The Solution Properties of Some Polyoxyethylene-Polyoxypropylene Surfactants in Nonaqueous Solvents[1]

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Abstract

Results obtained with Pluronic polyol homologues in benzene and in dioxane by light-scattering, ultracentrifugal and vapor pressure lowering measurements in addition to data obtained in water and in butyl chloride by light-scattering and ultracentrifugal determinations are described. The systems are examined over a wide range of solute concentrations at about 37C. Considerable difference appears to exist between weight and number-average micellar weight obtained by light-scattering and two methods of measuring vapor pressure lowering of the solutions. Divergence in micellar weight values appears to be less pronounced between the latter technique and ultracentrifugal determinations. Possible micellar configurations of these Pluronic polyols are presented.

Introduction

SURFACE ACTIVE AGENTS composed of polyoxyethylene-polyoxypropylene block copolymers, sold commercially as Pluronic surfactants, are unique in that the hydrophilic groups are placed on both the head and tail of the polyoxypropylene chain. This type of surfactant exhibits a critical micelle concentration in aqueous solutions as evidenced by dye absorption and by surface tension measurements (1), but apparently solute association was not detected by ultracentrifugal measurements (2) and no aggregation was found by light-scattering determinations (3). This communication presents additional information concerning the solution properties of several Pluronic polyols in aqueous and nonaqueous solvents.

Light-scattering and ultracentrifugal determinations were carried out in benzene, dioxane, butyl chloride and in water. Some light-scattering and "osmometric" measurements were attempted with one surfactant (F68) in moist benzene. Vapor pressure lowering determinations were made in benzene, using a vapor pressure "osmometer" and also by means of a sensitive differential mercury micromanometer, in rigorously dry benzene and in dioxane using milligram quantities of materials.

Experimental

Light-Scattering

Weight average molecular weights ($\overline{M}_w$) of F38, F68, F88, and F108 were measured by light-scattering using a Sofica P.G.D. Instrument which has been calibrated previously (4). All measurements were made using unpolarized blue light ($\lambda = 4358$ Å) on solutions contained in cylindrical cells which were thermostatted at 37.0 ± 0.2C, with the exception of aqueous solutions where the temperature was 25.0 ± 0.2C. Scattering intensities were read at 45°, 90°, and 135° and the instrument response was maintained by constantly checking it with a glass standard which had been calibrated against the 90° scattering of pure benzene at the temperature of measurement. Solutions were clarified by filtration into a heated cell through fine grade sintered glass filters, which were kept at 40C by water circulating in a jacket surrounding the filter.

The Rayleigh ratio of benzene was taken (4) as 49×10^{-6} and weight average molecular weights ($\overline{M}_w$) were calculated from the excess turbidity measured at 90°. Dissymmetries were also estimated.

The refractive index increment (dn/dc) at 37C was measured on a Brice-Phoenix differential refractometer using blue light ($\lambda = 4358$ Å). The value obtained in dry benzene was −0.028, in wet benzene −0.037, in dioxane 0.047, in butyl chloride 0.074 and in water at 25C, 0.138.

Ultracentrifuge

A value of ($\overline{M}_w$) for F68 was also obtained from the ultracentrifuge using the short column equilibrium method. A Spinco Model E ultracentrifuge equipped with a rotor temperature control unit and Schlieren phase plate optics was used. Solutions were injected into 12 mm double sector cells which allow simultaneous examination of solution pattern and solvent base line. The column length was normally 3 mm with 0.05 ml of mercury as the bottom layer to reduce the possibility of convective disturbances. However, in aqueous solutions a multichannel centrepiece was employed in which the liquid column height was 1 mm and FC 43 oil was used on the cell bottom.

The concentration range examined varied between 0.4% and 4.3% and rotor speeds of 35,600 rpm were used. The apparent molecular weight (M_w) was calculated as previously described (5) and was plotted against concentration to give $\overline{M}_w$ at zero concentration.

