(7) Bamelis, P.; Huyskens, P.; Meeussen, E. J. Chim. Phys. Phys.-Chim. Biol. 1965, 62, 158.
(8) Decroocq, D. Bull. Soc. Chim. Fr. 1963, 127.
(9) Maryott, A. A.; Smith, E. R. Table of Dielectric Constants of Pure Liquids. Natl. Bur. Stand. Circ. 1951, No. 514.
(10) Dannhauser, W.; Bahe, L. W. J. Chem. Phys. 1964, 40, 3058.
(11) Cunningham, G. P.; Vidulich, G. A.; Kay, R. L. J. Chem. Eng. Data 1967, 12, 336.
(12) Stokes, R. H.; Mills, R. Viscosity of Electrolytes and Related Properties; Pergamon: Oxford, U.K., 1965; Vol. 3, p 76 and references cited therein.
(13) Ulich, H.; Nesjutal, W. Z. Phys. Chem. 1932, 16B, 221.
(14) Cannon, M. R.; Monning, R. E.; Bell, J. D. Anal. Chem. 1960, 32, 355.
(15) Papanastasiou, G.; Papoutsis, A.; Kokkinidis, G. J. Chem. Eng. Data 1987, 32, 377.
(16) Papanastasiou, G.; Ziogas, I. J. Chem. Eng. Data 1991, 36, 46.
(17) Fort, R. J.; Moore, W. R. Trans. Faraday Soc. 1966, 62, 112 and references cited therein.
(18) Partington, J. L. An Advanced Treatise of Physical Chemistry; Longmans: London, 1951; Vol. II, p 94.
(19) Reynaud, R. Bull. Soc. Chim. Fr. 1971, 4269.
(20) Staveley, L. A.; Taylor, P. F. J. Chem. Soc. 1956, 200.
(21) Ibbitson, D. A.; Moore, L. F. J. Chem. Soc. B 1967, 76.
(22) Hudson, R. F.; Stelzer, I. Trans. Faraday Soc. 1958, 54, 213.
(23) Prigogine, I.; Desmyter, A. Trans. Faraday Soc. 1951, 47, 1137.
(24) Huyskens, P.; Henry, R; Gillerot, G. Bull. Soc. Chim. Fr. 1962, 720.
(25) Brot, C. J. Chim. Phys. Phys.-Chim. Biol. 1964, 61, 139.
(26) Syrkin, Y. K.; Dyatkina, M. E. Structure of Molecules and the Chemical Bond; Dover: New York, 1964; p 277.
(27) Santos, J. D.; Pineau, P.; Josien, M-L. J. Chim. Phys. Phys.-Chim. Biol. 1965, 62, 628 and references cited therein.
(28) Fletcher, A. N.; Heller, A. C. J. Phys. Chem. 1967, 71, 3742.
(29) Vinogradov, S. N. Hydrogen Bonding; Van Nostrand Reinhold: New York, 1971; pp 16, 127.
(30) Kay, R. L.; Evans, D. F.; Matesich, M. A. Solute-Solvent Interactions; M. Dekker: New York, 1976; Vol. 2, p 133.
(31) Becker, E. D. Spectrochim. Acta 1961, 17, 436.
(32) Eyring, H. J. Chem. Phys. 1936, 4, 263.
(33) Reynaud, R. Bull. Soc. Chim. Fr. 1972, 532.
(34) Douchêret, G.; Morênas, M. Can. J. Chem. 1979, 57, 608.
(35) Payne, R.; Theodorou, I. J. Phys. Chem. 1972, 76, 2892.
(36) Koolling, O. W. Anal. Chem. 1965, 57, 1721.
(37) Exner, O. Dipole Moments in Organic Chemistry; Georg Thieme: Stuttgart, 1975; p 127 and references cited therein.

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Interfacial Tensions of Two-Liquid-Phase Ternary Systems

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Interfacial tensions of seven aqueous ternary systems containing propionic acid, 1-propanol, or 2-propanol as solute were measured at 25 °C with a DuNouy ring interfacial tensiometer. A simple equation is given for the estimation of the interfacial tensions with equilibrium compositions from binary data alone.

