Phase transitions in electrolyte solutions

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A theory of the phase transition from weak to strong electrolyte is developed, making it possible to explain anomalous variations previously observed in the conductivity of electrolyte solutions when their dielectric permittivity ε changes. It is shown that as opposed to the usual Debye approximation for calculating fields acting on the carriers, it is necessary in principle to consider the interaction not only with free, but also with bound charges in solution. It was established that for realistic parameters, there exists a critical value ε_c, at which the degree of critical dissociation of electrolyte molecules changes discontinuously by more than an order of magnitude. The values found for ε_c agree well with experimental data.

Study of the properties of electrolyte solutions, as a rule, is conducted using the Debye approximation Refs. 1–3. Until now, changes in electrolyte solution properties (solubility,[1] carrier mobility,[4] etc.) have been studied in detail as functions of electrolyte concentration. Thus solvent properties enter essentially through the dielectric permittivity ε: the electrolyte ionic interaction energy is ε times smaller than in vacuum, where ε is taken to be constant. In such an approach, the electrolyte–solvent system is completely analogous to an ionized gas. However, the peculiarity of an electrolyte solution is that ε of the solvent can be changed relatively easily and over broad ranges. (Experimentally, this is achieved, for example, by diluting the solution using a liquid with a different dielectric permittivity.) It is noteworthy that the dependence of the thermodynamic properties of an electrolyte solution on the ε of the solvent has scarcely been studied theoretically, although rather extensive experimental material has been gathered in this area.[5]

In this work, the degree of electrolyte molecular dissociation x is studied as a function of the dielectric permittivity of the solvent. It is shown that when calculating fields, acting on a carrier, it is necessary to consider the interaction not only of the free, but also of the bound charges in solution. It is established that for realistic system parameters, there exists a critical value ε_c at which the degree of dissociation of electrolyte molecules changes discontinuously by more than an order of magnitude.

A symmetric binary electrolyte solution will be examined. The static dielectric permittivity of the solvent is ε, the number density of solvent molecules is N, and the degree of dissociation is x. The magnitude of x is determined by the law of mass action:[2]

$$\frac{x^2}{1-x}=\frac{\nu}{N}\exp\left[-\frac{u(x)}{T}\right],\qquad \nu=\frac{z_+z_-}{z_0},\tag{1}$$

where the entropy factor ν is of order R^{-3} (R is the radius of the ion); T is the temperature in energy units, z_+, z_-, z_0, are respectively, the numbers of possible states of positive and negative ions, and of electrolyte molecules per unit volume.

The dissociation energy takes the form

$$u(x)=u_0+u_-+u_+-u_M,\tag{2}$$

where the ε-dependent terms u_M and $u_\pm$ represent the electrostatic parts of the internal energy of an electrolyte molecule and the ion pair that forms as a result of dissociation; u_0 includes the energy expended in breaking the chemical bond during dissociation, as well as the difference in the internal molecular and ionic energies arising from short-range forces of nonelectrostatic origin (hydration energy and so on). For simplicity, we will assume that u_0 does not depend on ε.

The values of the energies $u_\pm$ are found by the usual method of electrolyte theory,[3] representing ions as vacuum spheres with radius R and with point charges $\pm q$ at the center. The remaining part of the solution is viewed as a continuous medium with a dielectric permittivity equal to the actual value of ε for the system. Free charges are described using the inverse Debye radius

$$\varkappa=(8\pi q^2xN/\varepsilon T)^{1/2}.$$

Within the scope of this model, in the case of interest, that of a dilute electrolyte with $\varkappa R<1$, we have

$$u_\pm=-\left\{\frac{q^2}{R_\pm}\left(1-\frac{1}{\varepsilon}\right)+\frac{q^2\varkappa}{\varepsilon}\right\}.\tag{3}$$

Note that Eq. (3) is the simplest expression for $u_\pm$ and its range of validity is limited. The question of the use of (3) is studied in detail in Ref. 6, where the error of this expression is determined numerically for different system parameters. The values of the parameters we used in studying phase transitions [see the discussion after Eq. (9) below], fall in the area where, in accordance with Ref. 6, (3) is accurate to 5–10%. This accuracy is found to be completely satisfactory inasmuch as the self-consistency of (1) introduces at least as much error in our computation.

The first term in Eq. (3) represents the energy u_{field} of interaction with bound charges and the second the Debye energy u_D of interaction with free charges in solution (in Ref. 3 where the dependence of x on the carrier concentration was studied, only the u_D term was taken into consideration).

