Osmometric Study of Commercial Surfactants

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Abstract

The micellar weights of Tergitol 15-S-9 (Union Carbide) and of Neodol 25-9 (Shell Chemical Co.) were determined by membrane osmometry in water as 98,000 and 82,000, respectively (36.5 C). Both surfactants contained a small amount of a nonassociating component. The micelles were found to be extremely stable. The micellar weight of Aerosol OT (American Cyanamid) was determined as $<5,900$ (toluene, 34 C). The results of this investigation indicate the usefulness of membrane osmometry in the determination of micellar weights of surfactants. Information with respect to the stability of the micelles and the dialytic behavior of surfactants in general can be obtained from the osmotic pressure-time curve.

Introduction

In a previous report (1) it was shown that membrane osmometry is suitable for determining the degree of micellization of surfactants. This was demonstrated in a study of an ionic detergent (sodium dodecyl sulfate) in aqueous solution.

The present investigation served mainly to compare two ethylene oxide alcohols, one (LPA) derived from linear primary alcohols (Neodol 25–9; Shell Chemical Co.), the other (RSA) derived from random secondary alcohols (Tergitol 15-S-9; Union Carbide).

Some measurements on a sample of Aerosol OT were included. Measurements on this surfactant in toluene preceded the work on sodium dodecyl sulfate. These earlier results demonstrated the feasibility of determining the molecular weight of association compounds by membrane osmometry, and encouraged the further investigations.

It should be borne in mind that the present surfactants are commercial products whose composition and purity are not precisely defined. Nevertheless, they are believed to be typical for their class of compounds.

Experimental Procedures

All measurements were made with automatic recording osmometers of Shell design (2). For aqueous solutions we used an instrument lent to us by Hallikainen Instrument Company (Richmond, Calif.), and a membrane with designation B 20 (Schleicher and Schuell, Keene, N. H.). The cell temperature was set at 36.5 C. For the measurements on Aerosol OT in toluene we used an osmometer manufactured by Dohrmann Instrument Co. (Mountain View, Calif.) and membranes of the type 0 8 (Schleicher and Schuell). The cell temperature was 34 C.

All readings of osmotic pressure were preceded by rinsing of the sample as well as the solvent cell of the osmometer and by a blank run (solvent in both cells). The subsequent pressure readings of the surfactant solutions were multiplied by 1.04 to correct for incomplete replacement of the previous contents of the sample cell (1,2).

The osmometer constants, RT, were 2.64×10^4 for the aqueous solutions and 3.02×10^4 in the case of toluene, the pressures being read as centimeters of solvent and the concentration expressed as grams per liter.

Some further experimental details are included in the following sections.

RSA

RSA (Tergitol 15-S-9; Union Carbide) is a commercial nonionic surfactant. It is a mixture of alkyl oxyethyleneglycol ethers derived from random secondary alcohols (C_{11} to C_{15}) containing, on the average, approximately 9 EO per molecule. At room temperature the sample showed a slight turbid sediment. The density was determined as 1.001 (25 C), the viscosity as 65 centistokes. The refractive index increment in water was found to be 0.132 cc/g ($\lambda = 5460$).

The solutions for osmometry were prepared with partially degassed water (or 0.03 M sodium chloride solutions). The samples were stirred for 1 hr or longer before being transferred to the osmometer. Stirring for a shorter period, until the liquid was homogeneous to the eye was apparently sufficient, since no effect of sample history on the osmotic pressure was discernible.

Figure 1 shows typical osmotic-pressure-time curves replotted on semilog paper. After an initial equilibration period of about 30 min a decrease of pressure occurred. After approximately 4 hr the pressure reached a level which remained virtually constant. This plateau value was then taken as the osmotic pressure (P) due to the RSA micelles. The

