Solubilization, Micellization, and Phase Equilibria of Polyoxyethylene Derivatives of Dehydroabietic Acid

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Poly(oxyethylene)dehydroabietates (DeHAb(EtO)_n) with polyoxyethylene chains of 11 and 22 units have been synthesized. Phase diagrams for the systems DeHAb(EtO)₁₁-decanol-H₂O and DeHAb(EtO)₂₂-decanol-H₂O have been determined. In both systems a lamellar liquid crystalline phase is formed. The surfactants behave similarly to nonionic surfactants with an alkyl or alkyl/aryl hydrocarbon chain. The solubilization of dehydroabietinol (I), 1-octadecanol (II), decahydronaphthalene (III), decane (IV), and octadecane (V) was investigated at 60 °C in solutions of DeHAb(EtO)₂₂ and compared with a technical polyoxyethylene nonylphenol ether with 20 EtO units. The maximum solubilization in micellar solutions decreased in the order I > II > III > IV \approx V \approx 0 for both surfactants. These results can be conveniently correlated with the location of the solubilizates in the micelles as predicted on the basis of polarities and partial molar volumes. In all cases larger amounts were solubilized in DeHAb(EtO)₂₂ than in the nonylphenol surfactant. This can be rationalized as a result of the lower cloud point of the DeHAb(EtO)₂₂, which is probably due to the differences in the hydrocarbon moieties of the two surfactants.

Introduction

In the digestion of wood in the pulp and paper industry an important group of by-products is the alicyclic rosin acids, the salts of which show surface activity as demonstrated many years ago.¹ We therefore thought it interesting to investigate the phase equilibria of surfactants with a hydrocarbon moiety consisting of a rosin acid type alicyclic compound and a nonionic hydrophilic part as well as the capacity of such surfactants to solubilize alicyclic compounds with a structure similar to that of the hydrocarbon moiety. For comparison we also studied the solubilization of such compounds by a nonionic surfactant with a similar polar nonionic part and an alkyl-aryl hydrocarbon chain as the hydrophobic group. The general behavior of the alicyclic surfactants toward such solubilizates was also compared with solubilization of simpler, weakly polar or completely nonpolar compounds. The comparisions cannot, of course, be very quantitative since the surfactants differ in cloud point, but they should indicate whether the surfactant based on an alicyclic compound has any remarkable solubilizing capacity, in particular toward compounds with a structure similar to that of the hydrocarbon part of the surfactant.

Experimental Section

Chemicals. Pyridine (dried over KOH), thionyl chloride, and 2-aminoethanol were purified by distillation. Benzene and toluene were of a thiophene-free grade. Ethyl diglycol, ethoxylated with approximately 10 and 20 mol of ethylene oxide (here abbreviated (EtO)₁₂ and (EtO)₂₂, respectively), was supplied by Berol Kemi AB (Stenungsund, Sweden). The chain length distribution of the EtO chains is similar to that of normally used commercial products except that short chains are rare. The shorter polyether was dried over P_2O_5 while the longer was dried by azeotrope distillation with toluene and stored over P_2O_5 . Dehydroabietic acid

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was obtained by recrystallization as the 2-aminoethanol salt of dehydroabietic acid from a commercial rosin acid mixture supplied by Bergvik AB (Sandarne, Sweden).²

The purity of the acid was checked by GLC after methylation (diazomethan). The dehydroabietic acid isomer fraction was more than 90% of total rosin acids. Dehydroabietyl chloride was prepared from dehydroabietic acid and thionyl chloride.³

Dehydroabietinol (Ic) was obtained by $LiAlH_4$ reduction of dehydroabietic acid. Decane, octadecane, decahydronaphthalene (decalin, a mixture of cis and trans isomers), 1-decanol, 1-octadecanol, and sodium chloride were of analytical quality. The water was distilled twice.

The technical product Berol 292 used in these experiments is a poly(oxyethylene) nonylphenol ether with about 20 ethylene oxide units in the hydrophilic chain, manufactured by Berol Kemi AB (Stenungsund, Sweden).

Dehydroabietic Acid. Ethylundecaoxyethylene Derivatives of Dehydroabietic Acid $(DeHAb(EtO)_{11})$ (Ia).



