Surface Tension of Binary Mixtures of Several Organic Liquids at 25° C.

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The surface tension was determined for the following pairs of organic liquid mixtures over the entire range of concentration by the differential capillary rise method: benzene and ethyl acetate, carbon tetrachloride and ethyl acetate, benzene and carbon bisulfide, carbon tetrachloride and carbon bisulfide, benzene and carbon tetrachloride, and benzene and acetone. The first four pairs showed negative deviation and the last two, positive deviation from the ideal mixture relationship. The density of the first three pairs was also measured. Both surface tension and density were measured at 25° C.

THIS INVESTIGATION was undertaken to obtain values of surface tension and density for several pairs of miscible organic liquids as a function of concentration. Such data, covering the whole concentration range, are currently available for only a few mixtures. No particularly useful interpretation of the data obtained in terms of any existing theory is immediately apparent, so the results are simply presented without any attempt at interpretation.

The surface tension and density were measured on the following pairs: benzene and ethyl acetate, carbon tetrachloride and ethyl acetate, and benzene and carbon bisulfide. The surface tension was measured and the density taken from the literature (*2*, *4*, *5*) on the following pairs: carbon tetrachloride and carbon bisulfide, benzene and carbon tetrachloride, and benzene and acetone.

EXPERIMENTAL

Materials. Benzene, carbon tetrachloride, and acetone were spectro grade from Eastman. Carbon bisulfide and ethyl acetate were Baker Analyzed Reagent. No further purification of these samples was considered necessary. The water used was prepared daily from once-distilled water by redistillation in an all-quartz still, the middle fraction being retained.

Surface Tension. The method chosen was that of measuring the rise of liquids in capillary tubes. To minimize several experimental problems, the difference, Δh, in the heights to which a liquid rises in two capillary tubes of different radii, r_1 and r_2, was measured (*3*). The two capillaries were mounted so that both could be seen in the field of view of a cathetometer.

The capillaries were placed in a circular cylinder, 2 inches in diameter and 8 inches in depth. They were then mounted in a constant-temperature bath, which was provided with a proportional temperature control, with its resistance element placed near the cylinder containing the capillary tubes. The temperature of this bath was maintained at 25.000 ±0.005° C., as determined with a Beckman differential thermometer that had been calibrated against a platinum resistance thermometer. The capillaries were adjusted for each measurement to bring the menisci to the same position in each capillary. This eliminated errors due to small irregularities in the radii. When a surface is exposed to air, it gradually becomes contaminated, and its properties change. To avoid this error, the solution was forced up into the capillary to obtain a clean fresh surface for each determination; time was then allowed for the system to come to equilibrium.

Densities were determined with a pair of 20-ml. pycnometers, calibrated with water, mercury, and benzene to one part in 10,000.

Fifty milliliters of each solution was prepared volumetrically by delivering the appropriate volume of each pure liquid into the cylinder from buretes with manufacturer's certification to 0.1 ml. at room temperature. Thus, the composition of the mixtures was known with an uncertainty of between 1 and 2%. The cylinder was then positioned in the constant-temperature bath, the capillaries were adjusted, and 20 minutes allowed for the system to reach thermal equilibrium. After determining the surface tension, this same mixture was used for the density determination.

Lines were etched at approximately 1-inch intervals on each of two 9-inch-long capillaries. The distance between each pair of lines was measured to ±0.001 cm. with a cathetometer. The volume of the capillary between each pair of lines was determined to ±0.0002 ml. by filling with distilled water from a precision microsyringe in a water bath controlled to ±0.001° C. This measurement was made by the Mass and Volume Section of the National Bureau of Standards. Between the lines used on capillary No. 1, the volume was 0.0106 ml.; on capillary No. 2, 0.0219 ml. The respective distances were 2.528 and 2.549 cm. Thus, the average radii in the intervals used were:

Capillary No. 1: 0.0365 ± 0.0004 cm.
Capillary No. 2: 0.0523 ± 0.0003 cm.

