Interfacial Tensions in Ternary Liquid-Liquid Systems

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Interfacial tensions over the two-phase concentration range have been measured for the ternary systems acetone-hexane-water, isopropanol-hexane-water, methyl ethyl ketone–hexane–water, methanol-benzene-water, isopropanol-benzene-water, and acetone–methyl isobutyl ketone–water. All measurements were made at 25° ± 1° C. The systems were selected to represent several types of irregularities.

RELIABLE DATA on the interfacial tension of ternary liquid-liquid systems are uncommon. In general, when available, the data do not extend over the full range of solubilities. The two most important sets of data are those of Bartell and Davis (*1*), and of Pliskin and Treybal (*4*).

A problem facing investigators attempting to correlate interfacial tensions is the absence of data on irregular systems—e.g., those passing through an isopycnic (two phases of equal density), through a solutrope (equal solute concentration in each phase), or that do not have a plait point (systems of type II). The systems that are presented here include all three types.

EXPERIMENTAL PROCEDURE

The interfacial tension measurements were made with a calibrated Cenco-duNouy ring tensiometer having a platinum-iridium ring with a 5.999-cm. circumference. The data so obtained were corrected to absolute values by means of the Zuidema and Waters compensation for interface distortion (*6*). The method was tested on materials of known surface tension, and was reliable to 0.1 dyne per cm.

All data were taken at 25° C. ± 1°. Several checks were made on the temperature coefficients, and the maximum effect was less than 0.06 dyne per ° C.

All organic systems were redistilled at high reflux in a laboratory column, retaining only the central 80% by volume of the distillate. The water was obtained as ion-free, organic-free redistillate from the University of Missouri Medical School. Its purity was verified by measuring the surface tension.

Glassware was cleaned by immersing for about 2 hours in a hot solution of sodium dichromate in concentrated sulfuric acid. Then, the glassware was rinsed in tap water, followed by a running jet of distilled water, and was allowed to drip on clean filter paper in a dust-free cabinet. This method, which follows the recommendations of duNouy (*2*), was found necessary to ensure reproducible data.

The ternary system equilibrium data used were those of Seidell and Linke (*5*). The components of any given system were added together in measured amounts, and the mixture was agitated in a constant temperature bath until equilibrium conditions were reached. After measuring the interfacial tension, the phases were separated and their densities were measured by a Westphal balance. The phases were identified by means of their refractive indices.

PRESENTATION OF DATA

Table I lists the compositions and densities of the equilibrium phases, together with their interfacial tension. Systems I to V have a nonpolar organic solvent and a polar solute. System VI, acetone–methyl isobutyl ketone–water, has no nonpolar component. System I, acetone-hexane-water, and system II, isopropanol-hexane-water, show no special irregularity. System V, isopropanol-benzene-water, has a solutrope about one-third of the way to the plait point. System III, methyl ethyl ketone–hexane–water, has no plait point. Apparently, type II solubility characteristics do not alter the mechanism responsible for the lowering of the interfacial tension. System IV, methanol-benzene-water, goes through an isopycnic about three quarters of the way to the plait point. A smooth curve was drawn through the points on each side of the isopycnic. This interpolation procedure gave a value of interfacial tension at the isopycnic concentration of methanol as approximately 3.2 dyne per cm.

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

Aqueous Phase Concn., mole fraction		Aqueous Phase Density, g./cc.	Organic Phase Concn., mole fraction		Organic Phase Density, g./cc.	Interfacial Tension, Dynes/Cm.
		ACETONE(S)-HEXANE(1)-WATER(2)				
(s)	(2)		(s)	(2)		
0.000	0.999	0.9973	0.000	0.0006	0.6610	50.1
0.002	0.998	0.9950	0.009	0.0006	0.6623	41.6
0.025	0.975	0.9865	0.034	0.0006	0.6625	20.5
0.051	0.949	0.9860	0.075	0.0006	0.6641	12.8
0.106	0.894	0.9584	0.137	0.0006	0.6671	6.3
0.143	0.857	0.9444	0.207	0.0006	0.6698	4.7
0.222	0.778	0.9155	0.337	0.0120	0.6790	2.9
0.266	0.733	0.9040	0.387	0.0240	0.6856	2.2
0.304	0.692	0.8931	0.448	0.0370	0.6904	1.5
0.342	0.652	0.8787	0.505	0.0460	0.6991	1.2
0.386	0.605	0.8674	0.555	0.0550	0.7092	1.0
0.444	0.541	0.8464	0.599	0.0850	0.7231	0.9

