

Electrolytes in Non-Aqueous Solvents

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Abstract - The features of a treatment of electrolyte solutions in the framework of a semi-phenomenological approach including short-range interactions are discussed. Applications are given in the fields of high-frequency permittivity, chemical kinetics, thermodynamic and transport properties. The temperature dependence of non-aqueous solution properties is a crucial point of this investigation.

1. INTRODUCTION

Since the first systematic investigations on non-aqueous electrolyte solutions by Walden, Kraus, and their coworkers, a steady growth of publications in this field has demonstrated the importance of non-aqueous electrolyte solutions in fundamental research as well as in applied electrochemistry and technology [cf. (1 to 11)]. Recent developments in theory as well as improvements of experimental techniques have enforced investigation on non-aqueous solutions.

Since Debye, Hückel and Onsager (12,13), any relevant theoretical treatment of electrolyte solution properties is based on ion-distribution functions [cf. (7,14,15)]. In actual theories they imply short range interaction forces which are taken into account either by appropriate potential terms [e.g. (15 to 19,57)] or by hypothesis of ion-association [cf. (7,20, 21,22,23,53)] as initially introduced by Bjerrum, however, with regard only to ion-ion Coulomb interaction in the vicinity of ions (24).

Ion association and related ion-solvent interaction yielding appropriate expressions for short range forces will be a crucial point of this contribution.

A perusal of published data on the temperature dependence or pressure dependence [cf. (25)] of non-aqueous electrolyte solution properties yields few items of information, the reason for the lack of reliable data being the difficulty of obtaining high accuracy of measuring data over a sufficiently large temperature or pressure range (20).

Temperature dependence of non-aqueous electrolyte solution properties will be a second crucial point of this paper. For a detailed description of the measuring equipment, Figure 1, cf. (20,26).

Further points are the dielectric properties of electrolyte solutions and the reactivity of electrolyte compounds in chemical reactions both giving insight into the role of short range forces around the ions and, finally, a discussion of transport phenomena in the framework of the new electrolyte theories.

Figure 2 shows an example of the instrumental set up for permittivity measurements in a narrow frequency range ($4 < f/\text{GHz} < 8$). A minimum of six to seven measuring lines is required to cover the relevant frequency region between 0.8 to 80 GHz in the usual solvents.

Spectroscopic methods and association derived from them are not considered in this context, many contributions of the 6th ICNAS dealing with this important matter. Let it suffice to notice that the way in which association is treated in the presented paper by means of partition functions permits the introduction of spectroscopic results, also.

All equations in this contribution are written to be used both with SI units and cgs units. For this purpose appropriate physical constants and conversion factors are summarised in Table 1 [cf. (7), also for further details]. Physicochemical symbols and the values of physical constants are used in accordance with (29). Concentration c is used throughout as $\text{mol}\cdot\text{l}^{-1}$, requiring a conversion factor 10^3 .

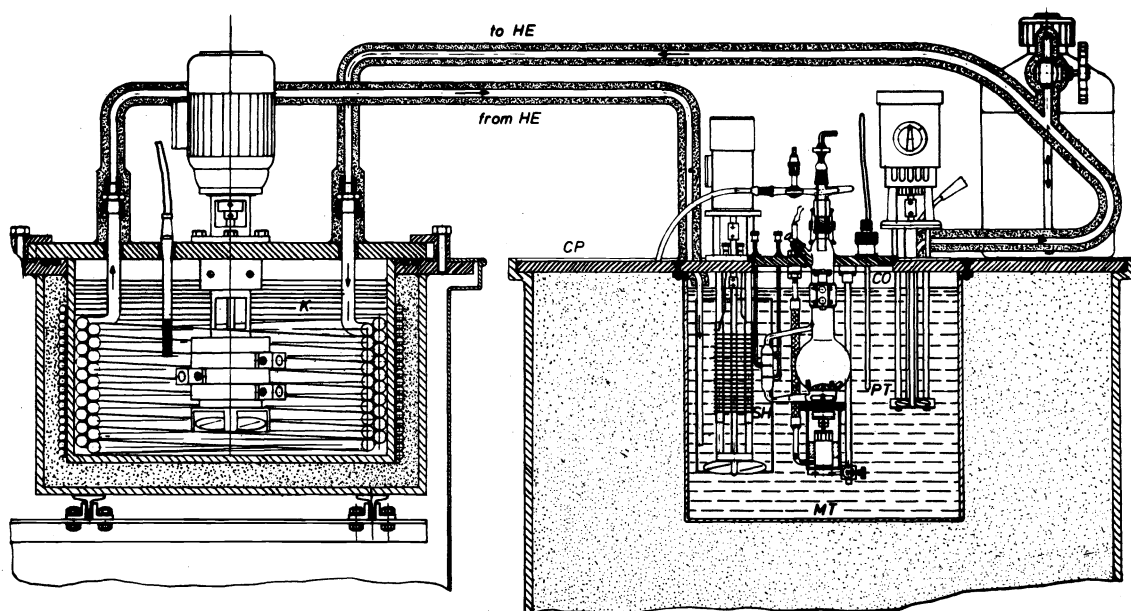


Fig. 1. Thermostat assembly for precise determination of solution properties over a large temperature range (20,26).

The measurement thermostat (MT; precision and reproducibility $\Delta\theta = 0.001$ K for $-60^\circ\text{C} \leq \theta < +50^\circ\text{C}$; cf. also Fig. 1a) is coupled to the cold bath (K) by means of a heat exchanger (HE). A circular opening (CO, $\varnothing 18.5$ cm) in the coverplate (CP) permits the immersion or connecting of different types of measuring cells (conductance, transference numbers, permittivity, viscosity, density, solubility etc.) which carry assembly plates guaranteeing hermetic sealing of the opening (CO). In Fig. 1 the thermostat contains a conductance cell, Fig. 1b. The temperature is controlled [source of heat (SH)] by a PID controller joined to an a.c. bridge containing the platinum resistance thermometer (PT).

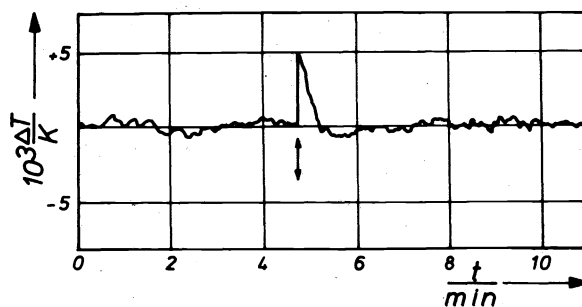


Fig. 1a. Precision and regulating properties of the thermostat, Fig. 1.

Both short and long-time deviations are within $\Delta\theta = 0.001$ K. A short-time perturbation introduced at time t (\downarrow) vanishes within 20 s without overshoot of temperature. Extended-time tests by regular comparison with temperature standards of the thermometric scale (IPTS 68) yield temperature stability better than 10^{-3} K per year.

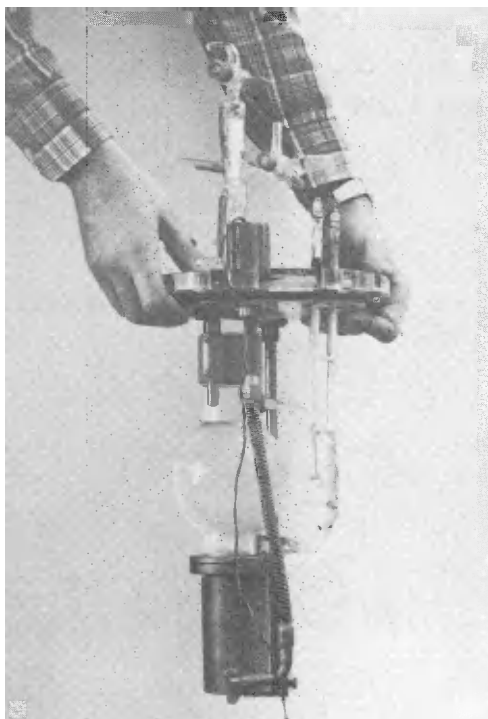


Fig. 1b. Conductance cell with assembly plate for immersion in the temperature bath [cf. Fig. 1].

Mixing chamber ($V \sim 1000$ ml) with inlet cap, encapsulated electromagnetic stirrer and three-electrode measuring cell. For further details see (20).

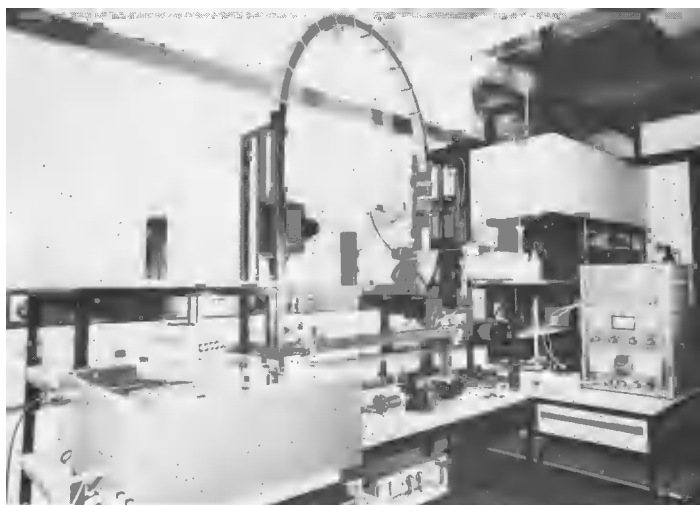


Fig. 2. View of the set-up for permittivity measurements at high frequencies [C-band, $4 < f/\text{GHz} < 8$]. The relevant measuring cell is represented in Fig. 4.

TABLE 1. Physical constants and conversion factors

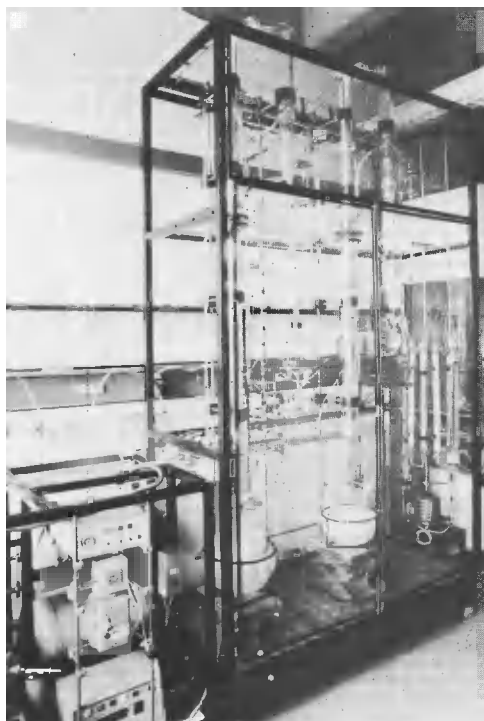
Quantity and symbol	Values with estimated uncertainty	
	SI	cgs
Charge of proton e_0	$1.60210 \cdot 10^{-19} \text{ C}$ ± 0.00007	$4.8029 \cdot 10^{-10} \text{ esu}$ ± 0.0002
Permittivity of vacuum ϵ_0	$8.85419 \cdot 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$ ± 0.00002	$1/(4\pi)$ exactly
Conversion factor E	1 exactly	$9.98755 \cdot 10^{11}$
Conversion factor m	+ 3 exactly	-3 exactly

2. NON AQUEOUS SOLVENTS

Electrolyte theory gives evidence of structural parameters only if precise measurements can be achieved. Such investigations require a very high degree of purity of products especially for the solvent in highly diluted solutions. Two classes of impurities must be distinguished (7);

- inert impurities changing by their presence only the physical properties of the solvent,
- interfering impurities which react with the added electrolyte compound, selective solvation included.

Impurities of the first class are largely rendered ineffective by the usual solvent corrections, those of the second one must be reduced to a non disturbing content. For examples cf. (30 to 36).



Chemical purification of the solvent with appropriate reactants takes place in the still ($V \sim 6000 \text{ ml}$) of the left part of the apparatus followed by a distillation into the still of the right part and from there over a packed column (~ 40 theoretical plates) in the fraction collector controlled by a conductance measuring cell. On the left side the electronic pressure governor and the pump stand for the highly purified protective gas are installed.

Fig. 3. Apparatus for the purification of solvents in an inert gas atmosphere at arbitrary pressure ($2 < p/\text{Torr} < 1000$).

In general, for purifying of products all steps must be done in an inert gas atmosphere. Figure 3 shows a type of plant for the complete purification of the solvent under inert gas as used in our laboratory. For a detailed description cf. (20,37).

Analysis of experimental data to determine properties of electrolyte solutions requires the knowledge of temperature and pressure dependent solvent properties: density, permittivity, viscosity etc. which up to now are available only for few solvents or solvent systems [cf. (38)].

3. DIELECTRIC PROPERTIES OF SOLVENTS AND ELECTROLYTE SOLUTIONS

Permittivity of polar compounds is composed of two parts arising from different physical causes. Displacement polarisation engenders the dielectric part and orientation polarisation the piezoelectric one, both showing a characteristic dispersion in different frequency ranges and thus performable separately.

The dispersion of permittivity ϵ is described as a complex function of the angular frequency ω

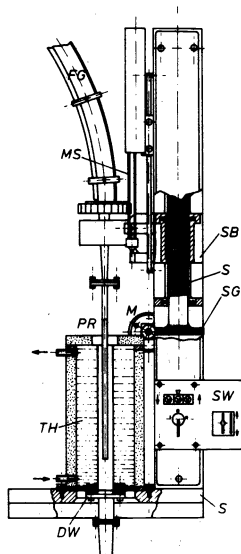
$$\epsilon(\omega) = \epsilon'(\omega) + j \epsilon''(\omega) \quad (1)$$

In electrically conducting systems the imaginary part $\epsilon''(\omega)$ of ϵ contains the contribution $\epsilon''_R(\omega)$ from relaxation processes as well as the loss $\sigma/\omega\epsilon_0$ from electric conductance σ

$$\epsilon''(\omega) = \epsilon''_R(\omega) + \sigma/\omega\epsilon_0 \quad (2)$$

This result is obtained directly from Maxwell's theory together with the information that the two contributions cannot be separately measured. As a rule, separation is performed with the help of the assumption of a frequency independent specific conductance σ which then is introduced from low frequency measurements ($f < 10\,000$ Hz).

