in which $\phi_1 = V_1/(V_1 + V_2)$ and $\phi_2 = V_2/(V_1 + V_2)$, and V_1 and V_2 are the volumes of the pure components. The A'' values were calculated using the n_D values obtained near the $x_1 = 0.5$ region, and are also listed in Table II. They may be represented linearly as a function of the number of C atoms of the aliphatic hydrocarbons. The differences between the experimental and calculated n_D values, using either Equation 2 or Equation 3 are summarized in Table III. The average difference is of the same order of accuracy as the refractometer's readings.

LITERATURE CITED

(1) Dow Chem. Co., Physical Properties of Chemical Compounds, 1953.
(2) Mrazek, R. V., Van Ness, H. C., *A. I. Ch. E. J.* **7**, 190 (1961).
(3) Redlich. O., Kister, A. T., *J. Chem. Phys.* **36**, 2002 (1962).

RECEIVED for review May 13, 1965. Accepted October 18, 1965.

Interfacial Tensions in Two-Liquid-Phase Ternary Systems

IRWIN PLISKIN[1] and ROBERT E. TREYBAL

New York University, New York, N. Y.

Interfacial tensions over the concentration range corresponding to two liquid phases have been measured in the following ternary systems: 1,1,2-trichloroethane–water–acetone (25.0° C.), 1,1,2-trichloroethane–water–methyl ethyl ketone (25.0° C.), benzene–water–acetone (30.0° C.), benzene–water–methanol (25.0° C), carbon tetrachloride–water–*n*-propanol (20.0° C), perfluoro-*n*-hexane–benzene–*n*-hexane (30.0° C.), and perfluoro-*n*-hexane–carbon disulfide–*n*-hexane (25.0° C.). In the case of the latter two, the ternary phase diagrams were also determined. Mutual solubilities and interfacial tensions were also measured in the binary systems, perfluoro-*n*-hexane–tetradecane (25.0° C.) and tetradecane–methanol (25.0° C.).

INFORMATION about the interfacial tension of two-liquid-phase ternary systems, as it varies with concentration within the systems, is relatively rare. Perhaps the most extensive study of great importance in liquid-liquid extraction, is that of Murphy, Lastovica, and Fallis (*9*), who confined themselves to aqueous systems. In the present study, which also includes aqueous systems, two nonaqueous systems which are regular in the Hildebrand sense (*8*) are included.

EXPERIMENTAL METHODS

Most of the measurements were made with a Cenco-DuNouy ring tensiometer having a platinum-iridium ring 5.999 cm. in circumference. Samples were kept in a constant-temperature bath until just before measurement. During measurement, the temperature was maintained by placing the sample dishes in a larger container and allowing water, pumped from the bath, to circulate around them. Corrections involving the densities of the two liquids, and the diameters of ring and wire (*15*) were then applied.

