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Conductometry of electrolyte solutions

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ABSTRACT. A review is given of the theories of the electrical conductance of electrolyte solutions of different ionic strengths and concentations, and of the models of ion association. An analysis is made of the methods for mathematical processing of experimental conductometric data. An account is provided of various theories describing the dependence of the limiting value of the ionic electrical conductance on the properties of the solute and solvent

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Introduction

Conductometry, i.e. measurement of the electrical conductivity, is used widely in fundamental investigations of electrolyte solutions and in tackling many applied problems. It is one of the simplest and yet most accurate methods for the investigation and analysis of substances. It makes it possible to carry out studies over a wide range of temperatures, pressures, and electrolyte solutions (from strongly dilute to melts), and this can be done using practically any solvent. The fact that the electrical conductance of electrolyte solutions can be measured with a high degree of precision at low concentrations makes it possible to apply quite rigorous theories and model representations which can give information on the state of particles in a solution, their effective size, mobility, and association. Combination of the conductometric method with determination of the transport (transference) numbers makes it possible to find the transport characteristics of individual ions without making any assumptions.

Many monographs and reviews have been published on the conductometric method.[1–9] However, the majority of them concentrate on the theory and practice of the determination of the resistance of electrolyte solutions and less prominence is given to theoretical interpretations of the results obtained. The present review therefore stresses a theoretical description of the dependence of the electrical conductance of an electrolyte solution on the concentration, temperature, pressure, and properties of the solvent, and also the problems encountered in mathematical processing of the experimental results, particularly selection of a suitable algorithm needed to find the parameters of interest.

II. Dependence of the electrical conductance on concentration

The existing theory of electrolyte solutions is incapable of describing, from a unified point of view, the concentration dependence of the electrical conductance of an electrolyte solution throughout the full range of compositions. There are different approaches to the interpretation of the electrical conductance of strong and weak electrolytes.

1. Dilute solutions of strong electrolytes

The theoretical problems of interpretation of the concentration dependence of the electrical conductance of dilute electrolyte solutions were considered by Onsager. The Onsager theory is based on the hypothesis that the limiting velocity v of an ion is determined by the action of three forces: 1) an external force eE; 2) average interionic forces F_r responsible for what is known as the relaxation effect; 3) forces of electrophoretic drag F_e which arise because the motion of a central ion does not occur in an immobile medium but in a medium moving in the opposite direction to this ion:

$$v = v_e + u_0(eE + F_r),$$

where v_e is the velocity of an ion under the action of the electrophoretic forces F_e; u_0 is the mobility of an ion at infinite dilution

$$u_0 = \frac{v_0}{E} = \lambda^0/zeF,$$

F is the Faraday; z is the charge of the ion.

The forces exerting the drag on an ion can be defined in terms of the distribution functions f and the pair interaction potentials U. Therefore, the theoretical problem of the electrical conductance reduces to estimating these quantities. The pair distribution functions f_{ij} and f_{ji} can be calculated by solving the continuity equation

$$-\frac{\partial}{\partial t} f_{ji} = \nabla_P f_{ij}\vec{V}_{ij} + \nabla_0 f_{ji}\vec{V}_{ji} = -\frac{\partial}{\partial t} f_{ji},$$

where $\vec{V}_{ij}$ and $\vec{V}_{ij}$ are the velocities of two particles; ∇_P and ∇_Q are the nabla operators acting in the vicinity of the points P and Q.

The continuity equation given in Ref. 10 contains the distribution functions for two, three, and four particles. A similar equation was obtained by Ebeling[11,12] directly from the Liouville equation.[13] This makes it possible to find the relationship between the Onsager approach to the problem of the electrical conductance from the point of view of diffusion and using an approach based on statistical physics.

When weak electric fields are applied to a system (as in measurements of the electrical conductance) the velocity of a charged particle can be regarded as directly proportional to the electric field E. This assumption makes it possible to solve the continuity equation by introducing the following approximations:

$$f_{ij} = f_{ij}^{0} + f_{ij}',$$

$$\psi_i = \overset{0}{\psi_i} + \psi_i,$$

where ψ_i is the potential of the mean force; f^0 and ψ^0 are quantities corresponding to the equilibrium state; f' and ψ' are the contributions due to the presence of an external electric field. The relationship between the pair distribution function and the mean-force potential can be described by the Poisson–Boltzmann equation. The selection of U_{ij} and f_{ij}^0, and of the appropriate boundary conditions, for solving the continuity equation, together with the different degrees of precision of this solution are the reasons for the multiplicity of equations proposed for the concentration dependence of the molar electrical conductance, such as the equations proposed by Pitts,[14] Fuoss, Onsager and Skinner,[15] Fuoss and Hsia,[16] Quint and Viallard,[17] Chen,[18] etc.

In their most general form all the equations describing the electrical conductance on the basis of the Debye–Hückel–Onsager theory can be represented as follows:

$$\lambda = \lambda^0\left(1 + \frac{\Delta X}{X}\right) + \Delta\lambda_e, \qquad (1)$$

where $\Delta X/X$ and $\Delta\lambda_e$ represent, respectively, the relaxation and electrophoretic contributions to the electrical conductivity. We can find the interpretation of $\Delta X/X$ and $\Delta\lambda_e$ in the original papers.

One primitive model considers the behaviour of a solid charged unpolarisable sphere of radius a_j in a continuum whose permittivity ε and viscosity η are the same as in the bulk of the solvent. When equations based on this primitive model are used, it is assumed initially that an electrolyte is fully dissociated and association is considered only at the second stage using the law of mass action. Dielectric saturation is ignored and the bulk value of ε is used right up to $r = a_{ij} = R$ (which is the distance of closest approach of the ions).

Expanding $\Delta X/X$ and $\Delta\lambda_e$ as a series in terms of the concentration, we can reduce Eqn. (1) to

$$\lambda = \lambda^0 - Sc^{1/2} + Ec\ln c + I_1 c + I_2 c^{3/2} + \ldots, \qquad (2)$$

where $S = \alpha^0\lambda^0 + \beta^0$, (2a)

$$E' = E_1'\lambda^0 - hE_2', \qquad (2b)$$

$$I_1 = \sigma_1\lambda^0 + \sigma_2, \qquad (2c)$$

$$I_2 = \sigma_3\lambda^0 + \sigma_4. \qquad (2d)$$

The coefficients S and E' can be calculated from the following relationships:

$$\alpha^0 = \frac{kab}{3\sqrt{c}}\frac{1/2}{1+1/\sqrt{2}} = \frac{kab}{3\sqrt{c}}0.29282 = 8.2042\cdot10^5(\varepsilon T)^{-3/2}, \qquad (3a)$$

$$\beta^0 = \frac{Fe|z|}{3\pi\eta C}\frac{k}{\sqrt{c}} = 82.4907\eta^{-1}(\varepsilon T)^{-1/2}, \qquad (3b)$$

$$E_1' = \frac{\beta^2k^2}{24c} = 2.9437\cdot10^{12}(\varepsilon T)^{-3}, \qquad (3c)$$

$$E_2' = \frac{\beta k\beta^0}{16\sqrt{c}} = 43.3244\eta^{-1}(\varepsilon T)^{-2}, \qquad (3d)$$

$$\beta = ab = (ze)^2/\varepsilon kT = 1.6712\cdot10^{-3}(\varepsilon T)^{-1}, \qquad (3e)$$

$$\frac{k}{\sqrt{c}} = \left[\frac{8\pi N(ze)^2}{1000\varepsilon Tk}\right]^{1/2} = 5.02956\cdot10^9(\varepsilon T)^{-1/2}, \qquad (3f)$$

$$\sigma_1 = 2E_1'\Delta_1,\ \sigma_2 = 2E_2'\Delta_2,\ \sigma_3 = -ZE_1'\Delta_3,\ \sigma_4 = -ZE_4'\Delta_4,\ Z = \frac{k\beta}{\sqrt{c}}.$$

The expressions for $\Delta_1 - \Delta_4$ and the values of h obtained using various theories are as follows:

Pitt (Ref.14)	Quint–Viallard (Ref.17)
$\Delta_1 = \frac{2}{b} + 1.7718 + \ln Z,$	$\Delta_1 = \frac{2}{b} + \frac{2}{b^2} - \frac{1}{b^3} + 0.9074 + \ln Z,$
$\Delta_2 = \frac{8}{b} + 0.01387 - \ln Z,$	$\Delta_2 = \frac{1}{b^2} + \frac{35}{6b} - 1.6764 - 2\ln Z,$
$\Delta_3 = \frac{5.1716}{b} + 6.2928,$	$\Delta_3 = \frac{3.8048}{b^2} + \frac{4.4296}{b} + 1.6094,$
$\Delta_4 = \frac{16}{\beta_0 b} + 1.25248,$	$\Delta_4 = \frac{34}{3b} - 3.7844,$
$h = 1;$	$h = 2;$

Fuoss–Hsia (Ref.16)	Fuoss–Justice–Chen (Ref.19)
$\Delta_1 = \frac{2}{b} + \frac{2}{b^2} - \frac{1}{b^3} + 0.9074 + \ln Z,$	$\Delta_1 = \frac{2}{b} + \frac{2}{b^2} - \frac{1}{b^3} + 0.9074 + \ln Z,$
$\Delta_2 = \frac{22}{3b} + 0.01422 - \ln Z,$	$\Delta_2 = \frac{1}{b^2} + \frac{35}{3b} - 1.0344 - 2\ln Z,$
$\Delta_3 = \frac{3.8284}{b^2} + \frac{4.4748}{b} + 0.6094,$	$\Delta_3 = \frac{3.8284}{b^2} + \frac{4.4748}{b} + 0.6094,$
$\Delta_4 = \frac{4}{3b^2} + \frac{16.3906}{b} + 2.6883 - 1.2922b + \frac{\beta_0}{Z\lambda^0}\left(\frac{4}{3} - 2.2194\right),$	$\Delta_4 = \frac{34}{3b} - \frac{2}{b^2} - 1.3693,$
$h = 1;$	$h = 2.$

The role of the ion–ion interactions increases on increase in the concentration and on reduction in the permittivity. This leads to association of ions, which lowers the electrical conductance of electrolyte solutions. Then Eqns. (1) and (2) assume the following form if we allow for the degree of dissociation of an electrolyte α:

$$\lambda = \alpha\left[\lambda^0\left(1 + \frac{\Delta X}{X}\right) + \lambda_e\right], \qquad (4)$$

$$\lambda = \alpha\left[\lambda^0 - S(\alpha c)^{1/2} + E'\alpha c\ln(\alpha c) + I_1\alpha c + I_2(\alpha c)^{3/2} + \ldots\right]. \qquad (5)$$

However, investigators are interested more in finding not the degree of dissociation of an electrolyte but the association constant:

$$K_a = \frac{(1-\alpha)\gamma_a}{\alpha^2 c\gamma_\pm^2}, \qquad (6)$$

where γ_a is the activity coefficient of ion pairs (usually assumed to be unity): $\gamma_\pm$ is the mean-ion activity coefficient, which is usually calculated employing the Debye–Hückel theory

$$\gamma_\pm = \exp\left(-\frac{qk}{1+kR}\right), \tag{7}$$

where $q = \beta/2$.

