

Effect of Inorganic Additives on Solutions of Nonionic Surfactants IV: Krafft Points

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Abstract □ Two polydisperse polyoxyethylated nonionic surfactants were found to possess Krafft points as well as cloud points. The significance of the Krafft point and the reason why it is rarely observed in nonionic surfactants are discussed. The values of the Krafft and cloud points of the two surfactants underwent only small changes as a function of surfactant concentration in the range of 0.5–7.5% (w/w). All electrolytes investigated, as well as urea, raised the Krafft points by between 1 and 4° in the concentration range of 0.5–4 molal. Included were salting-in electrolytes, which raised the cloud points, as well as salting-out electrolytes, which lowered them. Electrolytes that salt out nonionic surfactants strongly may depress the cloud point to the Krafft point temperature, rendering a water-soluble surfactant insoluble in salt solutions at all temperatures.

Keyphrases □ Surfactants, nonionic—aqueous solutions, effect of inorganic additives on Krafft and cloud points □ Electrolytes—effect on Krafft and cloud points of aqueous solutions of nonionic surfactants □ Inorganic additives—effect on Krafft and cloud points of aqueous solutions of nonionic surfactants □ Krafft point—aqueous solutions of nonionic surfactants, effect of inorganic additives □ Cloud point—aqueous solutions of nonionic surfactants, effect of inorganic additives □ Nonionic surfactants—Krafft and cloud points, effect of inorganic additives

During a study of the effect of electrolytes on the cloud points of four commercial polydisperse polyoxyethylated nonionic surfactants (1), two were found to possess Krafft points as well. These observations and the effect of electrolytes on the two Krafft points are reported.

SIGNIFICANCE OF KRAFFT POINT

The solubility–temperature relation of ionic surfactants in water follows a common pattern. At low temperatures, while the solubility remains below the critical micelle concentration (CMC), it is low and increases only slowly with rising temperature. A rapid increase in solubility takes place after the concentration limit reaches the CMC, at a temperature called the Krafft point. Above that temperature, the rate of increase of the solubility with temperature is high. Solubility–temperature plots consist of two segments. The one below the Krafft point has a small slope, while the one above it ascends steeply (2–5).

The temperature at which the sudden increase in solubility occurs has been interpreted as the melting point of the (hydrated) surfactant crystals or soap fibers (2, 6) or as the freezing point of the micelles (7, 8). The Krafft point increases regularly on ascending a homologous series of surfactants such as sodium alkyl sulfates (5, 9) or sodium soaps (5, 6) with even numbers of carbon atoms. In this respect, the Krafft point resembles the melting point, which undergoes regular increases on ascending the homologous series of normal paraffins or of normal fatty acids with even numbers of carbon atoms.

An alternative explanation for the sudden solubility increase is the necessity for a rapid increase in micellar concentration above the Krafft point (2). The aggregation of single surfactant molecules S into micelles S_n containing n surfactant molecules each is an equilibrium process: $nS \rightleftharpoons S_n$, for which the equilibrium constant is:

$$K = [S_n]/[S]^n \quad (\text{Eq. 1})$$

Brackets indicate concentration or, more exactly, activity. The equilibrium constant K and the CMC vary only gradually with

temperature. At the Krafft point, the CMC curve crosses over the solubility curve in Fig. 1 and micelle formation begins. At that point, the micellar concentration $[S_n]$ has to increase fast to catch up with $[S]^n$ to maintain the ratio K constant or, rather, to allow for the increasing value of K with rising temperature. This requirement leads to an abrupt increase in surfactant solubility in the form of micelles, because the aggregation number n is fairly large, usually falling in the 30–200 range. Micelles have a much higher solubility in water than single surfactant molecules, because the hydrocarbon moieties in the former are largely shielded from contact with water by the polar headgroups (3).

Krafft point phenomena have been observed for soaps (5, 6) and most other anionic and cationic surfactants whose solubility–temperature relation was investigated (2–9). To the knowledge of the authors, only a single, homogeneous nonionic surfactant, cetyl alcohol with exactly seven ethylene oxide units, has been reported to possess a Krafft point (10). For homogeneous and polydisperse polyoxyethylated nonionic surfactants, an upper consolute temperature called the cloud point, above which they precipitate from aqueous solutions as relatively concentrated gels due to dehydration, is commonly observed (11).

