

- (10) Sada, E., Kito, S., Yamashita, M., *J. Chem. Eng. Data*, **20**, 376-377 (1975).
- (11) Vogel, A., "Elementary Practical Organic Chemistry. Part 1: Small Scale Preparations", Longman, London, 1966, p 158.
- (12) Landolt-Börnstein, "Zahlenwerte und Functionen", Vol. 2, Part 2, Sec. C, Springer-Verlag, Berlin, 1964, p 610.
- (13) Mertsin, R. V., Nikurashina, N. I., Petrov, V. A., *Russ. J. Phys. Chem. (Engl. Transl.)*, **35**, 1369-1372 (1961).
- (14) Patterson, R. E., Ross, S., *Surface Sci.*, in press.
- (15) Bauer, N., Lewin, S. Z., "Physical Methods of Organic Chemistry", 3rd ed., Vol. I, Part I of "Technique of Organic Chemistry", A. Weissberger, Ed., Wiley-Interscience, New York, 1959, pp 165-166.
- (16) Zuidema, H. H., Waters, G. W., *Ind. Eng. Chem. (Anal. Ed.)*, **13**, 312-313 (1941).
- (17) Patterson, R. E., "Surface and Interfacial Tensions of Conjugate Solutions in Isothermal Ternary Systems", Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, N.Y., 1978.
- (18) Bancroft, W. D., Hubard, S. C., *J. Am. Chem. Soc.*, **64**, 347-353 (1942).
- (19) Cahn, J. W., *J. Chem. Phys.*, **66**, 3667-3672 (1977).

Received for review June 21, 1978. Accepted December 30, 1978.

Solubility of Toluene in Aqueous Sodium Alkylbenzenesulfonate Solutions

Patience C. Ho,* Chuen-huei Ho, and Kurt A. Kraus

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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

crude product was obtained. It was recrystallized twice from acetone-H₂O and dried over P₂O₅ under vacuum at room temperature. Proton NMR confirmed one sulfonate group para to the isopropyl group. Anal. Calcd: C, 48.64; H, 4.99; S, 14.43. Found: C, 48.53; H, 5.09; S, 14.53.

(c) **Sodium 2-Methyl-5-isopropylbenzenesulfonate (Sodium Cymenesulfonate)**. This compound was prepared from *p*-methylisopropylbenzene (Eastman) and 15% oleum with a procedure similar to that used with sodium *p*-isopropylbenzenesulfonate, except that temperature was kept at room temperature after addition of oleum. Carbon-13 NMR confirmed one sulfonate group ortho to the methyl group. Anal. Calcd: C, 50.83; H, 5.55; S, 13.87. Found: C, 50.88; H, 5.57; S, 13.43.

(d) **Sodium 2-Methyl-5-*tert*-butylbenzenesulfonate**. A 18.7-mL sample of 10% oleum was added slowly to a mixture of 0.5 mol of *p*-*tert*-butyltoluene (Aldrich) and 0.5 mol of thionyl chloride. The rest of the procedure was like that used for sodium *p*-ethylbenzenesulfonate. Carbon-13 NMR confirmed one sulfonate group ortho to the methyl group. Anal. Calcd: C, 52.78; H, 6.04; S, 12.81. Found: C, 52.71; H, 6.04; S, 12.96.

(e) **Sodium 2,5-Diisopropylbenzenesulfonate**. Fifty milliliters of 15% oleum was added dropwise to 50 mL of *p*-diisopropylbenzene (99%, Pfaltz and Bauer) at room temperature. After the oleum was added, the reaction mixture was heated to 50 °C for about 3 h. The reaction mixture was decomposed with 200 g of ice. White crude sulfonic acid was crystallized from water. The crude acid was recrystallized three times from water. The pure acid was redissolved in water and neutralized slowly with 10% NaOH. A white shining sodium salt was obtained after reducing the volume. The salt was dried overnight at 70 °C. Proton NMR confirmed one sulfonate group. Anal. Calcd: C, 54.53; H, 6.48; S, 12.13. Found: C, 54.75; H, 6.48; S, 12.25.