I a R= -CO-O{CH2-CH2-O}10CH2-CH3

b R= -CO-O(CH2-CH2-O)21CH2-CH3

c R⊧ -CH₂OH

Dehydroabietyl chloride (2.5 g), $(\text{EtO})_{12}$ (20 g), and pyridine (2 g) were stirred overnight at 60 °C. The reaction mixture was diluted with diethyl ether after cooling. Excess pyridine was removed by extraction with a small amount of dilute acid. The organic phase was then dried over Na₂SO₄. After evaporation of the solvent a viscous liquid was obtained. The reaction mixture was separated



Figure 1. The cloud point of a 2% solution of DeHAb(EtO)₂₂ as a function of the concentration of added NaCl.

by chromatography on a silica gel column eluted with diethyl ether-ethanol mixtures. The IR absorptions of the free acid (1690 cm⁻¹), the ester (1725 cm⁻¹), and the hydroxyl group (3500 cm⁻¹) were used to monitor the elution of compounds from the column. The fraction showing absorption at 1725 cm⁻¹ was collected for further use. The homogenity of the sample was checked by NMR spectroscopy. The ratio of NMR integrals of methylene protons adjacent to an ether link ($\delta = 3.6$) to aromatic protons of a sample of this fraction dissolved in CDCl₃ indicated binding of 11 ethylene oxide units per dehydroabietate.

Ethyldocosaoxyethylene Derivatives of Dehydroabietic Acid $(DeHAb(EtO)_{22})$ (Ib). The dehydroabietyl chloride and pyridine (ratio as above) were dissolved in toluene and heated to 70 °C. Melted $(EtO)_{22}$ was added to the stirred reaction mixture. When all acid chloride had reacted (1780 cm⁻¹) Norite (charcoal) was added and the reaction mixture was filtered while still hot. Toluene and excess pyridine were removed by distillation. NMR (CDCl₃) indicated binding of 22 ethylene oxide units per dehydroabietate.

Studies of Solubilization and Phase Equilibria. The phase boundaries were determined with a titration technique at constant temperature, ± 0.5 °C.

The liquid crystalline phases were examined in a microscope between crossed polaroids after centrifugation at 25 °C.

The solubilization studies were carried out by stepwise addition of solubilizate to a test tube containing the surfactant solution. Limits of solubilization and the separation of the solutions into two (or more) phases with changes in the temperature were detected visually. The solubilization limits were checked by adding surfactant to the turbid suspensions until they were again converted to isotropic solutions.

Results

1. Cloud Points. The cloud point of a 1% solution of DeHAb(EtO)₁₁ is 31 °C. For DeHAb(EtO)₂₂ it is 72 °C and for Berol 292 >95 °C.

The influence of added sodium chloride on the cloud point of DeHAb(EtO)₂₂ was investigated. The result for a 2% DeHAb(EtO)₂₂ solution is shown in Figure 1. NaCl (1 mol dm⁻³) decreases the cloud point by 18 °C. The cloud point of Berol 292 is decreased to 73 °C when 1.7 mol dm⁻³ of NaCl is added.

2. Solubilization. All solubilization studies were carried out at 60 °C which is a temperature below the cloud point of Berol 292 and DeHAb(EtO)₂₂ but above that of De-HAb(EtO)₁₁. Hence, studies were made with the two former compounds only. The solubilization of the following compounds was investigated: decane, octadecane, decahydronaphthalene, 1-octadecanol, and dehydro-



Figure 2. Solubilization of 1-octadecanol, decahydronaphthalene, and dehydroabietinol in aqueous solutions of DeHAb(EtO)₂₂ and Berol 292, given as partial phase diagrams for the three-component systems. The area below the curve is the single phase region.



Figure 3. The maximum solubilization of dehydroabietinol, decahydronaphthalene, and 1-octadecanol (in aqueous solutions of Berol 292 and DeHAb(EtO)₂₂.

abietinol (Ic). The results are summarized in Figures 2 and 3.

Only very small amounts of octadecane and decane were solubilized by the surfactants.

The maximum solubilization of octadecanol is 0.9 mol/mol of DeHAb(EtO)₂₂ and 0.39 mol/mol of Berol 292. The capacity of DeHAb(EtO)₂₂ to solubilize decahydronaphthalene is higher than for the aliphatic alcohol, 1.7 mol of decahydronaphthalene per mol of DeHAb(EtO)₂₂ while only 0.75 mol of decahydronaphthalene per mol of Berol 292 can be solubilized.

