

Effect of inorganic additives on solutions of nonionic surfactants — XVI. Limiting cloud points of highly polyoxyethylated surfactants

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Abstract

As their degree of polyoxyethylation is increased, the cloud points (CPs) of three homologous series of nonionic surfactants (NSs) rise steeply at first but then level off, converging asymptotically to the temperature range of 114–118°C, which corresponds to the CP of polyethylene oxide with a molecular weight of 10^4 . Six of the 14 surfactants investigated were octoxynols, five were nonoxynols and three were polyoxyethylene dodecyl ethers. Ten had an average number of oxyethylene units per molecule $p > 20$ and a CP $> 100^\circ\text{C}$. Three of these CPs were measured directly on 2.00% surfactant solutions sealed into ampoules. To avoid additional measurements under pressure, the other surfactants had their CPs lowered below the normal boiling point of their 2.00% solutions by adding the salting-out, CP-lowering salt NaNO_3 at various concentrations, measuring the depressed CPs and extrapolating them to zero salt concentration. The CPs decrease linearly with increasing molality m of NaNO_3 up to ca. $2.5 m$ and more steeply at higher concentration. For a given concentration of NaNO_3 , larger p values result in more extensive salting out: The more highly polyoxyethylated a surfactant is, the greater the reduction in CP it undergoes. As p increases, the curves of CP in water versus p for the octoxynols and nonoxynols rise steeply and nearly linearly, reaching 100 and 103°C at $p = 16$, and then begin to level off. The sharpest inflections are at $p = 22$ – 25 . The nonoxynol curve becomes horizontal at $p \cong 40$ and 115°C while the octoxynol curve rises gently from 3°C below the nonoxynol curve to merge with it at $p = 90$ and 114°C . The CPs of the three polyoxyethylene dodecyl ethers are slightly higher than those of the polyoxyethylated alkylphenols with comparable p values, peaking at 118°C . The most highly polyoxyethylated surfactant of each series contains 95% polyoxyethylene. Their CP range of 114 – 118°C equals that of polyethylene oxides with molecular weights between 8000 and 20 000. Published quantitative CP– p relations for polyoxyethylated NSs cover only CP values below 100°C and p values below 16. They fail to predict the levelling off of the CPs as the p values rise above 16. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cloud point limits; Highly polyoxyethylated nonionic surfactants; Nonionic surfactants; Nonoxynol cloud points; Octoxynol cloud points

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PII: S0927-7757(01)00491-5

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SENJU EXHIBIT 2034
LUPIN v. SENJU
IPR2015-01097

1. Introduction

1.1. Cloud points

Water-soluble polyoxyethylated nonionic surfactants (NSs) are more soluble in cold than in hot water. When heated above a characteristic lower consolute temperature or cloud point (CP), their aqueous solutions separate into a surfactant-rich phase and a very dilute solution as the NSs change from being primarily water-soluble to becoming primarily oil-soluble. Cooling below the CP reverses this process without hysteresis.

Because of such phase separation, NSs cease to perform many of their intended functions above the CP: Suspensions stabilized with NSs flocculate or coagulate, foams collapse, and O/W emulsions break. Incidentally, many of the organic liquids being emulsified raise or lower the characteristic CP values substantially.

CPs are commonplace. Most NSs have low critical micelle concentrations: At practical use levels, the bulk of the surfactants are aggregated into micelles. High micellar molecular weights cause the dissolved NSs to behave like polymers: Low entropies of mixing render micellar solutions far more prone to demixing or phase separation than solutions of nonaggregated molecules at comparable volume fractions.

1.2. Predicting cloud point values

Because of the practical and theoretical importance of the CP, procedures for predicting its values from the structure of NSs are of interest. CPs generally increase with increasing hydrophile-lipophile balance (HLB) of the NSs, corresponding either to an increasing number p of oxyethylene units per surfactant molecule or a shorter hydrocarbon moiety [1,2].

Within several homologous series pertaining to different categories of NSs, the CP was reported to be proportional to $\log p$ [3,4] and inversely proportional to the number n of carbon atoms in the hydrocarbon moiety [4]. This empirical method for estimating CPs was extended and refined by including topological indices characterizing the hydrocarbon moiety of the surfactants.

Thus, it became feasible to commingle different categories of NSs, resulting in a universal relation for estimating all CPs based on the p value and size and structure of the hydrocarbon moieties [5].