Partial Specific Volume

Solution densities in nonaqueous solvents were measured at 37C in a Sprengel-Ostwald pyknometer whose volume was approximately 21 ml. Partial specific volumes were calculated from the densities and values obtained were 0.904 ml/g in benzene, 0.891 ml/g in butyl chloride, 0.910 ml/g in dioxane, and 0.890 ml/g in water at 25C.

Viscosity

Intrinsic viscosities were measured using a Cannon-Ubbelohde semi-micro dilution viscometer which was reproducibly positioned, by a triple point suspension system, in a bath thermostatted at 37.0 ± 0.01C.

Vapor Pressure Lowering

In the vapor pressure work the commercial samples of Pluronic polyols L31, L33, L35, F38, F68 and F88 were used without further purification. The solute was evacuated at room temperature in order to remove volatile material. The experimental method

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TABLE I

$\overline{M}_w$ Micellar Weights of F68, F38, F108, and F88 in Different Solvents by Light-Scattering Determinations

Surfactant	Benzene		Dioxane		Butychloride		Water	
	$\overline{M}_w$	n	$\overline{M}_w$	n	$\overline{M}_w$	n	$\overline{M}_w$	n
F68 (8,750)	35,700	4	69,600	8	11,300	1.5	18,600	$\sim$2
F38 (4,750)	21,000	$\sim$4	13,050	$\sim$3	....	....	7,300	$\sim$2
F108 (16,250)	37,500	$\sim$2.5	27,870	$\sim$2	....	....	....	..
F88 (11,000)	....	....	34,800	$\sim$3	....	....	....	..

and the apparatus used for carrying out differential vapor pressure measurements between pure solvent and solutions have been described elsewhere (6). The determinations were carried out at about 37C and the apparent molecular weights were calculated from Raoult's law. Some measurements were also carried out in benzene at 37C using a Mechrolab vapor pressure "osmometer" Model 301. The instrument was calibrated with solutions of freshly recrystallized benzil (mol wt 210.22) below 0.01 molal in order to examine the surfactants at moderately low concentrations.

Results and Discussion

Results obtained by light-scattering for F68, F38, F88 and F108 in different solvents are shown in Table I. Sample F68 showed most evidence of micelle formation when examined by this method. The values of $\overline{M}_w$ are calculated from the scattering at 90° and are therefore minimum values. Dissymmetry measurements in benzene and in dioxane indicated the value (I_{45}/I_{135}) to be about 1.5 in both cases, and the resulting corrections increase the value of $\overline{M}_w$ to 49,000 in benzene and 95,000 in dioxane. Little evidence could be found of micelle formation in butyl chloride, while in water dimers were the only form observed. Measurements on F38 and F108 show only dimers, trimers and tetramers in the various solvents. Samples of F38 and F68 in water, benzene, and dioxane, behave as associating systems whereas F108 in benzene and dioxane, F88 in dioxane, and F68 in butyl chloride are similar to normal polymer systems in which the apparent molecular weight decreases with increasing concentration.

Light-scattering measurements were made on sample F68 in "dry" benzene and in benzene saturated with water; these results are shown in Figure 1. Turbidities are indicated in Figure 2. The effect of even this small amount of water is quite marked. The micellar weight increased from 35,700 to 64,000 in wet benzene. Dissymmetries were high and of questionable validity, thus the micellar weights quoted are, of necessity, minimum values. A marked increase in the excess turbidity in the case of wet benzene is reflected by an increase in the size of the micelle. It appears also that this polyoxyethylene-polyoxypropylene copolymer is strongly hydrophilic as evidenced by the apparent low association in water. The increased association in moist benzene is probably caused by the sorption of water by the polyoxyethylene portion of the surfactant. Water solubilized in the micelle can possibly bridge further quantities of detergent molecules into the system. This appears consistent with the results reported by Kitahara (7) for nonylphenol-ethylene oxide adducts in cyclohexane. An increase of less than 10% was indicated in the apparent number average molecular weight at finite concentrations with solutions of F68 in moist benzene.

