Interfacial Tensions of Two-Phase Ternary Systems

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Interfacial tensions of two-phase aqueous ternary systems are presented. Measurements are conducted by use of the capillary rise method of Bartell and Miller for seven systems at 25°C and under the condition of equilibrium distributions of solute concentrations between the phases.

Liquid-liquid interfacial tension is of considerable importance to chemical engineers in the design of liquid-liquid contact operations. Although interfacial tension data on many binary liquid-liquid systems are available, there is scant information on more than three-component systems. Valentine and Heideger (10) observed the interfacial tensions on three- and four-component aqueous mixtures and concluded that they were not easily predicted from the pure component relations. Murphy et al. (6) reported the interfacial tension data on various three-component systems and obtained an empirical correlating method which requires the plait point data by considering their experimental results. Pliskin and Treybal (8) and Paul and de Chazal (7) also presented experimental data for such systems.

In the present work interfacial tension data on seven two-phase three-component aqueous systems are presented to make available more experimental knowledge.

Experimental

Interfacial tensions were obtained by use of the capillary rise method of Bartell and Miller (1). Two capillary cells made of pyrex glass were used. Before each experimental run, they were cleaned with sodium hydroxide solution, sulfuric acid, freshly prepared chromic acid mixture, and double-distilled water, in sequence. The experimental procedure was almost identical to that of Bartell and Miller (1). With this method interfacial tension can be evaluated by using the following equation:

$$\gamma_{12} = \frac{rg}{2}(h_1 d_1 - h_2 d_2) \tag{1}$$

where γ_{12} is the interfacial tension; r and g are the radius and the acceleration of gravity, respectively; h_1 and h_2 are the heights of organic and aqueous phases; and d_1 and d_2 are the densities of organic and aqueous phases.

In the evaluation of interfacial tension, the radii of the capillary cells must be known accurately. In the present work the radii at the position where interfaces were always established were experimentally determined by applying the published data for the benzene-water system at 25°C (2-4) to Equation 1. This system was selected since more experimental data are available. The mean values were calculated to be 0.0230 and 0.0261 cm, respectively. Heights h_1 and h_2 were measured by use of a cathetometer with an accuracy of 0.0005 cm.

All measurements were carried out at 25° ± 0.02°C and

under the condition of equilibrium distributions of solute concentrations between two phases. The equilibrium condition was established as follows: the known amounts of each component in the system to be studied were measured and placed in a flask. The flask was shaken vigorously for a few minutes, and then the liquid mixture was kept to be stirred for about 24 hr in a constant temperature bath by use of a magnetic stirrer. The phases were then allowed to separate. Densities of each phase were measured by an Ostwald-type pycnometer.

Equilibrium-phase compositions were determined from the existing phase data in the literature where available.

The following seven aqueous ternary systems were studied in this investigation: water-benzene-ethanol, water-benzene-i-propanol, water-benzene-tert-butanol, water-toluene-ethanol, water-toluene-n-propanol, water-toluene-i-propanol, and water-cyclohexane-i-propanol.

To check the radii of capillary cells determined above, the interfacial tensions of water-toluene and water-cyclohexane systems were measured. The observed results were in good agreement with those in the literature (2, 5).

Throughout this work, reagent grade organic solvents of guaranteed purity were used without further purification. The densities and the refractive indices of these chemicals were measured by using the Ostwald-type pycnometer and Abbe refractometer, respectively. The observed results were in good agreement with those in the literature (9). Therefore, their purities can be considered to be satisfactory. Water was double distilled.

The accuracy of the interfacial tension measurement was estimated to be less than 3%.

Results and Discussion

The experimental results are tabulated in Table I and are also shown graphically in Figures 1 and 2. In these figures the abscissa represents the weight percent of solute (alcohol) in the organic phase. As can be seen from these figures, interfacial tension is decreased exponentially with increasing solute concentration for all systems; this is the same trend as those of other investigations.

