Micellar Properties of Polyoxyethylene Nonylphenol Ether in Anhydrous and Hydrous Cyclohexane[1]

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Abstract

A polyoxyethylated nonylphenol ether containing an average of about 10 moles ethylene oxide per mole of hydrophobe was examined in hydrous and in anhydrous cyclohexane by light-scattering at 45C and by vapor-pressure measurements with the dry solvent at 39.1C. Stability was assessed by carrying out turbidity measurements over a period of two weeks. The aggregation number was found to increase with added water. The difference between weight and number average molecular weight was very small in dry cyclohexane.

Introduction

THE NUMBER $\overline{Mn}$ AND WEIGHT AVERAGE $\overline{Mw}$ METHODS of molecular weight measurement have been shown to give considerably different values for the extent of aggregation of nonionic detergents in nonaqueous solvents (1,2). Results obtained with an ionic detergent, Aerosol OT, in toluene suggest that the larger value of $\overline{Mw}$ can be attributed to small quantities of water, solubilized by the surfactant. Initially a relatively small number of very large aggregates are formed, possibly owing to the formation of microemulsions. As the solution ages, it breaks down to smaller aggregates, and at equilibrium $\overline{Mw}$ and $\overline{Mn}$ were then found to be in good agreement (3). In this case water may be identified with the impurity suggested by Debye (3).

The apparent micellar weight of a Pluronic polyol, F68, increased by a factor of two in benzene saturated with water and by about 10% at 3–5% concentration when the solutions were examined by light-scattering and by vapor-pressure measurements respectively (4). Large differences in micellar weight, with added water, were observed by light-scattering measurements for several polyoxyethylene nonylphenol ethers in cyclohexane (5). The increase in molecular weight was more pronounced with the higher homologues.

A detailed assessment of the behavior of a similar substance in dry and in hydrous cyclohexane solutions is reported in this paper. A commercial polyoxyethylene nonylphenol ether, Renex 690 with an average of 9–10 moles of ethylene oxide per mole of hydrophobe, was used. Solutions prepared in dry and in hydrous cyclohexane were examined by light-scattering over periods of several weeks at 45C. Osmometric determinations were carried out in dry cyclohexane, in CCl_4, and in benzene at 39.1C.

Experimental Section

Light-scattering determinations were carried out on solutions of polyoxyethylated nonylphenol ether in cyclohexane, which had been stored and freshly distilled over CaH_2, at 40, 45, and 50C, and in moist solvent at 45C. The solutions at 45C were examined over a period of about two weeks, during which time they were kept at 45C in an air thermostat. Cylindrical cells provided with mercury seals were used to avoid changes in concentration owing to evaporation. A previously calibrated SOFICA PGD instrument, using unpolarized blue light ($\lambda = 4358Å$), was employed (6). Scattering intensities were read at 45°, 90°, and 135°.

Each solution was clarified by repeated filtration into a heated cell through fine-grade, sintered glass filters which were kept at 47C by water circulating in a jacket surrounding the filter. Conductivity water, used for making up hydrous solutions, was clarified in a centrifuge before being injected into the filtered dry solutions of known composition. The Rayleigh ratio of benzene was taken (6) as 49×10^{-6}, and weight average molecular weights were calculated from the excess turbidity measured at 90°. Dissymmetries were also estimated. The refractive index increment (dn/dc) at 45C was measured with a Brice-Phoenix differential refractometer by using blue light ($\lambda = 4358Å$). The value obtained in cyclohexane was 0.0644 mlg^{-1}.

Vapor-Pressure Lowering

Vapor-pressure depressions of solutions relative to the pure solvent were determined at 39.1C with a Mechrolab osmometer Model 301. The instrument was calibrated with solutions of freshly recrystallized benzil (mw 210.12). The calculation of the apparent molecular weight from the calibration curves has been described previously (7).