Gas Chromatography. Solubilities of toluene in the aqueous solutions were determined at least in duplicate by gas chromatography. Toluene and the aqueous solutions were mixed and equilibrated in a water bath at 25 and 55 °C at least 1 h before injecting samples (5 μL, Hamilton syringe) into the GC column. For duplicates, equilibration times were frequently several hours to several days. Duplicates agreed to within about 5%, as expected from the innate precision of the method.

A Perkin-Elmer Model 3920 gas chromatograph equipped with flame ionization detector was used. A 2 ft × 1/8 in. o.d. glass column packed with 60/80 mesh Tenax GC (Applied Science Laboratory) and coupled to the chromatograph with Swagelok fittings and graphite ferrules was used. Column temperature was programmed from 80 °C (2 min hold) to 130 °C with an increase of 4°/min. Inlet and detector temperatures were set at 250 °C; helium carrier gas was used with inlet pressure at 50 psig. The column was baked out overnight at 250 °C and gave a constant, low-level baseline at the most sensitive setting.

The instrument was calibrated using standard solutions of toluene in acetone. These were prepared by volume and converted to weight percentage with the known densities.¹² Differences in density from minor differences in temperature were ignored.

Tenax GC, a porous column packing material, is usually used for the separation of high boiling polar compounds such as acids.¹³ However, chromatograms from this study (Figure 1) show that Tenax GC is also suitable for the analysis of nonpolar lower boiling compounds (e.g., toluene in aqueous solutions).

Results and Discussion

Solubility of Sulfonates in Water. In order to establish the temperature and concentration ranges over which the measurements could be carried out, we have determined the solubility of the sodium salts of the various benzenesulfonates in water at 25 and 55 °C. The solubilities were obtained by saturating

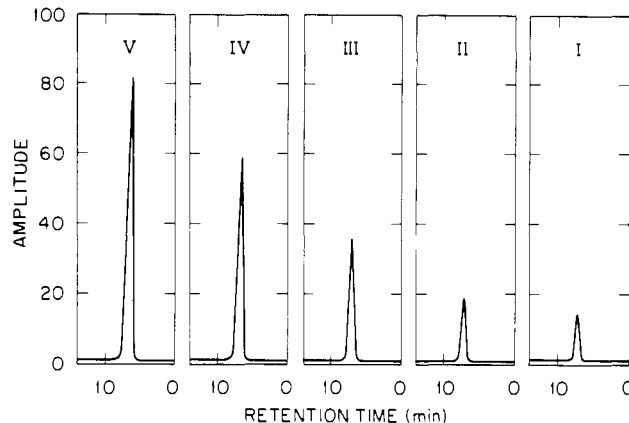


Figure 1. Determination of the solubility of toluene in 1.0 *m* substituted sodium benzenesulfonates (25 °C) by gas chromatography. Toluene in aqueous solution of: I, sodium benzenesulfonate; II, sodium *p*-toluenesulfonate; III, sodium *p*-ethylbenzenesulfonate; IV, sodium *p*-isopropylbenzenesulfonate; V, sodium 2-methyl-5-(isopropyl)-benzenesulfonate (sodium *p*-cymenesulfonate).

Table I. Effect of Temperature on Solubility of Benzenesulfonate and Substituted Benzenesulfonates in Water

sodium sulfonates of ^a	no. of C's in attached alkyl groups	solubility, mol/kg of H ₂ O	
		25 °C	55 °C
benzene	0	2.89	4.10
<i>p</i> -toluene	1	3.56	5.10
2,4-dimethylbenzene	2	2.88	3.90
<i>p</i> -ethylbenzene	2	2.57	3.56
<i>p</i> -isopropylbenzene	3	3.75	5.49
2,4,6-trimethylbenzene	3	1.36	2.49
2-methyl-5-isopropylbenzene	4	3.03	6.31
2-methyl-5- <i>tert</i> -butylbenzene	5	0.30	3.25
2,5-diisopropylbenzene	6	1.00	3.16

^a The sulfonate group is taken to be in the "1" position.

water with the salts at the appropriate temperature and then determining the salt content of weighed aliquots (ca. 0.5 g) by evaporation to dryness (70 °C). The results of the measurements are summarized in Table I, which also lists all the sulfonates studied here.

