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SOLVENT EFFECTS ON THE THERMODYNAMICS OF SOLVATION OF BARIUUM DIPHENYLAMINESULFONATE IN ETHANOL-WATER MIXED SOLVENTS

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ABSTRACT

Aims: *The aim of this study was to determine the thermodynamic functions, Gibbs energy, enthalpy and entropy for the solution processes of barium diphenylaminesulfonate in the mixed solvent (ethanol+water) were calculated from solubility values obtained at temperatures ranging from 293.15 K to 308.15 K. The respective thermodynamic functions for mixing and solvation processes as well as the activity coefficients for the solute were calculated. 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 diphenylaminesulfonate in the mixed solvent (ethanol + water by value percent of ethanol = 0, 20, 40, 60, 80 and 100% by volume), was determined at different temperature by the solvent evaporation method. The results enable us to estimate the value of thermodynamic solubility product,* $K_{op(th)}$*, of barium diphenylaminesulfonate in the mixed solvent. In addition, Gibbs energy, enthalpy, entropy for the solution processes and free energies of transfer of barium diphenylaminesulfonate 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.*

KEY WORDS: Solubility; thermodynamics; solubility product; mixed solvents; barium diphenylaminesulfonate

Place and Duration of Study:

1. Chemistry Department, Faculty of Science, Mansoura University, Egypt
2. Basic Science Department, Delta Higher Institute of Engineering and Technology, Dakhlia, Mansoura, Egypt between June 2012 and July 2013

RESUMO

O propósito deste estudo foi determinar as propriedades termodinâmicas tais com energia livre de Gibbs, entalpia e entropia para o processo de solubilização de difenilaminesulfonato de bário em solvente misto consistindo de etanol-água a várias temperaturas. Foi determinada a constante de solubilidade, Ksp , e foram analisados também fatores tais como interações soluto-solvente, propriedades eletrostáticas, solvatação de íons e a força iônica do meio.

PALAVRAS CHAVE: Solubilidade, termodinâmica, solventes mistos, Ksp, difenilaminesulfonato de bário

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1. INTRODUCTION

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 solvent's 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 [2-4].

The solvation of dissolved ions determines many of the properties of electrolyte solutions [5–7], including their redox, complexation, and kinetic behavior. Its particular importance to solubilities, the central topic of the international symposium on solubility phenomena, is illustrated by the thermodynamic cycle in Fig. 1. As shown, the (standard) Gibbs energy of solution, $\Delta_{soln}G^\circ$, is seen to be the sum of (the negative of the) lattice energy of the salt, $\Delta_{latt}G^\circ$, and the solvation energies of the ions, $\Delta_{solv}G^\circ$. This cycle makes it clear that the only reason that salts dissolve in solvents is because the very large lattice energies that are lost upon dissolution are compensated by the even larger solvation energies of the ions.

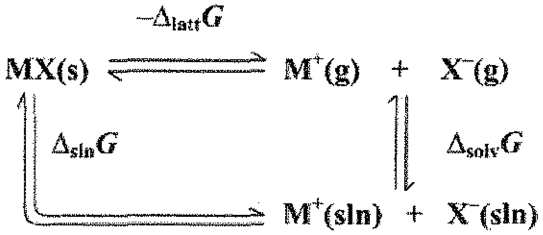

Fig. 1 Born–Haber cycle for dissolution of the salt MX.

Because both $\Delta_{latt}G^\circ$ and $\Delta_{solv}G^\circ$ are very large (negative) quantities, typically of the order of −1000 kJ/mol, it follows that relatively small changes in either, for example, arising from minor changes in the nature of the solvent or the salt, can result in dramatic changes in solubility. Given that $\Delta_{sln}G^o = -RT\ln K^o_{sp} = 2.303\ RT\ pK^o_{sp}$

where R and T have their usual meanings and $\mathbf{K^{o}_{sp}}$ is the (standard) solubility product of the salt:
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 [8-15].

2. EXPERIMENTAL

2.1 Chemicals and Reagents

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

2.2 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 diphenylaminesulfonate 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 (g.mole/Kg.solvent), of barium diphenylaminesulfonate in the mixed solvent at different temperature was determined gravimetrically by the solvent evaporating method. All the solubility experiments were repeated at least three times and the results were averaged.

