

Surface Tension of Aqueous Solutions of Some Glycols

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Abstract: The surface tensions of aqueous solutions of 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 1,4-butanediol were measured at 20, 30, and 40°C. The correlation between the surface tension of pure glycols at different temperatures and the volume contraction in an aqueous solution and volume fraction in surface phase of an aqueous solution are studied.

1. Introduction

Various behavior of aqueous glycol solutions has been reported in properties such as excess and partial volumes.⁽¹⁾ Although no complete study has been made of the laws governing hydrate formation and the transfer of glycol from bulk phase to surface phase in water. For the purpose of the study of hydrate formation, the surface tension of aqueous alcohol solutions have been reported,⁽²⁾ no surface tension data have been published except our paper⁽³⁾ for glycol-water solutions.

The surface tensions of aqueous solutions of five glycols were measured at 20.00, 30.00, and 40.00°C. The glycols used were 1,2-ethanediol (12ED), 1,2-propanediol (12PD), 1,3-propanediol (13PD), 1,3-butanediol (13BD), and 1,4-butanediol (14BD). Among the surface tensions, the data measured at 30°C were reported previously.⁽³⁾ However, for the purpose of a comparison of these data with the data measured at other temperatures, we used again.

2. Experimental

The samples used were of G. R. grade JIS guaranteed reagent and were purified further by dehydrating over anhydrous salts such as Na_2SO_4 and distilling repeatedly with a fractionating column until their gas chromatogram (polyethylene glycol as column and H_2 as carrier gas) showed minimum impurities. Estimated purity was 99.8%.

The capillary height method was used throughout the surface tension measurements. The uniformity in the inner diameter of capillaries was checked by measuring the length of a known amount of mercury in the capillary. The two-capillary method, a modification credited to Sugden⁽⁴⁾ and Richards *et al.*,⁽⁵⁾ was used. The diameters of capillaries

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were 0.50 and 0.27 mm. The height of capillary rise was determined with a traveling microscope. All the measurements were made at 20.00, 30.00, and 40.00°C, in a water thermostat, the temperature of which was controlled to $\pm 0.01^\circ\text{C}$. The accuracy of surface tension determination was estimated to be ± 0.3 dyn/cm.

3. Results

The surface tension data for an aqueous glycol solutions are given in Tables I and II. The Tables show that increasing the glycol content of the solution decreases the surface tension. However, the surface tension-composition lines differ in curvature with all the glycols at same temperature (As shown in Figure 1). The curve for the 12ED, 13PD, and 14BD solutions are smoother, and that for the 12PD and 13BD solutions are characterised by a sharper bend. As shown in Figure 2, the each curves for the same glycol solution are nearly parallel.

Table I : Surface tension of aqueous solution of glycols at 20.00°C

1,2-Ethanediol+H ₂ O			1,2-Propanediol+H ₂ O			1,3-Propanediol+H ₂ O		
ω	χ	γ	ω	χ	γ	ω	χ	γ
0.0	0.0	72.75	0.0	0.0	72.75	0.0	0.0	72.75
0.1478	0.0479	65.82	0.1292	0.0339	59.79	0.0995	0.0255	64.31
0.2779	0.1005	62.18	0.2490	0.0728	53.22	0.2500	0.0732	57.62
0.4740	0.2074	57.61	0.3962	0.1345	47.96	0.3206	0.1005	55.91
0.7751	0.5001	51.39	0.5268	0.2086	44.07	0.4252	0.1491	54.97
0.8731	0.6664	49.59	0.8036	0.4921	39.03	0.5485	0.2234	53.41
1.0	1.0	46.65	0.9117	0.7097	37.53	0.6495	0.3053	51.96
			1.0	1.0	36.73	0.7977	0.4829	50.17
						1.0	1.0	47.54
1,3-Butanediol+H ₂ O			1,4-Butanediol+H ₂ O					
ω	χ	γ	ω	χ	γ			
0.0	0.0	72.75	0.0	0.0	72.75			
0.1689	0.0391	51.51	0.2026	0.0484	57.60			
0.3745	0.1069	47.14	0.3053	0.0808	54.51			
0.5613	0.2037	43.65	0.4029	0.1189	52.38			
0.8382	0.5088	40.08	0.5519	0.1976	50.59			
0.9171	0.6887	38.87	0.6988	0.3169	48.65			
1.0	1.0	37.53	0.8008	0.4456	47.53			
			0.9002	0.6433	45.85			
			1.0	1.0	44.72			

