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STUDY OF THE THERMODYNAMIC PROPERTIES OF SOLUTIONS OF STRONG ELECTROLYTES IN SOLVENTS WITH HIGH DIELECTRIC CONSTANTS

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For studying the influence of the nature of the solvent on the thermodynamic properties of solutions of strong electrolytes, the activity coefficients of electrolytes in solvents having a dielectric constant (hereafter d.c.) substantially higher than that of water are of great interest. In the case of solvents with low d.c., the effect of ion-pair formation is, as a rule, dominant and masks other effects. The existing data (⁀1) on the activity coefficients of alkali-metal halides in formamide (d.c. 126) show that in this solvent, as in water, positive deviations of the activity coefficients $\gamma_\pm$ from the classical Debye–Hückel electrostatic theory are observed; moreover, the minimum on the $\lg \gamma_\pm$–concentration curves is shifted in this case toward more dilute solutions than in water. Therefore one may expect that in solvents with high d.c., owing to the decrease in the energy of electrostatic attraction between ions, the result of the interaction of the electrostatic fields of the ions with the solvent will manifest itself to a greater degree than, for example, in water.

In this connection, in the present work the activity coefficients of sodium chloride and cesium chloride in N-methylformamide (d.c. 182.4) and of cesium chloride in formamide (d.c. 109.6) at 25° were determined. For this purpose the emf of the corresponding cells without transference of the type:

$$\text{Ag—AgCl} \mid \text{MCl}\ (M) \mid M_x\text{Hg} \mid \text{MCl}\ (0{,}1) \mid \text{AgCl—Ag}, \qquad \text{(A)}$$

$$\text{Ag—AgCl} \mid \text{MCl} \mid M_x\text{Hg}, \qquad (\ )$$

was measured, where $M = \text{Na, Cs}$ for the cell of type (A) in N-methylformamide and $M = \text{Cs}$ for (B) in formamide. The measurements were carried out with

Fig. 1. Dependence of $\lg \gamma_\pm$ on $\sqrt{M}$.

Figure 1: Fig. 1. Dependence of $\lg \gamma_\pm$ on $\sqrt{M}$.

silver-silver chloride electrodes prepared by the thermoelectrolytic method, and with jet amalgam electrodes. The procedure of measurement, preparation of electrodes, and purification of N-methylformamide were described previously (ˆ2). Formamide of "pure" grade was purified by vacuum distillation with a 70 cm-high dephlegmator at a temperature of about 60°, treated with CaO with subsequent pumping off in vacuum, and finally distilled on a rectification column at a temperature of about 55°. The formamide obtained in this way had a specific electrical conductivity of about $5 \cdot 10^{-5}$ ohm$^{-1} \cdot$cm^{-1}. The working solutions were prepared without contact of the solvents with air. All concentrations of solutions are given in molalities.

The use of silver-silver chloride electrodes in such solvents as N-methylformamide and formamide deserves special attention.

In measurements in solutions of NaCl and CsCl in N-methylformamide it was established that in dilute chloride solutions, after several hours, a stationary potential of the silver-silver chloride electrode is established; the asymmetry potential between two electrodes amounts to several hundredths of a millivolt, as in aqueous solutions.

At concentrations above $0.1\,M$, the increase in the solubility of AgCl (ˆ3)

leads to unstable values of the potential of the Ag—AgCl electrode. In the case of NaCl solutions in N-methylformamide, the e.m.f. could be measured up to a concentration of 0.3 M, whereas for CsCl one often obtains overestimated e.m.f. values, which were erroneously used earlier (^{2}) for calculating activity coefficients. The behavior of Ag—AgCl electrodes in N-methylformamide will be considered in greater detail in another paper.

In formamide the solubility of AgCl in NaCl and CsCl solutions is considerably lower; therefore measurements of the e.m.f. of cell (B) with CsCl were possible up to a concentration of 0.7 M, above which a strong scatter was also observed. The results of e.m.f. measurements for cells (A) and (B) are given in Table 1, together with the maximum deviations of the e.m.f. from the mean value. The activity coefficients were calculated from the e.m.f. data by the least-squares method using the equation for the activity coefficients with a linear term. The dependence of the activity coefficients on the solution concentration is shown in Fig. 1. For comparison, the dependence of $\lg \gamma_\pm$ on $\sqrt{M}$ for CsCl in H_2O at 25° (^{4}) is also shown there.