The solubility of most of the sulfonates is rather high even at 25 °C; solubilities generally increase with temperature. Very large increases in solubilities are shown by the diisopropyl derivative (threefold increase in solubility). An even larger increase (tenfold) is shown for the methyl-*tert*-butyl derivative. If one assumes linear variation of the log of the solubility with the inverse of temperature, one calculates an apparent heat of solution of 15.5 kcal for this compound, a remarkably high value.

Because of the uniformly high solubilities at 55 °C, we have carried out most of our toluene-solubility measurements at this temperature. Somewhat less complete measurements have also been carried out at 25 °C. Even at the higher temperatures we could not carry out all toluene solubility measurements to our targeted 2.5 *m* salt concentration since in some cases crystallization of the salt occurred in the syringe used in the GC determinations.

Solubility of Toluene in Aqueous Sulfonate Solutions. The solubility of toluene in aqueous solutions of the nine sulfonates listed in Table I was determined at 25 and 55 °C. Table II summarizes the results obtained at 25 °C; they refer to 1.0 and where possible 2.5 *m* solutions of the sulfonates. Table III summarizes the 55 °C results for ca. 0.5, 1.0, 1.5, and 2.5 *m* sulfonate solutions. From several determinations we compute the solubility of toluene in water to be 0.008 mol/kg of H₂O at 25 °C and 0.015 mol/kg of H₂O at 55 °C.

Table II. Solubility of Toluene in Aqueous Sodium Alkylbenzenesulfonate Solutions (25 °C)

aqueous solution of the Na salt of	[sulfonate], mol/kg of H ₂ O	solubility, mol of toluene/kg of H ₂ O
benzenesulfonate	1.0	0.0078
	2.5	0.023
<i>p</i> -toluenesulfonate	1.0	0.015
	2.5	0.052
2,4-dimethylbenzenesulfonate	1.0	0.027
	2.5	0.13
<i>p</i> -ethylbenzenesulfonate	1.0	0.028
	2.5	0.14
<i>p</i> -isopropylbenzenesulfonate	1.0	0.047
	2.5	0.27
2,4,6-trimethylbenzenesulfonate	1.0	0.039
	2.5	
2-methyl-5-isopropylbenzenesulfonate	1.0	0.089
	2.5	0.34
2,5-diisopropylbenzenesulfonate	1.0	0.21
	2.5	

Table III. Solubility of Toluene in Aqueous Sodium Alkylbenzenesulfonate Solutions (55 °C)

aqueous solution of the Na salt of	[sulfonate], mol/kg of H ₂ O	solubility, mol of toluene/kg of H ₂ O
benzenesulfonate	0.0	0.015
	0.53	0.011
	1.00	0.013
	1.56	0.018
	2.50	0.029
<i>p</i> -toluenesulfonate	0.51	0.013
	1.00	0.015
	1.64	0.028
	2.50	0.052
2,4-dimethylbenzenesulfonate	0.54	0.015
	1.00	0.024
	1.74	0.047
	2.50	0.139
<i>p</i> -ethylbenzenesulfonate	0.49	0.015
	1.00	0.025
	1.79	0.058
	2.50	0.160
<i>p</i> -isopropylbenzenesulfonate	0.50	0.027
	1.00	0.046
	1.77	0.152
	2.44	0.35
2,4,6-trimethylbenzenesulfonate	0.50	0.022
	1.00	0.037
2-methyl-5-isopropylbenzenesulfonate	0.68	0.044
	1.00	0.082
	1.57	0.167
	2.50	0.72
2-methyl-5- <i>tert</i> -butylbenzenesulfonate	0.50	0.048
	1.00	0.125
	1.39	0.208
	0.52	0.063
	1.00	0.233
2,5-diisopropylbenzenesulfonate	1.52	0.51
	2.50	2.29

It can be seen from Tables II and III that the effect of temperature on solubility is small and that solubility generally increases with molality of the sulfonates. With benzenesulfonate the solubility of toluene first decreases with sulfonate concentration (Table III). A less pronounced solubility minimum occurs with toluene sulfonate. The more highly substituted sulfonates show pronounced increases in solubility with sulfonate concentration and no minima.

