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Thermodynamics of Ion Association in the Saturated Solution of Barium Diphenyl amine sulfonate in Ethanol-Water Mixed Solvent

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Abstract— The aim of this study was to determine the ion association phenomenon in the saturated solution of barium diphenylamine sulfonate in the mixed solvent (ethanol+water) from solubility and the mean activity coefficient values obtained at 298.15K. The solubility of solutes in mixed solvents depends primarily on the solvation of the solutes or their constituent ions by the components of the solvent mixtures. In this study, the solubility of this barium diphenylamine sulfonate in the mixed solvent (ethanol + water by value percent of ethanol = 0, 20, 40, 60, 80 and 100% by volume), was determined at 293.15K, 298.15K, 303.15K, and 308.15K by the solvent evaporation method. The results enable us to estimate the values of concentration and modeled solubility product data ($pK_{sp(c)}$ & $pK_{sp(m)}$) of barium diphenylamine sulfonate in the mixed solvent. In addition, the corresponding Gibbs free energy for the solution processes and free energies of transfer of barium diphenylamine sulfonate units from water to the ethanol solutions were also calculated in order to estimate the contributions solute-solvent interactions related ion association are based on changes in the electrostatic properties of the solvent, solute and ion solvation as well as on the ionic strength of the medium.

Keywords: barium diphenylamine sulfonate, mixed solvents, solubility, thermodynamics.

I. INTRODUCTION

Solid–liquid equilibrium of mixed electrolyte aqueous solution plays an important role in separation operation for many industrial processes involving electrolyte solutions. To meet engineering requirements, an accurate estimation method is necessary for engineering design because solid–liquid equilibrium data for mixed electrolyte solutions are scarcely available in literature. To perform the calculation of solid–liquid equilibrium for mixed electrolyte aqueous solution, a key problem is how to accurately express the activity coefficient of electrolyte in a saturated solution. The solubility of solutes of all kinds in mixed solvents is of great practical importance, since many industrial process as well as laboratory procedures call for the use of solvent mixtures, or such mixtures are used by default [1].

Most physicochemical properties of ionic solutions are influenced by ionic strength and the solvent's dielectric constant. Indeed, in the context of solution chemistry, solvent polarity, the dielectric constant of the solvent, and the ionic strength of the medium are of great interest as a measure of the solvents ability to stabilize charges or dipoles. As an example, the dissolution of an ionic salt in a solvent or in a mixed solvent depends on the relative permittivity and the polarity of the solvent as well as on the lattice energy of the solute and the ionic strength of the medium [2-7].

In turn, most of the theories that have been used to predict the extend of solubility of an ionic compound in a given solvent or in a mixed solvent and related ion association are based on changes in the electrostatic properties of the solvent, solute and ion solvation as well as on the ionic strength of the medium [8-14].

An activity coefficient [15] is a factor used in thermodynamics to account for deviations from ideal behavior in a mixture of chemical substances. Max Margules [16-17] introduced a simple thermodynamic model for the excess Gibbs free energy of a liquid mixture. After Lewis had introduced the concept of the activity coefficient, the model could be used to derive an expression for the activity coefficients of a compound i in a liquid. The activity coefficient is a measure for the deviation from ideal solubility. Activity coefficients may be measured experimentally or calculated theoretically, using the Debye-Huckel equation or extensions such as Davies equation, [18], Pitzer equations [19] or TCPC model [20 to 21]. Specific ion interaction theory (SIT) [24], may also be used. Alternatively correlative methods such as UNIQUAC [25], NRTL model [26], MOSCED or UNIFAC may be employed, provided fitted component-specific or model parameters are available.

II. EXPERIMENTAL

A. CHEMICALS AND REAGENTS

Barium diphenylamine sulfonate and ethanol were purchased from Merck Company with high degree of purity and used without further purification.

B.PREPARATION OF MIXED SOLVENT AND SATURATED SOLUTIONS

The mixed solvent, (ethanol + water by value percent of ethanol = 0, 20, 40, 60, 80 and 100% by volume), were prepared from deionized water and fairly pure ethanol. Then, saturated solutions of barium diphenylamine sulfonate were prepared by dissolving different amounts in closed test tubes containing different (ethanol + water) mixtures. These mixtures were then saturated with nitrogen gas an inert atmosphere. The tubes were placed in a shaking thermostat (Model Gel) for a period of four days till equilibrium reached. The solubility, ***S*** (mole/Kg.solvent), of barium diphenylamine sulfonate in the mixed solvent at 298.15K was determined gravimetrically by the solvent evaporating method. All the solubility experiments were repeated at least three times and the results were averaged.

