Preliminary results in this laboratory on the analysis of blood lipids have been encouraging.

The analyses as performed here do not permit measurement of individuals of all classes of fatty esters. If measurement of single components is desired, paper chromatography of the separated classes can be performed. Gas chromatography provides this function in the analysis of nonoxygenated esters, and may be extended to other classes of esters.

The method may also have some application to glyceride analysis in those oils which contain fatty acids of different polarity. For example, triglycerides containing one, two, or three epoxy fatty acids should be separable. Waxes, cholesteryl esters, and glycerides have been separated by thin-layer chromatography (20), and mixtures containing these can be analyzed by the proposed method. Thin-layer chromatography has proved to be a powerful tool for qualitative separations, and this and other reports (22,23) indicate that it is equally promising for quantitative measurements.

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The Adsorption and Chromatography of Alkyl Benzene Sulfonates on Charcoal

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A chromatographic procedure for the separation and characterization of sodium alkyl benzene sulfonates is outlined. It is based on properly sized activated charcoal and uses methanol with varying amounts of benzene and a small content of ammonia and water. Milligram quantities of surfactants are used and the fractions analyzed colorimetrically. The rationale of the method is established by adsorption measurements which indicate that in this system the surfactant is adsorbed by both van der Waals and ionic forces with strong dependence upon both molecular weight and structure.

THE DESIRABILITY of a simple, rapid, and accurate method for the identification of individual surfactants and the separation of their mixtures continues to be obvious. The present paper reports some progress in developing a chromatographic method for the identification and separation of alkyl benzene sulfonates which, however, is still far from being simple and rapid, and also discusses the principles underlying this separation.

Charcoal was originally chosen as the adsorbent in the hope that adsorption would involve only the hydrocarbon part of the surfactant and thus be highly selective to the structure of this moiety. Further work showed, however, that while the premise was incorrect, the desired selectivity was nevertheless obtained. The adsorptive power of charcoal proved also to be impractically strong in either water or alcohol, but by following the experience of the Analytical Methods Subcommittee of the AASGP (1), could be controlled over a wide range by addition of benzene and ammonia. In this way a workable chromatographic method could be devised capable of separating alkyl benzene sulfonates of same molecular weight and different structure or of same structure and different molecular weights. Branching affects adsorption, however, in the same way as a lower molecular weight so that complete resolution of more complex mixtures cannot always be obtained.

Experimental

Analytical Method. Used throughout was a methylene blue spectrophotometric method based on the work of Mukerjee (2). Since alcohol interferes with this method and was normally present in the solutions, all samples were first evaporated to dryness in a test tube placed in an oven at 80°C. The residue was typically dissolved in 20 ml. of water and aliquot portions made up to 20 ml. in a 125-ml. Erlenmeyer flask to which 2 or 3 drops of 0.1% aqueous methylene blue solution and 20 ml. of $CHCl_3$ were added. The flask then was shaken vigorously for a few minutes and allowed to settle for about 2 hr. A part of the bottom layer was then carefully pipetted out and its optical density at 655 mμ was determined in a Beckman DU spectrophotometer using covered 1-cm. cells. A separate blank was used for each series of measurements and was always quite small. Standard solutions of the detergents used or of freshly dissolved pure sodium lauryl sulfate were used for calibration.

Materials. The surfactants of known structure were kindly supplied by the Continental Oil Company Research and Development Laboratories, Ponca City, Oklahoma. As shown later by chromatographic analysis, these contained only small amounts of impurities (see Fig. 5).

Charcoal. Preliminary experiments showed that good chromatographic resolution required absence of particles larger than 150–100 mesh. Good flow through the chromatographic columns and good settling in adsorption experiments required absence of very fine particles. In addition it was thought desirable to use ash-free charcoals. Most of the experiments reported were performed using Darco G-60 from the Atlas Powder Co., Wilmington, Delaware, from which a fraction passing the 150-mesh sieve and retained on the 275-mesh sieve was obtained by prolonged and laborious wet sieving. Later an essentially equivalent sample of YJ-2 of 100- x 300-mesh size was obtained from the Barneby-Cheney Co., Columbus, Ohio.

Adsorption Measurements. Equilibration was conducted in 125-ml. Pyrex Erlenmeyer flasks with tight-fitting, long, ground-glass stoppers. Weighed amounts of charcoal and known volumes of solvent and of standard detergent solutions were placed in these and mechanically agitated in an air conditioned room at about 23°C. for 24 to 36 hr. After settling for 12 to 24 hr., small volumes (1–5 ml.) of the clear supernatant liquid were taken out for analysis. Experiments in which less than 50% of the detergent was adsorbed, or in which the optical density of the volumetric determination was less than about 0.1, were rejected.