3. RESULTS AND DISCUSSION

For an ionic compound, with the formula BA_2, we may consider the following equilibrium in its saturated solution at a given constant temperature.

$$\mathbf{BA_2(s) \quad \leftrightarrow \quad B^{2+}{}_{(aq)} + 2A^{-}{}_{(aq)}, \qquad K_{sp(th)} = a_{+} \cdot a_{-}^{2}} \qquad \mathbf{(1)}$$

Where $K_{sp(th)}$ denotes the thermodynamic solubility product constant and a_+ and a_- refer to activity of B^{2+} and A^- in the solution, respectively. If the solubility of BA_2 is very low, it may replace the activity of each ion by its concentration, S_o

$$K_{sp(th)} = 4S_o^3 \qquad (2)$$

Where S_o represents the molarity of BA_2 in the very dilute solution. The electrostatic interaction becomes very small and the ion association phenomenon may be negligible (the activity coefficient $\gamma_\pm \sim 1$) [16-21].
At low concentration, the activity coefficient may be determined by using the Debye-Huckel limiting law:

$$\log \gamma_\pm = -Z_+Z_-A\sqrt{I} \quad \textbf{applicable for } I < 10^{-2}\,M \qquad (3)$$

Where Z_+ and Z_- are the charges of ions in solutions, $A = 1.823 \times 10^6(\varepsilon.T)^{-3/2}$, 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 m_i 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 (ε) for ethanol-water mixtures were taken from previous publications [22].

On the other hand, it can be considered that at high concentration, the solubility product constant (K_{sp}) is given by:

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

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 single ion activity coefficients [15]. At relatively high concentration, the electrostatic interaction becomes very large [23-26]. The activity coefficient may be determined using the extend Debye-Hückel law:

$$\log \gamma_\pm = -\frac{Z_+Z_-A\sqrt{I}}{I + Br^\circ\sqrt{I}} \qquad \textbf{for} \quad I < 10^{-1}\,M \qquad (5)$$

Where $B = 50.29\,(\varepsilon.T)^{-1/2}$, and r° is the solvated radius.

At high concentrations, activity coefficients of electrolyte solutions can be determined by using the Davies equation [27] 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.

$$\log \gamma_{\pm} = -Z_{+}Z_{-}A\left(\frac{\sqrt{I}}{I+\sqrt{I}} - 0.3I\right) \qquad (6)$$

The second term, 0.3 *I*, 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.

The molal solubility , S (g.mole/Kg.solvent), of barium diphenylaminesulfonate in the mixed solvent at different temperature was determined gravimetrically by the solvent evaporating method. The solubility values and activity coefficients are cited in Table (1).

The solubility of saturated solution of barium diphenylaminesulfonate 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.

The solubility product was calculated by the use of equation (7).

$$pK_{sp} = -4(\log S^3 + \log \gamma_{\pm}^3)\ldots\ldots\ldots\ldots(7)$$

The solubility product (pK_{sp}) data are given in Table (2), the Gibbs free energies of solvation and the transfer Gibbs free energies from water to mixed solvents were calculated by using equations (8) and (9) [28-32]. Their values are tabulated also in Table (2) and Table (3).

$$\Delta G^{o} = 2.303\ RT\ pK_{sp} \qquad (8)$$

$$\Delta G_t = \Delta G_s - \Delta G_w \qquad (9)$$

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

The enthalpy change of solvation $(\Delta H)_s$ were calculated From the plots of log $K_{sp.}$ versus $\frac{1}{T}$ as shown in Figs. 1, where the slope equals $-\Delta H/2.303\ R$ using van 't Hoff equation [33]:-

$$\log \mathbf{K} = -\frac{\Delta \mathbf{H}^{\circ}}{2.303\mathbf{R}}\left(\frac{1}{\mathbf{T}}\right) + \mathbf{constant} \qquad \mathbf{(10)}$$

From equation (18) & (20) the values of $(\Delta G)_s$ and $(\Delta H)_s$ can be used to calculate the values of TΔS at different temperatures according to Gibbs-Helmholtz equation (12) [32] and all the results are reported in Table (3).

$$\mathbf{(\Delta G)_s = (\Delta H)_s - (T\Delta S)_s} \qquad \mathbf{(12)}$$

The magnitude of $\Delta G_{t\ (\text{solute, w} \rightarrow \text{w + s})}$ as shown in Figs. 2 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 diphenylaminesulfonate solubilization. This is due to more solvation behaviour 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 diphenylaminesulfonate solubilization in the aqueous carrier solution. Positive Gibbs free energy values indicate disfavourable conditions.

