

Figure 1. Temperature dependence of solubility of cuprous chloride.

is highly reactive in the presence of oxygen to form soluble cupric salts.

Results and Discussion

Solubilities of cuprous chloride in water and HCl solutions were determined at 20, 29, 40, and 50 °C. The concentration of HCl was varied from 0.129 to 0.603 g-mol/L. The data are presented in Table I. An experimental error in the solubility values estimated by repeating a single experiment three to four times was found to be less than 5%.

Various empirical equations were used to correlate the data and to obtain a relationship between solubility, temperature, and

Table II. Results of Regression Analysis

parameter	value
a	2.2265
b	-2.3480×10^3
c	1.0486
d	15.0
ΔH	4.696 kcal/g-mol
stand dev, σ	1.1513×10^{-3}

concentration of HCl. The following equation was found to represent the data most satisfactorily:

$$\ln S = a + b/T + c \ln(1 + dX) \quad (1)$$

where S and X are respectively solubility of cuprous chloride and concentration of HCl in g-mol/L, T is temperature in K, and a , b , c , and d are constants.

In order to obtain the best fit, regression analysis was carried out. The values of the constants a , b , c , and d and the temperature-dependent heat of solution, ΔH , are given in Table II. The solubility values estimated from eq 1, using the constants in Table II, and the experimental data agree within 2–5%. The Arrhenius type of temperature dependence of solubility is also evident from Figure 1, which is a plot of $\ln S$ vs. $1/T$.

Glossary

$a, b, c,$	constants in eq 1
d	
ΔH	temperature-dependent heat of solution, kcal/g-mol
S	solubility of cuprous chloride, g-mol/L
T	temperature, K
X	concentration of hydrochloric acid, g-mol/L
σ	standard deviation

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Surface and Interfacial Tensions of Conjugate Solutions in Ternary Systems

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A high-precision apparatus was constructed to measure surface and interfacial tensions of liquids by the pendent-drop technique. The method as used in this work requires control of temperature, photographic recording of the drop, precise measurement of dimensions, and the use of a computer to determine the surface tensions from the data input. The surface and interfacial tensions of conjugate solutions of compositions located in the isothermal miscibility gap of two ternary systems were measured. The systems investigated were benzene–water–ethanol and *n*-hexane–water–ethanol at 20.0 °C.

Knowledge of wetting and spreading is important to engineers in the design of liquid–liquid contact operations wherever matter passes across an interface. For this purpose not merely the interfacial tension but also the surface tensions of the two fluids are required. Such information is recorded for few ternary systems (1–4). Brun (1–3) measured the surface and interfacial tensions of conjugate phases in the water–3-methyl-1-butanol–ethanol system by the method of rising drops; he found that the surface tensions of the conjugate phases approach each other and become equal at the plait point and that the interfacial tension falls to zero at the same point (as would be expected). Murphy, Lastovica, and Fallis (4) report surface and interfacial tensions determined by the ring method for several ternary

Table I. Physical Properties of Purified Liquids

	density at 20.0 °C, g/cm ³		bp at 1 atm, °C		refractive index, n_D^{20}		surface tension at 20.0 °C, mN/m	
	obsd	lit.	obsd	lit.	obsd	lit.	obsd	lit.
water	0.9982	0.9982 ^a	99.9–100.0	100.0 ^a	1.3330	1.33299 ^a	73.06	72.88 ^b
ethanol	0.7895	0.7893 ^a	77.9–78.1	78.5 ^a	1.3612	1.3611 ^a	22.20	22.39 ^b
benzene	0.8792	0.879 ^c	79.6–79.8	80.1 ^a	1.5011	1.5011 ^a	29.27	28.88 ^b
<i>n</i> -hexane	0.6595	0.65937 ^a	68.4–68.5	68.7 ^c	1.3749	1.37486 ^a	18.1 ^d	18.40 ^b

^a "CRC Handbook of Chemistry and Physics", 48th ed., R. C. Weast and S. M. Selby, Ed., Chemical Rubber Co., Cleveland, Ohio, 1967. ^b J. J. Jasper, *J. Phys. Chem. Ref. Data*, 1, 841–1009 (1972). ^c "Lange's Handbook of Chemistry", 11th ed., J. A. Dean, Ed., McGraw-Hill, New York, 1973. ^d Measured by the ring method (other observed surface tensions measured by the pendent-drop method).

systems (but not those examined in the present work) and attempt to correlate these tensions with cosolvent concentrations along a line joining the plait point to the vertex representing pure cosolvent by an empirically determined equation. Several other workers (5–7) report interfacial (but not surface) tensions measured in ternary systems by the ring method. The systems studied in the present work, however, are not included. These are benzene–water–ethanol and *n*-hexane–water–ethanol at 20.0 °C.