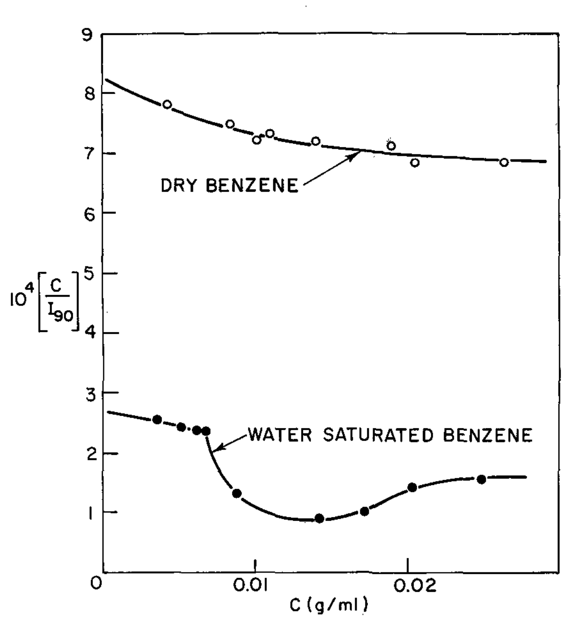

FIG. 1. Light-scattering measurements as a function of solute concentration for F68 in dry benzene and in wet benzene.

Ultracentrifuge

Results obtained with the equilibrium ultracentrifuge for F68 in benzene, dioxane, butyl chloride and in water are shown in Figure 3. This material behaved as a normal polymer system and only in the case of benzene was association detected. In benzene the association number is 3 compared to 4 (or 5.5 if dissymmetry is allowed for) as measured by light-scattering. However, the discrepancy in dioxane is much more marked as no association can be detected by centrifugal techniques, while light-scattering results would suggest that association numbers between 8 and 11 are to be expected. Possibly one could explain this by postulating the presence of a small number of large clusters which can be observed by light-scattering but are disrupted under the in-

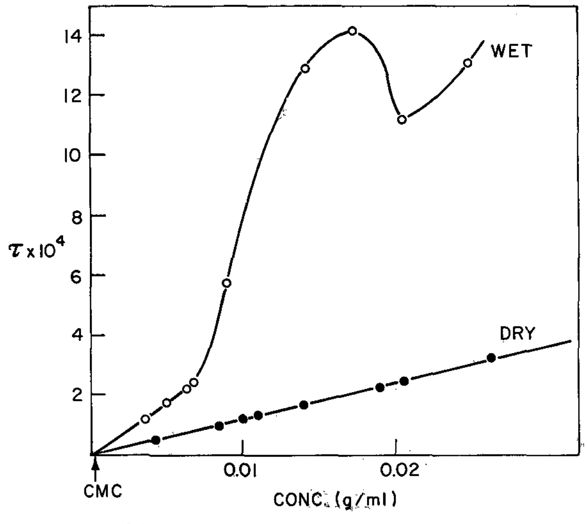

FIG. 2. Turbidity versus solute concentration for F68 in dry benzene and in wet benzene.

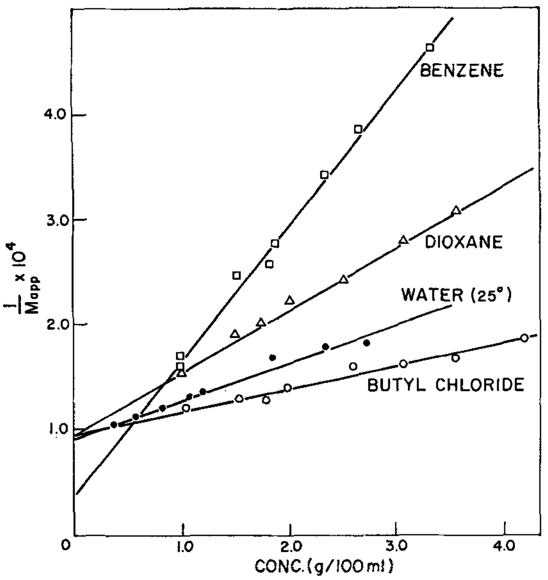

FIG. 3. Apparent weight average molecular weight versus solute concentration obtained by ultracentrifugal measurements for F68 in benzene, dioxane, butylchloride and in water.