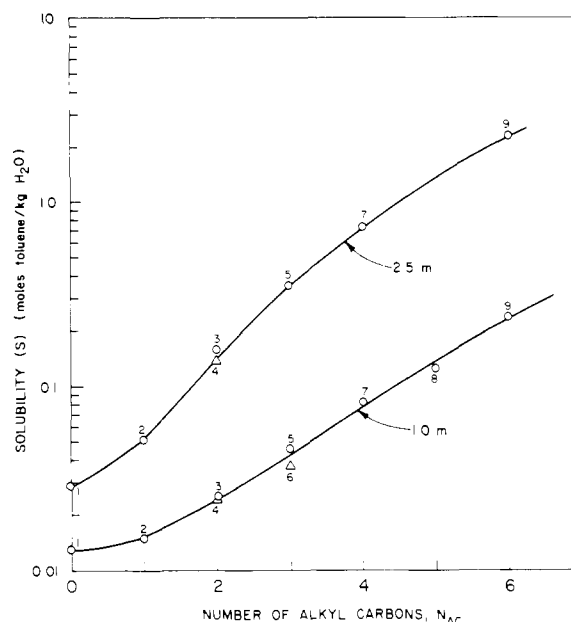


Figure 2. Solubility of toluene in aqueous solutions of various sodium benzenesulfonates (55 °C). Sodium sulfonates of: (1) benzene, (2) *p*-toluene, (3) *p*-ethylbenzene, (4) 2,4-dimethylbenzene, (5) *p*-isopropylbenzene, (6) 2,4,6-trimethylbenzene, (7) 2-methyl-5-(isopropyl)benzene, (8) 2-methyl-5-(*tert*-butyl)benzene, (9) 2,5-diisopropylbenzene.

Toluene solubility increases with the number of alkyl carbons attached to the benzene ring of the sulfonates. With the most highly substituted compound studied here (the sulfonate of diisopropylbenzene, six alkyl carbons) at 55 °C, the salting-in effect becomes very large, more than 1 mol of toluene dissolves/mol of sulfonate in a 2.5 *m* solution. Typical relationships between toluene solubility and number of alkyl carbons are shown in Figure 2. The log of the solubility (*s*) of toluene seems to increase almost linearly with the number of alkyl carbons N_{AC} attached to the benzene ring. For these relatively low molecular weight materials the specific isomeric structure seems of little importance. Thus the solubility of toluene in the sulfonates of ethylbenzene and of dimethylbenzene differ by less than 10%. The difference is somewhat larger between the sulfonates of isopropylbenzene and trimethylbenzene, but the similarity between the two is still striking.

Salting-in effects for various sulfonates have frequently been described in the literature, usually under the term hydrotropic behavior.^{1-4,6-9,14-17} The compound frequently cited as one of the best hydrotropic materials is cymenesulfonate (methylisopropylbenzenesulfonate). The diisopropyl compound studied here shows a much more pronounced hydrotropic effect than cymenesulfonate and thus should be an improvement over cymenesulfonate in many of the applications proposed for it. As implied by Figure 2, addition of further alkyl carbons to the benzene ring should further increase the hydrotropic properties of this series of compounds even under conditions where micelle formation does not occur.