A statistical approach consisted in using nonlinear regression analysis to correlate the CP with p at fixed n values within different categories of linear and branched polyoxyethylated aliphatic alcohols. The CP versus p plots were slightly concave towards the p axis [6].

These studies [1,3–6] have a common shortcoming: they are based on NSs with $p \leq 15$ and $CP < 100^\circ\text{C}$, presumably because CP data beyond these limits are scarce. However, NSs with p values up to 100 are commercially available and used in industrial formulations. Furthermore, temperatures exceeding 100°C are routinely used during the manufacture of aqueous disperse systems stabilized with NSs. For instance, steam sterilization of pharmaceutical and cosmetic suspensions, emulsions and ointments is generally carried out by autoclaving at $\geq 121^\circ\text{C}$. Ultrahigh-temperature pasteurization employs temperatures in the $87\text{--}132^\circ\text{C}$ range. In order to prevent destabilization of such disperse systems by high processing temperatures through surfactant phase separation, they should be formulated with NSs whose CPs exceed even these high temperatures.

This points to the importance of knowing the CP values of NSs with p in the 16–100 range, which exceed the normal boiling points of the aqueous surfactant systems. Estimating these CP values by extrapolating the published relations [1,3–6] would be particularly useful because the pertinent CP measurements, which involve pressurized systems, are more difficult to carry out.

Two observations suggest that the published relations between CP and p [1,3–6] cannot be extrapolated indefinitely with increasing p values. (i) While the CPs within individual homologous series of both normally distributed and homogeneous NSs always increase with p , the CP increments for each additional oxyethylene unit decrease [1]. (ii) A plot of CP versus p for 7 normally distributed polyoxyethylated octylphenols with p values ranging from 7 to 34 rises rapidly (although less than linearly) from $p = 7$ ($CP = 17^\circ\text{C}$) to $p = 19$ ($CP = 101^\circ\text{C}$), but shows

signs of levelling off at $p = 30$ (CP = 108°C) and $p = 34$ (CP = 110°C) [7]. This very informative 1959 publication [7] is being completely overlooked in the current literature, even though it was the first and almost only one to publish CPs above 100°C.

1.3. Research plan

The purpose of the present work is to investigate the CPs of extensively polyoxyethylated NSs, which are merely listed as $> 100^\circ\text{C}$ in the literature. Two homologous series based on alkylphenols were chosen because they are widely used in formulations and include surfactants with the highest p values available.

The CPs of highly polyoxyethylated NSs exceed the normal boiling points of their solutions. To avoid working with pressurized systems, the CPs of the solutions were depressed below 100°C by adding various amounts of a salting-out electrolyte and extrapolating them to zero electrolyte concentration. This approach is facilitated by the linear dependence of CP values on the concentrations of many 1:1 electrolytes up to ca. 3 m [8,9].

2. Experimental

2.1. Materials

The two series of polyoxyethylated alkylphenols used are commercially available in a wide range of p values. These surfactants are normally distributed. It was not feasible to use monodisperse (homogeneous) polyoxyethylated surfactants because these are only available with $p < 9$ and have CP values well below 100°C.

Polyoxyethylated octylphenols are designated as octoxynols [10,11]. The numbers following the word, octoxynol, represent average p values. The branched octyl moiety is an isobutylene dimer. Octoxynols are supplied by Union Carbide Corp. under the tradename Triton X. The highest p value of the series is 53 (Surfactant No. 5 in Table 1).

Polyoxyethylated nonylphenols are designated as nonoxynols [10,11]. The branched nonyl moiety is a propylene trimer. Nonoxynols are supplied by Rhodia Inc. under the tradename Igepal CO. The highest p value of the series is 94 (Surfactant No. 11 in Table 1).

Table 1

US Pharmacopeial names, trade names, average number of oxyethylene units per molecule (p) and hydrophile-lipophile balance (HLB) of the surfactants

Surfactant number	US pharmacopeial name	Trade name ^a	p	HLB
1	Octoxynol 12	Triton X-102	12	14.4
2	Octoxynol 16	Triton X-165	16	15.5
3	Octoxynol 30	Triton X-305	30	17.3
4	Octoxynol 40	Triton X-405	35	17.6
5	Octoxynol 70	Triton X-705	53	18.4
6	Octoxynol 90	–	90	19.0
7	Nonoxynol 15	Igepal CO-730	15	15.0
8	Nonoxynol 30	Igepal CO-880	29	17.1
9	Nonoxynol 50	Igepal CO-970	47	18.1
10	Nonoxynol 70	Igepal CO-987	70	18.7
11	Nonoxynol 100	Igepal CO-997	94	19.0
12	Polyoxyl 11 dodecyl ether	–	11	14.4
13	Polyoxyl 23 dodecyl ether	Brij 35	23	16.9
14	Polyoxyl 80 dodecyl ether	–	80	19.0

^a Triton, Igepal and Brij are registered trademarks of Union Carbide Corp., Rhodia Inc. and ICI Americas Inc., respectively.

