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Methods for the Theoretical Description of the Energy of Resolvation of Ions

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Present-day theories of ion solvation have been examined. The experimental values of the standard free energies of resolvation and the standard redistribution potentials of ions between water and organic solvents have been given. The contribution of dielectric saturation to the electrostatic component of the free energy of resolvation has been analysed. The results of theoretical calculations have been compared with the experimental dependence of the standard free energy of solvation on the static and optical dielectric constants of the solvents, and also on the size of the ions. The solvophobic contribution to the energy of resolvation has been estimated.
The bibliography contains 100 references.

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I. INTRODUCTION

In recent years there has been a sharp increase in interest in the experimental and theoretical determination of the values of the standard free energy of resolvation of ions. A knowledge of these quantities is required in the study of the electrochemistry of the interface between two immiscible electrolyte solutions,[1-5] the transport of ions through biological and synthetic membranes,[6] the mechanisms of interphase and surface catalysis,[7-10] the kinetics of charge transfer through an oil–water interface,[11-13] the coupling of heterogeneous reactions in bioenergetics,[5] extraction,[14] and the production of ion-selective electrodes.[15]

The term solvation refers to all the energetic and structural changes taking place in a system in the transfer of ions from the gas phase to the liquid phase of a solvent. The interaction of an ion with a solvent includes several effects: 1) electric polarisation of the medium; 2) the production in the medium of a cavity to accommodate the ion; 3) a change in the structure of the solvent, involving the breakdown of the old structure and the production of a new structure close to the ion (the formation of cavities and the change in the structure of the solvent close to the ion are sometimes combined in a single effect, called the solvophobic or hydrophobic effect); and 4) specific interaction of the ions with the solvent molecules (the formation of hydrogen bonds,

donor–acceptor interaction), etc. This division is to some extent arbitrary, since different effects may overlap; for example, the electric polarisation of a solution may have a significant influence on its structure. It is possible, however, to carry out the theoretical calculation of individual effects.[16]

In the present review, present-day theories of ion solvation will be characterised briefly. To find the standard free energy of resolvation $\Delta^{\alpha}_{\beta}G^0_i$ of an ion i, the Gibbs free energies of the ion in two media, α and β, are compared. If the phase β is a vacuum, the quantity

$$\Delta^{\alpha}_{vac}G^0_i = G^{0,\alpha}_i - G^{0,vac}_i$$

is called the energy of solvation of the ion i in the phase α. The energy of resolvation can obviously be represented as the difference between two solvation energies:

$$\Delta^{\alpha}_{\beta}G^0_i = \Delta^{\alpha}_{vac}G^0_i - \Delta^{\beta}_{vac}G^0_i. \qquad (1)$$

The standard free energies of resolvation of ions from water into different organic solvents are found by cyclic voltammetry, chronopotentiometry, polarography, data on the spin–lattice relaxation of the quadrupole moments of the nuclei of the ions, and also from solubility and extraction data.[1,12,14,17–30] These quantities are given in Table 1, which shows that the standard free energy of resolvation of ions depends markedly on the nature of the ion and the solvent.

Figs. 1 and 2 give the dependence of the energy of resolvation on the static and optical dielectric constants of non-aqueous solvents. Fig. 3 gives the dependence of the standard free energy of hydration on the radius of the ion. Figs. 1–3 and Table 1 show that the energy of resolvation (and hydration) decreases sharply with increase in the size of the ion and the static and optical dielectric constants of the medium.

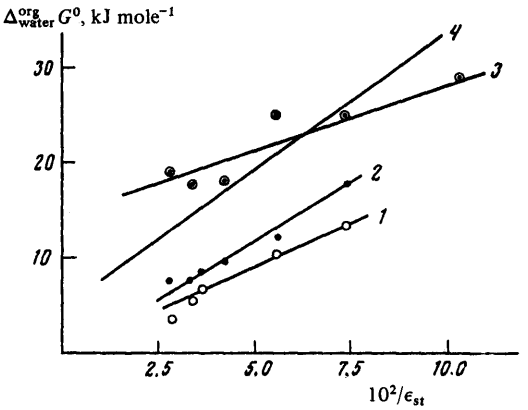


Figure 1. Dependence of the standard free energy of resolvation on the static dielectric constant of the non-aqueous phase; curves *1* (Me_4N^+), *2* (ClO_4^-), and *3* (I^-) give the experimental data from Table 1, and curve *4* gives the results of the calculation using the Born equation for Me_4N^+.

Table 1. Standard free energies of resolvation of the ions $\Delta^{org}_{water}G^0_i$ (kJ mole^{-1}) and distribution potentials $\Delta^{org}_{water}\phi^0$ (mV) of the ions between water and organic solvents at 298 K.[12,14,17–30]

Ion	Nitrobenzene		Acetophenone		Isobutyl methyl ketone		1,2-Dichloroethane		1,1-Dichloroethane		Dichloromethane	
	$\Delta^{org}_{water}G^0_i$	$\Delta^{org}_{water}\varphi^0_i$	$\Delta^{org}_{water}G^0_i$	$\Delta^{org}_{water}\varphi^0_i$	$\Delta^{org}_{water}G^0_i$	$\Delta^{org}_{water}\varphi^0_i$	$\Delta^{org}_{water}G^0_i$	$\Delta^{org}_{water}\varphi^0_i$	$\Delta^{org}_{water}G^0_i$	$\Delta^{org}_{water}\varphi^0_i$	$\Delta^{org}_{water}G^0_i$	$\Delta^{org}_{water}\varphi^0_i$
Li^+	38.4	−398	—	—	20.3	210	—	—	—	—	—	—
Mg^{2+}	71.4	−370	—	—	—	—	—	—	—	—	—	—
Na^+	34.5	−358	—	—	—	—	—	—	28.9	−299	—	—
Ca^{2+}	68.3	−354	—	—	—	—	—	—	—	—	—	—
Sr^{2+}	67.2	−348	—	—	—	—	—	—	—	—	—	—
H^+	32.5	−337	—	—	—	—	—	—	—	—	—	—
Ba^{2+}	63.3	−328	—	—	—	—	—	—	—	—	—	—
NH^+	27.4	−284	—	—	—	—	—	—	—	—	—	—
K^+	24.3	−252	—	—	—	—	—	—	29.7	−307	—	—
Rb^+	19.9	−206	—	—	—	—	—	—	28.9	−299	—	—
Cs^+	15.5	−161	—	—	—	—	17.9	−185	—	—	—	—
$(Me)_4N^+$	3.4	−35	—	—	—	—	17.6	−182	17.5	−181	18.8	−195
$(Et)_4N^+$	−5.8	60	—	—	8.7	−90	4.2	−44	10.8	−112	4.2	−44
$(Pr)_4N^+$	−15.5	161	—	—	—	—	−8.8	91	−2.2	23	−8.8	91
$(But)_4N^+$	−24.2	248 * [27]	−15.6	162	−19.3	200	−21.8	226	−11.7	121	−22.2	230
$(Ph)_4As^+$	−35.9	372	−16.2	168	—	—	−35.2	365	−27.3	283	—	—
Cl^-	30.5	316	—	—	50.2	520	46.5	481	57.8	600	46.4	481
Br^-	28.5	295	—	—	—	—	38.5	399	42.5	440	39.3	408
I^-	18.8	195	12.4	128	—	—	26.4	274	30.6	317	26.4	273
ClO_4^-	8.0	83	1.8	19	—	—	17.2	178	22.4	232	21.3	221
2,4-DNP$^-$	7.3	76	—	—	—	—	—	—	—	—	—	—
Pi^-	−4.5	−48	—	—	11.6	120	—	—	—	—	−6.7	−69
$(Ph)_4B^-$	−35.9	−372	−16.2	−168	—	—	−35.2	−365	−27.3	−283	—	—
DCC^-	−50.2	−520	—	—	—	—	—	—	—	—	—	—
SCN^-	16.0	176	11.0	144	—	—	25.5	264	—	—	—	—
IO_4^-	6.9	75	1.5	15	—	—	14.5	159	—	—	—	—
ClO_3^-	—	—	19.3	200	—	—	33.1	343	—	—	—	—
NO_3^-	24.4	253	20.4	211	—	—	33.9	351	—	—	—	—
BF_4^-	11.0	121	—	—	—	—	17.9	197	—	—	—	—

