SURFACTANTS & DETERGENTS TECHNICAL

Critical Surfactant Concentration in the Interaction Between Nonionic Surfactants and Polymeric Acids. Effects of Temperature, pH and Salts[1]

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Critical surfactant concentrations at which the binding of nonionic surfactants to polyacrylic acid, or complex formation, abruptly occurred in aqueous solution were lower than the CMC and were temperature-independent. The complex was precipitated by pH lowering or salt addition. At low pH, precipitation limit surfactant concentration (PLC) existed, below which no precipitation of the complex took place, and the PLC coincided with the critical concentration mentioned above. In this case the PLC did not change with temperature either. In the precipitation caused by $AlCl_3$ addition, the PLC was a little higher than that at low pH, because Al ions induced not only shrinking and agglomeration of the complex but at the same time blocked the sites on the polymeric acid for hydrogen bonding with the surfactant. By NaCl or $CaCl_2$ addition no PLC was found, because in both cases the salting-out effect dominated.

The interaction between nonionic surfactants of the polyoxyethylene type and polymeric acids in aqueous systems appears in various ways as properties of the single components (1). The interaction is believed to be mainly a micelle-like association of the surfactants on the polymer bound by hydrophobic interaction between both components and by hydrogen bonding between ether oxygens of the polyoxyethylene moiety of the surfactant and carboxyl groups of the polymer.

One of the features of the interaction is that the binding of the nonionic surfactant to polymeric acid occurs abruptly above a certain critical surfactant concentration lower than the CMC. This concentration depends on the polymeric acid concentration, or pH of the system, but when the pH is adjusted, it is independent of the polymeric acid concentration in a wide range. This concentration is dependent on the kind of polymeric acid (2). This critical concentration was deduced from the solubilization and viscosity measurements in nonionic surfactant-polymeric acid solutions (2). Existence of such a critical surfactant concentration was observed in the ionic surfactant interactions with nonionic polymers, polyelectrolytes, polypeptides, and proteins in aqueous solution (3-6).

As this critical surfactant concentration is related to a transition of bound states of surfactants on the polymer chain, and not to the bulk concentration, it seems appropriate to use the same notation T_1 as employed by Jones in a similar critical phenomenon in the interaction

between ionic surfactants and nonionic polymers in aqueous solution (6).

At low pH, when the ratio of nonionic surfactant and polymeric acid is appropriate, the surfactant is precipitated as a complex with the polymeric acid. In this case a precipitation limit surfactant concentration (PLC) exists below which no more precipitation of the surfactant takes place in a wide range of polyacid concentration added in a low pH range (7). The complex is also precipitated by addition of neutral salts, especially of multivalent cations (8).

Apparently, since below the T_1 no complex exists, no coprecipitation of the surfactant and polymeric acid can occur. In other words, the PLC could be the T_1 in the precipitated system. The question is whether or not, or to what extent, the T_1 in solution state will be influenced by these precipitants. In this paper the correlation between both the T_1 and PLC of nonionic surfactants in the interaction with polymeric acid was studied.

EXPERIMENTAL PROCEDURES

Materials. Polyoxyethylene (20 EO) octylphenyl ether, $(EO)_{20}$ OP, was a product of Nikko Chemical Co., Tokyo, polyoxyethylene (10 EO) octylphenyl ether, $(EO)_{10}$ OP, was Triton X100 of Rohm & Haas Co., U.S.A., and polyoxyethylene (20 EO) nonylphenyl ether, $(EO)_{20}$ NP, was a product of Tokyo Kasei Co., Tokyo. The pHs of their 1 mM aqueous solutions were about 5. Polyacrylic acid (PAA) and polymethacrylic acid (PMA) had molecular weights 1.5×10^5 and 1.4×10^6, respectively (9). HCl, NaCl, $CaCl_2$ and $AlCl_3$ were special grade reagents of Wako Pure Chem. Co., Osaka. Distilled water was employed.

Methods. Concentration of these surfactants was determined with a Shimadzu Spectrophotometer UV-160 with a 1 cm cell by a relation: molar concentration = optical density at 275 nm $\times$ 0.753 mM (7,10), because their chromophores are the same. This method was more accurate than the weight basis concentration determination, as done before (7).