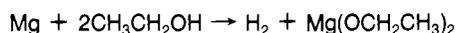
Franks and Ives (8) measured the effect of low concentrations of ethanol on the interfacial tension between water and hexane (a mixture of isomers) by the drop–volume method at 25 °C and other temperatures; their results cannot be compared with those obtained here for several reasons: the temperatures are different, the hexane they used was impure, and the highest concentration of ethanol used in their study was only about 0.1 M. No other data on surface or interfacial tensions in the *n*-hexane–water–ethanol system are known to us.

Other data are available on the interfacial tension between conjugate phases in the benzene–water–ethanol system, but only at 25 °C. Bartell and Davis (9) studied this system using the pendent-drop method and report an interfacial tension as low as 8.9 mN/m. Sada, Kito, and Yamashita (10) studied this system using the capillary-rise method and report an interfacial tension as low as 0.04 mN/m; they had difficulty in measuring so small a tension with this method, and their data do not agree well with those of Bartell and Davis even though both were determined at the same temperature. Neither group of workers reports surface tensions of the conjugate phases. Sada et al. (10) maintain that interfacial tensions decrease exponentially with increasing cosolvent (ethanol) concentration, but the data obtained in the present study do not verify that relation.

Materials

The materials used were reagent-grade chemicals, further purified by standard procedures. Benzene was passed through a column of activated alumina into a bottle containing small sodium spheres. After enough time was allowed for the sodium to remove any traces of water present, the benzene was fractionally distilled in an all-glass still with greaseless ground-glass joints. The first and last portions of the distillate were discarded. *n*-Hexane was purified in a similar manner; the treatment with sodium to remove water was not required.

Absolute ethanol from commercial sources typically contains about 0.5% water, but since water was added anyway to the ethanol used to prepare various mixtures in the three-component systems, no effort was made to remove the small quantity of water initially present. Ethanol used alone, however, for density and surface tension determinations was treated to remove residual water as follows (11):



The reaction proceeds readily provided the magnesium is ac-

tivated with iodine. The dried ethanol was fractionally distilled into a receiver protected by a drying tube.

Water obtained from a central still was redistilled from basic permanganate; the distillate was acidified with phosphoric acid and distilled a third time. Distillations were carried out under a nitrogen atmosphere.

Glassware was rinsed with hot ethanolic potassium hydroxide solution to remove traces of grease, followed by copious rinsing with distilled water, and then was allowed to drain on clean filter paper. Liquids were stored in glass flasks with tightly fitting ground-glass stoppers; benzene and ethanol flasks were kept in a desiccator.

Some physical properties of the purified liquids are reported in Table I.

Preparation of Solutions

Compositions of conjugate solutions at the end points of eight tie lines in each of the two systems benzene–water–ethanol (12) and *n*-hexane–water–ethanol (13) at 20 °C were taken from the literature. Solutions of composition corresponding to the midpoint of each tie line were prepared by weighing the liquids into clean tared flasks with tightly fitting ground-glass stoppers; 90 g of solution was prepared for each tie line. The precision of weighing always exceeds the reported precision of the composition. The solutions were shaken several times during the minimum of 24 h allowed for equilibration in a constant-temperature bath at 20.0 ± 0.05 °C. The time allowed was extended to several days for compositions containing cosolvent.

Experimental Section

Surface and interfacial tensions were measured by the pendent-drop method of Patterson and Ross, which is fully described elsewhere (14). In this method the drop was suspended from a syringe needle, which had been ground flat and inserted into a sample cell containing air or, in the case of measuring interfacial tensions, another liquid. The sample cell was surrounded by a jacket through which was circulated water from a constant-temperature bath. All measurements were made with the conjugate phases in equilibrium. The drop was illuminated by rays of light that were essentially parallel to the optical axis; it was placed between the light source and the camera lens so that a silhouette was obtained. A photomicrographic camera lens of relatively long focal length provided a long working distance with a minimum of distortion at high magnifications. The distance between the camera lens and the film was fixed so that the magnification of the system was constant (14.3 diameters in this case). Polaroid Type 55 film was used since it gives a dimensionally stable negative of 4 × 5 in., which is developed in only 20 s. The entire apparatus was housed in a subbasement room known to be relatively free of vibrations and was mounted on a vibration-isolation platform to reduce still further the already-small vibrations. The exact magnification of each negative was determined from the image of a precision ball bearing of known diameter placed on the