Note: $(Alk)_4N^+$ = tetra-alkylammonium, DCC^- = dicarbollylcobaltate, DNP^- = dinitrophenolate, Pi^- = picrate.
* 255 mV,[20] 275 mV.[26]

The standard free energies of resolvation of ions, obtained by different methods, do not always coincide exactly with one another. These quantities can be calculated or measured by two methods. It is possible to determine the energy of solvation of the ion in the two pure solvents α and β, and then to use Eqn.(1) to find the standard free energy of the transfer of the ion *i* from the solvent β to the solvent α. If two immiscible liquids α and β are in contact and in equilibrium, some solvent from each of these phases dissolves in the other phase. In this case the phases α and β will be mutually saturated. The corresponding energy of resolvation of the ion on its transfer between the two equilibrated solvents is called the standard free energy of distribution.[22] For most known ions and solvents, the standard free energies of transfer and distribution coincide with one another within the limits of accuracy of the measurements. It is not excluded, however, that for some solvents and ions these quantities differ.

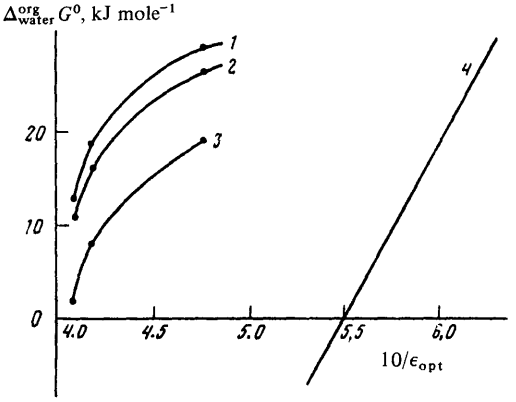


Figure 2. Dependence of the standard free energy of resolvation of the ions on the optical dielectric constant of the non-aqueous phase: curves *1* (I^-), *2* (SCN^-), and *3* (ClO_4^-) give the experimental data from Table 1, and curve *4* gives the results of the calculation using the Born equation for I^-, assuming that $\epsilon = \epsilon_{opt}$; the values of the optical dielectric constant were taken from Table 2.

Thus in the analysis and application of the values of the standard free energy of resolvation it is necessary to consider whether ion transfer takes place between the pure solvents or between the mutually saturated solvents.

II. ELECTRIC CONTRIBUTION TO THE SOLVATION ENERGY

There are two groups of models for calculating the electric component of the solvation energy. In the first group the medium is regarded as a structureless continuum, and in the second as a set of individual particles with real or simplified properties. In early work, the structure of the solvent was taken into account by calculating directly the energies of specific configurations of the solvent molecules close to the ion; the actual configuration and the number of molecules included in it were selected somewhat arbitrarily from various physical considerations, to give agreement between the calculated and experimental data. In these models, the statistical properties of the solution, which are undoubtedly important for a correct description of the phenomenon of solvation, were ignored completely. The modern approach involves the development of a statistical theory of the ion–dipole plasma, reflecting both the energetic and statistical aspects of the phenomenon.

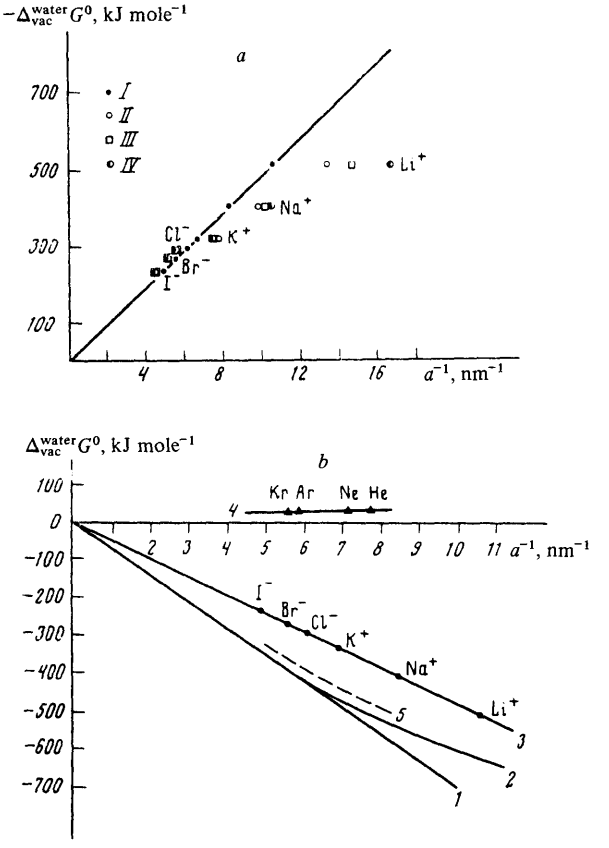


Figure 3. Dependence of the standard free energy of hydration of inorganic ions on their radius; the ionic radii were those of Gourary and Adrian (I),[31] Waddington (II),[37] Goldschmidt (III),[36] and Pauling (IV);[35] *a*: experimental data from Refs.29 and 30; *b*: *1*) calculated using the Born equation, *2*) calculated with allowance for dielectric saturation,[2] *3*) experimental data from Refs.29 and 30, *4*) standard free energies of solution of the inert gases (1 atm in the gas phase and a mole fraction of 1 in the aqueous solution at 298 K), *5*) sum of curves *2* and *4*.[2]

There is also an intermediate approach, in which, while remaining within the framework of continuum theories, attempts are made to take account of the influence of the discrete nature of the solvent on the effective parameters of the model. For this purpose, account is taken of non-linear dielectric effects, and the mutual correlation of the polarisation vectors of the solvent molecules, situated at short distances from one another, is analysed using the theory of non-local electrostatics. Each of these approaches, reflecting the role of different effects, has its own advantages.