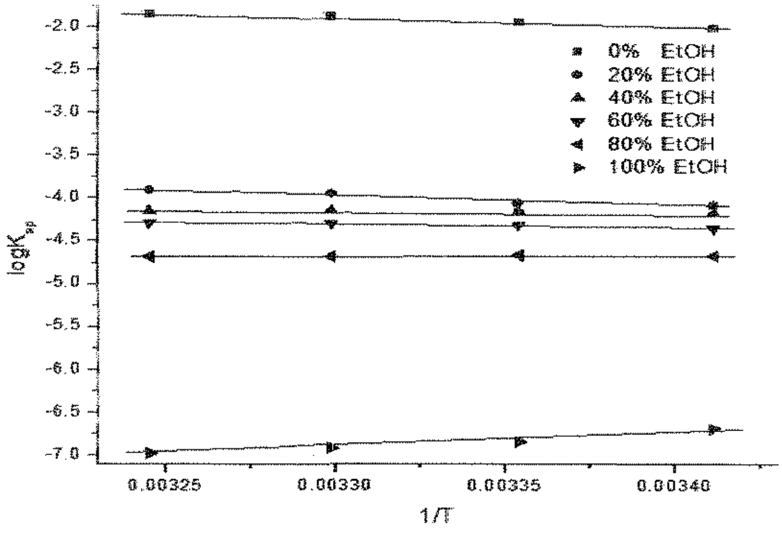

Fig. 1. Plots of log $K_{sp.}$ for barium diphenylaminesulfonate versus $\frac{1}{T}$ at different vol % of EtOH.

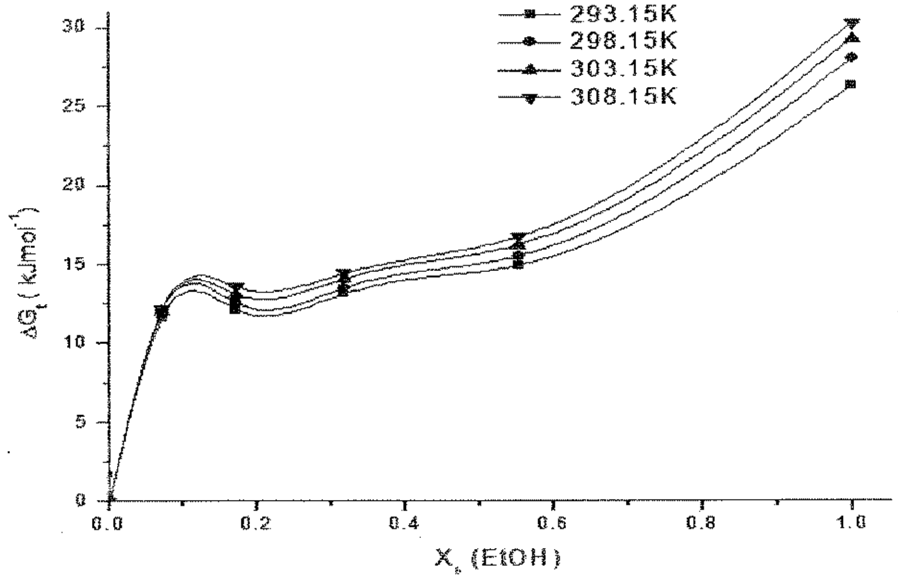

Fig. 2. Gibbs free energies of transfer (ΔGt) for barium diphenylaminesulfonate versus the mole fraction (X_s) of EtOH at different temperature.

Table 1. Solubilities and molal activity coefficients for barium diphenylaminesulfonate in mixed EtOH-H2O solvents at different temperature.

EtOH% By vol.	X_s EtOH	S,g. mol/kg solvent				log $\gamma_\pm$			
		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	0.5513	0.5518	0.5516	0.5508
20	0.0717	0.0468	0.0485	0.0538	0.0569	0.5792	0.5729	0.5605	0.5510
40	0.1708	0.046	0.0479	0.0489	0.049	0.5515	0.5428	0.5369	0.5316
60	0.3166	0.0451	0.0468	0.0476	0.0481	0.4924	0.4902	0.4868	0.4844
80	0.5527	0.0446	0.0464	0.0468	0.0474	0.3878	0.3757	0.3702	0.3631
100	1	0.0439	0.0459	0.0468	0.0470	0.0838	0.0711	0.0669	0.0631

Table 2. Solubility products and Gibbs free energies of solvation for barium diphenylaminesulfonate in mixed EtOH-H_2O solvents at different temperature.

X_s, EtOH	pK_{sp}				ΔG_s, kJ/mol			
	293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	2.0246	1.9543	1.8855	1.8553	11.364	11.157	10.944	10.947
0.0717	4.0974	4.0661	3.9608	3.9081	22.999	23.212	22.99	23.059
0.1708	4.1848	4.1526	4.1410	4.1519	23.489	23.706	24.037	24.497
0.3166	4.3591	4.3152	4.3102	4.2963	24.468	24.634	25.019	25.349
0.5527	4.6841	4.6745	4.6807	4.6891	26.292	26.686	27.169	27.667
1	6.7008	6.8562	6.9206	6.9812	37.612	39.141	40.171	41.191

Table 3. Transfer Gibbs free energies, enthalpy and entropy of solvation for barium diphenylaminesulfonate in mixed EtOH-H_2O solvents at different temperature.