At a relatively higher $(EO)_{20}$ OP concentration and in the presence of PAA, its absorption peak, when measured against the PAA solution of the same concentration, shifted to a slightly longer wavelength accompanied by some absorption increase. However, in a precipitated system treated in this report, in which the content of surfactant or polymeric acid or both in its supernatant was low, the supernatant was further diluted for absorption measurement, and surfactant concentration in the measured condition (below 0.2 mM) was usually lower than

the respective T_1. Thus, error due to the presence of a polymeric acid in determining the surfactant concentration by the above relation was negligible. Also, the absorption of $(EO)_{20}$ OP in its single solution was not influenced by pH drop to 2 by HCl addition. The absorption shift may be related to the complex formation of the surfactant with polymers (11). The same applies to the other surfactants.

CMC and T_1 were determined by solubilization of Yellow OB, an oil-soluble dye (2). The cross points in the dye solubilization-surfactant concentration relation in the absence and presence of a polymeric acid were referred to as CMC and T_1, respectively.

In determining the precipitation limit surfactant concentration (PLC), a solution of precipitant (HCl, NaCl, $CaCl_2$, and $AlCl_3$) was added to a mixture of nonionic surfactant and polymeric acid. Rate of the addition did not affect the amount of precipitation of the surfactant. Since the precipitation reaction usually occurred quickly, a precipitant solution was added to a complex solution at a regulated temperature. Aliquots were taken out from transparent supernatant solutions carefully, or centrifuged for a short period so that the temperature of the systems remained unchanged.

Polymer concentration was expressed in terms of unit mole.

RESULTS AND DISCUSSION

Critical surfactant concentration T_1 at various temperatures. The CMC of $(EO)_{20}$ OP and T_1 with 15.6 mM PAA at 4°, 14° and 25°C were given by the dye solubilization method in Figure 1. Previously it was found that, although T_1 depended on PAA concentration, PAA at 10–30 mM gave a constant T_1, because pH around 3.3,

or in this PAA concentration region, suppresses dissociation of PAA enough but not too low as to cause precipitation of the complex (2). In Figure 1, the CMC was dependent on temperature, but in the presence of PAA the dye solubilization relation at different temperatures converged to a constant point (0.15 mM). Thus, T_1 was lower than the respective CMC and independent of temperature. This T_1 value agreed with the former result (2).

The pH of a PAA solution rises slightly as a result of surfactant binding (12). In the legends for Figures 1–3, "initial pH" means the pH of the PAA solution before surfactant addition.

The CMC of $(EO)_{10}$ OP and its T_1 with 13.5 mM PAA at various temperatures were shown in Figure 2, and those of $(EO)_{20}$ NP in Figure 3. In both surfactants too, each T_1 (0.15 mM for $(EO)_{10}$ OP and 0.05 mM for $(EO)_{20}$ NP) was lower than the respective CMC and independent of temperature.

Supposedly, the nonionic surfactants are bound to a PAA chain firmly by a number of hydrogen bonds together with the hydrophobic interaction, and hence the binding of the surfactants to PAA is rather insensitive to temperature change. It is known that in the interaction between polyoxyethylene and PAA the mole ratio of the binding is not affected much by temperature (13).

Once bound to a PAA chain, the behavior of the surfactant molecules is governed by the hydrophobic moiety. Since $(EO)_{20}$ NP is more hydrophobic than $(EO)_{20}$ OP, it has a lower T_1 (0.045–0.05 mM). It is to be noted that $(EO)_{10}$ OP and $(EO)_{20}$ OP have the same T_1 value despite different polyoxyethylene chain lengths, and this trend will be discussed elsewhere together with further data on other surfactants (14).

In the system of sodium dodecylsulfate and polyvinylpyrrolidone, T_1 was almost independent of polymer
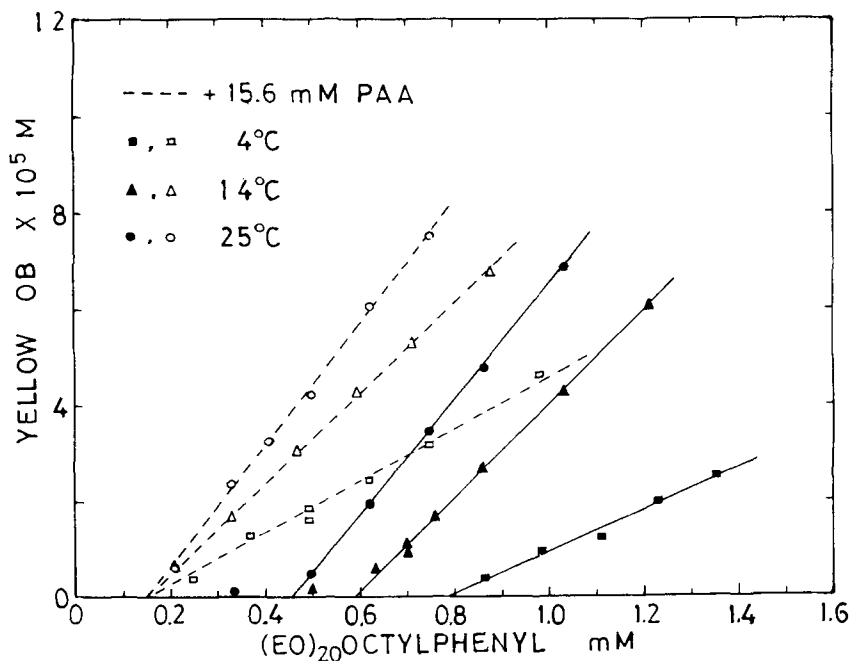

