Studies on Mixed Surfactant Systems: Effect of Some Anionic Surfactants on the Cloud Point of Poly(nona-)oxyethylated Nonylphenol

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The effect of some common anionic surfactants, namely LABS-Na, AOS-Na, SLS, SLES, di-octyl sulphosuccinate and sodium soaps of coconut, palm and rice bran oils on the cloud point of poly(nona-)oxyethylene nonylphenol has been determined. It is observed that sodium soaps have a larger effect on the cloud point than do anionic surfactants containing sulphate/sulphonate head groups. The influence on cloud point was found to decrease with an increase in hydrophobic chain length.

Studies on the binary mixtures of surfactant solutions have gained importance in recent years (1-5). A large variety of such systems are known to exhibit non-ideal behavior and as a consequence thereof offer appreciable surface and bulk synergistic effects. The surface activity-related synergistic phenomena are of technological interest (6). As a part of our investigations on binary mixtures of surfactant solutions (7, 8), we have determined the effects of some common anionic surfactants on the cloud point of poly(nona-)oxyethylated nonvlphenol (abbreviated as NP9EO). The nonionic was selected in view of its wide applications as an emulsifier, suspending, wetting and solubilizing agent in a variety of formulations. The anionic surfactants used in the present studies are some of the common surfactants, namely, sodium salt of alpha olefin sulphonate (AOS-Na); sodium salt of linear alkylbenzene sulphonate (LABS-Na); sodium lauryl sulphate (SLS); sodium lauryl ether sulphate (SLES); dioctyl(2-ethyl hexyl-)sulpho succinate (DOSS), and sodium soaps of coconut, palm and rice bran oils. These studies were aimed at determining the influence of anionic surfactants on

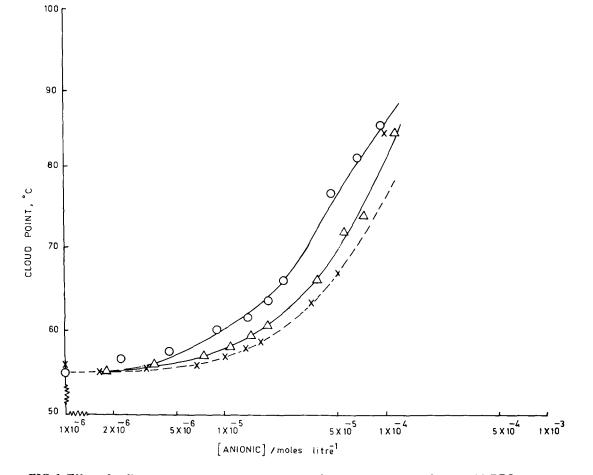


FIG. 1. Effect of sodium soaps on the cloud point of NP9EO. ○, CNO soap; △, palm soap; ×, RBO soap.

the micellar behavior of NP9EO. This information was required for development work on product formulations.

EXPERIMENTAL

The sample of NP9EO was procured from M/s Hico Products, Bombay, India. The mean molecular weight and hence the average chain length of the ethoxylate was determined from the hydroxyl value (9). The sample was found to contain an average of 9.3 moles of ethylene oxide/mole of surfactant. This nonionic falls into the polydisperse category; hence, its properties are close to those of the homogeneous compounds having the composition of the mean (10).

Sodium soaps of coconut, palm and rice bran oils were prepared from their respective fatty acids by following established procedures (11). The specifications of the fatty acids used were: Coconut oil fatty acid, I.V., 9.05; titer, 21.8°C; A.V., 256.2; palm fatty acid, I.V., 52.2; titer, 42.3°C; A.V., 202.6; rice bran fatty acid, I.V., 96.4; titer, 31.1°C; A.V., 184.6.

