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GEL FILTRATION CHROMATOGRAPHY OF PETROLEUM SULFONATES

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SUMMARY

Sulfonated fractions of partially refined petroleum were chromatographed on Sephadex beads in water-95% ethanol (9:1). Each petroleum sulfonate was separated into two portions, a polymeric colloid fraction and an association colloid fraction. The composition of each sample with respect to these two fractions was calculated on a dry weight basis. For each sample, the initial micelle concentration of the association colloid fraction was determined from surface tension measurements and from gel filtration data. A comparison of the results showed that the two techniques yield critical micelle concentrations which differ by as much as a factor of four.

INTRODUCTION

Gel filtration chromatography of micellar solutions on Sephadex beads has been reported by Nakagawa and Jizomoto¹, Suzuki and Sasaki², and Coll³. These articles stress the theoretical aspects of the transport of a micellar solution on a gel filtration matrix. For the most part, the experimental work reported by these workers consisted of analyzing purified laboratory surfactants. Experiments with sodium dodecyl sulfate demonstrated that the transport of a micellar solution proceeds in the following manner². The micelles, which are colloidal-sized species, are excluded from the beads and elute at the void volume. A plateau, the concentration of which equals the critical micelle concentration, trails the micelle peak. This situation arises because of the equilibrium between micelles and monomers. Micelles move faster down the column than monomers, therefore the micelles must dissociate to regenerate the equilibrium concentration of monomer (*i.e.*, the critical micelle concentration) during the transport process.

The chromatography of a surfactant mixture on a gel filtration matrix has been described by Nakagawa and Jizomoto⁴. In this latter paper, also, the authors' major concern was the theoretical aspects of the system. Nonetheless, interesting

observations of a practical nature were reported. In particular, Nakagawa and Jizomoto⁴ showed that if a property common to each surfactant in a mixture (*e.g.*, conductivity) were plotted as a function of eluted volume, the resultant elution profile would have a more or less characteristic shape as a consequence of the different physical properties of the constituent surfactants. We became interested in determining whether useful qualitative information about the surfactant composition of petroleum sulfonates could be obtained by this technique. In addition, we wanted to determine whether the critical micelle concentration of a petroleum sulfonate measured by this technique was essentially the same as that determined by a more classical procedure, *e.g.* surface tension measurements. Petroleum sulfonates have recently become popular as inexpensive surfactants for use in tertiary oil recovery systems^{5,6}.

EXPERIMENTAL

A 3:2 mixture of Sephadex G-25 and Sephadex G-50 was prepared on a dry weight basis and allowed to hydrate in a large excess of twice distilled water for 24 h. Fines were removed by decanting. The slurry was poured into a column to form a bed 2.8×44 cm. Subsequently, the bed was equilibrated with the solvent used for all of the studies described in this paper, water-95% ethanol (9:1).

Sulfonated fractions of partially refined petroleum were prepared as previously described⁷. Prior to analysis by gel filtration chromatography, each petroleum sulfonate was subjected to a solvent extraction procedure to remove inorganic salts and unsulfonated organic material⁸. Samples were prepared for chromatography by dissolving 40 mg of the active petroleum sulfonate in 2.0 ml of the solvent. Gentle heating with live steam and frequent swirling on a Vortex mixer were used to speed up the dissolving process. After a sample had cooled to ambient temperature, it was carefully placed on the bed of Sephadex beads. Eluent fractions of 5 ml were obtained with an automatic fraction collector.

The eluted fractions were assayed for conductivity with a YSI Model 31 conductivity bridge equipped with a microprobe. Dry weight was determined by pouring a 5-ml fraction into a pre-weighed aluminum weighing dish, drying at 65° for at least 36 h, and weighing the sample plus dish on a Mettler H-20 balance.

Surface tension measurements were made with a Cahn electrobalance, Model RM-2, equipped with a platinum/iridium ring. The solvent was water-95% ethanol (9:1).

Sulfur analyses were performed by Huffman Labs. (Wheat Ridge, Colo., U.S.A.).

RESULTS AND DISCUSSION

Composition of petroleum sulfonates

Profiles of conductivity *versus* elution volume are shown in Fig. 1 for three different petroleum sulfonates. For these surfactant mixtures, such profiles are much more complex than the analogous profile of a pure surfactant (see ref. 2). Also shown in Fig. 1 are profiles of dry weight *versus* elution volume. The trough in these profiles at about fraction 33 suggests that the material which elutes at the void volume is not

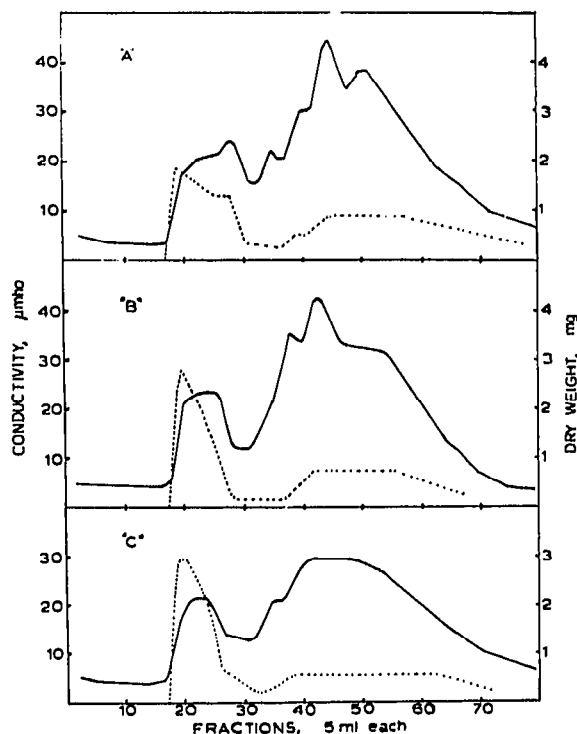


Fig. 1. Elution profiles for three different petroleum sulfonates. Conductivity (solid line) and dry weight (broken line) are plotted *versus* eluted volume in each case. Total bed volume = 270 ml.