The following results were obtained by an interferometric method of travelling waves described for the first time by Buchanan (39). The measuring equipment is realized according to present standard of technology (27,40 to 43). Figure 4 shows the measuring cell of the set-up in Figure 2 as an example (42). For the general background of permittivity measurements see (41,43), cf. also (44).



The electrolyte solution is contained in a thermostated cage (thermostat TH) which is composed of a part of the wave guide and limited by a dielectric window (DW). The dielectrically well-adapted probe (PR) is immersed by a motor-driven arrangement [motor (M); spindle (S) with spindle gearing (SG) and spindle bearing (SB); switchboard (SW) and motor governor] into the solution for measuring of damping and phase shift of the electromagnetic wave as a function of probe position. The measuring spindle (MS) permits a precision of $1\ \mu$ over a distance of 10 cm. A Flexaguide (FG) links the probe (PR) to the rigid part of the measuring line. (S): support of the cell-assembly.

Fig. 4. Measuring cell of the C-band equipment in Figure 2.

The results of these measurements are the real (ϵ') and the imaginary (ϵ'') parts of the permittivity of the solution at the frequency of the applied wave. In the context of this contribution discussion is limited to the frequency range of solvent molecule relaxations in pure solvents and in good-conducting electrolyte solutions, $\epsilon_s > 20$. The plots of $\epsilon''(\omega)$ vs. $\epsilon'(\omega)$ at various frequencies ω yield arcs with intersections on the ϵ' -axis at points of static permittivity $\epsilon_s = \epsilon(\omega \rightarrow 0)$ and high frequency permittivity $\epsilon_\infty = \epsilon(\omega \rightarrow \infty)$ [cf. Fig. 5]. The barycenter of relaxation times yields the frequency of the apex.

Some systems, especially pure solvents and their solutions at low electrolyte concentrations show diagrams of a Debye type

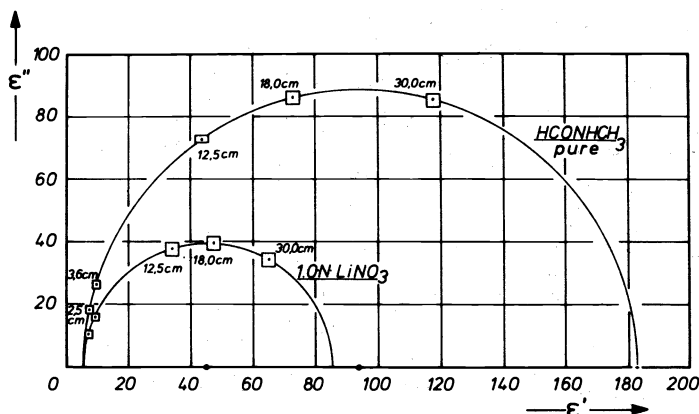


Fig. 5. Argand diagrams $\epsilon'' = f(\epsilon')$ of electrolyte solutions from measurements in the frequency region $2 < f/\text{GHz} < 40$ at 25°C (40,43): LiNO_3 in N-methylformamide.

- semicircles with center on the ϵ' -axis - indicating a single relaxation time of the solvent molecules. In general, however, more than one relaxation time is obtained and data analysis yields spectral functions like those shown in Fig. 6.

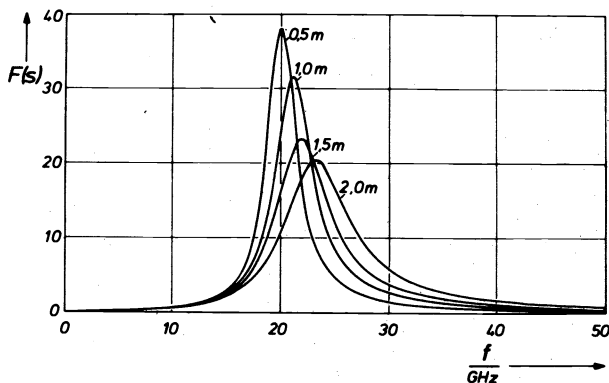


Fig. 6. Distributions of relaxation times for aqueous CsBr solutions (25°C) at various salt concentrations (27).

$F(s) = (\beta/\pi) [\cos(\beta\pi/2) \cos h(\beta s)] / [\cos^2(\beta\pi/2) + \sin^2(\beta s)]$ is the representation based on the Fuoss-Kirkwood theory [cf. (7,44,50)] with the loss function as $\epsilon''(\omega) = \epsilon''(\omega_0) \sec h(\beta s)$; $s = \ln \omega/\omega_0$; $\omega_0 = \tau^{-1}$ is the barycenter of the distribution.

The spectral distribution of solvent molecule relaxation times in solutions of varying salt concentration, Figure 6, illustrates the broadening of the frequency-range for the movement of solvent molecules with increasing electrolyte concentration. As a result, varying dielectric properties of the solutions are observed.

With amides [HCONH_2 , HCONHCH_3 , $\text{HCON}(\text{CH}_3)_2$] as the solvents a pronounced effect of an added salt is observed in solutions with N-methylformamide [Fig. 5] where a decrease of the static permittivity of $\epsilon_s = 182$ for the pure solvent to $\epsilon_s = 85$ for the 1 M LiNO_3 solution is

observed. A comparison of the frequencies (or wave lengths) at the apex shows values which correspond to relaxation times of 123 ps in the pure solvent and 91 ps in the 1 M solution. Both results, displacement of the static permittivity as well as decrease of relaxation time, are in accord with the destruction of the linear molecule associates of the pure solvent by the added salt. An appropriate application of the Kirkwood-Fröhlich theory on these data shows that about 10 solvent molecules are reorientated in the solvation shells of the ions (28). Formamide, a solvent with a two dimensional network of molecules, shows a percentage decrease of ϵ_s , similar to that of water [cf. Table 2]. In contrast to water, however, relaxation time increases with increasing salt concentration. The solvation number is 6 to 7. Dimethylformamide, finally, as a representative of non-associating solvents shows a slight decrease of the static permittivity with increasing salt concentration and no variation of relaxation time. Table 2 permits a comparison between these and further solvents; for more details see (7,40 to 43).

A linear decrease of ϵ_s with increasing salt concentration c

$$\epsilon_s = \epsilon_{\text{solv}} - \delta c \quad (3)$$

as postulated by Hückel is limited to low concentrations (46); a more satisfying relationship is extended to a quadratic term [cf. (7)]. Association can be deduced from ϵ_s values if different salts at the same concentration are compared in a given solvent, e.g. HCONH₂ in Table 2 [further examples (43)]. The higher association constant yields a lower ϵ_s -value.

TABLE 2. Static (ϵ_s) and high frequency (ϵ_∞) permittivities and relaxation times (τ) of polar solvents and their electrolyte solutions at 25°C.

Solvent	Electrolyte and concentration	ϵ_s	ϵ_∞	$\frac{\tau}{\text{ps}}$	Ref.
H ₂ O	-	78.4		8.3	40, 43
	1 M LiNO ₃	63.6		7.5	
CH ₃ OH	-	32.6	5.1	47	40
		32.6	5.6	52	48 (0,25 g H ₂ O/l)
	1 M LiNO ₃	18.2	5.5	51	40
C ₂ H ₅ OH	-	24.3	4.4		47 (v4 g H ₂ O/l)
	0.94 M LiClO ₄	11.5	4.8		(v4 g H ₂ O/l)
HCONH ₂	-	109.5	7.0	37	40
	1 M NaNO ₃	88.7	8.2	41	
	1 M LiNO ₃	87.4	8.6	39	
	1 M LiCl	87.0	8.4	42	
HCONHCH ₃	-	182	5.4	123	40
	1 M LiNO ₃	85	6.0	91	
HCONH(CH ₃) ₂	-	37.4	4.5	11	40
	0.5 M LiNO ₃	34.9	4.8	12	
(CH ₃) ₂ SO	-	47.3	5.7	17	40
	1 M LiNO ₃	39.4	4.7	27	
(CH ₃) ₆ N ₃ PO	-	29.6	3.3	80	40
	0.5 M LiNO ₃	21.3	3.3	88	

Relaxation times and their dependence on electrolyte concentration [Fig. 7] show increasing as well as decreasing values in H-bonded solvents. Up to now no decreasing relaxation times have been found in aprotic solvents. The relaxation time as a chemical rate process [cf. (44)] is characterised by the free energy of activation. Unfortunately, temperature dependent data are not yet available for quantitative discussion of this aspect.

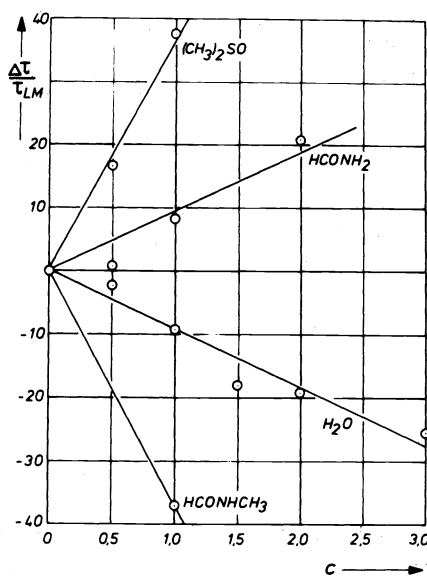


Fig. 7. Relative shift $\Delta\tau/\tau_{solv}$ of relaxation times as a function of concentration c of $LiNO_3$ in different solvents at 25°C (40).

Further significant information is obtained by a consideration of solutions at very high electrolyte concentrations. Figure 8 illustrates the result for $LiCl$ investigated on aqueous solutions of up to 13 M, corresponding to a molar fraction of $x_{LiCl} = 0.25$ in the binary system $H_2O-LiCl$ (43). As usual ϵ_s is the electrostatic permittivity of the aqueous $LiCl$ solution, ϵ_{solv} is the permittivity of the pure solvent. From Figure 8 a value of $\epsilon_s \approx 15$ can be assumed as the lower limit of ϵ_s in aqueous $LiCl$ solutions.

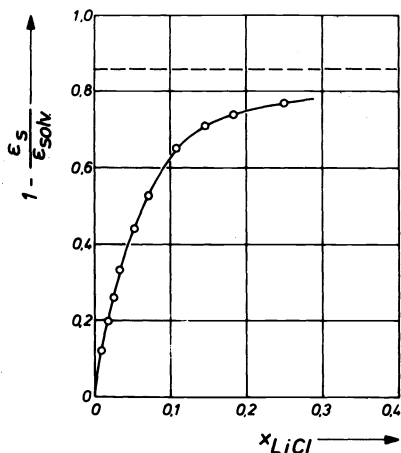


Fig. 8. Plot of $(\epsilon_{H_2O} - \epsilon_s)/\epsilon_{H_2O}$ vs. x_{LiCl} for $LiCl$ in aqueous solutions (25°C) (43). The dotted line at 0.859 corresponds to the permittivity of solid pure $LiCl$ $\epsilon_{LiCl} = 11.05$ (49).

A molar fraction $x_{LiCl} = 0.25$ describes a situation where all the cations and anions throughout the solution have approached to within a distance comparable to that of ion-pairs.

4. DISTRIBUTION FUNCTIONS

A consistent and useful classification of electrolytes is to distinguish ionophores and ionogenes [cf. (7,51,53)]. Ionophores [also: true electrolytes (52)] are substances which in their pure state already exist as ionic compounds, e.g. ionic crystals like alkali metal halides. Ionogenes [also: potential electrolytes (52)], such as acetic acid, form ions only by chemical reaction with solvent molecules. In contrast to the older definitions of strong and weak electrolytes this classification is independent of solvent properties and implies a distinction of the electrolyte compounds on the basis of short range interaction forces between their ions.

Ionophores are completely dissociated in solution and thus an electrolyte solution of a symmetrical ionophore $Y \equiv C^{Z+} A^{Z-}$ in a solvent S contains cations C^{Z+} , anions A^{Z-} , solvent molecules S and, if occasion arises, structures built up from these elements.

The distribution functions for the constituents of the solution are defined in statistical mechanics on the basis of a density function $\rho = \rho(\vec{r}_1 \dots \vec{r}_N, \vec{p}_1 \dots \vec{p}_N; t)$ of the position and momentum coordinates \vec{r}_i and \vec{p}_i of all particles and of time t in the $6N$ dimensional phase space (Γ -space) [cf. 53,54,55,56].

Integration of the density function $\rho(\vec{r}_i, \vec{p}_i; t)$ with respect only to the coordinates $\vec{r}_{s+1} \dots \vec{r}_N$, and momenta $\vec{p}_{s+1} \dots \vec{p}_N$ yields the s -particle distribution function

$$\rho^{(s)}(\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_s; t) = \sigma^{(s)} \int \rho(\vec{r}, \vec{p}, t) d\vec{r}_{s+1} \dots d\vec{r}_N d\vec{p}_{s+1} \dots d\vec{p}_N$$

which gives the probability of finding particles $i=1 \dots s$ in the position $\vec{r}_1 \dots \vec{r}_s$ and with momenta $\vec{p}_1 \dots \vec{p}_s$ regardless of the position of the remaining particles. The coefficient $\sigma^{(s)}$ takes into account whether equal or different particles are observed. Pursuing this method of integration molecular distribution functions $f^{(s)}(\vec{r}_1 \dots \vec{r}_s; t)$ are obtained if the functions $\rho^{(s)}$ themselves are integrated with respect to the remaining momentum coordinates $\vec{p}_1 \dots \vec{p}_s$.