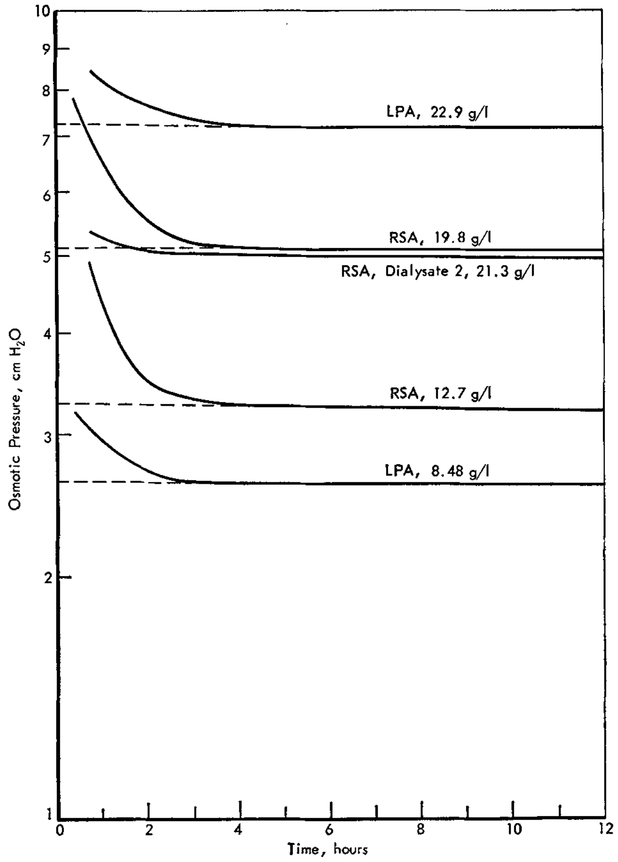

FIG. 1. Change of osmotic pressure with time.

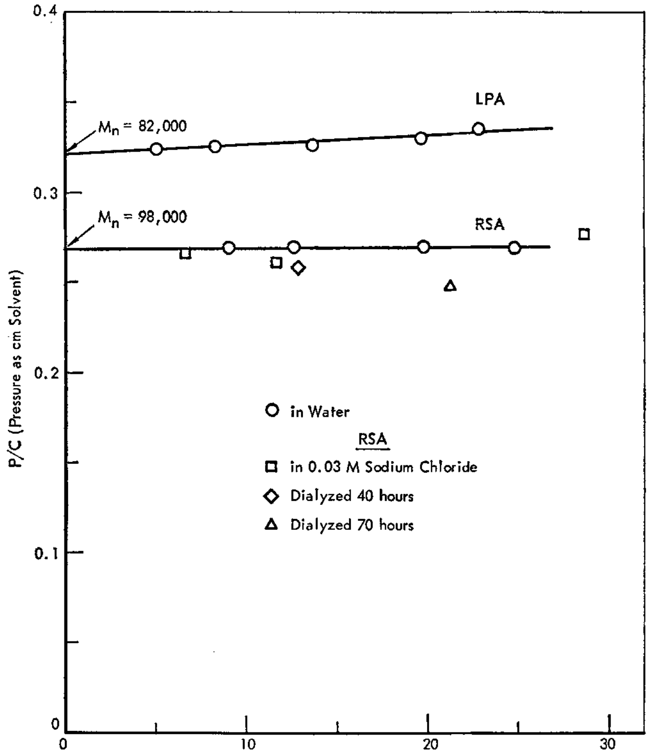

FIG. 2. Plot of reduced osmotic pressure vs. concentration.

results, plotted as P/c versus c are shown in Figure 2. The number-average micellar weight is calculated from the intercept as M = 98,000 (36.5 C, water). The osmotic pressures in 0.03 M sodium chloride solution are consistent with this result. The second virial coefficient, within experimental error, is equal to zero.