Chromatographic Procedure. Experiments were conducted with many variants in the procedure, but a typical one was as follows: A 25-ml. burette with a Teflon stopcock was carefully filled with the charcoal over a glass wool plug while methanol was constantly flowing and the charcoal added in small amounts. The column was then washed with 500 ml. of the mixed solvent used. A concentrated, or even supersaturated, solution containing about 1 mg. of the surfactant studied in the same solvent was then slowly added onto the column and the elution with the same solvent begun. The flow rate was of the order of 2 drops a minute, and the fractions were collected with a Packard Instrument Co., automatic fraction collector by drop count.

Results

No attempt was made to determine the full shape of the adsorption isotherm but the data obtained could be readily fitted to a Freundlich type, i.e., gave straight lines on a log-log plot of the amount adsorbed per unit adsorbent vs. the equilibrium concentration. In each case enough points were obtained to ascertain the relative level of the adsorption, but the precision of the determination often left doubt as to the exact slope of the lines.

Fig. 1 shows the effect of broad variation in solvent composition upon adsorption of 1-phenyl-n-decane sulfonate. It is clearly evident that adsorption from water is very much stronger than from methanol, that it is further lessened by addition of either benzene or ammonia to the methanol, but that simultaneous addition of ammonia and benzene is much more effective than that of either separately. These results seem to indicate that the alkyl benzene sulfonate is adsorbed both by van der Waal's forces acting upon the hydrocarbon moiety and by ionic forces of residual impurities of the charcoal acting upon the sulfonate group. Competition by alcohol and especially benzene reduces adsorption by van der Waal's forces while hydroxyl ions supplied by ammonia effectively compete with the polar group. When only one type of adsorption is reduced, the other is still active. Thus adsorption is especially reduced when both types of competition are present.

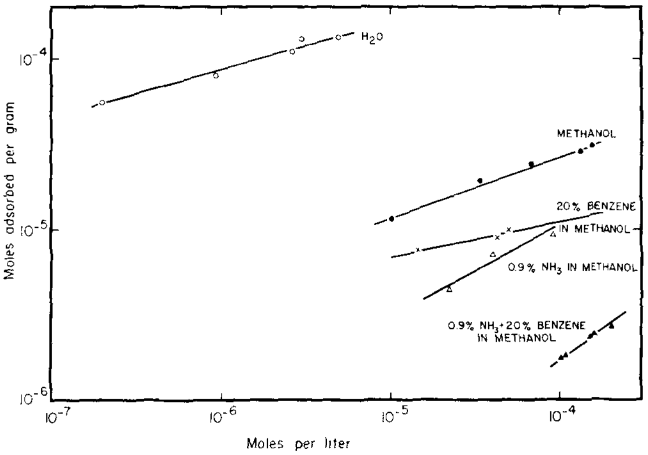

FIG. 1. Equilibrium adsorption of sodium 1-phenyl-n-decane sulfonate by charcoal from a number of solvents.

It may also be noted that the slope of the adsorption line for systems containing ammonia is significantly higher than the others and especially those containing benzene. In fact, the slope is close to 45°, i.e., direct proportionality of amount adsorbed to concentration (Cf. Fig. 4), and thus indicates considerable uniformity of the surface. If as indicated above, the role of ammonia is to reduce the effect of residual ionic impurities of the charcoal, this means that at the low coverages here involved, the carbon surface is relatively homogeneous while the impurities are quite heterogeneous.

Since it is well known that proportionality between the amount adsorbed and concentration lead to symmetrical chromatographic peaks, it is clear that the presence of ammonia is highly beneficial in a chromatographic procedure.

Fig. 1 indicates also that water may have a considerable effect upon adsorption. Because of the difficulty of maintaining strictly anhydrous conditions, all our experiments were conducted in the presence of a small but controlled amount of moisture, generally 3 volume % of the solvent.