(continued on page 106)

Table I. Interfacial Tensions of Ternary Systems at 25° C. (*Continued*)

Aqueous Phase			Organic Phase			Interfacial Tension, Dynes/Cm.
Concn., mole fraction		Density, g./cc.	Concn., mole fraction		Density, g./cc.	
(s)	(2)		(s)	(2)		
ISOPROPANOL(S)-HEXANE(1)-WATER(2)						
0.000	0.999	0.9982	0.000	0.0006	0.6622	50.1
0.002	0.998	0.9954	0.003	0.0006	0.6623	35.1
0.009	0.991	0.9901	0.010	0.0006	0.6627	19.1
0.023	0.977	0.9850	0.025	0.0006	0.6634	12.4
0.050	0.950	0.9739	0.049	0.0006	0.6645	8.4
0.077	0.923	0.9643	0.071	0.0006	0.6655	5.6
0.106	0.894	0.9527	0.102	0.0040	0.6690	4.5
0.130	0.870	0.9402	0.147	0.0090	0.6723	3.0
0.166	0.832	0.9241	0.175	0.0170	0.6770	2.4
0.223	0.767	0.8995	0.231	0.0300	0.6834	1.7
0.322	0.638	0.8450	0.327	0.0800	0.6973	0.9
0.398	0.517	0.7922	0.407	0.1760	0.7211	0.7
METHYL ETHYL KETONE(S)-HEXANE(1)-WATER(2)						
0.000	0.999	0.9983	0.000	0.0006	0.6629	50.1
0.001	0.999	0.9974	0.007	0.0006	0.6634	40.1
0.002	0.998	0.9963	0.014	0.0006	0.6638	35.7
0.012	0.988	0.9913	0.076	0.0006	0.6681	18.9
0.016	0.984	0.9895	0.129	0.0006	0.6718	17.0
0.020	0.980	0.9860	0.241	0.0006	0.6816	13.2
0.029	0.971	0.9840	0.324	0.0006	0.6917	10.7
0.032	0.968	0.9827	0.396	0.0040	0.7022	9.0
0.033	0.967	0.9808	0.452	0.0100	0.7133	8.0
0.042	0.958	0.9778	0.581	0.0270	0.7328	6.6
0.049	0.951	0.9756	0.686	0.0630	0.7617	4.2
0.058	0.942	0.9724	0.730	0.1460	0.7883	2.7
0.075	0.925	0.9612	0.692	0.3070	0.8313	1.1
METHANOL(S)-BENZENE(1)-WATER(2)						
0.000	0.999	0.9971	0.000	0.0031	0.8748	34.3
0.011	0.989	0.9932	0.002	0.0031	0.8745	30.8
0.052	0.948	0.9825	0.005	0.0031	0.8742	23.4
0.121	0.879	0.9658	0.012	0.0031	0.8740	18.8
0.188	0.812	0.9525	0.024	0.0031	0.8739	13.9
0.277	0.722	0.9300	0.045	0.0160	0.8736	8.8
0.361	0.637	0.9103	0.062	0.0200	0.8731	6.7
0.417	0.571	0.8952	0.080	0.0240	0.8727	5.2
0.517	0.450	0.8749	0.090	0.0320	0.8697	3.7
0.548	0.409	0.8672	0.112	0.0390	0.8695	2.7
0.561	0.387	0.8610	0.141	0.0380	0.8687	2.2
0.604	0.217	0.8468	0.253	0.0690	0.8632	1.0
ISOPROPANOL(S)-BENZENE(1)-WATER(2)						
0.000	0.999	0.9984	0.000	0.0031	0.8743	34.3
0.002	0.998	0.9959	0.001	0.0031	0.8731	30.1
0.003	0.997	0.9942	0.006	0.0031	0.8727	27.8
0.023	0.977	0.9853	0.023	0.0031	0.8724	13.7
0.047	0.953	0.9761	0.063	0.0031	0.8686	8.7
0.063	0.938	0.9701	0.122	0.0100	0.8638	6.0
0.077	0.922	0.9629	0.207	0.0240	0.8575	4.1
0.086	0.912	0.9584	0.284	0.0650	0.8529	3.1
0.097	0.900	0.9524	0.359	0.1310	0.8477	2.1
0.109	0.887	0.9460	0.405	0.2230	0.8463	1.6
0.121	0.873	0.9390	0.411	0.3070	0.8487	1.2
0.150	0.837	0.9271	0.379	0.4450	0.8587	0.9
ACETONE(S)-METHYL ISOBUTYL KETONE(1)-WATER(2)						
0.000	0.997	0.9973	0.000	0.115	0.8017	10.1
0.001	0.995	0.9972	0.009	0.116	0.8017	9.9
0.003	0.993	0.9956	0.018	0.128	0.8019	9.5
0.010	0.986	0.9903	0.093	0.132	0.8024	8.5
0.023	0.973	0.9849	0.179	0.144	0.8033	6.9
0.040	0.955	0.9786	0.237	0.158	0.8041	5.9
0.053	0.941	0.9717	0.313	0.190	0.8052	5.1
0.076	0.917	0.9644	0.353	0.214	0.8066	4.5
0.092	0.899	0.9584	0.385	0.255	0.8088	3.6
0.108	0.881	0.9477	0.410	0.325	0.8125	2.8
0.175	0.802	0.9168	0.332	0.578	0.8294	1.5

