Surface tension of aqueous solutions of alcohol and polyols at 298.15 K

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Surface tension of aqueous solutions of 1-propanol (*n*P), 1,2-propanediol (12PD), 1,3-propanediol (13PD) and 1,2,3-propanetriol (123PT) were measured using the method of capillary rise as a function of concentration at 298.15 K with emphasis in the very dilute region. The decrease of surface tension with mole fraction of alcohol becomes less pronounced as the number of OH groups increases. The surface enrichment effect, reflected by the slopes for the curves of surface tension versus composition, is correlated with the number of hydroxyl groups in the solute and the hydrophilic character of the solutes.

Keywords: Alcohol; Polyols; Mixed solvent; Surface tension

1. Introduction

Thermodynamic properties of aqueous solutions of alcohols are of interest in the elucidation of interactions between non-polar groups and water, solute effects on water structure and hydrophobic and hydrophilic hydration. Among them, solution surface tension is very important for the information it gives about molecular interactions [1–8] in liquids.

Studies on surface properties of alcohol–water mixtures have been reported, especially with monohydric alcohols of low molecular weight [9–13]. Few studies have been done with polyols, and even though some thermodynamic properties of aqueous glycol mixtures have been determined, the lack of precise experimental data in the very dilute region does not allow a systematic study of the effect of the relation of polar groups to apolar groups on the surface properties of these systems, nor of the effect of the position of the polar groups [14,17].

It is well known that the increase of hydroxyl groups changes the hydrophobic–hydrophilic balance. This is especially important at low concentration where the

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interaction of the hydrophobic hydration sphere with the hydrophilic hydration sphere defines the behavior of the aqueous mixture. However, the complexity of interactions present in these systems means that the behavior of these solutes in water is not well understood. The aim of this article is to analyze the effect of the relation between polar and apolar groups on the hydrophobic/hydrophilic character of alcohols and polyols from the behavior of surface tension of aqueous solutions of *n*-propanol, 1,2-propanediol, 1,3-propanediol and 1,2,3-propanetriol (glycerol) at 298.15 K. Surface tension measurements allowed us to examine in a systematical way the effect of the number of hydroxyl groups in the solute and the hydrophilic character of the solutes.

2. Experimental

The materials used were *n*-Propanol Merck 99.5%, 1,2-Propanediol Merck 99.5%, 1,3-Propanediol Sigma 99.0% and 1,2,3-Propanetriol Carlo Erba 99%. Alcohols were degassed before use and water content was determined in all cases by the Karl Fisher method. Water was doubly distilled, treated according to literature and degassed before use [18]. All solutions were prepared by weight using a Mettler balance AT 261 dual range with sensitivity $\pm 10^{-5}$ g in the lower range. Final concentrations were corrected according to the water content analysis.

The density and surface tension for the aqueous alcohol mixtures were determined at $25.00 \pm 0.01^\circ$C following literature recommendations [18,19]. Solution density was measured using pycnometers of the Wood–Brusie type with an uncertainty of $\pm 5 \times 10^{-5}$ g cm^{-3} and the results are reported elsewhere [20]. Surface tension was determined using the capillary rise method with a capillary tube of 27.0 cm length and 0.0422 cm inner radius, determined by calibration with water at $25.00 \pm 0.01^\circ$C. The height measurements were done with a cathetometer with minimum division of 1×10^{-2} cm.

Solution surface tension σ was calculated using the Poisson–Rayleigh equation in which ρ is the solution density, r is the capillary radius, h is the capillary height and g the gravitational constant. In all cases, the relative standard deviation is less than 0.3 mN m^{-1}.

$$\sigma = \frac{r\rho g}{2}\left(h + \frac{r}{3} - \frac{0.1288r^2}{h} + \frac{0.1312r^3}{h^2}\right). \tag{1}$$

3. Results

The surface tension values for the pure components obtained in this work behave well according to literature data as can be seen in table 1 [15–17].

Table 2 presents the experimental results for surface tension as a function of alcohol mole fraction. The decrease of surface tension with mole fraction of alcohol becomes less pronounced as the number of OH groups increases (figure 1). This is clearly exhibited by the values of the limiting slopes evaluated in the very dilute region which are: -2319.5 mN m^{-1} for 1-propanol, -312.2 mN m^{-1} for 1,2-propanediol, -158.33 mN m^{-1} for 1,3-propanediol and -44.30 for 1,2,3-propanetriol.

Table 1. Experimental values of surface tension for 1-propanol, 1,2-propanediol, 1,3-propanediol and 1,2,3-propanetriol at 298.15 K.

Substance	σ_{exp} (mN m^{-1})	σ_{lit} (mN m^{-1})
1-propanol	23.1	23.10[a], 23.28[a], 23.34[a], 23.50[a], 24.74[c]
1,2-propanediol	35.6	35.80[a], 35.47[c]
1,3-propanediol	45.8	53.125[b], 47.43[c], 45.62 at 20.0°C[a]
1,2,3-propanetriol	63.0	65.16[c]

References: [a][15], [b][14], [c][16].

Table 2. Experimental values of surface tension for aqueous solutions of 1-propanol, 1,2-propanediol, 1,3-propanediol and 1,2,3-propanetriol at 298.15 K.

