

Calculations of Ion-ion Interactions, Densities, and Different Volumes of Barium Diphenylamine Sulfonate in Ethanol-water at Different Temperatures

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ABSTRACT

The aim of this work is to calculate ion-ion interaction, dielectric constant, density of organic-aqueous mixtures of ethanol-water, density of saturated solutions of barium diphenylamine sulfonate (BDPA), solvation volumes (Van der Waals volume V_{Wp} , molar volume V_M , and electrostriction volume V_e), and solvated radii (r_o) from solubility experiments. It was found that values of the log activity coefficient (γ_{\pm}) of BDPA in (EtOH-H₂O) mixture were decreases by increasing in the content of the organic solvent used. The values of the log γ_{\pm} found to decrease with the increase in temperature. The densities and the molar volumes of the saturated solutions of BDPA decrease by increasing ratio of EtOH and also increase by increasing in temperature. All the electrostriction volumes calculated for BDPA having negative values. The electrostriction volumes increase in negativity on increasing the percentages of the organic solvent. The solvated radii of BDPA are increased as the organic solvent content increase and as the temperature increase.

Key words: Barium diphenylamine sulfonate, ion-ion interactions, solubility, solvation volumes

INTRODUCTION

The ionic strength of a solution is a measure of the concentration of ions in that solution. Ionic compounds, when dissolved in water, dissociate into ions. The total electrolyte concentration in solution will affect important properties such as the dissociation or the solubility of different salts. One of the main characteristics of a solution with dissolved ions is the ionic strength. Various models have been used to predict the cosolvent/water solubility profiles. These include parabolic and log-linear models. The log-linear model of Yalkowsky and Rosemann^[1] describes an exponential increase in non-polar drug solubility with a linear increase in cosolvent concentration. There are also numerous parabolic models that have been used to predict the cosolvent/water solubility profile for semi-polar solutes. Paruta *et al.*^[2] correlated the cosolvent solubility with a parabolic function of the dielectric constant of the solvent mixture. Martin *et al.*^[3-5] proposed a parabolic relationship between solute solubility and the solubility parameter of a solvent mixture. Recently, Ruckenstein *et al.*^[6] applied fluctuation theory to generate a new parabolic relationship. These parabolic relationships are based on regular solution theory. As was shown by Hilderbrand and Scatchard^[7] and later reiterated by Yalkowsky,^[8] regular solution theory

is not applicable to solutions where hydrogen bonding or ionic interactions are dominant. Ethanol is the most commonly used cosolvent due to its low toxicity and low cost. Ethanol/water systems have the most data available, and therefore, ethanol will be used as the model solvent for this study. A lot of published data^[9-12] for BDPA and other substances that states that they are very important materials for different fields.

MATERIALS AND METHODS

Materials

High grade of barium diphenylamine sulfonate ethanol was supplied from Merck, double-distilled water that has measured specific conductance 2×10^{-7} S/cm.

Preparation of Mixed Solvent and Saturated Solutions

The mixed solvent, (ethanol + water by percent values of ethanol = 0, 20, 40, 60, 80, and 100% by volume), was prepared from double-distilled water and fairly pure ethanol. Then, saturated solutions of BDPA were prepared by dissolving different amounts in closed test tubes containing different (ethanol + water) mixtures. The tubes were placed in a shaking thermostat (Model Gel) for 4 days till equilibrium reached. The solubility, S (mole/kg.solvent), of BDPA in the mixed solvent at different temperature was determined gravimetrically by the solvent evaporating method. All the solubility experiments were repeated at least 3 times and the results were averaged.

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RESULTS AND DISCUSSION

Ion-ion Interaction Calculations

For an ionic compound, with the formula AB_2 , we may consider the following equilibrium in its saturated solution at a given constant temperature.



Where, $K_{sp(th)}$ denotes the thermodynamic solubility product constant and a_+ and a_- refer to activity of A^{2+} and B^- in the solution, respectively. If the solubility of AB_2 is very low, it may replace the activity of each ion by its concentration, so,

$$K_{sp(th)} = 4s_o^3 \quad (2)$$

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 $\gamma_{\pm} \sim 1$).^[13-16]

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

Ion-ion interaction is a function of the mean activity coefficient (γ_{\pm}) of the ions. There are several theoretically-based expressions that can be used to estimate the activity coefficients. At very low concentration, the electrostatic interaction becomes very small and the ion association phenomenon may be negligible (the activity coefficient $\gamma_{\pm} \sim 1$).^[17,18]

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

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

Where, Z_+ and Z_- are the charges of ions in solutions, $A = 1.823 \times 10^6 (\epsilon T)^{-3/2}$, 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.