FIG. 1. Solubilization of Yellow OB in $(EO)_{20}$ OP solutions without and with 15.6 mM PAA at 4°, 14°, and 25°C at initial pH 3.4.

concentration and temperature (15,16), but its CMC was also hardly temperature-dependent.

Precipitation of complex by pH lowering and PLC. Figure 4 shows the precipitation results of $(EO)_{20}$ OP from an initial concentration 0.52 mM as a function of concentration of PAA or PMA at pH 2. The polyacid concentration around 15 mM gave a constant and the highest

FIG. 2. Solubilization of Yellow OB in $(EO)_{10}$ OP solutions without and with 13.5 mM PAA at 4°, 25° and 38°C at initial pH 3.5.

yield of precipitation, or PLC, from 0.52 mM $(EO)_{20}$ OP for both PAA and PMA. In a much higher polymer concentration range, the sediments tended to disperse. As shown in Figure 5, pH 2 was sufficient for inducing the maximum precipitation of the surfactant as a complex.

In Figure 4, by pH lowering from the initial value of 3.4 to 2, the PLC of $(EO)_{20}$ OP with 15.6 mM PAA at 4°, 14°, and 25°C were the same (0.15 mM) within experimental error and coincided with the T_1 determined by the dye solubilization method at pH 3.4, as shown in Figure 1. Although transparent supernatant solutions at 4°C became only slightly turbid at 25°C, no clear differences were observed between the corresponding PLCs. Between 14° and 25°C, no turbidity change was found.

With 14.8 mM PMA, the PLC by pH lowering from the initial pH 4.0 to 2 was 0.075 mM. The T_1 value for the PMA system by the Yellow OB solubilization method was, because a PMA solution alone has some solubilization capacity for the dye, not exact but around 0.05–0.10 mM (2).

Similarly, in the $(EO)_{10}$ OP solution at 0.53 mM in Figure 6, and in the $(EO)_{20}$ NP solution at 0.46 mM in Figure 7, the PLCs with PAA at pH 2 were 0.15 mM and 0.04–0.05 mM, respectively, and each PLC at different temperatures was the same within experimental error. Each PLC also was coincident with the respective T_1 and its temperature-independency, as indicated in Figures 2 and 3.