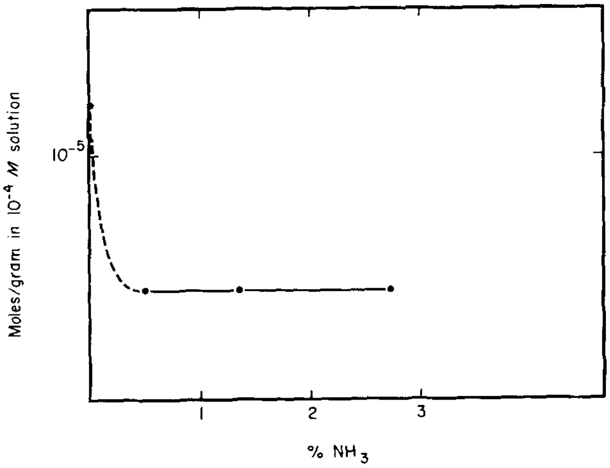

FIG. 2. The effect of small amounts of ammonia upon equilibrium adsorption of sodium 1-phenyl-n-decane sulfonate by charcoal from methanol containing 8% of benzene.

Fig. 2 shows the effect of increasing the concentration of ammonia in a methanol-benzene system. The amount adsorbed is recorded for a constant concentration of surfactant in the equilibrium solutions, namely 10^{-4} M/l as obtained by interpolation or slight extrapolation on a log-log plot such as Fig. 1. The important result is that the full effect of ammonia in reducing adsorption is obtained at very low concentrations and that small variations in the neighborhood of 1% have only a negligible effect. This is important because of the very real possibility of the loss of ammonia from the solvents during manipulation.

Fig. 3 shows in a similar way, but on a tenfold contracted scale, the effect of varying the proportion of benzene in the presence and absence of ammonia. It is apparent that in the presence of ammonia adsorption is quite sensitive to the proportion of benzene throughout the range studied, thus providing a useful method of controlling the rate of chromatographic migration by adjusting this concentration. The upper curve indicates that at high concentrations of benzene adsorption is again increased. This may be connected with the reduced solubility of surfactants in benzene-rich systems.

Fig. 4 shows the effect of structure and molecular weight upon adsorption from a mixed solvent containing methanol, benzene, water, and ammonia. All surfactants had a sulfonated benzene attached to a straight hydrocarbon chain. The solid lines refer to varying chain lengths from C_{15} to C_{10} in which the benzene was attached to the terminal carbon atom. The effect of shorter chains in reducing adsorption is clearly evident. The dashed lines refer to C_{15} chains in which the benzene is attached to the penultimate and the middle carbon atom, respectively. It is clear that the effect of structure is even more important than that of the molecular weight.

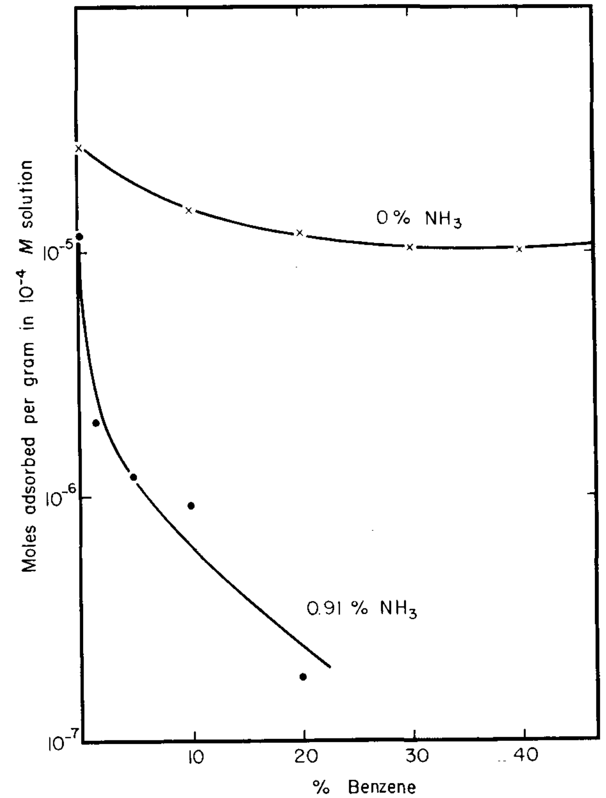

FIG. 3. The effect of benzene on equilibrium adsorption of sodium 1-phenyl-n-decane sulfonate by charcoal from methanol in the presence of 0 and 0.91% ammonia.