Fig. 1. Dependence of $\lg \gamma_\pm$ on $\sqrt{M}$: 1—NaCl in N-methylformamide; 2—CsCl in N-methylformamide; 3—$\lg \gamma_{\mathrm{DII}}$ for NaCl in N-methylformamide; 4—$\lg \gamma_{\mathrm{DII}}$ for CsCl in N-methylformamide; 5—$\lg \gamma_{\mathrm{DII}}$ for CsCl in formamide; 6—CsCl in formamide; 7—$\lg \gamma_{\mathrm{DII}}$ for CsCl in H_2O; 8—CsCl in H_2O according to (4).

Table 1

M	N-methylformamide, NaCl: e.m.f. in (cell A)	N-methylformamide, NaCl: max. dev., mV	N-methylformamide, NaCl: $\gamma_\pm$	N-methylformamide, CsCl: e.m.f. in (cell A)	N-methylformamide, CsCl: max. dev., mV	N-methylformamide, CsCl: $\gamma_\pm$	CsCl, formamide: e.m.f. in (cell B)	CsCl, formamide: $\gamma_\pm$
0,01	−0,1170	–	0,964	−0,1162	0,3	0,969	–	–
0,02	−0,0803	+0,96	0,963	−0,0809	–	0,963	–	–
0,03	–	–	–	–	–	–	2,1562	0,901
0,035	−0,0535	+0,14	0,949	−0,0527	−0,08	0,954	–	–
0,05	−0,0351	−0,07	0,950	−0,0345	−0,43	0,952	2,1306	0,865
0,06	–	–	–	−0,0255	+0,41	0,944	2,1224	0,856
0,07	−0,0181	+1,40	0,945	−0,0178	−0,34	0,940	2,1138	0,853
0,08	–	–	–	–	–	–	2,1083	0,843
0,1	–	–	0,940	–	–	0,931	2,0982	0,832
0,2	0,0348	–	0,926	–	–	–	2,0643	0,791
0,3	0,0566	+0,79	0,943	–	–	–	2,0457	0,763
0,5	–	–	–	–	–	–	2,0216	0,727
0,6	–	–	–	–	–	–	2,0127	0,726
0,7	–	–	–	–	–	–	2,0070	0,694

Since for CsCl in N-methylformamide at concentrations above 0.1 M it was not possible to measure the activity coefficients by the e.m.f. method, we attempted to do this by the cryoscopic method. The depression of the freezing points of CsCl solutions in N-methylformamide was determined by the kinetic method (^{5}) with a Beckmann thermometer. Unfortunately, the melting temperatures determined from heating curves proved to depend on

preliminary thermal conditioning both in the case of the pure solvent and in the case of the salt solution, probably because of the existence of nonequilibrium forms. This circumstance did not make it possible to attain an accuracy of measurement better than ±0.015°. In Fig. 2 two series are given for the relative depression of the melting temperature θ for solutions of CsCl in N-methylformamide. As can be seen from the figure, although the curves obtained by different methods do not coincide with one another, the general course of the curve $\frac{\theta}{M} - M$ shows that, in the concentration region above $0.1\,M$, the activity coefficients of CsCl decrease more slowly than in the region of low concentrations, which is in qualitative agreement with the curve for $\lg \gamma_\pm$ of CsCl in Fig. 1.

As can be seen from Fig. 1, the curves $\lg \gamma_\pm - \sqrt{M}$ for NaCl and CsCl in N-methylformamide and for CsCl in formamide lie higher than the limiting-law straight line of the Debye–Hückel theory. For a more detailed comparison

Fig. 2. Relative depressions of the freezing temperatures of CsCl solutions in N-methylformamide: 1—without preliminary thermal conditioning, 2—with preliminary thermal conditioning

Figure 2: Fig. 2. Relative depressions of the freezing temperatures of CsCl solutions in N-methylformamide: 1—without preliminary thermal conditioning, 2—with preliminary thermal conditioning

of the results with the electrostatic Debye—Hückel theory, one should use the second approximation of this theory (^{6}), which takes into account the distance of closest approach of the ions a^0, despite the lack of knowledge of the exact value of this quantity. From the regularities in the change of $\lg \gamma_{\pm}$ in aqueous solutions it is known (^{7}) that the value of a^0 for salts of strongly hydrated cations is appreciably greater than the sum of the crystallographic radii. In addition, in its physical meaning the value of a^0 cannot be smaller than this sum.

