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THERMODYNAMIC PROPERTIES OF AQUEOUS ALCOHOL AND POLYOL SOLUTIONS

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Abstract

In this work, we present experimental results for partial molar volumes and viscosities of aqueous solutions of *n*-propanol, 1,2-propanediol, 1,3-propanediol and 1,2,3-propanetriol at 25.00°C and literature data for other systems. The thermodynamic behavior of aqueous alcohol and polyol solutions is discussed in terms of the relationship between polar and non-polar groups and their effect on water structure.

The relationship of hydroxyl groups to the number of non-polar groups in the solute determines the balance between hydrophobic and hydrophilic interactions and as a direct consequence, the thermodynamic behavior of properties such as partial molar volumes, and viscosity.

Keywords: amino acid, mixed solvent, solute-solvent interactions, viscosity, volume

Introduction

Aqueous solutions of alcohols have been extensively studied looking for an explanation for their particular behavior, especially at low concentration [1–5]. Some of the properties that have called attention of many scientists are the pronounced minimum in the partial molar volume curves of the solutes, the maximum in the viscosity curves, the particular behavior of the excess enthalpy and the dependence on temperature of excess and partial molar volumes [1–16]. The presence of maxima and minima in the behaviour of these properties as a function of concentration indicates, as Franks points out, that they are related to structural changes that depend on the relation between hydrophobic and hydrophilic groups [5].

Even though there is not yet a definite explanation in terms of the intermolecular forces that determine their particular behavior, the experimental results suggest that any interpretation should take into account the complex nature of the alcohol–water mixtures mainly due to hydrogen bonding and the fundamental effect exerted by the alkyl chain especially at low concentration where the interaction of the hydrophobic

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hydration sphere with the hydrophilic hydration sphere define the behavior of the aqueous mixture [1, 2, 6, 8, 13, 18].

The presence of additional hydroxyl groups change the hydrophobic–hydrophilic balance and the peculiar behavior becomes less pronounced [16, 17]. Even though some thermodynamic properties of aqueous glycol mixtures have been determined, the lack of precise experimental data allowns neither a systematic study of the effect of the relation of polar groups to apolar groups on the thermodynamic properties of these systems nor of the effect of the position of the polar groups.

In this work we present a study of the partial molar volumes and the viscosities aqueous solutions of *n*-propanol, 1,2-propanediol, 1,3-propanediol and 1,2,3-propanetriol at 25.00°C. The dependence of the limiting partial molar volumes, and the viscosity *B* coefficient on concentration are analyzed in terms of the relation between polar and apolar groups and the relative position of the hydroxyl groups.

Experimental

The materials used were the following: 1-propanol Merck 99.5%, 1,2-propanediol Merck 99.5%, 1,3-propanediol Sigma 99.0% and 1,2,3-propanetriol Carlo Erba 99%. The four alcohols were analytical reagents and were distilled and degassed before use. Water content was determined in all cases by Karl Fisher method. Water was doubly distilled, treated according to literature and degassed before use. All solutions were prepared by mass using a Mettler balance AT 261 dual range with sensitivity of 10^{-5} g in the lower range. Final concentrations were corrected according to the water content analysis.

Density of solutions was measured using pycnometers of the Wood–Brusie type with an uncertainty of $\pm 5\cdot 10^{-5}$ g cm^{-3}. Viscosity was determined using two Ubbelohde viscometers with efflux times near 300 s for water. Reproducibility of efflux times was in all cases better than 0.05%. The results for pure compounds compare well with literature data. All measurements were realized in a constant temperature bath with temperature controlled to ±0.005°C. Density and efflux times were determined at 25.00°C for the aqueous alcohol mixtures in the whole concentration range.

The apparent molar volumes ϕ_v were calculated from the equation [17–19]:

$$\phi_v = M/d + 1000(d_0 - d)/mdd_0 \tag{1}$$

where M is the molecular mass of the solute, m its molar concentration, d and d_0 are the densities of the solution and the aqueous solvent. They were used to evaluate the partial molar volumes according to the relation:

$$\overline{V}_2 = \Phi_{V_2} + m\left(\frac{\partial \Phi_{V_2}}{\partial m}\right)_{T,P}$$

The viscosity data were obtained from the relation:

$$\eta = \alpha dt - \beta d/t \tag{2}$$

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 [18, 19].

Results

Figure 1 presents the behavior of the excess molar volume divided by X_1X_2, Vm^E/X_1X_2 as function of molar fraction X_2 for the four alcohols in water at 298.15 K. The partial molar volumes of alcohol and water at infinite dilution were evaluated from the Redlich–Kister approach, by extrapolation to $X_2=1$ and $X_2=0$ according to Desnoyers and Perron recommendation [17]. This procedure was chosen because the resulting curves are smoother than the partial molar volume curves, making easier the extrapolation procedure to obtain the limiting values at infinite dilution.