fluence of the strong force field experienced in the ultracentrifuge or to a very broad spectrum of molecular sizes present in the system. The possibility that nonequilibrium conditions exist in solutions examined by light-scattering and that the demicellization process is enchanced by the additional force experienced in the ultracentrifuge perhaps should not be overlooked.

Vapor Pressure Results

The variation of the apparent number average molecular weight ($\overline{M}n$) with solute concentration for a series of Pluronic polyols in benzene at about 37C as measured by vapor pressure lowering is shown in Figure 4, Curves 1, 2, 3, 4, and 5 for L31, L33, L35, F38, and F68, respectively. The points with open and solid circles were determined with a model 301 Mechrolab "osmometer," the others by employing rigorously dry solvent and the differential Mercury Micromanometer. The agreement between the two methods of measuring the colligative properties of solutions is good in moderately concentrated solutions. At low solute concentrations deviations appear to occur probably owing to deficient sensitivity of the "osmometer," to loss of low molecular weight volatile material from the solute while being repeatedly evacuated (in order to prepare solutions of different concentrations under hermetically sealed condition in the case of static vapor pressure measurements), or to the rigorous drying which is possible with this system. The data indicate, however, that the surfactants below about 2000 in molecular weight (L35, L33 and L31) behave like low molecular weight polymers and do not appear to associate in benzene when examined by this technique. On extrapolation to infinite dilution the $\overline{M}n$ is found to be in good agreement with the value expected from the Pluronic grid. The surfactants F38 and F68 which differ in the molecular weight of the hydrophobic base behave like moderately high molecular weight polymers and these show pronounced dependence on concentration. Assuming the formula weight given by the manufacturer, the extrapolation of the experimental points to infinite dilution suggests the presence of associated material in benzene. Since association of monomer and solvation effects are probably taking place simultaneously over the concentration range examined, it is difficult to estimate the micellar weight of the associated species. A value of about 12,000 at infinite dilution suggests, however, that dimers or possibly associated material of higher order are present in the case of F68.

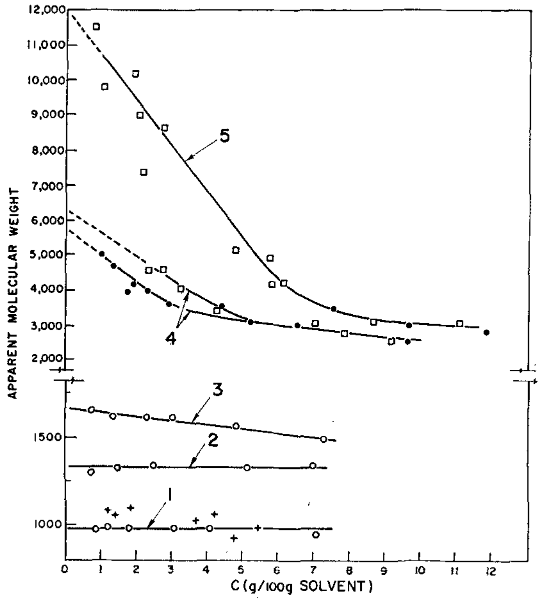

FIG. 4. Apparent molecular weight versus solute concentration for a series of Pluronic polyols in benzene at about 37C. The points with the open and solid circles were determined with the "Osmometer," the others by static vapor pressure measurements. Curve 1, L31; Curve 2, L33; Curve 3, L35; Curve 4, F38; and Curve 5, F68.