III. RESULTS AND DISCUSSION

For an ionic compound, with the formula BA_2, we may consider the concentration solubility product constant $(K_{sp(c)})$ in the saturated solution as;

$$BA_{2(s)} \leftrightarrow B^{2+}(aq) + 2A^{-}_{(aq)}, \qquad (1)$$

$$K_{sp(c)} = 4S^3 \qquad (2)$$

$$pK_{sp(c)} = -\log(4S^3) \qquad (3)$$

The estimation of the activity coefficient of ions in a given solution by using a suitable model and the calculation of the modeled solubility product, $Ksp(m)$, as;

$$K_{sp(m)} = 4S^3\,\gamma_\pm^{\,3} \qquad (4)$$

$$pK_{sp(m)} = -\log(4S^3\,\gamma_\pm^{\,3}) \qquad (5)$$

$$\textit{And} \qquad pK_{sp(m)} = pK_{sp(c)} - \log(\gamma_\pm^{\,3}) \qquad (6)$$

Where S is the molal solubility of BA_2 and $\gamma_\pm$ is the mean molal activity coefficient. There are several theoretically-based expressions that can be used to estimate the activity coefficients [18-26]. At very low concentration, the electrostatic interaction becomes very small and the ion association phenomenon may be negligible (the activity coefficient $\gamma_\pm$~1) [29-30].

At low concentration, the activity coefficient may be determined by using the Debye- Hückel limiting law:

$$\log \gamma_\pm = -Z_+Z_-A\sqrt{I} \qquad \text{Applicable for } I < 10^{-2}\,M \qquad (7)$$

Where Z_+ and Z_- are the charges of ions in solutions, $A = 1.823\chi10^6\,(D.T)$, the ionic strength, I, defined as, $I = \frac{1}{2}\sum_i m_i z_i^2$ (z_i is the charge on ion i, and mi is the molality of ion i) and the ionic strength, I emphasizes the charges of ions because the charge numbers occur as their squares. The values of dielectric constant (D) for ethanol-water mixtures were taken from previous publications [31].

The molal solubility, S (mole/Kg solvent) and ionic strength of barium diphenylamine sulfonate in the mixed solvent (ethanol + water by value percent of ethanol = 0, 20, 40, 60, 80 and 100% by volume) at 293.15K, 298.15K, 303.15K and 308.15K are cited in Table (1)

The solubility of saturated solution of barium diphenylamine sulfonate in mixed solvents found to decrease with the increase the mole fraction of EtOH in the mixed solvent and increase with increase temperature depends primarily on the solvation of the solutes or their constituent ions by the components of the solvent mixtures. The saturated solution of diphenyl amine barium salt in the mixed solvent is perfectly non-ideal. The non-ideality is partly due to the mean activity coefficient of ions in the solution and partly due to the ion association phenomenon.

At relatively high concentration, the electrostatic interaction becomes very large [32-34]. The activity coefficient may be determined using the extend Debye-Hückel law:

$$\log \gamma_\pm = -\frac{Z_+Z_-A\sqrt{I}}{I + Br^{o}\sqrt{I}} \qquad \text{for} \quad I < 10\text{-}1\,M \qquad (8)$$

Where $B = 50.29\,(\varepsilon.T)^{-½}$, and r° is the solvated radius.

At high concentrations, activity coefficients of electrolyte solutions can be determined by using the Davies equation [18] which is an empirical extension of Debye–Hückel theory. The final form of the equation gives the mean molal activity coefficient, $\gamma_\pm$, of an electrolyte which dissociates into ions having charges Z_+ and Z_- as a function of ionic strength, I.

$$\log \gamma_\pm = -Z_+Z_-A\left(\frac{\sqrt{I}}{I+\sqrt{I}} - 0.3I\right) \qquad (9)$$

The second term, $0.3I$, goes to zero as the ionic strength goes to zero, so the equation reduces to the Debye–Hückel equation at low concentration. However, as concentration increases, the second term becomes increasingly important, so the Davies equation can be used for solutions too concentrated to allow the use of the Debye–Hückel equation.