Introduction

The experimental data of interfacial tension are required by chemical engineers for the design of liquid–liquid contactors as well as by researchers for testing their methods used to predict or correlate interfacial tensions. The data for only 53 ternary systems were found in the literature (*1–8*). In the set of data of Murphy et al. (*1*) for 12 ternary systems containing acetic acid or acetone as solute, only the overall compositions of the whole liquid–liquid systems corresponding to the experimental interfacial tension data were given, and in that of Masamoto and Nakahara (*6*) for 5 ternary systems containing acetic acid as solute, only the mole fractions of solute in the two liquid phases were reported. For widening the data coverage for correlation, in the present work the interfacial tensions of seven ternary liquid–liquid aqueous systems are measured with a DuNouy ring tensiometer. We have given the compositions and densities of the two phases to more completely describe these seven ternary systems we have studied.

Experimental Section

All the measurements of interfacial tension were made at 25 ± 0.5 °C by use of a Kruss ring interfacial tensiometer with an accuracy of ± 0.1 mN m^{-1} and a resolution of ± 0.05 mN m^{-1}. The data so obtained were corrected to the actual values by means of the Zuidema and Waters compensation for interface distortion (*9*).

The seven ternary systems studied are carbon tetrachloride + water + propionic acid, chloroform + water + propionic acid, benzene + water + propionic acid, toluene + water + propionic acid, *n*-heptane + water + propionic acid, cyclohexane + water + 2-propanol, and cyclohexane + water + 1-propanol. For all the systems, the points near the plait points are excluded since the data may be less reliable and they are of less importance in chemical engineering calculations; for instance, in liquid–liquid extraction where the operation near the plait point is usually avoided for the difficulty in phase separation. For the cyclohexane + water + 2-propanol system in the paper of Masamoto et al. (*6*), there was a mistake. The equilibrium compositions used for preparing the mixtures within the two-phase region are found to be those for the system containing cyclohexene instead of cyclohexane. No interfacial tension data of the other six systems appeared in the literature. For all the systems the component 1 and the component 2 are partially miscible, and the component 3 is completely soluble in both liquid phases.

Benzene, chloroform, carbon tetrachloride, and cyclohexane of spectroscopic grade and *n*-heptane, propionic acid, and 1-propanol of guaranteed purity (Tokyo Kasei Kogyo Co., Ltd., Japan) were used directly. Toluene and 2-propanol of analytical purity (Beijing Chemical Reagent Plant, China) were distilled in a laboratory column prior to use, retaining only the central portion of the distillate. The claimed minimum purity for the compounds is 99.0% or 99.5% (see Table I). Water was double distilled.

The densities and refractive indices of all the organic reagents at 20 °C were measured by using a pycnometer and an Abbe refractometer, respectively. The interfacial tensions of benzene, toluene, chloroform, carbon tetrachloride, *n*-heptane, and cyclohexane with water at 25 °C were also measured. A comparison between the measured values and those from the literature for the physical properties was listed in Table I.

The liquid–liquid equilibrium data for all the ternary systems were obtained from the literature (*10*). The three components forming the mixture with an overall composition within the two-phase region were weighed to an accuracy of about 0.1 mg into a sealed bottle. The bottles were kept in a thermostat and shaken several times during the period of at least 24 h allowed for equilibrium (*5*).

When the interfacial tensions of the two aqueous systems containing chloroform or carbon tetrachloride as the organic

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Table I. Properties of Pure Liquids and Interfacial Tensions of Organic Solvents with Water

compd	purity min/%	ρ(20 °C)/(g cm⁻³) exptl	ρ(20 °C)/(g cm⁻³) lit.	n_D(20 °C) exptl	n_D(20 °C) lit.	σ(25 °C)/(mN m⁻¹) exptl	σ(25 °C)/(mN m⁻¹) lit.
benzene	99.5	0.8792	0.8792 (*5*)	1.5009	1.5008 (*18*)	34.0	33.8 (*8*)
toluene	99.5	0.8652	0.8670 (*19*)	1.4972	1.4969 (*19*)	35.8	35.4 (*8*)
cyclohexane	99.0	0.7754	0.77836 (*20*)	1.4264	1.4261 (*20*)	50.0	50.0 (*8*)
n-heptane	99.0	0.6815	0.6829 (*19*)	1.3880	1.3870 (*19*)	50.1	50.1 (*8*)
chloroform	99.0	1.4812	1.48911 (*21*)	1.4450	1.4459 (*21*)	31.1	30.8 (*8*)
carbon tetrachloride	99.5	1.5895	1.59417 (*21*)	1.4603	1.4602 (*21*)	44.1	44.3 (*8*)
1-propanol	99.5	0.8021	0.80375 (*21*)	1.3855	1.38556 (*21*)		
2-propanol	99.5	0.7874	0.78545 (*21*)	1.3775	1.37720 (*21*)		
propionic acid	99.0	0.9881[a]	0.9879[a] (*22*)	1.3873	1.3865 (*21*)		

[a] At 25 °C.