Table II. Compositions, Densities, and Surface and Interfacial Tensions in the System Benzene (1)–Water (2)–Ethanol (3) at 20.0 °C^a

tie line no.	aqueous phase			organic phase			interfacial tension, mN/m		
	compn, wt fraction (1)	compn, wt fraction (3)	density, g/cm ³	surface tension, mN/m	compn, wt fraction (1)	compn, wt fraction (3)		density, g/cm ³	surface tension, mN/m
0	0.000	0.000	0.9980	62.15	1.000	0.000	0.8792	28.69	34.08
1	0.002	0.148	0.9756	41.93	0.992	0.007	0.8781	28.02	15.90
2	0.006	0.280	0.9572	32.30	0.973	0.025	0.8764	28.53	7.03
3	0.014	0.368	0.9403	28.31	0.949	0.047	0.8747	28.55	3.76
4	0.036	0.446	0.9201	27.12	0.920	0.073	0.8712	28.58	2.06
5	0.095	0.504	0.8977	26.34	0.882	0.107	0.8695	28.02	0.94
6	0.211	0.526	0.8713	26.00	0.806	0.174	0.8650	26.52	0.230
7	0.276	0.510	0.8652	26.15	0.764	0.206	0.8631	26.00	0.100
8	0.368	0.470	0.8608	26.28	0.675	0.272	0.8603	25.80	0.0092

^a Composition at the plait point: 0.517 (1), 0.100 (2), 0.383 (3) [weight fractions]. Source of plait point data: Seidell, A., Linke, W., "Solubilities of Inorganic and Organic Compounds", Supplement to the 3rd ed., D. Van Nostrand, New York, 1952, p 921.

corner of the film. The image of a vertical reference line was also placed on the film. The dimensions of the image of the drop were measured using a high-precision x–y comparator capable of measuring distances as small as 1 μm . At least ten coordinate pairs were measured along the profile of each drop image and were used as input to a computer program that obtained the best curve-fit of a theoretical profile to the experimental points. The interfacial tension was calculated from the density difference between the conjugate phases, the local acceleration of gravity, and the parameters of the best theoretical curve through the experimental points. The accuracy of the measurements of interfacial tension was estimated to be better than 0.35%.

The Westphal balance (15) was used to determine densities, using a thermostatic receptacle for the liquid and making appropriate corrections for air buoyancy. A gravimetric balance accurate to 0.0001 g was adapted for these measurements. Temperature was maintained at 20.0 ± 0.05 °C.

One noteworthy difficulty occurred with the *n*-hexane–water–ethanol system. The hexane-rich phase, because of its very low surface tension, invariably spreads on the Teflon-coated syringe needle. This problem does not arise when the phase surrounding the pendent drop is liquid instead of vapor, even when the measured tension is still lower, because the attractive forces of a surrounding liquid compete more successfully with the drop for attachment to the needle than those of a vapor. When the sample cell is filled with vapor and the hexane-rich drop is first formed, the drop could not be made to hang from the tip of the needle long enough to be photographed; it climbed up the needle. Measurements taken from photographs of such drops, attached to the needle above the tip, gave erroneous values of surface tension. The ring method was therefore used to measure the surface tension of the hexane-rich phase for each of the tie lines in that system. The ring method was also used to measure the surface tension of the water-rich phase for the tie line closest to the plait point in this system; drops of that phase also spread on the syringe needle because of their low surface tension.

A Cenco-du Noüy interfacial tensiometer was used with a platinum–iridium ring having a 5.992 cm circumference. The ratio of the radius of the ring to the radius of the wire from which the ring is made is 53.6. The liquid was contained in a jacketed beaker through which water at 20.0 ± 0.05 °C was pumped from a constant-temperature bath. The data so obtained were corrected by the equation of Zuidema and Waters (16) to give the true surface tension. The instrument has a precision of 0.1 mN/m within the range of surface tensions measured in this study.

