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Thermodynamics of glycine in mixed solvents at 30° – 40° C

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Abstract: The ion solvent interaction of glycine in ethanol + water, methanol + water, isopropanol + water, glycol + water, glycerol + water obtained from conductance measurement have been compared at 10, 20 and 30% (w/w) solvent composition with temperature range of 30-40°C have been studied. The physical parameters like K, ΔG^o, $\Delta G^o_{(el)}$, and $\Delta G^0_{t (Ch)}$ have been calculated and ion-solvent interactions are inferred.

Keywords: Dielectric Constant, Walden Product, Ion-Solvent Interaction & Dipole Moment

1. Introduction

Amines in pure state are self associated through intermolecular hydrogen bonds. They are all electron donors which allow them to have specific interactions with other electron deficient molecules. The physical properties of the mixed solvents like ethanol + water, methanol + water, isopropanol + water, dioxane + water, glycol + water and glycerol + water viz. dielectric constant, dipole moments are very much different from that of water. These organic solvents are more or less aprotic. Water, the most commonly used solvent, is both polar and sustains hydrogen bonds. Water is both an electron donor and electron acceptor. These and several other properties make a study of their aqueous mixture an interesting thing to explore particularly of the ionic processes accompanying the solution of strong electrolytes.

Fig.1 represents a 2-dimensional section of an idealized electrolyte solution. The ions are shown as spheres with unit electrical charge. The solvent (pale blue) is shown as a uniform medium, without structure. On average, each ion is surrounded more closely by ions of opposite charge than by ions of like charge. Conductivity is traditionally determined by measuring the AC resistance of the solution between two electrodes. Dilute solutions follow Kohlrausch's Laws of concentration dependence and additivity of ionic contributions. Lars Onsager gave a theoretical explanation of Kohlrausch's law by extending Debye–Hückel theory.
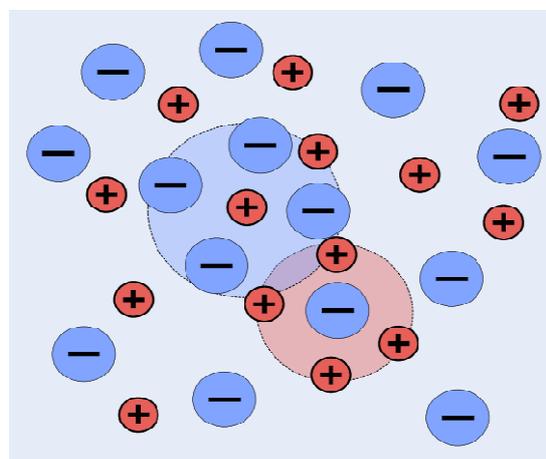
*Fig. 1. An idealized representation of a solution of a 1:1 electrolyte*

In the present communication conductivities of glycine in ethanol + water, methanol + water, isopropanol + water, dioxane + water, glycol + water, and glycerol + water mixture at 30o to 40oC have been measured to investigate the ion solvent interaction.

2. Experimental

The electrical conductivity of a solution of an electrolyte

is measured by determining the resistance of the solution between two flat or cylindrical electrodes separated by a fixed distance [8]. An alternating voltage is used in order to avoid electrolysis. The resistance is measured by a conductivity meter. Typical frequencies used are in the range 1–3 kHz. The dependence on the frequency is usually small, but may become appreciable at very high frequencies, an effect known as the Debye–Falkenhagen effect.

The salt used was of E-Merck' extra pure variety. The purification of solvent, preparation of solvent and solution and measurement of the conductance has been described previously [3]. The conductance measurements were within accuracy of 0.002 and within the concentration range from 0.01 to 0.001 equivalent litre-1. The temperature of investigation was from 303 to 313 + 0.01 K.

