analysis, and, in particular, showed that the temperature coefficient of the II → I reaction rate is greatest near a mole fraction of 0.5.

Differential thermal analysis gave the following results (mole fraction of ammonium chloride, transition temperature on heating (°C.), transition temperature on cooling (°C.): 0, 141.2, 138.1; 0.083, 129.7, 124.7; 0.269, 114.0, 108.9; 0.378, 110.8, 105.4; 0.498, 110.6, 107.7; 0.615, 118.9, 115.1; 0.785, 135.8, 138.7; 0.885, 153.5, unobservable; 1.000, 185.0, 184.1. These data are shown in Figure 1. Bridgman, (*1*) gives 137.8 and 184.3° and Pöyhönen (*5*), in a recent careful study, 137.2 and 183.1° for the pure bromide and pure chloride, respectively.

For the solid solutions, the observed temperatures of transition vary smoothly and pass through a minimum with changing composition. The II → I transitions occur at higher temperatures than the I → II, except for the solutions of highest chloride content where a large spread between the two equilibrium solidus lines is indicated (estimated, in the light of this investigation, as lying approximately as shown in Figure 1 by broken lines). This spread was further suggested by less noticeable thermal effects in this region.

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Interfacial Tension in Multicomponent Aqueous - Organic Systems

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Interfacial tension measurements are presented for four two-phase liquid systems: benzene–carbon tetrachloride–water, benzene–carbon tetrachloride–water–methanol, benzene–carbon tetrachloride–water–acetone, and benzene–carbon tetrachloride–water–cyclohexanol. Data are given both for freshly formed interfaces with the solute (4th component) originally in the organic phase, and for equilibrium phase compositions. The range of solute concentrations studied was from 0 to 50 mole %. Variations in interfacial tension as an effect of the solute ranged from 0 to 35 dynes per centimeter. Methanol decreased interfacial tension almost in proportion to concentration. Acetone had a proportionately greater effect at lower concentrations. The low concentration effect was even more pronounced with cyclohexanol.

ALTHOUGH INTERFACIAL TENSION data on many two-component, liquid-liquid systems are available in the literature (*1*), there is scant information on three or four component systems. Correspondingly, there are few, if any data on the effect of a solute, in either phase or in both phases, on interfacial tension in liquid-liquid systems.

This work presents interfacial tension data on the following multicomponent systems:

1. Water-Benzene-Carbon Tetrachloride
2. Water-Benzene-Carbon Tetrachloride-Methanol
3. Water-Benzene-Carbon Tetrachloride-Acetone
4. Water-Benzene-Carbon Tetrachloride-Cyclohexanol

In the last three systems, the final component was added initially to the organic phase. Thus freshly formed interfaces of nonequilibrium concentration distribution could be examined. The same systems were also studied with equilibrium distribution of concentration between the phases to provide interfacial tension data that was not time dependent.

APPARATUS

Interfacial tension data were obtained by use of a DuNouy interfacial tensiometer, catalog No. 93010 from Scientific Technical Supplies Co. of Frankfurt, Germany. The ring used was a No. 70542 platinum ring supplied by the Central Scientific Co. The mean circumference of the ring was 5.991 cm. The ratio of ring diameter to wire diameter, R/r, was 53.6. All experiments were conducted at ambient temperature.

Ternary phase diagrams for the systems studied were determined by titration where literature data were not available. Tie lines for the Benzene–methanol–water system were determined experimentally. Tie-line information for the other systems was obtained from Perry (*2*) and Seidell (*3*).

MATERIALS

All chemicals used in these experiments were Merck reagent grade, conforming to ACS specifications, with the exception of cyclohexanol. The latter chemical was provided by the Eastman Organic Chemicals Co.

EXPERIMENTAL

Interfacial tension data reported here are based on freshly formed interfaces with nonequilibrium concentration distribution and on equilibrium concentrations in each phase.

To obtain information on freshly formed interfaces, the following procedure was used: Phase 1, the organic phase, was made up to a known concentration by volumetric measurements. Phase 2, a known volume of distilled water, was kept separate from phase 1. The more dense of the two phases was placed in an evaporating dish. The less dense phase was then gently but rapidly placed upon the surface. Interface tension measurements were taken every minute or so by moving the ring through the interface from the aqueous to the organic phase. A plot of the interfacial tension as a function of time was then constructed. Extrapolation of this plot to zero time gave an estimate of the interfacial tension of the freshly formed interface.