Manufacturers obtain the p values from the weight increase during polyoxyethylation of the alkylphenols and/or by determining the hydroxyl number of the finished products. The surfactants contain small amounts of polyethylene glycols. These impurities generally have lower molecular weights than the surfactants and have two terminal hydroxyl groups compared to the surfactants' one. Therefore, the reported p values represent lower limits. Polyethylene glycol impurities have negligible effects on the CPs of highly polyoxyethylated surfactants [7].

The commercial surfactants were supplied either neat or as 70% aqueous solutions. Their moisture contents were determined by drying at room temperature first over Drierite and then over P_2O_5 . All neat products contained $< 0.1\%$ water.

Octoxynol 90 (Surfactant No. 6 in Table 1) was prepared by polyoxyethylation of molecularly distilled octoxynol 3 (Triton X-35) to $p = 90$. The catalyst was 0.7% NaOH; the temperature in the stirred autoclave was 160–180°C and the pressure 2–3 atm. The weight increase was 11.3-fold (1130%). The hydroxyl number of Surfactant 6 was 13.4₅ mg KOH/g surfactant.

Surfactants No. 12 and 14 were made by polyoxyethylating 1-dodecanol under similar conditions to $p = 11$ and 80, respectively. They are designated polyoxyl 11 and 80 dodecyl ether [10] or laureth-11 and -80 [11].

The other chemicals were ACS reagent grade. The water was double distilled. $NaNO_3$ was selected as the salting-out electrolyte to lower the CPs because the NO_3^- anion occupies an intermediate position in the lyotropic series and neither raises nor lowers the CPs of NSs [12]. Thus, the CP reductions are due entirely to the salting-out activity of the Na^+ ions. Plots of CP versus m_{NaNO_3} are linear up to 2.5 m , which simplifies the extrapolation to $m = 0$.

2.2. Solution preparation

Solutions containing surfactant and salt were prepared by adding water and analyzed, ca. 8 m $NaNO_3$ solutions to 20.00% surfactant solutions, all weighed out to the nearest milligram. As a rule, the CPs of normally distributed NSs depend only

slightly on surfactant concentration in the range of 0.2–7.5% [1,7,13]. The final concentration of all surfactants was 2.00% by weight; their percentage is based on the weight of water present. All mixtures were stored in the dark at 6–9°C for ≥ 20 h prior to measuring the CP to ensure full hydration of the micelles.

2.3. Cloud point determination

CPs were measured visually in triplicate as the temperatures at which the solutions suddenly turned nearly opaque on heating and the temperatures at which they just as suddenly cleared on cooling, without hysteresis. Observing the precautions described [14], the six CP values for a given solution agreed within 0.2°C.

Even though the CPs of Surfactants No. 6, 13 and 14 exceeded the normal boiling points of their 2.00% aqueous solutions, they were measured directly. Salt-free solutions sealed inside glass ampoules were heated and cooled at the rate of 0.1°C min^{-1} in the vicinity of the CP.

The CPs of aqueous NS solutions are known to increase with pressure. However, the rate of increase, ca. $1 \times 10^{-7} \text{ } ^\circ\text{C Pa}^{-1}$ [15] is three orders of magnitude smaller than the rate of increase of saturated steam pressure with temperature. Therefore, the CP increase due to pressure developed in the sealed ampoules is negligible.

3. Results and discussion

3.1. Cloud points versus molality of $NaNO_3$

The Na^+ ions salt out the NSs, lowering their CPs. The CPs decrease monotonically with increasing molality m of $NaNO_3$, linearly at first but more steeply at higher $NaNO_3$ concentrations. For Surfactant No. 1, which has the lowest degree of polyoxyethylation, the linear range extends only up to 1.0 m $NaNO_3$. The plots of all other surfactants are linear up to ca. 2.5 m (see Figs. 1 and 2).

The equation for the linear segments is:

$$CP = CP^0 + bm \quad (1)$$

The intercept CP^0 is the (extrapolated) CP at $m = 0$. This is the desired quantity.