1. The Born Model

In the first continuum model, developed by Born,[32] the ion was regarded as a solid sphere with a given radius a, immersed in a continuous medium with a constant dielectric constant ε (Fig. 4*a*). This was a macroscopic theory, which described the properties of the solvent at short distances from the ion by macroscopic laws. The energy of solvation (more accurately, its electric part), calculated for one particle, is given according to the Born theory by the familiar equation

$$\Delta^{\alpha}_{vac}G^{0}(el) = -\frac{z^2e_0^2}{8\pi\varepsilon_0 a}\left(1-\frac{1}{\varepsilon^{\alpha}}\right) \qquad (2)$$

where ε_0 is the electric constant, ε^{α} the dielectric constant of the medium, z the charge number of the ion, and e_0 the charge of the electron. From this equation, the energy of resolvation when an ion is transferred from the medium α to the medium β (that is the difference between the energies in the media β and α) is given by:

$$\Delta^{\beta}_{\alpha}G^{0}(el) = -\frac{z^2e_0^2}{8\pi\varepsilon_0 a}\left(\frac{1}{\varepsilon^{\alpha}}-\frac{1}{\varepsilon^{\beta}}\right) \qquad (3)$$

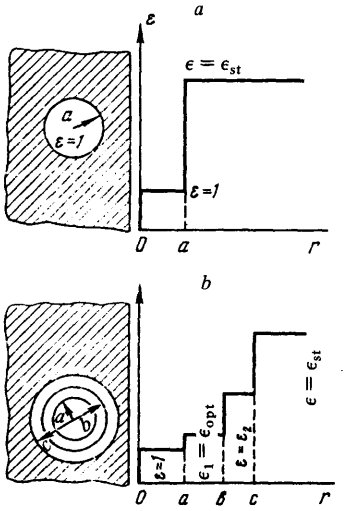


Figure 4. Models of Born (*a*) and Abraham and Liszi (*b*).[49,50]

Calculations using the Born equation give values of the solvation energy differing considerably from the experimental values.[2,33,34] Since the energy of resolvation is often the small difference between two comparatively large solvation energies, a relatively small uncertainty in the determination of each of these quantities may lead to a considerable overall uncertainty, even an incorrect sign. For example, it follows from Eqn. (3) that for $\varepsilon^{\alpha} > \varepsilon^{\beta}$, it is more favourable for the ion to be in the solvent α, irrespective of its actual size. This is not always observed experimentally, however. Small ions with a radius $a < 0.2$ nm are in fact found chiefly in a polar solvent with a high dielectric constant, but at the same time, large organic ions often enter the hydrophobic phase preferentially.

Distribution coefficients[1,14,17] and extraction, solubility[14,17] and voltammetric data[12,22,26] indicate that the standard free energy of the transfer of an ion from water to a less polar solvent is positive for ions with a small radius, and negative for ions with a large radius, whereas according to Eqn. (3) it is a constant-sign function of the radius.

Born's equation gives values of the solvation energy which are too high (too negative) (Figs. 1 and 3). When comparing specific values with experimental data, it is necessary to assign a radius to each ion. This procedure is to some extent arbitrary, since the ionic radius is only an effective parameter, the use of which makes possible the most successful description of various properties of ionic systems. It is often found that different properties of a system require the choice of different ionic radii for their description. It is pointless to raise the question of which value of the ionic radius is correct, and which is not, although naturally there are reasonable physical restrictions on the range within which the value of the effective radius of an ion may lie.

This is reflected in the fact that there are at least four scales of ionic radii, namely those of Pauling,[35] Goldschmidt,[36] Waddington,[37] and Gourary and Adrian,[31] calculated on the basis of different assumptions. The first three scales differ little from one another, but the fourth differs from the others. Blandamer and Symons[38] tried to select the most successful scale of ionic radii by comparing thermodynamic data on the Gibbs free energy and entropy of hydration of the ions. They showed that if any of these quantities is plotted as a function of $1/a^2$, all the points corresponding to the alkali metal cations and the halide anions lie on the same smooth curve if the Gourary–Adrian radii are used. The other sets of radii give two different curves, one for the cations and another for the anions. It is difficult to say what importance should be given to the observed regularity, since as yet it has no theoretical foundation.

Since Born's equation (2) gives the dependence of the solvation energy on $1/a$, the same coordinates are used in Fig. 3. Fig. 3*a* gives the experimental data for six cations and anions on all four ionic radius scales. The data on the Gourary–Adrian scale lie ideally on one straight line, confirming the observation made in Ref. 38. This fact undoubtedly deserves attention. The data using the other scales deviate from this straight line, although a significant deviation is observed only for the small ions Li^+, Na^+, and K^+, and the points for Cl^-, Br^-, and I^- deviate little. The experimental points are compared with the theoretical predictions in Fig. 3*b*. To avoid overloading the Figure, the experimental points are given only on the Gourary–Adrian scale (curve *3*). The non-electrostatic part of the free energy of hydration is given by curve *4*.

Different independent methods can be used to determine the hydration energy of the inert gases. If the radii of the ions and atoms of the inert gases coincide, the free energy of solution of the gas is simply the non-electrostatic component of the free energy of hydration.

The electrostatic part of the hydration energy, calculated from the Born equation, is given by curve *1* in Fig. 3*b*. It in fact is greater (by ~50%) than the experimental values. It may be noted that it is necessary to compare with experiment the sum of curves *1* and *4*; this improves the situation, but only very slightly. The sum of the electrostatic and non-electrostatic parts of the free energy of hydration corresponds to curve *5*; the values of the sum are in fact close

to the experimental points. The discrepancy between theory and experiment is smallest when the Gourary–Adrian scale of ionic radii is used.

Thus the Born theory requires improvement. Eqn.(2) contains only two experimental parameters, the ionic radius a and the dielectric constant ε. In principle, it is possible to achieve satisfactory agreement between theory and experiment by changing either of these quantities in appropriate fashion. This formal fitting of the parameters, however, leads to physically unreasonable values of a and ε, which do not lie on any one acceptable scale. Thus although this fitting gives an empirical equation showing good agreement with experiment, it cannot give a physical explanation of the phenomenon of solvation.

The use of ideas on the dielectric saturation of the medium in the field of the ion are more attractive from this viewpoint.[2,39–52] Allowance for this effect decreases the absolute magnitude of the electric component of the solvation energy. Again, formally, it is possible to achieve very good agreement between theory and experiment by selecting suitable saturation range dimensions and dielectric constant values. Ideal agreement was obtained in this way by Abraham and Liszi's group.[47–52] There still remains the question, however, of whether these results give a physical explanation of the phenomenon of solvation, or only a successful empirical equation, convenient for practical applications. Since published views on the role of saturation effects in the solvation of ions are contradictory, this question will be examined specially.

2. Non-linear Dielectric Effects

The simplest approach to the calculation of the electrostatic part of the solvation energy, based on the continuum description, and methods for its improvement by taking account of the dielectric saturation of the medium in the field of the ion, can be considered. Some time ago, it appeared that this problem had been sufficiently elucidated; allowance for dielectric saturation gave too small a correction to the Born theory.[17,18] In recent years, however, interest has again been shown in this problem.[2,47–52] Allowance for dielectric saturation gave new results, which unlike the previous results show ideal agreement with experimental data.[47–52] An attempt has been made to analyse the situation that has arisen and to propose simple equations for estimating the effect of dielectric saturation and its role in the phenomenon of ion resolvation.