Table II. Experimental and Calculated Results for Density ρ and Interfacial Tension at 25 °C

water-rich phase x_1	water-rich phase x_3	water-rich phase ρ/(g cm⁻³)	organic-rich phase x_1	organic-rich phase x_3	organic-rich phase ρ/(g cm⁻³)	σ/(mN m⁻¹) exptl	σ/(mN m⁻¹) calcd at K = 2	σ/(mN m⁻¹) calcd fitted
Carbon Tetrachloride (1) + Water (2) + Propionic Acid (3)								
0.0003	0.0196	1.0031	0.9578	0.0422	1.5617	16.3	13.1	14.0
0.0003	0.0334	1.0082	0.9056	0.0944	1.5343	10.8	9.7	10.6
0.0008	0.0584	1.0150	0.7942	0.1982	1.4784	7.3	6.2	6.9
0.0010	0.0743	1.0146	0.7404	0.2322	1.4510	5.1	5.3	5.9
0.0013	0.1078	1.0195	0.6583	0.3277	1.4117	3.0	3.7	4.3
0.0029	0.1414	1.0238	0.5964	0.3836	1.3844	2.1	2.8	3.2
0.0073	0.1887	1.0279	0.3462	0.4280	1.3484	1.4	1.9	2.3
0.0121	0.2193	1.0364	0.3053	0.4573	1.3324	0.9	1.5	1.8
0.0325	0.2852	1.0445	0.4107	0.4829	1.2921	0.4	0.6	0.8
Chloroform (1) + Water (2) + Propionic Acid (3)								
0.0013	0.0141	1.0018	0.9108	0.0764	1.4362	13.6	16.4	13.6
0.0013	0.0229	1.0048	0.8284	0.1532	1.4011	9.9	12.8	9.9
0.0015	0.0319	1.0080	0.7420	0.2286	1.3644	7.0	9.9	7.1
0.0016	0.0437	1.0104	0.6373	0.3127	1.3189	4.5	7.1	4.6
0.0016	0.0548	1.0137	0.5560	0.3650	1.2854	3.2	5.2	3.1
0.0039	0.0839	1.0182	0.3951	0.4153	1.2220	1.3	2.1	1.0
Benzene (1) + Water (2) + Propionic Acid (3)								
0.0005	0.0158	1.0020	0.9624	0.0333	0.8774	16.5	15.9	14.7
0.0008	0.0273	1.0058	0.8994	0.0921	0.8819	11.4	11.6	10.3
0.0014	0.0531	1.0099	0.7690	0.2182	0.8949	5.7	7.7	6.6
0.0021	0.0863	1.0154	0.6473	0.3317	0.9094	2.6	5.2	4.3
0.0066	0.1328	1.0165	0.5447	0.4063	0.9219	0.9	2.9	2.3
0.0172	0.1813	1.0117	0.4612	0.4302	0.9324	0.3	1.5	1.1
Toluene (1) + Water (2) + Propionic Acid (3)								
0.0002	0.0361	1.0092	0.8675	0.1276	0.8739	10.3	10.2	8.9
0.0005	0.0631	1.0124	0.7476	0.2428	0.8863	5.7	6.7	5.7
0.0013	0.0964	1.0173	0.6495	0.3364	0.8988	3.2	4.8	3.9
0.0023	0.1488	1.0168	0.5678	0.4183	0.9083	1.6	3.3	2.5
0.0094	0.2005	1.0137	0.5138	0.4679	0.9164	0.8	2.2	1.6
0.0293	0.2649	1.0041	0.4191	0.4875	0.9267	0.3	0.9	0.6
n-Heptane (1) + Water (2) + Propionic Acid (3)								
0.0002	0.0453	1.0108	0.9219	0.0727	0.6890	13.5	8.5	13.2
0.0006	0.1856	1.0185	0.7884	0.2064	0.7109	5.3	2.6	5.5
0.0010	0.2628	1.0183	0.7040	0.2808	0.7246	3.8	1.6	3.7
0.0036	0.3191	1.0153	0.6653	0.3146	0.7330	3.0	1.1	2.9
0.0086	0.3937	1.0096	0.6180	0.3574	0.7458	2.1	0.8	2.4
0.0126	0.4365	0.9996	0.5348	0.4364	0.7626	1.3	0.5	1.6
Cyclohexane (1) + Water (2) + 2-Propanol (3)								
0.0004	0.0136	0.9898	1.0000	0.0000[a]	0.7756	26.5	29.5	27.4
0.0012	0.0520	0.9747	0.9773	0.0180	0.7737	11.4	12.6	10.4
0.0005	0.0950	0.9578	0.9108	0.0801	0.7723	4.1	5.3	3.8
0.0025	0.1278	0.9417	0.8382	0.1485	0.7720	2.0	3.4	2.3
0.0084	0.1814	0.9141	0.7399	0.2178	0.7724	0.9	1.9	1.2
0.0299	0.2729	0.8739	0.5920	0.2995	0.7763	0.3	0.7	0.4
Cyclohexane (1) + Water (2) + 1-Propanol (3)								
0.0002	0.0181	0.9877	0.9874	0.0126	0.7726	16.8	17.2	15.0
0.0012	0.0464	0.9766	0.9395	0.0605	0.7727	5.9	8.4	6.7
0.0015	0.0601	0.9693	0.8118	0.1577	0.7746	2.6	5.1	3.9
0.0020	0.0674	0.9662	0.6709	0.2599	0.7796	1.5	3.5	2.5
0.0018	0.0734	0.9612	0.3660	0.4124	0.7932	0.7	1.3	0.8
0.0020	0.0781	0.9601	0.2101	0.4421	0.8128	0.4	0.7	0.4