At relatively high concentration, the electrostatic interaction becomes very large.^[19,20] The activity coefficient may be determined using the extended Debye-Hückel law:

$$\log \gamma_{\pm} = \frac{-Z_+ Z_- A \sqrt{I}}{I + B r^{\circ} \sqrt{I}} \text{ for } I < 10^{-1} M \quad (4)$$

Where $B = 50.29 \times 10^8 (\epsilon T)^{-1/2}$, and r° is the solvated radius.

At high concentrations, activity coefficients of electrolyte solutions can be determined using the Davies equation^[20] which is an empirical extension of Debye-Hückel theory. The final form of the equation gives the mean molal activity coefficient, γ_{\pm} , of an electrolyte which dissociates into ions having charges Z_+ and Z_- as a function of ionic strength, I .

$$\log \gamma_{\pm} = -Z_+ Z_- A \left(\frac{\sqrt{I}}{I + \sqrt{I}} - 0.3I \right) \quad (5)$$

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 results of the ionic strength for BDPA in (EtOH- H_2O) mixture are illustrated in Table 1. The values of the $\log \gamma_{\pm}$ for BDPA in (EtOH- H_2O) mixture are illustrated in Table 2 are shown in Figure 1.

It was found that values of the $\log \gamma_{\pm}$ of BDPA were decreases by increasing in the content of the organic solvent used (EtOH) due to decrease in its solubility which lead to a decrease of the electrostatic interaction becomes and the ion association. The values of the $\log \gamma_{\pm}$ found to decrease with the increase in temperature due to a decrease of the electrostatic interaction becomes and the ion association.

Density Measurements

Density of (organic-aqueous) mixtures

The results of the density measurements of the (organic-aqueous) mixtures (EtOH- H_2O) at different temperatures (293.15, 298.15, 303.15, and 308.15 K) are reported in Table 3.

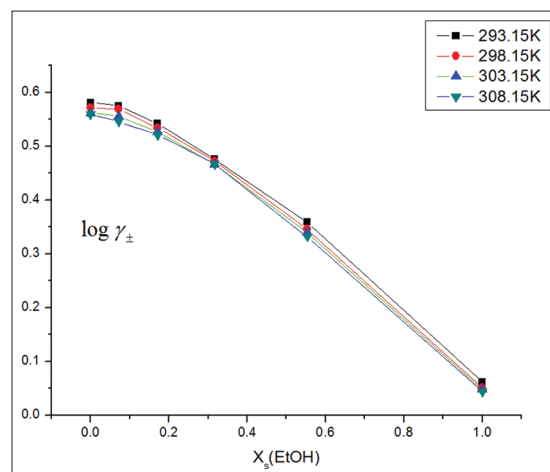


Figure 1: Relation between the activity coefficient ($\log \gamma_{\pm}$) of BDPA and the mole fraction of EtOH (X_s) in mixed solvents at different temperatures

Density of the saturated solutions

Table 4 summarizes the density of the saturated solutions of BDPA in (EtOH-H₂O) mixtures, at different temperatures (293.15, 298.15, 303.15, and 308.15 K). It is obvious that the densities of the saturated solutions of BDPA decrease by increasing ratio of EtOH and also increases by increasing in temperature.

Calculation of the Solvation Volumes

From density and molal solubility measurements of the saturated solutions of BDPA in (EtOH-H₂O) mixtures, the molar volumes (V)^[20,21] are calculated, at different temperatures (293.15, 298.15, 303.15, and 308.15 K) according to Equation (6):

$$V = \frac{M}{d} \quad (6)$$

Where, M is the molecular weight of BDPA, d is the density of the solution. The molecular weights of the binary solvents are calculated using Equation (7):

$$M = X_{S(1)(H_2O)} \cdot M_{(H_2O)} + X_{S(2)(O.S)} \cdot M_{(O.S)} \quad (7)$$

Where, M_(H₂O) and X_{S(2)(O.S)} are the molecular weights of water and organic solvent, respectively, X_{S(1)(H₂O)} and X_{S(2)(O.S)} are the mole fractions of water and the organic solvents used by are calculated by applying Equation (8):

$$X_{S(1)} \text{ by wt.} = \frac{\frac{\text{Vol.}\%(1) \times d(1)}{M}}{\frac{\text{Vol.}\%(1) \times d(1)}{M_1} + \frac{\text{Vol.}\%(2) \times d(2)}{M_2}} \quad (8)$$

Where, d₍₁₎ and d₍₂₎ are the densities of the organic solvent and water, respectively, and M₁ and M₂ are the molecular weights of the organic solvent and water, respectively, vol. % (1) and vol. % (2) are the volume percentages of the organic solvent and water, respectively.