One method of improving the Born theory is by taking account of non-linear dielectric effects. The dielectric constant of a medium containing polar molecules should change with change in the intensity of the external electric field. This is due both to breakdown of the actual structure of the associated dipoles and to dielectric saturation.[39–41]

A theoretical analysis of the properties of water[42] within the framework of the model used by the author showed that when an electric field is applied, the dielectric constant of water may decrease from the static value $\varepsilon_{st} \cong 80$ to the optical value, equal to the square of the refractive index, that is $\varepsilon_{opt} = 1.8$. Saturation is reached in fields whose intensity exceeds 10^9 V m^{-1}. Because of technical difficulties, it has been possible to verify the theory only in fields with an intensity not exceeding 2×10^7 V m^{-1}, where the decrease in the dielectric constant did not exceed 1% (Fig.5). A detailed discussion of this question can be found in Refs. 43–45.

The first attempt to take account of the dielectric saturation of the medium close to the ion in the calculation of the solvation energy was made in 1926.[46] Introduction of the corresponding correction makes it possible to move the calculated values obtained using the Born theory in the required direction. Subsequently, attempts to attribute the difference between the experimental values of $\Delta^{\alpha}_{vac}G^0$ and the values calculated using the Born theory entirely to dielectric saturation raised serious objections.[33,34]

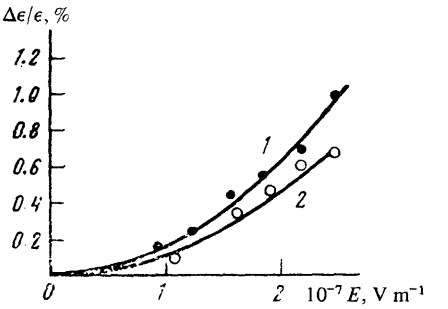


Figure 5. Influence of the intensity of the electric field E on the dielectric constant of nitrobenzene (*1*) and water (*2*);[40,41] $\Delta\varepsilon = \varepsilon_{st} - \varepsilon(E)$.

The density of the free energy of the electric field in a dielectric in the general case is described by the integral

$$g(\mathbf{r}) = \int_0^{\mathbf{D}} \mathbf{E}\,d\mathbf{D} \qquad (4)$$

where **E** is the intensity of the electric field, and **D** the electric induction. In weak fields with a linear relationship $\mathbf{D} = \varepsilon_0\varepsilon\mathbf{E}$, integration of the density of the free energy (4) over the whole of space outside the ion leads to the Born equation (2).

In the general case, the electric induction can be represented as follows:[42]

$$D = \epsilon_0\epsilon_{opt}E + N\mu L(E) \qquad (5)$$

where

$$\mu = \frac{\epsilon_{opt} + 2}{3}\mu_0\tilde{g}^{1/2} \qquad (6)$$

N is the number of molecules of the dielectric in unit volume, μ_0 their dipole moment in a vacuum, and $\tilde{g}^{1/2}$ the Kirkwood factor, which depends on the field and takes account of the associated character of the dipolar molecules (in a non-associated liquid and in high fields, $\tilde{g} = 1$). For the function $L(E)$ it is usual to employ the Langevin model function, but to estimate the effect it is sufficient to know the dependence of D on E in the most general form. From general physical considerations it is clear that with increase in E the function $L(E)$ should increase and tend to a limiting value of 1. As a result, the dependence of D on E moves from one limiting law to another. At low intensities

$$D \cong [\epsilon_0\epsilon_{opt} + N\mu(L'|_{E=0})]E = \epsilon_0\epsilon_{opt}E \qquad (7)$$

and at high intensities

$$D \cong \epsilon_0\epsilon_{opt}E + N\mu. \qquad (8)$$

On the graph giving the dependence of E on D (Fig.6), the straight line ac corresponds to the linear function. As saturation takes place, the curve begins to rise steeply, reaching another asymptote be. The density of the free

energy in the linear approximation is equal to the area of the triangle *acd*, and the value of the total integral (4) is equal to the much larger area of the curvilinear triangle *abd*. The difference between these values arises when the electric induction D is greater than the characteristic value D_{sat}, which can readily be shown to be equal to

$$D_{sat} = N\mu. \quad (9)$$

Since the electric induction in a spherically symmetrical field is independent of the dielectric constant

$$D = \frac{ze_0}{4\pi r^2} \quad (10)$$

it is possible to indicate the characteristic distance from the centre of the ion, within which the saturation effect has an influence:

$$r_{sat} = \left(\frac{|z|e_0}{4\pi N\mu}\right)^{1/2} \quad (11)$$

Thus the characteristic saturation radius r_{sat} is independent of the size of the ion and is determined only by its charge and the properties of the dielectric.[2]†

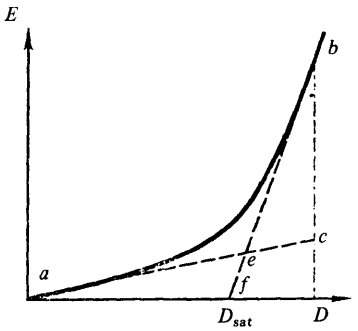


Figure 6. Dependence of the intensity of the electric field E on the electric induction D.

Comparison of the value of r_{sat} with the ionic radius a makes it possible to estimate how large a contribution the phenomenon of saturation may make to the energy of the electric field of the actual ion. For univalent ions in nitrobenzene with $N = 6 \times 10^{27}$ m^{-3} and $\mu_0 = 3.9$ D, it is found that $r_{sat} = 0.31$ nm, and in acetonitrile with $N = 1.1 \times 10^{28}$ m^{-3} and $\mu_0 = 3.97$ D, $r_{sat} = 0.29$ nm. For water ($N = 3.34 \times 10^{28}$ m^{-3}, $\mu_0 = 1.84$ D), the characteristic saturation radius is 0.22 nm.

The values obtained are greater than the radii of monatomic inorganic ions, and for these the contribution of dielectric saturation to the energy of polarisation of the medium should be considerable. To find this contribution, it is necessary to calculate the density of the free energy of the electric field g, that is the integral (4). Approximating the latter by the area of the triangles *acd* and *fbd* in Fig.6 gives:

$$g = \frac{D^2}{2\varepsilon_0\varepsilon} \text{ for } D < D_{sat}$$

$$g = D^2/2\varepsilon_0\varepsilon + (D - D_{sat})^2/2\varepsilon_0\varepsilon_{opt} \text{ for } D > D_{sat}. \quad (12)$$

Integrating the density of the energy over the whole of space outside the ion gives the electric component of the solvation energy:

$$\Delta^{\alpha}_{vac}G^0(el) = -\frac{z^2e_0^2}{8\pi\varepsilon_0 a}\left[1 - \frac{1}{\varepsilon^{\alpha}} - \frac{1}{\varepsilon^{\alpha}_{opt}}\left(1 - \frac{8}{3}x + 2x^2 - \frac{1}{2}x^4\right)\right] \quad (13)$$

where $x = a/r_{sat}$.

In addition to the Born term $1 - 1/\varepsilon^{\alpha}$, Eqn.(13) contains a correction to it which depends on the ratio of the radius of the ion a to the saturation radius. When $a = r_{sat}$, the correction becomes zero; it increases with decrease in a. This is understandable, since it is at short distances that dielectric saturation has an influence. For clarity, the equation obtained can be illustrated by numerical examples. Curve *2* in Fig.3 was constructed using Eqn.(13). It can be seen that allowance for saturation moves the Born straight line in the required direction, bringing it closer to the experimental points. The magnitude of the correction is different for different a. It is 16% for lithium ions. It was previously pointed out that for cations with a small radius, the deviation of the experimental points from the Born straight line reaches 30%. Thus in the case of lithium, allowance for saturation can eliminate more than half of the discrepancy. For potassium, the correction amounts to 4%, which covers 1/7 of the discrepancy between the theoretical and experimental values. Subsequently, the contribution from saturation decreases. It is 2.9% for rubidium, and 1.3% for caesium, corresponding to 0.1 and 0.04 times the required correction respectively.