[a] In calculation, the mole fraction of water in the cyclohexane phase of the cyclohexane–water binary system was used instead of the value of zero here, and the mole fraction of 2-propanol in the phase was obtained by the extrapolation of data.

solvent were measured, the equilibrium ternary mixture was poured into the sample dish, and immediately covered with a lucite sheet. The mixture in the dish was kept in the thermostat vessel for about 20 min to establish the equilibrium condition again. The interfacial tension was measured by pushing the ring through the upper phase (water phase) to the lower phase (organic phase) because the affinity of the water phase to the platinum iridium ring is higher than the affinity of the organic phase for the first two systems where the organic phase is the dense phase. For the other five systems, the measurement of interfacial tension was performed by moving the ring upward through the interface. Therefore, the cleaned ring was first put in selected place in the empty sample dish, and then the dish was filled with the heavier phase to immerse the ring. Then the lighter phase was carefully pipetted in above. After the interfacial tension was measured, the densities of the two phases were determined by means of a pycnometer.

The experimental results are tabulated in Table II.

Correlation of Interfacial Tensions

Three equations (*7*, *11*, *12*) each with two adjustable parameters have been proposed for correlating the interfacial tensions of ternary systems with the liquid–liquid equilibrium compositions, and a few methods (*13*–*16*) have also been established for predicting the interfacial tensions from pure component or binary data alone. For the correlation of data, the equation of Li and Fu (*7*) is convenient to use and generally applicable, and for prediction purposes, a recent unpublished method of Li and Fu (*16*) is satisfactory for the ternary systems when the interfacial tension of the partially miscible pair is less than 40 mN m^{-1}.

The simple correlation equation developed by Li and Fu (*7*) is also used to estimate the interfacial tensions of ternary systems from the interfacial tension of the partially miscible binary pair and their mutual solubilities. The equation is shown as follows:

$$\sigma = \sigma_0\left(\frac{X}{X_0}\right)^K \qquad (1)$$

where

$$X = -[\ln (x''_1 + x'_2 + x_{3p})] \qquad (2)$$

σ is the interfacial tension of a ternary system. σ_0 is the interfacial tension of the partially miscible binary pair in the ternary system, and X_0 is equal to X at $x_3 = 0$. x''_1 is the mole fraction of solvent 1 in the phase richer in solvent 2, x'_2 is that of solvent 2 in the phase richer in solvent 1, and x_{3p} is the mole fraction of solute in the phase poor in it. K is an adjustable parameter for the correlation of interfacial tensions with mutual solubilities, and it can be also fixed as a constant for approximate estimation. In our previous work (*7*), the parameter K was modified as a linear function of X, i.e., $K = a + bX$, where a and b are two adjustable parameters, and the overall average absolute deviation and relative deviation for 24 ternary systems found this way were 0.3 mN m^{-1} and 4.8%, respectively.