Pitzer [35-37] has provided osmotic and activity coefficient expressions for his model. Pitzer model is one of the most widespread methods for calculating activity coefficients in concentrated, multicomponent electrolyte solutions at room or elevated temperature. This method is semi-empirical, based on the definition of the excess Gibbs energy G^{ex} for electrolyte solution [38 and 39] using equations (10-17).

$$\left(G^{ex}\big/n_wRT\right) = f^{GX} + m^2(2\nu_M\nu_X)B^{GX}_{MX} + m^3\left[2(\nu_M\nu_X)^{3/2}\right]C^{GX}_{MX} \qquad (10)$$

Where

$$f^{GX} = -A_\varphi\left(4\,{}^{I}\!/_{b}\right)\ln\left(1 + bI^{1/2}\right) \qquad (11)$$

$$B^{GX}_{MX} = \beta^{(0)}_{MX} + \frac{2\beta^{(1)}_{MX}}{\alpha^2 I}\left[1 - e^{-\alpha I^{1/2}}\left(1 + \alpha I^{1/2}\right)\right] \qquad (12)$$

$$\text{And} \qquad C^{GX}_{MX} = (1/2)\,C^{\varphi}_{MX}$$

The expression for the mean ionic activity coefficient is;

$$\ln\gamma_{MX} = |Z_M Z_X|\,f^{\gamma} + m\left(\frac{2(\nu_+\nu_-)}{\nu}\right)B^{\gamma}_{MX} + m^2\left(\frac{2(\nu_+\nu_-)^{3/2}}{\nu}\right)C^{\gamma}_{MX} \qquad (12)$$

$$B^{\varphi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\,e^{-\alpha_1 I^{1/2}} + \beta^{(2)}_{MX}\,e^{-\alpha_2 I^{1/2}} \qquad (13)$$

$$f^{\gamma} = -A_\varphi\left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}\ln\left(1 + bI^{1/2}\right)\right] \qquad (14)$$

$$B^{\gamma}_{MX} = 2\beta^{(0)}_{MX} + \frac{2\beta^{(1)}_{MX}}{\alpha_1{}^2 I}\left[1 - e^{-\alpha_1 I^{\frac{1}{2}}}\left(1 + \alpha_1 I^{\frac{1}{2}} - \frac{1}{2}\alpha_1^2 I\right)\right] + \frac{2\beta^{(2)}_{MX}}{\alpha_2{}^2 I}\left[1 - e^{-\alpha_2 I^{1/2}}\left(1 + \alpha_2 I^{1/2} - \frac{1}{2}\alpha_2^2 I\right)\right] \qquad (15)$$

$$\textbf{And} \qquad C^{\gamma}_{MX} = \left(\tfrac{3}{2}\right)C^{o}_{MX} \qquad (16)$$

A_φ is a Debye – Hückel coefficient

$$A_\varphi = \left[\frac{1}{3}\left(2\pi N_A d_w/1000\right)^{1/2}\right]\left(e^2/DkT\right)^{3/2} \qquad (17)$$

With m concentration in molal, Z ionic charge, ν_M stoichiometric coefficient for the cation, nX stoichiometric coefficient for the anion, $\nu = \nu_M + \nu_X$, e unit charge, D dielectric constant of solvent, d_o dentistry of solvent, k Boltzmann constant, N_A Avogatro number, "Debye-Huckel" term, B_{MX} "Pitzer B term", containing the adjustable parameters and C_{MX} "Pitzer C term", containing adjustable parameters.

For each electrolyte, the adjustable parameters are $\beta_{MX}^{(0)}, \beta_{MX}^{(1)}$ and C_i . Usually C_i is very small and sometimes completely negligible. The optimal value for α_1 is set equal to 2.0 for all but 2-2 electrolytes: for these α_1 is equal to 1.4 and α_2 to 12.0. With the exception of 2-2 electrolytes, α_2 and β parameters are equal to 0 [39].

