

Study of The Effect of Solvation on Thermodynamic Parameters

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ABSTRACT

In the present research paper, we study about the effect of solvation on thermodynamic parameters. The main difference between reactions in solution and in the gas, phase is the formation and participation of ions. It is pertinent to consider the process of forming ions. It is pertinent to consider the process of forming ions from neutral molecules and the effect of solvent as the difference between ions in situ and in the gas, phase is the formation and participant of ions.

Keywords : Alkaline, Ester, Thermodynamic, Kinetic, Hydrolysis.

I. INTRODUCTION

It has been found that the change in heat content, ΔH^0 , and the change in entropy, ΔS^0 , in the gas phase of HCl are 327 K. Cals. and 11.6 E.U. respectively while in the aqueous solution of HCl these are about -25 K. Cals. and -19 E.U. respectively. The reaction in the gas phase, $\text{HCl}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{Cl}^-(\text{g})$ is thermodynamically unfavorable from an energetic point of view. The entropy increase, though favorable, is not sufficient to cause the reaction to go to any perceptible degree at ordinary temperatures. The aqueous solution $\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ is thermodynamically favourable in the same reaction. The change in the lowering of ΔH^0 in the gas form a large positive value (327 K. cal) to a small negative value (-25 K. cal) in solution is noteworthy¹. Thus,

the heat of solution ions from each other. This is very definite property of the solvent and is related to the orientation of solvent molecule dipoles around the ions in such a way as to lead to electrostatic attraction. The decrease in entropy observed in solution (from E.D. to 19 E.D) is also associated with the orientation of the solvent molecules around the ions with an attendant loss in freedom of motion². It leads to a striking coincidence between such oriented and strongly hold water molecules and "frozen" water molecules.

II. EFFECT OF SOLVATION ON THERMODYNAMIC PARAMETERS

According to this view the loss in entropy in an ionization includes not only the change in entropy of

the molecules which ionize but also the change in entropy of the solvent molecules which surround the ions. An important query in the effect of a change in solvent from water to something less polar³. Table 1 below shows the experimental results of gradually replacing water by molecular dioxan on the ionization of acetic acid.

TABLE – 1
CH₃COOH ⇌ H⁺ + CH₃COO⁻

Solvent	ΔH ⁰ (K.cals)	ΔS ⁰ (E. U.)
Water	-0.09	-22.2
20% Dioxan	-0.06	-24.5
45% Dioxan	-0.45	-30.4
70% Dioxan	-0.62	-40.2
82% Dioxan	-1.35	-50.9

Here also change is merely due to a more negative entropy of ionization. The heat of ionization changes in a direction opposite to that which might have been anticipated. Further prediction of the effect of different solvents on ionic equilibria is not possible. However, certain generalization can be made from a simple electrostatic picture, which views ionization as the separation of two-point charges of opposite sign in a continuous medium. If two such charges of opposite sign in a continuous medium⁴. If two such charges are separated from an equilibrium distancer. *r*, to an infinite distance in a medium of dielectric constant, *D*, then the electrical work done, given by coulomb's law, is

$$W_{el} = \frac{Z_A \cdot Z_B \cdot e^2}{D \cdot r} = -\Delta F_{el} \tag{1}$$

where *F_{el}* is the corresponding change in free energy. From the thermodynamic equation

$$\left[\frac{\delta(\Delta F)}{\delta T} \right]_p = -\Delta S \tag{2}$$

The change in entropy can also be calculated as

$$\Delta S_{el} = -\frac{Z_A \cdot Z_B \cdot e^2}{D \cdot r} \cdot \left[\frac{\delta \ln D}{\delta T} \right]_p \tag{3}$$

If Δ*F* and Δ*S* are known, then Δ*H* can readily be found from Δ*H*=Δ*F* + *T*Δ*S*. The values of *D*, Δ*F_{el}*, Δ*S_{el}* and Δ*H_{el}* for a number of representative solvents are given in Table 2.

TABLE – 2
Calculated Electrostatic Effects in Various Solvents

Solvent	<i>D</i> _{20°C}	Δ <i>F_{el}</i> (K.cals)	Δ <i>S_{el}</i> (K.cals)	Δ <i>H_{el}</i> (K.cals)
Vacuum	1.0	312.0	00	312
Hexane	1.9	164.0	-117	130
Chlorobenzen e	6.65	47.0	-136	7.1
Ethyl alcohol	25.0	12.5	-75	-.95
Water	80.0	3.9	-18	-1.5

For *Z_A* = +1. *Z_B* = -1, and *r* = 1*A*
The free energy change decreases consistently with increasing polarity of the solvent on expected lines. The entropy-change is always negative in a solvent but goes through an apparent minimum for solvents of moderate polarity. It is small for highly polar solvents, very large for solvents of moderate polarity, not so large for non-polar solvents and zero for a vacuum⁵. The entropy decrease is again seen to be a property of the solvent, since, when the solvent is completely removed, there is zero entropy of ionization. If the loss of freedom of solvent molecules when frozen around the ions is consider the variation of Δ*S_{el}* with polarity can be explained.

III. FACTORS RESPONSIBLE FOR

Two assumptions were concluded from the experimental values of the activation energies and entropies of activation for a number of reactions

involving the formation of ions from neutral molecules in a variety of solvents⁶.

1st: The activation energy (E_a) depends on the type of reaction and does not change rapidly from solvent to solvent.