The calculation of the electrostatic part of the molecular energy u_M is completely analogous to the calculation of $u_\pm$. The ratio of u_M to $u_\pm$ is of order $(p/qR_\pm)^2$, where p is the absolute value of the dipole moment of the molecule. We specialize to the case $p\ll qR_\pm$, in which u_M is negligible in comparison with $u_\pm$. (The calculation of u_M does not pose major difficulties and does not change the qualitative form of the results obtained below.)

Substituting expressions (2) and (3) into (1), we obtain the following equation determining x:

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$$\ln\frac{x^2}{1-x}=-W-\ln n-\frac{A}{\varepsilon}+\left(\frac{A^3nx}{\varepsilon^3}\right)^{1/3} \qquad (4)$$

where

$$W=\frac{u_0}{T}-\frac{q^2}{RT}-\ln 4\pi, \qquad A=\frac{q^2}{RT},$$
$$n=32\pi R^3N, \quad R^{-1}=R_-^{-1}+R_+^{-1}. \qquad (5)$$

Note that the second term in the right side of (4) is obtained by transformation of the coefficient of the exponential in Eq. (1). The difference in the magnitudes of N/v and the dimensionless concentration n in (5) causes the constant W to be renormalized slightly.

As is evident from Eqs. (1)–(4), the main contribution to the dependence $x(\varepsilon)$ is made by changes of the energy u_{field} of interaction with bound charges as ε is varied (since $u_{\text{field}}/u_D \sim (\varkappa R)^{-1} > 1$): As ε increases the energy u_{field} decreases and x increases. It is evident that this effect is most noticeable if at small ε ($\varepsilon \approx 1$) the electrolyte is weak ($x \ll 1$). In this case, in some range of values of ε (up to $x \ll 1$) x grows exponentially with ε and for $\varepsilon \gg 1$ the electrolyte becomes strong ($x \approx 1$).

These monotonic changes in the dependence $x(\varepsilon)$ occur when the Debye contribution u_D can be neglected. The situation changes qualitatively if the quantities u_0 and u_{field} cancel each other out to a significant degree and their difference is of the same order as u_D. In this case, it can be significant that as x grows the energy u_D increases (due to the interaction of ions with the Debye cloud), which in turn leads to a further increase in x. The positive feedback arising due to this under favorable conditions can lead to a discontinuous jump in x at some value of ε: a first-order phase transition occurs in the system, in which x changes more than an order of magnitude. The permittivity of the solution grows correspondingly. This transition can be called a weak electrolyte–strong electrolyte phase transition.

A quantitative examination of equation (4) for various choices of n, A, W shows that at large values of W and fixed values of A and n, the dependence of x on ε is monotonic. As W decreases below some value W^*, the dependence of x on ε becomes S-shaped (see Fig. 1). As usual, this is evidence that a first-order phase transition is occurring in the system.

The value of W at which $x(\varepsilon)$ becomes multivalued, can be determined by solving Eq. (4), as well as by using the conditions

$$\partial\varepsilon/\partial x=0,\ \partial^2\varepsilon/\partial x^2=0\ (\partial x/\partial\varepsilon=\infty,\ \partial^2x/\partial\varepsilon^2=\infty), \qquad (6)$$

for which the multivalued portion of the $x(\varepsilon)$ phase curve degenerates to a single point. The values of x_0 and ε_0, satisfying this condition are $x_0 = 0.44$, $\varepsilon_0 = 0.24An^{-1/3}$. Substituting them into (4) we find W^* and also conditions for the parameters W and n for which this phase transition is possible:

$$W<6{,}63-\ln n-4{,}20n^{-1/3}. \qquad (7)$$

In order to study in more detail the phase transition that takes place when condition (7) is satisfied (in particular, for determining the critical dielectric permittivity ε_c), it is necessary to construct the free-energy functional. The free energy of the system in the calculation is given by the expression

$$F=F_0+\int_0^x u(x)\,dx-TS, \qquad (8)$$

where

$$S=\ln\left\{\frac{(z_+)!\qquad(z_-)!\qquad(z_0)!}{(xN)\,(z_+-xN)!\,(xN)!\,(z_-+xN)!\,(N-xN)!\,(z_0-N+xN)!}\right\} \qquad (9)$$

and F_0 is the free energy of the system in the absence of dissociation ($x = 0$).

