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PARTIAL MOLAR VOLUME OF SOME ALKANOLAMINES IN WATER AT 298.15 K

VOLUMEN MOLAR PARCIAL DE ALGUNAS ALCANOLAMINAS EN AGUA A 298,15 K

VOLUME MOLAR PARCIAL DE ALGUMAS ALCANOLAMINAS EM ÁGUA A 298,15 K

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ABSTRACT

Densities of aqueous solutions of 3-amino-1-propanol, 2-amino-1-propanol, 3-amino-1,2-propanediol, and 1,3-diamino-2-propanol were measured at 298.15 K using the vibrating tube technique. The apparent molar volumes of the alkanolamines were determined as a function of composition from experimental data and the solute limiting partial molar volume was obtained through extrapolation. The results are discussed in terms of the effect of the number and the position of polar groups in the molecules.

Key words: Partial molar volume, molecular interactions, group contribution, alkanolamines.

RESUMEN

Las densidades de soluciones acuosas de 3-amino-1-propanol, 2-amino-1-propanol, 3-amino-1,2-propanodiol y 1,3-diamino-2-propanol fueron medidas a 298,15 K usando la técnica del tubo vibrante. Los volúmenes molares aparentes se determinaron en función de la composición a partir de los datos experimentales y los volúmenes molares parciales de los solutos a dilución infinita fueron obtenidos por extrapolación. Los resultados son discutidos en términos del efecto del número y la posición de los grupos polares en las moléculas.

Palabras clave: Volumen molar parcial, interacciones moleculares, contribución de grupo, alcanolaminas.

RESUMO

As densidades de soluções aquosas de 3-amino-1-propanol, 2-amino-1-propanol, 3-amino-1,2-propanediol and 1,3-diamino-2-propanol foram medidas a 298 K utilizando a técnica de tubo vi-

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bratório. Os volumes molares aparentes das alcanolaminas foram determinados como uma função de composição partindo de dados experimentais e parciais volumes molares de solutos na diluição infinita foram obtidos por extrapolação. Os resultados são discutidos em termos do efeito do número e da posição dos grupos polares nas moléculas.

Palavras-chave: Volume molar parcial, interações moleculares, grupo contribuição, alcanolaminas.

INTRODUCTION

Thermodynamic properties of aqueous solutions of model compounds of biological and industrial importance are of considerable interest due to their practical and theoretical importance. The information obtained contributes to understand the nature of interactions between non-polar and polar groups with water and the balance between hydrophobic and hydrophilic interactions (1-4).

Alkanolamines or aminoalcohols are small organic solutes that contain alkyl, amino, and hydroxyl groups. Their aqueous solutions have application in the removal of acid gases, such as carbon dioxide and principally hydrogen sulfide, from gas streams in the petroleum and natural gas industry. Additionally, they can be used as model systems for the study of molecular interactions in aqueous solution, additivity of polar group contributions and the effect of the number and position of polar groups (2).

The dependence of the apparent molar volumes on concentration gives useful information about (solute + solute) interactions, while the partial molar volumes at infinite dilution provide information about (solute + solvent) interactions. In the case of alkanolamines the information available in literature refers especially to the volumetric properties of the small alkanolamines such as glycolamines and those used in the petroleum industry (2, 5-18). Besides, density data for dilute aqueous solutions are scarce.

As continuation of our previous work on volumetric properties of small model compounds (19-24), in this article we report the effect of concentration on the apparent molar volumes of 3-amino-1-propanol, 2-amino-1-propanol, 3-amino-1,2-propanediol and 1,3-diamino-2-propanol in aqueous solution at 298.15 K. From these data, the solute limiting partial molar volume was determined through extrapolation. The solutes were selected to examine the effect of the position and number of polar groups on infinite partial molar volume in a systematical way. The results are discussed in terms of the nature of interactions between nonpolar and polar groups with water and their effect on water structure.

MATERIALS AND METHODS

Water was doubly distilled and deionized according to literature and degassed before use obtaining a product with conductivity less than 2 μS m-1 (25, 26). The solutes used in this work were 3-amino-1-propanol (Aldrich $\geq$99 %), 2-amino-1-propanol (Fluka $\geq$98.5 %), 3-amino-1,2-propanediol (Fluka $\geq$98 %), and 1,3-diamino-2-propanol (Fluka $\geq$98 %). All solutions were prepared by weight using a Mettler balance AT 261

dual range with sensitivity of 10^{-5} g in the lower range.

Densities were measured with an Anton Paar DSA 5000 densimeter with temperature control better than 0.01 K and uncertainty of $5x10^{-3}$ kg m^3. The densimeter was calibrated using air and water at 298.15 K. The density values reported for the aqueous solutions are the average of three independent measurements.

RESULTS AND DISCUSSION

Data for experimental density measurements and apparent molar volumes obtained in this work are presented in Tables 1-4. The measured density data were used to calculate the apparent molar volume V_ϕ using the equation:

$$V_\varphi = \frac{M_2}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0} \quad [1]$$

where M_2 is the molecular weight of the solute, m its molal concentration, ρ and ρ_0 are the densities of the solution and the aqueous solvent.

