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ION PAIRS AND SOLVENT-SOLUTE INTERACTION: Conductance of Sodium Chloride in Methanol-H_2O and Glycerol-H_2O Mixtures at Different Temperatures

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The conductance of sodium chloride over the approximate range of concentration up to 0.02M has been measured in methanol-H_2O and glycerol-H_2O mixtures at 25, 30, 35, and 40°. For mixtures with the same dielectric constant, the association constant, K_A, is over an order of magnitude greater in the glycerol mixtures. This mainly is due to effect of hydrogen bond. Glycerol-H_2O is more hydrogen bonded solvent than methanol-H_2O. Also, K_A values increase as the proportion of methanol or glycerol increases in the mixture. The thermodynamic parameters $\Delta H°$, $\Delta G°$, and $\Delta S°$ were also calculated. It turned out that the entire process of ionic association in those systems are endothermic ones. The results are discussed on the basis of ion solvent interaction.

Key words: Conductance, Association, Thermodynamics.

Introduction

In the course of our studies on association phenomena [1-6], it was necessary to study the effect of dielectric constant, D. However, in case of some mixed solvents, which have the same dielectric constant at constant temperature, the major role is due to another factor, i.e., the effect of hydrogen bonding [7]. The present work deals with conductometric measurements of sodium chloride, in some mixed solvents at different temperatures. Our measurements serve mainly two purposes. The first: study the effect on the association of NaCl of solvents which exhibit hydrogen bonding. Conductance of NaCl in glycerol-H_2O and in methanol-H_2O mixtures were measured. The ratios were adjusted in both mixtures to give methanol-H_2O and glycerol-H_2O solutions with the same dielectric constant. Secondly: in mixed solvent, NaCl exhibit ionic association to some extent. Actually interference from the association has been observed in our studies of the formation of complexes in some mixed solvents by using NaCl to control the ionic strength [8]. This interference causes systematic errors in the chemical quantities we want to measure. Therefore, in order to remove the interference we studied ionic association of NaCl in mixed solvents at different temperatures.

Experimental

Chemicals. Sodium chloride, analytical reagent grade, the individual stock solution was standarized by an ion-exchange procedure [9]. Glycerol was purified [10]. Methanol was refluxed over magnesium metal and iodine for 1 hr., then purified by distillation at 65° (boiling point of methanol) in water bath. Deionized distilled water was used for all dilutions.

Electric conductance. The measurements were carried out with conductivity meter, model LBR, equipped with a cell of model LTA 100. Temperature was maintained constant by circulating the cell compartment with water at the proper temperature ±0.01°. Full details concerning electrical equipment and general technique have been outlined elsewhere [1]. The conductance of NaCl has been measured in 20, 30, 40% mehanol-H_2O and in 30, 40, 60% glycerol-H_2O mixtures at 25, 30, 35, and 40°.

Physical properties of solvents. Viscosities and dielectric constants [11] of methanol-H_2O and glycerol-H_2O mixtures at various temperatures are summarized in Table 1.

Results and Discussion

The experimental data were analysed by using the conductance equation

$$\Lambda = \gamma [\Lambda_0 (1+\Delta X/X) - \Delta\Lambda_e] \dots\dots\dots\dots (1)$$

where Λ is the equivalent conductance, Λ_0 is the equivalent conductance at infinite dilution, Λ_e is the electrophoresis term, X is the field strength in volt cm^{-1}, ΔX is the relaxation effect correction to the field strength and, γ is the degree of dissociation.

The above equation is a version of the Hasia-Fuoss conductance equation [12] adapted by D'Aprano [13]:

(1). The relaxation term $\Delta X/X$ is the Hasia-Fuoss [12] function in which the variable Ka is replaced by $\tau = \beta k/2$, $\beta = \varepsilon^2/DKT$; this change [14] corresponds to using the Bjerrum radius $\beta/2$ as the lower limit in the integration instead of the contact distance "a", where τ is Fuoss-Onsager parameter, β is Boltzmann's constant, ε is the electronic charge in esu, D is dielectric constant, T is absolute temperature, K is reciprocal of average radius of ion atmosphere in cm^{-1}.