in equilibrium with the material eluting later. Presumably, a significant portion of each different petroleum sulfonate is composed of relatively large, polysulfonated compounds, *e.g.* polysulfonated asphaltines. These materials, due to their large size and, possibly, due to charge repulsion effects, elute at or near the void volume. For convenience, we have labelled this peak (*i.e.*, fractions $\approx 19-35$) the "polymeric colloid fraction". The pigments peculiar to petroleum, if present, always elute in this fraction. When isolated and re-chromatographed under the same conditions, the polymeric colloid fraction continues to elute at the void volume, *i.e.* as if it consisted of compounds large enough to be completely excluded from the Sephadex beads.

The second portion of the pronounced two-peak profiles (Fig. 1) has been labelled the "association colloid fraction" (*i.e.* fractions $\approx 40-70$). On the basis of UV, IR, and NMR spectra this material appears to be composed of monosulfonated compounds of the alkylaryl sulfonate class⁹. When the association colloid fraction is isolated and re-chromatographed under the same conditions, the elution behavior is strikingly similar to that of a pure surfactant. Such an observation suggests that this fraction is composed of a mixture of surfactants possessing similar physical properties. The compounds in the association colloid fraction appear to be strongly adsorbed by Sephadex, since solute elution extends significantly beyond the total bed volume.

The composition of each petroleum sulfonate with respect to the polymeric colloid fraction and the association colloid fraction has been calculated from the dry

TABLE I

DISTRIBUTION OF PETROLEUM SULFONATE INTO POLYMERIC COLLOID AND ASSOCIATION COLLOID FRACTIONS AND THE EQUIVALENT WEIGHT OF EACH FRACTION

Petroleum sulfonate	Polymeric colloid		Association colloid	
	Percentage of sample	Equivalent weight*	Percentage of sample	Equivalent weight*
"A"	43	400	57	280
"B"	54	480	46	265
"C"	56	430	44	275

* Based on sulfur content.

weight profiles of Fig. 1. The data are shown in Table I. Equivalent weights based on sulfur content are also shown in Table I. While the polymeric colloid fraction has the higher equivalent weight of each pair, the equivalent weights for the two fractions are not dramatically different.

We conclude that gel filtration chromatography of petroleum sulfonates does yield limited but useful qualitative information about the sample composition. In particular, it is possible to estimate the association colloid content of a sample by this technique. It seems reasonable to suggest that petroleum sulfonates with the greater association colloid content would be more effective, on a weight basis, in forming micellar solutions, stabilizing microemulsions, and so on. The polymeric colloid fraction should also be surface active, in the same sense that other polyelectrolytes (e.g. proteins) are. However, these large species diffuse to interfaces relatively slowly and once at the interface tend not to leave. Thus, the polymeric colloid fraction probably does not contribute to the general detergent properties of a solution containing petroleum sulfonates.

Critical micelle concentrations of petroleum sulfonates

The critical micelle concentration for the association colloid fraction of each different petroleum sulfonate was estimated from the plateau of constant dry weight per fraction observed in each experiment (Fig. 1). The critical micelle concentration was calculated by dividing the concentration in the plateau region (in g/l) by the equivalent weight of the association colloid fraction (from Table I). As a comparison, the critical micelle concentration for each petroleum sulfonate was determined by

TABLE II

COMPARISON OF CRITICAL MICELLE CONCENTRATIONS DETERMINED BY SURFACE TENSION MEASUREMENTS AND GEL FILTRATION CHROMATOGRAPHY

Petroleum sulfonate	Surface tension (mequiv./l)	Gel filtration (mequiv./l)
"A"	0.15	0.64
"B"	0.88	0.53
"C"	0.33	0.44

surface tension measurements. For this technique, the critical micelle concentration was obtained by multiplying the measured value (in g/l) for the petroleum sulfonate by the percentage of the sample attributed to the association colloid fraction, and then dividing by the equivalent weight of the association colloid fraction. The critical micelle concentrations determined by the two procedures are listed in Table II. A comparison of the data in Table II reveals that the two procedures yield critical micelle concentrations which differ by as much as a factor of four. However, as noted above, adsorption of the association colloid fraction onto Sephadex appears to be a significant factor in the transport process. The monomer concentration in the plateau of the elution profiles (Fig. 1) presumably arises from an equilibrium with both adsorption sites and micelles. Thus, the relatively large differences in critical micelle concentrations measured by the two techniques is not an unexpected result.

Concluding comments

A gel filtration column composed of only Sephadex G-50 gives a much better resolution of the two fractions present in petroleum sulfonates than that shown in Fig. 1. However, with the system described in Experimental, it is most difficult to estimate the critical micelle concentration with Sephadex G-50 because the number of fractions constituting the plateau is very small. On the other hand, a gel filtration column composed of only Sephadex G-25 does not resolve the petroleum sulfonate into polymeric colloid and association colloid fractions. But, in this case, the plateau includes slightly more fractions than are present in the data shown in Fig. 1. By empirical testing, a gel filtration column composed of a 3:2 mixture of Sephadex G-25 and G-50 was selected, so that both sample composition and critical micelle concentration could be estimated in one experiment.

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