It can be shown that the density function $\rho(\vec{r}_i, \vec{p}_i; t)$ tends toward a time-independent equilibrium distribution $\rho^{(eq)}(\vec{r}_i, \vec{p}_i)$ if time t tends toward ∞ (56).

$$\rho(\vec{r}_i, \vec{p}_i) = \frac{\exp[-H/kT]}{\int \exp[-H/kT] d\vec{r}_1 \dots d\vec{r}_N d\vec{p}_1 \dots d\vec{p}_N} \quad (4)$$

Introducing the Hamiltonian $H(\vec{r}_i, \vec{p}_i)$ in the usual form for conservative mechanical systems

$$H(\vec{r}_1 \dots \vec{r}_N, \vec{p}_1 \dots \vec{p}_N) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + U(\vec{r}_1, \dots, \vec{r}_N) \quad (5)$$

$$\text{with } U(\vec{r}_1 \dots \vec{r}_N) = \frac{1}{2} \sum_i \sum_j U_{ij}(|\vec{r}_i - \vec{r}_j|) \quad (6)$$

gives the molecular s -particle distribution function

$$f^{(s)}(\vec{r}_1, \dots, \vec{r}_s) = \frac{\sigma^{(s)}}{Q_K^{(N)}} \int \exp[-U(\vec{r}_1, \dots, \vec{r}_N)/kT] d\vec{r}_{s+1} \dots d\vec{r}_N \quad (7)$$

Eq. (6) is the representation of the potential energy $U(\vec{r}_1, \dots, \vec{r}_N)$ of the system as the superposition of two-particle interaction potentials. $Q_K^{(N)}$ in eq. (7) is given by the integral

$$Q_K^{(N)} = \int \exp[-U(\vec{r}_1, \dots, \vec{r}_N)/kT] d\vec{r}_1 \dots d\vec{r}_N$$

As the force \vec{K}_i acting on the particle i at position \vec{r}_i in a conservative system is $\vec{K}_i = -\partial U / \partial \vec{r}_i$ the mean value of this quantity with fixed particles $i=1 \dots s$ and regardless of the position of the remaining ones can be expressed as

$$\langle \vec{K}_i(\vec{r}_1, \dots, \vec{r}_s) \rangle = \frac{\int (-\frac{\partial U}{\partial \vec{r}_i}) \exp[-U(\vec{r}_1, \dots, \vec{r}_N)/kT] d\vec{r}_{s+1} \dots d\vec{r}_N}{\int \exp[-U(\vec{r}_1, \dots, \vec{r}_N)/kT] d\vec{r}_{s+1} \dots d\vec{r}_N} \quad (8)$$

Statistical-mechanical theory shows, e.g., via the BBGKY hierarchy of equations, that the properties of solutions can be derived from the knowledge of pair distribution functions

$$f_{ij}^{(2)}(\vec{r}_1, \vec{r}_2) = f_{ij}(\vec{r}_1, \vec{r}_2); \vec{r}_{21} = \vec{r}_2 - \vec{r}_1 = -\vec{r}_{12}$$

The factor $\sigma^{(2)}$, eq. (7), is $\sigma^{(2)} = N_i N_j$ for different particles i and j and $\sigma^{(2)} = N_i(N_i-1)$ for equal ones, N_i and N_j being the number of particles of i and j , respectively, in the solution. All interaction forces vanish with increasing distance $|\vec{r}_1 - \vec{r}_2|$ and

$$\lim_{|\vec{r}_1 - \vec{r}_2| \rightarrow \infty} f_{ij}^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{N_i}{V} \cdot \frac{N_j}{V} = n_i n_j$$

V is the volume occupied by the system and hence n_i, n_j are the particle densities within it. A pair correlation function $g_{ij}(\vec{r}_1, \vec{r}_2)$ can be introduced which measures the departure of the pair distribution function from its asymptotic value.

$$f_{ij}(\vec{r}_1, \vec{r}_{21}) = n_i n_j g_{ij}(\vec{r}_1, \vec{r}_{21})$$

Cations C^{z+} , anions A^{z-} , and solvent molecules S of an electrolyte solution contribute to the total potential energy of the system U , eq. (6), via ion-ion, ion-molecule, and molecule-molecule interaction energies U_{ij} due to polar, induction, dispersion and repulsive forces. The resulting two particle distribution functions

$$f_{ij}(\vec{r}_1, \vec{r}_{21}) = n_i n_j g_{ij}(\vec{r}_1, \vec{r}_{21}) = n_j n_i g_{ij}(\vec{r}_2, \vec{r}_{12}) = f_{ji}(\vec{r}_2, \vec{r}_{12}) \quad (9)$$

are related to these forces by eq. (8). Comparison of eqs. (7), (8) and (9) leads to the relationship, eq. (10), between the pair correlation function g_{ij} and the potential W_{ij} of the mean force $\langle \vec{K}_i(\vec{r}_1, \vec{r}_{21}) \rangle = \vec{K}_{ij}$.

$$W_{ij}(\vec{r}_1, \vec{r}_{21}) = -kT \ln g_{ij}(\vec{r}_1, \vec{r}_{21}) \quad (10)$$

Any attempt to set up a theory which takes into account all types of interaction energies U_{ij} , Table 3, with the aim and purpose of determining potentials of mean forces W_{ij} and, via these, pair distribution functions f_{ij} must prove unavailing as a result of insuperable mathematical difficulties.

TABLE 3. Potentials of Interaction of Ions and Molecules in Electrolyte Solutions

Type	Ion-Ion	Ion-Dipole	Dipole-Dipole
Electrostatic forces	$\frac{e_0^2 z_i z_j}{r_{ij}}$	$\frac{e_0 z_i m_j}{r_{ij}^2} f(\theta)$	$\frac{m_i m_j}{r_{ij}} f(\theta, \varphi)$
Induction forces		$\frac{e_0^2 z_i^2 \alpha_j}{2r_{ij}^2}$	$\frac{m_i^2 \alpha_j}{r_{ij}^6} f(\theta)$ $\frac{m_i^2 \alpha_j^2}{r_{ij}^9} f(\theta, \varphi)$
Dispersion forces	$\sim \frac{1}{r_{ij}^6}$ (v.d.Waals attraction)		
Repulsive forces	$e^{-\beta(r_{ij} - r_{ij}^0)}$ (electron shell)		

Symbols: z_i = ionic valency, m_i = dipole moment, α_i = polarisability, r_{ij} = mutual distance, r_{ij}^0 = equilibrium distance, θ, φ = angles of mutual orientation.

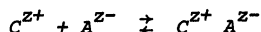
5. THE BASIC MODEL OF INTERACTION POTENTIALS AROUND AN ION IN SOLUTION

The feature of Debye's treatment of electrolyte solutions is the concept of using the fundamental potential equation of the electrostatic field in combination with a Boltzmann distribution of the ions to express charge density together with appropriate boundary conditions for determining the potential W_{ij} of an equilibrium distribution (12). At equilibrium the distribution of spherical charge distributions itself can be assumed to be of spherical symmetry, i.e., $|\vec{r}_{12}| = |\vec{r}_{21}| = r$ in the preceding equations and

$$\text{div grad } \psi_i(r) = -\frac{e_0}{\epsilon_0 \epsilon} \sum n_j z_j g_{ij}(r)$$

$$g_{ij}(r) = \exp[-W_{ij}(r)/kT] \approx 1 - \frac{W_{ij}(r)}{kT}; \quad W_{ij}(r) = e_0 z_j \psi_i(r)$$

As indicated in the second equation the series expansion of $g_{ij}(r)$ is truncated after the linear term meaning a restriction to highly dilute solutions. As a further restriction, the limitation to only long range forces must be remembered. Today this concept is no longer a matter of debate as far as the limiting laws of properties of electrolyte solutions are concerned. However, solutions with solvents of low permittivity show already at their lowest realisable concentrations deviations from the Debye-Hückel limiting law and these have been the reason for introducing a formal association equilibrium



of oppositely charged ions in the solution which leads to the hypothesis of ion-pair formation. The original work in this field considers in accordance with the Debye-Hückel theory only Coulomb forces between the ions (24).

The following treatment tries to combine the concept of the Debye-Hückel theory and the association hypothesis in a general way permitting the introduction of short range forces into the electrolyte theory (57). For this purpose, a basic model, Fig. 9, is used which differs from Debye's model in so far as in the vicinity of an ion which is considered as a 'free' ion, a region $a \leq r \leq R$ is assumed free of other single charges.

As a first type of short range interaction, a neutral particle interaction independent of the central ion charge can be introduced into theory [cf. 20,22,24,58 to 60]. The underlying forces have a range $a \leq r \leq R^*$, $R^* \leq R$.

Long range ion-ion interaction forces are maintained for $r \geq R$ as in the Debye-Hückel theory.

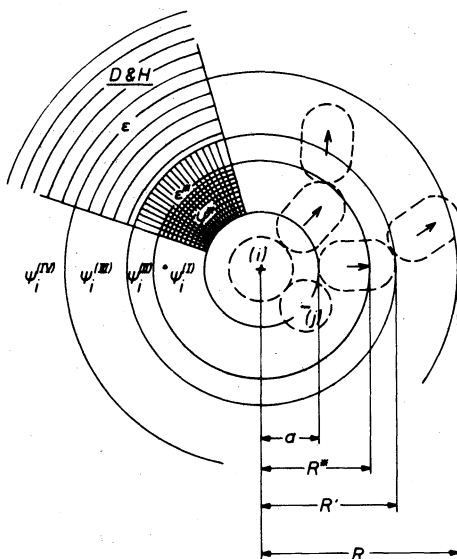


Fig. 9. The basic model of interaction regions in the vicinity of an ion in solution.

Permittivity measurements suggest taking into account special short range ion-solvent interactions by the possibility of reorientation of the solvent molecules in the strong field of the central ion giving rise to a local permittivity ϵ^* in the region $a \leq r \leq R'$ (e.g. in Fig. 9: $R^* \leq R' \leq R$) of the immediately adjacent solvent [cf. (20,23)]. The pertinent mean potential ψ_{ij} can be calculated within the theoretical framework based on Fig. 9. This type of separating different types of short range interactions is no requirement of theory and is of use only if a significant meaning can be attributed to the ad hoc introduced quantity ϵ^* .

The model described above implies the distinction between paired states of ions as paired states of 'free' ions ($r \geq R$) and as ion pairs ($a \leq r \leq R$). Concentration of 'free' cations or anions is αc , α being the degree of dissociation and c the analytical concentration of the electrolyte compound in the solution.

Extension to incompletely dissociated ionogenic electrolyte compounds is achieved with the help of partition functions regarding the reacting ions and molecules as particles in an energy cage ($a \leq r \leq R$) and, if circumstances demand, introducing their vibrational and rotational contributions of internal degrees of freedom [cf. Section 9].

6. CONTRIBUTION OF ELECTROSTATIC ION-ION INTERACTION POTENTIALS TO EQUILIBRIUM DISTRIBUTIONS

As a first step for discussion, a model with only long range forces is considered. Then the space around the central ion is subdivided into two regions, a charge free region (I), $a \leq r \leq R$, with an electrostatic potential $\psi_i^{(I)}(r)$ and the bulk solution, region (II) [$r \geq R$], with the potential $\psi_i^{(II)}(r)$. This model requires the following system of equations (57).

$$\operatorname{div} \operatorname{grad} \psi_i^{(I)}(r) = 0 \quad a \leq r \leq R \quad (11a)$$

$$\operatorname{div} \operatorname{grad} \psi_i^{(II)}(r) = \kappa^2 \psi_i^{(II)}(r) \quad r \geq R \quad (11b)$$

and the boundary conditions

$$\lim_{r \rightarrow \infty} \psi_i^{(II)}(r) = 0 \quad (12a)$$

$$\psi_i^{(I)}(R) = \psi_i^{(II)}(R) \quad (12b)$$

$$\left(\frac{\partial \psi_i^{(I)}}{\partial r} \right)_R = \left(\frac{\partial \psi_i^{(II)}}{\partial r} \right)_R \quad (12c)$$

$$-\epsilon_0 \epsilon \iint_{(R)} \operatorname{grad} \psi_i^{(I)}(r) = \epsilon_0 z_i \quad (12d)$$

Eq. (11b) is that of the Debye-Hückel theory with linear approximation of $g_{ij}(r)$. Thus the parameter κ has its usual meaning

$$\kappa^2 = 16 \pi q N_A (\alpha c) \cdot 10^m; \quad q = \frac{e_0^2 z^2}{8 \pi \epsilon_0 \epsilon kT} \quad (13a \text{ and } b)$$

The boundary conditions state the vanishing potential $\psi_i(r)$ with increasing distance [eq. (12a)] and the continuity of the potential and of the normal component of the dielectric displacement vector $\vec{D} = -\epsilon_0 \epsilon \operatorname{grad} \psi_i(r)$ on the surface $r = R$ [eqs. (12b) and (12c)]. Eq. (12d) ensures that the region $a \leq r \leq R$ is free of other charges than the central ion itself by the assumption that the total flow of the displacement vector \vec{D} through the surface $r = R$ is equivalent to the central charge.

Eqs. (11) and (12) yield the mean potentials in the form

$$w_{ij}^{(I)}(r) = e_0 z_j \psi_i^{(I)}(r) = -\frac{2qkT}{r} + \frac{2qkT}{1+\kappa R} \quad \kappa a \leq r \leq R \quad (14a)$$

$$w_{ij}^{(II)}(r) = e_0 z_j \psi_i^{(II)}(r) = -\frac{2qkT}{r} \frac{\exp[\kappa(R-r)]}{1+\kappa R} \quad r \geq R \quad (14b)$$

Separation of the contribution of the central i ion and that of the remaining ions to the potential $\psi_i^{(I)}(r)$, eq. (14a), yields the potential of the ion cloud $\tilde{\psi}_i^{(I)}(r)$ within $a \leq r \leq R$ in the usual way.

$$\tilde{\psi}_i^{(I)}(r) = \psi_i^{(I)}(r) - \frac{e_0 z_i}{4\pi \epsilon_0 \epsilon} \cdot \frac{1}{r}$$

and by a charging process the activity coefficient y_i of the central ion of type i , when this ion is a 'free' ion according to the initial definition

$$\ln y_i = \frac{N_A}{RT} \int_0^{e_0 z_i} \tilde{\psi}_i^{(I)}(r) d(e_0 z_i) \quad (15)$$

Then the mean activity coefficient of the dissociated part of a symmetrical electrolyte $C^{z+} A^{z-}$ follows as

$$\ln y_{\pm} = -\frac{\kappa q}{1+\kappa R} \quad (16)$$

in accordance with the activity coefficient of the Debye-Hückel theory which assumes all ions of an ionophoric electrolyte in solution to be 'free' ions.