ω : Weight fraction of glycol. χ : Mole fraction of glycol.
 γ : Surface tension in dyn/cm.

Table II : Surface tension of aqueous solution of glycols at 40.00°C

1,2-Ethenediol+H ₂ O			1,2-Propanediol+H ₂ O			1,3-Propanediol+H ₂ O		
ω	χ	γ	ω	χ	γ	ω	χ	γ
0.0	0.0	69.55	0.0	0.0	69.55	0.0	0.0	69.55
0.1478	0.0479	63.92	0.1018	0.0261	59.14	0.1863	0.0514	58.01
0.2779	0.1005	60.37	0.1863	0.0514	53.58	0.3405	0.1089	54.48
0.3499	0.1351	58.90	0.3408	0.1091	48.19	0.5262	0.2082	52.15
0.4740	0.2074	55.73	0.5252	0.2076	42.67	0.8119	0.5055	48.75
0.6014	0.3046	53.19	0.6478	0.3034	39.97	0.9118	0.7100	47.38
0.7751	0.5001	49.86	0.8004	0.4871	37.24	1.0	1.0	45.73
0.8731	0.6664	47.95	0.9027	0.6872	35.91			
1.0	1.0	45.76	1.0	1.0	34.28			
1,3-Butanediol+H ₂ O			1,4-Butanediol+H ₂ O					
ω	χ	γ	ω	χ	γ			
0.0	0.0	69.55	0.0	0.0	69.55			
0.1019	0.0222	55.77	0.2056	0.0492	55.17			
0.1728	0.0401	52.57	0.3767	0.1078	51.44			
0.3745	0.1069	45.56	0.5582	0.2017	49.00			
0.5613	0.2037	42.00	0.8372	0.5050	45.12			
0.8382	0.5088	38.22	0.9111	0.6721	44.26			
0.9171	0.6887	37.24	1.0	1.0	42.46			
1.0	1.0	35.83						

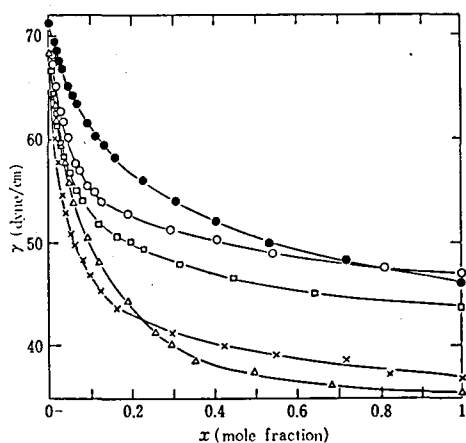
 ω : Weight fraction of glycol. χ : Mole fraction of glycol. γ : Surface tension in dyn/cm.

Fig. 1 : Surface tension of aqueous solution of glycol at 30.00°C ○2,2-ethanediol, △1,2-propanediol, ●1,3-propanediol, ×1,3-butanediol, □1,4-butanediol.