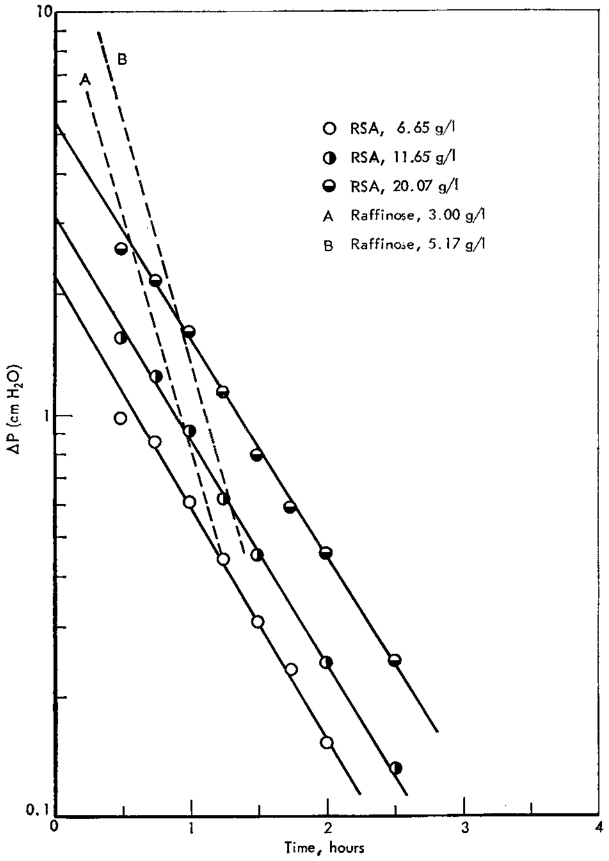

FIG. 3. Transient osmotic pressures.

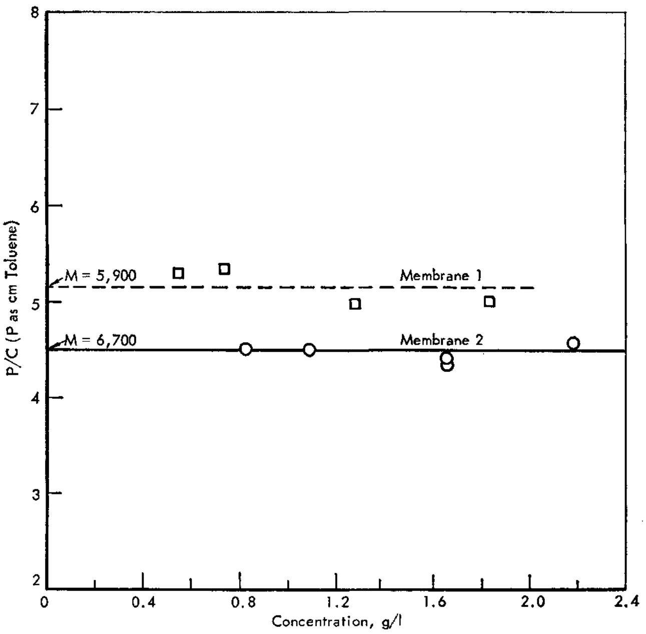

FIG. 4. Reduced osmotic pressure vs. concentration; Aerosol OT, 34 C.

A semilog plot of the transient part of the osmotic pressure time curve, $\Delta P = P_{total} - P_{plateau}$, is shown in Figure 3. The plots are linear within experimental error (half time = 35 min). This can be interpreted (3) as the presence of a monodisperse (or only slightly heterodisperse) component which is capable of permeating through the membrane. The rate of pressure decrease is compared with that of raffinose (mol wt 504.4). Raffinose diffuses more rapidly through the membrane (half time = 15 min). This suggests that the molecular weight of the RSA component is larger than 500, assuming that the permeability of the membrane is not affected by the presence of the surfactant and that structural effects on the rate of membrane permeation are not too different for the two substances (3). These assumptions appear to be reasonable. Measurements on the transients were made in 0.03 M sodium chloride, but there is no indication that the salinity of the solutions has any effect on the diffusion rate across the membrane.

We then tried to remove the diffusible component by dialysis through cellophane dialyzer tubing of 48 A nominal pore size (Arthur H. Thomas, Philadelphia, Pa.).

In the first experiment (dialysis 1) 200 ml of a 3% solution in water was dialyzed against 20 liters of water (changed once) for 40 hr. The dialyzer tube diameter was 27/32 in. About 60% of the diffusible component was removed.

The experiment was repeated with 100 ml of a 2.5% solution in ⅝ in. tubing for 70 hr against 20 liters of water which was stirred. As shown in Figure 1, this operation removed between 80% and 90% of the diffusible component (dialysis 2). The concentrations were subsequently determined by measuring the refractive index of the solution against water in an automatic differential refractometer (Shell design). The reduced osmotic pressures of the dialyzed solutions are recorded in Figure 2. These pressures fall somewhat below the other points of the Tergitol series. This disagreement may be due to differences of refractive index between solution components, for instance, since the determination of concentrations was based on measurements of this quantity. It may be concluded that the transient osmotic pressure is not caused by monomer in equilibrium with the micelles, as was the case in the measurements on sodium dodecyl sulfate (1). This conclusion is also supported by the results of Balmbra et al. (4) which suggest a very low critical micelle concentration.