The height of a liquid, h, in a capillary of radius r above the level in a large reservoir is (*1*)

$$h = \frac{2\gamma}{gr\rho} - r/3 \tag{1}$$

where γ is the surface tension; g, the acceleration of gravity; and ρ, the density of the liquid; h is measured to the bottom of the meniscus, and the liquid-air interface is assumed spherical. The density of the mixture vapor surrounding the capillary is about 0.1% of ρ and is ignored. Thus, from the difference in heights $\Delta h = h_1 - h_2$ in two capillaries of radii r_1 and r_2, the surface tension is given by

$$\gamma = \left[\Delta h - \frac{\Delta r}{3}\right] \frac{g\rho}{2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)} \tag{2}$$

where

$$\Delta r = r_2 - r_1$$

and $g = 980.1$ cm./sec.^{2}

The constants in Equation 2 using the values of r_1 and r_2 measured volumetrically are: $\Delta r/3 = 0.0053$ cm. and $(1/r_1 - 1/r_2) = 8.293$ cm.$^{-1}$ A check on the accuracy of these constants and the adequacy of the various assumptions involved in the derivation of Equation 1 was made by plotting Δh *vs.* $2\gamma/g\rho$ for pure liquids, using values of γ and ρ obtained from Timmermans (*4, 5*). A least squares fit gives an intercept of 0.0054 ± 0.002 cm. and a slope of 8.283 ± 0.002 cm.$^{-1}$, as shown in Figure 1.

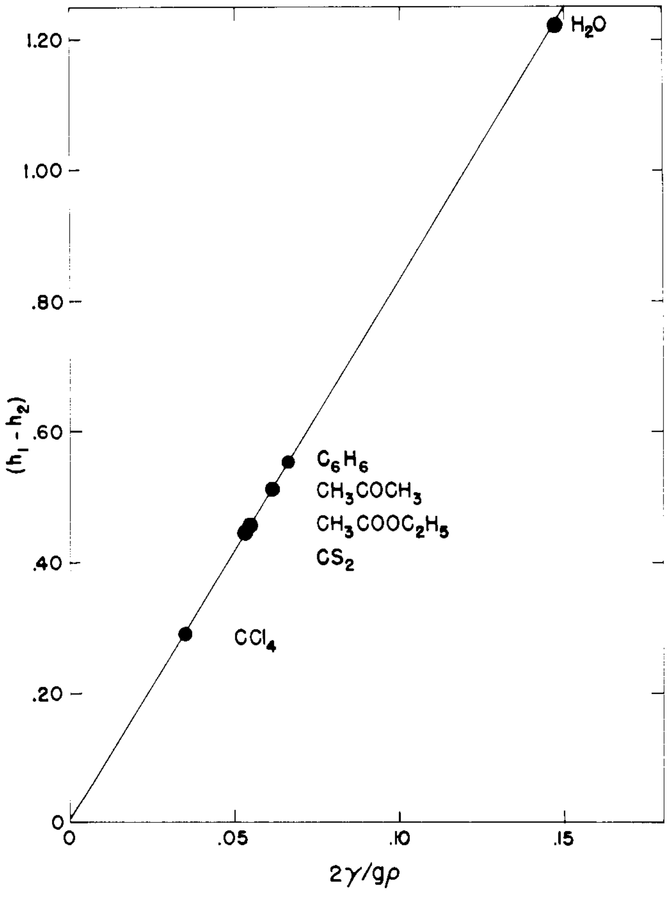

Figure 1. Height difference of pure organic liquids ($h_1 - h_2$) plotted against $2\gamma/g\rho$. The slope is equal to $(1/r_1 - 1/r_2)$ and the intercept, $1/3(r_2 - r_1)$

Table I. Surface Tension and Density for Pure Liquids

Sample	Density,[a] ρ, G./Cm.^{3}	Surface Tension,[a] γ, (Newtons/Meter) × 10^3 or Dynes/Cm.
H_2O	0.99708	71.97
C_6H_6	0.8733	28.34
CH_3COCH_3	0.7850	23.52
$CH_3COOC_2H_5$	0.8947	23.82
CS_2	1.2558	32.75
CCl_4	1.5847	26.86

[a] Ref. (*4, 5*).