Results and Discussions

Light-Scattering of Anhydrous Solutions

The results of the light-scattering determinations in dry cyclohexane at 45C are shown in Figure 1 as

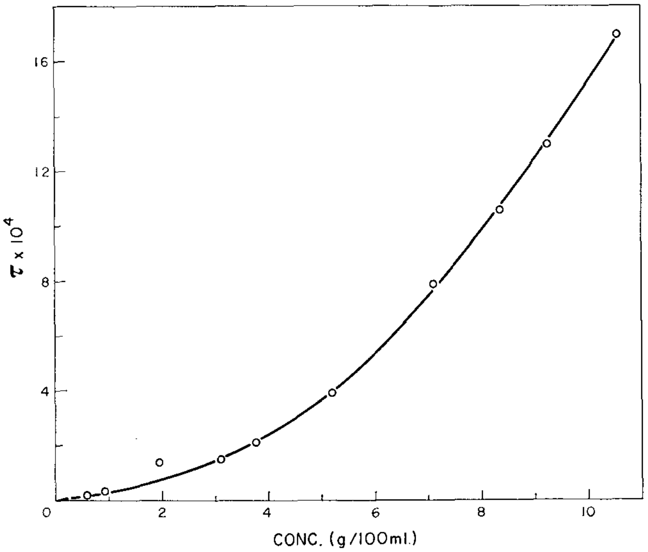

FIG. 1. Turbidity as a function of solute concentration for Renex 690 in dry cyclohexane at 45C.

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a plot of excess turbidity measured at 90° versus solute concentration. The data fit a line with an upward curvature. The measurements were carried out six days after preparing the solutions. In Figure 2 excess turbidity determinations with solutions of known concentration indicate that the associated species formed appear to be stable under the experimental conditions which were employed. The solutions were clear up to about 0.9%, then turbid to about 5.5%, and clear at higher concentrations. A similar phenomenon was reported previously for several purified polyoxyethylene nonylphenol ethers in cyclohexane (5). The dissymmetry (Z = 45°/135°) measured six days after the solutions were prepared rose to a maximum in the turbid region, then declined as the concentration of solution approached the clear region; it also became smaller as the temperature was raised from 40 to 50C. Examination of this parameter as a function of time for three different concentrations at 45C showed that the values remained virtually constant for the concentrated system whereas those of the dilute solutions near the turbid region appeared to increase after about six days of aging.

Turbidities were very low in the dilute solution range; however a reasonable estimate of $\overline{\mathrm{M}}\mathrm{w}$ could be obtained by extrapolation from high concentrations through the turbid region. Thus though values quoted will be of doubtful accuracy, they ought to be of the correct order of magnitude and should reflect relative trends quite reliably. The value of $\overline{\mathrm{M}}\mathrm{w}$ calculated for the system at 40C was 1200, indicating possible dimer formation.

Light-Scattering of Hydrous Solutions

Light-scattering measurements were carried out at 45C by using solutions of different solute concentration that contained a fixed mole ratio of water to surfactant. The maximum amount of water held per mole of solute appeared to be much less in the turbid region (circa 0.9 to 5.5%) than for the clear solutions immediately following this at the higher concentrations. It is quite possible that, in the turbid region, steric effects hinder the absorption of water by the polar groups. As more solute is added, the monomer acts as solvent, causing the aggregate to redissolve, and the solution clears. The light-scattering measurements were restricted to the clear solutions as being more meaningful.

The excess turbidity of the hydrous solution was found to increase with concentration up to a mole ratio of added water of about 0.28, where it was found to be virtually independent of concentration, and it finally decreased with concentration at the higher mole ratios of water to surfactant. The dissymmetry at a fixed mole ratio was close to unity when the solution was clear but increased sharply to about 1.2 as the turbid region was approached.

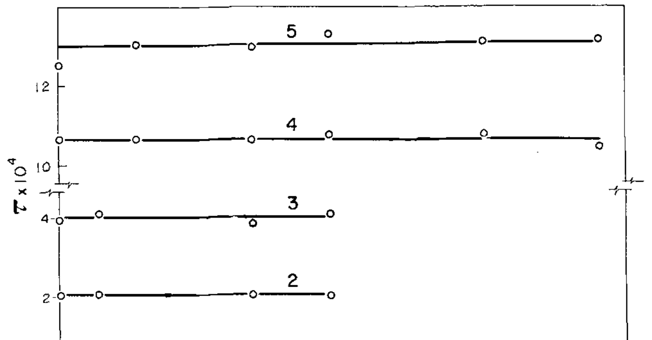

FIG. 2. Turbidity as a function of time for different concentrations of Renex 690 in dry cyclohexane at 45C. Curve 1, 0.60%; Curve 2, 3.79%; Curve 3, 5.20%; Curve 4, 8.34%; Curve 5, 9.26%.