LPA

LPA (Neodol 25–9; Shell Chemical Co.) is derived from primary alcohols (C_{12} to C_{15}) with over 75% normal alcohol content. Analysis by thin layer chromatography (5) revealed 2%, by weight, of unreacted alcohol and an ethoxylate (EO) distribution from 1 EO to 15 EO and beyond, with a maximum at 9 EO. This last figure is considered to be the average number of EO per molecule of surfactant. At room temperature the material was solid, but could easily be liquefied by warming in a water bath. The liquid was thoroughly stirred before weighing out samples for osmometry. The experimental procedure was the same as for Tergitol.

The osmotic pressure-time curves (Fig. 1) resemble those of Tergitol. Again, a transient part is evident, although somewhat smaller than in the previous case. Plots of ΔP were similar to the ones shown in Figure 2, although somewhat more erratic. The intercepts at $t = 0$ were smaller (lower concentration of the diffusing component). The slopes likewise appeared somewhat smaller, but the differences were not significant.

Again, after the initial transient portion, the osmotic pressure remained virtually constant. The micellar weight calculated from the plateau was 82,000. The second virial coefficient was slightly positive, $B = 2.2 \times 10^{-8}$ liter/g (36.5 C, water).

Balmbra et al. (4) have studied the micellization of pure alkyl hexaoxyethlene glycol monethers, which despite the lower EO content can be considered as very similar to LPA (and RSA) in their solution properties. These authors find that the micellar weight is not constant. Between the cmc and a concentration (c_L) which is several times as large as the cmc, the micellar weight increases with concentration. Beyond c_L the micellar weight remained essentially constant. In the present case of RSA and LPA all measurements were made above c_L; a further significant increase of micellar weight would give rise to a negative second virial coefficient which is not borne out by our plots of P/c vs. c. If we assume the uncharged micelles to be compact and spherical we can estimate B from the excluded volume effect as $B = 4v_2/M$, v_2 being the specific volume of the micelle, M the molecular weight. With $v_2 = 10^{-3}$ liter/g, and $M = 10^5$, $B = 4 \times 10^{-8}$ liter/g. This is the right order of magnitude in the case of LPA. In the case of RSA where $B = 0$ one may perhaps argue for a slight increase of micellar weight with concentration.

According to Balmbra et al. (4) the micellar weights of these nonionic surfactants are quite dependent on temperature, M increasing with temperature. Furthermore, chain length of the alcohol has a distinct effect on the micellar weight. Since LPA as well as RSA represent mixtures, we must expect the micellar weight to depend on the formulation of the sample. By comparison with data from light scattering, for instance, one can also establish whether the micelles are polydisperse.

Aerosol OT

Aerosol OT (di[2-ethylhexyl] sodium sulfosuccinate; monomer weight 444) is known to form micelles in nonaqueous solvents such as *n*-dodecane (6).

The material which we studied was supplied by American Cyanamid. Its water content was determined as 1.6%. The level of other impurities was not known. It dissolved readily in toluene.

Osmotic pressure-time curves were measured by the usual procedure. The experiments were repeated with a second membrane of the same designation (O 8) which gave pressures lower by 10–15% (Fig. 4). Typical pressure-time curves are shown in Fig. 5.

