

Effect of Solubilized Methanol on Micelle Size in a Nonpolar Solvent

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The behavior and state of aggregation of barium dinonylnaphthalene sulfonate in toluene, toluene-methanol, and methanol solutions were studied by ultracentrifugation and viscometry. The aggregation number of its micelles is reduced from about 10 in pure toluene to about 4 when the mole fraction of free methanol in the solvent is approximately 0.03. In pure methanol micelles do not exist, and the monomers dissociate ionically. Results of the investigation supplement an earlier observation that the solubilization of methanol diminishes the size of sulfonate and carboxylate micelles in nonaqueous solvents.

INTRODUCTION

Aspects of solubilization of hydrogen-bonding solubilizates by micelle-forming and polymeric species in nonpolar solvents have been investigated by ultracentrifugation and densimetry (1), spectrophotometry (2-4), fluorescence depolarization (3), viscometry (5), phase changes (6-8), a variety of methods of observing vapor pressures and vapor compositions over solutions (3, 10-15), and by chemical analysis of solutions (9). The solubilizing and detergency properties of polymers have been related to their performance characteristics in internal combustion engines (16).

Fluorescence depolarization data indicated that with increasing concentrations of methanol (MeOH) in toluene solutions, sulfonate and carboxylate micelles decreased in size, and eventually ceased to exist at free MeOH mole fractions less than 0.06 (3). Deductions from the fluorescence data were made with the assumption that a negligible effect upon aggregation number resulted from the low concentration of fluorescent dye present. A molecule of the dye used as a fluorescent marker or tracer was assumed to substitute for a sulfonate or carboxylate monomer in the micelle or aggregate with which it was associated.

However, since these are assumptions, and since alcohol could be suspected of modifying the fluorescence upon which the measurement depended, further evidence is required to establish the validity of the conclusion that the alcohol alone in low concentration substantially influences the aggregation number. It has been reported that the dye markedly affects the micelle size of calcium dinonylnaphthalene sulfonate in *n*-decane (17, 18). However, a careful ultracentrifugal study in the absence of dye (19) yielded essentially the same aggregation number for dry benzene solutions of barium dinonylnaphthalene sulfonate ($\text{Ba}(\text{DNNS})_2$) as was obtained by the fluorescence depolarization method (20). The present investigation was undertaken to test the previous conclusion that solubilized MeOH in the absence of dye in nonpolar solvents reduced micelle size.

EXPERIMENTAL

Materials. *Methanol*, absolute—J. T. Baker Chemical Co., ACS grade, selected lot, containing less than 0.0015 mole fraction moisture. *Silica gel*—W. R. Grace and Co., Davison grade 950, washed with dilute HCl, rinsed with H_2O , and dried at about 160°C. *Benzene*—J. T. Baker Chemical Co.,

ACS grade, thiophene free, percolated over silica gel and stored over sodium. *Diethyl ether*—J. T. Baker Chemical Co., anhydrous ACS grade, percolated over silica gel and alumina. *n-Hexane*—Phillips Petroleum Co., technical grade (95 mole per cent, minimum; principal impurity: methylcyclopentane), percolated over silica gel and alumina. *Toluene*—Phillips Petroleum Co., pure grade (99.9 mole per cent; principal impurity: benzene), percolated over silica gel and stored over sodium. *Dinonylnaphthalene sulfonic acid* (HDNNS)—King Organic Chemicals, Inc., Norwalk, Connecticut; a special research grade supplied in moist heptane-methanol solution, described in previous publications (20, 21). The acid, freed of solvents by evaporation at reduced pressure, was redissolved in hexane, and purified chromatographically. The solution was loaded on a hexane-saturated column of silica gel containing 6 gm of silica gel for each gram of acid. Benzene, which advanced the HDNNS only slightly, eluted 1% to 2% of a nontitratable, nearly colorless, viscous fraction the infrared adsorption spectrum of which showed it to be of hydrocarbon composition. The HDNNS was eluted with a 20% (by volume) solution of diethyl ether in benzene. Two principal bands of adsorbate developed, the first of which was an 80% fraction and faintly yellow; the second was considerably darker. It could not be distinguished readily from the first by infrared spectra but was discarded nevertheless. Repetition of the separation failed to yield a hydrocarbon fraction, but the acid again separated into two bands with a repetition of 80% yield for the first. The ether was removed from the product by evaporation at reduced pressure.