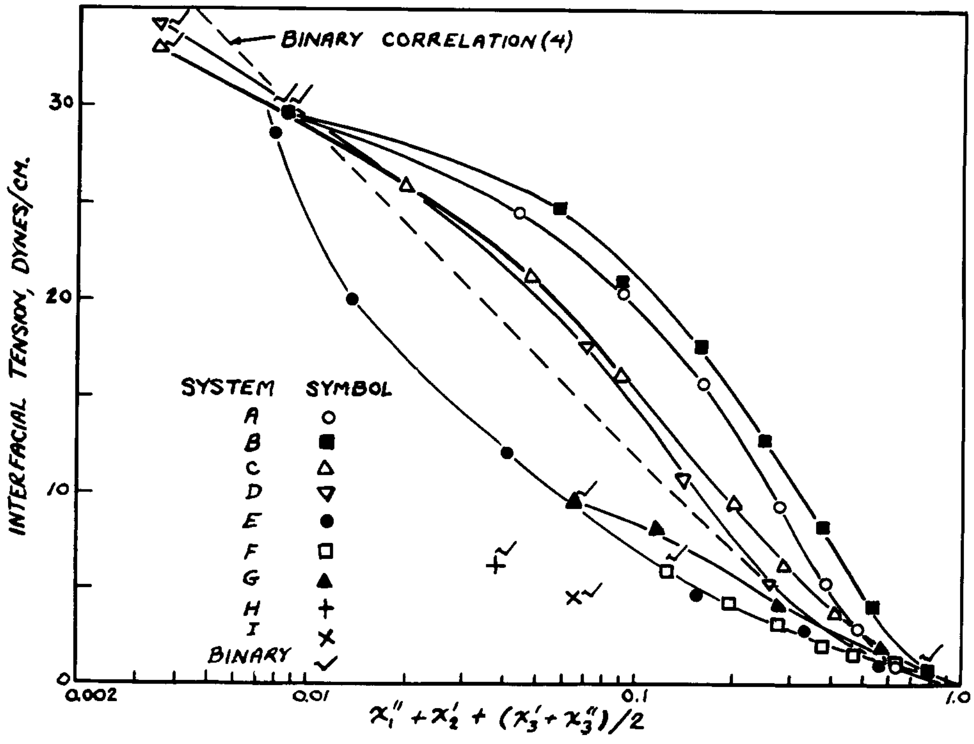

Figure 1. Correlation of interfacial tensions and phase compositions. Binary correlation of Donahue and Bartell (*4*)

---

[1] Present address: McGill University, Montreal, Quebec, Canada.

Some measurements were also made by the drop-volume method developed by Harkins (*5*, *6*). A smoothly polished glass drop-forming tip was used for the system 1,1,2-trichloroethane–water–acetone, in which the aqueous phase preferentially wetted the tip; for benzene–water–acetone, a carefully machined Teflon tip was used, so that the benzene phase wetted the tip. The tip diameters were measured by micrometer to the nearest 0.001 inch. The total volume of several drops was measured by a 2-ml. precision-bore pipet graduated in 0.01-ml. increments.

Table I. Comparison of Interfacial Tensions

System: Benzene–Water–Acetone, 30.0°C

Wt. % Acetone in		Interfacial Tension, Dynes/cm.		
Aqueous phase	Benzene phase	Drop-Volume	Du Nouy	Pendant drop
0	0	33.0	32.8	32.2
4.3	4.9	21.3	19.9	21.7
8.6	10.3	16.1	15.6	16.0
17.8	23.6	9.5	9.4	9.5

A few measurements were made by the pendant-drop method (*7*). Photographs of pendant-down drops were taken with a Leica Ig camera, with bellows attachment, having an *f* 4.5 lens of 42-mm. focal length, using a high contrast copy film. The drops, formed from the heavier aqueous phase, were suspended from a cylindrical, polished glass tip immersed in the lighter organic phase. The tip diameter was measured by micrometer to the nearest 0.001 inch. The organic phase was contained in a quartz cell normally used for measuring light absorption. The cell had parallel sides to minimize distortion of the photographed shapes, and was held at constant temperature by immersion in a water bath. The photographic negatives were made into slides, and measurements were made from projections of the slides.

Table I lists a comparison among measurements made on three two-phase mixtures by the three methods. Considering the difficulties of measurement, agreement is considered satisfactory.

All chemicals used were distilled in a laboratory column prior to use, retaining only the central portion of the distillate. The water was redistilled from an alkaline potassium permanganate solution.