The largest solubilizing capacity is found for the cyclic alcohol, dehydroabietinol. 3 mol/mol of DeHAb(EtO)₂₂ (corresponding to a weight ratio 2:3) and 2 mol/mol of Berol 292 (weight ratio 1.7:3) are solubilized.

Preliminary studies indicated no drastic changes in solubilization when the temperature was varied (from 25 to 90 °C).

Polyoxyethylene Derivatives of Dehydroabietic Acid



Figure 4. Phase diagram (incomplete) for the three-component system water–DeHAb(EtO)₁₁–1-decanol at 25 $^{\circ}$ C. The one-phase areas are LC lamellar liquid crystalline phase and L isotropic solutions.



Figure 5. Phase diagram (incomplete) for the three-component system water-DeHAb(EtO)₂₂-1-decanol at 25 °C. Notation as in Figure 4.

3. Phase Diagrams. The phase diagram of DeHAb-(EtO)₁₁-decanol-water at 25 °C is shown in Figure 4. The surfactant is completely miscible with water but has a low capacity for solubilization of decanol. When decanol is added in excess a liquid crystalline phase separates. The microscopic texture of this phase indicates that it has a lamellar structure.

Figure 5 shows the phase diagram of $DeHAb(EtO)_{22}$ decanol-water at 25 °C. In the concentration region of 0-25% surfactant, the maximum solubilization capacity for decanol represents a nearly constant ratio between the amount of solubilizate and surfactant. This ratio is 0.25 g of decanol/g of surfactant, corresponding to 2 mol of decanol/mol of DeHAb(EtO)₂₂. The microscopic appearance of the liquid crystalline phase obtained indicates a lamellar structure.

Discussion

Phase Diagrams. The phase diagrams shown in Figures 4 and 5 indicate that the surfactants behave similarly to nonionic surfactants with an aliphatic hydrocarbon chain and a PEO chain as the hydrophilic group. The binary solutions water-DeHAb(EtO)₁₁ at 25 °C are probably close to the cloud point of the solutions at all concentrations (the cloud point for a 1% solution is 31 °C). The addition of decanol lowers the cloud point as expected for a weakly hydrophilic substance.⁴ Very small amounts of decanol are needed to lower the cloud point to 25 °C and, consequently, the solubilization of decanol in dilute solutions is low. The solubility of water in solutions of DeHAb- $(EtO)_{11}$ in decanol is substantial at high concentrations of surfactant. The haze point of solutions of the surfactant in this lipophilic solvent probably is somewhat higher than the cloud point in aqueous solutions and the solubility of water can be considerable if the temperature is 5-10 °C above the haze point.⁵

 $DeHAb(EtO)_{22}$ behaves as expected for a nonionic compound at temperatures quite far below the cloud point.

Solubilization of decanol increases much more rapidly with increasing concentrations than for DeHAb(EtO)₁₁ and, due to the larger hydrophilic chain of the surfactant, larger amounts of water could also be solubilized than in De-HAb(EtO)₁₁-decanol solutions. Since the surfactant is solid at 25 °C, very concentrated systems could not be investigated in detail.

Cloud Point Depression by Salt. The cloud point of nonionic surfactants of the PEO type is strongly depressed by the addition of salt.⁶ The sensitivity of the cloud point of DeHAb(EtO)₂₂ to additions of NaCl (Figure 1) is normal for surfactants with this PEO chain length (1 mol dm⁻³ of NaCl decreases the cloud point of 2% DeHAb(EtO)₂₂ by 18 °C). However, the cloud point of Berol 292 is much higher than that of DeHAb(EtO)₂₂ (at least 20 °C higher) despite the similar PEO chains. Thus, the effect of replacing the flexible hydrocarbon moiety of Berol 292 with a bulky and stiff moiety of roughly the same molecular weight substantially lowers the cloud point.

Solubilization. It has been shown for nonionic compounds of the PEO type that solubilization increases rapidly at temperatures just below the cloud point. The cloud point can be increased by an increase in the length of the hydrophilic chain,⁶ can be changed by addition of a cosurfactant with a smaller hydrophilic group, can be increased by addition of an ionic surfactant,⁷ and can be decreased by addition of an electrolyte.⁸ The effect of size and structure of the hydrophobic moiety has received considerably less attention. For nonpolar compounds, e.g., aliphatic hydrocarbons, the solubilizing capacity increases linearly with the length of the hydrocarbon chain in a homologous series of surfactants,^{6,9} i.e., the maximum solubilization may be correlated with the size of the hydrocarbon moiety of the micelle and the total amount of micelles.