Barium dinonylnaphthalene sulfonate ($\text{Ba}(\text{DNNS})_2$)—The refined HDNNS was neutralized with NaOH to form the sodium salt, which was lyophilized, redissolved in benzene, and percolated through silica gel. A small undetermined amount of dark yellow material remained in a band at the top of the column. $\text{Ba}(\text{DNNS})_2$ was prepared from the sodium salt by metathesis and finally lyophilized repeatedly from dry

benzene to remove traces of alcohol and moisture. Details of the preparation have been described earlier (14).

Measurements. The data of a previous investigation (14) were used to choose the compositions of solutions to be studied. Solutions were prepared from the same batch of $\text{Ba}(\text{DNNS})_2$ used in the previous study. In the experimental range of $\text{Ba}(\text{DNNS})_2$ solutions in toluene-MeOH (0 to 0.05 mole fraction unsolubilized or unbound MeOH) it was shown that the ratio of bound MeOH to total $\text{Ba}(\text{DNNS})_2$ is fixed by the free (unbound or unsolubilized) MeOH concentration in the solvent, irrespective of the $\text{Ba}(\text{DNNS})_2$ concentration. It was further concluded that the free MeOH concentration determined the state of aggregation of the soap.

To study the effect of MeOH on micelle size, five groups of solutions were studied. Each group included nominal $\text{Ba}(\text{DNNS})_2$ concentrations (by weight) of 2%, 4%, and 6%; the ratio of solubilized MeOH to $\text{Ba}(\text{DNNS})_2$ was held constant within each group. These ratios were 0, 0.5, 1.0, and 3.0 moles MeOH per equivalent weight of $\text{Ba}(\text{DNNS})_2$ for the first four groups. The solvents for these groups were toluene containing 0%, 0.017%, 0.078%, and 0.900% MeOH (by weight), respectively; the solubilized MeOH is not considered to be a part of the solvent. The solvent for the fifth group was pure MeOH, for which the solubilization ratio is unknown; additional nominal $\text{Ba}(\text{DNNS})_2$ concentrations of 0.5% and 1% were studied in this group.

Sedimentation velocity and diffusion measurements were made at 25°C with the Model E Spinco analytical ultracentrifuge, using schlieren optics. Rotor speeds were 59,780 and 10,589 rpm, respectively, for sedimentation and diffusion measurements. A 12 mm, 4° single sector cell was used for all sedimentation measurements except those where the free MeOH concentration corresponded to 3 moles MeOH bound per equivalent weight of $\text{Ba}(\text{DNNS})_2$ and for solutions in which the solvent was pure MeOH. For these a 12 mm 2½° double sector capillary type synthetic boundary cell was used; the latter type cell was used for all diffusion measurements.

In the synthetic boundary runs, toluene, MeOH, or the appropriate mixture of these was layered over the Ba(DNNS)₂ solution. Each of these mixtures was of the precise composition corresponding to the free MeOH concentration of the underlayered sulfonate solution.

Viscosity measurements were made at 25.00° ± 0.01°C with a Cannon-Fenske size 50 viscometer.

Densities were determined at 25.00° ± 0.01°C with a 10 ml modified Ostwald-Sprengel pycnometer capped at both ends to prevent evaporation.

RESULTS AND DISCUSSION

Treatment of the results of measurements included extrapolation of sedimentation and diffusion coefficients to infinite dilution for each set of solutions, and computation of the molecular weight of the sedimenting species by the Svedberg equation (22),

$$M = \frac{sRT}{D(1 - \bar{v}\rho)},$$

where M = molecular weight of the sedimenting species;

s = sedimentation coefficient of the sedimenting species;

R = gas constant;

T = Kelvin temperature;

D = diffusion coefficient of the sedimenting species;

\bar{v} = partial specific volume of the sedimenting species; and

ρ = density of the liquid through which sedimentation occurs.

Sedimentation coefficients determined in the single sector cells were corrected for retardation of the schlieren peak (19) before extrapolation; retardation need not be considered in the synthetic boundary cell. All extrapolated sedimentation coefficients were corrected for the pressure effects on solvent density and viscosity (23, 24). Approximations of compressibilities and viscosities under pressure were interpolated from data in the literature (25, 26). Compressibility of the sulfonate was neglected, since no pertinent data were available; this factor would contribute least to the combined corrections. The

effect of the pressure corrections is to estimate the sedimentation coefficient under buoyancy and viscosity conditions at atmospheric pressure.

Diffusion coefficients were computed by the maximum ordinate method (27). No attempt was made to correct diffusion coefficients because at the pertinent rotor velocity (10,589 rpm) results should approach those corresponding to atmospheric pressure.

