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Apparent molal volumes and viscosities of DL-α-alanine in water–alcohol mixtures

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Abstract

A systematic study of the experimental behavior of apparent molal volumes and viscosities of DL-α-alanine in aqueous 1-propanol, 1-butanol and 1,2-propanediol mixtures at 25°C is presented. The concentrations of the alcohol–water mixtures used as solvents were selected taking into account their special thermodynamic behavior and in particular the abrupt change observed in the dependence of partial molal volumes with concentration.

The results are discussed in terms of changes in solvent structure.

Keywords: Amino acid; Mixed solvent; Solute–solvent interactions; Volume; Viscosity

1. Introduction

Properties of amino acids in aqueous solutions have been extensively studied trying to obtain a better understanding of solute–solvent interactions and their role on the conformational stability of proteins [1–25]. Eventhough in recent years attention has been given to their behavior in different aqueous mixed solvents [4,9,13,23–28], there are only very few studies about amino acid properties in water–alcohol mixtures [29,30] probably due to the complex nature of its interactions [31,32].

In this work, we present a study of the apparent molal volumes and viscosities of DL-α-alanine in 1-propanol, 1-butanol and 1,2-propanediol aqueous solutions at 25°C. Alanine was chosen because, according to previous studies, it has a very small effect on water structure, so it can be considered almost "neutral", due to the compensation between hydrophobic hydration effects and charge–water interactions. Thus it is plausible to expect that changes in solvent structure must be reflected on important changes in the behavior of the solute in the mixed solvent. Besides, there is a plenty of information about its physico-chemical properties in water.

The concentrations of the alcohol–water mixtures were selected according to their thermodynamic behavior [31–42], in particular to the dependence of partial molal volumes with mole fraction [31,32,38–42]. Thus for 1-propanol and 1,2-propanediol, of the mixtures selected one has a mole fraction around the minimum observed in the alcohol partial molal volume isotherm, and the other mixtures have mole fractions lower and higher than the minimum. For the system 1-butanol–water, no minimum is observed and the mixtures were selected in a concentration range that at 25°C they show complete miscibility.

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The results are compared with data obtained in ethanol aqueous mixtures, giving a global insight of the dependence of the limiting apparent molal volumes and the viscosity *B* coefficients of alanine on alcohol nature and concentration.

2. Experimental

The materials used were the following: DL-α-alanine, Merck, analytical reagent which was dried under vacuum for 48 h before use. 1-Propanol, 1-butanol and 1,2-propanediol were J.T. Baker analytical reagents and were distilled and degassed before use. Water was doubly distilled, treated according to literature [43] and degassed before use. All solutions were prepared by weight using a Mettler balance AT 261.

Density of solutions was measured using a magnetic float densimeter described elsewhere [44] with an uncertainty of $\pm 2\times 10^{-6}$ g cm^{-3}. Viscosity was determined using two Ubbelohde viscometers with efflux times nearly 300 s for water. Reproducibility of efflux times was in all cases better than 0.05%. All measurements were realized in a constant temperature bath with temperature controlled to ±0.005°C.

Density and efflux times were determined at 25°C for the aqueous alcohol mixtures used as solvents and for at least 8 solutions of DL-α-alanine in each one of the aqueous solvents, in a concentration range from 0.0100 to 0.1000 m.

The apparent molal volumes ϕ_v were calculated from the equation

$$\phi_v = M/d + 1000(d_0 - d)/mdd_0, \qquad (1)$$

where *M* is the molecular weight of the solute, *m* its molal concentration, *d* and d_0 are the densities of the solution and the aqueous solvent, respectively.

The viscosity data were obtained from the relation

$$\eta = \alpha dt - \beta d/t, \qquad (2)$$

where α and β are the viscometer constants, *d* is the density and *t* the efflux time. The relative viscosities $\eta_r=\eta/\eta_0$ were calculated from the solution and solvent viscosities, respectively.

3. Results

Table 1 presents the density and viscosity values at the alcohol molar fractions selected for all the alcohol–water mixtures considered in this work.The data obtained compare well with the values reported in literature for these systems.

The apparent molal volumes of alanine in the aqueous solvents were calculated by means of Eq. (1). In all cases, the dependence of the apparent molal volume on concentration is linear in the concentration range considered. The data were fitted by least squares to the well-known equation

$$\phi_v = \phi_v^0 + S_v m, \qquad (3)$$

Table 1
Density and viscosity of alcohol–water mixtures at 25°C

Solvent	X_{OH}	*d* (g cm^{-3})	10^{-3} η (kg m^{-1} s^{-1})
PrOH–H_2O	0.0100	0.991678	1.0267
PrOH–H_2O	0.0250	0.985067	1.2475
PrOH–H_2O	0.0450	0.977114	1.5497
PrOH–H_2O	0.0650	0.968939	1.8105
PrOH–H_2O	0.0800	0.962041	1.9687
BuOH–H_2O	0.0030	0.995064	0.9421
BuOH–H_2O	0.0060	0.993180	0.9940
BuOH–H_2O	0.0090	0.991419	1.0471
BuOH–H_2O	0.0120	0.989741	1.1001
1,2-Pr$(OH)_2$–H_2O	0.0300	1.005627	1.3114
1,2-Pr$(OH)_2$–H_2O	0.0600	1.013763	1.8506
1,2-Pr$(OH)_2$–H_2O	0.1000	1.022797	2.7329
1,2-Pr$(OH)_2$–H_2O	0.1200	1.026389	3.2329

in which ϕ_v^0 is the limiting apparent molal volume, S_v the experimental slope and m is the molal concentration. At infinite dilution, ϕ_v^0 becomes equal to the partial molal volume $\bar{V}^0$.