Table II. Experimental Values of Density and Surface Tension for Mixtures of Ethyl Acetate with Benzene, and with Carbon Tetrachloride at 25.0° C.

	Benzene		Carbon Tetrachloride	
Mole Fraction of Ethyl Acetate	Density, ρ, g./cm.^{3}	Surface tension, γ, (newtons/meter) × 10^3 or dynes/cm.	Density, ρ, g./cm.^{3}	Surface tension, γ, (newtons/meter) × 10^3 or dynes/cm.
0.00	0.8947	23.8	0.8947	23.8
0.10	...	...	0.9617	23.6
0.11	0.8920	24.2	...	...
0.20	...	...	1.0317	24.6
0.22	0.8894	24.5	...	...
0.30	...	...	1.1004	24.3
0.32	0.8868	24.8	...	...
0.40	...	...	1.1696	24.9
0.42	0.8848	25.3	...	...
0.50	...	...	1.2387	25.0
0.52	0.8824	25.7	...	...
0.60	...	...	1.3072	25.7
0.62	0.8803	26.2	...	...
0.70	...	...	1.3770	25.9
0.72	0.8783	26.9	...	...
0.80	...	...	1.4461	26.4
0.82	0.8764	26.5	...	...
0.90	...	...	1.5156	26.8
0.91	0.8747	27.8	...	...
1.00	0.8733	28.3	1.5847	26.8

The difference between the value of $(1/r_1 - 1/r_2)$ calculated from the measured dimensions and the slope of the curve in Figure 1 is 0.12%. The intercept differs by 2% from the calculated value of $\Delta r/3$, a negligible difference, since this term contributes less than 2% to values of γ reported here.

RESULTS

The values of density (measured during this work, unless a literature reference is shown) and measured values of surface tension are given in Tables I, II, III, and IV. The Δh values used for the calculation of surface tension were the averages of nine independent observations on a single mixture. An independent observation consisted in forcing the menisci up into the two capillaries to slightly above their equilibrium positions, and reading Δh after they had again reached equilibrium. In all cases, the individual observations of Δh differed by no more than ±0.5% from their mean value. Since, as is evident from Figure 1, Δh is very nearly proportional to γ/ρ, and since the densities are known with an uncertainty of about ±0.01%, this figure of ±0.5% also represents the reproducibility of the present measurements of γ. This figure may also be used as an

Table III. Experimental Values of Surface Tension for Mixtures of Carbon Bisulfide with Carbon Tetrachloride, and with Benzene at 25.0° C.

	Carbon Tetrachloride		Benzene	
Mole Fraction of Carbon Bisulfide	Density,[a] ρ, g./cm.^{3}	Surface tension, γ, (newtons/meter) × 10^3 or dynes/cm.	Density, ρ, g./cm.^{3}	Surface tension, γ, (newtons/meter) × 10^3 or dynes/cm.
0.00	1.5847	26.8	0.8733	28.3
0.14	...	...	0.9076	28.7
0.15	1.5450	27.2	...	...
0.27	...	...	0.9438	28.4
0.29	1.5110	27.6	...	...
0.39	...	...	0.9817	28.6
0.41	1.4772	28.1	...	...
0.49	...	...	1.0176	28.9
0.52	1.4430	28.3	...	...
0.60	...	...	1.0638	29.7
0.62	1.4118	28.6	...	...
0.69	...	...	1.0957	29.9
0.71	1.3783	29.0	...	...
0.78	...	...	1.1346	29.9
0.79	1.3452	29.9	...	...
0.86	1.3150	30.7	1.1688	30.3
0.93	...	...	1.2134	31.4
0.94	1.2840	31.2	...	...
1.00	1.2558	32.7	1.2558	32.7

[a] Ref. (*5*).