Activity Coefficients of Toluene in Substituted Benzenesulfonate Solutions. We may use the solubility measurements to determine the activity coefficients of toluene in these somewhat unusual electrolyte solutions. At equilibrium the chemical potential of toluene is the same in both liquid phases. If we use the same standard state for toluene in both phases, its activity is also the same

$$a_{T(T)} = a_T \quad (1)$$

where $a_{T(T)}$ is the activity of toluene in the toluene-rich phase and a_T its activity in the water-rich phase. If the solubility of water and of the various sulfonates is small in toluene, variations

of $a_{T(T)}$ can be approximated by Raoult's law

$$a_{T(T)} = Na_T^* \quad (2)$$

where N is the mole fraction of toluene in the toluene-rich phase and a_T^* its activity in pure toluene.

We have determined for the toluene-rich phase the water contents by Karl Fischer titrations and the solubilities of the various sulfonates by residue analyses over the whole experimental concentration range. Water contents were less than 0.1 wt %, corresponding to a mole fraction of less than 0.0051. Sulfonate concentrations were less than 0.05 wt % corresponding to mole fractions of less than 0.0002 (after taking into consideration that the sulfonates contribute 2 mol of ions/mol of component). The maximum mole fraction of water and electrolyte "impurities" in the toluene-rich phase is thus only 0.0053 and the minimum value of N is about 0.995. Hence the activity of toluene remains constant to within about 0.5%. For our calculations we therefore have assumed $a_{T(T)}$ to be constant.

For the various equilibrations we thus can write

$$a_{T(aq)} = m_{T(aq)}\gamma_{T(aq)} = m_T^\circ\gamma_T^\circ \quad (3)$$

Note that $a_{T(aq)}$, the activity of toluene in the aqueous phase, is not necessarily equal to a_T of eq 1, because reference states can be different. In eq 3, m_T° and γ_T° are the concentration (solubility) and activity coefficient of toluene in water; $m_{T(aq)}$ and $\gamma_{T(aq)}$ are its concentration and activity coefficient in the aqueous electrolyte (sulfonate) solutions. The ratio $\gamma_{T(aq)}/\gamma_T^\circ$ for the aqueous phases saturated in toluene is given by the ratio of the experimentally determined solubilities, $m_T^\circ/m_{T(aq)}$. The concentration m_T° is very small (0.015 mol/kg of water at 55 °C), and the value of γ_T° should be to a good approximation the value at infinite dilution of toluene in water. We shall make this approximation and assign $\gamma_T^\circ = 1$, the conventional value for this reference state. With this assignment

$$\gamma_{T(aq)} = m_T^\circ/m_{T(aq)} \quad (4)$$

The results of these computations are summarized in Figure 3.

Except for the lowest members of the series where activity coefficients first rise with salt concentration, activity coefficients decrease with salt concentration. For the highest members of the series this effect is very dramatic—a decrease of γ_T of more than 2 orders of magnitude in 2.5 m salt solution.

Hydrotropy, of course, implies decreases of activity coefficients of the organic (neutral) component with concentration of the hydrotropic agent. It may be worth recalling here that according to the Debye–McAuley theory the activity coefficient of the neutral component should vary linearly with ionic strength (synonymous here with concentration m). Thus one would expect here

$$\log \gamma_{T(aq)} = km \quad (5)$$

The salting coefficient k should be positive if, as is the case here, the dielectric constant of the neutral material is less than that of water. With simple salts this frequently occurs as shown in the general compilation of salting coefficients in Harned and Owen.¹⁸

With toluene dissolved in these aqueous sulfonate solutions a positive salting coefficient seems to occur only for the lowest members of the series and at low salt concentration. Generally the salting coefficients here are negative and the equation representing variation of $\log \gamma_{T(aq)}$ with m requires higher terms