It should be pointed out that when Eqns. (4) and (5) are used the coefficient should be interpreted bearing in mind that $c_i = \alpha c$. Fuoss[20] showed that when the series of parameters λ^0, K_a, and R are used, the values of the electrical conductance calculated from Eqn. (1) are always less than those obtained using the exact expression (2), and they agree satisfactorily with one another only up to $kR \approx 0.2$.

Justice[21] suggested making the parameter I_2 in Eqn. (5) a fitting variable and thus allowing for all the inaccuracies associated with calculation of the exponential integral. It should be pointed out that the validity of Eqns. (4) and (5) is limied to the maximum electrolyte concentration corresponding to the condition $kq \approx 0.5$.

Fuoss[22] and Lee and Wheaton[23–25] proposed equations describing the electrical conductivity on the basis of a more realistic physical picture than the primitive model described above. In the model of Lee and Wheaton it is assumed that an ion is surrounded by three different regions: in the first ($a_j < r < R_j'$, where a_j is the crystallographic radius of an ion) the solvent molecules are oriented in the electric field of an ion and the dielectric saturation effect applies; in the second region ($R_j' < r < R_j$, where R_j is the radius of the Gurney co-sphere of an ion[26]) the structure of the solvent is still modified by the field of the ion and the permittivity is not equal to the bulk value; in the third region ($r > R_j$) the properties of the solvent are the same as in the bulk.

In this way Lee and Wheaton allow for the dielectric saturation effects and also include the concept of ion association right from the beginning. This leads to the following equation

$$\lambda = \alpha\left\{\lambda_0\left[1 + C_1\beta k + C_2(\beta k)^2 + C_3(\beta k)^3\right] - \frac{\rho k}{1+t}\left[1 + C_4\beta k + C_5(\beta k)^2 + \frac{t}{12}\right]\right\}, \tag{8}$$

$$C_1 = \frac{\left(1-1/\sqrt{2}\right)\left[1\left(1+1/\sqrt{2}\right)t/2\right]}{3k_0k_3},$$

$$C_2 = -\frac{1}{24k_0k_3}\left[\frac{2\left[Tr\left(2+1/\sqrt{2}\right)t + 1/2\right]}{k_0} + \frac{H_1(t)}{k_3}\right],$$

$$H_1(t) = \left\{-1.91421356 - 1.35355t - 0.198t^2 - 3k_3Tr\left[\left(1+1/\sqrt{2}\right)t\right] + 4k_3k_2Tr(t) - k_1k_2Tr\left(t/\sqrt{2}\right)\right\},$$

$$C_3 = \frac{\left(3+1/\sqrt{2}\right)Tr\left[\left(3+1/\sqrt{2}\right)t\right]}{36k_0k_3\left(1+1/\sqrt{2}\right)},$$

$$C_4 = -\left\{H_2(t)/2 + \frac{\left[1+\left(1+1/\sqrt{2}\right)t/2\right]}{6k_0k_3\left(1+1/\sqrt{2}\right)}\right\},$$

$$H_2(t) = \left\{-Tr(t)/2 + \frac{3Tr\left[\left(1+1/\sqrt{2}\right)t\right]}{4k_3} + 0.436886 - 0.3085t\right\},$$

$$t = kR,\ \rho R = \beta_0(\alpha c)^{1/2},$$
$$k_0 = 1 + t,\ k_1 = 1 + t + t^2/2,\ k_2 = 1 + t/\sqrt{2},\ k_3 = 1 + t/\sqrt{2} + t^2/4.$$

In Ref. 27 the coefficients $C_1 - C_5$ are represented as a series in terms of t and $\ln t$, which is accurate to within 0.01% in the range $0.005 < t < 0.7$:

$$C_1 = -0.09753 + 0.08185t - 0.044144t^2 + 0.01114t^3,$$
$$C_2 = 0.11798 - 0.18737t + 0.09052t^2 - 0.02393t^3 + 0.08358\ln t,$$
$$C_3 = -0.19454 + 0.39764t - 0.37557t^2 + 0.25118t^3 - 0.07843t^4 - 0.10296\ln t,$$
$$C_4 = -0.04724 + 0.06445t - 0.07419t^2 + 0.01784t^3 + 0.12428\ln t + 0.09863t\ln t,$$
$$C_5 = 0.84185 - 0.90051t + 0.07809t^2 - 0.05333t^3 + 0.50097\ln t + 0.45252t\ln t.$$

In Refs. 22 and 28 Fuoss proposed an equation describing formation of ion pairs separated by solvent and those in direct contact:

$$M^+ + A^- \underline{K_1} (M^+ \ldots A^-) \underline{K_2} M^+A^-.$$

If α_1 is the fraction of free ions and α_2 is the fraction of contact ion pairs, the equation describing the electrical conductivity becomes

$$\lambda = [1 - \alpha_2(1-\alpha_1)]\left[\lambda^0\left(1 + \frac{\Delta X}{X}\right) + \Delta\lambda_e\right]. \tag{9}$$

Formation of ion pairs separated by solvent is described by the expression

$$K_1 = \frac{(1-\alpha_1)(1-\alpha_2)}{c\alpha_1^2\gamma_\pm^2},$$

whereas the formation of contact pairs from solvent-separated ones is given by

$$K_2 = \frac{\alpha_2}{(1-\alpha_2)}.$$

The association constant is

$$K_a = K_1(1 + K_2).$$

According to Fuoss, all the short-range effects can be represented by a single parameter LK_2 which can be calculated from

$$K_2 = \exp\left[\frac{\Delta E_s}{kT}\right],$$

where ΔE_s is the difference between the energies of the ions in the states $r = R$ and $r = a$.

An analysis of the experimental results using Eqn. (9) reduces to solution of the equaiton $\lambda = \lambda(c, \lambda^0, R, E_s)$. The value of K_1 is calculated on condition that R is known using the Fuoss equation for the association constant [Eqn. (28)].

Ebeling and his colleagues[29–31] used nonequilibrium thermodynamics and statistical physics in combination with the mean-sphere approximation and the law of mass action to propose the following equation for the electrical conductance:

$$\lambda = a\lambda^0[1 + S^{Rel}(t, b) + S^{Int}(t, b) + S^{Ext}(t, b)], \tag{10}$$

where

$$S^{\mathrm{Rel}}(t,b)=\frac{1}{6\sqrt{2}tb}\left[2-2b+\sqrt{2}tb-t^2\right]-\frac{\exp(-\sqrt{2}t)}{6\sqrt{2}tb}\left[2-2b+\right.$$
$$\left.+\ 2\sqrt{2}t-\sqrt{2}tb+t^2\right]+\frac{1}{3(1+\Gamma R)^2}\left[\left(1+\frac{t}{\sqrt{2}}-b\right)\exp\left(\frac{2-\sqrt{2}t}{2}t\right)\right.$$
$$\left.-1-t+b\right]-\frac{t^2}{12b}\left(\frac{1}{3}+b\right)(1+t-b)\exp(-t),$$

$$\frac{S^{\mathrm{Int}}(t,b)}{h}=\frac{tb}{2}E_i\left(-\frac{t}{\sqrt{2}}\right)\left[\left(\sqrt{2}-t\right)\exp\left(\frac{t}{\sqrt{2}}\right)-\left(\sqrt{2}+t\right)\exp\left(-\frac{t}{\sqrt{2}}\right)\right]-$$
$$-\frac{\exp(-\sqrt{2}t)}{t}\left[\left(\sqrt{2}+2t+\frac{t^2}{\sqrt{2}}\right)b-2\sqrt{2}-4t-\sqrt{2}t^2\right]+$$
$$+\frac{\sqrt{2}}{t}\left[\left(1-\frac{t^2}{2}\right)b-2+t^2\right]+\frac{2b^2\exp(t)}{(1+\Gamma R)^2}\left[\frac{t^2}{2}E_i\left(-\frac{t^2}{\sqrt{2}}\right)-t^2E_i(-t)+\right.$$
$$\left.+\left(1-\frac{2}{b}+\frac{t}{\sqrt{2}}-\frac{\sqrt{2}t}{b}\right)\exp\left(-\frac{t}{\sqrt{2}}\right)-\left(1-\frac{2}{b}+t\frac{2t}{b}\right)\exp(-t)\right]-t^2\left(\frac{1}{3}+b\right)$$
$$\left[\frac{t^2b}{2}E_i(-t)-\left(1-\frac{b}{2}+t-\frac{tb}{2}\right)\exp(-t)\right],$$

$$S^{\mathrm{Ext}}(t,b)=-\frac{8tbh}{(1+\Gamma R)^2},$$

$$\Gamma R=\frac{1}{2}(1+2t)^{1/2}-\frac{1}{2},$$

$$h=\frac{\varepsilon kTN}{3\pi\eta\lambda^0\cdot 9\cdot 10^{11}}=\frac{H}{\lambda^0},\ H=1.226956\cdot 10^{-6}\varepsilon T/\eta;$$

$$E_i(-x)=0.577215665+\ln(-x)+\sum_{n=1}^{\infty}\frac{(-x)^n}{n\cdot n!},\quad b=\frac{\beta}{R}.$$

In calculation of the degree of association in this approach the constant is obtained from the Ebeling equation[32]

$$K_a=8\cdot 10^3\pi R^3N\sum_{m=2}^{\infty}\frac{q^{2m}}{(2m)!(2m-3)},\qquad(11)$$

and the mean ion activity coefficient is found from the mean-sphere approximation

$$\ln\gamma_{\pm}=-\frac{10^3t}{4\pi cNR^3}\left[1+2t-(1+2t)^{1/2}\right].\qquad(12)$$

It should be stressed that all the equations given above describe only the concentration dependences of the electrical conductance of symmetric electrolytes.