2nd: The entropy of activation (ΔS^*) is always negative and changes with the solvent, becoming more negative as the polarity of the solvent decreases. Consequently, it can be concluded safely that the rates of reactions producing ions in solution increase with the polarity of the solvent and that the increase is governed largely by the change in entropy of activation⁷. To relate the entropy, decrease in going from reactants to activated complex it has been argued as due to the freezing of solvent molecules around the incipient ions. The activated complex is almost an ion pair at its distance of closest approach of at least and exceedingly polar complex approaching an ion-pair. Each and of the polar complex have already accumulated a layer of solvent molecules, whose presence is necessary to allow the process of separating the ions completely to continue. As the separating the ions completely to continue. As the separation occurs, the layer of solvent molecule is completed so that usually no further decrease in entropy occurs in going from the transition state to the products. From the same arguments given in regard to equilibria, the less polar solvents have a greater loss in freedom in becoming frozen to the ion than do the more polar solvents⁸. A polar reactant in a non-polar solvent will also tend to act as a solvating agent is also an established fact. (The hydrogen ion in particular is not formed without a considerable decrease in entropy). As the smaller ions are more highly solvated, the decrease in entropy is greater for a small ion than for a larger one. There may be some cases in polar media where large ions are formed with a positive entropy of activation. The relative insensitivity of the activation energy to the dielectric properties of the medium is not unexpected⁹. Of much

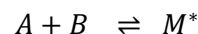
greater importance determine the activation energy for a reaction producing ions, as well as for any other kind of reaction, are the repulsive energies between the reactants as they are brought close together. Most of the factors that determine the energy barrier in forming the activated complex are properties of the reactants, and the solvent plays only a secondary role. Since the solvent lowers the energy of both the reactants and the activated state by solvation, even this effect tends to cancel. Because the activation energy is frequently somewhat greater in the more polar solvents the experimental results goes to the opposite against the expectation that the solvation would be greater for the polar complex¹⁰.

IV. ROLE OF THE DIELECTRIC CONSTANT

Kirkwood has given (a theory for the influence of the dielectric constant of the medium on the free energy of a polar molecule¹¹. By considering electrostatic forces only the difference in free-energy of a dipole in a medium with dielectric constant D and with a dielectric constant of unity is given by

$$\Delta F = -\frac{-\mu^2(D-1)}{r^3(2D+1)} \quad (4)$$

where μ is the dipole moment and r the radius of the molecule. Applying this to the transition state theory for the reactions:



where A , B and M^* are polar species, and for which the rate expression is

$$k = \frac{RT}{Nh} \cdot e^{-\Delta F^*/RT} \quad (5)$$

Integrating these equations, we get

$$\ln k - \ln k_0 = \frac{N(d-1)}{RT(2+1)} \left[\frac{\mu^A}{r_A^3} + \frac{\mu^2 A}{r_B^3} - \frac{\mu_*^2}{r_*^3} \right] \quad (6)$$

where k is the rate constant in the medium of dielectric constant D , and k_0 is the rate constant in a

condenses medium of dielectric constant unity, where the non-electrostatics forces are the same for the activated complex as for the reactants¹². The equation above predicts that, if the activated complex is more polar than the reactants (as would be true if the products are ions) the rate of reaction would increase with the dielectric constant of the medium. For many such reactions in mixtures of two solvents of such composition that the dielectric by plotting $\log k$ against $(D-1)/(2D+1)$. However, this equation is not obeyed, and is not valid in general, if the reaction rates in different solvents of various dielectric constants are compared, using above equation, it is also possible to calculate the electrostatic contribution to the entropy of activation.

$$\Delta S_{el}^* = - \left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \right] \frac{30}{(2D+1)^2} \left[\frac{\delta \ln D}{\delta T} \right]_P \quad (7)$$

Table 3 shows the results of such calculations for a number of solvents¹³.

TABLE – 3

Calculated Values of ΔF_{el}^* , ΔH_{el}^* and ΔS_{el}^* for a reaction

Where, $\left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \right]$

Solvent	D_{20^0C}	ΔF_{el}^* (k.cals)	ΔH_{el}^* (k.cals)	ΔS_{el}^* (E.U.)
Hexane	1.9	11.2	14.4	10.6
Carbon tetrachloride	2.2	13.7	17.1	11.4
Benzene	2.3	13.8	17.2	11.5
Ethyl alcohol	25.0	28.2	31.3	10.4
Methyl alcohol	32.5	28.6	30.8	7.3
Nitrobenzene	35.5	28.8	30.7	6.3
Water	80.0	29.6	30.3	2.4

The values of ΔH_{el}^* are fairly in agreement with experiment for all the polar molecules in that they show little variation from one solvent to another¹⁴. For the polar solvents the values of ΔS_{el}^* are also

reasonable in that they are always negative and decrease with decreasing polarity of the solvent. For the non-polar solvents such as benzene or hexane the calculated results do not agree with experimental values for reactions in such solvents¹⁵.

The prediction is that activation energies would be very large and that the entropies of activation would be only moderately negative. The facts for non-polar solvents are that the activation energies are roughly comparable to those for polar solvents and that the entropies are most negative of all. In these cases, the use of gross dielectric constant is very misleading. The interaction of the ion or dipole with a non-polar molecule is much greater than would be expected. This is particularly true for aromatic solvents, which often are surprisingly good for ionic solutes or ionic reactions.

V. CONCLUSIONS

It can safely be concluded that the use of a classical electrostatic model the dielectric constant is only a very rough guide to the efficiency of a solvent in promoting rates of ionic reactions. There are many examples in which a solvent shows specific effects. Thus, solvents such as nitromethane, although having high dielectric constants, are poor solvent for ionic materials because they cannot effectively coordinate anions. The positive end of the dipole of the solvent molecule is somewhat buried in this case and so is not easily available like the positive hydrogen atom of water or alcohol. The specific effect of the benzene ring is related to the highly polarizable cloud of electrons above and below the aromatic ring. Solvents can be classified such as aromatic, aliphatic, and hydroxylic or donor and non-donor keeping in view of the contributing factors.

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