The mean molal activity coefficient (using Davis and Pitzer equations) of barium diphenylamine sulfonate in the mixed solvent at 293.15K, 298.15K, 303.15K, and 308.15K are cited in Table (2)

The concentration solubility product ***(pK$_{sp(c)}$)*** using equation (3) and modeled solubility product ***(pK$_{sp(m)}$)*** using equation (6) and Pitzer mean molal activity coefficient data are given in Table (3), the corresponding Gibbs free energies of solvation Δ***G*** and the transfer Gibbs free energies ΔG_t from water to mixed solvents were calculated by using equations (18) and (19) [40- 43].

$$\Delta G^o = 2.303\ RT\ pK_{sp} \tag{18}$$

$$\Delta G_t = \Delta G_s - \Delta G_w \tag{19}$$

Where ***(s)***, ***(w)*** denote solvent and water, respectively.

The concentration Gibbs free energies of solvation ΔG_c and modeled Gibbs free energies of solvation ΔG_m for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperature are tabulated in Table (4).

The transfer Concentration Gibbs free energies of solvation $\Delta G_{t.c}$ and transfer modeled Gibbs free energies solvation $\Delta G_{t.m}$ for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperature are tabulated in Table (5).

.The magnitude of $\Delta G_{t\ (solute,\ w \rightarrow w+s)}$ as shown in Table. (5) is a measure of the overall change in the solvation (energy) of an ion upon its transfer from water to an organic − aqueous mixture. Such quantities are usually "well behaved" in the sense that they vary smoothly as a function of solvent composition, even though they may show great diversity. It was concluded that the Gibbs free energies of transfer increase in negativity by increasing the mole fraction of EtOH in the mixed EtOH -H_2O solvents indicating the decrease in spontaneous nature of barium diphenylamine sulfonate solubilization. This is due to more solvation behavior in water than that of the mixed solvents where the Gibbs free energy values provide information on whether the process conditions favor or disfavor barium diphenylamine sulfonate solubilization in the aqueous carrier solution. Positive Gibbs free energy values indicate disfavourable conditions.

The difference in Gibbs free energies of solvation for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperature were calculated by using equations (20) and their values are cited in Table (5).

$$\Delta G_i = \Delta G_m - \Delta G_c \tag{20}$$

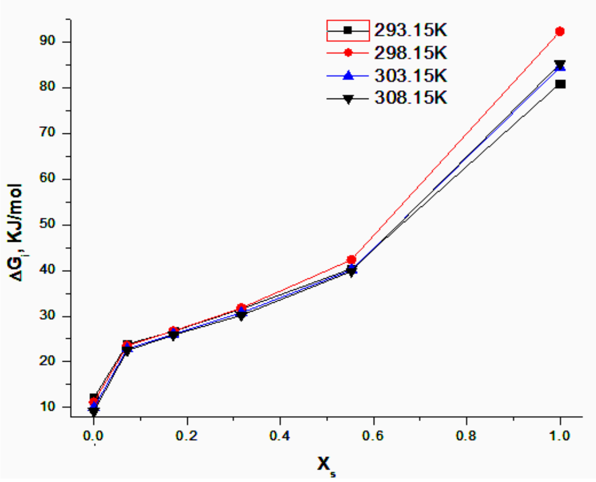

Fig. 1. Difference in Gibbs free energies of solvation (ΔG_i) for barium diphenylaminesulfonate versus the mole fraction (X_s) of EtOH at different temperatures.

IV. CONCLUSION

The solubility of saturated solution of barium diphenylamine sulfonate in mixed solvents found to decrease with the increase the mole fraction of EtOH in the mixed solvent and increase with increasing the temperature. In addition, Gibbs energy, enthalpy, entropy for the solution processes and free energies of transfer were also calculated in order to estimate the contributions solute-solvent interactions related ion association are based on changes in the electrostatic properties of the solvent, solute and ion solvation as well as on the ionic strength of the medium. The saturated solution of diphenyl amine barium salt in the mixed solvent is perfectly non-ideal. The non-ideality is partly due to the mean activity coefficient of ions in the solution and partly due to the ion association phenomenon. By choosing a suitable model for estimating the mean activity coefficient and using the iteration calculations, we obtained the value of ion-pair concentration and the activity coefficient contribution and ion association contribution to the solubility of the considered ionic compound in the considered mixed solvent at different temperature.

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APPENDIX

Table 1. Molal solubility and ionic strength for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperatures.