X_{nP}	σ (mN m^{-1})	X_{12PD}	σ (mN m^{-1})	X_{13PD}	σ (mN m^{-1})	X_{123PT}	σ (mN m^{-1})
0.0000	71.8	0.0000	71.81	0.0000	71.8	0.0000	71.8
0.0005	67.6	0.0062	68.2	0.0040	71.0	0.0397	69.7
0.0026	61.8	0.0237	61.1	0.0051	70.4	0.0472	69.5
0.0047	56.5	0.0352	57.7	0.0248	66.8	0.0660	68.8
0.0090	48.3	0.0444	57.1	0.0500	63.7	0.0724	68.6
0.0200	39.7	0.0517	55.5	0.0674	62.0	0.0914	68.3
0.0400	32.1	0.0810	52.3	0.0908	60.3	0.1120	67.9
0.0549	28.7	0.0930	50.8	0.1003	58.7	0.1533	67.3
0.0600	28.0	0.1212	48.3	0.1503	56.5	0.1749	67.1
0.0689	27.3	0.1389	47.1	0.1998	54.5	0.2285	66.9
0.1000	24.7	0.1529	45.7	0.2991	53.6	0.3065	66.4
0.1498	24.9	0.1701	45.6	0.3983	51.8	0.4224	65.8
0.1998	24.6	0.1925	44.2	0.5929	49.4	0.4936	65.3
0.2498	24.4	0.2243	43.2	0.6976	48.7	0.5992	64.7
0.2998	23.2	0.2429	42.8	1.0000	45.8	0.6523	64.4
0.4496	24.5	0.3002	41.8			0.7132	63.6
0.5472	23.8	0.3382	40.7			0.7505	63.5
0.5862	23.6	0.3565	40.3			0.7937	63.5
0.6004	23.4	0.4028	39.4			0.9195	62.9
0.7499	23.6	0.4338	39.0			1.0000	63.0
0.8495	23.4	0.4597	38.1				
0.9002	22.4	0.5253	37.5				
1.0000	23.1	0.5579	36.8				
		0.5815	36.6				
		0.6227	36.1				
		0.6689	35.8				
		0.7537	35.6				
		0.8055	35.6				
		0.8361	35.6				
		0.8834	35.6				
		0.9037	35.6				
		1.0000	35.6				

The negative sign is characteristic of polar solutes, and the magnitude of the slope which becomes smaller as the number of OH groups increases reflects the increasing hydrophilic character of the solute. The negative slopes indicate that in all cases the surface excess is positive. Even though the surface excess is not calculated because there is not enough information about the activity coefficients for all the alcohols considered in this work, the surface enrichment effect reflected by the slopes for the curves of surface tension versus composition is related to the presence of hydrophobic groups and is less pronounced as the number of OH groups increases. Thus, the results
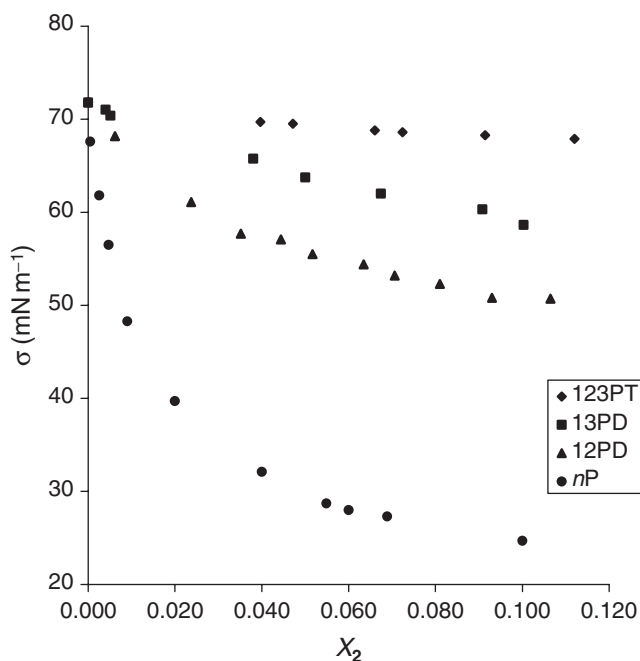
Figure 1.   Surface tension for dilute aqueous solutions of alcohols and polyols at 298.15 K.

show that *n*-propanol, which has the largest negative slope, is the alcohol that exhibits the most pronounced hydrophobic character followed by 1,2-propanediol, 1,3-propanediol, and 1,2,3-propanetriol, confirming the results obtained from volumetric properties for this system [20]. Further, the behavior of propanediols in water follows the same trend exhibited by butanediols in aqueous solution [21].

The observed behavior for limiting slopes suggests that the order is related to the accessible surface area in each case. Propanol has the largest hydrophobic domain. The hydrophobic region diminishes with the increase of OH groups, and in the case of diols depends on the OH position. 1,2-propanediol has a larger hydrophobic domain than 1,3-propanediol. For 1,2,3-propanetriol, the hydrophobic and hydrophilic domain are almost compensated and this is reflected in the low value of the limiting slope.

Acknowledgements

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