A Krafft point or lower consolute temperature is rarely found because the CMC values of water-soluble nonionic surfactants are usually low and their solubility does not diminish appreciably with decreasing temperature. The Krafft point is the temperature at which the solubility of the surfactant equals its CMC. Thus, the solubility usually does not drop below the CMC before the freezing point of water is reached. Alternatively, most hydrated nonionic surfactants remain liquid down to temperatures in the vicinity of 0°; i.e., their melting point is below the freezing point of water.

EXPERIMENTAL

The four surfactants employed are commercial polydisperse polyoxyethylated compounds. Surfactant I, octoxynol NF, is a branched octylphenol containing an average of nine to 10 ethylene oxide units¹. Surfactants II, III, and IV consist of cetyl, stearyl, and oleyl alcohol with an average of 10 ethylene oxide units, respectively². Their properties and formulas were given in Ref. 1. All other chemicals were ACS reagent grade; water was double distilled.

The assay methods for determining the electrolyte content of the concentrated stock solutions and the preparation of the ternary mixtures were described in Ref. 12. The electrolyte concentrations are given in molality, and the surfactant concentrations are expressed as percent weight to weight based on the amount of water present.

To measure its Krafft point, the 30-g portion of a solution was contained in a 60-ml (2-oz) bottle closed with a rubber stopper bearing a thermometer. The contents were first heated well above the Krafft point, but below the cloud point, to dissolve the surfactant and hydrate it completely. Cooling below the Krafft point caused the surfactant to separate as thin, needle-shaped crystals, which imparted a pearlescent appearance to the liquid. The suspensions of these crystals were heated at the rate of 1°/15 min.

The Krafft point was taken as the temperature at which the crystalline solid dissolved completely. The solutions often exhibited a slight turbidity above the Krafft point. Triplicate measurements were made on each system, which agreed within 0.5°. The few experiments in which the rate of heating was 1°/30 min gave the same values for the dissolution temperatures of the needles as were obtained at the faster heating rate.

¹ Triton X-100; supplied by Rohm and Haas Co.

² Brij 56, 76, and 96, respectively; supplied by Atlas Chemicals Division of ICI United States Inc.

Table I—Krafft Points and Cloud Points of Surfactants II and III as a Function of Concentration

Surfactant Concentration, % (w/w)	Consolute Temperatures of			
	Surfactant II		Surfactant III ^a	
	Krafft Point	Cloud Point	Krafft Point	Cloud Point
0.50	32.5°	67.0°	45.5°	64.0°
1.00	34.0°	64.0°	46.0°	63.0°
1.50	34.0°	63.5°	47.5°	62.0°
2.00	34.5°	62.5°	48.0°	62.0°
3.00	35.0°	62.0°	48.5°	63.5°
5.00	36.0°	61.0°	49.0°	64.0°
7.50	37.0°	—	49.0°	65.5°
10.00	37.5°	66.0°	—	—

^aA different batch from that used for determining the data of Table III.

For cloud point determinations, the solutions were heated and cooled at rates from 1°/2 min to 1°/5 min. The cloud points were taken as the temperatures at which the solutions became turbid on heating and clear on cooling. The four cloud point values obtained from duplicate heating and cooling cycles agreed within 0.5°.

RESULTS AND DISCUSSION

The crystallization of Surfactants II and III upon cooling their solutions below the Krafft points was a slow process. It required about 0.5 hr after reaching that temperature without any additive or in the presence of the nitrates of lithium, sodium, potassium, or cesium or the bromide, iodide, or perchlorate of sodium. Crystallization required about 1 hr in the presence of the nitrates of calcium or lead or in the presence of sulfuric or hydrochloric acid. The nitrates of magnesium, aluminum, nickel, and cadmium delayed the crystallization of the two surfactants even more, requiring about 2 hr in the presence of low concentrations of these salts and overnight standing at high concentrations.

Very slow cooling of solutions containing surfactants, at rates of 1°/hr or 1°/2 hr, caused the crystals to separate about 10° below the temperature at which they cleared on heating. Because of this supercooling, attempts to determine Krafft points from above as well as from below were abandoned.

Only Surfactants II and III underwent phase separation on cooling. A cryoscopic study of Surfactant I indicated that micelles existed at the freezing point of its aqueous solutions (13), *i.e.*, its extrapolated Krafft point is below 0°. Aqueous solutions containing 2.00 and 3.00% (w/w) of Surfactant IV remained clear down to 2°. Therefore, the Krafft point of Surfactant IV is below that temperature.