Figures 1 and 2 show the dependence of the apparent molar volumes of alkanolamines with molality. The apparent molar volumes do not show a linear dependence on molality in the concentration range considered. For all the solutes in the dilute region, partial molar volumes decrease as the solute concentration increases and the limiting slopes are negative. The behavior changes as concentration increases. 3-amino-1-propanol and 2-amino-1-propanol exhibit a minimum that is not observed for 3-amino-1,2-propanediol and 1,3-diamino-2-propanol.

As can be seen from equation [2], at infinite dilution the apparent molar volume is equal to the limiting partial molar volume.

$$\overline{V_2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} = V_\phi + n_2\left(\frac{\partial V_\phi}{\partial n_2}\right)_{T,P,n_1} \quad [2]$$

The values of the limiting molar partial volume were determined by extrapolation of the behavior of the apparent molar volume as a function of molality and the results are shown in Table 5 together with literature data when available.

It can be seen that the change of position of the amine group does not affect the value of partial molar volume at infinite dilution and the experimental behavior of the apparent molar volumes at infinite dilution of the isomers 3-amino-1-propanol and 2-amino-1-propanol is nearly the same within uncertainty limits. The value obtained in this work for 3-amino-1-propanol agrees with the corresponding literature value (2). The small difference can be attributed to differences in the concentration range used and the resulting differences in least-squares fitting of the experimental data. No results have been found in the literature for the other alkanolamines reported in this study.

Apparent molar volumes of alkanolamines show an important concentration dependence. The sign and magnitude of the limiting slopes reflect the size of the hydrocarbon chain (2, 21, 27, 28, 30). In this study the observed limiting slopes are negative indicating that although the polar groups influence the hydration sphere of the molecules, the solute behavior is determined by the interaction of water with the alkyl groups as it is

Table 1. Density and apparent molar volume for aqueous solutions of 3-amino-1-propanol at 298.15 K.

3-amino-1-propanol		
m mol kg^{-1}	ρ 10^{-3} kg m^{-3}	V_ϕ 10^6 m^{3}mol^{-1}
0.27665	0.997372	76.5
0.44461	0.997427	76.2
0.56485	0.997482	76.1
0.70575	0.997561	76.0
0.82997	0.997646	76.0
1.02548	0.997805	76.0
1.31837	0.998106	76.1
1.56321	0.998413	76.1
2.01427	0.999114	76.2
2.17948	0.999414	76.2

Table 2. Density and apparent molar volume for aqueous solutions of 2-amino-1-propanol at 298.15 K.

2-amino-1-propanol		
m mol kg^{-1}	ρ 10^{-3} kg m^{-3}	V_ϕ 10^6 m^{3}mol^{-1}
0.28551	0.997193	75.9
0.47671	0.997204	75.7
0.83005	0.997294	75.6
0.88372	0.997316	75.6
1.24293	0.997515	75.7
1.30714	0.997561	75.7
1.48246	0.997700	75.7
1.87082	0.998090	75.8
1.88097	0.998102	75.8
2.05881	0.998319	75.9

Table 3. Density and apparent molar volume for aqueous solutions of 3-amino-1,2-propanediol at 298.15 K.

3-amino-1,2-propanediol		
m	ρ	V_ϕ
mol kg^{-1}	10^{-3} kg m^{-3}	10^{6} m^{3}mol^{-1}
0.04232	0.997832	110.0
0.05159	0.997983	109.6
0.05198	0.997989	109.6
0.09756	0.998731	108.6
0.47507	1.004692	106.8
0.72362	1.008441	106.0
0.88222	1.010760	105.6
1.18179	1.014984	104.8
1.47448	1.018915	104.0
2.33489	1.029346	102.0

Table 4. Density and apparent molar volume for aqueous solutions of 1,3-diamino-2-propanol at 298.15 K.

1,3-diamino-2-propanol		
m	ρ	V_ϕ
mol kg^{-1}	10^{-3} kg m^{-3}	10^{6} m^{3}mol^{-1}
0.04961	0.997582	101.3
0.11271	0.998231	100.9
0.23893	0.999514	100.5
0.50630	1.002168	100.1
0.77562	1.004752	99.6
0.85284	1.005476	99.5
1.00933	1.006922	99.2
1.17847	1.008450	99.0
1.43499	1.010700	98.6
1.59604	1.012071	98.4
2.38679	1.018340	97.3