Thus saturation of the dielectric constant has a significant influence on the electric component of the solvation energy only for the smallest ions, but in this case its influence may be extremely marked. Thus any continuum theory must take account of the saturation of the dielectric constant, at least in the calculation of the hydration energy of ions with a radius smaller than 0.15 nm.

The above estimate of the solvation energy with allowance for dielectric saturation was carried out within the framework of a rigorous continuum model. All the quantities were calculated from first principles. It was assumed that the dielectric constant changes regularly in space, without undergoing any sharp changes. For this reason, Eqn.(13) does not contain fitting parameters. In its derivation, no attempt was made to obtain a detailed description of the dependence of the electric induction on the intensity of the external electric field, and it was merely assumed that the true curve is fairly close to the two asymptotes (see Fig.6). For the complete curve, as already noted, there is a model description in the form of the Langevin function. It can be shown that in this approximation, the function $E(D)$ rapidly reaches the second asymptote.

It should also be noted that the piecewise-linear approximation examined above leads to a slightly low value of E (for a given D), so that the values obtained for the solvation energy represent an upper estimate (absolute magnitude), although they are apparently close to the true value. The accuracy of the approximation increases with decrease in the radius of the ion. Detailed calculations based on the use of the Langevin function were carried out in Ref.53.

A simpler description of the phenomenon of saturation is given in Refs.47–52. To obtain simple analytical expressions, it is assumed that the dielectric constant changes in

†See V.S.Markin and A.G.Volkov, J.Electroanal.Chem.(1987) (in the press).

stepwise fashion in space (see Fig. 4*b*). In this model it is assumed that the ion of radius a is surrounded by two solvate layers with radii b and c respectively. Within the first layer, complete dielectric saturation is assumed, and the dielectric constant is taken as equal to its optical value ($\varepsilon_1 = \varepsilon_{opt}$). At the boundary between the two layers, the dielectric constant undergoes an abrupt change, and in the second layer it has a new constant value ε_2, estimated from the Onsager–Booth equations.[42] Thus the electrostatic component of the solvation energy is given by the equation

$$\Delta^{\alpha}_{vac}G^0(el) = -\frac{z^2e_0^2}{8\pi\varepsilon_0}\left[\left(1-\frac{1}{\varepsilon_1}\right)\left(\frac{1}{a}-\frac{1}{b}\right)+\left(1-\frac{1}{\varepsilon_2}\right)\left(\frac{1}{b}-\frac{1}{c}\right)+\left(1-\frac{1}{\varepsilon_2}\right)\frac{1}{c}\right] \quad (14)$$

The use of the fitting parameters a, b, c, ε_1, and ε_2 gave almost complete agreement between the calculated and experimental data.[48] The value of $\Delta^{\alpha}_{vac}G^0(el)$ is practically insensitive to the parameter c; the use of the fitting parameter b gives the main contribution only if its value is so large as to be unreasonable. According to Ref. 48, to obtain the closest agreement between the theoretical and experimental results it must be assumed that for singly-charged inorganic ions within a radius of 0.4 nm round the ion there is complete dielectric saturation of the solvent, and $\varepsilon_1 = \varepsilon_{opt}$. From what has been said above, however, it is clear that this approach is unsound.

3. The Method of Non-local Electrostatics

To calculate the electrostatic contribution to the solvation energy, use is made of another semi-macroscopic approach, namely the method of non-local electrostatics, which has been developed extremely intensively in recent years. The method of non-local electrostatics takes account of the fact that the fluctuations of the polarisation of the solvent correlate with one another in space as a result of the presence in the liquid of a structure determined by the quantum-mechanical interaction between its molecules. Thus the average polarisation at each point depends on the induction at all other points in space, correlating with the given one.[54]

The relationship between the intensity of the electric field **E** and the electric induction **D** in the method of non-local electrostatics is expressed by means of the tensor $\varepsilon_{mn}(r)$:

$$D^m(\mathbf{r}) = \sum_n \int d\mathbf{r}\varepsilon_0\varepsilon_{mn}(\mathbf{r}-\mathbf{r}')E^n(\mathbf{r}') \quad (15)$$

where $m, n = x, y, z$. A noteworthy feature is that this relationship, which has complex spatial character, remains linear. The subsequent calculations are carried out by the Fourier transformation of the tensor $\varepsilon_{mn}(\mathbf{r})$, which is called the static dielectric function $\varepsilon(\mathbf{k})$:

$$\varepsilon(k) = \sum_{m,n}\frac{k_m k_n}{k^2}\int d(\mathbf{r}-\mathbf{r}')e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')}\varepsilon_{mn}(\mathbf{r}-\mathbf{r}') \quad (16)$$

The electric potential created in the medium by a charged sphere with a radius a at a distance r from its centre is

$$\varphi(\mathbf{r}) = \frac{ze_0}{2\pi^2\varepsilon_0}\int_0^{\infty}\frac{dk}{\varepsilon(k)}\frac{\sin kr}{kr}\frac{\sin ka}{ka} \quad (17)$$

This gives the electric contribution to the solvation energy:

$$\Delta^{\alpha}_{vac}G^0(el) = -\frac{z^2e_0^2}{4\pi^2\varepsilon_0}\int_0^{\infty}dk\frac{\sin^2 ka}{k^2a^2}\left[1-\frac{1}{\varepsilon(k)}\right] \quad (18)$$

To calculate the integral in Eqn. (18), it is necessary to specify in some way the functional dependence $\varepsilon(k)$. It is possible, as was done in Refs. 33 and 34, to break down the fluctuations of the polarisation of the medium into three modes related to different degrees of freedom: electronic or optical (index 1), vibrational or infrared (index 2), and orientational or Debye (index 3). If the radius of the correlation of the i^{th} mode of a fluctuation is λ_i, then

$$1-\frac{1}{\varepsilon(k)} = 1-\frac{1}{\varepsilon_1}+\left(\frac{1}{\varepsilon_1}-\frac{1}{\varepsilon_2}\right)\frac{1}{1+k^2\lambda_2^2}+\left(\frac{1}{\varepsilon_2}-\frac{1}{\varepsilon_3}\right)\frac{1}{1+k^2\lambda_3^2} \quad (19)$$

The correlation radius of the electronic mode λ_1 is here taken as zero. It is impossible to indicate beforehand the exact values of the correlation radii λ_2 and λ_3, but an approximate estimate can be carried out from physical considerations. For the infrared vibrations, the magnitude of λ_3 depends on the type of liquid. For non-associated liquids, the correlation radius of the orientational vibrations is approximately equal to the intermolecular distance, but for associated liquids, for example water, the scale of λ_3 is indicated by the characteristic length of the chain of hydrogen bonds, which amounts to ~0.5–0.7 nm.[33,34]