The degree of association $(1-\alpha)$ is obtained by counting the paired states of ions within $a \leq r \leq R$

$$1-\alpha = 4\pi\alpha n_j \int_a^R r^2 \exp\left(-\frac{W_{ij}^{(I)}(r)}{kT}\right) dr \quad (17)$$

Replacing the density function n_j by $n_j = N_A(\alpha c) 10^m$ and using eq. (16) the relationship

$$\frac{1-\alpha}{\alpha^2 c} = 4\pi N_A \cdot 10^m \cdot y_{\pm}^{\prime 2} \int_a^R r^2 \exp\left(\frac{2q}{r}\right) dr \quad (18)$$

is obtained which encompasses Prue's association constant (32,61) and hence also Bjerrum's constant ($R = q$) as special cases.

7. EXTENSION OF THE THEORY TO SHORT RANGE INTERACTION

As a next measure, short range forces which are independent of the central ion charge can be introduced into theory. These forces act in the range $a \leq r \leq R^*$ [cf. Fig. 9]. The simplest possible model which takes into account this type of interaction is to assume a mean force potential

$$W_{ij}^*(r) = W_{ij}^* = \text{const} \quad a \leq r \leq R^* \quad (19a)$$

$$W_{ij}^*(r) = 0 \quad r \geq R^* \quad (19b)$$

A superimposition of the foregoing electrostatic model which yields potentials $W_{ij}^{(el)} = e_0 z_j \psi_i(r)$ and the neutral interaction potentials of type W_{ij}^* leads to pair correlation functions based on the potentials (57)

$$W_{ij}^{(I)}(r) = -\frac{2q kT}{r} + \frac{2q kT}{1+\kappa R} \kappa + W_{ij}^* \quad a \leq r \leq R^* \quad (20a)$$

$$W_{ij}^{(II)}(r) = -\frac{2q kT}{r} + \frac{2q kT}{1+\kappa R} \kappa \quad R^* \leq r \leq R \quad (20b)$$

$$W_{ij}^{(III)}(r) = -\frac{2q kT}{r} \cdot \frac{\exp[\kappa(R-r)]}{1+\kappa R} \quad r \geq R \quad (20c)$$

As a consequence of the assumption of this further interaction, eq. (18) must be replaced by

$$\frac{1-\alpha}{\alpha^2 c} = 4\pi N_A \cdot 10^m \cdot y_{\pm}^{\prime 2} \left[\int_{R^*}^R r^2 \exp\left(\frac{2q}{r}\right) dr + a \int_a^{R^*} r^2 \exp\left[\frac{2q}{r} - \frac{W_{ij}^*}{kT}\right] dr \right] \quad (21a)$$

The resulting association constant with $\Delta G_A^* = N_A W_{ij}^*$

$$K_A^{\text{tot}} = 4\pi N_A \cdot 10^m \left[\exp\left[-\frac{\Delta G_A^*}{RT}\right] \int_a^{R^*} r^2 \exp\left(\frac{2q}{r}\right) dr + \int_{R^*}^R r^2 \exp\left(\frac{2q}{r}\right) dr \right] \quad (21b)$$

has been applied within the framework of modern theories (7,20,22,57 to 60).

The application of the complete model, Fig. 9, including a region of local permittivity, requires a system of three Poisson equations for the evaluation of the electrostatic potential $\psi_i(r)$ in the regions (I,II): $a \leq r \leq R'$, (III): $R' \leq r \leq R$, and (IV): $r \geq R$. The boundary conditions of the system of partial differential equations are chosen as follows

$$\lim_{r \rightarrow \infty} \psi_i^{(IV)}(r) = 0 \quad (22a) \quad \psi_i^{(III)}(R) = \psi_i^{(IV)}(R) \quad (22b)$$

$$\left(\frac{\partial \psi_i^{(III)}}{\partial r}\right)_R = \left(\frac{\partial \psi_i^{(IV)}}{\partial r}\right)_R \quad (22c) \quad \psi_i^{(III)}(R') = \psi_i^{(I)}(R') \quad (22d)$$

$$\epsilon \left(\frac{\partial \psi_i^{(III)}}{\partial r}\right)_{R'} = \epsilon^* \left(\frac{\partial \psi_i^{(I)}}{\partial r}\right)_{R'} \quad (22e) \quad \lim_{R' \rightarrow \infty} \psi_i^{(I)}(r) = \frac{e_0 z_i}{4\pi \epsilon_0 \epsilon^*} \cdot \frac{1}{r} \quad (22f)$$

In comparison with eqs. (11) and (12) the new boundary at $r = R'$ is characterised by conditions [eqs. (22d) and (22e)] taking into account the differing permittivities in the two

regions. Eq. (12d) is replaced by the condition (22f) which is a more appropriate form for further generalizations, e.g. a non-symmetrical charge distribution of the central particle as introduced in Section 10.

The mean potential $W_{ij}(r)$ according to the model in Fig. 9, is finally obtained as the superimposition of $W_{ij}^{(el)}$ and W_{ij}^* [cf. eqs. (20a) to (20c)]. In our present state of knowledge a distinction between R^* and R' is scarcely possible, i.e. these parameters are equalized, $R' = R^*$, in the further context. Then the association constant eq. (21b) is replaced by

$$\begin{aligned} \mu_A^{\text{tot}} = 4\pi N_A \cdot 10^m \left[\exp \left[-\frac{\Delta G_A^*}{RT} - \frac{2q}{R^*} \frac{\epsilon - \epsilon^*}{\epsilon^*} \right] \int_a^{R^*} r^2 \exp \left(\frac{2q}{r} \frac{\epsilon}{\epsilon^*} \right) dr \right. \\ \left. + \int_{R^*}^R r^2 \exp \left(\frac{2q}{r} \right) dr \right] \end{aligned} \quad (23)$$

8. THERMODYNAMIC PROPERTIES OF ELECTROLYTE SOLUTIONS

The thermodynamic properties of a completely dissociated electrolyte compound $Y \equiv C^{z+} A^{z-}$ in a solvent S are available from the knowledge of the chemical potentials (7,14,57,62).

$$\mu_Y = \mu_Y^\infty + 2 RT \ln c_{\pm} y_{\pm} \quad (24a)$$

$$\mu_Y^\infty = \lim_{x_S \rightarrow 1} [\mu_Y(p,T) - 2 RT \ln c_{\pm}]; \lim_{x_S \rightarrow 1} y_{\pm} = 1 \quad (24b \text{ and } c)$$

$$\mu_S = \mu_S^0 + RT \ln x_S f_S \quad (25a)$$

$$\mu_S^0 = \lim_{x_S \rightarrow 1} \mu_S(p,T); \lim_{x_S \rightarrow 1} f_S = 1 \quad (25b \text{ and } c)$$

In eqs. (24) and (25), $\mu_Y = \mu_Y(p,T)$ and $\mu_S = \mu_S(p,T)$ are the chemical potentials of the two constituents of the electrolyte solution and μ_Y^∞ (infinitely dilute electrolyte) and μ_S^0 (pure solvent) their potentials in the reference states. c_{\pm} is the mean concentration of the electrolyte compound in the molar scale, y_{\pm} the relevant mean activity coefficient. For the solvent the mol fraction x_S is chosen as the appropriate concentration measure, f_S means the corresponding activity coefficient.

Eqs. (24) are based on the assumption

$$\mu_Y(p,T) = \mu_+(p,T) + \mu_-(p,T) \quad (26)$$

with $\mu_+(p,T)$ as the chemical potential of the cation C^{z+} and $\mu_-(p,T)$ as that of the anion A^{z-} in solution. If, however, the electrolyte compound is not completely dissociated (ionogenic electrolyte) or if we assume partial association of the ions to ion-pairs of type $X = [C^{z+} A^{z-}]$ according to



eq. (26) must be replaced by

$$\mu_Y(p,T) = \alpha [\mu_+^i(p,T) + \mu_-^i(p,T)] + (1-\alpha) \mu_X^i(p,T) \quad (28)$$

where $\mu_+^i(p,T)$, $\mu_-^i(p,T)$ and $\mu_X^i(p,T)$ are the chemical potentials of free cations, free anions and the species X (undissociated molecule or ion-pair of equal stoichiometric composition). α is the degree of dissociation.

Eq. (28) is subject to the equilibrium condition

$$\mu_X^i(p,T) - \mu_+^i(p,T) - \mu_-^i(p,T) = 0 \quad (29)$$

Taking into account the relationships $\mu_Y^\infty = \mu_Y^i$ and $c_{\pm}^i = \alpha c_{\pm}$, eq. (24) is also obtained from eqs. (28) and (29); i.e. eq. (24) remains valid for the incompletely dissociated or for the partially associated electrolyte compound Y when y_{\pm} is set

$$y_{\pm} = \alpha y_{\pm}^i \quad (30)$$

From the equilibrium condition, eq. (29),

$$\mu_X^\infty - \mu_+^\infty - \mu_-^\infty = -RT \ln \frac{c_X^i}{c_{\pm}^i} \frac{y_X^i}{y_{\pm}^i} \quad (31)$$

is obtained as a further result. The left side of eq. (31) is the molar Gibbs' energy ΔG_A^0 of formation of an ion-pair in the infinitely dilute solution from the initially infinitely separated ions. The right side of eq. (31) contains the equilibrium constant

$$K_A = \frac{c'_X}{c_{\pm}^{\prime 2}} \frac{y_X}{y_{\pm}^{\prime 2}} = \frac{1-\alpha}{\alpha^2 c} \frac{y_X}{y_{\pm}^{\prime 2}} \quad (32)$$

relating to the chemical process in eq. (27). Hence eq. (30) can be written

$$\Delta G_A^0 = -RT \ln K_A \quad (33)$$

The foregoing investigation based on the existence of an ion-pair of composition $[C^{z+} A^{z-}]$ can easily be generalized. E.g., if the electrolyte $Y \equiv C_{w_+}^{z_+} A_{w_-}^{z_-}$ is assumed to build aggregates of type $X \equiv C_{w_+}^{z_+} A_{w_-}^{z_-}$, the activity coefficient is given as (7)

$$y_{\pm}^v = y_{\pm}^{\prime v} \alpha^{v+} \left[1 - (1-\alpha) \frac{w_-}{w_+} \frac{v_+}{v_-} \right]^{v-}$$

etc. Extensions to the more general cases of simultaneous equilibria, competitive or consecutive, can easily be performed, too.

Calculation of the equilibrium constant K_A is possible by means of statistical thermodynamic methods [cf. (63)]

$$K_A = \frac{Q_X}{Q_+ Q_-} \exp \left[-\frac{\Delta E_0}{RT} \right] \quad (34a)$$

In eq. (34a) Q_X , Q_+ , and Q_- are the reduced partition functions of species X, cation C^{z+} , and anion A^{z-} . ΔE_0 is the difference in energy between the reacting species in their lowest energy levels.

$$\Delta E_0 = E_0(X) - E_0(C^{z+}) - E_0(A^{z-}) \quad (34b)$$

The partition function of type Q_i can be divided into a translational part $Z_{\text{trans}}^{(i)}$ and a part Z_i due to the contributions of the internal degrees of freedom of species i .

$$Q_i = Z_{\text{trans}}^{(i)} Z_i = \frac{1}{N_A} \cdot \frac{(2\pi m_i kT)^{3/2}}{h^3} \cdot Z_i \quad (34c)$$

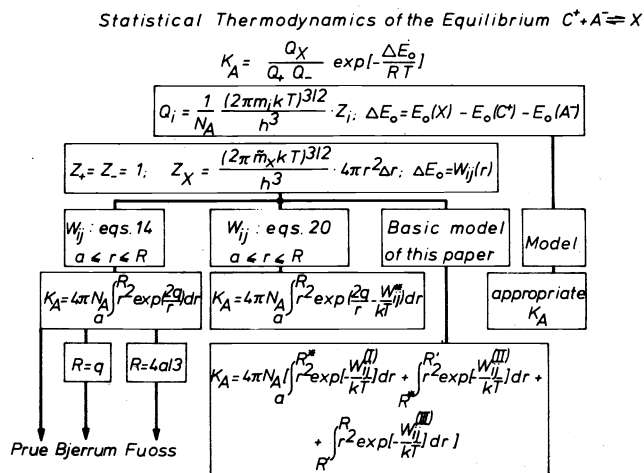


Fig. 10. Association constants and their origin.

Eqs. (34) apply to both, to an equilibrium between ions and an undissociated molecule or complex as well as to that between ions and an ion-pair [cf. Fig. 10]. A first approximation to ion-pair formation on an ionophore considers the cations C^{Z+} and the anions A^{Z-} to be charged spheres and no contribution from internal degrees of freedom is taken into account, i.e. $Z_+ = Z_- = 1$.

$$Q_+ = \frac{1}{N_A} \frac{(2\pi m_+ kT)^{3/2}}{h^3}; \quad Q_- = \frac{1}{N_A} \frac{(2\pi m_- kT)^{3/2}}{h^3} \quad (35a \text{ and } b)$$

The ion-pair X is formed whenever the region $a \leq r \leq R$ contains both an anion and a cation. As a chemical species the ion-pair contributes to Z_X by internal translational degrees of freedom only and

$$Q_X = \frac{1}{N_A} \frac{(2\pi m_X kT)^{3/2}}{h^3} \cdot \frac{(2\pi \bar{m}_X kT)^{3/2}}{h^3} \cdot \Delta V \quad (35c)$$

ΔV is the volume of the energy cage in which the paired state of ions is considered, $\Delta V = 4\pi r^2 \Delta r$, and \bar{m}_X is the reduced mass $\bar{m}_X^{-1} = m_+^{-1} + m_-^{-1}$.