For equilibrium measurements, the procedure was as follows: known volumes of each component in the system to be studied were measured and placed in a container. The container was shaken vigorously for several minutes. The phases were then allowed to separate. The interfacial tension was determined by moving the tensiometer ring from the aqueous to the organic phase as before. Equilibrium phase compositions were determined from existing phase data in the literature where available. Other necessary equilibrium data were obtained by construction of phase diagrams from experimental titrations to the cloud point. In cases where the solute was essentially nondistributive, such as methanol in the benzene-methanol-water system, the equilibrium-concentration in the aqueous phase (phase 2) was given to define the system. In all other cases, the concentration of the organic phase (phase 1) was used to define the system.

Reliability of the data presented here is estimated to be as follows: Concentrations were believed to be accurate to within ±1%. Reproducibility of individual points was

Table I. Interfacial Tension Between Phases

System: Phase 1. Benzene-Carbon Tetrachloride
Phase 2. Water

	Concn., Phase 1		Interfacial[a] Tension, Dynes/Cm.
Mole % Benzene	0	20° C.	44.3
	15.8		43.2
	42.4		38.9
	64.1		37.2
	100		33.4

[a] Freshly-formed interface.

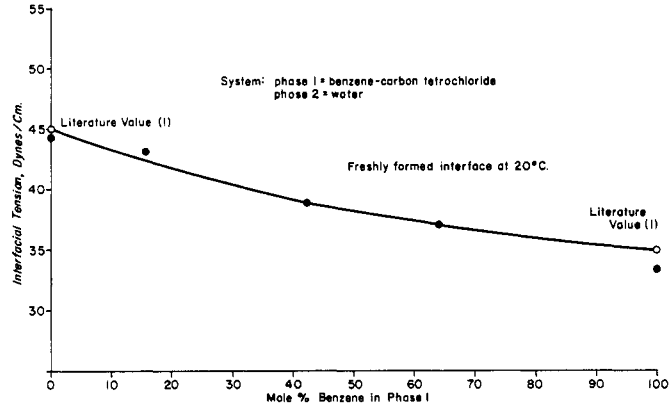

Figure 1. Interfacial tension between benzene-carbon tetrachloride mixtures and water

Table II. Interfacial Tension Between Phases

(Second phase in all systems is water)

Methanol, Mole %: Concn., phase 1	Methanol, Mole %: Equil. concn., phase 2	Interfacial Tension, Dynes/Cm.: Freshly-formed		Interfacial Tension, Dynes/Cm.: Equilibrium	
System: Benzene-Methanol					
		20° C.		20° C.	
0	0	33.9[a]		32.1	
8.9	1.8	27.6		29.2	
22.5	4.2	20.1		26.8	
26.8	7.7	17.5		23.0	
33.5	11.0	13.3		19.8	
	18.0			15.1	
System: Benzene–Carbon Tetrachloride–Methanol					
		24° C.	20° C.[c]	24° C.	20° C.[c]
0[d]	0	36.0	38.8[a]	...	...
8.5[d]	1.7	33.3	33.6	32.0	32.3
18.6[d]	4.3	27.8	28.1	28.8	29.1
31.4[d]	8.2	22.0	22.2	24.4	24.6
40.8[d]	11.8	15.8	16.0	19.5	19.7
53.5[d]	18.2	9.5	9.6	14.3	14.4
System: Carbon Tetrachloride–Methanol					
		20° C.		20° C.	
0	0	43.4		...	
8.8	1.8	35.5		37.9	
19.3	4.3	30.4		32.6	
32.3	8.2	23.4		26.2	
41.8	11.8	18.0		23.4	
54.4	18.2	13.0		18.3	