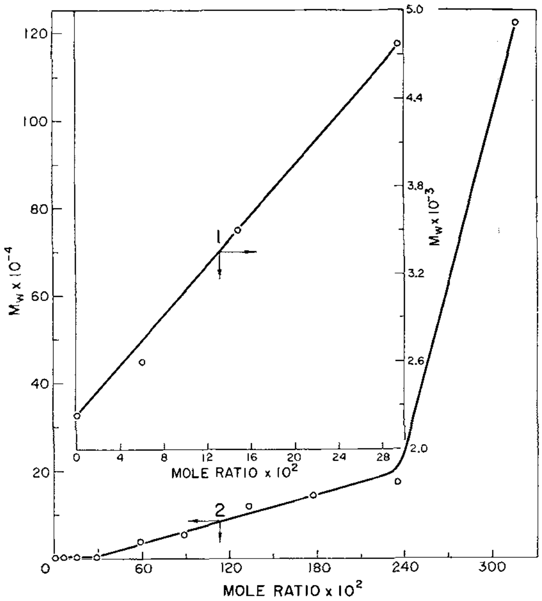

FIG. 3. Variation of $\overline{\mathrm{M}}\mathrm{w}$ with added water for Renex 690 in cyclohexane at 45C; Curve 1, up to about 0.28 mole ratio and Curve 2 up to about 3.2 mole ratio.

The variation in $\overline{\mathrm{M}}\mathrm{w}$ with added water is shown in Figure 3. Curve 1 was obtained up to about 0.28 mole ratios, which include measurements below the water content reported previously (5), and Curve 2 incorporates measurements up to a mole ratio of 3.2. These values were calculated for each mole ratio by extrapolating to infinite dilution the apparent molecular weight obtained at finite concentrations. Again $\overline{\mathrm{M}}\mathrm{w}$ was obtained by employing a rather long extrapolation through the turbid region and thus, although the trend in $\overline{\mathrm{M}}\mathrm{w}$ can be readily obtained, the absolute values are determined with some uncertainty. However the values thus obtained are in reasonably good agreement with the molecular weights reported by Kitahara (5) for a similar system. Water appears to have a marked effect on the aggregation of the polyoxyethylated nonylphenol ether in cyclohexane, yet it is difficult to assign micellar properties to the reasonably dry solutions. The aggregation number at 45C rises from about 4 to 8 as the mole ratio of water which is added is increased to about 0.28. The value rises more steeply at higher water concentrations, and phase separation occurs with further additions beyond a mole ratio of 2.4.

No evidence of micellar disintegration was obtained when a clear solution of 6.04% (g/100 ml), containing 0.579 mole ratios of water, was examined by light-scattering for about three weeks at 45C. Without disturbing the solution, the measurements at 90° decreased with time but, after shaking the system, the original reading was always reproduced. This supports the notion that a small fraction of large aggregates are formed, which settle out rather than rearrange into smaller units.

Vapor-Pressure Lowering

The variation of the apparent number average molecular weight as a function of concentration in dry

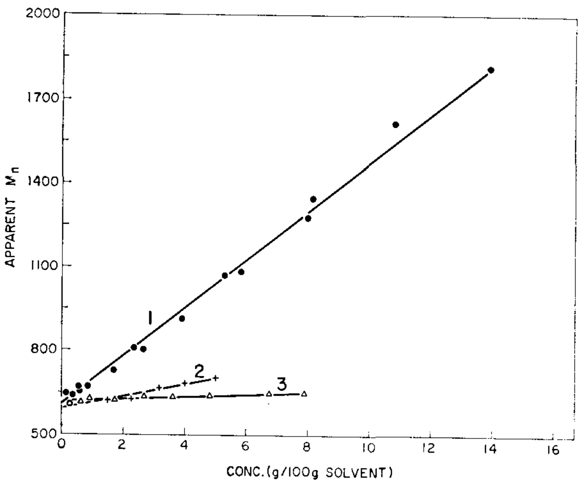

FIG. 4. Apparent $\overline{Mn}$ versus solute concentration for Renex 690 in different solvents as 39.1C. Curves 1, 2, and 3 were obtained in cyclohexane, carbon tetrachloride, and in benzene respectively.

cyclohexane, carbon tetrachloride, and in benzene, at 39.1C, is shown in Figure 4. Solute association increases with concentration in cyclohexane, but no apparent discontinuities are observed over the entire concentration range which was examined. At infinite dilution the extrapolated value of the molecular weight is about 595. Values of 615 and 580 were indicated in benzene and in carbon tetrachloride respectively.