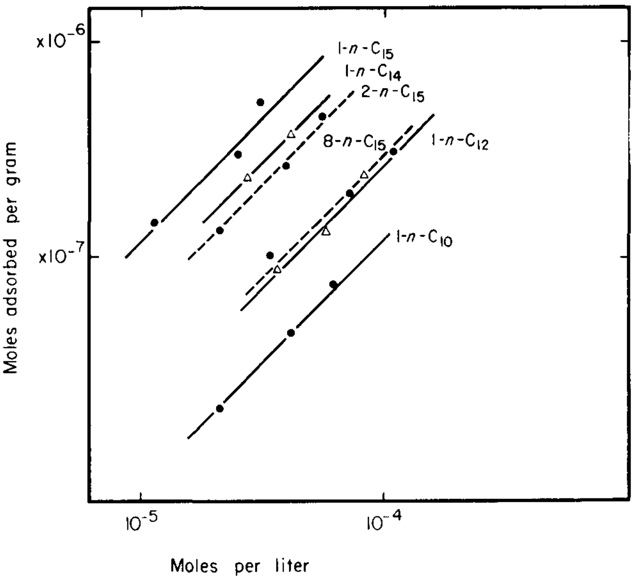

FIG. 4. The effect of molecular weight and structure upon the equilibrium adsorption of sodium n-alkyl benzene sulfonates by charcoal from methanol containing 8% benzene, 1.3% ammonia, and 3% water. Solid lines, terminally attached phenyl; dashed lines, phenyl displaced along straight C_{15} chain.

The overlap of the structural and molecular weight effects upon adsorption shows that complete separation and structural elucidation of a complex mixture cannot be possible by this method. Nevertheless, extensive fractionation of a complex mixture or resolution with structural implications of a simple mixture should be possible. The sensitivity to structure should be particularly interesting in the determination of purity of individual compounds.

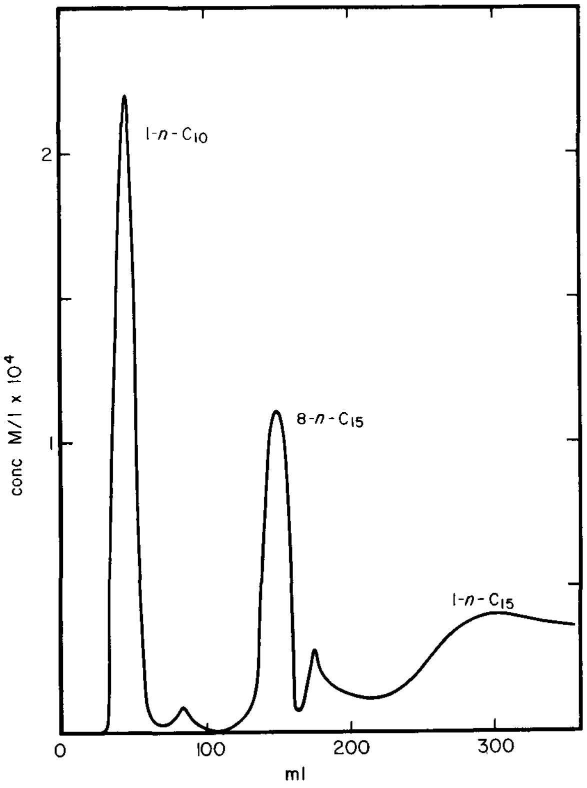

FIG. 5. Chromatogram of a synthetic mixture of 3 sodium alkyl benzene sulfonates on charcoal with methanol containing 8% benzene, 1.3% ammonia, and 3% water showing the presence of small amounts of impurities.

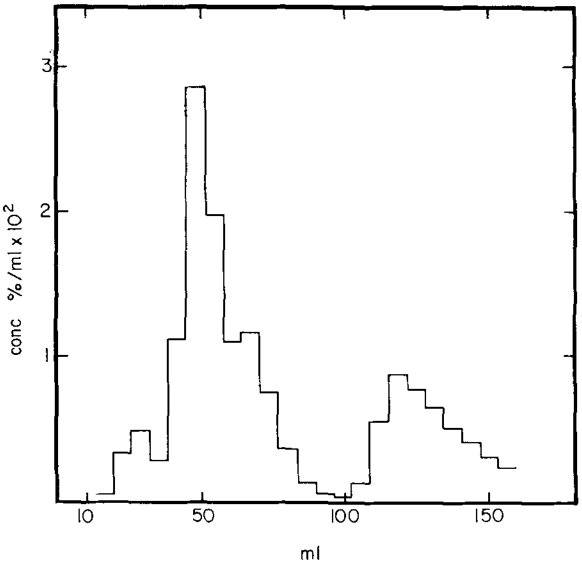

FIG. 6. Chromatogram of a mixture of isomeric sodium phenyl-n-decane sulfonates on charcoal using methanol containing 8% benzene, 1% ammonia, 2% water. Four of the possible five isomers are resolved.