The ring method has also been used in this laboratory to measure interfacial tensions in the benzene–water–ethanol system. The method was found to be highly inaccurate for interfacial tensions less than about 2 mN/m, when compared

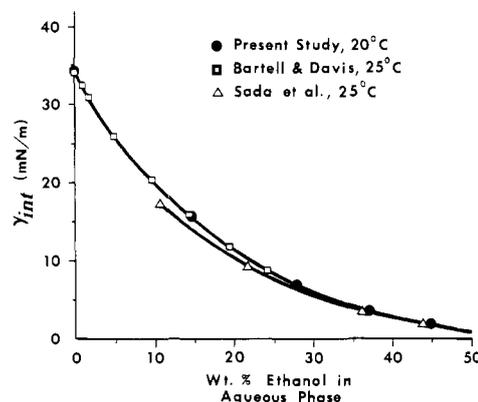


Figure 1. Interfacial tensions in the system benzene–water–ethanol at 20 °C—present study compared with published results of other workers.

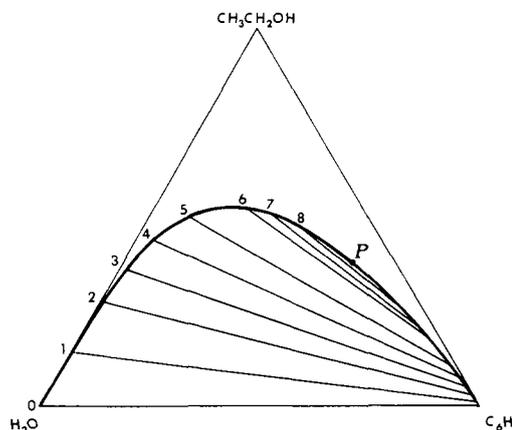


Figure 2. Phase diagram for benzene–water–ethanol at 20 °C.

with the pendent-drop method. A more complete discussion of the choice of method for the measurement of interfacial tension is given elsewhere (17).

Results and Discussion

In Figure 1 the results obtained in this work are compared with those already on record (9, 10) for the benzene–water–ethanol system. The agreement between the interfacial tensions obtained by Bartell and Davis at 25 °C and those obtained here at 20 °C (both with the pendent-drop method) is remarkable, considering the temperature difference; but the phase diagrams for this system at 20 °C (12) and at 25 °C (18) are nearly identical.

Phase diagrams for the two systems are shown in Figures 2 and 3. The eight tie lines chosen for study in each system are numbered on the diagrams; tie line "0" is located at the base

Table III. Compositions, Densities, and Surface and Interfacial Tensions in the System *n*-Hexane (1)-Water (2)-Ethanol (3) at 20.0 °C^a

tie line no.	aqueous phase			organic phase					
	compn, wt fraction (1)	compn, wt fraction (3)	density, g/cm ³	surface tension, mN/m	compn, wt fraction (1)	compn, wt fraction (3)	density, g/cm ³	surface tension, mN/m	interfacial tension, mN/m
0	0.000	0.000	0.9982	66.32	1.000	0.000	0.6595	18.1	49.75
1	0.000	0.232	0.9640	37.11	0.997	0.003	0.6595	18.5	14.70
2	0.001	0.325	0.9490	31.50	0.995	0.005	0.6595	18.5	9.82
3	0.002	0.383	0.9382	30.18	0.994	0.006	0.6599	18.5	7.83
4	0.003	0.440	0.9263	28.14	0.992	0.008	0.6601	18.4	6.67
5	0.006	0.518	0.9085	27.93	0.988	0.012	0.6600	18.5	5.26
6	0.020	0.612	0.8924	26.68	0.980	0.020	0.6610	18.7	3.82
7	0.082	0.730	0.8286	23.74	0.939	0.060	0.6635	18.8	1.50
8	0.300	0.640	0.7521	18.9	0.862	0.132	0.6787	18.7	0.096

^a Composition at the plait point was not found.

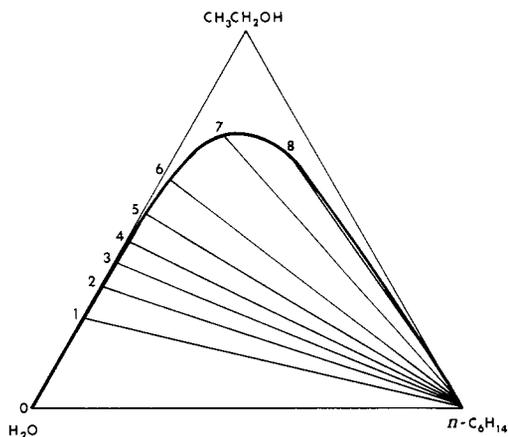


Figure 3. Phase diagram for *n*-hexane-water-ethanol at 20 °C.