For its use in the Svedberg equation, the value of \bar{v} , the partial specific volume of the sedimenting species for each set of solutions, was derived from the apparent density of the solute. Where the solvent was either pure toluene or pure methanol, the evaluation is straightforward; the apparent density of the solute was extrapolated to infinite dilution after its computation from the solvent density and the concentration and density of each solution in the group. The evaluation of \bar{v} in mixed solvents was derived by extrapolation of apparent densities computed in a less direct manner. In the latter case, the solute is the sulfonate and its bound MeOH combined. Thus the weight of the Ba(DNNS)₂ plus the solubilized MeOH was taken as the weight of solute in the solution. The composition of the solvent phase was selected on the basis of previous experience (14) as mentioned above, and its density could be determined separately.

Numerical results derived from the ultracentrifugal and densimetric measurements are tabulated in Table I. The slight reversal of order in diffusion coefficients of such measurements for small molecular weights by the ultracentrifugal method; this minor irregularity does not affect the more important qualitative conclusions. Although only a small decrease in aggregation is apparent when up to 1 mole of MeOH is solubilized per equivalent weight of soap, the computed aggregation number diminishes from about 10 to about 4 as the solubilization ratio proceeds from 0 to 3. At the solubilization ratio 3.0, it should be observed that the free MeOH concentration in the solvent is less than 1% by weight,

TABLE I
EFFECT OF SOLUBILIZED METHANOL ON PROPERTIES OF BARIUM
DINONYLNAPHTHALENE SULFONATE MICELLES

Free MeOH concentration in solvent (weight %)	Solubilization ratio R_s (moles MeOH / equiv. wt. sulfonate)	Sedimentation coefficient s (sec $\times 10^{13}$)	Diffusion coefficient D ($\text{cm}^2/\text{sec} \times 10^7$)	Partial specific vol. of solute \bar{v} (cc/gm)	Solvent density ρ (gm/cc)	gm-equivalent wt. of solute	gm-micelle wt. of solute	Aggregation no. (Acid residues aggregate)
0	0	1.98	33.5	0.851	0.8623	528.37	5505	10.4
0.017	0.5	1.90	34.7	0.854	0.8622	544.39	5138	9.4
0.078	1.0	1.73	33.3	0.877	0.8623	560.41	5275	9.4
0.900	3.0	1.06	45.0	0.901	0.8615	624.49	2605	4.2
100.000	^b	0.83	67.2	0.752	0.7866	528.37 ^b	750	1.4

^a Extrapolated to infinite dilution.

^b See text.

and its mole fraction is less than 0.03. The results confirm the trend in aggregation number observed by measurements of fluorescence depolarization with sodium and magnesium dinonylnaphthalene sulfonates and magnesium phenylstearate in benzene (3). The results for solutions in pure MeOH are consistent with the general trend, and demonstrate that micelles of Ba(DNNS)₂ do not exist in this solvent. Light-scattering studies of Aerosol OT in methanol and ethanol have indicated the absence of micelles (28), and conductivity studies have shown lithium and cesium dinonylnaphthalene sulfonates to be ionically dissociated in the same solvents (29). The extent of solvation of the sulfonate in pure MeOH cannot be deduced from the experimental data obtained here, but previous measurements (14) assure that it is greater than 5 moles of MeOH per equivalent weight of soap (10 moles MeOH/mole Ba(DNNS)₂).

Viscometric data obtained are displayed in Figs. 1 and 2. The ordinate in these plots is $(\eta - \eta_0)/\eta_0\phi$, where η and η_0 are the viscosities of the solution and solvent, respectively, and ϕ is the volume fraction of the solute in the solution. The abscissa is the concentration of the solute species in grams solute per cubic centimeter of solution. The solute is considered the sulfonate plus the MeOH solubilized by it. The solvent, as in the considerations of sedimentation and diffusion, is the toluene-MeOH mixture whose equilibrium free

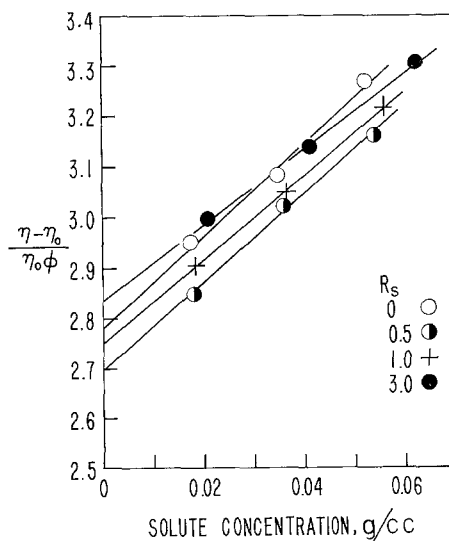


FIG. 1. Viscosity functions of barium dinonylnaphthalene sulfonate-methanol species in toluene-methanol solutions at constant solubilization ratios, R_s . R_s = moles MeOH solubilized/equivalent wt. sulfonate.