For weakly polar or polarizable compounds, however, the picture is more complicated, due to the tendency of these substances to arrange themselves in the micelles with their polar parts in close contact with the polar surface of the micelles. It has also been shown that solubilizing capacities and the formation of different liquid crystalline phases can be correlated.¹⁰⁻¹² Comparatively little, however, is known about the effects of changes in the structure of the hydrocarbon moiety of the surfactant on the solubilization of weakly polar substances.

The solubilizates in this study were chosen to represent aliphatic and alicyclic compounds that are expected to be located in different parts of the micelles due to their different degrees of polarity. In view of the many factors that affect solubilizing capacity (note that in addition to the different hydrocarbon groups the EtO chain of De-HAb(EtO)₂₂ ends with an ethyl group and has an ester linkage to the hydrophobic part, whereas in Berol 292 the chain ends in a hydroxyl group and is linked to the hydrocarbon chain with an ether bond) only very drastic solubilization effects can be interpreted as indicating specific interactions.

Saturated nonpolarizable hydrocarbons are solubilized in the core of the micelle, and solubilization is mostly fairly low.¹³ It is therefore not surprising that the amounts of decane and octadecane that are solubilized are very small.

The solubilization of decahydronaphthalene in Berol 292 as well as in DeHAb(EtO)₂₂ is considerably higher than that of decane, and comparable to that of octadecanol (see Figure 2). A possible explanation is that decahydronaphthalene has a molar volume that is much smaller than that of decane despite the small difference in molecular weight (M_w (decane) = 142, M_w (decahydronaphthalene) = 138). It has been shown by Höiland and Vikingstad¹⁴ that alkanes that are solubilized in the interior of micelles exhibit the same partial molar volumes and compressibilities as in the liquid alkanes. For decane and decahydronaphthalene the molar volumes are 194 and $155 \text{ cm}^3/\text{mol}$, respectively. The larger volume requirement of the decane should render it less soluble in the micellar interior than decahydronaphthalene, while the greater flexibility of decane should cause larger solubility. When the large difference in molar volumes of the two molecules is considered, it appears reasonable that the volume effect predominates over the effect of differences in flexibility.

Octadecanol has the same hydrocarbon chain as octadecane, but the effect of the polar end group is to increase the solubilization capacity for this compound in micelles of Berol 292 and DeHAb(EtO)₂₂ (Figure 2). Long-chain alcohols are incorporated into micelles with their hydroxyl group close to the polar layer of the micelles and, hence, the solubilizing capacity for these compounds is generally quite high.¹⁰ Hence, DeHAb(EtO)₂₂ behaves quite as may be expected in this respect.

As is seen in Figure 3, on molar basis, the solubilization of decahydronaphthalene as well as of octadecanol is higher in $DeHAb(EtO)_{22}$ than in Berol 292. However, there is no marked difference between the relative solubilization of these compounds in DeHAb(EtO)₂₂ or in Berol 292 solutions. The cloud point of DeHAb(EtO)₂₂ is about 20 °C lower than that of Berol 292 and the result, hence, conforms with the phenomenological rule that solubilization of nonpolar compounds increases close to the cloud point of a nonionic surfactant.¹⁰

The solubilization of dehydroabietinol is much greater than the solubilization of the other investigated compounds. Again, the solubilization in DeHAb(EtO)₂₂ is considerably higher than in Berol 292. Dehydroabietinol is a weakly polar alcohol with a polarizable lipophilic part. Polarizable compounds are solubilized close to the polar groups of the micelle and the tendency of the molecule to orient itself in close contact with the PEO shell of the

micelles should be strongly augmented by the presence of the hydroxyl group. As a consequence, a high solubilization is found for systems which are not so close to the cloud point that the solubility of the alcohol is limited by depression of the cloud point. If we consider the differences in the cloud points the difference in solubilization between DeHAb(EtO)₂₂ and Berol 292 does not appear to be remarkable.

We conclude that the alicyclic surfactant investigated has a good solubilizing capacity for most compounds investigated. On the basis of the available data we cannot, however, conclude that it has markedly more favorable interactions with, e.g., alicyclic compounds than the corresponding nonylphenyl compound. All differences can be reasonably rationalized by differences in cloud points.

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