Integration in Eqn. (18) using the function (19) gives the expression

$$\Delta^{\alpha}_{vac}G^0(el) = -\frac{z^2e_0^2}{8\pi\varepsilon_0 a}\left[1-\frac{1}{\varepsilon_1}+\left(\frac{1}{\varepsilon_1}-\frac{1}{\varepsilon_2}\right)\psi\left(\frac{2a}{\lambda^2}\right)+\left(\frac{1}{\varepsilon_2}-\frac{1}{\varepsilon_3}\right)\psi\left(\frac{2a}{\lambda_3}\right)\right] \quad (20)$$

where

$$\psi(x) = 1-(1-e^{-x})/x \quad (21)$$

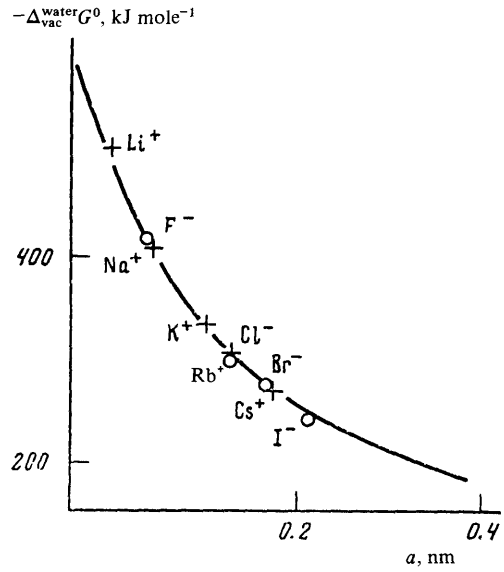


Figure 7. Dependence of the hydration energies of ions on their radius; the points give the experimental data,[29,30] and the continuous line the calculated data;[34] the values of a were taken from Ref. 31.

The electric contribution to the hydration energy, calculated[34] using these equations, is given in Fig. 7, together with the experimental data for a number of small univalent ions. The dielectric constant values used are given in Table 2. The correlation radii were chosen to be close to the characteristic values indicated from the condition for best

agreement between the theoretical and experimental data: $\lambda_2 = 0.1$ nm and $\lambda_3 = 0.7$ nm. Fig.7 shows that good agreement was obtained between theory and experiment.[34] As far as the sensitivity of the results to the fitting parameters λ_i is concerned, λ_2 has the greatest weight, and a less significant role is played by λ_3, as shown in Fig.8. A detailed analysis was carried out in Ref.33. The method of non-local electrostatics essentially uses continuum models, but the effective parameters required for the calculation are derived from an analysis of the structure of the solvent. This method makes it possible to obtain extremely accurate values of the solvation energy for small ions, and then, using Eqn.(1), the values of the energy of resolvation. At the same time, for large ions, appreciable discrepancies are observed between theory and experiment. This indicates the need to take account of additional effects, in this case the work of formation of a cavity in the solvent, or the solvophobic effect.

Table 2. Values of the dielectric constants ε_i [28] used in the model of three polarisation modes (T = 293 K).

Solvent	$\epsilon_1 = \epsilon_{opt}$	ϵ_2	$\epsilon_3 = \epsilon_{st}$
Water	1.8	4.9	78.8
Nitrobenzene	2.4	3.7	35.0
1,2-Dichloroethane	2.0	—	10.4
Acetophenone	2.45	—	17.4
Dichloromethane	2.04	—	9.1
Methyl butyl ketone	1.9	—	14.9

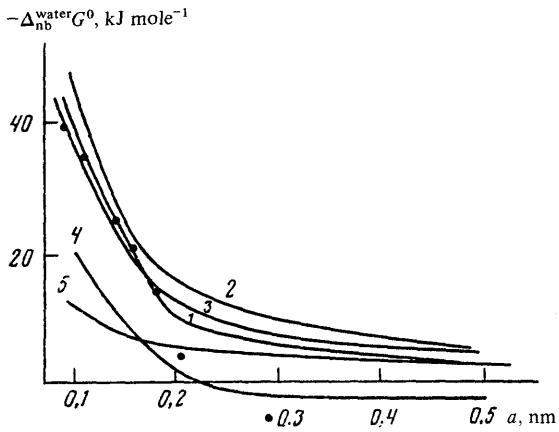


Figure 8. Influence of the spatial dispersion of the dielectric constants of the aqueous and nitrobenzene phases on the electrostatic contribution to the free energy of resolvation; the calculation was carried out by the published method[33] with $\lambda_2^{water} = 0.1$ nm and $\lambda_3^{water} = 0.7$ nm and the dielectric constants from Table 2; correlation radii, nm: *1)* $\lambda_2^{nb} = 0.1$, $\lambda_3^{nb} = 0.5$; *2)* $\lambda_2^{nb} = 0.1$, $\lambda_3^{nb} = 0.3$; *3)* $\lambda_2^{nb} = 0.13$, $\lambda_3^{nb} = 0.3$; *4)* $\lambda_2^{nb} = 0.1$, $\lambda_3^{nb} = 0.7$; *5)* calculated using the Born equation; the experimental data were taken from Table 1.

The chief disadvantage of the continuum and semi-continuum approaches to the problem of solvation lies in the actual model of the solvent. Allowance for saturation of the dielectric constant or correlation of the dipoles represents an attempt to reflect the discrete properties of the solvent while essentially remaining within the framework of the continuum model. Other similar approaches are known, in which, in the calculation of the thermodynamic properties of the system, attempts are made to take account of the unknown influence of the molecular structure of the solvent.[55] A true solution to the problem can be achieved, however, only by taking account of the discrete structure in the statistical theory of the solvent.

4. Statistical Models of the Solvent

A complete solution of the problem of solvation involves the development of a statistical theory which would regard the ions and solvent molecules "as equals", that is which would take account of their discrete molecular nature, even at the price of the introduction of model potentials.

In contrast to "primitive" models of an electrolyte, in which a continuum description of the solvent is used, in the "non-primitive" model used in present-day statistical analysis, or the ion–dipole plasma model, a solution of an electrolyte is regarded as a system of solid spheres with radii a and a_d, carrying at their centres a point electric charge or a constant point dipole respectively. It is assumed that there are the usual electrostatic interactions between the charges and the dipoles. The system is described in terms of many-particle correlation functions, for which corresponding chains of equations are written.[56–58] For their solution it is necessary to resort to various simplifications, among which the most popular is the mean-spherical approximation.[59] This model should make it possible to calculate the solvation energy of ions, and also the dielectric properties of a pure dipolar liquid.#

The dielectric constant of a dipolar liquid in the mean-spherical approximation was calculated in Ref.58, where the following equation was obtained:

$$\varepsilon = q(2\xi)/q(-\xi) \qquad (22)$$

in which

$$q(x) = (1+2x)^2/(1-x)^2 \qquad (23)$$

and the parameter ξ is obtained by solving the equation:

$$q(2\xi) - q(\xi) = n_d\mu^2/3\varepsilon_0 kT \qquad (24)$$

Here, n_d is the number of particles of the solvent in unit volume, and μ the dipole moment of the solvent molecule. This approach made it possible to refine considerably the familiar Onsager equation.

