5	18·5	
25	0·125	1·0491	1·0462	1·0495	(1)
	0·25	1·1042	1·1059	1·1083	
	0·375	1·1669	1·1641	1·1642	
	0·5	1·2290	1·2242	1·2310	
	0·75	1·3704	1·3622		
	1·0	1·5413			

1. Padova, *J. chem. Phys.*, 1963, **38**, 2635.

Sodium Acetate—$NaOCOCH_3$

Temp. °C	c	η/η^0 for various wt. percentages of C_2H_5OH							Ref.
		0	8·5	18·5	29·5	40·4	52·0	60·2	
25	0·125	1·0432	1·0398	1·0305	1·0284	1·0362	1·0268	1·0449	(1)
	0·25	1·0859	1·0795	1·0713	1·0570	1·0699	1·0563	1·0852	
	0·375	1·1299	1·1138	1·1071	1·0962	1·0978	1·0930	1·1331	
	0·5	1·1756	1·1600	1·1320	1·1213	1·1269	1·1137	1·1704	
	0·75	1·2732	1·2402	1·2107	1·1902	1·2019	1·1875		
	1·0	1·3753	1·3310	1·3085	1·2596	1·2805	1·2674		

1. Padova, *J. chem. Phys.*, 1963, **38**, 2635.

SOLVENT—METHANOL/WATER

POTASSIUM CHLORIDE—KCl

Temp. °C	c	η/η^0 for various wt. percentages of CH_3OH					Ref.
		10	20	30	40	50	
35	0·010	1·0005	1·0001	1·0001	1·0006	1·0014	(1)
	0·025	1·0008	1·0005	1·0005	1·0013	1·0025	
	0·050	1·0011	1·0004	1·0011	1·0022	1·0045	
	0·075	1·0015	1·0007	1·0016	1·0031	1·0064	
	0·100	1·0016	1·0008	1·0022	1·0040	1·0083	
	0·125	1·0018	1·0013	1·0022	1·0048	1·0101	
	0·150	1·0022	1·0016	1·0028	1·0056	1·0119	
	0·175	1·0022	1·0019	1·0030	1·0065	1·0137	
	0·200	1·0022	1·0019	1·0033	1·0073	1·0155	

1. SINGH, DAS and PATNAIK, *J. Ind. Chem. Soc.*, 1957, **34**, 494.

APPENDIX 3

Relative Viscosities of Aqueous Solutions of Mixed Electrolytes

The salt components of these mixtures are listed alphabetically hereunder. The tables in which they appear are given in parentheses alongside.

Ammonium sulphate (5)
Barium chloride (1), (2)
Cadmium chloride (2)
Calcium chloride (3)
Copper sulphate (4)
Hydrogen chloride (1), (2)
Hydrogen sulphate (4)
Magnesium chloride (1), (2), (5)
Potassium chloride (1), (4), (5)
Potassium sulphate (1)
Sodium chloride (1), (5)
Sodium nitrate (1)
Zinc chloride (3)
Zinc sulphate (5)

N.B. Where necessary, an explanation of the nature of the concentration units used, is given at the bottom of these tables.

TABLE 1

Temp. °C	Salt pairs	Mole Ratio	η/η^0	Remarks	Ref.
35	$NaCl + BaCl_2$	3:1	$1 + 0{\cdot}009\sqrt{c} + 0{\cdot}132c$	$\delta \sim 0{\cdot}01\%$ to 0·07 M	(1)
		1:1	$1 + 0{\cdot}011\sqrt{c} + 0{\cdot}170c$		
		1:3	$1 + 0{\cdot}015\sqrt{c} + 0{\cdot}205c$		
	$NaCl + MgCl_2$	4:1	$1 + 0{\cdot}009\sqrt{c} + 0{\cdot}165c$	$\delta \sim 0{\cdot}01\%$ to 0·07 M	(1)
		3:2	$1 + 0{\cdot}011\sqrt{c} + 0{\cdot}220c$		
		2:3	$1 + 0{\cdot}013\sqrt{c} + 0{\cdot}282c$		
	$K_2SO_4 + KCl$	3:1	$1 + 0{\cdot}017\sqrt{c} + 0{\cdot}12c$	$\delta \sim 0{\cdot}03\%$ to 0·07 M	(2)
		1:1	$1 + 0{\cdot}014\sqrt{c} + 0{\cdot}08c$		
		1:3	$1 + 0{\cdot}011\sqrt{c} + 0{\cdot}04c$		
	$NaNO_3 + NaCl$	3:1	$1 + 0{\cdot}007\sqrt{c} + 0{\cdot}07c$	$\delta \sim 0{\cdot}03\%$ to 0·07 M	(2)
		1:1	$1 + 0{\cdot}007\sqrt{c} + 0{\cdot}08c$		
		1:3	$1 + 0{\cdot}005\sqrt{c} + 0{\cdot}0875c$	$\delta \sim 0{\cdot}1\%$ to 0·2 M	
	$NaNO_3 + KCl$	3:1	$1 + 0{\cdot}007\sqrt{c} + 0{\cdot}042c$	$\delta \sim 0{\cdot}03\%$ to 0·2 M	(2)
		1:1	$1 + 0{\cdot}007\sqrt{c} + 0{\cdot}031c$		
		1:3	$1 + 0{\cdot}007\sqrt{c} + 0{\cdot}015c$		
	$NaNO_3 + HCl$	3:1	$1 + 0{\cdot}005\sqrt{c} + 0{\cdot}058c$	$\delta \sim 0{\cdot}03\%$ to 0·1 M	(2)
		1:1	$1 + 0{\cdot}005\sqrt{c} + 0{\cdot}058c$		
		1:3	$1 + 0{\cdot}006\sqrt{c} + 0{\cdot}06c$	$\delta \sim 0{\cdot}06\%$ to 0·2 M	