3. Discussion

The Onsager equation [1] for a completely dissociated electrolyte is

$$\wedge = \wedge^o - (A+B\wedge^o) \sqrt{C} \qquad (1)$$

where A and B are independent of concentration of the electrolytes. It satisfactorily accounts from the change in the equivalent conductivities with concentration. Correct evaluation of Λ^o can be made by extrapolating to zero concentration of the line obtained by plotting $\wedge$ vs. $C^{1/2}$. However the above method of extrapolation has been reported to the unreliable in case of a number of electrolytes involving incomplete dissociation or ion association. Davies has extended the Onsager's equation and has tabulated the dissociation constants of a variety of salts, specially of higher valency type. Electrolytic conductivities have been used to study ion solvent interaction and salvation of various cations and anions in aqueous and non-aqueous solution.

The equivalent conductivity of glycine investigated weight % of ethanol, methanol, isopropanol, dioxane, glycol, glycerol (10, 20 and 30%) water mixture at 30-40°C and found to be almost linear with $C^{1/2}$. The theoretical Slope (S_T) calculated from the determined $\wedge^o$ values for different electrolytes at different solvent composition have been obtained and compared with the experiment slope (S). Dielectric constants were calculated from the data of Akenlof and short, viscosities were determined experimentally. The S_T and S values are almost in fair agreement and differ by 2 to 3%; $\wedge^o$ values are given in table-1.

The Walden product [2] $\wedge^o\eta_0$ (table 2) has been actually employed to study ion-solvent interaction in solution from conductivity data. The plot of $\wedge^o\eta_0$ vs. t are found to be linear and is almost independent of temperature. Further the mere constancy of the Walden product at different temperature is most presumably due to compensating contribution of the temperature coefficient of the conductivity by the negative temperature coefficient of the viscosity of the solvent. The lesser the value of $\wedge^o\eta_0$ the greater is the ion solvent interaction. Also electrostatic charge density of the ion plays an important role in inducing

ion solvent interaction and salvation. It also appears that during these migration ions are covered with a sheath of solvent molecules resulting in a larger size of the solvodynamic unit, and a decrease in $\wedge^o\eta_0$ (Table-2), so that the size of the solvated ions and the ion-solvent interaction is of the order ethanol + water > methanol + water: isopropanol + water > dioxane + water > glycol + water > glycerol + water is in agreement with the viscosity and apparent molar volume data. (To be published later).

Because of the use of aquo-organic solvents, the dielectric constant of the medium is lowered and there is more probability of ion-pair formation. Hence the method of Fuoss and Krauss [3] and that of Shedlovsky [4] have been utilized to calculate the dissociation constant and $\wedge^o$ simultaneously; K values calculated by both the methods are in good agreement and are recorded in table-3. The K values decrease with the decrease in dielectric constant, i.e. with increase in non-aqueous solvent.

Table 1. $\wedge^o/\Omega^1.cm^2$

	Temp oC	10%	20%	30%
Methanol	30	125	99	96
+	35	130	106	100
Water	40	142	114	104
Ethanol	30	122	97	92
+	35	142	105	102
Water	40	160	128	127
Isopropanol	30	120	100	97
+	35	140	110	109
Water	40	160	130	120
Dioxane	30	110	96	87
+	35	120	99	90
Water	40	128	102	96
Glycol	30	125	109	100
+	35	131	114	104
Water	40	137	118	109
Glycerol	30	127	110	98
+	35	138	120	109
Water	40	145	132	120