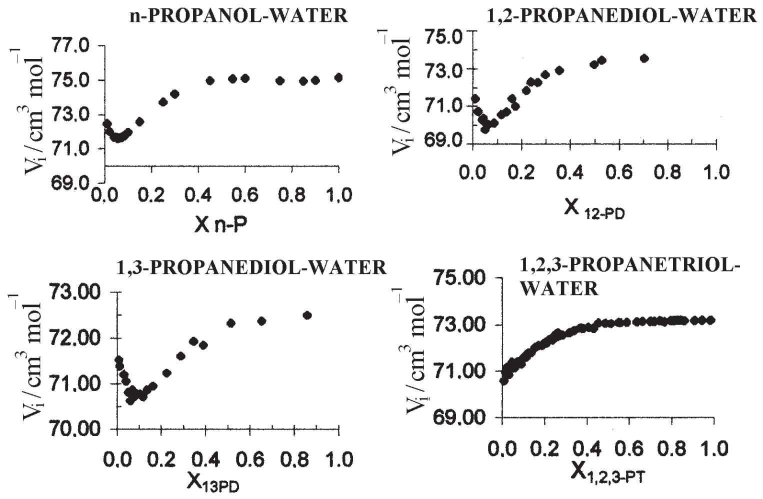

Fig. 1 Partial molar volumes of alcohols at 298.15 K

Table 1 shows the results for the partial molar volumes of alcohols and water at infinite dilution as well as the volume and alcohol molar fraction corresponding to the minimum where the transition in partial molar volume takes place. The limiting slope ($\delta V/\delta X_2$) when $X_2 \to 0$ is also included.

According to the hydrophobicity criteria based on volumetric properties, that is on the sign and magnitude of the limiting slope ($\delta V/\delta X_2$) when $X_2 \to 0$ [1, 2, 19, 20], the hydrophobicity order is:

n-propanol>1,2-propanediol>1,3-propanediol.

1,2,3-Propanetriol does not show a minimum and its behaviour is characteristic of a hydrophilic solute.

Table 1 Volumetric properties of alcohols in water at 298.15 K

Solute	*n*-P	1,2-PD	1,3-PD	1,2,3-PT
$X_{\min}$	0.053	0.057	0.095	No
$\bar{V}_{\min}$/cm^3 mol^{-1}	71.63	70.04	70.40	No
$\bar{V}^0_{OH}$/cm^3 mol^{-1}	70.64	71.68	71.47	69.97
$\bar{V}^0_{H_2O}$/cm^3 mol^{-1}	15.59	15.92	16.67	14.30
$\bar{V}^0_{OH}$/cm^3 mol^{-1}	75.14	73.70	72.55	73.19
$(d\bar{V}_2/dX_2)$ $X_2\to0$	–130.19	–30.40	–14.75	16.12

From the results shown, it can be seen that the addition of a second OH group causes a very small change in volumetric properties and its contribution is highly dependent on position. As a consequence, the volumetric contribution of OH groups is not additive.

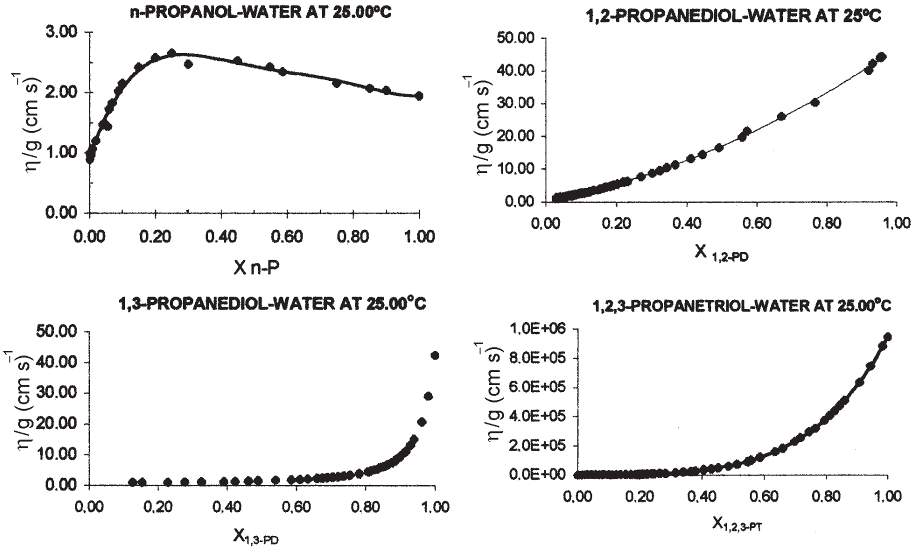

Fig. 2 Absolute viscosity for alcohols in aqueous solution at 298.15 K

Results for the absolute viscosity are shown in Fig. 2. Viscosity increases with alcohol concentration and *n*-propanol solution shows a clear maximum that is not observed for the diols or propanetriol. These results were used to evaluate the relative viscosity and the values thus obtained were adjusted by least-squares to a second order equation as proposed by Tsangaris–Martin:

$$\eta_r=1+Bm+Dm^2 \tag{4}$$

Table 2 *B* coefficient and infinite dilution partial molar volumes for alcohols in water at 298.15 K

Alcohol	B/kg mol^{-1}	V_2^0/cm^3 mol^{-1}	K
n-Propanol	0.2582	70.64	4.04
1,2-Propanediol	0.2756	71.68	3.83
1,3-Propanediol	0.0160	71.47	0.24
1,2,3-Propanetriol	0.1999	69.97	2.85

Coefficient B and the constant K defined as 1000 B/V_2^0 show that *n*-propanol and 1,2-propanediol have a hydrophobic character, followed by propanetriol and that the alcohol that has the most important hydrophilic contribution is 1,3-propanediol.

Finally, it can be seen that 1,2-propanediol and 1,3-propanediol have a completely different behaviour probably due to the tendency of 1,3-propanediol to form intramolecular H bonds, while the structure and conformation of 1,2-propanediol favors the formation of intermolecular hydrogen bonds.

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