1. CHACRAVARTI and PRASAD, *Trans. Faraday Soc.*, 1940, **36**, 557.
2. CHACRAVARTI, *J. Ind. chem. Soc.*, 1943, **20**, 41.

Both c and M refer to the *total* concentration of electrolyte in g moles l.^{-1}

TABLE 2

Temp. °C	Salt pairs	Molarity of HCl	η/η^0	Remarks	Ref.
35	$CdCl_2 + HCl$	0·100	$1{\cdot}0081 + 0{\cdot}0080\sqrt{c} + 0{\cdot}117c$	$\delta \sim 0{\cdot}03\%$ to 0·08 M	(1)
	$BaCl_2 + HCl$	0·002	$1{\cdot}0004 + 0{\cdot}014\sqrt{c} + 0{\cdot}240c$	$\delta \sim 0{\cdot}03\%$ to 0·04 M	(2)
		0·004	$1{\cdot}0006 + 0{\cdot}012\sqrt{c} + 0{\cdot}260c$	$\delta \sim 0{\cdot}01\%$ to 0·04 M	
		0·007	$1{\cdot}0009 + 0{\cdot}009\sqrt{c} + 0{\cdot}280c$	$\delta \sim 0{\cdot}02\%$ to 0·04 M	
		0·01	$1{\cdot}0012 + 0{\cdot}006\sqrt{c} + 0{\cdot}270c$	$\delta \sim 0{\cdot}02\%$ to 0·04 M	
		0·015	$1{\cdot}0016 + 0{\cdot}322c$	$\delta \sim 0{\cdot}02\%$ to 0·04 M	
		0·05	$1{\cdot}0044 + 0{\cdot}295c$	$\delta \sim 0{\cdot}02\%$ to 0·04 M	
	$MgCl_2 + HCl$	0·0025	$1{\cdot}0005 + 0{\cdot}014\sqrt{c} + 0{\cdot}400c$	$\delta \sim 0{\cdot}01\%$ to 0·05 M	(2)
		0·005	$1{\cdot}0007 + 0{\cdot}011\sqrt{c} + 0{\cdot}415c$	$\delta \sim 0{\cdot}02\%$ to 0·0475 M	
		0·0075	$1{\cdot}0010 + 0{\cdot}008\sqrt{c} + 0{\cdot}430c$	$\delta \sim 0{\cdot}02\%$ to 0·05 M	
		0·01	$1{\cdot}0012 + 0{\cdot}004\sqrt{c} + 0{\cdot}445c$	$\delta \sim 0{\cdot}01\%$ to 0·04 M	
		0·0125	$1{\cdot}0014 + 0{\cdot}002\sqrt{c} + 0{\cdot}450c$	$\delta \sim 0{\cdot}02\%$ to 0·05 M	
		0·05	$1{\cdot}0044 + 0{\cdot}430c$	$\delta \sim 0{\cdot}01\%$ to 0·05 M	

1. CHACRAVARTI and PRASAD, *J. Ind. chem. Soc.*, 1938, **15**, 479.
2. CHACRAVARTI and PRASAD, *Trans. Faraday Soc.*, 1940, **36**, 561.

Both *c* and M in this table refer to the concentration of electrolyte *other* than HCl.