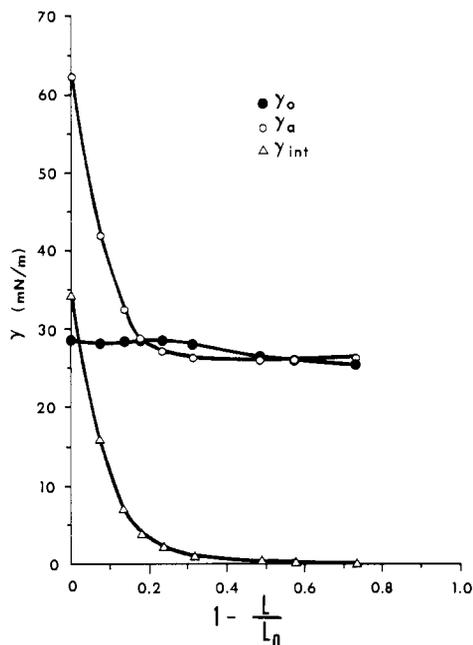


Figure 4. Variation of surface and interfacial tensions with a function of tie line length in the system benzene-water-ethanol at 20 °C. γ_o is the surface tension of the organic phase, γ_a is the surface tension of the aqueous phase, and γ_{int} is the interfacial tension between the two phases.

of each diagram (i.e., no added ethanol).

Tables II and III report the compositions of the conjugate phases, their densities, and their surface tensions, as well as the interfacial tension between them. The surface tensions reported to only one decimal place in Table III were measured by the ring method rather than by the pendent-drop method for the reasons previously mentioned.

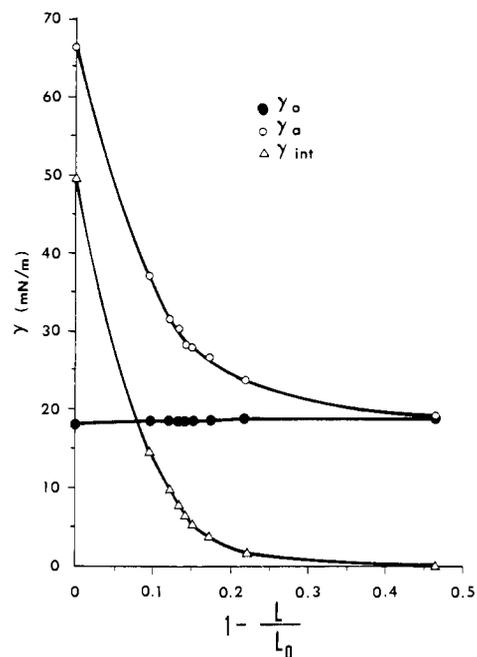


Figure 5. Variation of surface and interfacial tensions with a function of tie line length in the system *n*-hexane-water-ethanol at 20 °C. γ_o is the surface tension of the organic phase, γ_a is the surface tension of the aqueous phase, and γ_{int} is the interfacial tension between the two phases.

The surface and interfacial tensions are presented graphically in Figures 4 and 5. The abscissas in these diagrams are a function of the length of each tie line, L ; L_0 is defined as the length of the longest tie line, which in these systems is practically the distance between the vertices of the triangle. The function $1 - (L/L_0)$ equals zero when no ethanol is present and equals unity at the plait point. These diagrams show that at compositions of conjugates near the plait point, the interfacial tension is always closer to zero than is the difference between the surface tensions, a result also obtained by Brun (1, 3) for another ternary system. In this respect the ternary systems are seen to be analogous to binary systems in which temperature takes the place of concentration of cosolvent (19).