The Krafft and cloud points of Surfactants II and III as a function of concentration are listed in Table I. The upper and lower consolute temperatures of the two surfactants did not increase appreciably with increasing surfactant concentration in the concentration range tested. This finding agrees with previous reports (10,

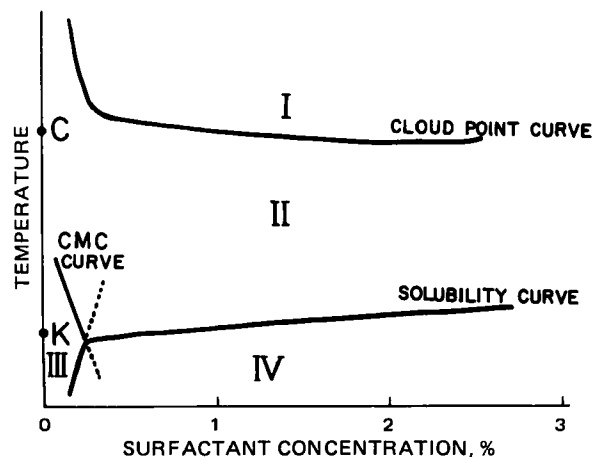


Figure 1—Schematic phase diagram representing the binary system of nonionic surfactant-water. Key: C, cloud point; K, Krafft point; phase field I, isotropic solution plus gel; phase field II, isotropic undersaturated solution containing nonassociated molecules and micelles; phase field III, isotropic solution of nonassociated molecules; and phase field IV, isotropic solution of nonassociated molecules plus crystals.

11). Hence, in Fig. 1, the main branches of the boundaries between phase fields I and II (labeled "cloud point curve") and between phase fields II and IV (labeled "solubility curve") are nearly horizontal. In this schematic figure, the Krafft point, defined by the intersection of the solubility curve and the CMC curve, resembles a triple point.

Phase field I corresponds to very dilute surfactant solutions plus relatively concentrated gels. Phase field II represents isotropic undersaturated solutions containing nonassociated surfactant molecules plus micelles. Dilute isotropic solutions of nonassociated surfactant molecules exist in phase field III, while such solutions coexist with solid surfactant crystals in phase field IV.

Surfactants II and III have the same number of ethylene oxide units per molecule. The Krafft point of Surfactant III, the stearyl alcohol adduct, exceeds that of Surfactant II, the cetyl alcohol adduct, by between 12.0 and 13.5°. This is due to the fact that the hydrocarbon moiety of the former is two methylene groups longer than that of the latter. The difference of 13° is comparable to the increase in Krafft point within a homologous series of ionic surfactants when the chain length is increased by two methylene groups (3, 5, 9). Replacement of a stearyl (Surfactant III) by an oleyl (Surfactant IV) group lowered the Krafft point from 47.5° to below 2°. This finding duplicates observations made with anionic surfactants (4) and parallels the drop in melting point when going from stearic to oleic acid.

The effect of additives on the Krafft points of Surfactants II and III was determined at the 1% surfactant level. The results are listed in Tables II and III. All additives in the 0.5–4 molal range raised the Krafft points of the two surfactants by between 1 and 4°. Inasmuch as increases in the lower consolute temperature

Table II—Effect of Additives on the Krafft Point of Surfactant II^{a, b}

Additive	Krafft Point at Additive Molalities of							
	0.10	0.25	0.50	1.0	2.0	3.0	4.0	5.0
Sodium nitrate	37.2°	37.8°	37.8°	38.0°	37.2°	37.8°	—	—
Potassium nitrate	36.9°	37.3°	37.5°	37.8°	37.9°	38.0°	38.5°	—
Lithium nitrate	35.8°	—	37.2°	37.7°	38.3°	37.2°	36.9°	36.3°
Hydrochloric acid	—	—	37.2°	37.5°	37.7°	37.3°	36.9°	36.6°
Sulfuric acid	—	—	38.5°	38.3°	38.3°	38.8°	39.0°	—
Magnesium nitrate	—	—	38.3°	38.5°	38.5°	38.2°	—	—
Calcium nitrate	—	—	37.0°	37.3°	38.0°	37.5°	—	—
Cadmium nitrate	35.8°	36.4°	36.8°	36.8°	37.0°	36.5°	35.7°	—
Aluminum nitrate	—	—	38.4°	38.6°	38.6°	37.5°	—	—
Lead nitrate	36.5°	37.0°	37.5°	37.5°	37.8°	—	—	—
Urea	35.0°	—	35.5°	35.5°	35.5°	35.5°	—	—

^aSurfactant concentration is 1.0%, based on weight of water. ^bKrafft point of Surfactant II without additive is 34.0–34.5° at 1.0%.