In Figure 1 the experimental results for the water-benzene-i-propanol system reported by Paul and de Chazal (7) are also plotted. To a certain extent, there is a discrepancy in the density results of this work and those of Paul and de Chazal (7). However, it is impossible to explain the discrepancy since Paul and de Chazal (7) did not show how to establish equilibrium.

In this work the method of Bartell and Miller (1) was not suitable to measure the interfacial tensions at the concentration range near the plait point. When increasing the concentration of solute to the plait point, the density difference between both phases and interfacial tension becomes very small. Therefore, the interface becomes very unstable. The difference in refractive indices of both phases also becomes negligible. As a result, it is very difficult to establish the stable interface successfully and to make it easily visual. In the present work the minimum interfacial tension that could be determined was 0.04 dyn/cm, and the corresponding density difference was 0.0118 g/cm³.

Table I. Interfacial Tensions of Ternary Systems at 25°C

| Aqueous phase		Organic phase		Inter-facial tension, dyn/cm
Concn, wt %	Density, g/cc	Concn, wt %	Density, g/cc	
Benzene(1)—water(2)—ethanol(s)				
(1)	(s)	(1)	(s)	
0.2	10.8	0.9782	98.6	1.2	0.8726	17.20
0.3	21.7	0.9626	97.1	2.6	0.8711	9.37
1.6	36.2	0.9365	94.0	5.4	0.8679	3.64
3.6	43.7	0.9172	91.3	7.9	0.8656	1.99
8.6	50.1	0.8944	87.3	11.4	0.8629	1.09
21.2	52.0	0.8690	79.3	18.0	0.8588	0.04
Benzene(1)—water(2)—i-propanol(s)				
(1)	(s)		(1)	(s)	
0.3	4.6	0.9869	98.9	1.1	0.8722	19.99
0.1	9.2	0.9803	97.5	2.5	0.8706	13.27
0.4	16.8	0.9699	92.3	7.6	0.8647	5.92
0.4	19.6	0.9656	87.9	11.9	0.8604	4.42
0.6	21.5	0.9620	82.8	16.6	0.8564	2.84
0.8	25.8	0.9530	65.0	31.6	0.8474	1.47
1.0	27.9	0.9481	56.4	38.3	0.8454	1.05
Benzene(1)—water(2)—tert-butanol(s)				
(1)	(s)		(1)	(s)	
0.1	4.8	0.9891	97.7	2.1	0.8706	14.20
