Precipitation of Nonionic Surfactants by Polymeric Acid

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ABSTRACT

Nonionic surfactants of the polyethylene oxide type are precipitated by carboxy vinyl polymer (CVP) in its acid form. While the reduced viscosity of the CVP solution is affected more markedly by a surfactant with a longer polyethylene oxide chain, the binding to CVP of the nonionic surfactants with the same hydrophobic parts occurs more effectively with shortening of the polyethylene oxide chain or with lowering of the critical micelle concentration. The structure of the complexes formed is discussed.

INTRODUCTION

Studies on the interaction between polyacrylic acid and nonionic surfactants of the polyethylene oxide type in aqueous solution have shown that water soluble complexes are formed by cooperation of mutual hydrophobic interaction and hydrogen bonding between the acids and ether oxygen atoms (1,2). Recently we have found that carboxyl vinyl polymer (CVP) forms insoluble complexes with the nonionic surfactants including those of the polyalcohol type. In this paper some results on this interaction are shown and the structure of the complexes is discussed. It seems that the nature of this interaction may lead to a new way of precipitating the nonionic surfactants from aqueous solution, other than by inorganic heteropoly acids (3).

On the same principle, some acid form cation exchange resins are useful for adsorbing nonionic surfactants dissolved in water, on which we will report elsewhere.

EXPERIMENTAL PROCEDURES

Two kinds of polyethylene oxide octylphenyl ethers ($[EO]_nOP$, *n*: 10 and 30 in average) were supplied by the Laboratory of Kao Soap Company, Japan. Their aqueous solutions were deionized by ion exchangers Amberlite IR-120B and Amberlite IRA-400 (Rohm & Haas Co.). Although these nonionic surfactants are adsorbed by acid-form cation exchangers, Amberlite IR-120B is not an effective adsorbent (to be published). CVP (Carbopol® 940, B.F. Goodrich Chemical Co., Cleveland) is a loosely interlinked polymeric acid, whose basic unit is reportedly acrylic acid. It is dissolved clearly in water by neutralization with alkalis, but in its acid form at low concentrations it gives a translucent dispersion, which can be sedimented with an ordinary centrifuge. The mixture of CVP and nonionic surfactants is more turbid than the original CVP dispersion solution, and the complexes formed are rather stable but can be separated from the solvent also by centrifugation.

The viscosity of the transparent upper layer solution of a centrifuged aliquot of a turbid mixture of CVP and nonionics was found to be almost equal to that of water, and furthermore, in order to amplify the existence of CVP, if any, in the upper layer solution, the viscosity of the transparent solution was measured in addition of NaOH; these results confirm that by centrifugation the polyacid is fully removed combined with the nonionics. The transparent upper layer solutions were appropriately diluted and submitted to spectrophotometry at 275 mμ to determine the concentration of the equilibrium surfactant solution. A very small contribution of absorption at this wave length, stemmed from the CVP solution, was subtracted. Viscosity was measured as described previously (2). All the experiments were done at 25 C.

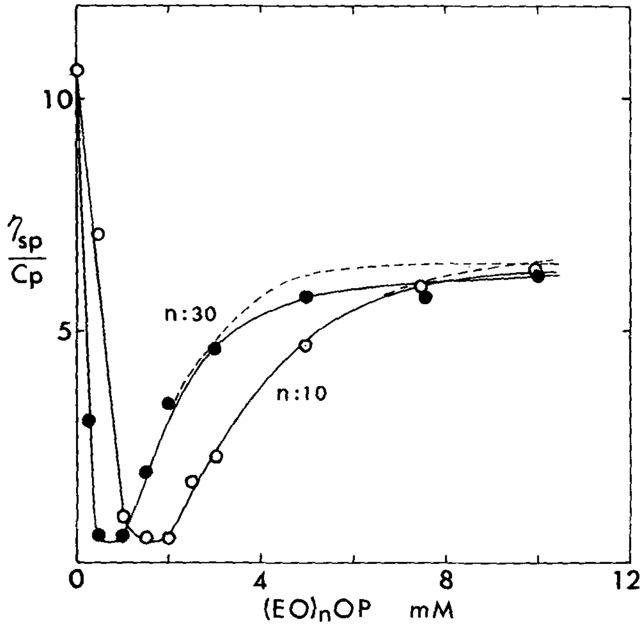

FIG. 1. Reduced viscosity of 0.05% CVP solution relative to surfactant solution as function of concentration of polyethylene oxide octylphenylether $(EO)_nOP$ (*n*: 10 and 30) added at 25 C. Dotted curves, see text. pH of CVP solution without additives is 3.94.