In the calculation using the simple equation for 37 ternary systems (*17*), better prediction results than other methods were obtained when the parameter K was taken to be 1.5 for the systems containing acetone or 2-butanone as solute or nonaqueous systems and 2 for all other systems. An overall average deviation for the 314 data points of the 37 systems was found to be only 1.5 mN m^{-1}.

Using the above equation for the seven systems in this investigation, the overall average deviation between the calculated and experimental interfacial tension was 1.5 mN m^{-1} with a constant K taken to be 2 and 0.7 mN m^{-1} with the K's obtained by fitting the data. The calculated results are also given in Table II. The interfacial tensions of binary systems included were found in the literature (*8*), and X_0 was calculated with the mutual solubilities from the literature (*10*).

Registry No. CCl_4, 56-23-5; $CHCl_3$, 67-66-3; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; n-C_7H_{16}, 142-82-5; cyclohexane, 110-82-7; 1-propanol, 71-23-8; 2-propanol, 67-63-0.

Literature Cited

(1) Murphy, N. I.; Lastovica, J. E.; Jallis, J. G. *J. Chem. Eng. Data* **1957**, *49*, 1035.
(2) Pliskin, I.; Treybal, R. E. *J. Chem. Eng. Data* **1966**, *11*, 49.
(3) Paul, G. W.; de Chazal, L. E. M. *J. Chem. Eng. Data* **1967**, *12*, 105.
(4) Sada, E.; Kito, S.; Yamashita, M. *J. Chem. Eng. Data* **1975**, *20*, 376.
(5) Ross, S.; Patterson, R. E. *J. Chem. Eng. Data* **1979**, *24*, 111.
(6) Masamoto, H.; Nakahara, S. *Kagaku Kogaku Ronbunshu* **1988**, *14*, 108.
(7) Li, B.; Fu, J. *Hua Kung Hsueh Pao* (*Chin. Ed.*) **1989**, *40* (3), 355.
(8) Backes, H. M.; Ma, J. J.; Bender, E.; Maurer, G. *Chem. Eng. Sci.* **1990**, *45*, 275.
(9) Zuidema, E. A.; Waters, G. W. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 312.
(10) Sørensen, J. M.; Arlt, W. *Liquid-Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, 1979; Vols. 1 and 2.
(11) Cotton, D. J. *J. Phys. Chem.* **1968**, *74*, 4139.
(12) Fleming, P. D.; Winatieri, J. E. *J. Chem. Eng. Data* **1981**, *26*, 173.
(13) Pliskin, I.; Treybal, R. E. *AIChE J.* **1966**, *12*, 795.
(14) Paul, G. W.; de Chazal, L. E. M. *Ind. Eng. Chem. Fundam.* **1969**, *8*, 104.
(15) Fu, J.; Li, B.; Wang, Z. *Chem. Eng. Sci.* **1986**, *41*, 2673.
(16) Li, B.; Fu, J. Beijing Institute of Chemical Technology, unpublished paper, 1991.
(17) Li, B. Ph.D. Dissertation, Beijing Institute of Chemical Technology, Beijing, China, 1991.
(18) Gultekin, N. *J. Chem. Eng. Data* **1990**, *35*, 130.
(19) Katayama, H.; Watanabe, I. *J. Chem. Eng. Data* **1980**, *25*, 107.
(20) Papanastasiou, G.; Ziogas, I. *J. Chem. Eng. Data* **1991**, *36*, 46.
(21) *Selected Values of Properties of Chemical Compounds*; Thermodynamics Research Center Data Project, Texas A & M University, College Station, TX, 1981.
(22) Kato, M.; Yamaguchi, M.; Yoshikawa, H. *J. Chem. Eng. Data* **1990**, *35*, 85.

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