On Deviations of the Thermodynamic Properties of Solutions of Strong Electrolytes from the Limiting Law in the Debye Region of Concentrations

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Abstract

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On Deviations of the Thermodynamic Properties of Solutions of Strong Electrolytes from the Limiting Law in the Debye Region of Concentrations

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In the Debye–Hückel theory (^{1}) the solvent is treated as a continuous medium characterized by a macroscopic dielectric constant D_0, independent of the distance from the ion center and of the electrolyte concentration; in calculating the free energy of the solution, no account is taken of the contributions introduced by the presence of ion pairs and by the dependence of the free energy of solvation on concentration. It is still insufficiently clear how essential the inclusion of these phenomena in the Debye concentration region (^{2}) is for explaining deviations from the limiting law. Evidently, their role will manifest itself to different degrees in different properties of solutions. The non-electrostatic contributions to the free energy of a solution, associated with the formation of ion pairs (ΔG_c) and with changes in the structure of the solvent (ΔG_p), may be small in comparison with the electrostatic contribution to the free energy ΔG_D, determined by the equation of the first approximation of Debye–Hückel (^{1}); however, their temperature derivatives may, generally speaking, be of the same order of magnitude. Therefore, in the case of heats of dilution one may expect significant deviations of the experimental values of the heats of dilution ΔW from the theoretical ΔW_D, especially at temperatures close to the melting point t_m of the solvent, when its structure is little disturbed by thermal motion.

For the heats of dilution of nonaqueous solutions of strong electrolytes in the Debye region, or at its boundary, the literature contains data only for NaCl in ethylene glycol at 25° (^{4}) ($D_0 = 37.7$), HCl in mixtures of H_2O–dioxane of various composition at 0-50° (^{5}) ($D_0 = 10 \div 80$), and for intermediate heats of dilution $\Delta W_{c_1}^{c_2}$ of solutions of NaCl, NaBr, and NaJ in formamide at 25° (^{6}) ($D_0 = 109$). In the first two cases, discrepancies between ΔW and ΔW_D of the same order as for aqueous solutions are observed. In the case of formamide, $\Delta W_{c_1}^{c_2}$, unlike aqueous solutions at the same concentrations, are opposite in sign to the theoretical values.

We measured the integral heats of solution ΔH_m of NaCl, KCl, RbCl, and CsCl in H_2O_2 at 0° ($D_0 = 84.2$; $t_\mathrm{m} = -0.49°$ (^{3})) from $c = 0.004$ mol/l and higher. The measurements were made in an ice calorimeter. The accuracy of determining ΔW from ΔH_m is ±7-15% in the case of NaCl solutions in 99.99%

H_2O_2 and ±10-30% in all other cases. From the graphs in Fig. 1 it is seen that the divergence of ΔW and ΔW_D in sign begins in H_2O_2 at much lower concentrations than in H_2O.

Allowance for $D = f(c)$, multiple collisions, the intrinsic volume of ions, change in the distance of closest approach of ions a with temperature, etc., is not capable of explaining the appearance of positive heats of dilution in the Debye concentration region. The only conceivable causes of this are the formation of ion pairs and a change in the structure of the solvent with concentration.

Accounting for ΔG_c in the most general form can be carried out on the basis of the Brønsted-Guggenheim theory of "specific interaction" of ions ([7,8]). Guggenheim ([8]) in fact assumes $U_c(r_{ij}) = u_k(r_{ij})$, where $u_k(r_{ij})$ is the potential energy of the quantum-mechanical interaction. The actual picture is more complicated. We regard the specific interaction of ions as the result of their approach to distances $r_{ij} < a_i + a_j$ (a_i and a_j are the radii of the solvation spheres of the ions). Then, for any ion pair,

$$U_c(r_{ij}) = \begin{cases} 0, & \text{for } r_{ij} > a_i + a_j, \\ U_c(r_{ij}), & \text{for } a \le r_{ij} < a_i + a_j, \\ +\infty, & \text{for } r_{ij} < a. \end{cases} \tag{1}$$

For $a < r_{ij} < a_i + a_j$, the inequalities $1 < D(r) < D_0$ and $u_k(r_{ij}) < 0$ hold. If $r_{ij} = a + 4r_p$ (r_p is the radius of a solvent molecule), then one may consider ([9]) that $D(r) \approx n^2 \approx 3 \div 4$ (n is the refractive index). This gives

$$-\left[u_e(r_{ij}) + u_k(r_{ij})\right] \gg kT, \tag{2}$$

where

$$u_e(r_{ij}) = \frac{e_i e_j}{r_{ij} D(r)},$$

and e_i and e_j are the ion charges. According to (2), strong association should occur, which is not observed experimentally in the case of strong electrolytes. This can be explained by the fact that, during the formation of an ion pair, partial desolvation of the ions occurs. The difference between the solvation potential energies of the ion pair and of the free ions, $\Delta u_c(r_{ij})$, plays the role of an effective repulsion energy of the ions, so that finally*

$$U_c(r_{ij}) = u_e(r_{ij}) + \Delta u_c(r_{ij}) + +u_k(r_{ij}) \tag{3}$$

and

$$|U_c(r_{ij})| < kT. \tag{4}$$

In the Debye-Hückel theory, relation (4) is achieved artificially, by taking $D(r) \equiv D_0$ for all r_{ij}, which contradicts the actual physical picture of the phenomenon. Therefore, the introduction into (3) of an expression of the type $\Delta u_c(r_{ij})$, describing short-range (but more "long-range" than the corresponding term $u_k(r_{ij})$) repulsive forces, is physically necessary.