The choice of one or another theoretical equation for the calculation λ^0, K_a, and R is quite subjective. The majority of these equations give the same value of λ^0, but the values of K_a agree only to within an order of magnitude. Therefore, a correct analysis of the dependences of the conductometric parameters on the temperature of an electrolyte solution and on the ion radius should involve treatment of all the experimental data on the basis of the same equation.

In obtaining reliable values of λ^0 and K_a it is important not only to select in a reasoned manner a theoretical equation, but also a mathematical approach for its solution.

All the equations given above can be represented in the form

$$\lambda_i=f(c_i,\varepsilon,\eta,T,|z|,\lambda^0,K_a,R),$$

where λ_i is the molar electrical conductance of a symmetric electrolyte with the ion charge z and a molar concentration c_i; ε is the permittivity and η is the viscosity of the solvent at a temperature T; λ^0, K_a, and R are the unknown parameters.

The task then reduces to finding such λ^0, K_a, and R that the values of the electrical conductance calculated on the basis of theoretical equations are as close as possible to the experimental data. We shall bear in mind that an analysis of the experimental data using the above equations for the electrical conductance may be carried out only within a certain range of concentrations. Since these equations are based on the concept of formation of ion pairs, the upper limit to the concentration range is limited by that value at which associates of higher orders can be ignored. An approximate estimate of the upper concentration limit can be obtained (ignoring the degree of dissociation) using the relationship $kq \approx 0.5$,[10] which corresponds to $c_{\max} = 1.4 \times 10^{-4}(\varepsilon T)^3$. The lower limit of the concentration is set by the experimental capabilities and it is usually $(0.5-1.0) \times 10^{-4}$ mol/dm^3. Moreover, it is important to stress that the values of upper and lower limits of the concentration range should differ by at least one order of magnitude.

From the mathematical point of view the finding of the unknown parameters (λ^0, K_a, R) reduces to solution of a redundant system of nonlinear equations: a) the concentration dependence of the electrical conductance [Eqns (5), (8), and (10), or others]; b) the law of mass action [Eqn. (6)]; c) the expressions for the mean ion activity coefficient [Eqns. (7) and (12)]. The solution of a system of such equations is then obtained by minimisation of the function

$$\sigma(\lambda)=\sum_{i=1}^{n}\omega_i(\lambda_i^{\mathrm{calc}}-\lambda_i^{\mathrm{exp}})^2/(n-m-1),\qquad(13)$$

where n is the number of experimental points; m is the number of unknown parameters; ω_i is a weighting coefficient.

The coefficient ω_i is usually assumed to be 1, but since the precision of the experimental data decreases on reduction in the solute concentration, Kay et al.[33] suggested using a weighting coefficient proportional to $c^{1/2}$. A more rigorous way of calculating the weighting coefficient for each point involves using the overall r.m.s. deviation $\omega = 1/\sigma_\lambda$.

The solution of the problem of minimisation of the function $\delta(\lambda)$ is most frequently tackled employing the nonlinear least squares method, which is not difficult when using modern computers.

One should point out however that calculations carried out by the method of least squares require the knowledge of the derivatives with respect to the parameters being sought. Analytic differentiation of such complex dependences as the equations describing the electrical conductance meets with certain difficulties. Therefore, these derivatives are frequently found by numerical differentiation but this increases the computer time. However, the derivatives with respect to λ^0 and K_a can be obtained employing the approximate equation

$$\left(\frac{\partial\lambda}{\partial K_a}\right)=-\frac{\gamma_{\pm}^2c\alpha}{(1+K_a\gamma_{\pm}^2c\alpha)}.$$

If we employ the Lee–Wheaton equation, then

$$\left(\frac{\partial\lambda}{\partial K_a}\right)\simeq\frac{E_s c\alpha}{\left(1+K_a\gamma_\pm^2 c\alpha\right)},$$

where $E_s c\alpha$ corresponds to the expression in the first square brackets of Eqn. (8).

If we use an equation of the (5) type, then

$$\left(\frac{\partial\lambda}{\partial K_a}\right)\simeq\frac{1-\alpha^0(\alpha c)^{1/2}+E_1'(\alpha c)\ln(\alpha c)+\sigma_1\alpha c+\sigma_3(\alpha c)^{3/2}}{\left(1+K_a\gamma_\pm^2 c\alpha\right)}.$$

If we employ Eqn. (1), then

$$\left(\frac{\partial\lambda}{\partial K_a}\right)\simeq\alpha\left(1+\frac{\Delta X}{X}\right).$$

We can in this way obtain derivatives with respect to λ^0 also from Eqn. (10).

In tackling such problems one may encounter cases when the derivatives with respect to K_a and R have opposite signs. Consequently, the search for a minimum may continue indefinitely. Moreover, in the case of some of the theoretical equations for the electrical conductance [Fuoss–Hsia or Fuoss (1975)] the dependence $\sigma(\lambda) = f(R)$ may have two minima in the range of physically reasonable values of R,[10] which in the opinion of these authors is related to the internal inconsistency of the equations themselves. Moreover, in solutions of specific problems it is frequently found that there is a wide range of values of K_a and R which yield practically the same value of $\sigma(\lambda)$. Difficulties are therefore encountered in an analysis of the data for such systems.

Such difficulties can be avoided either by varying R, as suggested by Fuoss[22] [then the values of λ^0, K_a, and R are selected on the basis of an analysis of the dependence $\sigma(\lambda) = f(R)$] or by reducing the problem to one with two parameters by selecting a physically reasonable value of R (it is usually the Bjerrum distance, equal to the sum of the crystallographic radii of ions and the diameter of the solvent molecule). It should be pointed out that many of these shortcomings are avoided also if the problem of minimisation is solved by the direct search method (Powell, deformed polyhedron, Rosenbrock, coordinate descent, and other methods[34]). However, in contrast to the least-squares method, the direct search methods do not yield the standard errors of the required parameters.

In tackling the task of minimisation of the function (13) we need to know the initial approximations in respect of the required parameters. In the case of λ^0 we can find this quantity approximately by: a) graphical extrapolation of the function $\lambda_i = f(c^{1/2})$ to zero concentration; b) from the Walden rule ($\lambda^0\eta_0$ = const); c) from the Fuoss–Kraus[35] or Shedlovsky[36,37] equations. The first approximation for K_a can be selected either from the Ostwald equation (if we specify λ^0 first), which gives

$$K_a=\frac{(\lambda^0)^2(1-\lambda/\lambda^0)}{c\lambda^2},$$

or from the Fuoss–Kraus and Shedlovsky equations. The first approximation for R is frequently taken to be the sum of the crystallographic radii of the ions.

We can find also other approaches to the solution of the electrical conductance equation in the published literature. They are based on a selection of an analytic relationship between K_a and R, so that the task of minimisation can be reduced to a two-parameter problem. However, we must then bear in mind that the selection should be based on the same model which underlies the theoretical equation for the electrical conductance. This approach is employed most frequently in Refs. 12, 29, 30, and 38 when the relationship between K_a and R is of the type given by Eqn. (11). On the other hand, in using the Lee–Wheaton equation the best grounded is the expression for K_a which allows for the short-range effects [Eqn. (32)]. Therefore, the number of the unknown parameters does not decrease and one of them (K_a) is simply replaced with another (U^*).

An approach developed by Justice[21] is also very popular and it involves solving equations of the (5) type. The fitting parameters are then λ^0, K_a, and I_2; the values of I_1 and $\gamma_\pm$ are then calculated on the assumption that R is equal to the Bjerrum distance (q).

The descriptions of the algorithms and the computer programs used in an analysis of conductometric data can be found in a number of original papers.[25,27,39–41]

All the equations given above describe the concentration dependence of the electrical conductance of symmetric electrolytes. In the case of solutions of asymmetric electrolytes (particularly asociated solutions) or mixtures of electrolytes the number of suggested equations is considerably less, although such solutions are encountered more frequently (they include natural water, solutions used in various technologies, etc.). The first attempts to provide a quantitative description of the electrical conductance of asymmetric electrolytes were made by Righellato and Davis,[42] and by Fuoss and Edelson.[43] The equations derived for associated 2–1 (or 1–2) electrolytes are based on the limiting Onsager law and on a number of other assumptions. Subsequently, Quint and Vialliard,[17] Murphy and Cohen,[44] and Chen[18] used the framework of the primitive model to calculate more accurately the contributions of the electrophoretic and relaxation effects to the electrical conductance of solutions of asymmetric and mixed electrolytes. The final equations for the electrical conductance can be found in the original papers. We shall give here the equation of Lee and Wheaton[23,24] obtained on the basis of their new model of a solution containing s types of charged particles:

$$\lambda(j)=\lambda^0(j)\left\{1+z_j\sum_{p=2}^{s}\chi_j^p\sum_{\nu=1}^{s}t_\nu\chi_\nu^p\left[A_\nu^p(t)(\beta k)+B_\nu^p(t)(\beta k)^2+C_\nu^p(t)(\beta k)^3\right]\right\}-$$

$$-\frac{|z_j|\beta^0 c_j^{1/2}}{(1+t)}\left[1+V_j^{(1)}(t)(\beta k)+V_j^{(2)}(t)(\beta k)^2+\Pi_j^{(3)}t/6\right], \qquad (14)$$

$$\lambda=\sum_{j=1}^{s}\left(|z_j|c_j\lambda(j)/c\right).$$

An interpretation of the coefficients in Eqn. (14) can be found in Ref. 24. However, even such a complex equation is only approximate and the expressions for C_ν^p and $V_j^{(2)}$ are incomplete.