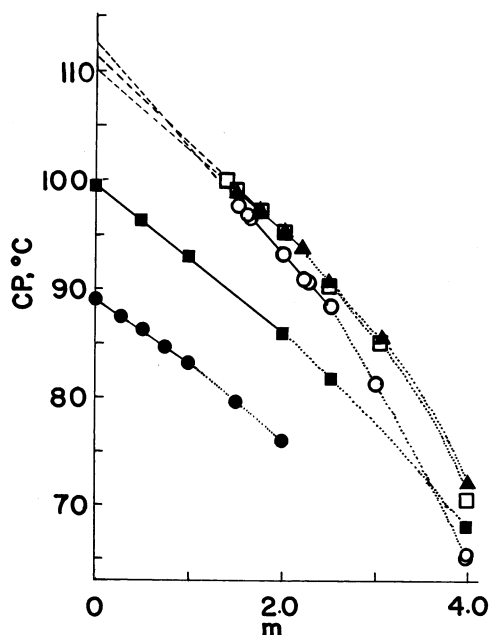


Fig. 1. Cloud point CP ($^{\circ}\text{C}$) of octoxynols as a function of the molality m of added NaNO_3 . The linear segments used for extrapolation are shown as solid lines. Nonlinear segments are shown as dotted lines. The dashed lines represent linear extrapolation to $m=0$. Key: ●, octoxynol 12 (Surfactant No. 1); ■, octoxynol 16 (No. 2); ▲, octoxynol 30 (No. 3); □, octoxynol 40 (No. 4); ○, octoxynol 70 (No. 5).

The empirical extrapolation procedure is validated by the following observations: Since the CPs of the salt-free solutions of Surfactants No. 1, 2 and 7 were below the respective normal boiling points, their CP^0 values were also measured directly.

The measured CP^0 values agree with corresponding extrapolated CP^0 values within an experimental error of 0.2°C (see Table 2). Furthermore, all negative correlation coefficients for the linear segments of Fig. 2, described by Eq. (1) and based on 4–6 points each, have absolute values ≥ 0.999 . This confirms the high precision of the CP extrapolations to $m=0$.

3.2. Statistical comparison of the linear segments of the CP versus m plots

In order to compare the linear segments of Fig. 1 and those of Fig. 2 by means of analysis of

variance (ANOVA) employing small-sample t - and F -tests, the residual or error variances must be homogeneous. It then becomes permissible to pool the estimated variances of the slopes and of the intercepts of the individual regression lines when using ANOVA [16,17]. Since the CP values of all octoxynols and nonoxynols except those of Surfactants No. 6 and 12–14 were measured by the same procedure and with the same precision, the expected homogeneity of the residual variances was observed.

3.3. (Extrapolated) intercepts: cloud points in water

The increase in the intercepts (CP^0 values) of the octoxynols with increasing p values shown in Tables 1 and 2 is significant at the 5% probability level. The intercepts of nonoxynols 50, 70 and 100 (Surfactants No. 9–11) do not differ significantly at the 5% probability level. Likewise, the CP^0 value of Surfactant No. 6 is indistinguishable

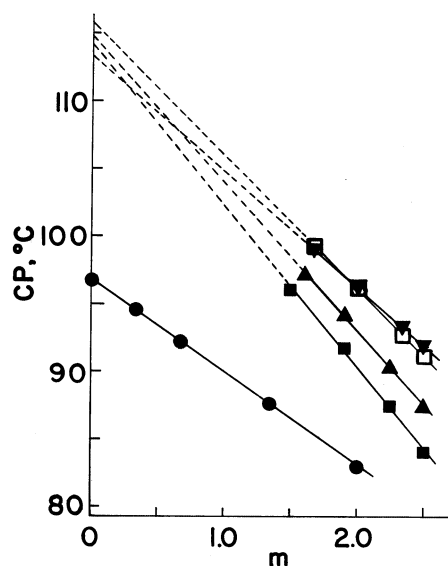


Fig. 2. Cloud point CP ($^{\circ}\text{C}$) of nonoxynols as a function of the molality m of added NaNO_3 . The linear segments used for extrapolation are shown as solid lines. The dashed lines represent linear extrapolation to $m=0$. Key: ●, nonoxynol 15 (Surfactant No. 7); ▼, nonoxynol 30 (No. 8); □, nonoxynol 50 (No. 9); ▲, nonoxynol 70 (No. 10); ■, nonoxynol 100 (No. 11).

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