The difference in energy ΔE_0 is identical to the potential of the mean force, W_{ij} . On the basis of eqs. (14) the association constants of Bjerrum, Fuoss and Prue are obtained. Eq. (20) leads to those based on a short range interaction term besides Coulomb ion-ion interaction, eq. (21b). The basic model, Fig. 9, yields the still more differentiating association constant, eq. (23). Further improvements are possible, especially when the restrictions $Z_+ = Z_- = 1$ and the resulting restrictions on Z_X are suppressed [cf. also (20,64 to 66)]. Thus it is possible to introduce for polyatomic ions contributions of internal degrees of freedom or to link solvent molecules to the ions and to the ion-pair. The most general model ['Model' in Fig. 9] permits the application to ionogenes and thus the introduction of binding forces. Short range as well as binding forces act in thermodynamic theories via the degree of dissociation α , eq. (30). The feature of Bjerrum's and related concepts based on eqs. (14) proves to be the introduction of that part of the Coulomb force within the region $r \leq R$ which is suppressed by Debye's linear approximation in $g_{ij}(r)$ [cf. Section 5].

9. ION-PAIRS IN NON AQUEOUS SOLUTIONS

The foregoing brief analysis of ion-ion and ion-solvent interactions in electrolyte solutions shows that the notion 'ion-pair' is related to the physicochemical phenomenon which has been used to determine it, just like e.g. the notion 'solvation number'. Spectroscopic methods yield association constants for paired states of ions which differ from those obtained by thermodynamic processes or transport phenomena. If the former exist, they are contained as partial equilibrium constants in the over-all constants K_A^{tot} of the latter type.

In accordance with the model, eq. (9), an ion-pair is considered to be any paired state of oppositely charged ions for which the ions have approached to within a distance $r \leq R$. R is called the upper limit of association and is determined from conductance measurements. Conductance is chosen as the definition method as a result of its very general applicability to electrolyte solutions and its high precision with solutions ranging from very dilute to saturated. Evaluation of conductance data with the aim of obtaining K_A -values as thermodynamic quantities containing the pertinent Gibbs excess energies must be based on conductance equations which are complete up to a concentration term $c^{3/2}$. This problem will be considered in Section 11.

Classical conductance work is based on equations of type eq. (18) which yields Bjerrum's constant if R is chosen $R = q$ (24). This distance q , eq. (13b), depends only on the permittivity ϵ and the temperature of the solvent

$$K_A^{\text{exp}} = K_A^B = 4\pi N_A 10^m \int_a^q r^2 \exp\left(\frac{2q}{r}\right) dr \quad (36)$$

Eq. (36) contains the lower limit a_K^B as the only parameter for adaptation to experimentally determined association constants, K_A^{exp} . a_K^B -values from this procedure are listed for the investigated electrolytes in Tables 4a and 4b. A perusal of these values confirms their unrealistic magnitude when compared to crystallographic radii 'a' in the same tables. Fig. 11 showing K_A -values of tetraalkylammonium salts in propanol as a function of temperature, illustrates also a behaviour which is incompatible with eq. (36).

The interpretation of experimentally determined K_A -values as association constants K_A^{tot} , eq. (21b), which has been also shown to be a thermodynamic equilibrium constant [cf. Sec. 8],

is more successful. Tetraalkylammonium salts $R_4N^+A^-$, especially those with longer chains ($R = Pr, n-Bu, n-Am, i-Am$) and big anions ($A^- = (C_6H_5)_4B^-, I^-, ClO_4^-$) have a small density of ionic surface charge. As far as permittivity is concerned, orientation of adjacent solvent molecules yields only small changes when compared to the orientation of solvent molecules in a solvation shell and thus short range interactions can be represented by W_{ij}^* , eqs. (19).

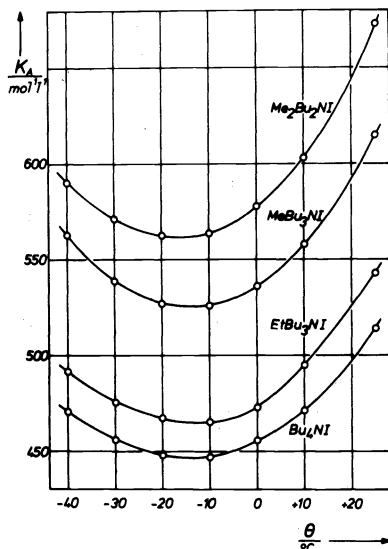


Fig. 11. Association constants of tetraalkylammonium salts in propanol in the temperature range ($-45 \leq \theta/^\circ C \leq +25$) (26).

The limits a , R^* and R in eq. (21b) are fixed as follows [cf. Fig. 9]: the lower limit ' a ' is no longer used as a parameter for adaptation. It is fixed as the hard core radius by the center-to-center distance of the ions from crystallographic radii where these exist or else is calculated from bond lengths or van der Waals volumes (68,69,70) [cf. (59)]. As far as tetraalkylammonium salts are concerned, the latter procedure is only possible for methyl and ethyl groups. a -Parameters for bigger ions are calculated from the molar volumes of the isosteric alkanes (69). For nonsymmetrical ions like $Me(n-Bu)_3N^+$ or $C_3H_7O^-$ the shortest possible distance between the localised positive and negative charges is taken to be the distance of closest approach, e.g. the distance $I^- \dots Me \dots N^+$ in $Me(n-Bu)_3NI$ (59).

The choice of $R = q$ with q as the Bjerrum distance which was made preferentially in preceding contributions (20,59,60) is consistent with electrolyte theory (22,71,72) but is a necessary condition neither there nor for the association concept (20,53,59,60). For $(n-Bu)(i-Am)_3N-B(C_6H_5)_4$ in ethanol or $(n-Bu)_4NClO_4$ in acetonitrile, $a > q$ at low temperature and no association should occur, whereas, e.g., $K_A^{exp} [(n-Bu)(i-Am)_3N B(C_6H_5)_4] = 475 \text{ l mol}^{-1}$ in ethanol at $-45^\circ C$ [$a = 10.77 \text{ \AA}$ (73), $q = 9.64 \text{ \AA}$].

In accordance with thermodynamics of the association process, paired states of ions are considered as ion-pairs if the ions have approached to within a distance smaller than the dimensions ' s ' of a solvent molecule; i.e. $R = a+s$ [cf. (20,59)]. This assumption is to be limited for the time being to big cations and anions, e.g. tetraalkylammonium ions, $(C_6H_5)_4B^-, I^-, SCN^-$ and ClO_4^- .

As a further and consistent assumption when a minimum of parameters is striven for, the short range interactions are limited to a maximum distance ' s ', i.e. $R = R^* = a+s$ in the actual discussion, keeping in mind that this distance is perhaps unrealistically large for this type of interaction, especially in solvents with big molecules. A comparison of different salts in the same solvent, however, can be made.

On the basis of these assumptions, eq. (21b) yields the association constant

$$K_A^{exp} = K_A^{tot} = 4\pi N_A 10^m \exp \left[-\frac{\Delta G_A^*}{RT} \right] \int_a^{a+s} r^2 \exp \left(\frac{2q}{r} \right) dr \quad (37)$$

In eq. (37) $\Delta G_A^* = N W_{ij}^*$ is that part of the molar Gibbs energy of ion-pair formation which is due to the short range interactions. Table 4a contains evaluations of ΔG_A^* and the derived quantities ΔH_A^* and ΔS_A^* from K_A^{exp} -values obtained by conductance measurements on tetraalkylammonium salts in the temperature range $-45 \leq \theta/^\circ C \leq +25$. Table 4b shows such results and results from further evaluations for alkali salts. As long as the diagrams $\Delta G_A^*/T$ vs. T^{-1} do not yield straight lines, the slopes at 298 K are used to determine ΔH_A^* and ΔS_A^* (59).

TABLE 4a. Ion-pair formation of tetraalkylammonium salts. Thermodynamic functions of short range interactions of ion-pair formation in some non aqueous solvents ($-45 \leq \theta/^\circ\text{C} \leq +25$).

Electrolyte	$\frac{a_K^B}{\bar{a}}$	$\frac{\Delta G_A^O(298)}{J \text{ mol}^{-1}}$	$\frac{a}{\bar{a}}$	$\frac{\Delta H_A^*}{J \text{ mol}^{-1}}$	$\frac{\Delta S_A^*}{J \text{ mol}^{-1} \text{ K}^{-1}}$
A. ETHANOL ($s = 5.30 \bar{a}$)					
Pr ₄ NBr	3.28	-12100±100	6.47	-2700±100	0.0±0.3
Pr ₄ NI	2.92	-12800	6.68	-3800	-1.0±0.2
Pr ₄ NC10 ₄	2.51	-14000	6.90	-5200	-1.3±0.4
Bu(i-Am) ₃ NI	2.85	-13100	7.10	-4000	-0.7±0.3
Bu(i-Am) ₃ N B(C ₆ H ₅) ₄	2.64	-13800	10.77	-6600	-6.7±0.5
B. PROPANOL ($s = 6.90 \bar{a}$)					
MeBu ₃ NI	2.85	-15900±100	5.64	-4300±150	+0.1±0.5
Me ₂ Bu ₂ NI	2.79	-16100	5.64	-3900±200	+2.2±0.5
Et ₄ NI	2.93	-15600	6.17	-3600±200	+2.1±0.5
EtBu ₃ NI	2.93	-15600	6.17	-3900±150	+1.0±0.5
Pr ₄ NI	2.97	-15500	6.68	-3700±200	+2.1±0.5
Bu ₄ NI	2.95	-15500	7.10	-3400±200	+3.1±1.0
Bu(i-Am) ₃ NI	2.89	-15700	7.10	-3700±150	+3.2±0.5
Bu ₄ NC10 ₄	2.91	-16900	7.64	-5900±100	-0.1±0.6
i-Am ₄ NI	2.89	-15700	7.10	-3900±200	+2.7±0.5
n-Am ₄ NI	2.94	-15600	7.45	-3600±200	+3.4±0.5
C. ACETONITRILE ($s = 5.12 \bar{a}$)					
Me ₄ NI	2.28	- 9100±2000	5.64	- 450±100	+4.5±0.5
Et ₄ NC10 ₄	2.78	- 8100±100	6.35	+ 500± 50	+4.2±0.2
Pr ₄ NC10 ₄	2.78	- 8000	7.22	+ 500±100	+4.5±0.3
Bu ₄ NC10 ₄	2.92	- 7900	7.64	+ 200±100	+2.5±0.4

Tetraalkylammonium salts [cf. Table 4a] in the protic solvents EtOH and PrOH as well as in the aprotic solvent MeCN show small entropy changes indicating that ion-pair formation occurs without sensible reorientation of solvent molecules adjacent to the ions. This observation confirms the initial assumption concerning the permittivity of the solvent in this region. In both protic solvents negative enthalpies ΔH_A^* of the same order of magnitude are obtained independent of the cation size. This result suggests the assumption of like interaction forces for all listed electrolytes in those solvents. ΔH_A^* -values in solutions in acetonitrile as the solvent are about one order of magnitude smaller and also comparable with one another. Satisfactory linear functions $\Delta G_A^*/T$ vs. T^{-1} within the whole temperature range $-45^\circ\text{C} \leq \theta \leq 25^\circ\text{C}$ yielding temperature-independent values of ΔH_A^* and ΔS_A^* are a further characteristic of short range interactions in tetraalkylammonium salt solutions.

Alkali salts [cf. Table 4b] in the same solvents show a quite different behaviour if their association constants K_A^{exp} are treated by eq. (37). Cesium salts and more or less also potassium salts with big anions show comparable properties in alcoholic solutions, i.e. large positive enthalpies ($\Delta H_A^* > 0$) and entropies ($\Delta S_A^* > 0$) indicating types of short range interaction which differ from those of tetraalkylammonium salts ($\Delta H_A^* < 0$, $\Delta S_A^* \approx 0$). With regard to ΔH_A^* and ΔS_A^* , the data of KI and KClO₄ in acetonitrile are of the same order of magnitude as those of potassium salts in the protic solvents. Neglecting the uncertainty caused by the very small association constants of KPF₆ in propylene carbonate [cf. Table 7], a tentative evaluation according to eq. (37) yields $\Delta H_A^* = +750 \text{ J mol}^{-1}$ and $\Delta S_A^* = -1.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

Short range interactions should be small in this case.

TABLE 4b. Ion-pair formation of alkali salts. Thermodynamic functions of short range interactions of ion-pair formation in some non aqueous solvents ($-45 \leq \theta/^\circ\text{C} \leq +25$)

Electrolyte	$\frac{B}{a_K}$ $\frac{\text{Å}}{\text{Å}}$	$\frac{\Delta G_A^\circ(298)}{J \text{ mol}^{-1}}$	$\frac{a}{\text{Å}}$	$\frac{\Delta H_A^*}{J \text{ mol}^{-1}}$	$\frac{\Delta S_A^*}{J \text{ mol}^{-1} \text{ K}^{-1}}$
A. ETHANOL ($s = 5.30 \text{ Å}$)					
NaI	5.09	- 9300±100	3.17	+ 400±100	- 7±1
NaB(C ₆ H ₅) ₄	7.68	- 8400	6.80	+ 200±100	- 2±1
NaI {a'}	-	-10100	5.98	+2500±200	+10±1
NaB(C ₆ H ₅) ₄ {a'}	-	- 9600	9.61	+ 900± 50	+ 5±1
KI	3.99	-10700	3.53	+2300±100	+ 6±1
KSCN	4.00	-10900	4.70	+3100±200	+12±1
CsI	3.06	-12300	3.87	+ 750± 50	+ 8±1
B. PROPANOL ($s = 6.90 \text{ Å}$)					
LiCl	3.49	-13900±100	2.49	+ 550± 50	-10±1
NaI	4.38	-12800	3.17	+ 900±100	- 3±1
LiCl {a'}	-	-14100	5.30	+6700±600	+28±4
NaI {a'}	-	-13100	5.98	+4400±400	+18±2
KI	3.41	-14200	3.53	+3900±200	+15±1
KSCN	3.30	-14300	4.70	+4900±300	+22±1
CsOPr	2.60	-16800	3.20	+8000±300	+34±3
C. ACETONITRILE ($s = 5.12 \text{ Å}$)					
KI	3.42	- 7300±100	3.52	+3000±200	9±1
KClO ₄	2.53	- 8500	3.70	+2000±200	10±1

On the basis of ΔH_A^* and ΔS_A^* values, no fundamental distinction can be made between interaction forces in electrolyte solutions of potassium salts with alcohols or acetonitrile as the solvents. This observation is in accordance with some results on protic and aprotic solvents of electrolyte solutions obtained from dispersion of permittivity, e.g. displacement of relaxation time. The entropy changes for cesium and potassium salts, Table 4b, indicate that solvent molecules in the immediate vicinity of the ions are involved in the formation of ion-pairs either by withdrawal from the solvation shell or by reorientation in a larger sense.