A correlation between interfacial tension and composition of ternary systems has been developed by the authors (*3*). The correlation also fits aqueous and nonaqueous interfacial tension data for binary systems with good accuracy.

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A Study of the Nuclear Magnetic Resonance Spectra of Aryl Nitrogen Derivatives of Some Estratriens

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The nuclear magnetic resonance chemical shifts and coupling constants are reported for seven aryl nitrogen derivatives of estratriens. This study confirmed the position of the group on the aromatic ring.

IN THE PAST, workers (*2, 4, 5, 6*) have studied the positions of substituents on the aromatic ring of estratriens. This laboratory would like to confirm these assignments, by means of their nuclear magnetic resonance spectra. The results are given in Table I.

This type of problem is particularly susceptible to solution by this method since the coupling patterns of the various types of aromatic substitution are thoroughly established (*1*). This evidence is, therefore, direct and unequivocal.

The mononitroestrone, which was assigned as

Table I Chemical Shifts, τ^a, and Coupling Constants, J^b, of Characteristic Protons in the NMR Spectra and Melting Points

Compound	Solvent	13 $-CH_3$	3 $-OCH_3$	1 & 2 or 1 & 4 Aromatic	2 or 4 $-NH_2$	M.P., ° C.
4-Nitroestrone	$CDCl_3$ & DMSO	9.09 $J = 0$		2.68 & 3.08 $J = 9$ $J = 9$		272[c]
4-Nitroestrone, 3-methyl ether	$CDCl_3$	9.09 $J = 0$	6.09 $J = 0$	2.51 & 3.02 $J = 9$ $J = 8$		253–256
4-Aminoestrone, 3-methyl ether	$CDCl_3$	9.09 $J = 0$	6.08 $J = 0$	3.18 $J = 0$	6.28[d]	188–191
4-Aminoestrone, 3-methyl ether	$CDCl_3$ + DCl	9.08 $J = 0$	6.08 $J = 0$	2.52 & 3.02 $J = 8$ $J = 8$		
2-Nitroestrone	$CDCl_3$	9.08 $J = 0$		1.99 & 3.12 $J = 0.4$ $J = 0.4$		172–175
2-Aminoestrone, 3-methyl ether	$CDCl_3$	9.10 $J = 0$	6.15 $J = 0$	3.23 & 3.40 $J = 0.5$ $J = 0.5$	6.45[d]	171–175
2-Aminoestrone, 3-methyl ether	$CDCl_3$ & DCl	9.12 $J = 0$	6.17 $J = 0$	2.42 & 3.44 $J = 0.5$ $J = 0.5$		
4-Nitroestrone, 3-benzyl ether	$CDCl_3$	9.12 $J = 0$		2.71 & 3.14 $J = 9$ $J = 9$		199–201
4-Aminoestrone, 3-benzyl ether	$CDCl_3$	9.11 $J = 0$		3.27 $J = 0$	6.28[d]	223–226
4-Aminoestrone, 3-benzyl ether	$CDCl_3$ + DCl	9.12 $J = 0$		2.67 & 3.13 $J = 9$ $J = 9$		

[a] Proton NMR spectra were measured at 60 Mc. on the Varian A-60 spectrometer using 5 to 10% solution in $CDCl_3$, except where noted, containing tetramethylsilane (TMS) as an internal reference standard. Chemical shifts are expressed in τ units measured downfield from the reference (τ0). [b] In c.p.s. [c] Decomposed. [d] Broad peaks and coupling constants could not be determined.