The simplest case in which we can apply Eqn. (14) is that of 2–1 electrolytes in which ions are associated in accordance with the scheme

$$K^{2+} + A^- \leftrightarrow KA^+.$$

In the case of such a solution we find that Eqn. (14) contains five unknown parameters: the values of the limiting electrical conductance of three ions, K_a, and R. In the presence of such a

large number of unknown parameters the solution of the above equation becomes multivalued. It was shown in Refs. 27 and 45 how the number of unknown parameters can be reduced to three and in Ref. 41 an algorithm was given for calculation of the parameters of complex associated and asymmetric electrolytes.

We described above the most frequently employed theoretical approaches to the description of the electrical conductance of dilute solutions of weakly associated electrolytes. We must stress again that all these equations give practically the same value of λ^0, whereas the values of K_a are in agreement only to within an order of magnitude. As far as the parameter a (or r) is concerned, we can *a priori* expect its value to depend on the nature of the equation, because it is governed by the selection of the boundary conditions and the mathematical approximations adopted in the treatment. Moreover, we cannot expect the parameter R to have a real physical meaning if we use equations based on the primitive model because the model itself does not describe reality. Therefore, an experimentalist should bear in mind that the conductometric parameters can be compared only if they are obtained on the baiss of the same equation.

Several statistical-mechanical theories have been put forward recently and they make it possible to describe quite rigorously the transport properties of electrolyte solutions right down to the average concentrations.[30,46–49] However, the equations derived using such theories are too complex for practical use.

2. Concentrated electrolyte solutions

There is as yet no theoretically rigorous equation for the description of the electrical conductance of concentrated electrolyte solutions. Therefore, the transport properties of such solutions are being interpreted on the basis of three main approaches: 1) 'generalisation' of equations for dilute solutions by introduction of empirical terms; 2) use of the equations applicable to molten salts; 3) description of the experimental data by purely empirical or semi-empirical equations. Among the first group of equations tl most widely used is the equation of Robinson and Stokes[1], corrected for the viscosity and allowing for the influence of the relaxation effect, as estimated by Falkenhagen et al.:[51]

$$\lambda = \left(\lambda^0 - \frac{\beta^0\sqrt{c}}{1+ka}\right)\left(1 - \frac{\alpha^0 F\sqrt{c}}{1+ka}\right)\frac{\eta_0}{\eta}, \qquad (15)$$

where $F = [\exp(0.2929ka) - 1]/(0.2929ka)$.

Equation (15) describes satisfactorily the electrical conductance of some salts in water up to concentrations of 5–6 mol/litre,[52,53] whereas in the case of other salts there is no satisfactory agreement[54] even at concentrations less than 1 mol/litre. In all probability this equation works well as long as the ratio η/η_0 is small.[55] Otherwise in calculation of the coefficient β^0 [Eqn. (3b)] it is necessary to use the viscosity of a solution with a given concentration. The authors of Ref. 56 suggest extending the validity of Eqn. (15) by calculating the coefficients employing both the viscosity of a solution and its permittivity (so that the quantities β^0, α^0, and k become concentration-dependent). If calculations based on Eqn. (15) give values of the electrical conductance lower than those found experimentally, this is evidence of ion association and can be allowed for by introducing the degree of dissociation α into Eqn. (15):

$$\lambda = \alpha\lambda'(\alpha c),$$

where $\lambda'(\alpha c)$ is given by Eqn. (15) with the actual ion concentration amounting to αc; α can be found by successive approximation or by applying the law of mass action. Equation (10) allows us to describe the concentration dependence of the electrical conductance of strong (concentrated) electrolytes in water right up to a concentration of $\sim$1 M.

Among the second group of equations one should mention particularly the Vogel–Fulcher–Tammann equation describing the temperature dependence of the transport properties of glass-forming liquids and molten salts:

$$x(T) = AT^{-1/2}\exp\left(-\frac{B}{T-T_0}\right),$$

where A and B are constants, and T_0 is the ideal or theoretical vitrification temperature.

If the solubility of an electrolyte is sufficiently high, the isotherms of the composition dependence of the electrical conductance have a maximum whose position and amplitude are governed by the nature of the components of the solution. These dependences are described most frequently employing the empirical equation of Castel and Amis:[57]

$$\frac{\kappa}{\kappa_{max}} = \left(\frac{m}{m_{max}}\right)^2 \exp\left[b(m-m_{max})^2 - \frac{a}{m_{max}}(m-m_{max})\right],$$

where κ_{max} and m_{max} are the values of the electrical conductivity and of the concentration corresponding to an extremum of the dependence $\lambda = f(m)$: a and b are empirical coefficients.

Among the empirical dependences describing the electrical conductivity of electrolyte solutions, we may mention a correlation equation which allows for a whole range of the solvent and salt parameters:[53]

$$\varkappa = A\exp\{aDN(r_+)^2 + bAN/(r_-)^2 + \mu[c/(r_+)^2 + d/(r-)^2] + e/\varepsilon\}/\eta_0 V_m^{1/3}, \qquad (16)$$

where A is the coefficient of proportionality; DN is the donor number; AN is the acceptor number; μ is the dipole moment of the solvent; a, b, c, d, e are empirical coefficients.

In some cases Eqn. (16) simplifies. For example, in the case of 1 M solutions of lithium salts in aprotic solvents we can ignore the solvation of the ions, so that Eqn. (16) becomes[53]

$$\varkappa = A\exp(aDN + b\mu + c/\varepsilon)/\eta_0 V_m^{1/3},$$

where the empirical coefficients are constant for a given salt in all the aprotic solvents.

In Ref. 58 it is assumed that the electrolytic properties of electrolyte solutions are governed by the processes of association in an electrolyte

$$nA \xleftrightarrow{K_1} A_n \xleftrightarrow{K_2} aA_j^{b+} + bB_j^{a-} \qquad (17)$$

and by its interaction with the solvent

$$mA + lS \leftrightarrow A_mS_l \leftrightarrow cA^{d+} + dB^{c-}, \qquad (18)$$

which leads to equations for the iostherms of the electrical conductance of binary liquid electrolyte–solvent systems.

In the case of noninteracting systems, we have

$$\kappa\eta = \kappa_A\eta_A\left(\frac{V_A}{V}\right)^{n/2} X^{n/2}, \qquad (19)$$

where κ_A, η_A, and V_A are the electrical conductivity, viscosity, and molar volume of the electrolyte, respectively; V is the molar volume of the solution; n is the stoichiometric equilibrium coefficient of Eqn. (17); X_A is the molar fraction of the electrolyte.

The electrical conductivity of interacting systems is then

$$\kappa\eta = \kappa_A\eta_A\left(\frac{V_A}{V}\right)^{n/2} X^{n/2} + Q_i\frac{X_A^{m/2}(1-X_A)^{1/2}}{V^{(m+l)/2}}, \qquad (20)$$

where Q_i is a constant governed by the values of the equilibrium constants K_3 and K_4 of Eqn. (18), by the molar volume, and by the conductance of the resultant electrolyte A_mS_l (Q_i is found from experimental data by calculation); m and l are the stoichiometric equilibrium coefficients of Eqn. (18).

Equations (19) and (20) are derived subject to the following assumptions: 1) the mechanism of the flow of the current involves ion migration; 2) the mobility of ions is inversely proportional to the viscosity of the solution; 3) the equilibrium constants in Eqns. (17) and (18) are smaller than 1×10^{-3}; 4) the ratio of the activity coefficients of different particles in a solution varies little with the concentration.

These equations describe satisfactorily the isotherms of the electrical conductance of a wide range of systems formed by alkylammonium salts with solvents of different types in the range of concentrations ranging from molten salts to dilute solutions (the latter with 1–2 mol%).

Moreover, several more empirical and semi-empirical equations have been proposed in the literature for the description of the electrical conductivity of solutions.[59,67] Some of these equations apply only to specific systems.

3. Solutions of weak electrolytes

In the case of weak electrolyte solutions the value of λ falls steeply on increase in the concentration and this is primarily due to a strong aggregation of current-carrying particles. In the case of such systems the ionicity of the medium is low so that the Debye–Hückel–Onsager effects make a relatively small contribution and the electrical conductivity of the solution is then described by simpler equations. The best of these are the Fuoss–Kraus[35] and Shedlovsky[36,37] equations

$$\frac{1}{\lambda S(Z)} = \frac{1}{\lambda^0} + \frac{c\lambda f_A S(Z)}{(\lambda^0)^2}, \qquad (21)$$

where $Z = S\sqrt{\lambda c}/\lambda^0$, S is the limiting Onsager coefficient, described by

$$\frac{1}{S(Z)} = F(Z) = 1 - Z\left\{1 - Z\left[1 - Z(\ldots)^{-1/2}\right]^{-1/2}\right\}^{-1/2}$$

in the Fuoss–Kraus method and by

$$S(Z) = \left\{\frac{Z}{2} + \left[1 + \left(\frac{Z}{2}\right)^2\right]^{1/2}\right\}^2 = 1 + Z + \left(\frac{Z}{2}\right)^2 + \left(\frac{Z}{2}\right)^3 + \ldots$$

in the Shedlovsky method. The coefficients $F(Z)$ and $S(Z)$ can be found in Refs. 68 and 69, respectively. In the first approximation the degree of dissociation α is calculated from $\alpha = \lambda/\lambda^0$. Then, the dependence $1/\lambda S(Z)$ on $c\lambda f_{\pm}^2 S(Z)$ is linear and it can be used to find the values of K_a and λ^0. These values can then be employed as the first approximation for the association constant and the limiting electrical conductance, respectively, which can then be used to calculate a new value of the degree of dissociation from $\alpha = \lambda S(Z)/\lambda^0$. Such a calculation is carried out until the required precision of the degree of dissociation (usually 1×10^{-4}) is achieved by the method of successive approximations.