MeOH concentration corresponds with the appropriate solubilization ratio.

For rigid, unsolvated spheres the Einstein equation (30) requires $(\eta - \eta_0)/\eta_0\phi$ to be 2.5 at infinite dilution. Restricted conditions for validity have given rise to many modifications of the Einstein equation, but the simple formulation is adequate for the purpose intended here (31). Extrapolated values in Fig. 1 fall between 2.70 and 2.84 for all the systems where the solvent is

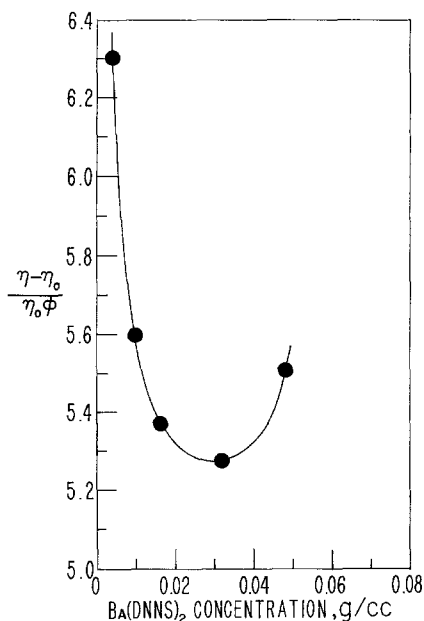


FIG. 2. Viscosity function of barium dinonylnaphthalene sulfonate in pure methanol.

either pure toluene or toluene-methanol (solubilization ratio, R_s , 0 to 3.0 moles MeOH per equivalent weight of sulfonate). Deviations from the value of 2.5 are usually attributed either to asymmetry of the particles or to solvation. Inasmuch as the solvate has been explicitly included with the solute, it is likely that the deviation is essentially due to asymmetry. With this assumption, and considering the solute to be present as prolate ellipsoids (32), the asymmetry is estimated to be 1.6 to 1.9 (33), which is a small deviation from sphericity.

The plot in Fig. 2, however, shows characteristics radically different from those in Fig. 1. Here the solvent is pure MeOH, and there is no information about the extent of solvation of the sulfonate. Hence the solute is taken as the sulfonate alone for purposes of this plot.

The ultracentrifugal results indicate a monomeric or more finely divided dispersion (aggregation number less than 2 acid residues per particle) in pure methanol, but the viscometric data are more revealing. The Einstein viscosity function is properly

applicable only when the solute species does not change with concentration, and it normally decreases monotonically with decreasing concentration. The anomalous behavior in pure methanol suggests increasing ionic dissociation with dilution. As the concentration decreases, the increasing proportion of charged ions can be expected to increase the effect of solute on viscosity, both because of the electroviscous effect and because of the greater interaction of the dipolar solvent with the separated ions.

SUMMARY

The data confirm the previous conclusion (3) that free methanol concentrations of less than 1% in toluene interfere with micelle formation of dinonylnaphthalene sulfonates. With increasing methanol concentration, the progressive solubilization decreases the degree of aggregation, but the approximate spherical shape of the diminishing aggregate is retained. In pure methanol at concentrations above 0.04 g/cc, the solute may be considered essentially monomeric, but with further dilution it dissociates ionically.

The formation of association micelles in nonpolar solvents may be visualized as the result of a greater decrease in free energy by bonding between the polar sulfonate monomers than by interaction with the nonpolar solvent species. The geometry of the species leads to a closed aggregate of limited size if no other polar species is present to compete for these bonds. However, the highly polar methanol successfully competes, and the methanol-sulfonate bond results in a greater decrease in free energy than the self bonding of the sulfonate molecules. As a consequence a quantity of methanol is demobilized (solubilized), with a resulting decrease in its activity coefficient (34). Simultaneously, the availability of the micelle-forming species for self bonding is lessened, and any increase in the total methanol concentration further decreases this availability until no self association can take place between the sulfonate molecules, and the micelles cease to exist.

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