With pH reduction, dissociation of PAA is more suppressed, and hence, a possibility of hydrogen bonding with ether oxygens of the polyoxyethylene moiety of the nonionic surfactant may be enhanced. The fact that, in spite of the pH difference, the T_1 and the PLC with PAA generally agreed might suggest that the increased hydrogen bonding, which leads to agglomeration and eventually to precipitation of the complex, did not encourage further complex formation but was enforced, instead, only within the existing complex. However, since the pK of dissociation of PAA is 5.6 (17), the degree of
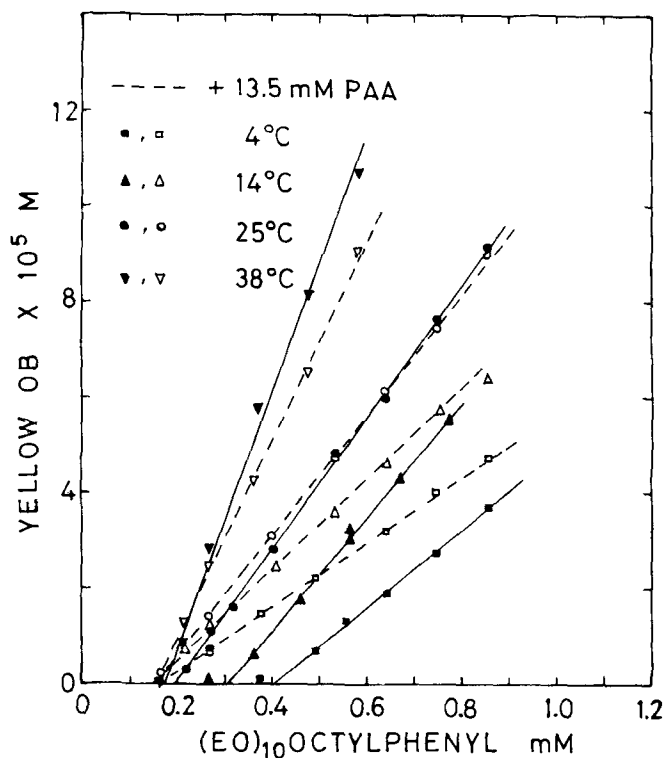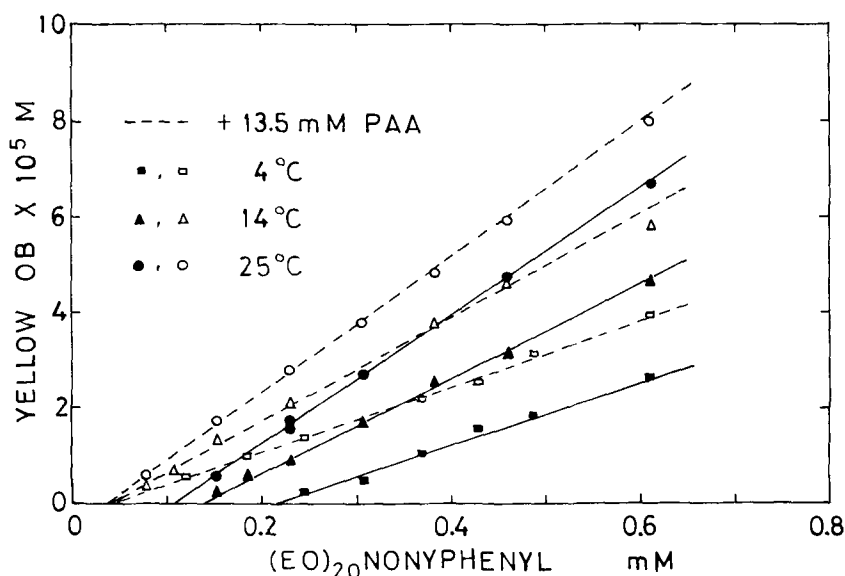