The solution is assumed to be dilute ($xN \ll z_+, z_-; N - xN \ll z_0$), so the entropy of the system is determined by the independent distribution of xN positive and negative ions in the z_+ and z_- states and the distribution of $N - xN$ electrolyte molecules in the z_0 state. Using Stirling's formula ($\ln y! = y\ln y - y$) we obtain

$$F=F_0+\ln z_0-\ln N+1+\int_0^x u(x)\,dx$$
$$-T\left[x\ln\frac{z_+z_-}{Nz_0}+x-(1-x)\ln(1-x)-2x\ln x\right]. \qquad (10)$$

Note that the law of mass action (1), as usual, follows from

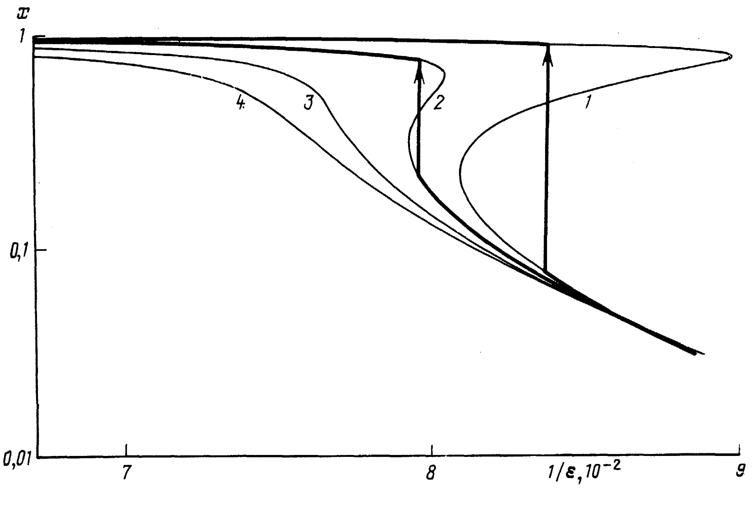

FIG. 1. Dependence of the degree of dissociation of the electrolyte molecule on inverse dielectric permittivity of the solvent at $A = 200$, $W = -5$ and at various values of dimensionless concentration n: 1—$n = 2.3\cdot10^{-2}$, 2—$2.0\cdot10^{-2}$, 3—$1.7\cdot10^{-2}$, 4—$1.5\cdot10^{-2}$. Phase transitions are indicated by arrows, bold lines indicate physically realized states.

the condition $\partial F/\partial x = 0$.

For $W < W^*$ there is a region of ε where Eq. (4) has three solutions for each value. The maximum and minimum values of x in the multivalued region for a fixed value of ε give local minima of the free energy F (10). The intermediate value corresponds to the maximum free energy. At some value $\varepsilon = \varepsilon_c$ the values of F, corresponding to the local minima become equal. For $\varepsilon < \varepsilon_c$ the phase with a low ion concentration is stable, while for $\varepsilon > \varepsilon_c$ the phase with a high ion concentration is stable. Thus ε_c determines the point of the phase transition. There the concentration changes discontinuously by more than a factor of ten.

In Fig. 1 the characteristics $x(\varepsilon)$ are shown for different values of the dimensionless concentration n and fixed $W = -5$ and $A = 200$ (the minimum value of the dimensionless concentration $n_{\min}$ at which a phase transition is possible, in accordance with (7), in this case is equal to $1.9 \cdot 10^{-2}$). When inequality (7) is satisfied (curves 1, 2), a first-order phase transition occurs (indicated in the figure by an arrow). At $n = 2 \cdot 10^{-2}$, the critical value of the dielectric permittivity is equal to $\varepsilon_c = 12.58$, and at $n = 2.3 \cdot 10^{-2}$, $\varepsilon_c = 11.98$. Thus, the phase transition is possible at reasonable values of the physical parameters. If the inequality (7) is not met (for values of the dimensionless concentration less than $n_{\min}$), x grows monotonically with ε, but, in the region $\varepsilon \sim \varepsilon_c$, sharp growth in the degree of dissociation x is observed.

Similar changes in the carrier concentration when the dielectric permittivity of the solvent was changed were observed in the experiment for LiCl dissolved in a mixture of methanol and dioxan.

In conclusion, note that when ε is close to the critical value ε_c and other parameters of the system are varied, e.g., the temperature T, anomalous changes in the degree of dissociation are possible. We did not consider temperature-dependent phase transitions, since this would require more detailed information regarding the dependence of ε on T.

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