The standard thermodynamic parameter ΔG^o and ΔS^o have been calculated in the usual manner. The plots of ΔG^o and ΔS^o vs. solvent composition are found to be linear. The extrapolated values give the thermodynamic parameter for water. The standard thermodynamic quantities (ΔG_t^o and ΔS_t^o) for transfer process for water from water to 10, 20 and 30% of organic solvent + water have been calculated by using Feakin's and Tuner's[5] method. ΔG_t^o values are tabulated in table-7 and 8. The ΔG_t^o values are all negative, which indicates that the ion pairs are in a lower free energy state in aquo-organic solvent than in water and hence the ion pair formation is favoured by decreasing the dielectric constant of the medium. Since single ion values of free energies are not available presently for the solvent mixtures studied, the method adopted by Khoo [6] is followed to study ion solvent content is increased. It is possible to split the ΔG_t^o values into two parts as suggested by Roy et al. [7] i.e. chemical contribution denoted in their terminology by $\Delta G_{t\,(Ch)}^o$ and an electrostatic contribution $\Delta G_{t\,(el)}^o$, which has been calculated from the Born equation:

$$\Delta G^o_{t(ed)} = (Ne^2/2) \, [(1/\varepsilon_s + 1/\varepsilon_w)(1/r_+ + 1/r_-) \qquad (2)$$

Table 2. $\wedge^o \eta_0/\Omega^{-1} \, cm^2$

	Temp ºC	10%	20%	30%
Methanol	30	1.11	1.12	1.11
+	35	1.12	1.12	1.12
Water	40	1.12	1.11	1.12
Ethanol	30	1.09	1.09	1.10
+	35	1.09	1.09	1.09
Water	40	1.09	1.09	1.09
Isopropanol	30	1.13	1.12	1.12
+	35	1.13	1.13	1.11
Water	40	1.12	1.13	1.11
Dioxane	30	1.14	1.14	1.15
+	35	1.15	1.16	1.15
Water	40	1.15	1.15	1.14
Glycol	30	1.11	1.12	1.11
+	35	1.08	1.09	1.08
Water	40	1.10	1.10	1.10
Glycerol	30	1.16	1.24	1.17
+	35	1.17	1.25	1.18
Water	40	1.18	1.25	1.19

Table 3. $K \times 10^2$

	Temp ºC	10%	20%	30%
Methanol	30	19.12	14.71	9.78
+	35	18.52	15.61	11.71
Water	40	18.12	15.71	10.61
Ethanol	30	16.42	14.21	10.50
+	35	17.42	14.53	10.44
Water	40	16.51	14.23	10.23
Isopropanol	30	17.52	15.41	11.72
+	35	17.62	15.5	11.84
Water	40	17.39	15.3	11.95
Dioxane	30	20.6	16.5	12.4
+	35	20.5	16.4	12.5
Water	40	20.4	16.4	12.5
Glycol	30	18.4	15.2	11.2
+	35	18.5	15.5	11.4
Water	40	18.6	15.9	11.9
Glycerol	30	19.2	17.2	9.51
+	35	19.4	17.4	9.2
Water	40	19.3	17.6	9.3

Table 4. $-\Delta G_t^o/J \, mol^{-1}$

	Temp ºC	10%	20%	30%
Methanol	30	950	1620	2470
+	35	915	1515	2440
Water	40	948	1598	2080
Ethanol	30	1040	1719	2568
+	35	1000	1615	2505
Water	40	1050	1715	2520
Isopropanol	30	851	1800	2470
+	35	862	1850	2390
Water	40	865	1780	2450
Dioxane	30	714	1415	2203
+	35	815	1415	2340
Water	40	815	1414	2345
Glycol	30	664	1114	1825
+	35	715	1214	2050
Water	40	744	1312	2092
Glycerol	30	694	1280	1845
+	35	700	1215	1850
Water	40	710	1275	1820

Table 5. $-\Delta G^o_{t(Ch)}/J \, mole^{-1}$

	Temp ºC	10%	20%	30%
Methanol	30	820	998	1670
+	35	815	1065	1750
Water	40	810	1062	1686
Ethanol	30	940	1080	1640
+	35	915	1100	1790
Water	40	910	1090	1680
Isopropanol	30	720	980	1700
+	35	705	970	1680
Water	40	715	990	1715
Dioxane	30	680	814	1752
+	35	640	912	1614
Water	40	500	914	1555
Glycol	30	620	930	1455
+	35	580	870	1415
Water	40	570	815	1392
Glycerol	30	580	870	1415
+	35	560	850	1380
Water	40	550	840	1390