Fig. 2. Relative depressions of the freezing temperatures of CsCl solutions in N-methylformamide: 1—without preliminary thermal conditioning, 2—with preliminary thermal conditioning.

For comparison of the regularities for $\gamma_{\pm}$ of NaCl and CsCl in water, formamide, and N-methylformamide, let us assume that the distances of closest approach of their ions do not change greatly on going from one solvent to another. Then, taking for CsCl a^0 equal to the sum of the crystallographic radii, 3.46 Å, and for NaCl in N-methylformamide the value 4.8 Å, as in water (^{8}), we obtain, with the aid of the second-approximation equation of the Debye—Hückel theory, the curves $\lg \gamma_{\mathrm{DII}}$ for the activity coefficients shown in Fig. 1. As can be seen from the figure, the activity coefficients of NaCl and CsCl in N-methylformamide at concentrations above $0.05\,M$ already appreciably exceed the values of $\lg \gamma_{\mathrm{DII}}$. Moreover, on the curve $\lg \gamma_{\pm} - \sqrt{M}$ for NaCl a flat minimum is observed already in the region of $0.2\,M$. It is interesting to note that in N-methylformamide the values of the activity coefficients for NaCl and CsCl differ from one another considerably less than in water, and up to a concentration of $0.05\,M$ both curves coincide within the experimental error, which requires practically identical a^0 values in the equation for $\lg \gamma_{\mathrm{DII}}$, equal to 8 Å.

As for CsCl in formamide, the values of $\lg \gamma_{\mathrm{DII}}$ with $a^0 = 3.46$ Å turn out to be larger than the experimental ones. If a^0 is calculated from the experimental data in the concentration interval up to $0.7\,M$, one obtains a value of a^0 close to 3 Å, which is smaller than the sum of the crystallographic radii, i.e., close to the value obtained for aqueous solutions (^{7}). Thus, in this case a formal analogy of the properties of the solutions is observed.

To estimate the change in the solvation of CsCl on going from water to formamide and N-methylformamide, the standard molal e.m.f. (E^0) in the three solvents was determined from the e.m.f. of cell ( ) for a cesium amalgam containing 0.44% Cs by weight. For water, formamide, and N-methylformamide the -

The values of E^0, respectively, are 2.0536 V, 1.9696 V, and 1.9073 V. The change in the logarithm of the activity coefficient of CsCl in the standard state on going from water to another solvent, $\lg \gamma_0$, determined from (^{9}), is 0.710 for formamide and 1.237 for N-methylformamide. If the solvation energy of the ions is represented as the sum of two terms—the Born term and a term determined by the interaction of the ion with the nearest solvent molecules (A_{sol}), then the value ΔA_{sol} for the transfer of the ions* Cs^+ and Cl^- from water to formamide is 1.94 kcal/mol, and to N-methylformamide 3.38 kcal/mol. This shows that the energy of nearest solvation of ions in a CsCl solution increases somewhat on going from a solution in water to formamide and N-methylformamide. The increase in ΔA_{sol} can be understood if one takes into account that the dipole moment of the formamide and N-methylformamide molecules is considerably larger than in water (^{10}); therefore, in these solvents the energy of ion-dipole interaction increases in comparison with water. However, the dipole moments of the formamide and N-methylformamide molecules differ only slightly (^{10}), so that the change in ΔA_{sol} cannot be attributed solely to an increase in the dipole moment of the solvent. For a more detailed analysis of the influence of the nature of the solvent on the change in the activity coefficients of ions with concentration, additional data are required on the values of $\gamma_\pm$ for different salts in various solvents with high dielectric constants; however, on the basis of the data obtained in this work on the activity coefficients of NaCl and CsCl in formamide and in N-methylformamide, it can already be concluded that, with increasing dielectric constant of the solvent, in a number of cases the positive deviations of $\gamma_\pm$ from the electrostatic Debye-Hückel theory increase, whereas, according both to the theory itself and to its statistical justifications (^{11}), the opposite should be expected. At the same time, as is seen from the example of CsCl, where there is no reason to expect an increase of a^0 from 3 to 8 Å on going from formamide to N-methylformamide, these deviations cannot be explained only by an increase of a^0.

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* The expression for ΔA_{sol} and the method of calculation are given in ([9]).

Note: Figure translations are in progress. See original paper for figures.