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Abstract

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ON THE INFLUENCE OF THE SOLVENT ON IONIC AND ION-MOLECULAR REACTIONS

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It is known (^{1}) that if the solvent is regarded as a homogeneous continuous dielectric, and the transition complex and the ion as charged spheres immersed in this dielectric, then in the case of ionic and ion-molecular reactions there must be a linear dependence of the logarithm of the reaction-rate constant $\lg k$ on the reciprocal of the dielectric constant, $1/D$.

Analysis of a large body of experimental data shows that the linearity of the dependence $\lg k = f(1/D)$ is indeed observed in many reactions of the indicated type whose rates were measured in mixtures of two solvents. However, very often substantial deviations (^{2}) of the dependence $\lg k = f(1/D)$ from linearity are observed both in the study of reactions in mixtures and in individual solvents. Moreover, there are cases (^{1,2}) in which, for one and the same reaction, the indicated linear dependence is obeyed in mixtures of some solvents and is not obeyed in mixtures of others. Deviations of this kind are usually explained by selective solvation, meaning that the more "polar" component is present near the ion in excess relative to the average composition of the solvent. Quite apart from the fact that there is no rigorous definition of solvent polarity (see below), such an explanation is completely unsuitable in those cases where the influence on the kinetics of individual solvents, rather than their mixtures, is studied. Therefore the natural conclusion suggests itself that either electrostatic interaction plays a secondary role in chemical reactions of the ionic and ion-molecular type, or the existing electrostatic theories of this interaction are too approximate. The first conclusion immediately falls away, since there are many facts indicating precisely the predominance of Coulomb interaction, and perhaps the only fact against electrostatic theories is their disagreement with kinetic data. It is therefore natural that, before rejecting a theory based on certain experimental facts but whose conclusions do not agree with other experimental facts, one should try to clarify the correctness of the premises of the theory.

We have already pointed out at the beginning that the modern treatment of the influence of the solvent on the kinetics of chemical reactions is based on electrostatic theories of interaction between the dissolved substance and the solvent, proceeding from the manifestly incorrect conception of a solution as a continuous homogeneous dielectric in which dissolved particles are distributed according to a known law; but as early as 1933, i.e., during the period when these theories were being created, Bernal and Fowler (^{3}) proposed another method of approaching this question. Bernal and Fowler showed that the hydration energy of ions can be calculated with good approximation from the molecular structure of salt solutions in water. Since then a number of authors (see the review of papers in (^{4})) have attempted to improve this method of calculation. As a result of a generalization (^{4}) of such attempts, a formula was given for calculating the free energy of solvation

ions. This formula makes it possible, to a good approximation, to calculate the energy of solvation of ions in water. With its aid N. Izmailov (^{5}) succeeded in quantitatively explaining the influence of the solvent on the energy of solvation, dissociation, solubility, and other properties of electrolytes, which indicates the correctness of the assumptions underlying the derivation of the formula and serves as yet another confirmation of the validity of the electrostatic approach to explaining the properties of electrolyte solutions. Incidentally, in addition to taking Coulomb interaction into account, the indicated formula also includes quantum-mechanical effects, but in comparison with the electrostatic ones they are not of great significance. However, owing to a number of assumptions that are not sufficiently justified, calculation by the indicated formula in nonaqueous solvents gives rather large discrepancies with experiment.

Taking into account the errors of previous authors and basing ourselves on the molecular structure of the solution, we derived (^{6}) a formula that makes it possible to calculate, with satisfactory accuracy, the solvation energies of alkali-metal halide salts in various solvents:

$$\Delta Z_x = -nE\,(0.958\,\mu + 0.458\,\mu_i) + nb\,(\bar{\mu} + \mu_i)^2/r^3 - \\ -e^2(1-1/D)/2r_s + Z_s, \qquad (1)$$

where n is the coordination number; E is the field strength at the center of the dipole; μ is the permanent dipole of the molecule with a correction for thermal motion; μ_i is the induced dipole; b is a geometric factor; r is the distance from the center of the ion to the center of the resultant dipole $(\bar{\mu}+\mu_i)$; e is the charge of the ion; r_s is the radius of the solvate sphere; Z_s is the London (^{7}) dispersion term.

The quantities E and μ_i are determined from the system of equations

$$\mu_i = \alpha E, \qquad E = e/r^2 - 2b\,(\bar{\mu} + \mu_i)/r^3,$$

where α is the electronic polarizability, determined from the molar refraction.