For strongly associated liquids, the theoretical results do not show very good agreement with the experimental data. There is nothing surprising in this, since the model does not include a whole range of complex forces acting between real solvent molecules. For example, for a dipolar liquid having the same dipole moment of the molecules (1.8 D) as water, the dielectric constant obtained from Eqn.(22) at room temperature is 48. To obtain the correct value of $\varepsilon_{st} = 80$, it is necessary to take the value 2.62 D for the dipole moment of the molecules of the liquid.

A dipolar liquid is a model system consisting of solid spheres with dipoles situated at their centres. It is used in theoretical calculations of the properties of a liquid.

A model in the form of a set of solid spheres with constant dipole moments naturally cannot describe all the properties of water, but this system may serve as a reasonable model for organic solvents, and in any case this is the first necessary step in obtaining a model of water. In particular, the study of this model made it possible to detect a number of fundamentally important effects related to the solvation and interaction of ions and associated with the discrete nature of the solvent.

In Ref.59, the solvation energy of an ion (the "Born" energy) was calculated in the mean-spherical approximation:

$$\Delta^{\alpha}_{vac}G^0 = -\frac{(ze_0)^2}{8\pi\varepsilon_0(a+a_d/\lambda)}\left(1-\frac{1}{\varepsilon}\right) \qquad (25)$$

where a_d is the diameter of the solvent molecule. The value of λ is determined by solving the equation

$$\lambda^2(1-\lambda)^4 = 16\varepsilon \qquad (26)$$

For all values of ε, the parameter λ lies in the range 1–3; for $\varepsilon = 80$ it is equal to 2.6. This parameter, together with the radius of the dipolar solvent molecule, defines in accordance with Eqn.(25) a new characteristic length a_d/λ, which arises naturally from the solution of the equations. This characteristic length is determined exclusively by the properties of the dipolar liquid, and depends on two of its parameters, the radius of the molecules and the dielectric constant.

Formally, Eqn.(25) looks like the equation for determining the Born energy, with a renormalised ionic radius, which has been increased by the section a_d/λ. An interesting feature is that there exists an empirical equation for describing the experimental solvation energies and free energies of resolvation, whose form is identical to that of Eqn.(25).[60] In aqueous electrolyte solutions, this correction lies in the range 0.64–0.84 Å for cations and 0.10–0.42 Å for anions. According to Eqn.(25), if the radius of the solvent molecule is taken as 1.5 Å, then $a_d/\lambda = 0.58$ Å.

The apparent increase in the radius of the ion in Eqn.(25) is related to the discrete nature of the solvent. It is obvious that the bulk value of the dielectric constant cannot be established directly at the actual "surface" of the ion. Eqn.(25) makes it possible to calculate that this value is effectively reached at a distance of $a + a_d/\lambda$ from the centre of the ion. It should be remembered, however, that this picture of a stepwise change in the dielectric constant represents only an effective approximation which can be used to describe a fairly accurate physical result obtained using the discrete model. Moreover, an analysis of this model shows that it is in general impossible to use the concept of local dielectric constant at such short distances, and it is necessary to return to the more accurate concept of the polarisation of the medium. In the macroscopic description of a dielectric, its polarisation at a distance r from the ion is given by the familiar equation $P_{macr}(r) = (\varepsilon-1)ze_0/4\pi\varepsilon r^2$.

Fig.9*a* gives the calculated[59] dependence of the polarisation of the medium, normalised to its macroscopic value P_{macr}, on the distance r. The most important feature of this dependence is its oscillatory character. This means that, as a result of the strong ordering of the dipoles nearest to the ion, the subsequent dipoles may adopt the opposite orientation. For this reason, the description of a medium in terms of the local dielectric constant (for example, the use of the stepwise function), even if it gives good agreement with experiment, leads to erroneous ideas about the true physical picture at short distances, and this description must be approached with care.

An important consequence should be noted. The interaction of ions in a discrete medium differs fundamentally from that predicted by the macroscopic theory. This interaction is described by a potential of mean force W_{ij}, which, in addition to the Coulomb potential, includes the averaged interaction with all the solvent molecules. As shown by the same authors,[59] the potential of mean force also oscillates at short distances (Fig.9*b*). For example, the curve for ions of different kinds has a deep potential minimum W_{+-}, when the centres of the ions are at a distance of $4a$. This is a relatively stable configuration, in which the ions are separated by one dipolar molecule; it can be regarded as the result of the formation of ion pairs in the solution. The potential for ions of the same kind W_{++} also has a deep minimum, at $r = 3a$. This configuration gives as it were a "double" ion, for which the increase in the Coulombic energy is more than compensated by the negative displacement of the Born energy of solvation of the highly charged structure.

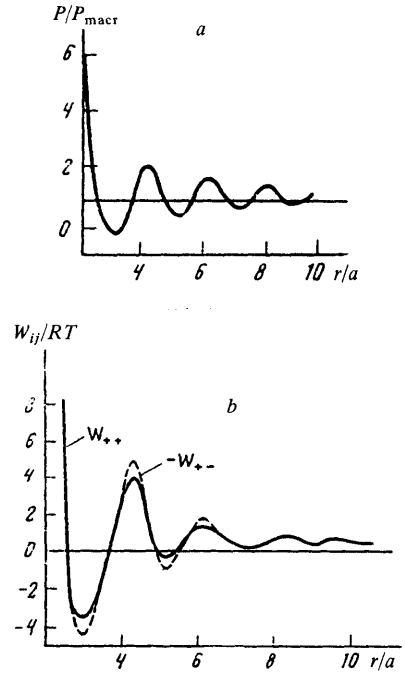


Figure 9. The normalised density of the polarisation P/P_{macr} (*a*) and the potential of the average force W_{ij} between two univalent ions i and j (*b*) as a function of the distance r from the centre of the ion.[59]

The results obtained in the mean-spherical approximation are mainly qualitative in character, but they make it possible to obtain a more correct representation of the true physical picture of solvation and to re-evaluate other theories on the basis of an understanding of how they achieve agreement with experiment.

III. THE SOLVOPHOBIC EFFECT

Present-day approaches to the calculation of the energy of the solvophobic interaction of an ion with a solvent are based on phenomenological[61,62] or statistical-mechanical molecular models,[63] which contain parameters, not always unknown, characterising the ion and the solvent. To avoid unnecessary indeterminacy, the estimation of the solvophobic contribution to the free energy of resolvation is sometimes carried out using Uhlig's semi-empirical equation,[64] the essential features of which reduce to the following.

If the concept of the surface tension at the boundary of the ion and the solvent $\gamma_{0,\alpha}$ is used, the surface energy is $4\pi a_2\gamma_{0,\alpha}$. The difference in the surface energies in the media α and β is $4\pi a^2(\gamma_{0,\alpha}-\gamma_{0,\beta})$. According to Antonov's rule

$$\gamma_{0,\alpha} - \gamma_{0,\beta} \approx \gamma_{\alpha\beta}\,\mathrm{sgn}\,(\gamma_\alpha - \gamma_\beta) \qquad (27)$$

where sgn $x = +1$ if $x \geq 0$, and sgn $x = -1$ if $x < 0$, $\gamma_{\alpha\beta}$ is the interfacial tension at the planar boundary between the media α and β, and γ_α and γ_β the surface tensions at the boundaries between air and the solvents α and β respectively at the same pressure and temperature. In this case, Uhlig's equation for the solvophobic contribution to the energy of resolvation has the form:

$$\Delta_\beta^\alpha G^0(\mathrm{svph}) = 4\pi a^2\gamma_{\alpha\beta}\,\mathrm{sgn}\,(\gamma_\alpha - \gamma_\beta) \qquad (28)$$

The contribution is obviously greater, the larger the radius of the ion a.