FIG. 3. Solubilization of Yellow OB in $(EO)_{20}$ NP solutions without and with 13.5 mM PAA at 4°, 14°, and 25°C at initial pH 3.5.
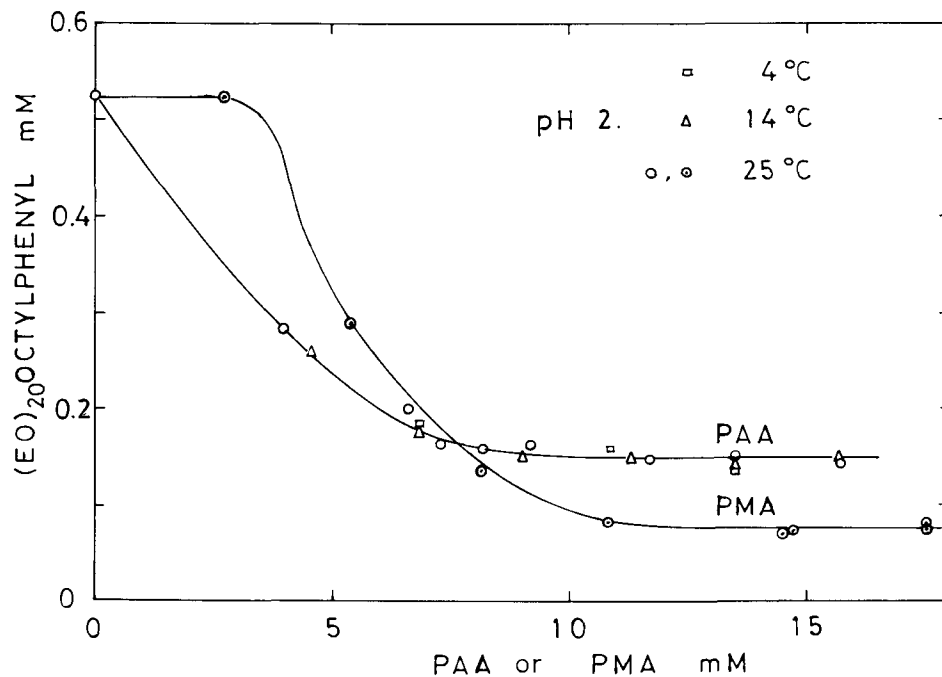
FIG. 4. Concentration of supernatant $(EO)_{20}$ OP in the precipitated system from 0.52 mM surfactant plotted against PAA or PMA concentration at pH 2 at 4°, 14°, and 25°C. The difference from 0.52 mM is the amount of surfactant precipitated.
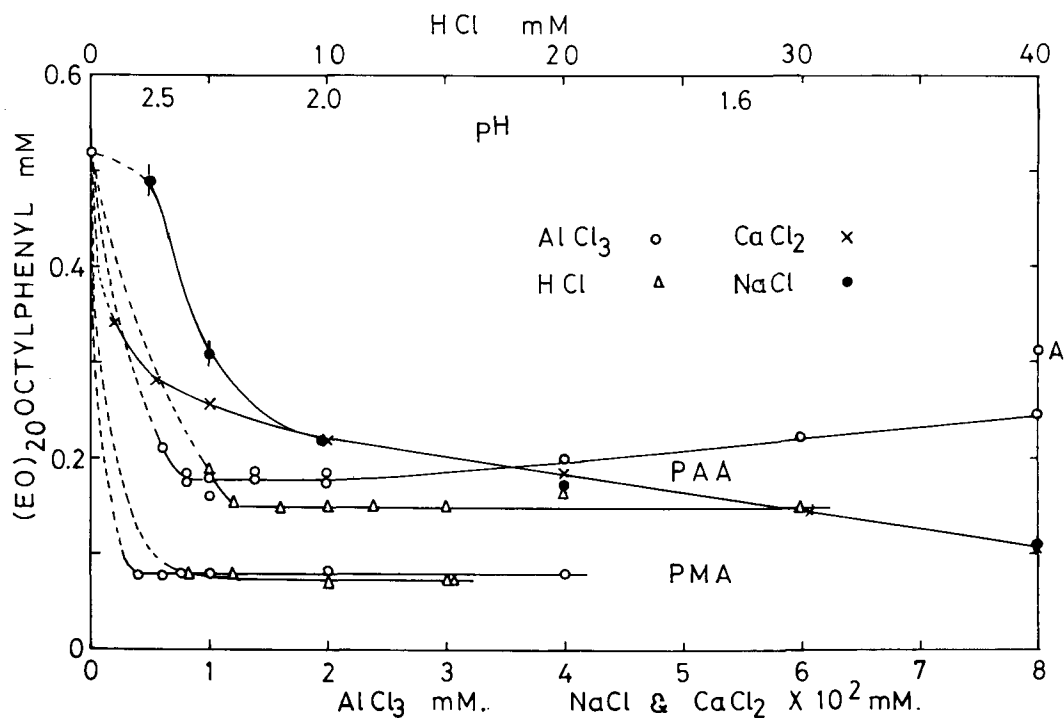