Acetone, Mole %: Concn., phase 1	Acetone, Mole %: Equil. concn., phase 1	Interfacial Tension, Dynes/Cm.: Freshly-formed		Interfacial Tension, Dynes/Cm.: Equilibrium	
System: Benzene-Acetone					
		24° C.	20° C.[c]	24° C.	20° C.[c]
0	0[b]	33.8	34.0	...	...
4.6	2.7[b]	26.2	26.4	26.9	27.1
10.8	6.2[b]	20.1	20.2	21.5	21.6
19.6	10.5[b]	15.2	15.3	16.3	16.4
26.6	15.5[b]	12.0	12.1	13.2	13.3
37.8	24.0[b]	8.1	8.2	9.1	9.2
System: Benzene–Carbon Tetrachloride–Acetone					
		22° C.	20° C.[c]	22° C.	20° C.[c]
0[d]	0[e]	38.4	38.5	35.7	35.8
4.8[d]	2.0[e]	27.8	27.9	27.0	27.1
11.2[d]	4.7[e]	21.1	21.2	21.8	21.9
20.2[d]	9.1[e]	16.5	16.6	16.5	16.6
27.6[d]	13.9[e]	13.6	13.7	14.1	14.2
38.7[d]	22.5[e]	10.2	10.3	11.3	11.4
System: Carbon Tetrachloride–Acetone					
		22° C.	20° C.[c]	22° C.	20° C.[c]
0	0[f]	43.5	43.7	38.7	38.9
5.0	1.2[f]	28.6	28.8	26.6	26.8
11.6	3.2[f]	22.5	22.6	23.2	23.3
20.9	7.6[f]	17.5	17.6	17.7	17.8
28.6	12.2[f]	14.7	14.8	15.7	15.8
39.7	21.0[f]	10.7	10.8	11.2	11.3

Cyclohexanol, Mole %; Concn., Phase 1	Interfacial Tension, Dynes/Cm., Freshly-Formed	
System: Benzene-Cyclohexanol		
	22° C.	20° C.[c]
0	33.8	33.9
3.3	15.3	15.4
7.9	11.3	11.4
14.6	9.6	9.6
20.4	8.5	8.5
29.9	7.1	7.1
System: Benzene–Carbon Tetrachloride–Cyclohexanol		
	23° C.	20° C.[c]
0[d]	35.4	35.6
3.4[d]	16.7	16.8
8.1[d]	12.4	12.5
15.1[d]	10.4	10.4
21.0[d]	9.3	9.3
30.7[d]	8.3	8.3
System: Carbon Tetrachloride–Cyclohexanol		
	22° C.	20° C.[c]
0	43.4	43.6
3.6	16.0	16.1
8.5	13.3	13.3
15.7	10.7	10.7
21.8	10.5	10.5
31.6	9.3	9.3

[a] From Figure 1. [b] (2). [c] Estimated from (*1*). [d] Volume benzene = to carbon tetrachloride. [e] Interpolated from data of b and f. [f] (*3*).

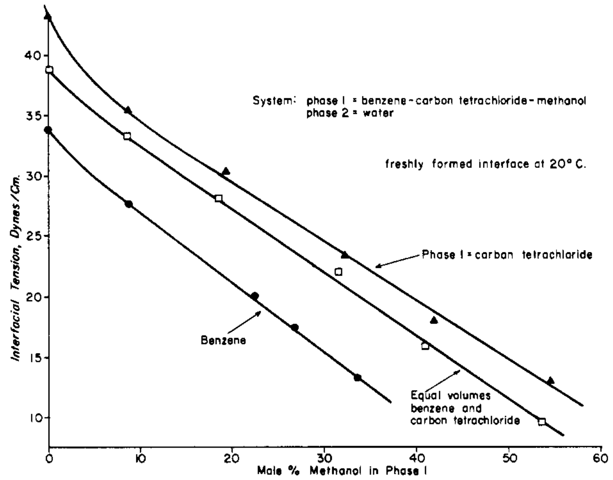

Figure 2. Effect of methanol on interfacial tension at a freshly formed interface

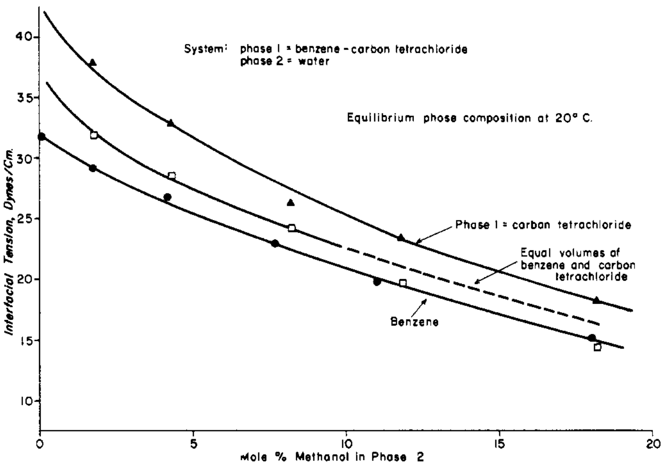

Figure 3. Effect of methanol on interfacial tension at equilibrium phase composition