Fig. 1. Integral heats of dilution at 0°. A—limiting law, H_2O_2; B—limiting law, H_2O. 1—KCl in H_2O (recalculated by us to 0° according to data (^{11}) at 12.5°), H_2O_2 99.99%: a—NaCl, b—KCl, v—RbCl, g—CsCl. H_2O_2 94.29%: d—KCl. Solid lines—experimental data; dashed lines—theoretical according to equation (6).

Since the potential energy of solvation depends on the structure of the solution, and the latter changes with concentration, $U_c(r_{ij})$ must depend on concentration through $\Delta u_0(r_{ij})$. But $\Delta u_c(r_{ij})$ is a difference quantity; in a first approximation it may be assumed that the change in the structure of the solution affects equally the solvation potential energy of the ion pair and of the free ions, and that $\Delta u_c(r_{ij})$ is independent of concentration. This assumption is the more accurate, the lower the concentration.

With the same degree of approximation it may be assumed that, in the Debye concentration region, ΔG_p contributes to ΔW a term of the form $\Delta W_p = K_2 c$.

It is not at present possible to find an explicit expression for $U_c(r_{ij})$. Let us denote

$$\beta = \int \left(e^{-\frac{U_c(r_{ij})}{kT}} - 1 \right) d\omega \quad \text{and} \quad \varphi = \frac{1}{V} \frac{\partial V}{\partial T}. \tag{5}$$

Using the usual thermodynamic relations, and taking ΔW_p into account, we obtain

$$\Delta W = \Delta W_D + K_1 c + K_2 c = \Delta W_D + Kc, \tag{6}$$

where

$$K_1 = RT^2 N \cdot 10^{-3} \left(\varphi \cdot \beta - \frac{\partial \beta}{\partial T} \right) \tag{7}$$

(N is Avogadro' s number).

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* In such a model, the requirement $U_c(r_{ij}) = 0$ for $r_{ij} \geq a_i + a_j$ is purely formal. It is necessary in order to satisfy the condition $\Delta G_c = 0$ for $r_{ij} \geq a_i + a_j$. This can also be achieved in other ways; however, since the integral in (1) is not evaluated further, the choice of method is of little importance.

It is seen from Fig. 1 that satisfactory agreement between calculation and experiment holds up to $c = 0.025$, i.e., up to the boundary of the Debye region. For comparison, the corresponding calculations were also carried out from literature data for NaCl in ethylene glycol at 25° (4), NaCl, NaBr, and NaJ in formamide at 25° (6), NaCl in H_2O at 25 and 10° (10), and KCl in H_2O at 25, 12.5, and 0° (11). The curve of ΔW for KCl in H_2O at 0° is given as typical for aqueous solutions of the group of salts studied, NaCl—CsCl. It turned out that agreement between the calculated and experimental values of ΔW is observed up to the highest concentrations, $c > 0.1$, in the case of aqueous solutions, and up to the lowest in the case of solutions in H_2O_2; the sharpest divergence, after a certain concentration is reached, between the experimental and calculated values of ΔW occurs in H_2O_2, and the least sharp in H_2O. Ethylene glycol and formamide occupy an intermediate position.

According to equations (3) and (4), $U_c(r_{ij})$ is a small difference of large quantities; therefore small changes in $\Delta u_c(r_{ij})$ upon changes in the structure of the solution can cause appreciable changes in K_1; at the same time K_2 will also change. Consequently, sharper divergences between the calculated and experimental ΔW should be expected in those cases where the structure of the solution changes more strongly with concentration.

Table 1

Solvent	t°C	$-\delta \cdot 10^3$	$\varphi \cdot 10^4$	Source
Water	0	4.56	−0.7	(19, 21)
Water	25	4.54	2.57	(19, 20)
Ethylene glycol	25	5.16	6.48	(22)
Formamide	25	6.54	7.41	(6)
H_2O_2	0	7.55	8.41*	(3)

* In the interval 0–10°.

Starting from the known information and ideas on the structure of H_2O (12) and of dilute aqueous solutions of salts (13–15), it may be assumed that the change in the structure of aqueous solutions with concentration, in the case of small spherical ions, will be small, at least up to $c = 0.1$. According to Randall’ s X-ray data (16), H_2O_2 is a liquid with close packing of molecules. It is reasonable to expect that the same ions will disturb, to a greater extent, the structure of a closely packed liquid with nonspherical molecules (H_2O_2) than that of water. It is known, further, that the perturbing action of ions on the structure of a liquid is to a certain extent similar to the action of temperature (see, for example, (17,18)). Therefore one may think that ions will have a stronger influence on the structure of that liqfor which the structure is more sensitive to changes in temperature. The latter can be characterized by the coefficients $\delta = \frac{1}{D_0}\frac{\partial D_0}{\partial T}$ and φ (Table 1), from comparison of which it is seen that, in terms of structural stability, H_2O and H_2O_2 occupy the extreme positions. Thus, the conclusions following from equation (6) are in qualitative agreement with the structural properties of the solvents.

The difference in the course of the experimental curve ΔW for KCl in 99.99% H_2O_2 from the course of the curves ΔW for NaCl, RbCl, and CsCl, in our opinion, is connected with $K \approx 0$. A known confirmation of this may be seen in the fact that the sign of the derivative $\partial(\Delta W)/\partial\sqrt{c}$ in this case is the same over the entire length of the curve ΔW as in all the other cases at higher concentrations. Another confirmation is provided by the simplest model calculation, showing the possibility that $[U_c(r_i)]_{\mathrm{KCl}} \approx 0$. Finally, from data on the lowering of the freezing temperature of H_2O_2 in the presence of NaCl (23) and KCl (24), it follows that Δt is larger in KCl solutions, which may also serve as an indication of the smaller association of KCl.

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