Table IV. Experimental Values of Surface Tension for Mixtures of Benzene with Carbon Tetrachloride, and with Acetone at 25.0° C.

	Carbon Tetrachloride		Acetone	
Mole Fraction of Benzene	Density,[a] ρ, g./cm.^{3}	Surface tension, γ, (newtons/meter) × 10^3 or dynes/cm.	Density,[b] ρ, g./cm.^{3}	Surface tension, γ, (newtons/meter) × 10^3 or dynes/cm.
0.00	1.5847	26.8	0.7850	23.5
0.08	...	...	0.7944	24.0
0.11	1.5125	27.0	...	...
0.21	1.4425	27.1	...	...
0.26	...	...	0.8123	24.7
0.32	1.3685	27.3	...	...
0.36	...	...	0.8218	25.6
0.42	1.3000	27.3	...	...
0.45	...	...	0.8308	25.6
0.50	...	...	0.8353	26.2
0.52	1.2300	27.5	...	...
0.62	1.1580	27.9	...	...
0.66	...	...	0.8491	27.0
0.72	1.0875	27.8	...	...
0.77	...	...	0.8576	27.6
0.81	1.0175	28.5	...	...
0.88	...	...	0.8655	28.0
0.91	0.9440	28.6	...	...
1.00	0.8733	28.3	0.8733	28.3

[a] Ref. (*2*). [b] Ref. (*4*).

estimate of the accuracy of these surface tension determinations of the mixtures because of the close agreement between the instrument constant calculated from the radii of the capillaries and that calculated from measurements on the pure components.

Measured values of Δh and density (ρ) were plotted against concentration and smoothed curves drawn. The values for the surface tension in increments of 0.05 mole, shown in Table V, were calculated using values of Δh read from these curves. For two pairs of mixtures, benzene and carbon tetrachloride and benzene and acetone, the plot of surface tension *vs.* composition lies above a straight line through the values for the pure components. In the other mixtures measured, the curve is below the straight line between the two pure components.

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Table V. Surface Tension: Smoothed Data

Mole Fraction of Component 2	C_6H_6 and $CH_3COOC_2H_5$	CCl_4 and $CH_3COOC_2H_5$	CS_2 and C_6H_6	CS_2 and CCl_4	C_6H_6 and CCl_4	C_6H_6 and CH_3COCH_3
0.00	28.3	26.9	32.8	32.8	28.3	28.4
0.05	28.1	26.7	31.8	31.9	28.5	28.3
0.10	27.9	26.6	31.1	31.2	28.5	28.1
0.15	27.6	26.4	30.5	30.6	28.5	28.0
0.20	27.3	26.2	30.1	30.0	28.4	27.8
0.25	27.0	26.1	29.9	29.5	28.3	27.6
0.30	26.7	25.9	29.7	29.1	28.2	27.3
0.35	26.4	25.8	29.5	28.8	28.0	27.0
0.40	26.1	25.6	29.3	28.6	27.8	26.7
0.45	25.9	25.4	29.1	28.5	27.7	26.4
0.50	25.6	25.3	29.0	28.4	27.6	26.1
0.55	25.3	25.1	28.8	28.1	27.5	25.8
0.60	25.2	24.9	28.7	28.0	27.4	25.5
0.65	25.0	24.7	28.6	27.8	27.4	25.4
0.70	24.8	24.5	28.6	27.8	27.2	25.0
0.75	24.6	24.2	28.5	27.6	27.2	24.8
0.80	24.5	24.0	28.4	27.4	27.2	24.5
0.85	24.3	23.8	28.4	27.3	27.1	24.3
0.90	24.1	23.7	28.3	27.1	27.1	24.0
0.95	24.0	23.7	28.3	27.0	27.0	23.8
1.00	23.8	23.8	28.3	26.8	26.9	23.5