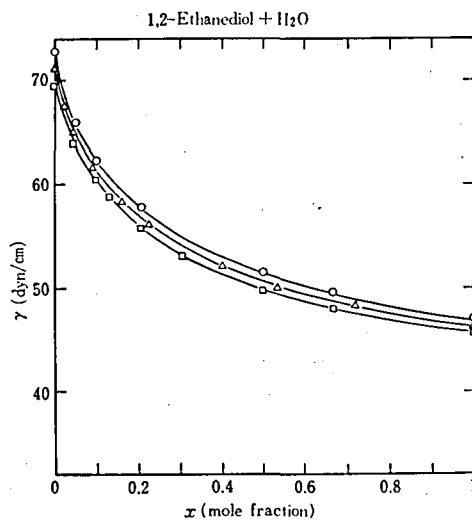


Fig. 2-1

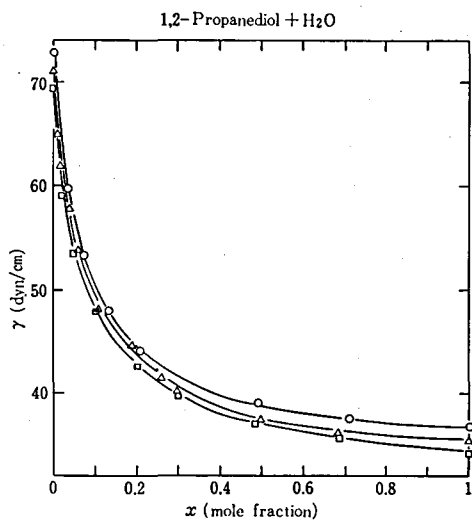


Fig. 2-2

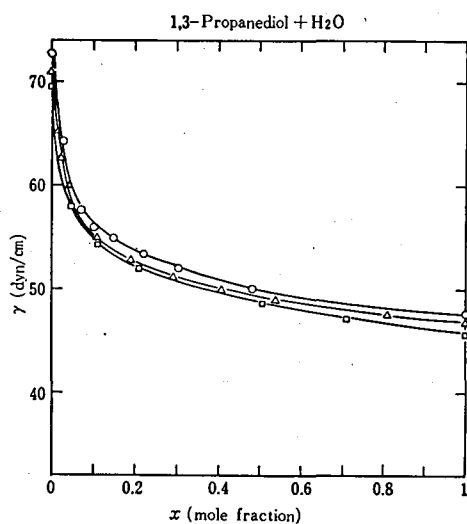


Fig. 2-3

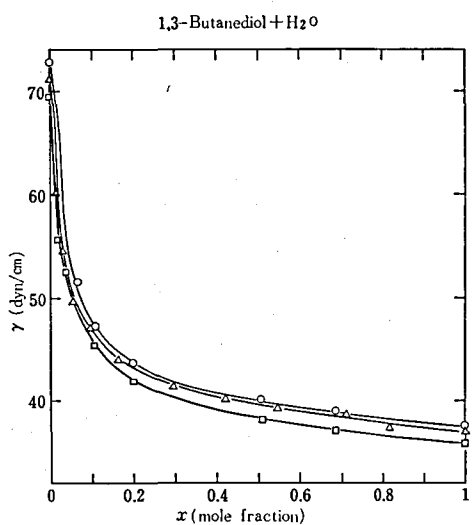


Fig. 2-4

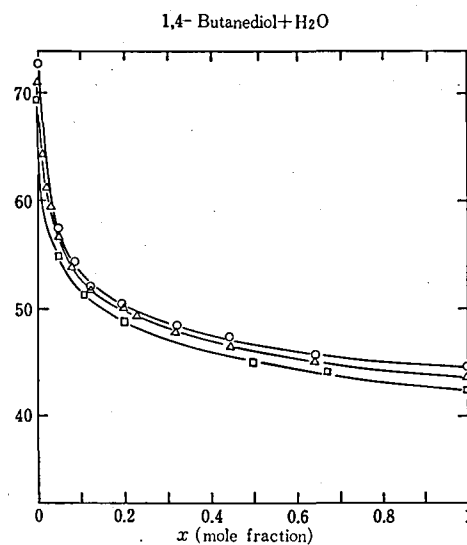


Fig. 2-5

Fig. 2: Surface tension of aqueous solution of glycols at 20.00, 30.00 and 40.00°C.

○: 20.00°C △: 30.00°C □: 40.00°C.