(2). The associaton constant K_A

$$K_A = (1 - \gamma)/C\gamma^2 f^2$$

where f is activity coefficient is given by the relation:

$$K_A = (4\pi N B^3/6000)\ F(b),\ b = \beta/a$$

which contains the function

$$F(b) = E_p(b) - (e^b/b)\ [1 + (1 + (1/b) + 2.435] \quad \text{..........}\ (2)$$

derived in 1961 by Fuoss and Onsager [15] and replaces the 1958 equation [16].

$$K_A = (4\pi\ Na^3/3000)e^b$$

where C is the molar concentration, f is activity coefficient, N is Avogadro's Number, "a" is distance of closest approach of two ions in cm. The electrophoretic term $\Delta\Lambda_e$, and the relaxation term $\Delta X/X$ are given expilictly in the Appendix 1.

(3). Activity coefficients are computed by:

$$-\ln f = \tau / (1 + \tau)$$

instead of the Debye Huckel limiting equation.

(4). The electrophoresis term Λ_e, formerly approximated [12] by:

$$\Delta\Lambda = [B_e C^{1/2} (1 + ka)]\ (1 + \Delta X/X)$$

has been replaced by

$$\Delta\Lambda_e = [B_e C^{1/2} \ /(1 + \tau)]\ F(\tau)$$

where F (τ) explicitly gives the effect of interaction between relaxation and velocity fields instead of approximating it by multiplying the limit value $B_o C^{1/2}$ by $(1 + \Delta X/X)$. Its principal effect is to introduce a previously missed term $[-E_2 C \ln C]$ in the electrophoresis [16], where B_o is electrophoretic coefficient of Onsager equation.

TABLE 1. VALUES OF VISCOSITIES AND DIELECTRIC CONSTANTS FOR METHANOL-H_2O AND GLYCEROL-H_2O MIXTURES AT VARIOUS TEMPERATURES.

%by weight	Property	298 °K	303 °K	308 °K	313 °K
METHANOL-H_2O MIXTURES					
20	Viscosity (cP)	0.3922	0.3231	0.2621	0.2154
	dielectric constant	69.20	67.86	66.52	65.18
30	Viscosity (cP)	0.5852	0.5062	00.3935	0.3124
	dielectric constant	64.30	63.20	62.10	61.00
40	Viscosity (cP)	0.7530	0.6837	0.6232	0.5563
	dielectric constant	60.94	59.33	57.72	56.17
GLYCEROL-H_2O MIXTURES					
30	Viscosity (cP)	2.157	1.876	1.637	1.385
	dielectric constant	70.00	68.23	66.53	64.87
50	Viscosity (cP)	5.041	4.247	3.591	2.835
	dielectric constant	64.00	62.35	60.71	59.55
60	Viscosity (cP)	8.823	7.312	5.348	3.506
	dielectric constant	60.00	58.61	57.10	55.34

(5). The volume term in volume fraction has been omitted.

The revised conductance equation (1) has been programmed for the electronic computer to find the conductometric parameters (Λ_o and K_A). The program is a two parameter search; given a set of data (C_j, A_j), dielectric constant, viscosity and temperature, it finds the values of Λ_e and K_A. Then b is obtained by solving the inverse of eq. (2) and the contact distance is given by (a = B/b).

All calculations were made on a M S X computer. The results are summarized in Tables 2, 3, where Λ_o is the limiting

TABLE 2. COMPUTED VALUES OF K_A, Λ_o AND σ FOR NaCl IN METHANOL-H_2O MIXTURES AT VARIOUS TEMPERATURES.