We found, by plotting the values of α calculated from the formula $\alpha = (n_d^2 - 1)M/(n_d^2+2)d$ (n_d is the refractive index, M is the molecular weight, d is the density), that for all alcohols (up to C_8, except C_5 and tertiary alcohols) and ketones a linear dependence is obeyed: $\alpha = (183/D - 2.3)$ Å^3. Substituting this expression for α through the dielectric constant into formula (1), we found that ΔZ_x is well approximated by the polynomial:

$$\Delta Z_x = a_1/D^4 + a_2/D^3 + a_3/D^2 + a_4/D + a_5. \tag{2}$$

All coefficients a_i are calculated from formula (1).

It is of interest that the equation (2) obtained by us gives the correct character of the dependence of the solvation energy in alcohols on the dielectric constant (^{6}).

Thus, we see that calculation of the solvation energy on the basis of taking into account the molecular structure of electrolyte solutions gives a complex form of the dependence of ΔZ_x on $1/D$ (see formula (2)), and not a linear one, as follows from Born' s formula.

Earlier (^{8}) we proposed a cycle according to which the free energy of activation $\Delta Z^{\neq}$ of a chemical reaction is represented as the sum

$$\Delta Z^{\neq} = \Delta Z_0^{\neq} + \Delta Z_s^{\neq} + \Delta Z_x,$$

where $\Delta Z_0^{\neq}$ is the free energy of activation of the given reaction in vacuum, and $\Delta Z_s^{\neq}$, ΔZ_x are the solvation energies of the activated complex and of the reactants, respectively. Since the quantities $\Delta Z_0^{\neq}$ and $\Delta Z_s^{\neq}$ change little in going from solvent to solvent, the change in $\Delta Z^{\neq}$, and hence in $\lg k$, in the case of ionic and ion-molecular reactions will be determined practically completely by the change in ΔZ_x of the ion participating in the reaction. But since ΔZ_x is a complex function of $1/D$ (see (2)), $\lg k$ will be the same complex function of $1/D$, which is in fact most often observed in practice.

But since, in studying kinetics in mixed solvents, one often encounters cases in which the dependences of rate constants on the dielectric properties of the medium predicted by the simplest electrostatic theories (see above) are fulfilled, the natural question arises: how does the theory we propose explain this fact? It turns out that this problem is solved quite simply.

Considering equation (1), it is easy to see that a large part of the energy of a solvated ion is due to interaction with solvent molecules that are in direct contact with the ion, and only one Born term takes into account the interaction with the solvent as a whole (the energy of interaction of the molecules of the solvation complex Z_s with neighboring solvent molecules is small and may be neglected). If the energy of interaction of molecules of one component of a mixed solvent with the ion is considerably greater than the energy of interaction with molecules of the other component, then, independently of the stoichiometric composition of the mixture over wide limits, the coordination layer of the solvation complex will be formed from molecules of the first component. This means that in equation (1) all terms except the Born term will remain constant until the quantity of the more strongly interacting component becomes insufficient to fill the coordination spheres of all ions. Consequently, as long as this component is present in excess, the free energy of solvation of the ion—and hence also the free energy of activation in the case of a spherical complex—must depend linearly on $1/D$. When a deficiency of the strongly interacting component begins to appear, the dependence of these quantities begins to deviate from linearity. The work in (9) may serve as an illustration of this.

In those cases where there is no predominant interaction of one of the solvent components with the dissolved substance, the dependences of $\lg k$ and ΔZ_x on $1/D$ may deviate strongly from linearity at any mixture compositions, as is observed in the case investigated in (10).

In the discussion given above we deliberately avoided the expressions "more polar component of the solvent" and "less polar component." The point is that the solvent which has the larger dielectric constant and dipole moment is usually considered the more polar one. Thus, for example, water is considered a much more polar solvent than methanol. But from formula (1) we see that the solvation energy of an ion (and consequently the activation energy as well) is determined not only by the dielectric constant and the dipole, but to a considerable extent also by such quantities as the polarizability of the molecule, its dimensions, and the distribution of charge in the molecule. Therefore there is nothing surprising in the fact that, for example, the solvation energy of J^- in water is 62 kcal/mole, and in methanol 61.4 kcal/mole, i.e., there is no noticeable difference; but it is precisely the solvation energy, as we have already pointed out more than once, that determines all the thermodynamic properties of the dissolved substance and governs the course of the chemical process. Consequently, the polarity of the solvent, if it can be applied at all, can be applied only within narrow limits.

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