The packing density (i.e., the relation between the Van der Waals volumes and the partial molar volumes) of relatively large molecules (>40) is found to be constant. Therefore, it is possible to calculate the Van der Waals volumes (V_w) of BDPA in (EtOH-H₂O) salt mixtures in at different temperatures (293.15, 298.15, 303.15, and 308.15 K) by applying Equation (9).

$$\text{Packing density (P)} = \frac{V_w}{V} = 0.661 \pm 0.017 \quad (9)$$

Where, V_w and V are the Van der Waals and partial molar volumes, respectively.

The electrostriction volume (V_e)^[21,22] which is the volume of the solute compressed by the solvent is calculated using Equation (10).

$$V_e = V_w - V \quad (10)$$

Table 1: Ionic strength (I) for BDPA in (EtOH-H₂O) mixed solvents at different temperatures

EtOH vol. %	X _s	Ionic strength, I			
		293.15 K	298.15 K	303.15 K	308.15 K
0	0	0.604	0.6369	0.6704	0.6884
20	0.0788	0.1171	0.1213	0.1344	0.1423
40	0.1857	0.115	0.1198	0.1222	0.1224
60	0.3391	0.1127	0.1171	0.1191	0.1202
80	0.577	0.1115	0.1159	0.1171	0.1186
100	1	0.1098	0.1148	0.116	0.1176

Table 2: Log activity coefficient (log γ_±) for BDPA in (EtOH-H₂O) mixed solvents at different temperatures

EtOH vol. %	X _s	log γ _±			
		293.15 K	298.15 K	303.15 K	308.15 K
0	0	0.5511	0.5513	0.5516	0.5494
20	0.0788	0.5755	0.5689	0.5558	0.546
40	0.1857	0.5425	0.5334	0.5268	0.5212
60	0.3391	0.4758	0.4729	0.4661	0.4663
80	0.577	0.3588	0.346	0.3397	0.3322
100	1	0.0619	0.0508	0.0473	0.0439

Table 3: Density (d_o) of (EtOH-H₂O) mixed solvents at different temperatures

EtOH vol. %	(d _o)			
	293.15 K	298.15 K	303.15 K	308.15 K
0	1.0004	0.997	0.9942	0.9912
20	0.9853	0.982	0.9789	0.9758
40	0.9643	0.9612	0.9577	0.9544
60	0.9335	0.9306	0.9264	0.9229
80	0.8836	0.8811	0.8756	0.8717
100	0.7889	0.7873	0.7789	0.7738

Table 4: Density (d) of saturated solution of BDPA in (EtOH-H₂O) mixed solvents at different temperatures

EtOH vol. %	(d)			
	293.15 K	298.15 K	303.15 K	308.15 K
0	1.53	1.61	1.734	1.835
20	1.207	1.211	1.214	1.217
40	1.163	1.165	1.167	1.169
60	1.111	1.114	1.116	1.119
80	1.05	1.053	1.057	1.063
100	1.013	1.019	1.025	1.029

Table 5: Molar volume (V), Van der Waals volume (V_w), electrostriction volume (V_e), and solvated radii (r_o) of BDPA in different (EtOH-H₂O) mixed solvents at 293.15 K (cm³.mol⁻¹)

EtOH vol. %	V	V _w	V _e	r _o
0	412.87	272.91	-140.0	4.6246
20	521.01	344.39	-176.6	5.0050
40	540.78	357.46	-183.3	5.0673
60	566.15	374.22	-191.9	5.1452
80	598.81	395.81	-203.0	5.2430
100	619.59	409.55	-210.0	5.3060

Table 6: Molar volume (V), Van der Waals volume (V_w), electrostriction volume (V_e), and solvated radii (r_o) of BDPA in different (EtOH-H₂O) mixed solvents at 298.15 K (cm³.mol⁻¹)

EtOH vol. %	V	V _w	V _e	r _o
0	392.22	259.26	-133.0	4.5467
20	519.33	343.28	-176.1	4.9994
40	539.94	356.91	-183.0	5.0644
60	564.63	373.22	-191.4	5.1405
80	597.11	394.69	-202.4	5.2379
100	615.78	407.03	-208.7	5.2956

The values of V , V_w , and V_e of BDPA in (EtOH-H₂O) mixtures; at different temperatures (293.15, 298.15, 303.15, and 308.15 K) are listed in Tables 5-8, respectively.