In the case of very weak electrolytes the slope of the dependence $1/\lambda S(Z) = f[c\lambda f_{\pm}^2 S(Z)]$ is so steep that the extrapolation procedure becomes uncertain and gives rise to large errors in the values of K_a and λ^0. In this case we can estimate λ^0 from the Kohlrausch law on the independence of ion migration and by combining the values of the limiting electrical conductance of strong electrolytes. For example, in the case of a solution of acetic acid in water, we can write down

$$\lambda^0_{CH_3COOH} = \lambda^0_{HCl} + \lambda^0_{CH_3COONa} - \lambda^0_{NaCl}.$$

It should be pointed out that Eqn. (21) is derived on the assumption that ion association produces only ion pairs. However, in solvents with a low permittivity we can expect also attachment of ions to an ion pair, forming ion triplets:

$$MA + M^+ \xleftrightarrow{K_1} M_2A^+,$$

$$MA + A^- \xleftrightarrow{K_2} MA_2^-.$$

These processes are most typical of solutions of electrolytes containing large organic ions.[70,71] It is usual to assume that the equilibrium constants of both processes are equal ($K_1 = K_2 = K_t$). In this case the results are usually analysed employing the Fuoss–Kraus equation[35]

$$\lambda c^{1/2} = \lambda^0 K_a^{-1/2} + \lambda_t^0 K_t K_a^{-1/2} c,$$

where λ_t^0 is the limiting electrical conductance due to ion triplets. We can find the association constant K_t representing the formation of triplets if the values of λ^0 are calculated by the method described above using the electrical conductances of strong electrolytes and λ_t^0 is obtained from the approximate expression $\lambda^0 = 3\lambda_t^0$.

Another approach to find the K_t and λ_t^0 was suggested by Beronius.[72] If we denote the equilibrium concentrations of the M^+ and A^- ions by $\alpha_1 c$ and the corresponding concentrations of M_2A^+ and MA_2^- by $\alpha_2 c$, we find that the electrical conductance is given by

$$\lambda = m(\alpha_1\lambda^0 + \alpha_2\lambda_t^0),$$

where m is a coeffficient allowing for the reduction in the conductance because of the ion–ion interaction and given by

$$m = \left(\lambda^0 - Sc_i^{1/2} + Ec_i \ln c_i + I_1 c_i + I_2 c_i^{3/2}\right)/\lambda^0,$$

m can be calculated using Eqns. (2) and (3); $c_i = c(\alpha_1 + \alpha_2)$. The expressions for the association constants are:

$$K_a = (1 - \lambda_1 - 3\lambda_2)/(c\lambda_1^2 f_{\pm}^2),$$

$$K_t = \lambda_2/[c\lambda_1(1 - \lambda_1 - 3\lambda_2)].$$

However, once again we can calculate λ_t^0 and K_t only if we find first the values of λ^0 and K_a.

A combined method is suggested in Ref. 41 and a description is given there of an algorithm for the processing of conductometric data in the case of complex associated electrolytes; this is done employing the Brickley formalism to describe chemical equilibria in solutions, the modified Newton second-order method for optimisation of the required parameters, and the equation of Lee and Wheaton for the concentration of the dependence of the molar electrical conductance of an electrolyte.

III. Limiting molar ionic electrical conductance

The value of the limiting electrical conductance due to ions can be calculated using λ^0 for the electrolyte in question and the limiting transport (transference) number t^0 for one ion forming a given electrolyte. In the case of our binary electrolyte we have

$$\lambda_+^0 = t_+^0\lambda^0,$$

$$\lambda_-^0 = (1 - t_+^0)\lambda^0.$$

Similar equations can be written down if we know t_-^0.

Determination of the transport numbers of nonaqueous solvents meets with major difficulties because of the frequent use of indirect methods for calculation of λ_{ion}^0 and subject to various assumptions. An analysis of these methods can be found in Refs. 73 and 74. The author of Ref. 73 is of the opinion that a physically more justified method uses the product $\lambda^0\eta_0$ for large tetraalkylammonium ions (beginning from Bu_4N^+) in various organic solvents and at different temperatures. The physical justification is the hypothesis that large tetraalkylammonium ions do not become solvated in organic solvents at any temperature. The following indirect methods of separation into ion components are given in Ref. 73:

$$\left(\lambda_\pm^0\right)_{(CH_3)_2CO} = \left(\lambda_\pm^0\right)_{H_2O}\frac{\eta_{0\,H_2O}}{\eta_{0\,(CH_3)_2CO}},$$

$$\lambda^0_{(Pi^-)}\eta_0 = 0.267,$$

$$\lambda^0_{(Et_4N^+)}\eta_0 = 0.296,$$

$$\lambda^0_{(Bu_4N^+)}\eta_0 = \begin{cases}0.208\\0.206\\0.209,\\0.201\\0.233\end{cases}$$

$$\left[\lambda^0_{(iso-Am_3BuN^+)}\eta_0\right]_{n-PrOH,n-BuOH} = \left[\lambda^0{}_{(iso-Am_3BuN^+)}\eta_0\right]_{EtOH},$$

$$\left[\lambda^0_{(Hept_4N^+)}\eta_0{}_{n-PrOH,n-BuOH}\right. = \left[\lambda^0_{(Hept_4N^+)}\eta_0\right]_{EtOH},$$

$$\lambda^0_{R_4N^+} = ZF^2/6\pi N\eta_0[R_i - (0.0103\varepsilon + r_j)],$$

$\lambda^0_{M^+} = \lambda^0_{A^-}$, where M^+ and A^-: iso-Am_4N^+ and iso-Am_4B^-, Bu_4N^+ and BPh_4F-, Bu_4N^+ and Ph_4B^-, $MeOctN^+$ and $OcldSO_4^-$, and Ph_4B_-, Me_3PhN^+ and $PhSO_3^-$, Bu_4N^+ and Bu_4B^-, Ph_4As^+ and Ph_4B^-;

$$\lambda^0_{Bu_4N^+} = 1.08\lambda^0_{iso\text{-}Am_4N^+},$$

$$\lambda^0_{Ph_4B^-} = 1.01\lambda^0_{iso\text{-}Am_4B^-},$$

An analysis of the transport numbers of ions in a number of solvents was given in Refs. 75–77, but the results reported have been obtained mainly at 289 K. There have been only few studies of the temperature dependences of the transport numbers.[78–80]

The dependence of the limiting ionic electrical conductance on the various factors can be analysed conveniently in the form of an expression for the friction coefficient ξ (kg/s):

$$\xi_i = \frac{Z_i^2F^2}{N_A\lambda_i^0}, \qquad (22)$$

where N_A is the Avogadro number.

Different theories give the following expressions for the friction coefficients† of spherical ions of radius R_i.

Continuum models

1. $\xi = \xi_v = A\pi\eta R_i$.

In the above case only the viscous friction forces are allowed for.[1]

2. $\xi = \xi_v + \Delta\xi$, $\Delta\xi = B\dfrac{(Ze)^2(\varepsilon - \varepsilon_\infty)\tau}{R_i^3\varepsilon(2\varepsilon + 1)}$.

The viscous and dielectric friction forces are now included.[81]

3. $\xi = \xi_V + \Delta\xi$,

$\Delta\xi = \eta_0 R_{x0}\sum_{j=1}^{j=4} a_j(R_{x0})^j$ [values of a; can be found in (Ref.82)],

$R_i^4/R_{x0} \to 0$, $\xi = \xi_T = 15.624\eta R_{x0}^{1/4}$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi = A\pi\eta R_i[A_1(R_{x0}/R_i^4) - A_2(R_{x0}/R_i^4)^2]$,

$R_{x0} = \dfrac{(Ze)^2}{16\pi\eta}\dfrac{\varepsilon - \varepsilon_\infty}{\varepsilon^2}\tau$.

The viscous and dielectric friction forces are included.[83–85]

3.1. $\xi = \xi_V + \Delta\xi + \Delta\xi_{DH}$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi_{DH} = A\pi\eta R_i\left[A_3\dfrac{R_{x0}}{R_i^4}\dfrac{R_{HK}}{R_i^4}\right]$,

$R_{HK} = -\dfrac{\alpha(Ze)^2(\varepsilon - 2\varepsilon_\infty)}{\varepsilon^2(\varepsilon - \varepsilon_\infty)}$.

† The values of the coefficients can be found also in the original papers (the references to these papers alongside the name of the model).

The effects of dielectric saturation are included.[86]

3.2. $\xi=\xi_V+\Delta\xi+\Delta\xi_{BB}$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi_{BB} = A\pi\eta R_i\left[A_4\frac{R_{x0}}{R_i^4}\frac{R_R}{R_i^4}\right]$,

$R_R=R_{x0}\eta/\eta_R$, where η_R- is the 'rotational viscosity'

$R_i^4/R_{x0}\to 0$, $\xi=\xi_T=14.089\eta R_{x0}^{1/4}$ when $R_R\to\infty$,

$\xi=\xi_T=15.624\eta R_{x0}^{1/4}$ when $R_R\to 0$.