The viscosity data obtained for alanine in the aqueous solvents were adjusted by least squares to a second-order equation of the type proposed by Tsangaris–Martin [21]:

$$\eta_r = 1 + Bm + Dm^2. \quad (4)$$

Eventhough B and D are empirical coefficients, B has been related to solute–solvent interactions and apparently depends on the size, shape and charge of the solute molecule.

The values of ϕ_v^0, and B for alanine in 1-propanol 1-butanol and 1,2-propanediol in water and in the aqueous mixtures used as solvents are summarized in Table 2. The data obtained in a previous work for alanine in ethanol–water mixtures are also included for comparison in Table 3.

The data reported in literature for the limiting apparent molal volume and the viscosity B coefficient of alanine in water have important differences that make difficult the selection of one of them. In this work, we selected the best values [1–28] taking into account the method used, the uncertainty in measurements, number of measurements, concentration range, and temperature control. These data were treated to calculate the average values which are given in Table 2. The average of 20 selected values for the apparent molal volume of alanine in water is 60.47 cm^3 mol^{-1} and the standard deviation is 0.09 cm^3 mol^{-1}. The average of six selected values for the B coefficient is 0.2525 kg mol^{-1} and the standard deviation is 0.0048 kg mol^{-1}; two uncertain digits are kept since some of the averaged values have four significant figures.

Table 2
Apparent molal volumes and viscosity B coefficients of DL-α-alanine in water and aqueous alcohol solutions at 25°C

Solvent	X_{OH}	ϕ_v^0 (cm^3 mol^{-1})	B (kg mol^{-1})
H_2O		60.47	0.2525
PrOH–H_2O	0.0100	60.36	0.2476
PrOH–H_2O	0.0250	60.69	0.2327
PrOH–H_2O	0.0450	59.24	0.2168
PrOH–H_2O	0.0650	60.99	0.1959
PrOH–H_2O	0.0800	61.18	0.2061
BuOH–H_2O	0.0030	60.35	0.2507
BuOH–H_2O	0.0060	60.34	0.2328
BuOH–H_2O	0.0090	60.66	0.2498
BuOH–H_2O	0.0120	60.37	0.2672
1,2-Pr(OH)$_2$–H_2O	0.0300	60.01	0.2523
1,2-Pr(OH)$_2$–H_2O	0.0600	60.67	0.2514
1,2-Pr(OH)$_2$–H_2O	0.1000	61.59	0.2468
1,2-Pr(OH)$_2$–H_2O	0.1200	61.94	0.2632

Table 3
Apparent molal volumes and viscosity B coefficients of DL-α-alanine in aqueous ethanol solutions at 25°C [30]

X_{OH}	ϕ_v^0 (cm^3 mol^{-1})	B (kg mol^{-1})
0.0000	60.47	0.2525
0.0200	58.71	0.2173
0.0375	57.80	0.1618
0.1000	56.11	0.1223
0.1435	57.82	0.1913

The values of the experimental slopes S_v for alanine in the alcohol–water mixtures present very small changes when compared to the corresponding value in water. Being the magnitude of the changes near the experimental uncertainty and taking into account the considerable scatter of the data reported in literature [1,2,4,5,12,18,19,22–25], we will not attempt in this work an interpretation of the observed changes.

4. Discussion

The behavior observed for the aqueous solvents follows the trend reported by other authors for the excess partial molal volumes of alcohols in water. The large and negative excess partial molal volumes $\bar{V}^{0E}$ become more negative with increase in length of the alcohol chain and the minimum in the $\bar{V}^{0E}$ (X_{OH}) isotherms occurs at lower concentration, except for the 1-butanol–water system whose low miscibility does not allow to reach the concentration where the minimum should appear. Because of the importance of these facts in the following analysis, the values for the excess partial molal volumes along with the alcohol mole fractions at which minimum are observed are reported in Table 4.