FIG. 5. Concentration of supernatant $(EO)_{20}$ OP in the precipitated system from 0.52 mM surfactant in the prsence of 15.6 mM PAA or 14.8 mM PMA by addition of HCl, or pH lowering (upper scale), NaCl, $CaCl_2$ (lower scale $\times 10^2$) and $AlCl_3$ (lower scale) at various temperatures. Point A on the right-side ordinate indicates supernatant surfactant concentration at 20 mM $AlCl_3$ in the PAA system. The dotted portion shows no precipitation.
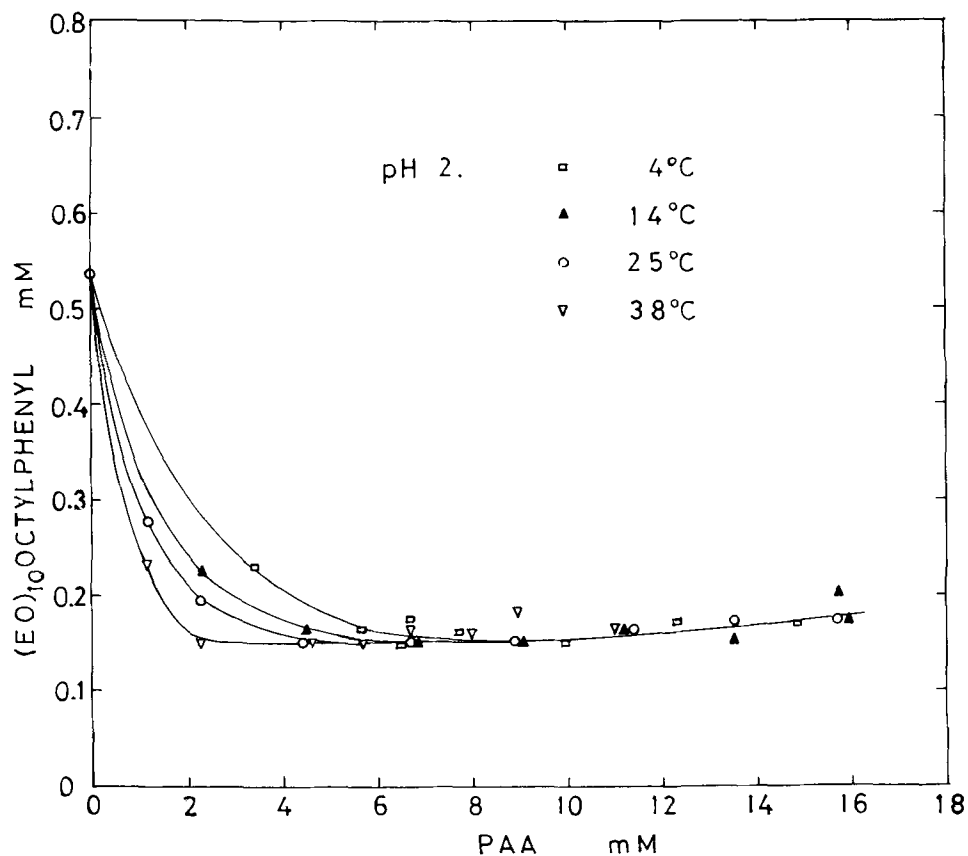
FIG. 6. Concentration of supernatant $(EO)_{10}$ OP in the precipitated system from 0.53 mM surfactant plotted against PAA concentration at pH 2 at 4°, 14°, 25° and 38°C. The difference from 0.53 mM is the amount of surfactant precipitated.
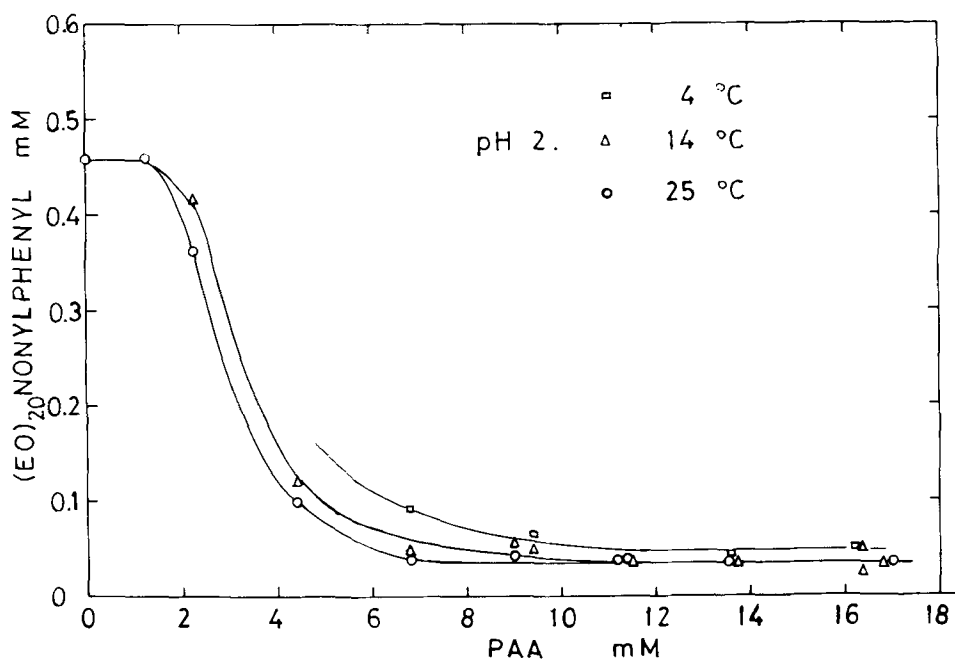

FIG. 7. Concentration of supernatant $(EO)_{20}$ NP in the precipitated system from 0.46 mM surfactant plotted against PAA concentration at pH 2 at 4°, 14°, and 25°C. The difference from 0.46 mM is the amount of surfactant precipitated.

dissociation is estimated to be about 0.6% in 15.6 mM PAA at pH 3.42. Thus, by decreasing the pH to 2 the contribution of the increase in the extent of hydrogen bonding to the formation of a low solubility complex seems to be minor. It is supposed that because a low pH makes the PAA configuration shrink, the complex is more tightly compressed and agglomerated. This explanation could be applied to that of precipitation by salt addition, as discussed below.