TABLE 3

Temp. °C	Salt pair	Mole ratio	Total molarity M	η/η^0	Ref.
25	$CaCl_2$		6	14·6	(1)
	$CaCl_2 + ZnCl_2$	3:1	6	7·28	
	$CaCl_2 + ZnCl_2$	1:1	6	4·14	
	$CaCl_2 + ZnCl_2$	1:3	6	3·84	
	$ZnCl_2$		6	4·13	
	$CaCl_2$		4·5	5·48	
	$CaCl_2 + ZnCl_2$	3:1	4·5	3·45	
	$CaCl_2 + ZnCl_2$	1:1	4·5	2·56	
	$CaCl_2 + ZnCl_2$	1:3	4·5	2·62	
	$ZnCl_2$		4·5	2·67	
	$CaCl_2$		3	2·49	
	$CaCl_2 + ZnCl_2$	3:1	3	2·02	
	$CaCl_2 + ZnCl_2$	1:1	3	1·81	
	$CaCl_2 + ZnCl_2$	1:3	3	1·81	
	$ZnCl_2$		3	1·87	
	$CaCl_2$		2	1·73	
	$CaCl_2 + ZnCl_2$	3:1	2	1·56	
	$CaCl_2 + ZnCl_2$	1:1	2	1·54	
	$CaCl_2 + ZnCl_2$	1:3	2	1·52	
	$ZnCl_2$		2	1·58	

1. MEAD and FUOSS, *J. phys. Chem.*, 1945, **49**, 480.

TABLE 4

Temp. °C	Salt pairs	Molar % $CuSO_4$	η/η^0	Remarks	Ref.
25	$CuSO_4$–KCl	100	$1 + 0{\cdot}0080\sqrt{\Gamma} + 0{\cdot}068\Gamma$	$\delta \sim 0{\cdot}01\%$ to $0{\cdot}07\Gamma$	(1)
		82·3	$1 + 0{\cdot}0077\sqrt{\Gamma} + 0{\cdot}064\Gamma$		
		64·8	$1 + 0{\cdot}0070\sqrt{\Gamma} + 0{\cdot}060\Gamma$		
		47·9	$1 + 0{\cdot}0067\sqrt{\Gamma} + 0{\cdot}054\Gamma$		
		31·9	$1 + 0{\cdot}0057\sqrt{\Gamma} + 0{\cdot}045\Gamma$		
		21·0	$1 + 0{\cdot}0052\sqrt{\Gamma} + 0{\cdot}036\Gamma$		
		10·3	$1 + 0{\cdot}0042\sqrt{\Gamma} + 0{\cdot}019\Gamma$		
		4·3	$1 + 0{\cdot}0038\sqrt{\Gamma} + 0{\cdot}010\Gamma$		
		0	$1 + 0{\cdot}0036\sqrt{\Gamma}$		
	$CuSO_4$–H_2SO_4	100	$1 + 0{\cdot}0080\sqrt{\Gamma} + 0{\cdot}068\Gamma$		
		84·3	$1 + 0{\cdot}0071\sqrt{\Gamma} + 0{\cdot}064\Gamma$		
		72·9	$1 + 0{\cdot}0064\sqrt{\Gamma} + 0{\cdot}059\Gamma$		
		56·8	$1 + 0{\cdot}0055\sqrt{\Gamma} + 0{\cdot}057\Gamma$		
		43·4	$1 + 0{\cdot}0049\sqrt{\Gamma} + 0{\cdot}053\Gamma$		
		15·4	$1 + 0{\cdot}0037\sqrt{\Gamma} + 0{\cdot}049\Gamma$		
		0	$1 + 0{\cdot}0032\sqrt{\Gamma} + 0{\cdot}037\Gamma$		

1. ASMUS, *Ann. Phys., Lpz.*, 1939, **36**, 166.

Γ is the total ionic concentration, i.e. $\Gamma = \Sigma C_i Z_i^2$, where C_i is the number of g ions/litre^{-1} of i and Z_i is the valence.

TABLE 5

Temp. °C	Salt pairs	Molar %	Total concn.	η/η^0	Ref.
20	NaCl + KCl	100 + 0	2 M	1·2094	(1)
		65 + 35		1·1271	
		60 + 40		1·1165	
		57 + 43		1·1093	
		55 + 45		1·1051	
		50 + 50		1·0944	
		48 + 52		1·0901	
		40 + 60		1·0734	
		25 + 75		1·0428	
		0 + 100		1·9895	
	$MgCl_2$ + KCl	100 + 0	1 M	1·4854	
		70 + 30		1·3104	
		60 + 40		1·2556	
		55 + 45		1·2323	
		52 + 48		1·2172	
		50 + 50		1·2072	
		48 + 52		1·1979	
		45 + 55		1·1863	
		0 + 100		1·9869	
	$(NH_4)_2SO_4$ + $ZnSO_4$	100 + 0	0·5 M	1·1052	
		90 + 10		1·1263	
		80 + 20		1·1494	
		65 + 35		1·1865	
		50 + 50		1·2252	
		40 + 60		1·2515	
		35 + 65		1·2654	
		30 + 70		1·2795	
		25 + 75		1·2941	
		20 + 80		1·3089	
		15 + 85		1·3248	
		0 + 100		1·3886	

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1. TOLLERT, *Z. phys. Chem.*, 1939, A 184, 150.

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* Since the tables in the appendices are alphabetically arranged (see p. 73), separate index entries for substances are not made unless they are also discussed in the text. Similarly, topics are not indexed where they are adequately located by chapter-headings (see p. vii).