In all micellar systems it has generally been assumed that the concentration of the detergent monomer increases linearly with concentration until the critical micelle concentration (CMC) is reached, during which time the concentration of micelles is zero. Above the CMC the concentration of monomer remains constant, but that of the micelles increases at a rate proportional to the concentration divided by, n, the aggregation number. However this model, which postulates the absence of an equilibrium between the monomer and the micelle at different concentrations, seems to be inconsistent with some published data for a number of surfactants in nonaqueous solvents (10–12), where the amount of monomer is shown to increase with concentration even after the CMC is reached. This can have a marked effect on the number average molecular weight whereas the weight average obtained from light-scattering is considerably less affected, particularly if a small number of large aggregates are formed.

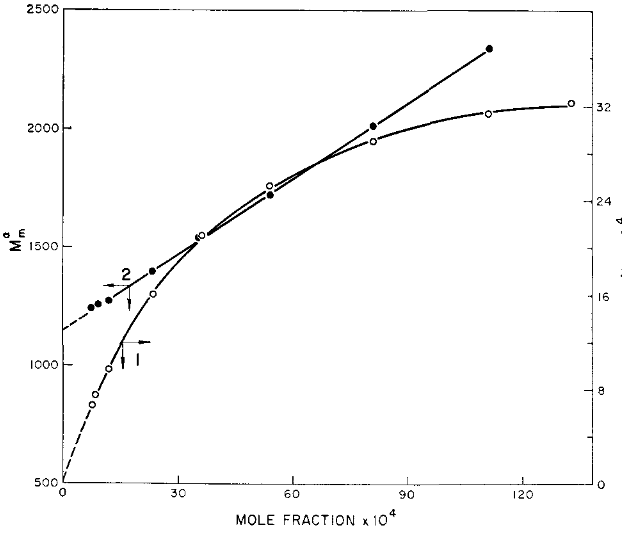

FIG. 5. Monomer concentration (Curve 1) and the apparent molecular weight of the associated material (Curve 2) as a function of total concentration for Renex 690 in dry cyclohexane at 39.1C.

The monomer concentration at each finite total concentration of solute was calculated by using Kreuzer's equation (8), which makes no assumption regarding the nature of the associative equilibria involved. The equation can be expressed in terms of mole fractions (9) as

$$\text{in}\ (1/\alpha) = (f-1)/f + \int_0^n \{(f-1)/fN\}dN,$$ where $\alpha =$ fraction of solute present as monomers, $f = \dfrac{M_a}{M_1}$, mean degree of association, N = total concentration. The apparent micellar weights M_m^a were calculated according to the following relation,

$$M_m^a = (M_a\overline{N} - N_1M_1)/N_m$$

where

M_1 = molecular weight of the monomer
M_a = apparent number of average molecular weight
N_1 = Mole fraction of free monomer
N = Mole fraction of total solute expressed as monomer
$\overline{N}$ = NM_1/M_a = effective mole fraction of solute
N_m = $\overline{N}$—N_1 = mole fraction of associated species.

The data calculated in this fashion are shown in Figure 5, where M_m^a and N_1 are plotted against the mole fraction of solute. At infinite dilution the molecular weight of the associated species is about 1140, which is in good agreement with 1200 as indicated from light-scattering measurements at 40C.

The presence of low-molecular-weight impurities can have a pronounced effect on the vapor pressure lowering and thus on $\overline{N}$. Provided the concentration of monomer is known, no soluble impurities are present and only one type of associated species is formed, the results indicate that no major differences exist between $\overline{Mw}$ and $\overline{Mn}$ for this surfactant in dry cyclohexane. If a correction is applied to allow for this increase in monomer concentration, then $\overline{Mn}$ will approach much more closely the value of $\overline{Mw}$ as it does for the very simple system being investigated, and it may be that in certain other systems, where $\overline{Mn}$ and $\overline{Mw}$ differ greatly, this could be a contributing factor. If this were the case, both number and weight average molecular weight measurements should be used to characterize these systems.

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