When the concentration of PAA was lowered greatly from 15.6 mM, i.e., when the pH was higher than ca. 4, the T_1 value determined by the dye solubilization method was not constant but closer to the CMC (2), and of course different from the PLC at pH 2.

The second critical concentration T_2, the saturation binding surfactant concentration on polymer in solution (6), was not clearly detected in the surfactant concentration region measured.

Precipitation of complexes by salt. The precipitation results of $(EO)_{20}$ OP with PAA and PMA by addition of various salts are also included in Figure 5. Since hydrogen bonding is basically involved in this case, the polyacid concentrations used for precipitation by pH lowering were considered to be appropriate also for that by addition of salts.

The addition of $AlCl_3$ was most effective for precipitation of the complex as shown previously (8). Whereas the PLCs of $(EO)_{20}$ OP with PAA and PMA were independent of pH below 2.2, that in $AlCl_3$ systems had a minimum with respect to salt concentration, though not clearly recognized in the PMA systems, and it was not

lower than the PLC by the pH lowering. This is different from the tendencies by NaCl and $CaCl_2$, whose concentration increase resulted in a steady rise of the amount of the surfactant precipitation; no definite PLC seems to exist.

The salt addition causes not only a salting-out or salting-in effect but also a binding of the cations to carboxyl groups of PAA. In the salting-out by chlorides, PAA solutions without nonionic surfactants become only slightly turbid. In the mixture of the complex, neutral salts, especially of multivalent cations, make the complex shrink and agglomerate and at the same time inhibit the complex formation, because the cations occupy a number of carboxyl groups of the polymeric acid and reduce a possibility of hydrogen bonding with the surfactant. Moreover, salts may alter the binding equilibrium between the surfactant and the polymer. Thus, generally the precipitation of the complex by salts depends on the balance of these effects.

The blocking of carboxyl sites by cations was reflected by the pH change in 15.6 mM PAA with 0.52 mM $(EO)_{20}$ OP by the salt addition, as shown in Figure 8. With an increase in the $AlCl_3$ concentration, the pH of the supernatant solutions dropped rapidly at first and then gradually, accompanied by increasing precipitation, as shown in Figure 5. In a comparison of both figures, it is thought that the complex was precipitated in the low $AlCl_3$ concentration region, whereas carboxyl groups continued being blocked further by Al ion binding, which prevents the polymer from the binding of the surfactant, and eventually a minimum appeared in the precipitation
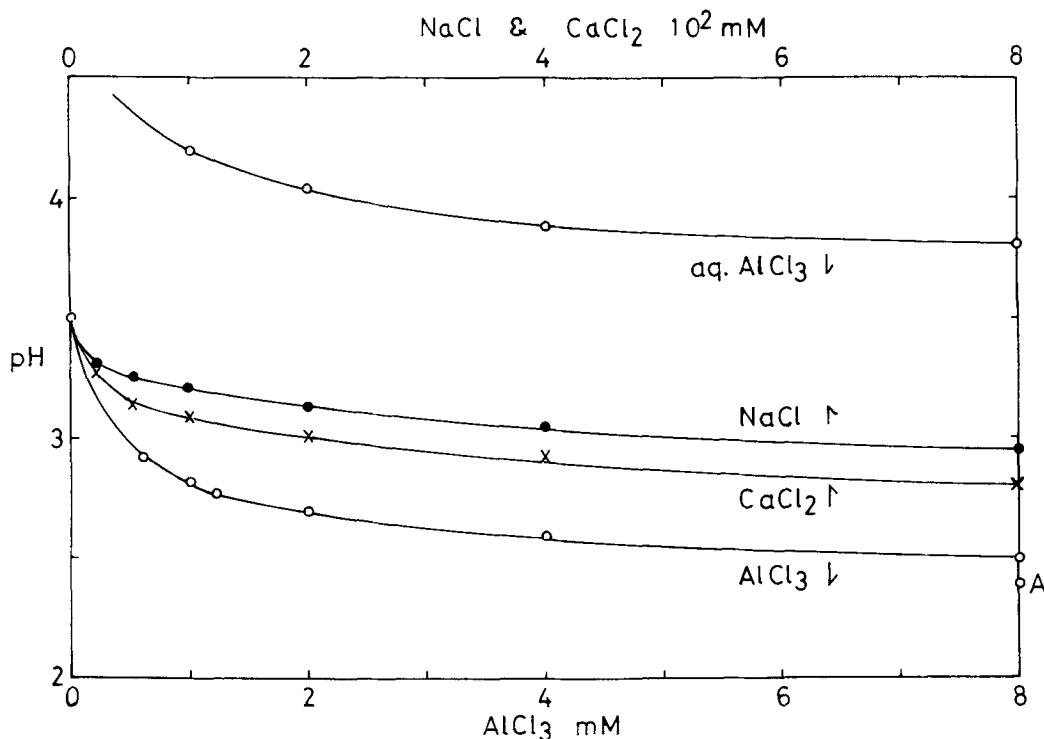