The influence of 'rotational' viscosity is allowed for.[87]

3.3. $\xi=\xi_V+\Delta\xi+\Delta\xi_e$,

$R_i^4/R_{x0} >> 1$, $\Delta\xi_e = A\pi\eta R_i\left(\frac{b-c}{R_i^4}\right)$,

$C = A_5\frac{(Ze)^2}{4\pi\varepsilon}\left(\frac{\partial\ln\eta}{\partial P}\right)_T$,

$b = A_6\frac{C}{\beta_T}\left(\frac{\partial\ln\eta}{\partial P}\right)_T$,

The influence of electrostriction is included.[88]

4. $\xi=\xi_V+\Delta\xi$,

$\Delta\xi = A_7\frac{(Ze)^2(\varepsilon-\varepsilon_\infty)}{R_iD\varepsilon^2}$.

The Debye relaxation mechanism is supplemented by a nonlocal translational diffusion of molecules along a gradient of a nonequilibrium polarisation field.[89]

5. $\xi=\xi_V+\Delta\xi$,

$R_i^4/R_{x0} > 1$, $\Delta\xi = A\pi\eta Ry(1-g)$,

$R_i^4/R_{x0} < 1$, $\Delta\xi = x\cdot 15.624\eta R_{x0}^{1/4}$,

$xy = f\left(g, R^4/R_{x0}\right)$,

$0 > g > 1/3$.

The ion is assumed to have a finite polarisability and the polarisation changes abruptly at the surface of an ion. The solvent may have more than one relaxation time.[90]

6. $\xi = 2\pi\eta R_i\left\{\sigma+2+\frac{R_{x0}}{R_i^4}\left[\frac{1}{105}\left(56-69\sigma+59\sigma^2\right)+\left(\frac{\lambda_e}{\lambda_h}-1\right)\sigma(1-\sigma)\right]\right\}$,

$\sigma = R_i/(R_i+3\lambda_h)$.

In the above case the energy dissipation in polar liquids is allowed for. The boundary conditions on the surface of an ion are governed by electrical (λ_e) and hydrodynamic (λ_h) parameters.[91]

Continuum-molecular models

1. $\xi=\xi_V'+\xi_D$,

$\xi_V' = 4\pi\eta_0\sigma\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$; $\xi_D = \frac{(Z_e^2(\varepsilon-\varepsilon_\infty)}{\varepsilon(2\varepsilon+1)R_i^4}\tau A_D\left[1+3\left(\frac{R_i}{\sigma}\right)_y^4\right]$,

$y = \left[\left(1+2\frac{\varepsilon}{\varepsilon_R}+\left(-\frac{\varepsilon-\varepsilon_\infty}{\varepsilon}\right)\left(\frac{\varepsilon_R}{\varepsilon_R-\varepsilon_\infty}\right)\left(\frac{2\sigma}{A_D}-\frac{3B_0}{A_D}\right)-\frac{2c\sigma}{A_D}+\right.\right.$

$\left.\left.+\frac{2\sigma}{R_i}\left(\frac{3\varepsilon_R+1}{2\varepsilon_R+1}\right)\left(1-\frac{\varepsilon}{\varepsilon_R}\right)\right]/\left[\left(1+\frac{2\varepsilon}{\varepsilon_R}\right)-2\left(\frac{R_i}{\sigma}\right)^3\left(\frac{\varepsilon_R-1}{2\varepsilon_R+1}\right)\left(1-\frac{\varepsilon}{\varepsilon_R}\right)\right.\right.$

$B_0 = \frac{\sigma}{2}\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$, $\sigma = R_i+2R_s$,

$A_D = \frac{\sigma}{2}\frac{\eta}{\eta_{\text{eff}}}\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$, $\Delta = \eta\rho_R/\eta_{\text{eff}}\rho(0\leqslant\Delta\leqslant 1)$,

$C = \frac{\sigma}{R_i}\frac{\eta}{\eta_{\text{eff}}}\left[1+\Delta\left(\frac{\sigma}{R_i}-1\right)\right]^{-1}$, $\rho_R, \eta_R, \varepsilon_R, \tau_R$ – for $R < r < \sigma$, ρ, η, ε, τ, – in the bulk,

$\eta_{\text{eff}} = \eta_R+\frac{\tau_R}{6M_s}\rho\left[\left(\frac{\rho_R}{\rho}\right)^2-1\right]\left(\frac{\sigma}{R_i}-1\right)\left(\rho\frac{dV(r)}{dr}\right)_{r=\sigma}$.

If $\varepsilon_R = \varepsilon$, then

$$\xi_D = \frac{1}{2}\frac{(ze)^2(\varepsilon-\varepsilon_\infty)\tau}{\varepsilon(1+2\varepsilon)}\frac{\sigma}{R_i^4}\times$$

$$\times\left\{\frac{(\rho/\rho_R)\Delta+(R_i/\sigma)^4\left[1+4\Delta(4\sigma/R_i-1)-(4\sigma/R_i-3)(\rho/\rho_R)\Delta\right]}{1+\Delta(\sigma/R_i-1)}\right\}.$$

If $\varepsilon_R = \varepsilon$ and $\rho_R = \rho$, we have

$$\xi_D = \frac{1}{2}\frac{(ze)^2(\varepsilon-\varepsilon_\infty)\tau}{\varepsilon(1+2\varepsilon)}\frac{\sigma}{R_i^4}\left\{\frac{\Delta+(R_i/\sigma)^4\left[1+\Delta(12\sigma/R_i-1)\right]}{1+\Delta(\sigma/R_i-1)}\right\}.$$

If $\varepsilon_R = \varepsilon_\infty \approx 1$, then

$$\xi_D = \frac{1}{2}\frac{(ze)^2(\varepsilon-\varepsilon_\infty)\tau}{\varepsilon(1+2\varepsilon)}\frac{1}{\sigma^3}\left[\frac{1+4\Delta(\sigma/R_i-1)}{1+\Delta(\sigma/R_i-1)}\right].$$

The local changes in the properties of the solvent near an ion are allowed for in the above expressions.[92]

2. $\xi = A\pi\eta R+\frac{2}{3}(ze)^2\frac{\varepsilon-\varepsilon_\infty}{\varepsilon^2}\frac{\tau}{R_e^3}$.

The short-range order around an ion is allowed for. The finite size of the solvent molecule is taken into acocunt.[93]

Molecular models[94–96]

1. $\xi=\frac{1}{kT}\int_0^\infty\left\langle F^R(0)F^R(t)\right\rangle dT = \xi^{HH}+\xi^{SH}+\xi^{HS}+\xi^{SS}$,

where S and H are, respectively, the soft and hard forces between an ion and the solvent molecules; ξ^{HH} is due to the hard interaction of particles considered as solid spheres and it is given by $\xi^{HH} = 4\pi\eta R_i$; ξ^{SS} corresponds to the soft interactions and is given by

$$\xi^{SS}=\frac{1}{kT}\left\langle\left(F^S\right)^2\right\rangle\tau_F;$$

$\langle(F^S)^2\rangle$ is the mean-square vibration of the soft component of the force; τ_F is the characteristic decay time; ξ^{HS} and ξ^{SH} are cross terms.

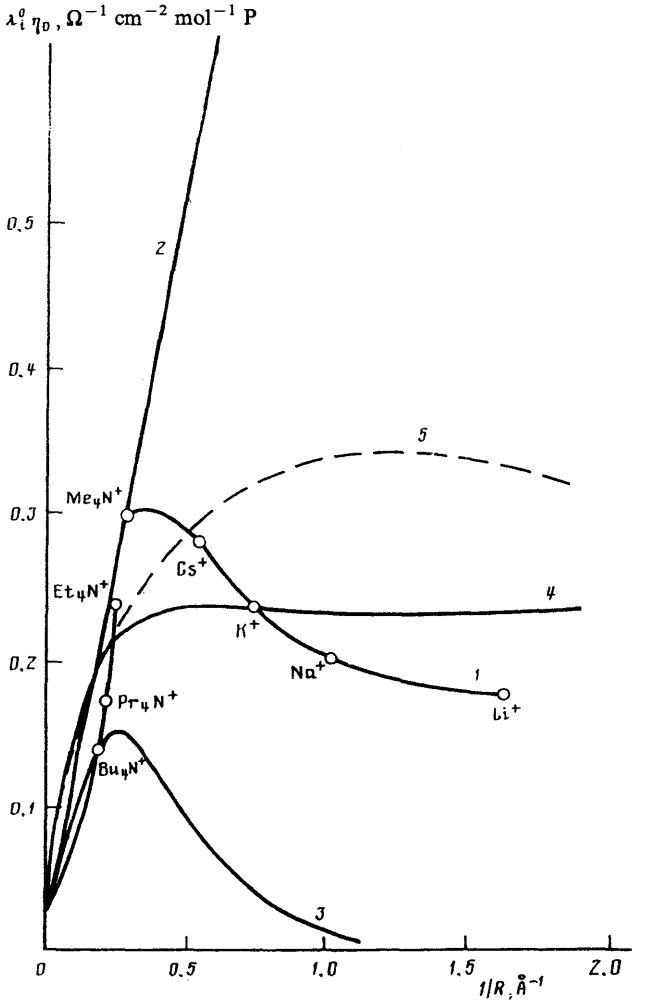


Figure 1. Experimental (*1*) and theoretical (*2*–*5*) dependences of $\lambda_i^0\eta_0$ for methanol on the reciprocal ionic radius at 298.15 K.[85] Theory: *2*, Stokes; *3*, Zwanzig; *4*, Hubbard–Onsager; *5*, Wolynes.