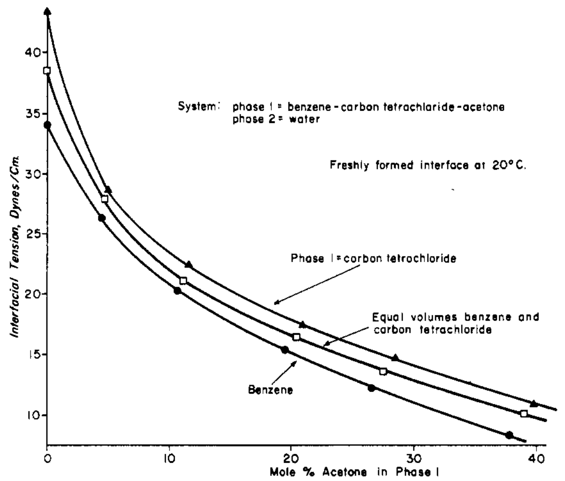

Figure 4. Effect of acetone on interfacial tension at a freshly formed interface

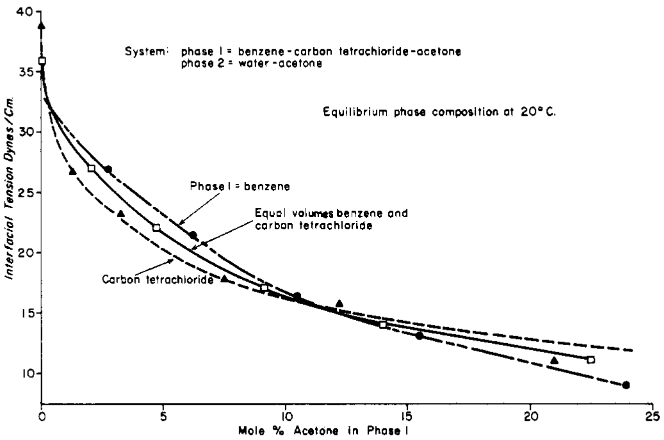

Figure 5. Effect of acetone on interfacial tension at equilibrium phase composition

accurate to ±0.2 dynes/cm. Freshly formed interface data were obtained by extrapolation of experimental data, and are estimated to be accurate to ±1 dyne/cm. Other causes of errors, such as incomplete wetting of the ring or foreign materials at the interface would tend to lower the values of interfacial tension obtained. Trace constituents of the reagents used in this study could influence the data by the migration of surface active agents to the interface. Measurements on pure benzene, carbon tetrachloride, and water, the major reagents used in this study, showed a maximum variation of 2 dynes/cm. or about 4% from the literature values. This amount is small in relation to the 10–30 dyne/cm. changes as a result of concentration variations. However, these errors could account for the low values found on some otherwise well defined curves. All curves presented here were drawn by visual estimate of the best fitting of the data points.

RESULTS

System 1. Table I gives the experimental results of interfacial tension measurements between mixtures of benzene with carbon tetrachloride (phase 1) and water (phase 2): These data are plotted in Figure 1. In drawing this plot, consideration was given to the relatively well defined values for pure benzene and pure carbon tetrachloride as given in the literature (*1, 2*).

System 2. In this system, the effect of a solute, methanol, on the interfacial tension between benzene–carbon tetrachloride mixtures and water is studied. Data are presented in Table II. Methanol was originally placed only in the organic phase (phase 1) for the freshly formed interface data. For the equilibrium data, on the other hand, essentially all of the methanol was found to be in the aqueous phase. Methanol appears to be nondistributive in this system.

In most cases, the interfacial tension data are presented at two temperatures. The first is the experimentally measured temperature. The second is 20° C. to provide a common basis for comparison. The data at 20° C. were estimated by correcting the data at other temperatures by the following factors, as given by the International Critical Tables (*1*):

For carbon tetrachloride $(d\gamma_i/dT) = -0.098$ (dynes/cm.)/° C.

For benzene $(d\gamma_i/dT) = -0.058$ (dynes/cm.)/° C.

where γ_i is the interfacial tension and T is the temperature in ° C.