FIG. 8. The pH of supernatant solutions from systems of 15.6 mM PAA–0.52 mM $(EO)_{20}$ OP at varied concentrations of NaCl, $CaCl_2$ (both the upper scale) and $AlCl_3$ (the lower scale) at 25°C. The pH of $AlCl_3$ solutions without the surfactant is also shown (the uppermost curve). Point A on the right-side ordinate indicates pH value at 20 mM $AlCl_3$, corresponding to the point A in Figure 5.

limit concentration curve. This minimum concentration is to some extent higher than the constant PLC at low pH. Since $AlCl_3$ is a weak electrolyte and the concentration added was very low, its salting-out effect is considered weak.

Calcium chloride ($CaCl_2$) was a stronger precipitant than NaCl at lower concentrations but both required much higher concentrations than $AlCl_3$ for precipitation of the PAA complex, and the pH changes of PAA–$(EO)_{20}$ OP mixtures by NaCl and $CaCl_2$ were, despite higher salt concentration, much smaller than $AlCl_3$, as demonstrated in Figures 5 and 8, respectively. Clearly, the blocking by Na ions was weaker than that by Ca ions and was much less than that by Al ions even in the high concentration region. The reasons for absence of minimum in the precipitation curves for NaCl and $CaCl_2$ in Figure 5 may be that in both salts the salting-out effect not only covers the blocking effect but also increases the surfactant binding to PAA, and eventually dominates for precipitation of the complex, because they are strong electrolytes and their addition concentrations were higher than $AlCl_3$.

REFERENCES

1. Saito, S., in *Nonionic Surfactants. Physical Chemistry*, edited by M.J. Schick, Marcel Dekker, New York, 1987, Chapter 15.
2. Saito, S., *Colloid & Polym. Sci. 257*:266 (1979).
3. Robb, I.D., in *Anionic Surfactants, Physical Chemistry of Surfactant Action*, edited by E.H. Lucassen-Reynders, Marcel Dekker, New York, 1981, Chapter 3.
4. Nagarajan, R., *Colloids & Surfaces 13*:1 (1985).
5. Goddard, E.D., *Colloids & Surfaces 19*:255, 301 (1986).
6. Jones, M.N., *J. Colloid & Interface Sci. 23*:36 (1967).
7. Saito, S., *Tenside 14*:113 (1977).
8. Saito, S., T. Taniguchi and H. Matsuyama, *Colloid & Polym. Sci. 254*:882 (1976).
9. Saito, S., *Colloids & Surfaces 19*:351 (1986).
10. Nadeau, H.G. and S. Siggia, in *Nonionic Surfactants*, edited by M.J. Schick, Marcel Dekker, New York, 1967, Chapter 26.
11. Green, F.A., *J. Colloid & Interface Sci. 35*:481 (1971).
12. Saito, S. and T. Taniguchi, *J. Colloid & Interface Sci. 44*:114 (1973).
13. Kokufuta, E., A. Yokota and I. Nakamura, *Polymer 24*:1031 (1983).
14. Saito, S., Presented at the ACS 62nd Colloid and Surface Science Symposium in June 19-22, 1988 in State College, PA.
15. Murata, M. and H. Arai, *J. Colloid & Interface Sci. 44*:475 (1973).
16. Arai, H., M. Murata and K. Shinoda, *J. Colloid & Interface Sci. 37*:223 (1971).
17. Ikawa, T., K. Abe, K. Honda and E. Tsuchida, *J. Polym. Sci. Polym. Chem. Ed. 13*:1505 (1975).