% of methanol by weight	T °K	K_A LM^{-1}	Λ_o $mho.cm^2$	σ
20	298	1.60	121.30	0.003
	303	2.05	132.43	0.003
	308	2.51	144.56	0.004
	313	2.98	156.69	0.004
30	298	2.75	118.50	0.015
	303	3.15	129.35	0.018
	308	3.54	141.20	0.020
	313	4.04	153.05	0.025
40	298	3.82	115.40	0.032
	303	4.41	125.94	0.035
	308	4.84	137.48	0.038
	313	5.32	149.02	0.039

TABLE 3. COMPUTED VALUES OF K_A, Λ_o AND σ FOR NaCl IN GLYCEROL-H_2O MIXTURES AT VARIOUS TEMPERATURES.

% of glycerol by weight	T °K	K_A LM^{-1}	Λ_o $mho.cm^2$	σ
30	298	3.40	76.24	0.0003
	303	4.01	82.86	0.0028
	308	4.55	90.48	0.0031
	313	5.12	98.11	0.0035
50	298	6.40	41.88	0.0004
	303	7.08	46.01	0.0036
	308	7.62	50.29	0.0039
	313	8.21	54.18	0.0042
60	298	8.12	24.48	0.0045
	303	8.71	27.10	0.0041
	308	9.44	29.52	0.0048
	313	10.14	31.98	0.0056

conductance; K_A is the association constant, and σ is the standard deviation.

It can be seen from the data in Tables 2, 3 that Λ_0 values of NaCl in both glycerol-H_2O and methanol-H_2O mixtures are smaller than those in aqueous medium. The values of Λ_0 are very low in glycerol-H_2O mixtures in comparison with those in methanol-H_2O. This is mainly due to the relatively higher viscosity of glycerol in comparison with methanol. Also, it is clear that Λ_0 values decrease slightly with increasing fraction of methanol in the mixtures, but the values of Λ_0 are drastically decreased as the fraction of glycerol increase. This possibly suggests that intramolecular hydrogen bonding taking place in glycerol-H_2O mixture must be diminishing the mobility of the ions and hence resulting in a decrease of the values of the equivalent conductances. Such hydrogen bonds are expected to be greater in the glycerol-H_2O solvent [18]. The Λ_0 values for all systems under study increased when the temperature increases. The thermal motion probably destroys the solvent structure and hence the mobility of the ions should increase, causing higher conductance.

The association constants, K_A, increased when the temperature is increased for all systems investigated. Also, it increases as the proportion of methanol or glycerol in the mixture increase.

However, although the dielectric constants of glycerol-H_2O and methanol-H_2O mixtures are in the same range of the values (D = 64.0, =64.3, respectively at 25°), sodium chloride is less associated in methanol-H_2O ($K_A = 2.75$) than in glycerol-H_2O ($K_A = 6.4$). The differences between two values is due to the effect of hydrogen bonding, where hydrogen bonds form the solvate cluster, which is followed by desolvation of the ions causing higher association between Na^+ and Cl^-. The solvation of the ions is weakened as soon as the ion pair is formed, and therefore, NaCl becomes more solvated in methanol-H_2O than in glycerol-H_2O.

In case of electrolytes with small ions, such as sodium chloride in mixtures containing water, specific ion-solvent interactions have been observed. Frank and Wen [19] postulated that the solvent around an ion can be divided into three regions of different structure. The region nearest the ions is one of dielectric saturation, because the ionic field is of the order of hundreds of megavolts/cm. The third region is the solvent at relatively large distance from the ion, where the solvent can be completely described by its macroscopic properties. The second region is a rather vaguely defined region of transition between completely oriented or hydrogen-bonded molecules and completely free solvent molecules. Gurney [20] had previously introduced the convenient term of cosphere to refer to the solvent in the first two regions. The approximation can be made that the cosphere for sodium ions is due to ion-dipole forces [21,22] and the cosphere for anions due to hydrogen-bonded solvent molecules [23]. We assume that the energies of interaction are high enough to hold the solvent molecules, even in the ion pairs. In the case of hydrogen bonded solvents, the resulting solvent structure can in some cases be reinforced by the presence of ions and in other cases will be destroyed.