Table II. Interfacial Tensions of Aqueous Ternary Systems

Aqueous phase			Organic phase			Interfacial Tension, Dynes/Cm.
Concn. wt.%		Density, grams/ml.	Concn. wt.%		Density, grams/ml.	
(2)	(3)		(2)	(3)		
A. 1, 1,2-Trichlorethane(1)–Water(2)–Acetone(3), 25.0° C.[a]						
99.56	0	0.9986	0.11	0	1.4304	29.6
97.5	2.0	0.9968	0.18	2.5	1.4013	24.6
95.4	4.1	0.9941	0.29	6.2	1.3651	20.3
91.7	7.7	0.9888	0.50	12.3	1.3048	15.7
83.7	15.6	0.9778	1.0	23.6	1.1983	9.3
76.0	23.1	0.9670	1.9	34.7	1.1136	5.4
66.7	32.1	0.9541	3.4	44.4	1.0414	2.8
56.6	41.3	0.9393	6.8	54.9	0.9827	1.0
B. 1, 1,2-Trichloroethane(1)–Water (2)–Methyl ethyl ketone(3), 25.0° C.[b]						
99.2	0.4	0.9979	0.2	3.4	1.3944	24.8
98.2	1.4	0.9965	0.3	7.7	1.3405	20.9
97.0	2.6	0.9950	0.5	15.5	1.2704	17.6
94.1	5.6	0.9907	0.8	29.8	1.1562	12.8
90.5	9.3	0.9857	1.6	45.5	1.0491	8.3
84.8	15.1	0.9774	3.9	68.4	0.9250	4.2
75.6	24.4	0.9620	10.0	90.0	0.8305	0.9
C. Benzene(1)–Water(2)–Acetone(3), 30.0° C.[a]						
99.8	0	0.9954	0.07	0	0.8682	33.0
98.1	1.8	0.9929	0.1	1.9	0.8663	25.9
95.6	4.3	0.9889	0.2	4.9	0.8638	21.3
91.2	8.6	0.9832	0.2	10.3	0.8581	16.1
81.9	17.8	0.9710	0.6	23.6	0.8465	9.5
75.8	23.8	0.9611	1.1	34.1	0.8388	6.3
68.2	30.9	0.9493	2.7	45.5	0.8317	3.8
D. Benzene(1)–Water(2)–Methanol(3), 25.0° C.[b]						
80.0	19.5	0.9648	0.1	0.5	0.8716	17.7
62.5	36.0	0.9369	0.1	1.5	0.8708	10.9
43.0	53.5	0.8990	0.15	3.0	0.8711	5.4
E. Carbon tetrachloride(1)–Water(2)–*n*-Propanol(3), 20.0° C.[b]						
97.8	2.1	0.9950	0.01	0.3	1.5880	28.6
95.1	4.8	0.9913	0.01	0.4	1.5841	20.0
91.4	8.5	0.9862	0.1	1.5	1.5748	12.1
84.9	14.8	0.9790	0.5	8.6	1.4486	4.8
83.4	16.4	0.9755	2.0	23.0	1.2785	2.8
80.8	18.9	0.9756	8.0	43.2	1.0832	1.0
...	0	...	...	0	...	43.3

[a] Drop-volume method.
[b] DuNouy ring method.

Table III. Ternary System F

Perfluoro-*n*-hexane(1)–Benzene(2)–*n*-Hexane(3)

30.0° C.

Binodal Curve

Concn., wt.% (1)	Concn., wt.% (2)	Density, grams/ml.	Concn., wt.% (1)	Concn., wt.% (2)	Density, grams/ml.
97.018	2.982	1.5986	26.41	31.17	0.8386
87.04	3.65	1.3673	17.00	47.41	0.8246
77.17	4.99	1.2310	12.79	58.60	0.8260
60.34	8.48	1.0314	7.16	78.34	0.8456
51.15	11.82	0.9577	5.01	87.10	0.8579
41.98	16.53	0.8955	3.947	96.053	0.8770
34.58	22.99	0.8630			

Tie Lines and Interfacial Tensions (Du Nouy)

C_6F_{14} phase Concn., wt.% (1)	C_6F_{14} phase Concn., wt.% (2)	Benzene phase Concn., wt.% (1)	Benzene phase Concn., wt.% (2)	Interfacial Tension, Dynes/Cm.
97.02	2.98	3.95	96.05	5.8
95.6	3.0	5.2	86.1	4.4
94.2	3.1	8.8	72.1	3.3
92.4	3.2	13.7	56.1	2.0
90.3	3.3	19.8	41.9	1.4
87.5	3.5	31.5	25.8	1.8

Table IV. Ternary System G

Perfluoro-*n*-hexane(1)–Carbon disulfide(2)–*n*-Hexane(3)

25.0° C.

Binodal Curve

Concn. wt.% (1)	Concn. wt.% (2)	Density, grams/ml.	Concn. wt.% (1)	Concn. wt.% (2)	Density, grams/ml.
98.49	1.51	1.6530	18.80	26.04	0.8443
91.99	1.21	1.4891	14.42	33.61	0.8542
87.07	1.98	1.3812	5.70	55.98	0.9289
79.46	1.48	1.2540	2.01	78.11	1.0585
58.30	2.73	1.0042	0.50	99.50	1.2558
29.82	15.17	0.8535			

Tie Lines and Interfacial Tensions (Du Nouy)

C_6F_{14} phase Concn. wt.% (1)	C_6F_{14} phase Concn. wt.% (2)	CS_2 phase Concn. wt.% (1)	CS_2 phase Concn. wt.% (2)	Interfacial Tension, Dynes/Cm.
98.49	1.51	0.50	99.50	9.6
97.3	1.7	0.8	92.7	7.8
95.6	1.9	3.9	64.5	4.1
92.3	2.0	14.3	33.5	2.0

Table V. Binary Systems, 25.0° C.