From the theoretical viewpoint, the range of applicability of Uhlig's equation is not quite clear. At the same time, it has proved surprisingly useful in calculations of distribution coefficients in systems consisting of two immiscible liquids.[33,34] Slight deviations from Uhlig's equation are observed when the interfacial tension between the two pure immiscible solvents is less than 10 mN m^{-1} and the dissolved species have dimensions of less than 0.2 nm.[35] This can readily be explained, since Uhlig's equation neglects the dependence of the surface tension on the curvature of the surface. At low values of $\gamma_{\alpha\beta}$ and for small particles, the contribution of the solvophobic effect is slight.

An important advantage of Uhlig's equation is that it does not contain fitting parameters, since $\gamma_{\alpha\beta}$ is taken from experiment. Fig.10 gives as an example the dependence of the solvophobic contribution to the energy of resolvation on the radius of the particle, calculated from Eqn.(28), for the water-nitrobenzene and water–1,2-dichloroethane systems.

IV. THE TOTAL ENERGY OF RESOLVATION

Various effects making a contribution to the energy of resolvation of ions were listed above. For most solvents of interest, the most significant role is played by electrostatic and solvophobic effects.[33] This has made it possible to represent the energy of resolvation as the sum of the contributions of two effects:[33]

$$\Delta_\beta^\alpha G^0 = \Delta_\beta^\alpha G^0(\mathrm{el}) + \Delta_\beta^\alpha G^0(\mathrm{svph}). \qquad (29)$$

The non-electrostatic part of the energy is usually taken as equal to the energy of solvation of the hypothetical discharged ion, all of whose other characteristics remain unchanged. It is usually estimated by comparing with a suitable neutral analogue, for example a noble gas. It is assumed that the energies of the formation of the cavity and the change in the structure of the solvent are the same for particles with the same shape and size, irrespective of the charge. This approach has an important advantage, emphasized in Ref.48. If identical standard states in the gas phase and the solution are taken for the ion and the neutral species imitating it, this procedure removes completely the problem of the recalculation and loss of the translational entropy of the solute in the solution in the comparison of the theoretical results with the experimental data.

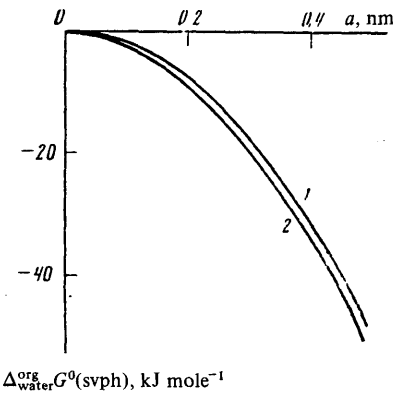


Figure 10. Solvophobic contribution to the energy of resolvation of a particle of radius a from water into nitrobenzene (*1*) and 1,2-dichloroethane (*2*), calculated using Uhlig's equation.[34]

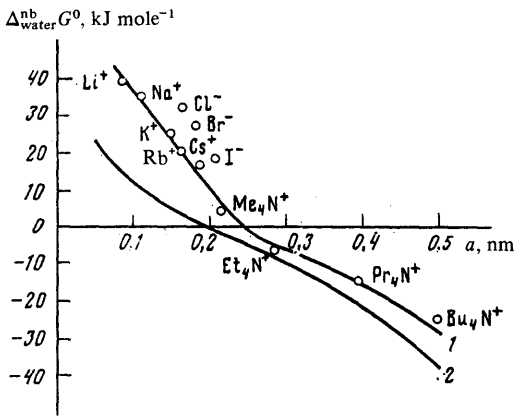


Figure 11. Dependence of the energy of resolvation on the radius of the ion in the water–nitrobenzene system, calculated from Eqn.(29): *1*) using the method of non-local electrostatics;[33,34] *2*) using the Born equation; the points give the experimental data (see Table 1).

In Ref.33, the electrostatic contribution was calculated by the method of non-local electrostatics, and the solvophobic contribution using Uhlig's equation. The results of the calculation for the most extensively studied experimental water–nitrobenzene system are given in Fig.11 (curve *1*). Comparison with curve *2*, obtained by calculation using

Born's equation, shows that allowance for the solvophobic effect alone does not make it possible to compensate the inadequacies of this simple equation.

Fig.11 shows that as a result of the solvophobic effect, the energy of resolvation may change sign with change in the radius of the ions. The results of the calculation show very good agreement with the experimental data. The deviations observed for anions in the range of small radii may be due to the formation of hydrogen bonds between the anions and the solvent molecules, or to the phenomenon of defect annihilation. The magnitude of these deviations corresponds approximately to the energy gain resulting from the formation of a weak hydrogen bond between the anion and the solvent.

The values of the energy of resolvation of small anions obtained by different authors differ considerably from one another.

V. STANDARD DISTRIBUTION POTENTIALS

When the energy of resolvation of an ion is known, it is possible to calculate the standard distribution potential $\Delta_\beta^\alpha\phi_i^0$ from the equation

$$\Delta_\beta^\alpha\varphi_i^0 = -\frac{\Delta_\beta^\alpha G_i^0}{z_i F} \qquad (30)$$

where F is the Faraday constant.

Table 1 gives the distribution potentials for different ions between water and organic solvents. In the separation of the standard free energy of resolvation into ionic components and the determination of the distribution potentials, the tetraphenylborate hypothesis was used.[65-69]

It is known from thermodynamics that the absolute value of a difference in electric potentials can be measured only in conductors with the same composition. For the same reason, the difference in the galvanic potentials between a point in an aqueous phase and a point in the depth of an organic solvent cannot be measured experimentally.

If identical reversible electrodes are introduced into each of the phases of two immiscible electrolyte solutions in thermodynamic equilibrium, the inter-phase potential difference between them will be zero, since the system, being in equilibrium, cannot perform work.[70] If the reversible electrodes are different, the measured potential difference will be equal to that which would have been observed if these electrodes had been placed in the same solution.[70]

The following experimental methods are now used to measure distribution potentials and also to determine $\Delta_\beta^\alpha G^0$: polarography at a dropping electrolyte electrode;[1,12,15,27,71,72] polarography with scanning of the current at a dropping electrolyte electrode;[73-75] polarography at a rising aqueous electrode;[76] alternating-current polarography;[77-80] chronopotentiometry;[80-82] chronoammetry;[80,83] cyclic voltammetry;[12,18,22,71,84-88] measurement of the EMF of liquid circuits;[25,89,90] calculation using data on solubility,[14] distribution coefficients,[24,91-95] extraction,[91,96,97] the spin–lattice relaxation of the quadrupolar nuclei of the ions,[23,98,99] and calorimetry.[100] The accuracy of the measurement of $\Delta_\beta^\alpha\phi^0$ and $\Delta_\beta^\alpha G^0$ reaches 1 mV and 0.1 kJ mole^{-1} respectively.

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The present review has described the most effective present-day methods for calculating the free energy of resolvation of ions. The most successful approach involves the use of the electrostatics of the media with spatial dispersion with allowance for solvophobic effects.

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