Note that in Figure 2 the interfacial tension appears to vary in a nearly linear fashion with methanol concentration over most of the range. In Figure 3, the interfacial tension is shown as a function of methanol concentration in the aqueous phase. The equilibrium concentration of methanol

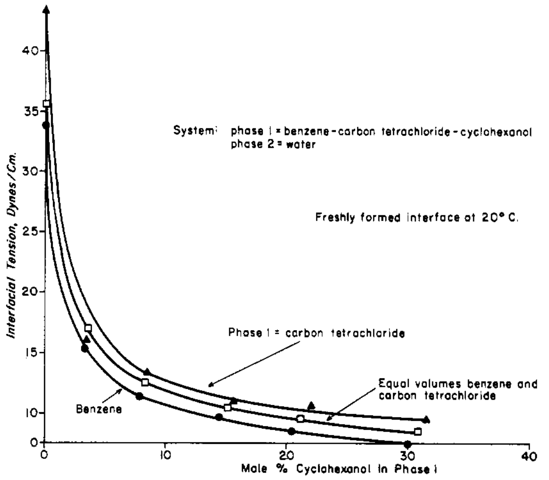

Figure 6. Effect of cyclohexanol on interfacial tension at a freshly formed interface

in the organic phase was negligible for any benzene–carbon tetrachloride mixture.

System 3. Data for this system are also presented in Table II. Temperature corrections to estimate results at 20° C. were applied where necessary. For the interfacial tension data at equilibrium, the concentration of acetone in the organic phase (phase 2) is given. Since acetone is distributive between the phases, giving the concentration of either phase will define the system.

Interfacial tension data for the freshly formed interface is given in Figure 4. The change in interfacial tension per unit change in acetone concentration was greatest at low concentrations of acetone. This suggests that the concentration of this solute at the interface may be higher than in the bulk of the organic phase. It is obvious, however, that there can be no concentration gradient in the organic phase when the interface is freshly formed. What we measure as the tension of the fresh surface must be that occurring at zero-plus time—i.e., after the molecules have had time to orient themselves at the interface but before appreciable amounts of solute have transferred between phases. This maximum effect generally decreases with time to the equilibrium value.

Figure 5 gives the relationship between equilibrium acetone concentration and interfacial tension. Note that the curves for the various benzene–carbon tetrachloride mixtures cross. The explanation for this is found in the ternary phase equilibrium diagrams for the systems benzene-acetone-water and carbon tetrachloride–acetone–water. The tie lines show that in the former system the acetone is distributed preferentially into the organic phase; in the latter, the acetone favors the aqueous phase. Thus for a given organic phase concentration, the amount of solute in the aqueous phase (phase 2), would be expected to be higher in the case of carbon tetrachloride. Interfacial tension, however, should vary in relation to concentration at the interface. Since the pure component interfacial tension is higher for carbon tetrachloride, the lines necessarily must cross.

System 4. Table II also gives experimental results of interfacial tension measurements between mixtures of benzene–carbon tetrachloride and water with cyclohexanol as the solute. The data were again corrected to 20° C. where necessary. The results are presented in Figure 6. A small amount of cyclohexanol has a very great effect on the interfacial tension. Cyclohexanol appears to act as a surface active agent, aggregating in higher concentration at the interface than in the bulk of the liquid. Presumably the cyclohexanol molecules orient themselves at the interface with the hydroxyl group pointing towards the aqueous phase. As the concentration of cyclohexanol is increased, the interfacial tension effect is smaller, since the number of sites at the interface which may be taken by cyclohexanol have been, for the most part, previously filled.

No data were obtained for this system at equilibrium concentration. Since cyclohexanol is only sparingly souble in water, the distribution would be expected to favor the organic phase strongly. Thus the equilibrium interfacial tension data would not differ appreciably from the freshly formed interface data.

CONCLUSION

The above experiments illustrate that interfacial tension in multicomponent, aqueous-organic systems is not easily predicted from the pure component relations. In some systems the decrease in interfacial tension is nearly a linear function of the solute concentration. This behavior is characteristic of the benzene–carbon tetrachloride–methanol–water system. If, however, the methanol is replaced by another solute such as acetone or cyclohexanol, the behavior is different. Particularly in the case of cyclohexanol, interfacial tension lowering per unit change in concentration of solute is greatest at low solute concentrations. Above 20 mole % cyclohexanol, the interfacial tension varies only slightly with further concentration increase. This information may be helpful in explaining some of the unusual behavior often noted at interfaces in the presence of mass transfer and the attendant concentration gradients.

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