4. Discussion

The best calculated method available is probably that proposed by Tamura *et al.*⁽⁶⁾ formula:

$$\gamma^{\frac{1}{4}} = (1-v_1)\gamma_A^{\frac{1}{4}} + v_1\gamma_B^{\frac{1}{4}}$$

$$\ln \left\{ \frac{v_1 (1 - v_L)}{v_L (1 - v_1)} \right\}^P = \frac{P(\gamma_A - \gamma_B)}{nkT}$$

γ : Surface tension of solution. γ_A : Surface tension of water. γ_B : Surface tension of glycol. v_L : Volume fraction of bulk phase. v_1 : Volume fraction of surface phase. P : Number of carbon atoms in glycol. k : Constant of Boltzmann. n : Number of molecules of water in a unit area.

Comparison of this method with the experimental data at 30°C indicates that the calculated γ value of 13PD is almost same value, and that the other calculated γ values are lower than the experimental ones, indicating an over-estimating of the surface concentration of the glycol (As shown in Figure 3).

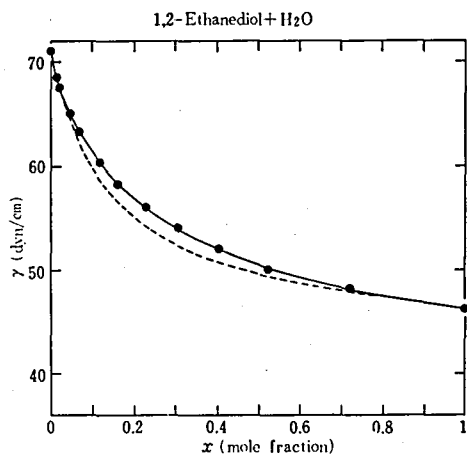


Fig. 3-1

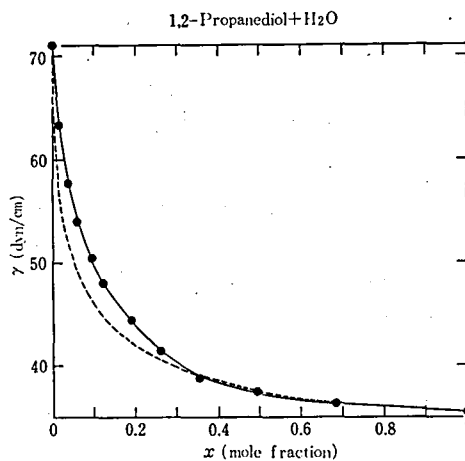


Fig. 3-2

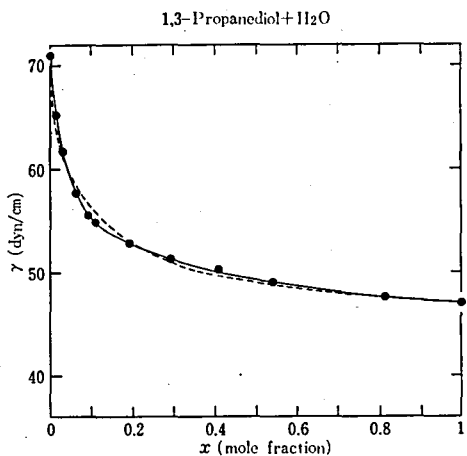


Fig. 3-3

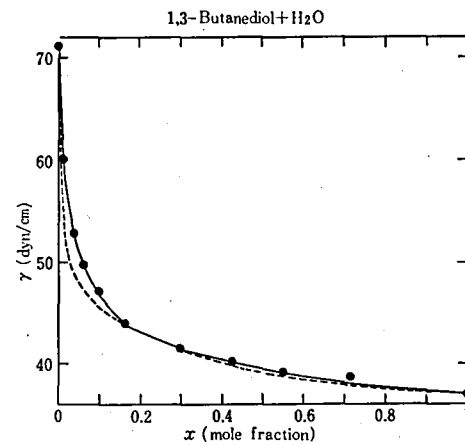


Fig. 3-4

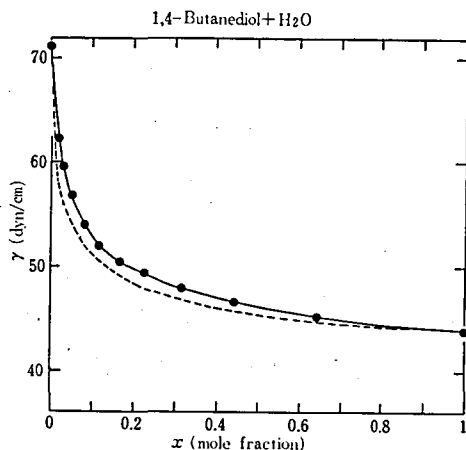


Fig. 3—5

Fig. 3 : Comparison of calculated values with experimental ones at 30.00°C
 experimental : —
 calculated :

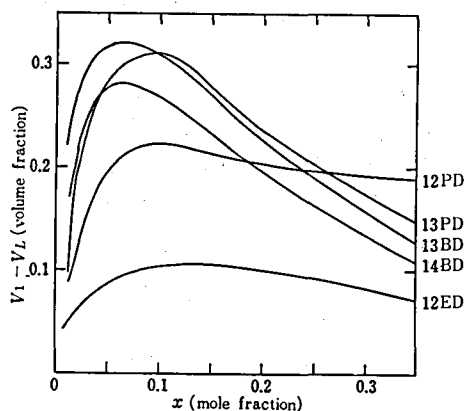


Fig. 4: The differences in volume concentration of glycols between bulk phase and surface phase at 30°C near their maximum.

The differences in volume concentration of glycols between bulk phase and surface phase, calculated by the experimental γ values are shown in Figure 4. It shows that the positions of maximum, where are about 0.14 mole fraction in 12ED, 0.09 mole fraction in 12PD and 13PD, and 0.06 mole fraction in 13BD and 14BD, are dependent of the sizes of glycols. Furthermore, it shows that the curves for the difference in volume concentration of glycols are characterised by the position of two hydroxyl groups which are contained in the molecule of glycol. Since, the curves for 12ED and 12PD are lower