0.3	9.4	0.9815	92.9	6.7	0.8620	9.19
0.2	13.1	0.9777	81.2	17.6	0.8535	4.50
0.4	15.1	0.9748	66.2	30.5	0.8432	2.61
0.5	16.2	0.9735	54.6	39.6	0.8379	1.66
0.5	17.4	0.9710	41.7	48.6	0.8358	1.07
0.5	18.6	0.9682	30.1	55.0	0.8381	1.04
Toluene(1)—water(2)—ethanol(s)				
(1)	(s)		(1)	(s)	
0.1	11.0	0.9797	99.7	0.2	0.8616	20.28
0.4	19.2	0.9684	99.2	0.7	0.8611	12.73
1.1	34.8	0.9414	97.2	2.6	0.8592	5.35
1.8	41.7	0.9247	94.9	4.7	0.8581	3.59
3.0	46.9	0.9117	94.3	5.3	0.8571	2.47
4.2	50.0	0.9018	93.0	6.5	0.8566	1.87
7.0	53.6	0.8900	90.9	8.4	0.8561	0.98
Toluene(1)—water(2)—n-propanol(s)				
(1)	(s)		(1)	(s)	
0.4	8.4	0.9844	97.2	2.5	0.8602	11.68
0.3	11.4	0.9807	94.6	4.9	0.8585	7.70
0.3	14.0	0.9755	87.2	11.8	0.8545	5.10
0.3	14.6	0.9745	78.6	19.5	0.8512	3.45
0.3	15.8	0.9727	67.0	29.2	0.8478	2.38
0.3	17.7	0.9693	54.5	38.9	0.8448	1.60
0.4	19.3	0.9665	37.8	50.2	0.8455	1.40
Toluene(1)—water(2)—i-propanol(s)				
(1)	(s)		(1)	(s)	
0.0	6.9	0.9852	98.9	0.9	0.8611	19.23
0.3	12.2	0.9776	97.5	2.2	0.8596	12.14
0.4	19.3	0.9670	92.4	7.0	0.8555	5.81
1.0	29.0	0.9473	71.9	24.9	0.8439	1.85
2.0	34.1	0.9335	54.9	37.5	0.8409	0.92
4.2	39.9	0.9156	36.4	48.5	0.8476	0.47
Cyclohexane(1)—water(2)—i-propanol(s)				
(1)	(s)		(1)	(s)	
0.2	8.8	0.9824	99.3	0.6	0.7735	19.34
0.3	15.0	0.9706	97.1	2.6	0.7732	10.13
0.8	19.4	0.9639	94.3	5.3	0.7728	6.72
0.8	29.6	0.9353	80.9	17.6	0.7730	2.31
1.7	34.8	0.9106	68.0	28.5	0.7744	1.41
2.4	37.5	0.8974	60.0	34.6	0.7751	1.16
3.4	40.4	0.8799	50.0	41.3	0.7775	0.95
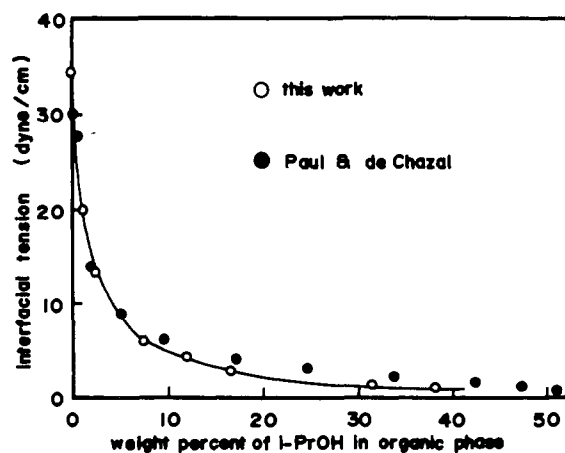
Figure 1. Variation of interfacial tension with solute weight fraction (1)
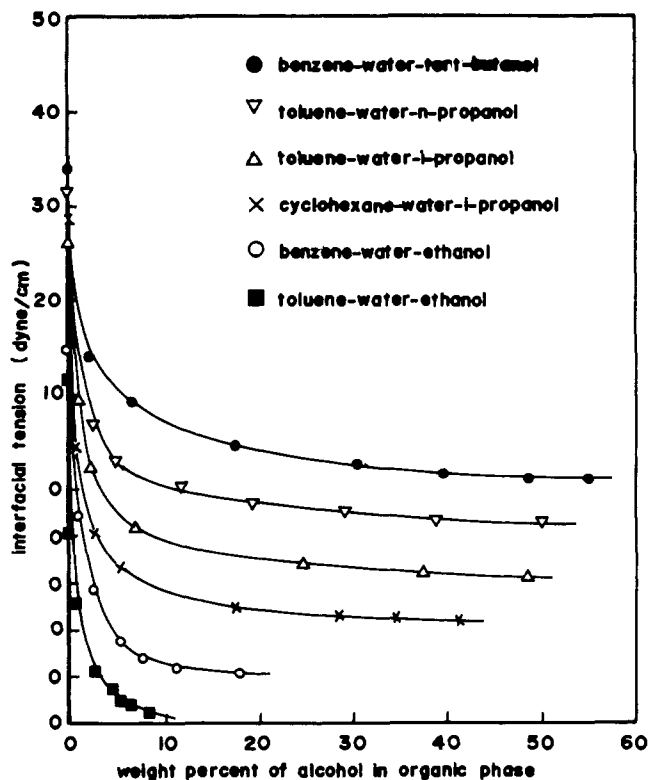

Figure 2. Variation of interfacial tension with solute weight fraction (2)

Point 10 on abscissa is 10 for benzene–water–tert-butanol system only. It is 15 for toluene–water–n-propanol system and 20 for toluene–water–i-propanol system, etc.

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