Commercial grade samples of LABS-Na, SLS, SLES and DOSS were procured from M/s Hico Products, Bombay, India, and AOS-Na was obtained from M/s Godrej Soaps Ltd., Bombay, India. The detailed analyses of these samples are: LABS-Na salt; aqueous paste., av. mol. wt., 356; active content, 82.4%; sodium sulphate, 1.6%; unsulphonated matter, 1.1%. AOS-Na; aqueous paste., blend of C_{14} and C_{16} ; av. mol. wt., 324; active content, 69.3%; free oil, 1.2%; sodium sulphate, 1.9%. SLS, powder; av. mol. wt., 298; active content, 94.7%; sodium sulphate, 1.6%; sodium chloride, 0.3%; unsulphated matter, 0.8%. SLES; aqueous paste., av. mol. wt., 408; active content, 29.6%; sodium sulphate, 1.8%; unsulphated matter, 0.8%; average ethoxylation, 2.5 mol of oxyethylene/mole of surfactant. DOSS, aqueous paste., av. mol. wt., 444; active content, 95.3%; sodium sulphate, 1.5%; free alcohol, 0.8%.

The surfactants were used as such without any purification.

Aqueous solutions of NP9EO and anionic surfactants containing 1.0% NP9EO and varying amounts of anionics were prepared by weight in distilled water. The cloud points of these solutions were determined by heating the solution until it clouds and then measuring the temperature at which clearing occurs on cooling (12). A pre-calibrated precision thermometer graduated to 0.1 °C was used to measure the temperature.

RESULTS AND DISCUSSION

Figures 1 and 2 show the effect of anionic surfactants on the cloud point of NP9EO. It is observed that the cloud point of the nonionic surfactant remains unaffected by the addition of a small amount of anionic surfactant (corresponding to $\tilde{}$ 5 mole percent of the critical micelle concentration of NP9EO). As the con-

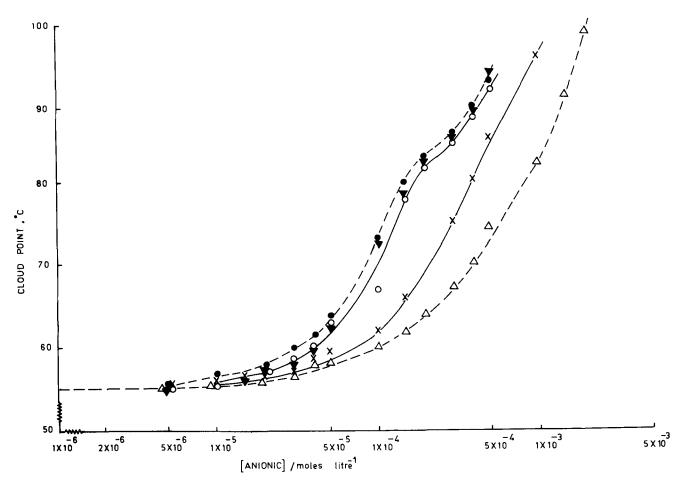


FIG. 2. Effect of some anionic surfactants on the cloud point of NP9EO.♥, AOS-Na; ●, SLS;○, LABS; ×, DOSS; △, SLES.

centration of the anionic surfactant is increased beyond this, the cloud point shows an increase. The increase is dependent on the amount and nature of the anionics and follows the order: CNO soap > palm soap > RBO soap > SLS > AOS-Na > LABS-Na > DOSS > SLES. Sodium soaps have a larger effect on the cloud point than do anionic surfactants containing sulphate/ sulphonate head groups. The influence on cloud point was found to decrease with an increase in hydrophobic chain length for surfactants having the same head group.

The increase in cloud point is attributed to the increased potential between the micelles arising from the electrostatic effects due to introduction of charge on the surface of the micelles when an anionic surfactant enters a nonionic micelle. Our results imply that at low concentration of the anionic surfactant nonionic micelles are predominant in the system maintaining the cloud point at the original value. As the concentration of the anionic surfactant is increased, it tends to get entrapped in the micelles and the cloud point increases from 55° C to $> 95^{\circ}$ C due to the formation of mixed micelles.

The coalescence of the resultant mixed micelles is also influenced by their relative tendencies to bring about structural changes in the solvent media (12-14). We find that the order of anionic surfactants for bringing about the change in cloud point corresponds to their relative ability to act as hydrophobic bond breakers.

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