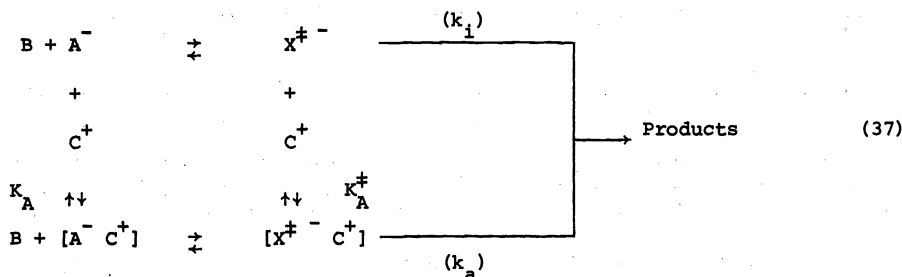
Data analysis of lithium and sodium salts in the alcoholic solutions when performed on the same base as used for potassium and cesium salts, i.e. by assuming the association limits to be a and $a+s$, yields unrealistic results like small ΔH_A^* -values and large negative entropy changes ΔS_A^* . Exclusion of the possibility of forming contact ion-pairs leads to more reliable results. For this purpose the lower association limit is fixed to a new value $a' = a+a_{OH}$ which exceeds the contact distance ' a ' by an increment $a_{OH} = 2.81 \text{ Å}$. The distance a_{OH} is calculated from the van der Waals volume of $-O-H$ [cf. (59)]. This procedure yielding the structure $C^+[O-H]A^-$ as the smallest possible ion-pair is indicated in Table 4b by the symbol ($a \rightarrow a'$). The resulting properties ΔH_A^* and ΔS_A^* fit better in the series of alkali salts. For comparison with an aprotic solvent, only the data of LiClO₄ in propylene carbonate are available up to now. Taking into account their uncertainty, $K_A^{*P} < 5 \text{ l}\cdot\text{mol}^{-1}$, they are consistent with those of KPF₆ in the same solvent without changing the lower association limit [$\Delta H_A^* = +650 \text{ J mol}^{-1}$, $\Delta S_A^* = -2 \text{ J mol}^{-1} \text{ K}^{-1}$] showing that contact ion-pairs should be allowed.

An inspection of alkali salt data and the underlying presuppositions of their data analysis

suggests the assumption of a local permittivity ϵ^* and hence the use of eq. (23) for interpreting K_A^{exp} . Up to now this procedure has not yielded convincing results for two reasons. On the one hand the integral in this equation varies sensitively with R^* and therefore requires an exact value R^* ; on the other hand, our knowledge of local permittivity is at present insufficient and ϵ^* -values are still a matter of debate. Tentative evaluations recommend the use of high permittivities as obtained by determination of the limiting value [Fig. 8] rather than the classical assumption $\epsilon^* = n_D^2$.

10. REACTIVITY OF IONS AND ION-PAIRS IN CHEMICAL REACTIONS

As an example of a more detailed charge distribution inside the ionic species of the model, Fig. 9, the formation of an activated complex X^\ddagger in chemical reactions is investigated when this species can be both an ion and an ion-pair. If a reaction takes place between a species B, ion or molecule, and an electrolyte compound $Y = C^+ A^-$ under conditions (solvent, temperature etc.) permitting the electrolyte compound to exist in both forms, free ions and ion-pair, generally one of the free ions, e.g. A^- , as well as the ion-pair A^-C^+ act as reactants. The reaction runs along different energetic paths with differing rate constants [e.g. eq. (41)], each of them involving the appropriate activated complex. The reaction scheme is as follows



The total velocity v of a reaction in which both reaction paths are assumed to be second order is

$$\begin{aligned}
 v &= k_i c_B(t) c_{A^-}(t) + k_a c_B(t) c_{[A^- C^+]}(t) \\
 &= [k_i \alpha + k_a (1-\alpha)] c_B(t) c_Y(t) = k_{\text{tot}} c_B(t) c_Y(t)
 \end{aligned} \quad (38)$$

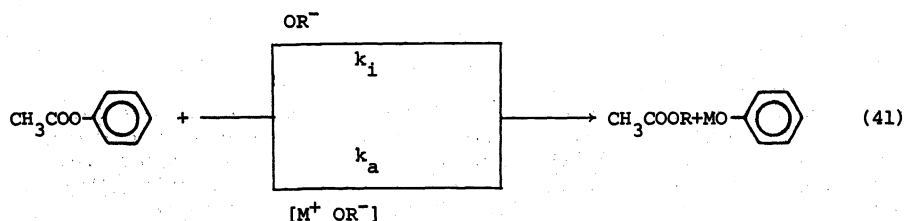
The degree of dissociation α is introduced with the help of eq. (28). The theory of absolute reaction rates permits expression of the specific reaction rates k_i and k_a via the Gibbs energies of activation ΔG_i^\ddagger and ΔG_a^\ddagger

$$k_i = \frac{kT}{h} \exp[-\Delta G_i^\ddagger/RT], \quad k_a = \frac{kT}{h} \exp[-\Delta G_a^\ddagger/RT] \quad (39a \text{ and } b)$$

and yields the relationship

$$\ln k_a - \ln k_i = \frac{1}{RT} [\Delta G_i^\ddagger - \Delta G_a^\ddagger] \quad (40)$$

The transesterification reaction of phenyl acetate by alkali metalalcoholates MOR in the corresponding alcohols as the solvents [Fig. 12] is a reaction of this type (74,75)



An analysis of the kinetic data with the inclusion of the appropriate association constants K_A of the alkali alcoholate ion-pair formation (76) yields the data of Table 5. Obviously in methanol and with alkali methylates as the reactants, no ion-pair reaction is observed, in contrast to the reactions in the solutions of higher alcohols. For all reactions in all the solvents, the rate constant k_i of the ion reaction is independent of the counterion, and

the variation of k_a reflects that of the association constant K_A of the base $[M^+ OR^-]$, here an increase from Li^+ to K^+ and a decrease from K^+ to Cs^+ .

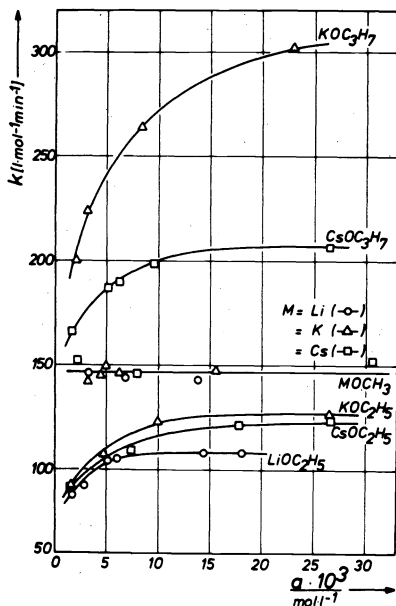


Fig. 12. Rate constants k_{tot} [eq. (38)] of the transesterification reaction [eq. (41)] in various alcohols ROH as a function of the initial concentration a of base MOR (74). M: Li, K, Cs; R = Me, Et, n-Pr.

TABLE 5. Rate constants k_i and k_a of the transesterification of phenyl acetate in methanol and ethanol as solvents (25°C).

Solvent (HOR)	Base (MOR)	$\frac{K_A}{1 \text{ mol}^{-1}}$	$\frac{k_i}{1 \text{ mol}^{-1} \text{ min}^{-1}}$	$\frac{k_a}{1 \text{ mol}^{-1} \text{ min}^{-1}}$
Methanol	LiOCH ₃	(12)	149±1	-
	KOCH ₃	(0)	146±3	-
	CsOCH ₃	(5)	150±3	-
Ethanol	LiOC ₂ H ₅	212	75±4	157±12
	KOC ₂ H ₅	90	80±4	234±25
	CsOC ₂ H ₅	121	82±1	188±3

A theoretical treatment of the reaction rates on the basis of a model as used to set up eqs. (11) and (12) requires starting with a more detailed internal charge distribution than Fig. 9 contains. Particles must come into contact before entering into the act of reaction and in this situation the exact local charge distribution near the reaction center must be known.

Fig. 13 shows the model postulated for the activated complex (76,77). The three bonds of carbon with the oxygen atoms are in a tetrahedral configuration, the negative charge being distributed equally on the three groups, O, OR, and C₆H₅O. The bond lengths, angles, and moments can be taken from standard reference tables. Thus the structural model contains no parameters which can be manipulated so as to fit kinetic measurements. From this model, the coefficients $b_j^{(m)}$ of the potential $\psi_i^{(T)}$ which has to replace eq. (12d) can be obtained as a series expansion with Legendre polynomials [cf. eq. (22f)]

$$\lim_{R \rightarrow \infty} \psi_i^{(T)}(r, \theta, \phi) = \sum_{j=0}^{\infty} \sum_{m=-j}^{+j} b_j^{(m)} \frac{1}{r^{j+1}} P_j^{(m)}(\cos \theta) e^{im\phi} \quad (42)$$

As a consequence of the symmetry of the new boundary condition (42) the potential ψ_i in eqs. (11) and (12) is no longer a function of distance 'r' alone, i.e. $\psi_i = \psi_i(r, \theta, \phi)$ (77).

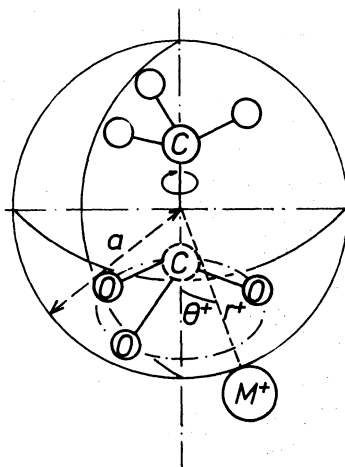


Fig. 13. Model of the activated complex of the transesterification reaction with an ion-pair $[M^+ OR^-]$ as a reactant [cf. eq. (41)].

In this paper the ion-pair formation



is of special interest. For the ion-pair $[x^{\ddagger-} c^+]$ as a kinetic species, a fixed position (r^+, θ^+, ϕ^+) of the counterion M^+ is required to form the activated complex in the ion-pair reaction. These coordinates are used for the calculus [eq. (11) and (12) with (42) instead of (12d)]. Results are summarised in Table 6.

TABLE 6. Activation energy, -enthalpy, and -entropy of the transesterification reaction of phenyl acetate with $CsOC_3H_7$ in n-propanol at various temperatures (75).

	$\frac{\Delta G_a^\ddagger - \Delta G_i^\ddagger}{J \text{ mol}^{-1}}$	$\frac{\Delta H_a^\ddagger - \Delta H_i^\ddagger}{J \text{ mol}^{-1}}$	$\frac{\Delta S_a^\ddagger - \Delta S_i^\ddagger}{J \text{ mol}^{-1} K^{-1}}$
Experimental value, eq. (43)	- 1800	+ 6700	+ 30
Electrostatic part calculated from distribution fig.5	- 1300	+ 1400	+ 9
Non electrostatic part, by difference	- 500	+ 5300	+ 21

The data of Table 6, when compared with the data of the ion-pair formation of alkali salts in propanol [cf. Table 4b] show comparable values for the non-electrostatic parts ΔH_A^* and ΔS_A^* of enthalpy and entropy.

11. ELECTROLYTE CONDUCTANCE

Conductance equations are obtained on the basis of Onsager's continuity equation (13) for the stationary case [cf. (7,14,15,51)]

$$\text{div}_1 [f_{ij} \vec{v}_{ij}] + \text{div}_2 [f_{ji} \vec{v}_{ji}] = 0$$

where the differential operators are applied with regard to the coordinates \vec{r}_1 and \vec{r}_2 . $\vec{v}_{ij}(\vec{r}_1, \vec{r}_2)$ and $\vec{v}_{ji}(\vec{r}_2, \vec{r}_1)$ are the velocities of the j ion in the vicinity of the i ion, and vice versa. A more general treatment starts from Liouville's theorem and uses the BBGKY hierarchy of equations (16,56). f_{ij} and f_{ji} are the two-particle distribution functions disturbed by the external field. A local hydrodynamic flow in the solvent as a consequence of the forces acting on the ions yields the electrophoretic velocity (16,51,78). The solvent is treated as a homogeneous medium of permittivity ϵ and viscosity η .

The information that can be provided by a conductance equation depends on the form of the mean potential $W_{ij}(r)$ on which its distribution function is based, on the form of the boundary conditions imposed on the problem, and on the nature of the factors affecting ion mobility that are taken also into account. For comparison of different equations see (7,16,20) and literature quoted there.

Conductance equations are obtained in the form

$$\Lambda = \Lambda^\infty - \Lambda^{\text{rel}}(\alpha c; \Lambda^\infty, R, \epsilon, T) - \Lambda^{\text{el}}(\alpha c; R, \epsilon, \eta, T) \quad (44)$$

with Λ^∞ as the equivalent conductance at infinite dilution, $\Lambda^\infty = \lim_{c \rightarrow 0} \Lambda$, and with a relaxation term, Λ^{rel} , and an electrophoretic term Λ^{el} , relative to the underlying conductance inhibiting effects.