As pointed out in Spiro's review,[4] the Stokes equation 'does not work' until the ionic radius reaches 5.5 Å in water and 10 Å in such solvents as sulpholane. The reason for this is the hydrodynamic model, in which the solvent is regarded as a structure-free continuum. There have been many attempts to develop empirical and theoretical modifications of the Stokes theory among which we should mention the work reported in Refs. 1 and 97. It is assumed in the continuum models that an ion experiences not only the hydrodynamic, but also the dielectric friction. A moving ion orients the solvent dipoles around itself and they return back to a disordered distribution after a certain time (which is the dielectric relaxation time τ). Therefore, an additional electrostatic force acts on an ion.

The continuum models allowing for the dielectric friction have been checked for a large number of electrolytic systems, including protic, aprotic, and mixed solvents.[82,98,99] The results of such calculations are diappointing, particularly in the case of small ions for which the dielectric friction effect in the largest (Fig. 1 shows, by way of example, the experimental and theoretical dependences of λ^0 on $1/R_i$ for methanol). Introduction of dielectric saturation yields an effect which is far too small to improve the results significantly. Moreover, none of the continuum theories can account for the physical nature of the investigated phenomena.

An ideal theory of the ionic electrical conductance should account for the motion of an ion allowing for the ion–solvent interaction, for the structure of the solvent surrounding the ion, and for the motion of the solvent molecules. Wolynes started[94–96] to develop such a molecular approximation. The numerical calculations reported in Ref. 95 were carried out using only the solid-sphere radial distribution functions and the ion-dipole potentials: they showed that the calculated values of the electrical conductance due to small ions were higher than the experimental values, exactly as in the case of the continuum theories (Fig. 1). A theoretical investigation of the dielectric friction coefficient considered from the molecular positions was reported in a recent paper.[100] In principle, such an approach is analogous to that of Wolynes, but there are also some differences.

It should be pointed out that the Walden product is used widely in the interpretation of the electrical conductance data. As assumed in Ref. 101, one of the reasons for the popularity of the product $\lambda^0\eta_0$ is the erroneous view that multiplicaiton of the electrical conductance by the viscosity avoids the problem of the influence of the viscosity on the motion of an ion and makes it possible to consider the influence of other factors. However, this approach should be treated with caution. Since an ion carries a charge, the neglect of the influence of temperature, pressure, and nature of the solvent on the electrostatic interaction of an ion with the solvent may result in an unjustified stress on the structure of the pure solvent. On the other hand, the treatment given in Ref. 102 demonstrates the correctness of the use of the Walden product in diagnostics of structural features of solvents. The relationships governing the changes in the product $\lambda^0\eta_0$ with the properties of the solvent and with the ion size are investigated in Ref. 103.

It is stressed in several papers[82,101] that it is essential to analyse the conductometric data allowing for the residual friction coefficient

$$\Delta\xi = \xi - \xi_V,$$

where ξ is the overall ionic fraction coefficient [deduced from Eqn. (22)]; ξ_V is the Stokes friction coefficient under glide conditions.

In the continuum theories the quantity $\Delta\xi$ reflects mainly the dielectric friction. In the Hubbard–Onsager theory the expression for $\Delta\xi$ includes both dielectric and viscous properties of the solvent, whereas in the theory of Zwanzig only the dielectric properties are

allowed for, because of the separate description of the viscous and dielectric frictions.

The expression for the residual friction coefficient is also in agreement with the formalism of the molecular Wolynes theory. The following assumptions are made in this case: the component of the coefficient of friction due to hard collisions is equated to the Stokes friction coefficient $\xi^{HH} = \xi_V$; the cross terms ξ^{SH} and ξ^{HS} are ignored. We then have $\Delta\xi = \xi^{SS}$. However, it is shown in Refs. 100 and 104 that the neglect of the cross terms is an unjustified simplification.

In the molecular-continuum theory of Chen and Adelman,[92] in contrast to the continuum theories, the dielectric friction contribution is small even in the case of small ions. However, the function Δ introduced there to represent the degree of solvation of an ion is not determined on the basis of microscopic data but is selected to ensure agreement with the experimental conductometry results and is therefore a fitting parameter.

Since the approximation of an ion by a sphere is fairly rough, other geometric approximations have been used to describe the configuration of an ion (ellipsoid, disk, cylinder, etc.). The equations for calculation of Δ is the case of these ion configurations can be found in Spiro's review.[4]

The Hubbard–Onsager theory of dielectic friction and the Onsager–Kirkwood–Fröhlich theory of insulators are used in Ref. 105 to propose a new quantitative characteristic (θ) of the influence of an ion on the dynamic structure of the solvent. The value of θ is calculated using the limiting molar electrical conductance due to ions and it agrees well with the other characteristics of ion solvation (such as the energy of close solvation of ions proposed by Samoilov and denoted by ΔE_i and a coefficient B in the Jones–Dole equation).

One of the quantitative methods for describing the temperature dependence of the electrical conductance is the kinetic approach based on the theory of a transient state. It is shown in Ref. 106 that this theory can be used as the basis of various methods for calculating the thermodynamic characteristics of ion migration. We shall give here only one of the possible variants of such a calculation. If the motion of an ion is regarded as migration across a liquid by a series of jumps from one equilibrium position to another, the distance between which is l, we can write down

$$\lambda_i^0 = \frac{z_i e_i F l^2}{6h} \exp\left(\frac{\Delta G_{\lambda^0}^*}{RT}\right), \tag{23}$$

where h is the Planck constant and $\Delta G_{\lambda^0}^*$ is the free Gibbs energy of activation of electrical conduction.

If we assume that $l = (V_M/N_N)^{1/3}$, then differentiation of Eqn. (23) with respect to temperature and presure yields the following relationships:

$$\left(\frac{\partial \ln \lambda_i^0}{\partial T}\right)_P = \frac{\Delta H_{\lambda^0}^*}{RT^2} + \frac{3}{2}\alpha, \tag{24}$$

$$\left(\frac{\partial \ln \lambda_i^0}{\partial T}\right)_V = \frac{\Delta U_{\lambda^0}^*}{RT^2},$$

$$\left(\frac{\partial \ln \lambda_i^0}{\partial T}\right)_T = \frac{\Delta V_{\lambda^0}^*}{RT} - \frac{2}{3}\beta,$$

where α is the thermal expansion coefficient; β is the isothermal compressibility of the solvent. The first expression in the system (24) is obtained only on the assumption that the entropy of activation of electrical conduction is independent of temperature.

The electrical conductance data can also be used to calculate the number of physicochemical characteristics of solutions and then these characteristics can be useful in tackling many practical problems.[2,4] For example, using the Stokes law, we can determine the radius of a moving solvated ion (Stokes radius):

$$R_s = \frac{zF^2}{6\pi N_A \eta_0 \lambda^0} = \frac{0.82z}{\eta_0 \lambda^0},$$

and then the value of R_s can be used to calculate the solvation number of an ion

$$n_s = \frac{V_c - V_{cv}}{V_s} = \frac{1}{V_s}\frac{4}{3}\pi(R_s^3 - R_{cv}^3),$$

where V_{cv} is the volume of an ion with the crystallographic radius R_{cv} and V_c is the volume of a solvated ion of radius R_s.

It was also suggested in Ref. 97 that the radius of a solvated ion can be calculated using the semi-empirical relationship based on the Stokes law:

$$R_s = \frac{zF^2}{6\pi N_A \eta_0 \lambda^0} + 0.0103\varepsilon + r_y,$$

where $r_y = 0.85$ Å describes dipolar unsassociated solvents and $r_y = 1.13$ Å applies to protic and other associated solvents.

The limiting molar conductance of an individual ion is related to its limiting diffusion coefficient D_i by the Nernst–Einstein equation:

$$D_i = \frac{RT\lambda_i^0}{z_i^2 F^2}.$$

The limiting diffusion coefficient of an electrolyte is

$$D^0 = \frac{RT}{F^2}\frac{z_+|z_-|}{z_+|z_-|}\frac{\lambda_+^0\lambda_-^0}{|z_-|\lambda_+^0 + z_+\lambda_-^0}.$$

The electrical conductance data can be used to calculate the parameters of self-dissociation (autoprotolysis) of water ($K_w = c_H + c_{OH^-}$) and of other pure solvents. Since the ionicity of a medium in a pure solvent is low ($\lambda = \lambda^0$), we can write down

$$\kappa = \frac{\lambda^0 c_{H^+}}{1000} = \frac{\lambda^0 K_w^{1/2}}{1000}. \tag{25}$$

the value of λ^0 is obtained in the same way as in the case of electrolytes, for example, $\lambda_{HOH}^0 = \lambda_{HCL^+}^0 + \lambda_{KOH}^0 - \lambda_{KCl}^0$. By analogy with Eqn. (25), saturated solutions of low-solubility completely dissociated 1–1 electrolytes can be described, in the first approximation, by the expression

$$\varkappa = \frac{\lambda_{sat}^0}{1000} = \frac{{}^0SP^{1/2}}{1000}.$$

If an electrolyte is associated in the solution, then

$$SP^{1/2} = c_{sat} = \frac{1000\varkappa}{\lambda^0} + \left(\frac{\varkappa \times 1000}{\lambda^0}\right)^2 K_a.$$

This makes it possible to calculate the solubility product (SP) of low-solubility salts.

IV. Parameters of ion association

The association constant is introduced into the equations for the electrical conductance of electrolyte solutions using the law of mass action. Therefore, the association constant obtained by solving these equations is an experimental quantity which does not require selection of the ion association model, but depends on the selection of the ionic conductance model. We must mention straight away that the association constant obtained in this way is preferred to the molar scale of concentrations. Therefore, in comparing the ion association processes in different solvents and at different temperatures it is preferable to use the association constant referred to the scale of molar fractions $[K_a(X)]$, which is related to K_a on the molar concentration scale by

$$K_a(X) = \frac{1000\rho}{M_s} K_a.$$

On the other hand, K_a can be calculated using different theories of ion association.