	System H Perfluoro-*n*-hexane(1)–Tetradecane(2)	System I Tetradecane(1)–Methanol(2)
Mutual Solubility		
Wt. % (1)	99.52 4.94	99.00 3.48
Interfacial		
Tension (Du Nouy) Dynes/Cm.	6.1	4.6

The ternary phase diagrams of aqueous systems were available in the literature (*1, 2, 3, 10, 14*). Mixtures having over-all compositions within the two-phase region were agitated in the water bath to reach equilibrium, and the phases separated. Densities of the equilibrium phases were determined by pycnometer. For all except two aqueous systems, the literature included the refractive indices of the equilibrium solutions, and the phases were identified by measuring refractive index with a Bausch and Lomb Model 33-45-03-01 Precision Refractometer. Phase densities were used in the case of 1,1,2-trichloroethane–water–methyl ethyl ketone. In the case of benzene–water–methanol, the compositions were made identical with those of known tie-lines.

In the case of the perfluoro-*n*-hexane systems, the ternary binodal solubility curves were determined by titration to a cloud point. Densities of the saturated phases were recorded. Equilibrium phase compositions were then determined from the densities by reference to the densities along the binodal curve. The two tetradecane binary solubilities were determined by titration to a cloud point.

PRESENTATION OF DATA

Tables II to V list the data and the method of measurement of interfacial tension. Generally, components 1 and 2 are partially miscible, and component 3 is completely soluble in both. In the case of the methyl ethyl ketone system, only components 1 and 3 are completely soluble.

Only the system 1,1,2-trichloroethane-water-acetone at 25.0° C. seems to have been measured earlier (*9*), and the present interfacial tensions in this system are a little higher (maximum difference about 3.6 dynes per cm.). However, in the case of the earlier measurements, many of the binary tensions reported were lower than literature values.

Donahue and Bartell (*4*) suggested a simple correlation between interfacial tension and mutual solubility of aqueous binary systems. On the basis of fragmentary data then available, it was further suggested (*13*) that this might be extended, on the coordinates of Figure 1, to include ternaries as well. The data reported here, as plotted in Figure 1, indicate that the nonaqueous binary data are not handled by the Donahue-Bartell correlation, and that extension to include ternaries is inadequate for these. Elsewhere (*11, 12*), a theory is advanced which permits prediction of both aqueous and nonaqueous binary interfacial tensions, and also those of regular ternary systems.

ACKNOWLEDGMENT

This work was done under a grant from the Petroleum Research Fund of the American Chemical Society, for whose support we are most grateful. Thanks are also due the Minnesota Mining and Manufacturing Co., who donated the perfluoro-*n*-hexane.

NOMENCLATURE

x = mole fraction concentration

Subscripts

1, 2, and 3, refer to components 1, 2, and 3, respectively, with 1 and 2 only partly soluble

Superscripts

$'$ = component—1—rich phase
$''$ = component—2—rich phase

LITERATURE CITED

(1) Barbaudy, J., *Compt. Rend.* **182,** 1279 (1926).
(2) Briggs, S.W., Comings, E.W., *Ind. Eng. Chem.* **35,** 413 (1943).
(3) Denzeler, C.G., *J. Phys. Chem.* **49,** 358 (1945).
(4) Donahue, D.J., Bartell, F.E., *Ibid.,* **56,** 480 (1952).
(5) Harkins, W.D., Brown, F.E., *J. Am. Chem. Soc.* **41,** 499 (1919).
(6) Harkins, W.D., Humphrey, E.C., *Ibid.,* **38,** 228 (1916).

