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Abstract

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Dielectric Permittivity of Organic Solvents and the Thermodynamic Properties of Sodium Iodide Solutions in Water, Methanol, Acetone, and in the Mixed Solvent Dioxane-Water

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If, in the limiting-dilution region of solutions of strong electrolytes in media with high values of dielectric permittivity (DP), sufficiently accurate calculations are possible that include the DP of the pure solvent, then the use of this quantity in treating experimental data relating to medium and high concentrations gives rise to legitimate doubts. First, the DP of the medium itself changes with concentration, and beyond the boundary of complete solvation it generally loses its meaning, since here the determining factor becomes the DP of the electrolyte, which also changes with increasing content (1,2). Second, with increasing concentration the individual properties of the solvent molecules, i.e., short-range interaction forces that suppress Coulombic long-range action, come increasingly to the fore. This idea was expressed relatively long ago by O. Ya. Samoilov (3), and in recent years Debye arrived at the same conclusion, as is evident from his introductory lecture at the Symposium on Electrolytes in 1959 (4).

The thermochemical characteristics of sodium iodide solutions in various media presented by us in this article, in our opinion, illustrate these propositions well.

In our laboratory, using a special calorimeter adapted for the study of non-aqueous systems, with a thermistor and a number of other improvements (5,6), integral heats of solution (ΔH_m) of sodium iodide in methanol (7) and acetone (8) were measured over the entire concentration range at 25°. In addition, one of the authors re-examined ΔH_m for NaJ in water, since the tabulated data raised certain doubts (9,10).

In Fig. 1 the curves $\Delta H_m = f(m)$, where m is the concentration in moles per 1000 g of solvent, refer, respectively, to (a) solutions in acetone (DP = 19.1); (b) solutions in methanol (DP = 31.5); and (c) solutions in water (DP = 78.5) at 25°.

As we have already indicated (7,8,11,12), the heats of solution in the mentioned organic media are more exothermic, and the change in ΔH_m with increasing salt concentration is significantly steeper than in water. The latter is undoubtedly connected with the formation of ion pairs in solvents with lower DP (12).

For a clearer determination of the role of DP, we applied the method of "modeling" media with DPs corresponding to those of acetone, methanol, and ethylene glycol (DP = 37.7), using mixtures of dioxane and water of different composition as the solvent. The DP of this system has been characterized in sufficient detail as a function of composition and temperature by Akerlöf (13). We prepared mixtures of dioxane and water with DPs equal to 19.1 and 31.5. In the same Fig. 1, curves (g) and (d) characterize $\Delta H_m = f(m)$ for "pseudoacetone" and "pseudomethanol," respectively. Because of the different solubility, ΔH_m was determined for acetone up to $m = 2.68$; for methanol, up to $m = 5.0$; for the aqueous-dioxane mixture with DP–19.1 up to $m = 1.57$; and for the mixture with DP = 31.5, up to $m = 2.65$ moles per 1000 g of solvent.

It is evident that even the first integral heats of solution ΔH_0 at $m = 0$ do not coincide, although these quantities are determined by the algebraic sum of the lattice energy of NaI and the heats of solvation of the cation and anion. Thus, in acetone $\Delta H_0 = -10.54$ kcal/mol, whereas in "pseudoacetone" it is -6.63 kcal/mol. The same quantities for the pair methanol and "pseudomethanol" are, respectively, -7.25 and -5.44 kcal/mol NaI. Consequently, the chemical heats of solvation in acetone and methanol are appreciably more exothermic than in model mixtures of dioxane and water. Even here, at infinite dilution, the role of the nature of the solvent particles and of the structure of its liquid phase is clearly manifested. Apparently, the presence and increase in the number of dioxane particles disrupts the primary structure of water, reducing the endothermic term associated with the expenditure of energy required to detach water molecules from its tetrahedral framework so that they may enter the solvation shells of ions (14, 15).

Of particular interest is the form of the curves $\Delta H_m = f(m)$ in the case of the model systems (curves g and d in Fig. 1). We see that after a rather steep drop in the region of small concentrations, already at $m \simeq 0.7$-1.1 mol NaI per 1000 g of solvent they become horizontal; i.e., ΔH_m, within the limits of measurement accuracy ($\sim \pm 0.5\%$), ceases to depend on concentration. For comparison, Fig. 1 also gives a graph of the dependence $\Delta \bar{H}_m = f(m)$ for a weak electrolyte, picric acid, in methanol (16). Here the transition to the horizontal coincides with the concentration at which the degree of dissociation of the acid approaches zero. It may be assumed that NaI in mixtures of dioxane and water likewise behaves like a weak electrolyte, which agrees with the results of work (17) on the determination of the dissociation constants of strong (in water) electrolytes in dioxane-water solvents with a dioxane content of 20% and higher.*

[Figure 1 and Figure 2 are visible on the page.]

Fig. 1. Integral heats of solution of sodium iodide in acetone (a) (DP = 19.1), methanol (b) (DP = 31.5), water (v) (DP = 78.5), aqueous dioxane solvent (g) (DP = 19.1), and aqueous dioxane solvent (d) (DP = 31.5).

Fig. 2. First heats of solution of sodium iodide in various solvents: **1**—in

aqueous dioxane solvents of different composition with DP = 19.1; 31.5; 37.7 and in water. **2**—in acetone, methanol, ethylene glycol, and water.

* In our case, the model systems with DP = 19.1 and DP = 31.5 contain 68.15 wt.% and 53.55 wt.% dioxane, respectively.

The role of the chemical nature of the solvent particles appears especially sharply if one considers the comparison made by us in Fig. 2. Here the solid line shows the dependence of the first heats of solution ΔH_0 at $m = 0$ on the dielectric constant of the initial dioxane-water mixtures. The third point from the left corresponds to $D = 37.7$, corresponding to "pseudo-ethylene glycol," and the extreme right-hand point is ΔH_0 for NaI in water. We see that in this case all four points lie on one straight line, i.e., D retains its determining character, since the liquid phase consists of the same molecules of dioxane and water, only in different proportions, and the electrolyte is at infinite dilution. An analogous picture is given in the work of A. F. Kapustinskii and co-workers ([18]) for integral heats of solution of KCl in dioxane-water mixtures of various compositions and in water ($m \simeq 0.058$). Here, apparently, one may agree with the conclusions of work ([18]). All our data confirm that so long as there are enough water molecules to form filled first solvation layers around the ions, the environment of the hydrated ions contains a mixed solvent only slightly polarized by the action of the ionic fields. As a result, with a smooth change in the composition of the dioxane-water medium, the composition of the solvates remains constant and the linear dependence on D is logical. Unfortunately, the sharp decrease in the solubility of NaI with increasing dioxane content does not make it possible to pass experimentally beyond the limit of complete hydration, after which a violation of linearity should be expected.

A quite different picture is obtained if the first heats of solution of NaI in acetone, methanol, ethylene glycol* and water are plotted as a function of D of these pure solvents (Fig. 2, dashed line). No rectilinear dependence can be involved here. The individuality of the nature of the molecules and the structure of the liquid phase come to the fore, despite the infinite dilution of the solution. It seems to us that the facts presented rather convincingly confirm the propositions stated at the beginning of this article.

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* The integral heats of solution of sodium iodide in ethylene glycol were measured in our laboratory by V. P. Tungusov.

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

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