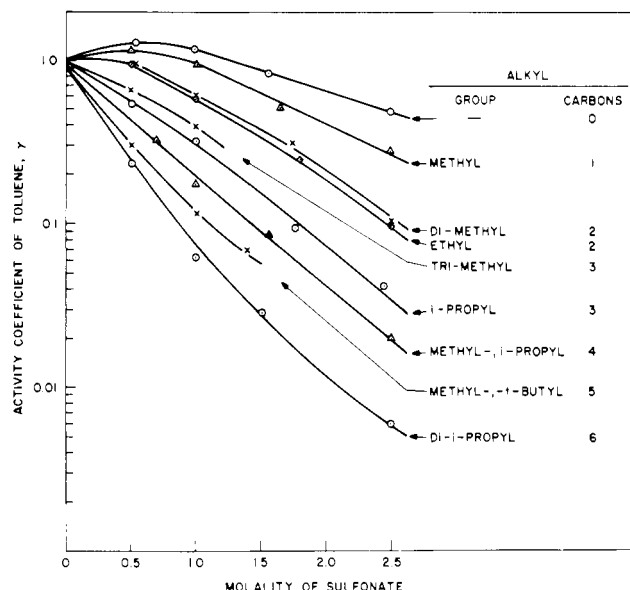


Figure 3. Activity coefficients of toluene in substituted sodium benzenesulfonate solutions at 55 °C.

in m than eq 5. An attempt was made to fit the results to the quadratic equation

$$\log \gamma_{T(aq)} = Bm + Cm^2 \quad (6)$$

Values of B varied from ca. +0.3 for benzenesulfonate to -1.3 for the diisopropylsulfonate and seemed to vary almost linearly with the number of alkyl carbons on the benzene ring.

Acknowledgment

We are indebted to L. L. Brown of the Oak Ridge National Laboratory Chemistry Division for the NMR work.

Literature Cited

- (1) R. H. McKee, U.S. Patent 2 308 564 (1943).
- (2) R. H. McKee, *Ind. Eng. Chem.*, **38**, 382 (1946).
- (3) N. Migita, J. Nakano, S. Hirai, and C. Taktuka, *Sen'i Gakkaishi*, **12**, 632 (1956).
- (4) H. Rath, *Tenside*, **2** (1), 1 (1965).
- (5) T. H. Vaughn and E. G. Nutting, *Ind. Eng. Chem., Anal. Ed.*, **14**, 454 (1942).
- (6) H. S. Booth and H. E. Everson, *Ind. Eng. Chem.*, **40**, 1491 (1948).
- (7) H. S. Booth and H. E. Everson, *Ind. Eng. Chem.*, **41**, 2627 (1949).
- (8) H. S. Booth and H. E. Everson, *Ind. Eng. Chem.*, **42**, 1536 (1950).
- (9) W. Licht, Jr., and L. D. Wiener, *Ind. Eng. Chem.*, **42**, 1538 (1950).
- (10) J. A. Bradley, P. Perkins, and J. J. Polison, paper presented at the 138th National Meeting of the American Chemical Society, New York, N.Y., Sept 1960.
- (11) J. LeFevre, *J. Chem. Soc.*, 1501 (1934).
- (12) "Handbook of Chemistry and Physics", 49th ed., CRC Press, Cleveland, Ohio, 1968–1969.
- (13) C.-h. Ho, B. R. Clark, and M. R. Guerin, *J. Environ. Sci. Health, Part A*, **A11** (7), 481 (1976).
- (14) C. Neuberg, *Biochem. Z.*, **76**, 107 (1916).
- (15) H. Rath, J. Rau, and D. Wagner, *Millind Textilber.*, **43**, 718 (1962).
- (16) M. Ueda, A. Katayama, and N. Kuroki, *Colloid Polym. Sci.*, **252**, 486 (1974).
- (17) S. N. Aminov, E. A. Aripov, K. S. Akhmedov, and D. Kunishev, *Colloid J. USSR (Engl. Transl.)*, **37** (5), 836 (1975).
- (18) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd ed., Reinhold, New York, N.Y., 1958, p 533 and Table 12-10-1A.

Received for review June 29, 1978. Accepted November 27, 1978. Research sponsored by the Division of Oil, Gas and Shale Technology, U.S. Department of Energy under Contract W-7405-eng-26 with Union Carbide Corp.