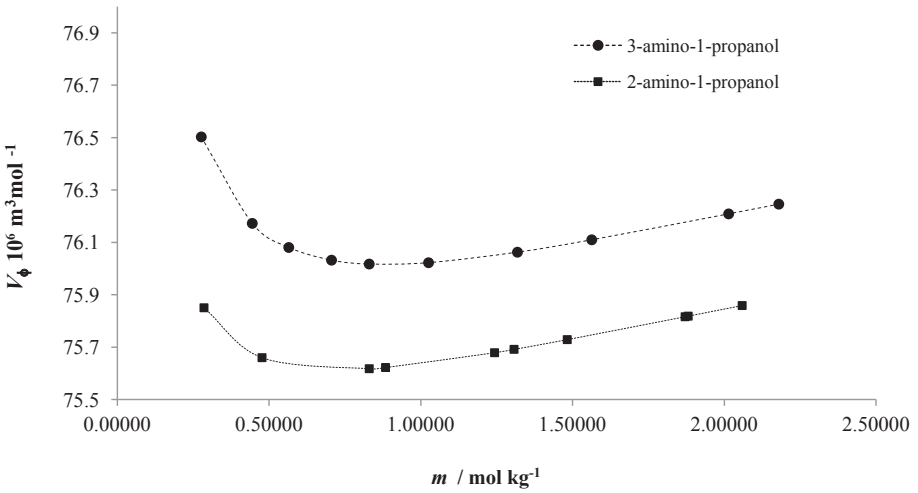

Figure 1. Apparent molar volume for aqueous solutions of 3-amino-1-propanol and 2-amino-1-propanol at 298.15 K.

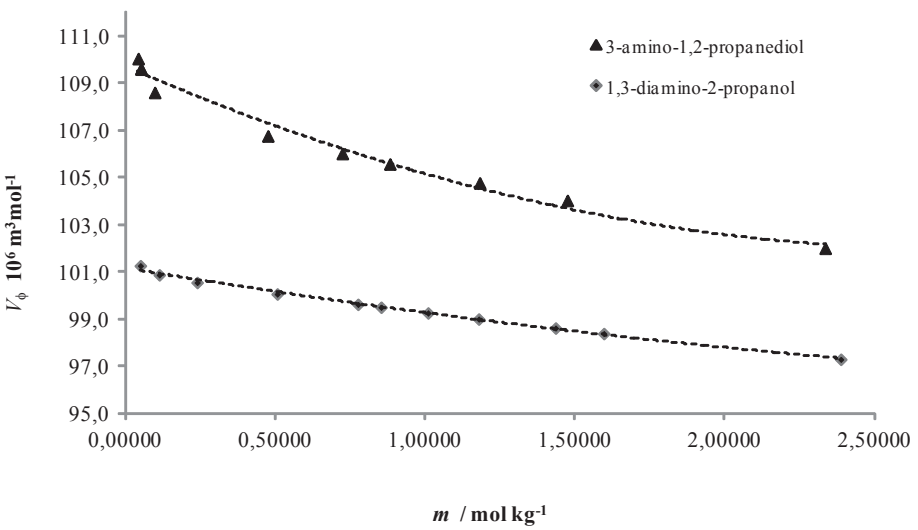

Figure 2. Apparent molar volume for aqueous solutions of 3-amino-1,2-propanediol and 1,3-diamino-2-propanol at 298.15 K.

observed with other polar compounds (1-3, 21, 22, 24, 27-31). However, the concentration dependence of the apparent molar volumes is different as can be seen in Figures 1 and 2. For 3-amino-1-propanol and 2-amino-1-propanol the minimum in the water-rich region is clearly observed. The concentration at which the minimum is observed is slightly lower for 2-amino-1-propanol showing that the

Table 5. Partial molar volume at infinite dilution for aqueous solutions of alkanolamines at 298.15 K.

Solute	V_ϕ /10^6m^{3}mol^{-1}	
3-amino-1-propanol	76.8	75.04 (2)
2-amino-1-propanol	76.4	
3-amino-1,2-propanediol	109.5	
1,3-diamino-2-propanol	101.2	

influence of the alkyl chain, with a larger hydrophobic domain, improves its promoting effect toward hydrophobic interactions (2, 21, 22). For 3-amino-1,2-propanediol and 1,3-diamino-2-propanol the partial molar volumes decrease as concentration increases and no minimum is observed, reflecting the effect of the increase of polar groups in the behavior of solute molecules.

According to the results obtained, the influence of the number of polar group on the volumetric properties does not follow a clear trend. From the data reported in literature for the partial molar volume at infinite dilution of n-propylamine, 74.0 cm^3 mol^{-1} (2) and 74.12 cm^3 mol^{-1} (31), it can be seen that the addition of a hydroxyl group in the isomers 3-amino-1-propanol and 2-amino-1-propanol does not cause a significant increase in this property and thus the volumetric contribution due to the hydroxyl group can not be considered additive as has been observed in previous works with alcohols and polyols (21-22). However, a comparison between 3-amino-1-propanol and 3-amino-1,2-propanediol shows that the addition of a hydroxyl group produces an increase of 32.7x10^{-6} m^3 mol^{-1} in the partial molar volume, while the addition of a second amino group as in the 1,3-diamino-2-propanol, causes an increase of 24.4x10^{-6} m^3 mol^{-1} in the partial molar volume at infinite dilution.

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