X_s, EtOH	ΔG_t, kJ/mol				ΔH_s, kJ/mol	$(T\Delta S)_s$, 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	20.006	8.642	8.850	9.062	9.060
0.0717	11.634	12.055	12.046	12.112	23.206	0.188	0.205	0.216	0.224
0.1708	12.125	12.549	13.092	13.550	3.889	-19.601	-19.818	-20.148	-20.609
0.3166	13.104	13.478	14.074	14.402	6.714	-17.754	-17.920	-18.305	-18.635
0.5527	14.928	15.529	16.225	16.720	-0.717	-27.009	-27.403	-27.886	-28.384
1	26.247	27.984	29.226	30.244	-31.432	-69.043	-70.572	-71.602	-72.622

4. CONCLUSIONS

The solubility of saturated solution of barium diphenylaminesulfonate 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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REFERENCES

[1] Marcus, Y., Pure Appl. Chem., 1990, 62, 2069-2076.
[2] Water and aqueous solutions, in: R.A. Home (Ed). 1972.
[3] M. Aghaie; H. Aghaie, J. Mol. Liq., 135, (2007), 72.
[4] M. Aghaie, S. Ghafoorain, B.Sh. Broojeni, H. Aghaie, J. Phys. Theor Chem, 5, (2009), 223.
[5] Y. Marcus. Ion Solvation, John Wiley, New York (1985).
[6] G. A. Krestov, N. P. Novosyolov, I. S. Perelygin, A. M. Kolker, L. P. Safonova, V. D. Ovchinnikova, V. N. Trostin. Ionic Solvation, Ellis Horwood, Chichester, UK (1994).
[7] O. Popovych and R. P. T. Tomkins. Nonaqueous Solution Chemistry, John Wiley, New York (1981).
[8] M. Aghaie, B. Sh. Broojeni. J. Phys. Theor. Chem, 3, (2007), 249.
[9] M. Aghaie, E, Samaie, J. Mol. Liq. 126, (2006), 305.
[10] N. Bjerrum, K. Danske vidensk. Selsk (Match. Fys. Medd), 7, (1926), 9
[11] Ion Assiciation, by Davies, C. W, 1962.
[12] R.W.Margaret. L. J. P.Lain. D. M. H. Kenneth, J. Chem. Ed. 75/3 (1998) 352.

[13] H. Aghaie, M. Aghaie, A. Ebrahimi, J. Phys. Theor. Chem, 2, (2005), 151.
[14] M. Aghaie, S. Gafoorian, J. Chem. Eng. Data, 55 (2010) 1867.
[15] P. Debye, E. Huckel, Z. Phys. 24 (1923)185, 305.
[16] M. Aghaie, B. S. Broojeni, J. Phys. Theor. Chem, 3 (2007) 249.
[17] M. Aghaie, E. Samaie, J. Mol. Liq, 126 (2006) 72.
[18] M. Aghaie, F. Ghaemi. A, M. Giahi, J. Phys. Theor. Chem, 2 (2005) 33.
[19] H. Aghaie, A. AliABA2di, B. Sohrabi, M. Aghaie, M. R. Sohrabi, J. Phys. Theor. Chem, 1 (2004) 143.
[20] M. R. Wright, I.L.L. Patterson, K.D. M. Harris, J. Chem. Educ, 75930
(1998) 352.
[21] E. C. Zhong, H. L. Friedman, J. Phys. Chem, 92 (1988) 1685.
[22] El-khouly, A. A., Gomaa, E. A., and Abou El-leef, S., (Bulletin of electrochemistry 19(5) May 2003, pp193-202).
[23] N. Bjerrum, Mat. Fys. Medd. K. Dan. Vidensk. Selsk, 7 (1926) 1.
[24] M. Aghaie, S. Gafoorian, B. S. Broojeni, H. Aghaie, J. Phys. Theor. Chem, 5 (2009) 223.
[25] M. Aghaie, H. Aghaie, A. Ebrahimi, J. Mol. Liq. 135 (2007) 72.
[26] D. E. Smith, Y. V. Kalyuzhnyi, A. D. J. Haymet, J. Chem. Phys, 95 (1991) 9165.

[27] Davies, C.W. Ion Association. London: Butterworths. (1962) p. 37–53.
[28] Gomaa, E. A., Eur. Chem. Bull., 2013, 1(5) 254-261.
[29] Gomaa, E. A., and Al-Jahdali, Science and Technology, 2012, 2(4) 66-76.
[30] Gomaa, E. A., Global Ad. Rescarch J. of Chem. and Material Science, 1(2), 35-38, 2012.
[31] Gomaa, E. A., AbuEl-Nader, H. M. and Rashed, Sh. E., Physical Chemistry, 2012, 2(3) 9-17.
[32] Dickerson R.E. and Geis I.,Chemistry, Matter and the Universe, W.A. Benjamin, Menlo Park, CA., 1976.
[33] Chemical Thermodynamics, D.J.G. Ives, University Chemistry, Macdonald Technical and Scientific, 1971.