The relations between logarithm of association constants, K_A and reciprocal of absolute temperatures, 1/T, are straight lines, with slope equals - ΔH°/R. Therefore, standard enthalpy changes, ΔH°, can be evaluated. Also, standard free energy changes, ΔG°, calculated from: $\Delta G^\circ = -RT\ 1nK_A$. Then, standard entropy changes, ΔS°, calculated by differences: $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$. Thermodynamic parameters ΔG°, ΔH° and ΔS° which were obtained for NaCl in different solvents are presented in Tables 4, 5.

In all the systems studied, the standard enthalpy change, ΔH°, values are found to be positive indicating that heat must be added to reactants for the equilibrium to take place in forming the ion pairs. It is clear that the association of NaCl in methanol-H_2O mixtures is more endothermic than that of NaCl in glycerol-H_2O media. Also, the endothermicsity is decreased as the proportion of glycerol or methanol in the mixture increased. This again in harmony with the fact that the association of NaCl is increased as the proportion of solvent increased.

In our previous paper [1], we studied the association of KBr in 10% glycerol-H_2O mixture at different temperatures, where ΔH° and ΔS° have negative values and K_A decrease with temperature. However, in the present paper, ΔH° and Δ°S have positive values and K_A increase with temperature for NaCl in

TABLE 4. THERMODYNAMIC PARAMETERS FOR ASSOCIATION OF NaCl IN METHANOL-H_2O MIXTURES AT VARIOUS TEMPERATURES.

% of methanol by weight	T K	$-\Delta G^\circ$ $kJ.mol^{-1}k$	ΔH° $J.mol^{-1}$	ΔS° $J(mol.^\circ K)^{-1}$
20	298	1.16	14.35	52.05
	303	1.81	14.35	53.33
	308	2.36	14.35	54.25
	313	2.84	14.35	54.92
30	298	2.51	9.10	38.96
	303	2.89	9.10	39.57
	308	3.24	9.10	40.06
	313	3.63	9.10	40.67
40	298	3.32	6.65	33.46
	303	3.74	6.65	34.29
	308	4.04	6.65	34.71
	313	4.35	6.65	35.14

glycerol-H_2O. The reversal in the signs of thermodynamic parameters ΔH° and ΔS° can be explained as follow: according to the results of thermodynamic functions in Tables 4 and 5, if we consider that from a rudimentary standpoint the ion pair is formed with only the action of the coulombic force in a continuum medium, both the values of ΔH° and ΔS° of the ion pair formation will be negative. In general, however, the solvation of ions is weakened as soon as the ion pair is formed. This situation turns out to increase in both ΔH° and ΔS°. Therefore, all the experimental values of ΔH°and ΔS° in Tables 4 and 5 are positive.

For all systems studied, the standard free energy change, ΔG°, have negative values, which indicate that the association process proceed spontaneously in the direction. The values of ΔG° for glycerol-H_2O are higher than those for methanol-H_2O mixtures, which agree well with the previous fact. The standard entropy change, ΔS°, have positive values which again in harmony with negativity of ΔG°. The ΔS° values for glycerol-H_2O mixtures are larger than those for methanol-H_2O. The association is accompanied by the loss of hydration, resulting in an increase in the disorder of the system. This is most likely the reason behind the higher values for ΔS° of NaCl in glycerol-H_2O over the methanol-H_2O media.

TABLE 5. THERMODYNAMIC PARAMETERS FOR ASSOCIATION OF NaCl IN GLYCEROL-H_2O MIXTURES AT VARIOUS TEMPERATURES.

% of methanol by weight	T °K	-ΔG° kJ.mol^{-1}	ΔH° kJ.mol^{-1}	ΔS° J(mol.°K)$^{-1}$
30	298	3.03	9.09	40.67
	303	3.50	9.09	41.55
	308	3.88	9.09	42.11
	313	4.25	9.09	42.62
50	298	4.65	6.35	36.91
	303	4.93	6.35	37.23
	308	5.20	6.35	37.50
	313	5.48	6.35	37.80
60	298	5.19	4.83	33.62
	303	5.45	4.83	33.93
	308	5.75	4.83	34.35
	313	6.03	4.83	34.70

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