NOMENCLATURE

g = acceleration due to gravity, 980.1 cm. per sec.^{2}
h = capillary height, cm.
r = capillary radius, cm.
γ = surface tension, dynes per cm. or (newton per meter) $\times 10^3$
ρ = density of the liquid, grams per cm.^{2}
Δ = difference of two quantities

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Salting Effects in Several Alcohol-Electrolyte-Water Systems

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Salting effects of sodium sulfate, potassium fluoride, potassium chloride, sodium perchlorate, and perchloric acid on cyclohexanol, 1-pentanol, and 1-butanol were determined by measuring the solubilities of the alcohols in the various electrolyte solutions. Solubilities were determined by color development and spectrophotometry. The relevant Setschenow parameters are reported. There was no apparent correlation between the salting effect and the dipole moment of the alcohol.

DATA on the salting effect of various electrolytes on several alcohols in aqueous solution were obtained during studies of the competitive adsorption of alcohols and salts at the dropping mercury electrode. To make meaningful comparisons, the activity coefficients of the alcohols were calculated from the solubilities of each alcohol in the various electrolyte solutions used. Since these data could be of use in other investigations, they are separately reported here together with details of the method used, which appears to be applicable to the range of alcohols.

"Salting effect" refers to the increase or decrease in the activity coefficient of the dissolved alcohol in the presence of a salt; an increased coefficient corresponds to salting out, a decreased coefficient in salting in. The activity coefficients are related to the solubilities of the alcohol by

$$fS = f^\circ S^\circ \tag{1}$$

where S° and S are the solubilities of the alcohol in pure water and in the salt solution, respectively, and f° and f are the corresponding activity coefficients. Taking the activity coefficient in pure water as unity, one obtains

$$f = S^\circ / S \tag{2}$$

Strictly speaking, the activity coefficient so defined refers only to a saturated solution of the alcohol. However, the variation of the activity coefficient of a nonelectrolyte with changing concentration of the nonelectrolyte is small compared to the salting effect, and consequently we refer to the coefficient defined by Equation 2 as "the" activity coefficient of the alcohol in the relevant salt solution.

Solubility determinations and calculations according to Equation 2 were performed for 1-butanol, 1-pentanol, and cyclohexanol in solutions of potassium fluoride, potassium chloride, sodium sulfate, sodium perchlorate, and perchloric acid; the concentrations of the electrolytes ranged from 0.1 to 1.4M. Previous workers have generally found that the logarithm of the activity coefficient of the nonelectrolyte is a linear function of the electrolyte concentration—i.e.,

$$\log f = KC_s \tag{3}$$

where C_s is the electrolyte concentration in moles per liter of solution and K, the Setschenow parameter, is a constant for a given alcohol and a given electrolyte. We found this relationship to hold for all systems studied. Values of the Setschenow parameters obtained are shown in Table I.

The salting effect of a given electrolyte is essentially the same toward 1-pentanol and cyclohexanol, except perhaps in perchlorate solutions, whereas there is an appreciable difference with 1-butanol. The molar solubilities of the alcohols in distilled water are: 1-pentanol, 0.243; cyclohexanol, 0.389; 1-butanol, 1.01.

Nonpolar nonelectrolytes have been used in recent studies of salting-out—and, more rarely, salting-in—effects. Examples are benzene (*5*) and hydrogen (*6*). However, dipole moments and salting effects observed in potassium chloride solutions have been compared; it seemed that the

Table I. Setschenow Parameters for Several Alcohols in Aqueous Electrolytes

(24.5° ± 0.5° C.)

Electrolyte in Solution[a]	Alcohol 1-Pentanol	 Cyclohexanol	 1-Butanol
Na_2SO_4	0.610[b]	0.596[b]	0.561
KF	0.301	0.319[b]	0.287
KCl	0.215	0.222	0.178
$NaClO_4$	0.14[c]	0.125[c]	0.084
$HClO_4$	−0.096[c]	−0.033[c]	−0.153

[a] Three concentrations of electrolyte used, except where otherwise indicated. [b] Four concentrations. [c] One concentration.