The association constant is related to the distribution function which gives the distribution of ions of opposite change around the central ion. The distribution function is related to the mean-force potential by

$$W^{(s)}(\bar{r}_1 \ldots \bar{r}_s) = -kT \ln f^{(s)}(r_1 \ldots r_s).$$

There are many ways of finding the relevant distribution functions and the mean-force potentials. However, all of them are based on similar assumptions. Firstly, it is postulated that the mean-force potential can be represented as a sum of the long-range (Coulomb) and short-range parts. In fact, such a separation is justified at low concentrations. Secondly, the mean-force potential corresponding to the short-range component is replaced with the pair potential describing this interaction. The second step is again justified by the low concentrations and short distances between ions with opposite signs, when they can be regarded as ion pairs.

In connection with such a separation of the meanforce potential into components, it is usual to solve the problem of the long-range component, since it is the most significant in the formation of an ion pair, and the parameters representing the short-range part are introduced only during the second stage.[22,107,108] There have been recent treatments[23,24,109,110] in which right from the beginning both types of interaction have been allowed for. However, it must be pointed out that it is quite difficult to treat the problem rigorously in view of the mathematical difficulties which are encountered and, therefore, many authors sacrifice the physical and mathematical rigour in order to obtain easily analysable results.

Without going into details of the various theories of ion association, we can point out that for the majority of them an analytic expression for the calculation of the association constant can be represented in the form

$$K_a = \frac{4\pi N_A}{1000} \int_a^R r^2 \exp\left(-\frac{U_\pm}{kT}\right) \omega(r) dr, \qquad (26)$$

where $\omega(r)$ is a weighting function which determines the weight of a paired state of ions as a function of the distance between them. The real potential $U_\pm$ (of Fig. 2*a*) is most frequently represented by the primitive model with an apparent distance a' between the solid spheres (Fig. 2*b*) or a model potential which allows for the long- and short-range components (for example, that shown in Fig. 2*b*),

The equations for calculation of the association constants based on the primitive model allow only for the electrostatic interaction between the ions ($U_\pm/kT = 2q/r$) and they differ in respect of selection of the upper limit of integration and in respect of the expression used for $\omega(r)$. For example, in the Bjerrum theory the value of R is governed by the distance q between the ions at which the energy of the electrostatic interaction is $2kT$. The value is $\omega(r) = 1$ for $a \leqslant r \leqslant q$ and $\omega(r) = 0$ for $r > q$.

The expression for K_a then becomes

$$K_a = \frac{4\pi N_A}{1000} \int_a^q r^2 \exp\left(\frac{2q}{r}\right) dr = \frac{4\pi N}{1000} \left(\frac{|z_+ z_-| e^2}{\varepsilon kT}\right)^3 Q(b), \qquad (27)$$

where

$$Q(b) = \frac{1}{6}\left[e^2 - E_i(2) + E_i(b) - \frac{e^b}{b^3}\left(2 + b + b^2\right)\right].$$

The value of $Q(b)$ is tabulated in Ref. 1 for different values of b.

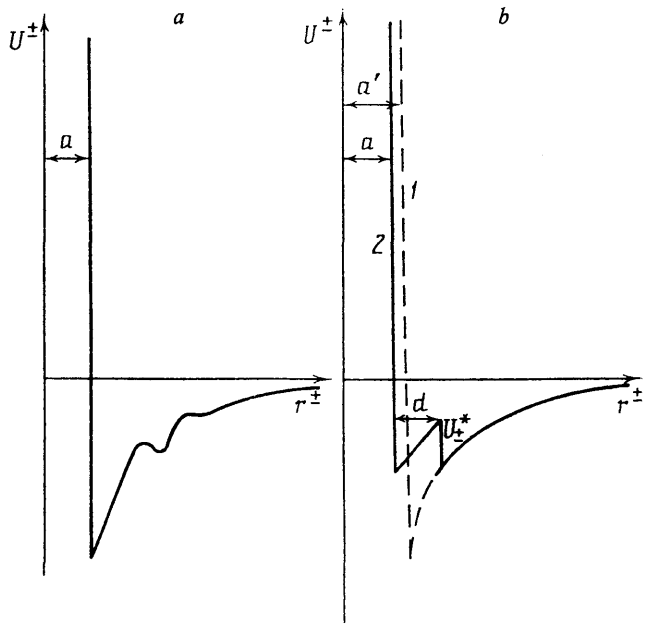


Figure 2. Representation of the cation–anion potential:[10,115] *a*, real potential; *b*, equivalent primitive model with an apparent distance a' between the hard spheres (*1*) and one of the simplest models allowing for the long- and short-range components (*2*).

In the theory of ion association proposed by Fuoss only the contact ion pairs are considered and the value of r is assumed to be $(4/3)a$. Then $\omega(r) = 1$ for $a \leqslant r \leqslant (4/3)a$ and $\omega(r) = 0$ for $r > (4/3)a$. The association constant is then given by

$$K_a = \frac{4\pi N_A a^3}{3000} e^h \ . \qquad (28)$$

A better justified selection of the weighting function $\omega(r)$, which allows us to obtain an expression for the ion association constant using the primitive model, is made by Ebeling[12,32]

$$\omega(r) = 1 + \exp\left(\frac{2q}{r}\right) - 2\exp\left(\frac{2q}{r}\right) - \left(\frac{2q}{r}\right)^2 \exp\left(\frac{2q}{r}\right).$$

The upper limit of integration [see Eqn. (26)] is ∞. As a result, we obtain Eqn. (10).

However, the most satisfactory description of the process of ion association can be obtained by employing a model potential that allows for the long- and short-range effects. There are various ways of representing the combined potential as a function of the distance:

$$\frac{U_\pm(r)}{kT} = \begin{cases} \infty, & r \leqslant a \\ \dfrac{U_\pm}{kT} = \text{const}, & a \leqslant r \leqslant R' \\ \dfrac{2q}{r}, & R' \leqslant r \leqslant R, \end{cases} \tag{29}$$

$$\frac{U_\pm(r)}{kT} = \begin{cases} \infty, & r \leqslant a \\ \dfrac{2q}{r} + \dfrac{U_\pm^*}{kT}\left(U_\pm^* = \text{const}\right), & a \leqslant r \leqslant R' \\ -\dfrac{2q}{r}. & R' \leqslant r \leqslant R, \end{cases} \tag{30}$$

$$\frac{U_\pm(r)}{kT} = \begin{cases} \infty, & r \leqslant a \\ -\dfrac{2q}{r} + \dfrac{U_\pm^*(r)}{kT}, & a \leqslant r \leqslant R' \\ -\dfrac{2q}{R} & R' \leqslant r \leqslant R. \end{cases} \tag{31}$$

Depending on the assumptions made by the authors, one can find other designations for the quantity $U_\pm^*$: $W_\pm^*$,[110] $d_\pm$,[111] and ν_1.[112] The lower limit of integration a in Eqn. (26) is equal to the 'hard-sphere' contact distance between the ions calculated from the crystallographic radii. The upper integration limit R may be specified in a variety of ways: it may be equated to the Bjerrum distance q: it may be equal to the distance found by solving the electrical conduction equation; it may also be selected using some other approach. The intermediate distance R' is most frequently expressed in the form $R' = a + S$, where S is equal to one or several diameters of the solvent molecule or some fragment of this molecule. The effective diameter of the solvent molecule d_S can be calculated from its molar volume V_S:

$$d_S = \left(\frac{6V_S}{\pi N_A}\right)^{1/3}$$

or from the geometric parameters of the solvent molecules. If in the case of $U_\pm$ we use the model potential of the type given by Eqn. (30), we find that K_a is given by

$$K_a = \frac{4\pi N}{1000}\left[\exp\left(-\frac{U^*}{kT}\right)\int_a^{R'} r^2 \exp\left(\frac{2q}{r}\right)dr + \int_{R'}^{R} r^2 \exp\left(\frac{2q}{r}\right)dr\right]. \tag{32}$$

Then,

$$\exp\left(-\frac{U_\pm^*}{kT}\right) = \frac{K_a - (4\pi a/1000)\int_{R'}^{R} r^2 \exp(2q/r)dr}{(4\pi N/1000)\int_a^{R'} r^2 \exp(2q/r)dr}. \tag{33}$$

Eqn. (33) is frequently written in the form

$$\exp\left(-\frac{U^*}{kT}\right) = \frac{K_a - (4\pi N/1000)\int_{R'}^{R} r^2 \exp(-2q/r)dr}{(4\pi N/1000)\int_a^{R} r^2 \exp(2q/r)dr - (4\pi N/1000)\int_{R'}^{R} r^2 \exp(2q/r)dr} =$$

$$= \frac{K_a - K_a(R')}{K_a(a) - K_a(R')},$$

where $K_a(R')$ and $K_a(a)$ are calculated using either the Bjerrum equation (27) or the Ebeling equation (28).

The selection of a specific form of the functional dependence $U_\pm^*(r)$ [Eqn. (31)] of Refs. 113 and 114 widens the concentration range of the validity of this equation, but it greatly complicates the problem. Therefore, it is not used much in practical applications when an analysis is made of conductometric data.

Knowledge of the ion association constants at different temperatures allows us to calculate all the thermodynamic characteristics of the association process using the following relationships:

$$\Delta G_a^0 = -RT \ln K_a,$$

$$\Delta H_a = \frac{RT^2 d\ln K_a}{dT},$$

$$\Delta S_a = \frac{\Delta H_a^0 - \Delta G_a^0}{T}$$

If the pair interaction potential is given by Eqns. (29)–(31) then ΔG_a can be represented as a combination of the long-range (Coulomb) and short-range contributions.

It follows from our review that conductometry of electrolyte solutions can provide in a fairly reliable way of obtaining some important information on the state and mobility of ions in solvents of different kinds and in a wide range of parameters. This is largely due to a good theoretical basis of this branch of physical chemistry of solutions and the experimental capabilities of the method itself.

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