The appearance of these curves is unusual. From theoretical considerations as well as on the basis of a large number of previous experiments (3) one should expect the plot of log P vs. time to be either linear or exhibit slopes which decrease with time. The steepening of the slopes towards the end of the run cannot be readily explained. Also, the much slower permeation in the case of the highest concentration in Figure 5 is unexpected. We suspected sorption of the surfactant in the membrane as a possible cause for this behavior. Sorption is indeed suggested by the following observation; when solute permeates through the membrane the osmotic pressure decreases and ultimately approaches zero as the concentrations in the sample and solvent cell become equal. The two cells in our instruments are of equal volume, hence, the final concentration $c_f = c_o/2$. If one now flushes the solvent cell with pure solvent, a concentration difference, $c_{sample} - c_{solvent} = c_o/2$ is

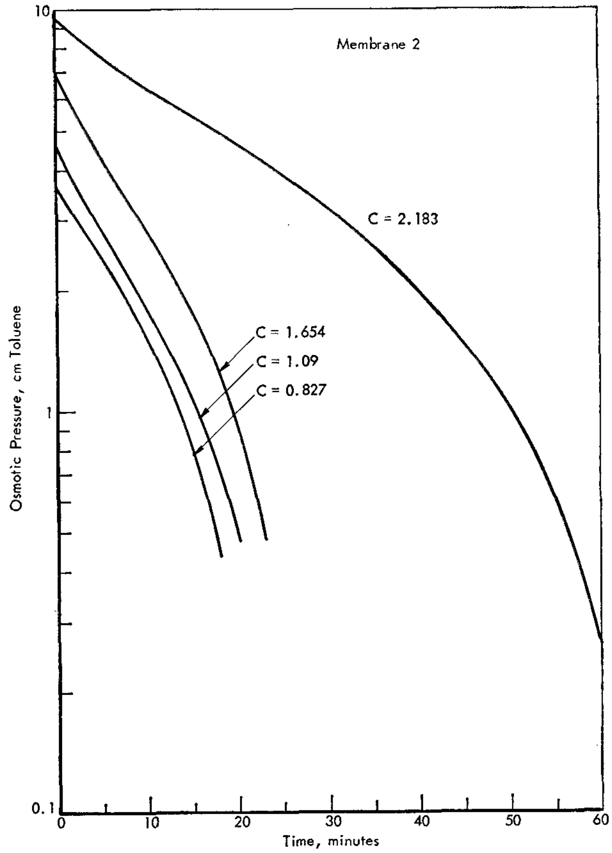

FIG. 5. Osomotic pressure vs. time; Aerosol OT in Toluene.

reestablished across the membrane, and the osmotic pressure should be approximately one half of the value measured initially. This effect was found, for instance, with n–$C_{36}H_{74}$ as the solute. The same test, when applied to Aerosol OT solutions, however, did not raise the pressure from its very small terminal value. Apparently, there was no Aerosol OT in the solvent cell, although the osmotic pressure had declined almost to zero. This strongly indicates that extensive sorption in the osmometer membrane takes place.

The osmotic pressures, extrapolated to $t = 0$ gave very reasonable and rather consistent values (Fig. 4). This extrapolation to $t = 0$ differs from the procedure applied in the case of LPA and RSA when the molecular weight was calculated from a plateau value of the osmotic pressure. Such a plateau does not exist in the present case. Moreover, the initial transient of the pressure is less pronounced. The pressure at $t = 0$ is therefore the most meaningful quantity for the purpose of calculating the micellar weight, although the resulting M_n includes a small contribution from nonassociating components if they are present in the sample. From the two sets of data in Figure 4, obtained with different membranes, one calculates $M = 5{,}900$ and 6,700. Because of solute permeation even the lower value is likely to be somewhat high (Staverman effect) (7).

The agreement with $M_n = 5{,}900 \pm 1{,}000$, reported by Corkill et al. (8) the result of vapor pressure measurements in toluene, is surprisingly good. Their substances, however, were probably of greater purity, and we may suspect the good agreement to be fortuitous.

Aerosol OT in water, without supporting electrolyte, gave high osmotic pressures as a result of ionic dissociation of the surfactant. In 0.03 M sodium chloride solution, at a concentration of 3.5 g/liter, the pressure initially declined with a half-time of about 1 hr and then leveled at the rather low value of approximately 0.5 cm H_2O. But about the same osmotic pressure-time curve was obtained with a solution containing 10.1 g/liter Aerosol OT. The solutions appeared turbid. Heating to some extent cleared up the turbidity, which reappeared upon cooling. This observation together with the unusual result from osmometry suggested that a phase separation occurred; the invariance of the osmotic pressure with concentration can be explained by the limited solubility of Aerosol OT in aqueous solution. It did not appear profitable to pursue this particular study any further.

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