(7) Hauser, E.A., Michaels, A.S., *J. Phys. & Colloid Chem.* **52,** 1157 (1948).
(8) Hildebrand, J.H., Scott, R.L., "Regular Solutions," Prentice-Hall, New York, 1962.
(9) Murphy, N F , Lastovica, J E , Fallis, J.G., *Ind. Eng. Chem.* **49,** 1035 (1957).
(10) Newman, M., Hayworth, C.B., Treybal, R.E., *Ibid.,* **41,** 2039 (1949).
(11) Pliskin, I., Ph.D. thesis, New York University, New York, N. Y., 1965.
(12) Pliskin, I., Treybal, R.E., New York University, New York, N. Y., unpublished data, 1965.
(13) Treybal, R.E., "Liquid Extraction," 2nd ed., pp. 131–2, McGraw-Hill, New York, 1963.
(14) Treybal, R.E., Weber, L.D., Daley, J.F., *Ind. Eng. Chem.* **38,** 817 (1946).
(15) Zuidema, E.A., Waters, G.W., *Ind. Eng. Chem., Anal. Ed.* **13,** 312 (1941).

RECEIVED for review July 6, 1965. Accepted October 21, 1965.

Thermal Conductivity of Fluids. Methane

L. T. CARMICHAEL, H. H. REAMER, and B. H. SAGE

Chemical Engineering Laboratory, California Institute of Technology, Pasadena, California

The thermal conductivity of methane was measured at five temperatures between 40° and 340° F. and at pressures between atmospheric and 5000 p.s.i.a. The data were obtained with a spherical thermal conductivity cell and are in good agreement with the measurements of of other investigators at low pressures but show a smaller effect of high pressure upon the thermal conductivity than would be expected from earlier measurements. Within the uncertainty of the present measurements, the thermal conductivity excess is a single-valued function of specific weight. The results are presented in tabular and graphical form.

THE THERMAL conductivity of methane at atmospheric pressure has been studied in some detail. The earlier work of Eucken (*1*) has been supplemented by the more recent measurements of Mann and Dickens (*12*), Johnston and Grilly (*5*), Lambert *et al.* (*9*), and Kannuluik and Donald (*6*). Rather recently, Svehla (*18*) reported values calculated from statistical mechanical considerations and experimental measurements of viscosity at temperatures between −280° and 8540° F. for atmospheric pressure. Schottky (*17*) and Geier and Schafer (*2*) also carried out experimental measurements of thermal conductivity at atmospheric pressure. There is reasonable agreement among these data, and they serve to establish the thermal conductivity of methane satisfactorily at atmospheric pressure. Keyes (*8*) carried out a series of measurements at temperatures between 122° and 572° F. and at pressures as high as 890 p.s.i.a. These data and the measurements by Lenoir and Com-

Table I. Thermal Conductivity of Helium from Several Sources at Atmospheric Pressure

			Thermal Conductivity, B.t.u./(Hr.) (Ft.) (° F.)			
Date	Pressure, P.S.I.A.	Temperature, ° F.	Authors	Keyes[a]	Hilsenrath, Touloukian[b]	Wilson[a]
July 1961	16.3	40	0.08204	0.08273	0.08257	
June 1959	15.0	100	0.08853	0.08864	0.08854	0.0890
July 1960	18.9	100	0.08854			
Aug. 1961	16.6	100	0.08859			
Dec. 1964[c]	18.1	100	0.08824			
Mar. 1962	17.5	130	0.09158	0.09150	0.09135	
Aug. 1962	18.5	130	0.09233			
Dec. 1962	17.2	130	0.09116			
May 1963	15.4	130	0.09138			
Oct. 1963	17.3	130	0.09122			
Jan. 1964[c]	17.4	130	0.09117			
Mar. 1964[c]	17.9	130	0.09071			
May 1964[c]	16.6	130	0.09095			
June 1959	17.7	220	0.09947	0.09960	0.09941	
July 1960	18.8	220	0.09946			
June 1959	15.0	340	0.10941	0.10957	0.10936	
Dec. 1959	15.0	340	0.10966			
July 1960	18.8	340	0.10927			
Aug. 1960	18.0	340	0.10927			
Average deviation[d]				0.00305	0.00291	0.00588

[a] Statistical mechanical calculations and experimental data (*7*, *20*).
[b] A critical review (*4*).
[c] Thermal conductivity of methane measurements taken during this time. (January 1964–May 1964, check measurements, December 1964).
[d] Average deviation expressed in fraction and defined by:

$$S' = \frac{\sum_{1}^{N_p} \left| \frac{(k_e)_{av} - k_r}{(k_e)_{av}} \right|}{N_p}$$