RESULTS AND DISCUSSION

Figure 1 illustrates the change of the reduced viscosity of the CVP solution by addition of $(EO)_nOP$. A deep valley appears in each reduced viscosity curve, as observed in polyacrylic acid solution (2). In parallel with the reduced viscosity rise at high surfactant concentrations, turbidity of the dispersed solutions is slightly decreased. In this figure

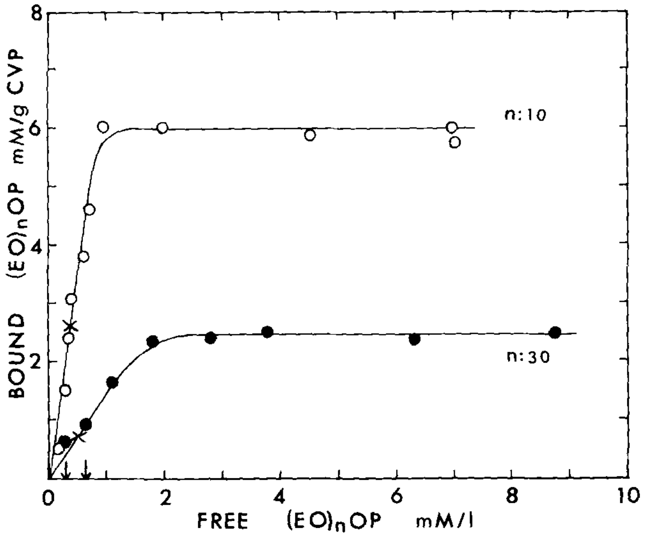

FIG. 2. Binding of polyethylene oxide octylphenylether $(EO)_nOP$ (*n*: 10 and 30) per 1 g CVP as function of free equilibrium surfactant concentration at 0.05% CVP at 25 C. Cross point marks binding at reduced viscosity minimum point shown in Figure 1. Arrow indicates critical micelle concentration (0.32 mM/liter and 0.65 mM/liter for *n* = 10 and 30, respectively) of free surfactant.

the reduced viscosity is conventionally expressed relative to the total nonionics solution as the solvent (this approach corrected later; see dotted curves in same figure), and without considering change in the polymer volume by complex formation.

As shown before (2), pH of a polymeric acid solution rises as a result of complex formation with the nonionic surfactants. At 0.05% CVP, its incipient pH (3.94) is raised ca. 0.2 units by an enough addition of $(EO)_nOP$.

The turbid complexes of CVP and the nonionics are separated from the solution of unbound surfactants by centrifugation. The sediments of the complexes at the reduced viscosity minimum point are rather compact, but with further increase in initial surfactant concentration they become more pasty and swollen corresponding to the reduced viscosity increase; they are fluffy when the CVP concentration is high.

In Figure 2 the amounts of binding of $(EO)_nOP$ per 1 g CVP (containing ca. 13 meq acid units) in its 0.05% solution are shown as a function of concentration of the free surfactant in equilibrium with the complex.

Now that the extent of binding is known and the free surfactant concentration in the solvent phase is determined, the reduced viscosity curves in Figure 1 are redrawn relative to the true solvent by the dotted lines; but the trend of the curves does not change substantially.

The binding at each reduced viscosity minimum point in Figure 1 is marked on the curve by a cross, which falls on the region of the critical micelle concentration (CMC) of each surfactant (0.32 and 0.65 mM/liter [interpolated value from Table 15.1 in Reference 4] for $[EO]_{10}OP$ and $[EO]_{30}OP$, respectively [4]). This means that the shrunken complex redisperses intramolecularly above the CMC of the equilibrium solution.

While the effect on the reduced viscosity by $(EO)_{30}OP$ is stronger than by $(EO)_{10}OP$, the binding of $(EO)_{10}OP$ actually occurs more effectively and reaches the higher saturation level at the lower concentration of free surfactant than that of $(EO)_{30}OP$. This indicates that—although hydrogen bonding is essential in the present interaction and therefore some properties of the polyacid solution, such as the reduced viscosity and pH, are affected more strongly by the longer polyethylene oxide chain of the surfactant (2)—the uptake of the nonionics is basically of hydrophobic nature, as in the binding to a nonionic polymer (5), to some proteins (6) and on carbon black (7,8).

The ratio of total oxygen atoms of the surfactants to acid units in the complex at the reduced viscosity minimum point is ca. 2, and at the saturation it is ca. 5, for both surfactants. This implies that only a small fraction of the total oxygen atoms of surfactants in the complex is really able to hydrogen bond to the acid units because of steric effect and competition with water molecules. It is therefore conceivable that above CMC the polyethylene oxide chain of a nonionics bound may form some loops and, especially, its end portion may be dangling in the solvent phase; this may be more so with larger *n* and with increasing binding degree, as proposed for a model structure of the complex (2).

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