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Solubility of Toluene in Aqueous Sodium Alkylbenzenesulfonate Solutions

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The solubility of toluene in aqueous solutions of nine substituted sodium benzenesulfonates with short side chains was determined at 25 and 55 °C using gas chromatography for the analysis of the saturated solutions. Tenax GC, which is used mostly for the separation of high boiling polar compounds, was found suitable for the analysis of aqueous solutions of toluene, a nonpolar, lower boiling compound. The solubility of toluene generally increases with sulfonate concentration except for the lowest members of the series (benzene- and toluenesulfonate) where a slight decrease in solubility (salting out) occurs at low concentrations. Toluene solubility in the aqueous phase generally increases with the number of alkyl carbons on the benzene ring. The compound with the largest number of alkyl carbons studied here (2,5-diisopropylbenzenesulfonate) shows a very high toluene solubility (ca. 1 mol of toluene/mol of sulfonate in 2.5 *m* sulfonate); its hydrotropic properties thus seem very much larger than of sodium *p*-cymenesulfonate, frequently cited as the best hydrotropic material available.

Introduction

The micellar flood process for enhanced oil recovery, which has been widely tested in laboratories and the field in recent years, involves very complex phenomena. To help understand some of the phenomena, a study seemed desirable of simpler systems which contain a hydrocarbon and a model surfactant, which does not form micelles. For this purpose we selected toluene and aqueous solutions of benzenesulfonates with short aliphatic side chains, since sulfonates with long side chains are commonly used in the micellar flood process. By such a study we hoped to help separate the effect of micelles on dispersion of the hydrocarbon from simple solubility effects.

The sodium salts of benzenesulfonates with short side chains, especially those of xylene and cymene (methylisopropylbenzene), are well-known as hydrotropic salts (or salting-in agent) suggested for use in wood pulp and other industries.¹⁻⁴ Aqueous solutions of hydrotropic salts can dissolve substances normally slightly soluble in water. Solubility of benzene and other organic substances in aqueous solutions of benzenesulfonates has been determined by a residue-volume method,⁵ volume change measurements,⁶⁻⁸ and evaporation-weight methods.⁹ There are several difficulties involved in these methods, especially the need

for large sample size and the problem of accurately reading volume changes. We have chosen a gas chromatographic method by which the solubility of toluene (and of other hydrocarbons) in aqueous solutions can rapidly and conveniently be determined.

Experimental Section

Materials. Toluene (certified ACS grade, Fisher Scientific Co.) and acetone (analytical reagent, Mallinckrodt) were used as received without further purification. Sodium benzenesulfonate, toluenesulfonic acid monohydrate, and 2,4,6-trimethylbenzenesulfonic acid were obtained from Fluka A. G. and the acids were converted to the sodium salt by neutralization with 10% NaOH. Sodium 2,4-dimethylbenzenesulfonate (Eastman) was recrystallized twice from acetone-water. The other substituted sodium benzenesulfonates used were synthesized as described below. The microanalysis of each synthetic compound was done by Galbraith Laboratories, Inc., Knoxville, Tenn. NMR spectra (proton and carbon-13) were obtained on a Varian FT80 by L. L. Brown of the Oak Ridge National Laboratory, Chemistry Division. The aqueous solutions were prepared by weight with distilled water, and concentrations are expressed as molality (mol/kg of water).

Preparation of Substituted Sodium Benzenesulfonates. (a) Sodium *p*-Ethylbenzenesulfonate.¹⁰ To a mixture of 1.5 mol of ethylbenzene (Matheson Coleman and Bell, bp 134-136 °C) and 1.2 mol of thionyl chloride (Fisher Scientific Co.), 1.0 mol of concentrated H₂SO₄ was added slowly at room temperature with stirring. The stirring was continued overnight. The reaction mixture was poured into 500 mL of ice water. The solution was neutralized with powdered sodium bicarbonate and heated to boiling. After being cooled, the solution was reduced to about 1/4 volume at 40 °C under reduced pressure. The crude product was crystallized from water, recrystallized from ethanol, and then dried over P₂O₅ under vacuum at room temperature. Proton NMR confirmed there was only one sulfonate group para to the ethyl group. Anal. Calcd: S, 15.40. Found: S, 15.49.

(b) Sodium *p*-Isopropylbenzenesulfonate.¹¹ Fifty milliliters of 15% oleum was added slowly to 50 mL of isopropylbenzene (Eastman) at room temperature. After complete addition of oleum, the reaction mixture was heated to 90 °C for about 3 h with stirring. The stirring was continued at room temperature overnight. The resultant sulfonic acid mix was poured onto 200 g of ice and neutralized with powdered Na₂CO₃. The solution was evaporated to about 1/4 volume and then chilled; a white