in the values of maximum, and then decrease slowly, but the curves for 13PD, 13BD, and 14BD are higher in the values of maximum, and then decrease rapidly. On the other hand, the calculating of surface entropy is inaccuracy since the data of different temperatures are few, for reference, the surface entropy curves have except 12ED maximum, corresponding to the hydrates. Their maximums indicate the existence of the hydrates $\text{CH}_2\text{OHCHOHCH}_3 \cdot 4\text{H}_2\text{O}$, $\text{CH}_2\text{OHCH}_2\text{CH}_2\text{OH} \cdot \text{H}_2\text{O}$, $\text{CH}_2\text{OHCH}_2\text{CHOHCH}_3 \cdot 2\text{H}_2\text{O}$, and $\text{CH}_2\text{OHCH}_2\text{CH}_2\text{CH}_2\text{OH} \cdot 3\text{H}_2\text{O}$.

In conclusion, the volumetric behavior of the glycols in water, is followed by three effects. The first effect is methyl group, which present in 12PD and 13BD, the lower surface tensions of their pure glycols are observed, as have been suggested by Nakanishi *et al.*,⁽⁴⁾ this fact is consistent with the larger volume contractions are observed at their glycols. The second effect is the position of two hydroxyl groups containing in the glycol, in the aqueous 12ED and 12PD solutions, the smaller differences in volume concentration of their glycols between bulk phase and surface phase are observed at low mole fraction. This fact is suggest, which may be due strong intermolecular hydrogen bonding between

to neighboring hydroxyl groups. The third effect is the number of methylene groups, the positions of maximum of difference in volume concentration of glycols between bulk phase and surface phase shift to low mole fraction as the number of methylene groups increase. Furthermore, as the surface tensions of aqueous glycol solutions at different temperatures are nearly parallel, these three effects are stronger as the temperature rise, but it may be not seen that the quite different behavior of the glycols in water takes place.

Acknowledgment

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