In comparing the data of solvation, it was observed that the values of the molar volume of ethanol mixtures with water are increased by increasing the organic solvents content in the mixtures due to the increase in the volume of organic solvent compared to water.

All the electrostriction volumes calculated for BDPA in (EtOH-H₂O) mixtures having negative values. The electrostriction volumes increase in negativity on increasing the percentages of the organic solvent, indicating the more work (energy) is done by the solvent on the solvation sheaths of the salts.

Calculation of the Solvated Radii

The solvated radii of the organic-aqueous mixtures; (EtOH-H₂O) at different temperatures (293.15, 298.15, 303.15, and 308.15 K) were calculated using Equation (11) by considering the spherical form of the solvated molecules.^[21,22]

$$V = \frac{1}{6} \pi N \sigma^3 \quad (11)$$

Where, V is the molar volume calculated from the densities as described before and σ is the solvated diameter. The solvated radii of BDPA in mixtures were calculated by adding the crystal radius of the salt to the radii of solvent

Table 7: Molar volume (V), Van der Waals volume (V_w), electrostriction volume (V_e), and solvated radii (r_o) of BDPA in different (EtOH-H₂O) mixed solvents at 303.15 K (cm³.mol⁻¹)

EtOH vol. %	V	V _w	V _e	r _o
0	363.97	240.58	-123.4	4.4357
20	518.32	342.61	-175.7	4.9954
40	538.98	356.26	-182.7	5.0616
60	563.61	372.54	-191.1	5.1375
80	594.71	393.10	-201.6	5.2314
100	612.02	404.54	-207.5	5.2853

Table 8: Molar volume (V), Van der Waals volume (V_w), electrostriction volume (V_e), and solvated radii (r_o) of BDPA in different (EtOH-H₂O) mixed solvents at 308.15 K (cm³.mol⁻¹)

EtOH vol. %	V	V _w	V _e	r _o
0	343.76	227.22	-116.5	4.3527
20	517.18	341.85	-175.3	4.9913
40	538.00	355.6	-182.4	5.0587
60	562.02	371.49	-190.5	5.1329
80	591.21	390.78	-200.4	5.2215
100	609.49	402.87	-206.6	5.2784

in BDPA (EtOH-H₂O) mixtures at different temperatures (293.15, 298.15, 303.15, and 308.15 K).

The calculated values of the solvated radii of BDPA (EtOH-H₂O) mixtures at different temperatures (293.15, 298.15, 303.15, and 308.15 K) as well as the solutions of BDPA in (EtOH-H₂O) mixtures are listed in Tables 5-8.

It is obvious that the solvated radii of BDPA in (EtOH-H₂O) mixtures are increased as the organic solvent content increase and as the temperature increase. This may be due to the excess solvation processes, and the higher solvated radii of the organic solvent used than those of water and also to increasing in the electronic clouds around the solvated molecules as a result of the increase in their vibration and rotation motions with increasing the temperature.

CONCLUSION

In this work, we calculate ion-ion interaction, dielectric constant, density of organic-aqueous mixtures of ethanol-water solvents, density of saturated solutions of BDPA, solvation volumes (Van der Waals volume V_w , molar volume V_M , and electrostriction volume V_e), and solvated radii from solubility experiments. It was found that values of the $\log \gamma_{\pm}$ of BDPA in (EtOH-H₂O) mixture were decreases by increasing in the content of the organic solvent used (EtOH). The values of the $\log \gamma_{\pm}$ found to decrease with the increase in temperature. The densities of the saturated solutions of BDPA decrease by increasing ratio of EtOH and also increase by increasing in temperature. The values of the molar volume of ethanol mixtures with

water are increased by increasing the organic solvents content in the mixtures due to the increase in the volume of organic solvent compared to water. All the electrostriction volumes calculated for BDPA having negative values. The electrostriction volumes increase in negativity on increasing the percentages of the organic solvent. The solvated radii of BDPA are increased as the organic solvent content increase and as the temperature increase.

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