Fig. 1 shows the influence of alcohol mole fraction on the limiting apparent molal volumes of alanine. The curves for alanine in ethanol, 1-propanol and 1,2-

Table 4
Excess partial molal volumes for alcohols in water at infinite dilution at 25°C

Alcohol	$\bar{V}^{0E}$ (cm^3 mol^{-1})	X_{min}
Ethanol	−3.7 [32]	0.08 [31,32]
1-Propanol	−4.5 [32]	0.07 [31,32]
1-Butanol	−5.0 [32]	
1,2-Propanediol	−2.0 [41]	0.06 [41]

propanediol are quite similar. ϕ_v^0 decreases with the increase of alcohol mole fraction in the solvent until a minimum is reached. This occurs at mole fractions of 0.1000 of ethanol, 0.0450 of 1-propanol and 0.0300 of 1,2-propanediol. At higher values of alcohol mole fraction, ϕ_v^0 shows a noticeable increase. When the 1-butanol–water mixtures are used as solvents the ϕ_v^0 values of the amino acid are slightly lower than those in pure water, and do not show a significant change with alcohol concentration. When the behavior of alanine in alcohol mixtures is compared with the volumetric behavior of alcohols in water, it can be seen that the minimum apparent molal volume of alanine in the mixtures appears at mole fractions equal or slightly lower than those at which the minimum for the corresponding alcohol–water isotherm is obtained. Besides, the minimum in the alcohol–water mixtures is more pronounced as the length of the alcohol chain increases, while the minimum shown in the curves of alanine is more pronounced as the length of the alcohol chain in the aqueous solvent decreases.

The effect of alcohol concentration on the viscosity B coefficient of alanine can be observed in Fig. 2. The values for B coefficients decrease with alcohol mole fraction until a minimum is reached. In the ethanol–water solvent system, the minimum is reached at X_{et}=0.1000, in 1-propanol–water, the minimum is reached at X_{pr}=0.0650, and in 1,2-propanediol–water, the minimum is at 0.1000. In 1-butanol–water, the behavior is similar showing a minimum at X_{bu}=0.0060.

The results show that at low alcohol mole fraction, the limiting apparent molal volume and the viscosity B coefficient of alanine in monohydric alcohols are always lower than the corresponding values in water, being the changes of these properties more pronounced as the hydrocarbon chain of the alcohol is shorter. Furthermore, changes in the volumetric behavior of alanine in 1,2-propanediol are less pronounced than the observed changes in 1-propanol.

The behavior of alanine at low alcohol concentrations may be attributed to induced modifications of water structure caused by the addition of alcohols and depends on aliphatic chain length and is also related to the number of OH groups. However, more information is necessary to attempt a definite explanation of the

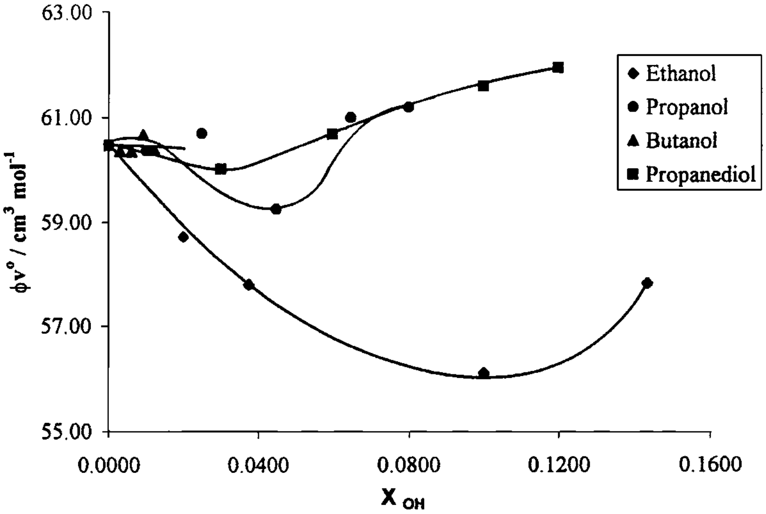

Fig. 1. Limiting apparent molal volumes of DL-α-alanine in aqueous alcohol mixtures at 25°C.

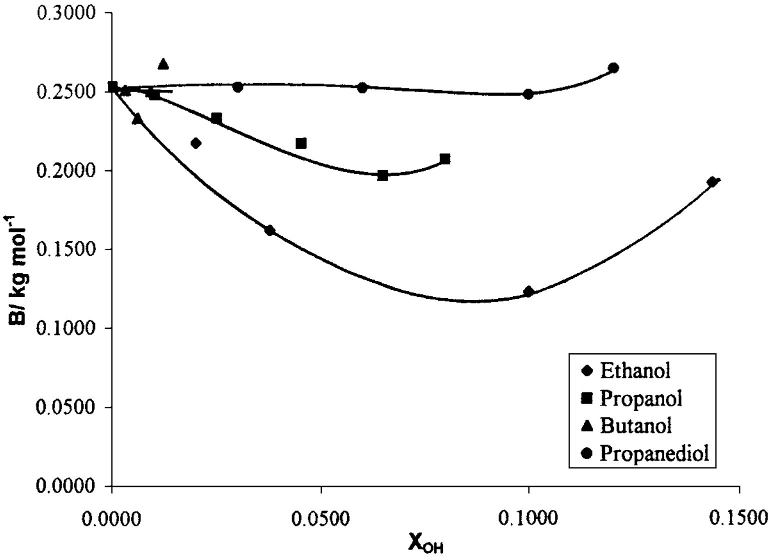

Fig. 2. Viscosity B coefficients of DL-α-alanine in aqueous alcohol mixtures at 25°C.

effect of alcohols on the behavior of alanine in aqueous mixtures.

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