Table 6. $-\Delta S^o_{t(Ch)}/JK^{-1}. \, mole^{-1}$

	Temp ºC	10%	20%	30%
Methanol	30	5.45	11.41	13.21
+	35	5.22	11.52	13.42
Water	40	5.51	11.52	13.41
Ethanol	30	6.72	12.50	13.91
+	35	6.22	12.12	14.56
Water	40	6.52	12.05	14.14
Isopropanol	30	4.81	11.34	13.14
+	35	4.62	11.25	13.25
Water	40	4.67	11.78	13.45
Dioxane	30	4.22	10.34	12.64
+	35	4.82	10.34	12.64
Water	40	4.92	10.54	11.95
Glycol	30	3.1	8.2	10.1
+	35	3.2	8.6	10.5
Water	40	3.6	8.9	10.9
Glycerol	30	3.1	8.4	10.0
+	35	3.2	8.6	10.2
Water	40	3.3	8.7	10.4

where r_+ and r_- are the crystallographic radii of the

$$d \lfloor n \varepsilon_w /dT \; \& \; d \lfloor n \varepsilon_s /dT$$

can be evaluated from the simple empirical equation :

$$d \lfloor n \varepsilon^o /dT = -1/\theta \qquad (3)$$

in which θ is a constant characteristic of the medium, so equation may be written as :

$$\Delta S^o_{t(el)} = Ne^2/2[(1/\varepsilon_s \theta_s - 1/\varepsilon_w \theta_w) \, (1/r_+ + 1/r_-) \qquad (4)$$

From the knowledge of $\Delta G^o_{t(el)}$ and $\Delta G^o_{t(el)}$, the chemical contribution of the free energy transfer, $\Delta G^o_{t(Ch)}$ and entropy transfer, $\Delta S^o_{t(Ch)}$ could be calculated by subtracting the respective electrostatic contribution values from the molar quantities and are tabulated in table 4 to 6. It is evident that the chemical contribution of the free energy transfer is negative in all cases and hence is thermodynamically favourable as far as the chemical interactions are concerned, and is of the order:

Ethanol + water > methanol + water > isopropanol +
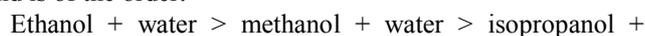
water > dioxane + water > glycol + water > glycerol + water.

The $\Delta S^o_{t\ (Ch)}$ is also negative in all cases indicating chemical interaction and is of the order:

Ethanol + water > methanol + water > isopropanol + water > dioxane + water > glycol + water > glycerol + water.

The reasons for this behaviour are as follows:

Ethanol, methanol and isopropanol have got one –OH and water is both an electron donor and acceptor. Hence, the former could accept a proton from water and hence the three dimensional water structures are easily broken down.

The addition of a small amount of dioxane to water may give rise to two effects; if the dioxane is accommodated in the solvent structure, it may strengthen the water structure because dioxane is a proton acceptor. If it cannot be accommodated because of its bulky size then it may cause a breakdown in three dimensional water structures. Several authors have observed that dioxane + water is less ordered than pure water. It is observed that ΔE and ΔG increase with increase in dioxane content and hence the three dimensional water structure is broken down though the quanta are less than that of ethanol and methanol + water mixtures.

Glycol has got two –OH groups and glycerol has got 3-OH groups. So it should have more tendencies to break hydrogen bond more readily than methyl alcohol and ethyl alcohol, but the reverse is seen to be true. This is probably due to the low ion solvent dipole interaction energy which is unable to break the strong intermolecular hydrogen bond.

Hydrogen bonding has an effect on the activation energy and conduction mechanism. In literature, the high electrical conductivity obtained was due to hydrogen bonding. It is known that the increase in conductivity with temperature is related to the increase in the population of electrons in the conduction band.

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