The results obtained in dioxane are shown in Figure 5 where apparent molecular weight versus solute concentration is plotted. Curves 1, 2, and 3 were obtained for F38, F68, and F88, respectively. These materials contain 80% ethylene oxide and are in the order of increasing molecular weight of the hydrophobic base. Above about 3% concentration the solutions behave as normal polymers and with the possible exception of F88, curve 3, the experimental points fall reasonably well on a linear plot. The number average molecular weights of F38, and F68 at infinite dilution appear to be slightly higher than the formula weight of these compounds. In the case of F68, this is in good agreement with the data obtained by ultracentrifuge measurements. The value is at considerable variance with the light-scattering results, however.

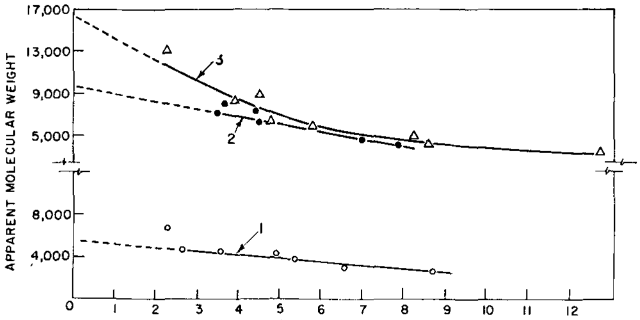

FIG. 5. Apparent molecular weight versus solute concentration for a series of Pluronic polyols in dioxane at about 37C, using a differential micromanometer. Curve 1, F38; Curve 2, F68; and Curve 3, F88.

One could possibly presume that nonequilibrium states exist in dioxane solutions in which a small number of large clusters gradually demicellize with time. As shown in the case of Aerosol OT in toluene (8), these have very little effect on the number average molecular weight but appear to have a marked effect on the weight average molecular weight obtained by light-scattering (8).

Micellar Shape

The shape of the micelle is somewhat difficult to determine as the evidence is internally inconsistent. The dissymmetry measurements indicate values considerably greater than unity which would suggest that the micelle is not spherical in shape. However, the intrinsic viscosity of F68 in benzene indicates that the micelle might approximate an unsolvated sphere as it was in close agreement with the Einstein equation for spherical particles.

$$\text{(i.e. } [\eta_{\mathrm{sp}}/\phi]_{\phi=0} = 2.2 \text{ instead of } 2.5)$$

Scherage and Mandilkern have related various models to shape a factor β defined as

$$\beta = N_A S [\eta]^{1/3}\ \eta/M^{2/3}\ (1 - \overline{V}\rho)$$

where N_A is Avogardo's Number, S the sedimentation constant, $[\eta]$ the intrinsic viscosity, η the solvent viscosity, ρ the solvent density, and $\overline{V}$ the partial specific volume of the solute.

The sedimentation constant of F68 in benzene at 37C was determined using a double sector capillary type synthetic boundary cell. A value of $S = 2.3 \times 10^{-13}$ was obtained, which gives $\beta \approx 3 \times 10^{-6}$ if the molecular weight corrected for dissymmetry is used in the equation. This would be representative of a prolate spheroid with an axial ratio of about 50 and suggests that the micelle is nonspherical. Thus the dissymmetry and sedimentation results indicate that nonspherical association complexes exist in solution.

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REFERENCES

1. Schmolka, I. R., and A. J. Raymond, JAOCS *42*, 1088 (1965).
2. Dwiggins, C. W., Jr., R. J. Bolen, and H. N. Dunning, J. Phys. Chem. *64*, 1175 (1960).
3. Mankowich, A. M., J. Phys. Chem. *58*, 1027 (1954).
4. Cowie, J. M. G., and S. Bywater, Polymer *6*, 197 (1965).
5. Sirianni, A. F., J. M. G. Cowie and I. E. Puddington, Can. J. Chem. *40*, 957 (1962).
6. Sirianni, A. F., and I. E. Puddington, Can J. Chem. *33*, 755 (1955).
7. Kitahara, A., J. Phys. Chem. *69*, 2788 (1965).
8. Corkill, J. M., J. F. Goodman and T. Walker, Trans. Faraday Soc. *61*, 589 (1965).

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