At our present state of knowledge we prefer to use eq. (44) in the form of a truncated series which contains concentration terms up to $c^{3/2}$. The equivalent conductance of an incompletely dissociated or partially associated symmetrical electrolyte is then given by the expression

$$\Lambda = \alpha[\Lambda^\infty - S\sqrt{\alpha c} + E \alpha c \log \alpha c + J_1(R_1) \alpha c + J_2(R_2) (\alpha c)^{3/2}] \quad (45a)$$

$$\frac{1-\alpha}{\alpha^2 c} \frac{y_x}{y_\pm^2} = K_A^{\text{exp}} \quad (45b)$$

The coefficients S , E , J_1 and J_2 depend on the assumptions on which a theory is based. A tabular survey of these expressions appropriate to the different theories has been catalogued (7,30). K_A^{exp} is the overall association constant of the electrolyte compound as determined by an *ad hoc* classification into 'free' ions as the conducting species on the one hand and non-conducting species like non-dissociated molecules, complexes or any other type of non-conducting paired state of ions on the other hand. y_\pm as usual is the mean activity coefficient in the molar scale of the dissociated part of the electrolyte and y_x that of the associated part.

The measuring points were obtained by a method of stepwise concentration and isologous sections (53). The curves result from a least-square fit of these measuring data according to eq. (45). The tangent at $c=0$ represents the Debye-Hückel limiting law at 25°C.

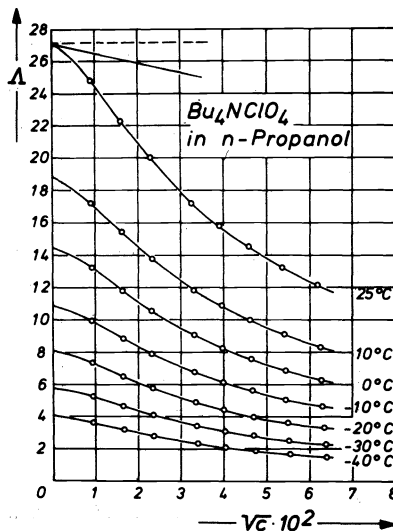


Fig. 14. Λ - c - T diagram of Bu_4NClO_4 in PrOH ($-40 \leq \theta/^\circ\text{C} \leq +25$).

Fig. 14 shows the equivalent conductance Λ as a function of concentration and temperature. The curves through the measuring points were plotted by the computer on the basis of a least squares fit according to eqs. (45). The initial slope represents the limiting law ($E=J_1=J_2=0$)

Using the model Fig. 9 and the resulting undisturbed electric potential $\psi_i(r)$ of the symmetrical ion distribution to engender the disturbed potential in the form

$$\psi_i(\vec{r}_1, \vec{r}_{21}) = \psi_i(r) + \psi'_i(\vec{r}_1, \vec{r}_{21})$$

and applying the boundary conditions

$$\left(\frac{\partial \psi'_i}{\partial r}\right)_{\infty} = 0; \quad \psi'_i(R-0) = \psi'_i(R+0); \quad \left(\frac{\partial \psi'_i}{\partial r}\right)_{R-0} = \left(\frac{\partial \psi'_i}{\partial r}\right)_{R+0}$$

$$([\vec{f}_{ij} \vec{v}_{ij} - \vec{f}_{ji} \vec{v}_{ji}])_{r=R} = 0 \quad (46a \text{ to } d)$$

to the conductance problem within the framework of the Fuoss-Onsager treatment, an equation of type eq. (45) is obtained in which

$$y_{\pm}' = \exp \left[-\frac{Kq}{1+KR_y} \right]; \quad y_x = 1 \quad (47)$$

Theory requires the compatibility condition

$$R_1 = R_2 = R_y = R \quad (48)$$

with R as the upper limit of associated paired states of ions. As a consequence of incompleteness of the linear and higher concentration terms in the truncated series expansion, eq. (45a), this compatibility condition is only approximately fulfilled. It can be handled to be of use in data analysis, however.

Table 7 summarises the results from a data analysis in which the coefficients S and E and the association limit $R_y = R$ are fixed at calculated values and Λ^{∞} , J_1 , J_2 and K_A are determined by a least squares method. This procedure is indicated in the following by a symbol 4 after the specification of the equation, e.g. FHFP 4 (= equation of Fuoss and Hsia (82)) which was brought to the form of eq. (45a) by Fernández-Prini (83) (evaluation of four parameters) or FJ4 (= form given by Justice (76)).

Any four-parametric evaluation yields the same set of Λ^{∞} , J_1 , J_2 , and K_A values when the same values for S and E are used. There is no question about the coefficient S . Slight variations can arise from the use of differing expressions for E (84) [cf. (7,20)]. In so far as the set of eqs. (45), (47) or (44), (47) is only used to determine Λ^{∞} and K_A without regard to the structure of the coefficients $J_1(R)$ and $J_2(R)$, these values are independent of the theoretical concept behind eq. (44) or (45a). Furthermore, the association limit $R = R_y$ can be varied within large limits around $R = q$ [Bjerrum's distance parameter, eq. (13b)] to yield coefficients of the same accuracy. Λ^{∞} is not affected by the choice of R_y and K_A^{tot} varies slightly in the expected manner [cf. Table 8].

DISTANCE PARAMETERS R_1 and R_2 , if evaluated within the framework of any conductance theory which is developed up to $c^{3/2}$, emerge compatible with the association limit and not as the radii of the collision cross-sections of the ions. For further four-parametric evaluations see (20,53,59,60,71). The four-parametric procedures require very high experimental accuracy which is often difficult to realize, especially when good-conducting solutions with low association constants are investigated. In these cases a three-parametric evaluation fixing S , E and $R_1 = R_y$ at calculated values and determining Λ^{∞} , J_2 and K_A by a least squares method, can be used. It has been shown repeatedly that four- and three-parametric methods yield comparable data where both procedures are performable (20,59). A three-parametric evaluation is indicated by a symbol 3 in connection with the used equation, e.g. FHFP 3 or FJ 3. Compatibility of data according to eq. (48) is checked by comparing the distance parameter R_2 as determined from J_2 to the fixed value $R_1 = R_y$. Table 7 shows various examples; for further applications see (7,20,71). Low solubility of the electrolyte in a given solvent may limit the concentration range to an extent that even three-parametric evaluations cannot be performed. This situation can also arise independently of solubility from a poorly asso-

ciating electrolyte. Two-parametric fits have been successfully achieved in these cases. Table 7 contains examples of FJ 2 evaluations in which R_2 is also fixed to the calculated value of R_y , $R_2 = R_1 = R_y$, and permits the comparison with the corresponding FJ 3 and FJ 4 data. An inspection of Tables 7 and 8 and the further quoted examples clears beyond doubt the role of the distance parameter $R_1 = R_2$ in the conductance equation as a measure of the association limit R .

TABLE 7. Comparison of four-, three-, and two-parametric evaluations for electrolytes in various solvents. Conductance equation eq. (45,47) with coefficients FJ (76); $R_y = a+s$.

Electrolyte	fixed values	$\frac{\Lambda^\infty}{\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$	$\frac{K_A}{\text{mol}^{-1} \text{ l}}$	$\frac{R_1}{\text{\AA}}$	$\frac{R_2'}{\text{\AA}}$
E T H A N O L (s = 5.30 \text{\AA})					
n-Bu(1-Am) ₃ NI a = 7.10 \text{\AA} 25°C; q=11.51 \text{\AA}	S, E, R _y	45.475±0.004	187 ± 2	11.2±0.3	10.7±0.3
	S, E, R ₁ =R _y	45.487±0.004	194 ± 1	(12.4)	11.8±0.1
	S, E, R ₁ =R ₂ =R _y	45.43 ±0.02	188 ± 1	(12.4)	(12.4)
-45°C; q=9.64 \text{\AA}	S, E, R _y	9.190±0.001	212 ± 3	12.2±0.8	12.5±0.7
	S, E, R ₁ =R _y	9.190±0.001	213 ± 1	(12.4)	12.7±0.1
	S, E, R ₁ =R ₂ =R _y	9.195±0.002	215 ± 1	(12.4)	(12.4)
P R O P A N O L (s = 6.90 \text{\AA})					
(n-Am) ₄ NI a = 7.60 \text{\AA} 25°C; q=13.71 \text{\AA}	S, E, R _y	23.510±0.004	511 ± 4	11.6±0.5	10.8±0.6
	S, E, R ₁ =R _y	23.530±0.006	538 ± 2	(14.5)	14.1±0.1
	S, E, R ₁ =R ₂ =R _y	23.509±0.009	531 ± 2	(14.5)	(14.5)
KSCN a = 4.70 \text{\AA} 25°C; q=13.71 \text{\AA}	S, E, R _y	26.591±0.005	329 ± 2	11.5±0.2	10.8±0.3
	S, E, R ₁ =R _y	26.593±0.002	329 ± 1	(11.6)	10.8±0.1
	S, E, R ₁ =R ₂ =R _y	26.51 ±0.03	317 ± 2	(11.6)	(11.6)
-40°C; q=11.48 \text{\AA}	S, E, R _y	3.817±0.001	105 ± 6	12.6±1.0	11.5±0.8
	S, E, R ₁ =R _y	3.815±0.001	99 ± 2	(11.6)	10.7±0.1
	S, E, R ₁ =R ₂ =R _y	3.806±0.003	92 ± 2	(11.6)	(11.6)
A C E T O N I T R I L E (s = 5.12 \text{\AA})					
KClO ₄ a = 3.70 \text{\AA} 25°C; q=7.77 \text{\AA}	S, E, R ₁ =R _y	187.48 ±0.01	31.3±0.2	(8.8)	8.5±0.2
	S, E, R ₁ =R ₂ =R _y	187.46 ±0.01	30.9±0.2	(8.8)	(8.8)
P R O P Y L E N E C A R B O N A T E (s = 5.40 \text{\AA})					
KPF ₆ a = 3.00 \text{\AA} 25°C; q=4.28 \text{\AA}	S, E, R ₁ =R _y	28.976±0.002	3.9±0.1	(8.4)	8.3±0.1
	S, E, R ₁ =R ₂ =R _y	28.973±0.002	3.8±0.1	(8.4)	(8.4)
-45°C; q=4.30 \text{\AA}	S, E, R ₁ =R _y	2.214±0.003	2.0±1.0	(8.4)	10.5±1.2
	S, E, R ₁ =R ₂ =R _y	2.218±0.002	3.5±0.2	(8.4)	(8.4)

ASSOCIATION CONSTANTS obtained from conductance measurements can be subjected to treatment as K_A^{loc} -values by eqs. (18), (21b) or (23) [cf. Section 10].

TABLE 8. Effect of R_y on conductance data of KSCN and $(n\text{-Pr})_4\text{NI}$ in n-propanol at $+10^\circ\text{C}$ [$q = 13.0 \text{ \AA}$] and -20°C [$q = 12.0 \text{ \AA}$]; R_1 and R_2 obtained by FHFP 4 evaluations.

$\frac{R_y}{\text{\AA}}$	$\frac{\Lambda^\infty}{\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}$	J_1	J_2	$\frac{K_A^{\text{tot}}}{1 \text{ mol}^{-1}}$	$\frac{R_1}{\text{\AA}}$	$\frac{R_2}{\text{\AA}}$
KSCN; $+10^\circ\text{C}$						
	± 0.006	± 50	± 500	± 5	± 0.5	± 0.5
17.78	18.262	1780	-6370	257	14.8	12.1
15.05	.261	1680	-5950	251	13.6	11.7
13.68	.260	1630	-5750	247	13.0	11.5
12.31	.259	1570	-5560	243	12.4	11.3
10.94	.258	1520	-5380	240	11.8	11.1
$(n\text{-Pr})_4\text{NI}; +10^\circ\text{C}$						
	± 0.002	± 40	± 500	± 4	± 0.5	± 0.5
17.78	18.060	1840	-7990	483	15.6	13.5
15.05	.059	1700	-7100	474	14.1	12.8
13.68	.059	1640	-6810	470	13.3	12.5
12.31	.059	1570	-6440	466	12.5	12.2
10.94	.059	1500	-6090	461	11.8	11.9
KSCN; -20°C						
	± 0.002	± 20	± 200	± 5	± 0.8	± 0.6
17.78	7.657	580	-1910	148	13.8	11.2
15.05	7.657	540	-1810	143	12.8	11.0
13.68	7.657	530	-1770	140	12.3	10.9
12.31	7.657	510	-1720	137	11.8	10.7
10.94	7.656	500	-1690	135	11.3	10.6
$(n\text{-Pr})_4\text{NI}; -20^\circ\text{C}$						
	± 0.002	± 30	± 400	± 5	± 0.9	± 1.0
17.78	7.585	570	-2100	452	13.7	11.8
15.05	7.585	520	-1800	445	12.2	11.0
13.68	7.585	490	-1670	442	11.4	10.6
12.31	7.585	470	-1540	438	10.6	10.2
10.94	7.585	440	-1410	434	9.8	9.7

LIMITING CONDUCTANCE Λ^∞ is related to limiting ionic conductances λ_+^∞ and λ_-^∞ by an additive rule

$$\lambda_+^\infty + \lambda_-^\infty = \Lambda^\infty \quad (49)$$

Eq. (49) can provide approximate values of $\lambda_+^\infty = \lambda_-^\infty$ from Λ^∞ if electrolytes of equally shaped ions and equal ion-solvent interactions of cation and anion are investigated. Further methods of approximate character are based on the constancy of the Walden product $\eta\lambda_+^\infty$ or $\eta\Lambda^\infty$ (85). Precise ionic conductances are available only from direct measurements, e.g. by a moving boundary method for determining transference numbers t_+^∞ and t_-^∞

$$t_+^\infty = \lambda_+^\infty / \Lambda^\infty, \quad t_-^\infty = \lambda_-^\infty / \Lambda^\infty \quad (50)$$

Table 9 gives an example of results obtained for Et_4NClO_4 in acetonitrile ($-40 \leq \theta/^\circ\text{C} \leq +25$).

TABLE 9. Transference numbers t_+^∞ of Et_4N^+ determined by a moving boundary method in the temperature range $-40 \leq \theta/^\circ\text{C} \leq +25$ (87).