EtOH % By vol.	X_s, EtOH	S, mol/kg solvent				*I*			
		293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	0	0.2416	0.2548	0.2682	0.2753	0.604	0.6369	0.6704	0.6884
20	0.072	0.0468	0.0485	0.0538	0.0569	0.1171	0.1213	0.1344	0.1423
40	0.171	0.046	0.0479	0.0489	0.049	0.115	0.1198	0.1222	0.1224
60	0.317	0.0451	0.0468	0.0476	0.0481	0.1127	0.1171	0.1191	0.1202
80	0.553	0.0446	0.0464	0.0468	0.0474	0.1115	0.1159	0.1171	0.1186
100	1	0.0439	0.0459	0.0468	0.0470	0.1098	0.1148	0.116	0.1176

Table 2. Davis and Pitzer molal activity coefficients for barium diphenylaminesulfonate in mixed EtOH-H_2O solvents at different temperatures.

EtOH % By vol.	$\gamma_{\pm}$ Davies				$\gamma_{\pm}$ Pitzer			
	293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	0.5513	0.5518	0.5526	0.5508	0.4108	0.3989	0.3896	0.3794
20	0.5792	0.5729	0.5605	0.551	0.5101	0.4960	0.4877	0.4738
40	0.5515	0.5428	0.5369	0.5316	0.4712	0.4470	0.4523	0.4449
60	0.4924	0.4902	0.4838	0.4844	0.3925	0.3677	0.3815	0.3826
80	0.3878	0.3757	0.3702	0.3631	0.2677	0.2226	0.2477	0.2402
100	0.0838	0.0711	0.0669	0.0631	0.0231	0.0102	0.0158	0.0143

Table 3. Concentration and modeled solubility product ($pK_{sp(c)}$) and modeled solubility product ($pk_{sp(c)}$) for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperatures.

EtOH% By vol.	$pK_{sp(c)}$				$pK_{sp(m)}$			
	293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	1.2487	1.1796	1.1127	1.0783	2.4078	2.377	2.3409	2.341
20	3.3859	3.3403	3.2066	3.1317	4.263	4.2539	4.1421	4.1049
40	3.4096	3.3565	3.3308	3.3287	4.3899	4.4055	4.3645	4.3839
60	3.436	3.3862	3.3644	3.352	4.6545	4.6897	4.6199	4.6038
80	3.4499	3.3992	3.386	3.3694	5.167	5.3566	5.2042	5.2277
100	3.4698	3.4123	3.3979	3.3803	8.379	9.3865	8.8019	8.9143

Table 4. Concentration Gibbs free energies of solvation ΔG_c and modeled Gibbs free energies of solvation ΔG_m for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperatures.

EtOH% By vol.	ΔG_c KJ/mol				ΔG_m KJ/mol			
	293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	7.0091	6.734	6.4589	6.3624	19.101	17.919	16.385	15.484
20	19.005	19.069	18.612	18.478	42.867	42.634	41.412	40.939
40	19.138	19.161	19.333	19.64	45.814	45.898	45.392	45.516
60	19.286	19.331	19.528	19.778	50.849	51.095	50.244	49.935

80	19.364	19.405	19.654	19.88	59.726	61.742	59.758	59.689
100	19.476	19.48	19.723	19.944	100.39	111.8	104.22	105.15

Table 5. Transfer Concentration Gibbs free energies of solvation $\Delta G_{t,c}$ and transfer modeled Gibbs free energies solvation $\Delta G_{t,m}$ for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperatures.

EtOH% By vol.	$\Delta G_{t,c}$ KJ/mol				$\Delta G_{t,m}$ KJ/mol			
	293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	11.996	12.335	12.153	12.115	23.766	24.715	25.026	25.454
40	12.129	12.427	12.874	13.277	26.713	27.978	29.007	30.032
60	12.277	12.597	13.070	13.415	31.748	33.176	33.859	34.451
80	12.355	12.671	13.195	13.518	40.625	43.823	43.373	44.205
100	12.467	12.746	13.264	13.582	81.291	93.883	87.840	89.661

Table 6. Difference in Gibbs free energies of solvation for barium diphenylamine sulfonate in mixed EtOH-H_2O solvents at different temperatures

EtOH% By vol.	X_s, EtOH	ΔG_i KJ/mol			
		293.15K	298.15K	303.15K	308.15K
0	0	12.092	11.185	9.926	9.122
20	0.072	23.862	23.565	22.799	22.461
40	0.171	26.676	26.737	26.059	25.876
60	0.317	31.562	31.764	30.716	30.157
80	0.553	40.362	42.337	40.104	39.809
100	1	80.916	92.322	84.502	85.201