Table III—Effect of Additives on the Krafft Point of Surfactant III^{a, b}

Additive	Krafft Point at Additive Molalities of								
	0.10	0.25	0.50	1.0	2.0	3.0	4.0	5.0	
Sodium sulfate	50.0°	—	—	—	—	—	—	—	
Sodium chloride	49.0°	—	49.5°	—	—	—	—	—	
Sodium bromide	48.5°	49.2°	49.5°	49.8°	49.5°	48.8°	—	—	
Sodium iodide	—	—	50.5°	50.5°	50.3°	50.0°	—	—	
Sodium perchlorate	—	—	49.7°	49.8°	49.3°	49.0°	—	—	
Sodium nitrate	—	—	48.8°	48.5°	48.3°	—	—	—	
Potassium nitrate	47.6°	—	48.3°	48.7°	49.0°	—	—	—	
Cesium nitrate	48.6°	—	48.5°	49.0°	49.3°	—	—	—	
Lithium nitrate	—	—	49.3°	49.5°	50.5°	50.4°	—	—	
Hydrochloric acid	48.8°	—	49.3°	49.6°	48.5°	48.3°	48.0°	47.6°	
Sulfuric acid	—	—	48.8°	49.0°	49.3°	49.3°	49.5°	49.5°	
Magnesium nitrate	—	—	50.3°	50.5°	51.5°	47.2°	—	—	
Calcium nitrate	—	—	49.6°	49.4°	49.3°	48.7°	—	—	
Cadmium nitrate	—	—	48.3°	49.3°	49.8°	49.3°	—	—	
Aluminum nitrate	—	—	49.5°	49.5°	49.7°	48.8°	—	—	
Lead nitrate	—	—	50.0°	50.3°	—	—	—	—	
Nickel nitrate	—	—	50.5°	51.0°	51.0°	49.0°	—	—	
Urea	—	—	48.8°	49.2°	49.0°	48.7°	48.0°	—	

^a Surfactant concentration is 1.0%, based on weight of water. ^b Krafft point of Surfactant III without additive is 47.5° at 1.0%.

shrink the area on the phase diagram where undersaturated isotropic surfactant solutions prevail, this result represents a salting-out phenomenon. Even additives that raised the cloud points of Surfactants I–IV, salting them in (1, 12), raised the Krafft points of Surfactants II and III.

There were no major differences between the effects on the Krafft point of cloud point-raising and cloud point-lowering additives. Sodium iodide, which raised cloud points by destroying the structure of water, and the nitrates of lead and nickel, which raised them through complexation of the cations with the ether oxygens of the surfactants, raised the Krafft point of Surfactant III more than did sodium or potassium nitrate, which lowered the cloud points of polyoxyethylated surfactants by salting them out. Sulfuric acid and magnesium nitrate, which raised cloud points by complexation, and sodium or potassium nitrate, which lowered them through salting out, increased the Krafft point of Surfactant II to about the same extent.

Urea raised the Krafft points of both surfactants the least. While urea increased the cloud points of Surfactants II–IV only moderately (1), it increased the CMC of Surfactants I and IV more than did the salting-in electrolytes (14).

The limited effect of solution additives on the Krafft points of Surfactants II and III is not surprising when the Krafft point is considered as the melting point of the hydrated surfactant crystals. In that case, it involves primarily the hydrocarbon portion of the surfactant molecules in their crystalline lattice.

Even though the increases in Krafft point produced by the additives are limited to the narrow range of 1–4°, it can be seen from Tables II and III that the effect of additive concentration on the Krafft point follows one of three trends. As the concentration of the additive was progressively increased, the Krafft points increased monotonically, went through a maximum, or remained constant after an initial increase at low additive concentration. Even when the Krafft points went through a maximum and then decreased, they never dipped below the Krafft point of the surfactant in pure water. Generally, the nitrates of sodium, potassium, and cesium, which lowered the cloud points of the four surfactants through salting out (1), fell into the first category. Salting-in additives generally fell into the second or third category.

In the case of Surfactant II, the effect of the nitrates of sodium and potassium on the cloud point (1) as well as on the Krafft point was investigated over a wide concentration range. Increasing salt concentrations lowered the cloud point strongly and raised the Krafft point moderately. The two temperatures coincided in ap-

proximately 3 molal salt solutions and then overlapped. Thus, Surfactant II is practically insoluble in solutions having this or higher concentrations of sodium or potassium nitrate at all temperatures. A transition from crystalline solid to amorphous gel presumably occurs at the combined Krafft/cloud point.

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