$\theta/^\circ\text{C}$	-40	-30	-20	-10	0	+10	+25
t_+^∞	0.44759	0.44819	0.44880	0.44941	0.45002	0.45064	0.45158
$\sigma(t_+^\infty) \cdot 10^5$	9	8	8	7	7	6	7

Interpretation of ionic conductance is based on a hydrodynamic model [cf. (88)], a kinetic model (89) or on proton-jump or electron-jump mechanisms (90) [cf. (7,20,88)].

The most elaborate hydrodynamic model at present was achieved by Boyd and Zwanzig (91,92). It assumes the ion to be a sphere of radius r_i moving through a continuous incompressible fluid of viscosity η . Solvent molecules immediately adjacent to the moving ions are partially subject to a relaxation process, the relaxation time τ being that of the pure solvent [cf. Section 3, also for ϵ_s and ϵ_∞]

$$\lambda_i^\infty = \frac{1}{\Xi} \frac{N_A e^2 |z_i|}{k_i^\infty + \frac{3}{4s} \frac{1}{4\pi\epsilon_0} \frac{(e_0 z_i)^2}{r_i^3} \frac{(\epsilon_s - \epsilon_\infty)\tau}{\epsilon_s (2\epsilon_s + 1)}} \quad (51)$$

k_i^∞ is the friction coefficient which varies from $6\pi\eta r_i$ for a sphere dragging the adjacent solvent along with it (sticking movement) to $4\pi\eta r_i$ for a sphere moving through the solvent without drag (slipping movement). $s = 2$ for a sticking and $s = 1$ for a slipping movement. Neglecting of the contribution of solvent relaxation in eq. (51) yields Stokes' law.

The kinetic model is based on transition state theory and explains λ_i as a process of interchange of sites separated by a mean distance L . The ionic migration is related to an activation energy ΔG^\ddagger .

$$\lambda_i^\infty = \frac{1}{\Xi} \frac{N_A e^2 |z_i| L^2}{6h} \exp\left[-\frac{\Delta G^\ddagger}{RT}\right]; \quad \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (52)$$

If transference numbers t_i can be assumed to be temperature-independent, the combination of eqs. (50) and (52) yields (20).

$$\ln \Lambda^\infty + \frac{2}{3} \ln \rho = -\frac{\Delta H^\ddagger}{RT} + B \quad (53)$$

Figs. 15 and 16 give examples for both theories. Fig. 15 shows that tetraalkylammonium ions and big anions, between 25°C and -40°C in acetonitrile as the solvent move essentially without dragging solvent molecules. Fig. 16 shows that ΔH^\ddagger , eq. (53) is mainly a function of solvent properties: $\Delta H^\ddagger \approx 13 \text{ kJ mol}^{-1}$ for solutions of 1,1-electrolytes in ethanol, $\Delta H^\ddagger \approx 18 \text{ kJ mol}^{-1}$ for these in propanol and $\Delta H^\ddagger \approx 8.5 \text{ kJ mol}^{-1}$ in acetonitrile.

Temperature-dependence of the limiting conductance provides information about structural effects arising from the solvent. The conductivity viscosity product $\lambda^\infty \eta$ shows a positive or negative temperature gradient in accordance with structure-promoting or -breaking properties of an ion. Water is considered to build a three-dimensional hydrogen-bonded network of water molecules, amides a two-dimensional network. The molecules of N-methylamides and alcohols form linear associates. Inert solvents interact with ions by means of their dipole moments.

The Me_4N^+ ion as well as the larger alkali metal ions disorganize water structure in their immediate vicinity and yield a negative temperature coefficient of $\lambda^\infty \eta$ whereas Pr_4N^+ and higher homologues behave in just the opposite manner (93). A temperature gradient of $\lambda^\infty \eta$ or $\Lambda^\infty \eta$ can be detected in dipolar aprotic solvents and in inert solvents for neither tetraalkylammonium salts nor alkali salts (20). Solutions in methanol are comparable to aqueous solutions. Tetrapropylammonium salts in ethanol and propanol, higher tetraalkylammonium and

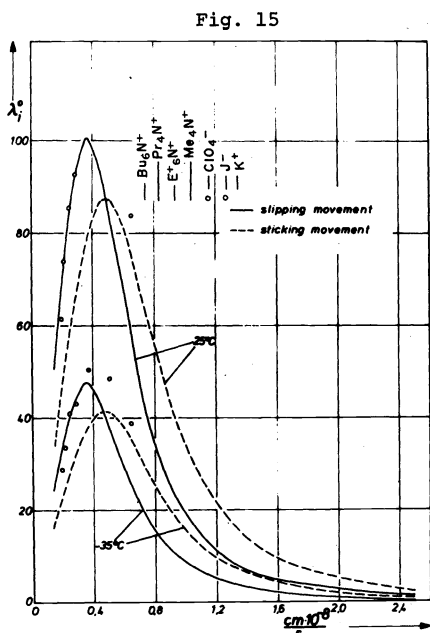


Fig. 15. Representation of ionic limiting conductance λ_i^∞ according to eq. (52) in acetonitrile at 25°C and -40°C (26); slipping movement [$s = 1$, $k_i^\infty = 4\pi\eta r_i$], sticking movement [$s = 2$, $k_i^\infty = 6\pi\eta r_i$].

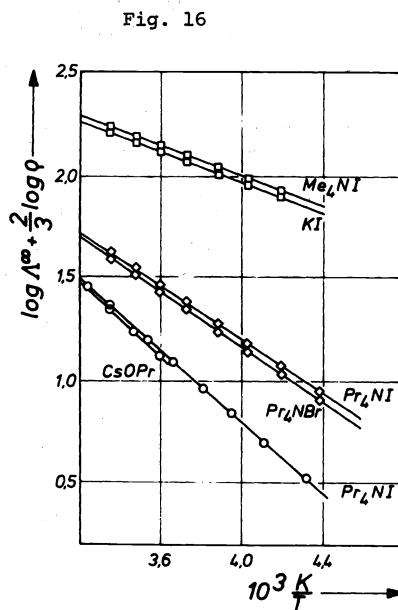


Fig. 16. Plot of $\log \Lambda^\infty + \frac{2}{3} \log \rho$ vs. T^{-1} according to eq. (54) ($-45 \leq \theta/^\circ\text{C} \leq +25$) for various salts in ethanol (\diamond), propanol (\circ) and acetonitrile (\square) (20).

potassium and sodium salts in propanol show no significant variations of the Walden product whereas LiCl yields a decrease. For solutions in formamide, reliable values are not available. In N-methylamides, all tetraalkylammonium salts yield negative temperature coefficients of λ_{\pm}^∞ or Λ^∞ and so do alkali salts [cf. (20) and quoted literature].

12. CONDUCTANCE OF CONCENTRATED ELECTROLYTE SOLUTIONS

In spite of the technological interest of concentrated non-aqueous solutions, e.g. for high energy batteries, only few items of information are available for discussions the conductance-determining factors as a function of electrolyte concentration m [mol kg^{-1}], temperature T (or θ), and solvent composition ξ [weight %] if binary solvent mixtures are considered. Review articles contain only few dependences of specific conductance κ of the type $\kappa = \kappa(m, T)$ or $\kappa = \kappa(\xi)$ together with data for single concentrations at 25°C (10,94,95). The most comprehensive data are available for the systems $\text{LiClO}_4/\text{PC}/\text{THF}$ ($-20 \leq \theta/^\circ\text{C} \leq +50$) (96) and $\text{X}/\text{PC}/\text{DME}$ ($-45 \leq \theta/^\circ\text{C} \leq 25$; $\text{X} = \text{LiClO}_4, \text{LiPF}_6, \text{KPF}_6, \text{KSCN}, \text{EtNPF}_6, \text{PrNPF}_6$ and BuNPF_6) (97) over the whole concentration range and for several salts in *N,N*-dimethylformamide (100) and in propylene carbonate (99) at moderate concentrations over a large temperature range. The following discussion is based on the results from ref. (97) and limited to the investigation of maximum conductance of electrolytes in a pure solvent, propylene carbonate, as a point of crucial interest.

Specific conductance κ is related to equivalent conductance Λ as

$$\kappa = k \cdot \Lambda c \quad (54)$$

with k as the conversion factor appropriate for the chosen system of units. Experimental evidence allows the assumption that $d\Lambda < c$ if $dc > 0$ and hence a maximum of specific conductance appears if (101)

$$d\kappa = k[\Lambda dc + cd\Lambda] = 0 \quad (55)$$

The existence of κ_{max} follows from the competition of two effects, a conductance-increasing term caused by an increase of the density of free ions and an inhibiting term resulting from a lowering of ionic mobilities when electrolyte concentration increases.

Fig. 17 shows the plots of the specific conductance $\kappa = \kappa(m, \theta)$ for LiClO_4 in propylene carbonate. Maximum specific conductance κ_{max} is attained at concentration μ of the solute. An empirical equation (98)

$$\frac{\kappa}{\kappa_{\max}} = \left(\frac{m}{\mu}\right)^a \exp [b(m-\mu)^2 - \frac{a}{\mu}(m-\mu)] \quad (56)$$

has proved to fit well data of all investigated solutions in a wide concentration range around μ and at all temperatures. The quantities κ_{\max} , μ and the constants a and b of eq. (56) are adjusted by a least-squares method. The curves through the measuring points in Fig. 17 are plotted by the computer according to this programme. Eq. (56) fulfils the conditions $\kappa(\mu) = \kappa_{\max}$ and $\kappa(0) = 0$. The displacement of μ to higher values with increasing temperature $(\partial\mu/\partial\theta) > 0$, is generally observed in organic solvents (96,97,99).

Fig. 17

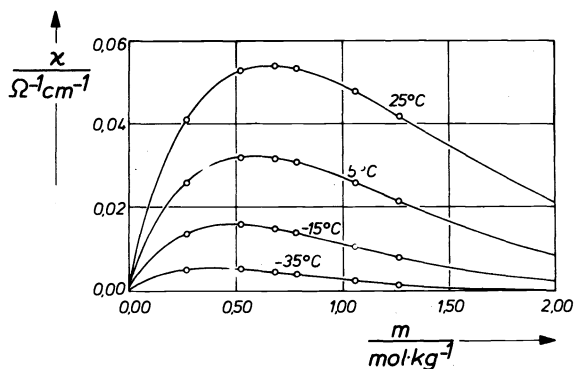
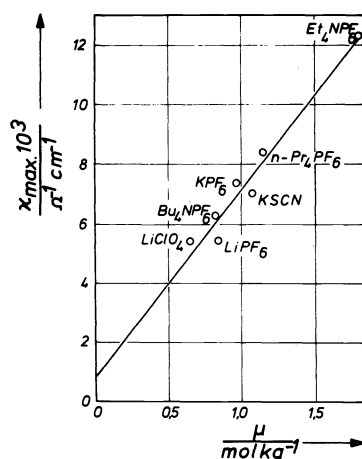


Fig. 17. Specific conductance $\kappa = \kappa(m, \theta)$ of LiClO_4 in propylene carbonate ($-45 \leq \theta/^\circ\text{C} \leq +25$).

The curves through the measuring points were obtained by a least-square fit according to eq. (56) (97).

Fig. 18. Linear dependence κ_{\max} vs. μ for various salts in propylene carbonate at 25°C (20).



A representation of κ_{\max} vs. μ for all investigated salts yields a linear function [Fig. 18]. If μ is attained only at high values, the decrease of ionic mobility caused by ion-solvent and ion-ion interaction submerges the increase of charge density only at this high concentration. The appropriate high charge density yields high conductance. The reasons for high μ -values can be quite varied: weak ion-solvent interactions, small ionic radii or low solvent viscosity. Thus lithium salts as well as tetrabutylammonium salts allow the expectation of small μ -values in contrast to tetraethylammonium salts.

The kinetic model of conductance [cf. eq. (52)] provides the same information as the hydrodynamic model. Activation energies for all electrolytes become equal at low concentrations indicating that these values are controlled mainly by the properties of the solvent. This result agrees well with the statement of Sears et al. that the ratio of activation energies of conductance and viscosity is independent of concentration, temperature, and electrolyte (99,100). At high concentrations, e.g. $m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$ at 0°C, the sequence of activation energies of the electrolytes $\text{LiClO}_4 > \text{Bu}_4\text{NPF}_6 > \text{KPF}_6 \approx \text{KSCN} > \text{Et}_4\text{NPF}_6$ is in accordance with the sequence of these electrolytes in Fig. 18 (20). The electrolyte submitted to the strongest interactions, LiClO_4 , has to cross the highest activation barrier. However, at concentration $m = 1.0 \text{ mol}\cdot\text{kg}^{-1}$ the maximum specific conductance of Et_4NPF_6 has not yet been attained whereas it has been largely surpassed for LiClO_4 . If activation energies are compared at concentration μ , they become equal for all electrolytes at any temperature (cf. Table 10).

Constancy of activation energy can be chosen to be an alternative criterion of the position μ of maximum specific conductance.

Maximum specific conductance for an electrolyte is obtained when the conductance-determining effects have established a critical energy barrier which depends only on solvent and temperature.

Investigations in concentrated non-aqueous solutions open new aspects and stimulate thought about the concept of electrolyte solutions. After the progress of the last years in understanding non-aqueous dilute solutions the technically important field of higher electrolyte concentrations should gain increasing weight in time to come.

TABLE 10. Activation energies of maximum specific conductance at various temperatures. Electrolyte solutions in propylene carbonate as solvent (20).

Electrolyte	$\theta = -35^{\circ}\text{C}$		$\theta = -15^{\circ}\text{C}$		$\theta = +15^{\circ}\text{C}$	
	μ	E_a^{\ddagger}	μ	E_a^{\ddagger}	μ	E_a^{\ddagger}
	mol kg^{-1}	kJ mol^{-1}	mol kg^{-1}	kJ mol^{-1}	mol kg^{-1}	kJ mol^{-1}
LiClO_4	0.394	30.4	0.495	24.5	0.624	16.2
KPF_6	0.509	30.3	0.655	24.8	0.881	16.7
KSCN	0.505	29.6	0.674	24.7	0.977	17.5
Et_4NPF_6	0.885	29.9	1.131	24.7	1.590	16.1
Bu_4NPF_6	0.475	29.7	0.601	25.0	0.778	16.9

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