Fig. 5 shows the chromatography of a synthetic mixture of three alkyl sulfates which could be completely resolved and the presence of impurities indicated. It is clear, however, that if impurities in the linear C_{15} surfactant were to be determined, a better solvent, i.e., one containing more benzene, should be used.

Fig. 6 shows the chromatogram of 3.11 mg. of a synthetic mixture of n-C_{10} alkyl benzene sulfonates. Twenty-eight per cent of the mixture had the benzene ring attached to the terminal carbon atom, and formed the last peak. Seventy-two per cent of the mixture that was formed by the other isomers and three of these are clearly resolved. The total recovery was 96%.

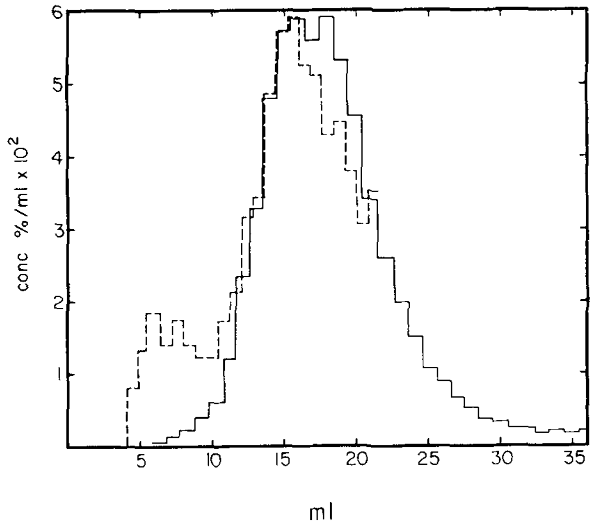

FIG. 7. Chromatograms of 1-mg. samples of two commercial sodium dodecyl benzene sulfonates on charcoal using methanol containing 4% benzene, 1% ammonia, and 2% water.

Fig. 7 shows the chromatograms of 1-mg. samples of two different commercial alkyl benzene sulfonates. Since exactly the same analytical technique was used in both runs, it is clear not only that they are quite different in composition, but also that one is much more complex than the other.

Acknowledgment

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Solvent-Blown, Rigid Urethane Foams from Low Cost Castor Oil-Polyol Mixtures[1]

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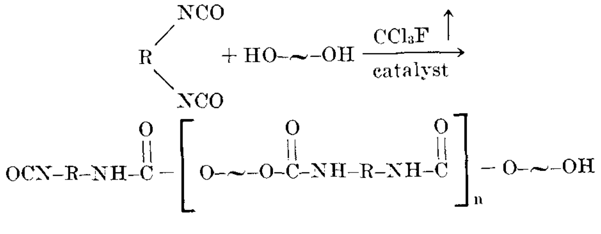
The preparation of solvent-blown rigid urethane foams from low cost castor oil-polyol mixtures was investigated. Solutions of triisopropanolamine, and of mixtures of triisopropanolamine and triethanolamine in castor oil, were used as the polyol component of these foams. Foams were prepared by reacting these polyol mixtures, in the presence of catalyst, surfactant, and trichlorofluoromethane, with prepolymers prepared from toluenediisocyanate and certain polyether polyols or mixtures of these polyether polyols with castor oil. The effect of polyol and prepolymer composition and blowing agent concentration on such foam properties as density and compressive strength was investigated. The properties of the castor oil-based foams were comparable to those of foams obtained from more costly polyols.

RIGID URETHANE FOAMS are cellular plastics which are being used in increasing amounts as insulating material, in low density structural panels, and in flotation gear such as life rafts and buoys. These materials can be foamed in place or in some cases sprayed on.

These foams are polyurethane polymers produced by the reaction of polyisocyanates with polyhydroxy compounds or polyols as shown in the equation



$$R\begin{matrix}\diagup NCO\\ \\ \diagdown NCO\end{matrix} + HO\text{-}\sim\text{-}OH \xrightarrow[\text{catalyst}]{CCl_3F\uparrow}$$

$$OCN\text{-}R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}\left[O\text{-}\sim\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}R\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\right]_n\text{-}O\text{-}\sim\text{-}OH$$

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[2] A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.