Technical

The Mutual Solubilization of Soap and Lime Soap Dispersing Agents

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ABSTRACT AND SUMMARY

Krafft point measurements were used to show that lime soap dispersing agents (LSDA) and soaps solubilize each other. Addition of as little as 5% soap to amphoteric LSDA of limited water solubility (high Krafft point) brought about a substantial lowering of the Krafft point and thus markedly improved water solubility. On the other hand, addition of 10% amphoteric LSDA to sodium palmitate lowered the Krafft point of the soap by 10 to 14 C. Addition of anionic LSDA to sodium palmitate showed smaller Krafft point depressions. Addition of a builder-type salt, such as sodium metasilicate, had essentially no effect on the Krafft points of soap LSDA mixtures.

INTRODUCTION

Soap has two major shortcomings as a laundry detergent: it forms an insoluble scum in hard water and thus washes poorly, and it does not dissolve readily in cool water. It has been shown in a series of previous publications that the first shortcoming can be overcome by the addition of up to 20% various lime soap dispersing agents (LSDA) to the soap (1,2). In the course of this study of lime soap dispersants, it was also observed that even water-insoluble dispersants were capable of functioning and were apparently solubilized by up to 20% of soap. Inversely, it was noted that the Krafft points of soaps were lowered by the addition of lime soap dispersants. Accordingly, a more systematic study of these phenomena was undertaken with the LSDA of greatest importance in our ongoing soap-based detergent studies. Obviously the improvement of the cold water solubility of soap-based detergents would be of substantial practical value.

EXPERIMENTAL PROCEDURES

Sodium palmitate was prepared by neutralization at room temperature of an alcoholic solution of palmitic acid (96.4% palmitic, 3.0% myristic, 0.5% stearic acids) with the theoretical quantity of aqueous sodium hydroxide. Titration of a sample confirmed that the soap was neutral to phenolphthalein, and sodium analysis by sulfated ash agreed with theory. Sodium oleate and tallow soap were similarly prepared from USP oleic acid and tallow fatty

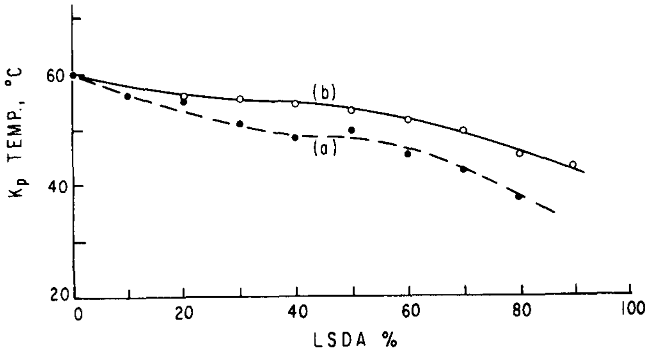

FIG. 2. Krafft points of blends of soap with anionic LSDA. Curve **a**: sodium palmitate + anionic compound 6; curve **b**: sodium palmitate + anionic compound 7.

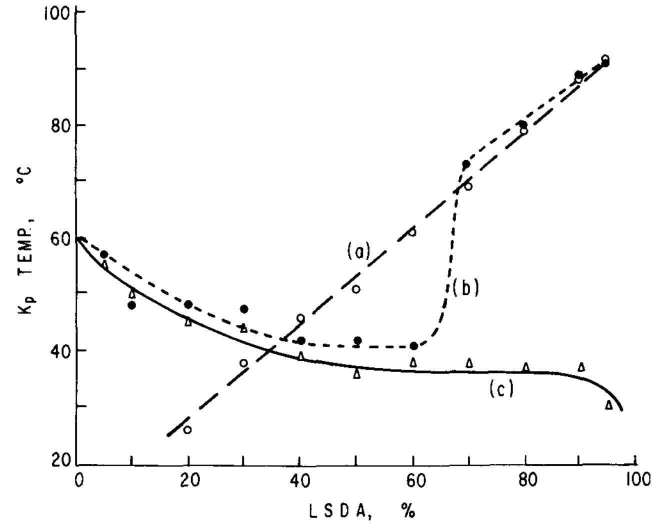

FIG. 1. Krafft points of blends of soaps with amphoteric LSDA. Curve **a**: Sodium oleate + amphoteric compound 3; curve **b**: sodium palmitate + amphoteric compound 3; curve **c**: sodium palmitate + amphoteric compound 1.

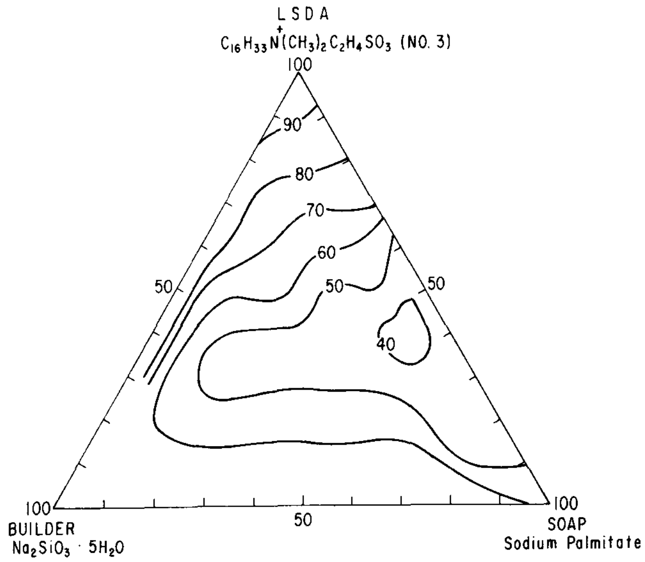

FIG. 3. Krafft points of ternary mixtures of sodium palmitate, amphoteric compound 3, and sodium metasilicate pentahydrate.

TABLE I

Krafft Points for Various Soap-LSDA Mixtures

Type of soap	Code no.	Structure	Ref.	Krafft points °C of 1% solutions of: 100% soap	90% soap + 10% LSDA	50% soap + 50% LSDA	10% soap + 90% LSDA	5% soap + 95% LSDA	100% LSDA
Sodium palmitate	1	$C_{15}H_{31}CONHC_3H_6N^+(CH_3)_2C_3H_6SO_3^-$	3	60	50	36	37	30	< 0
	2	$C_{16}H_{33}N^+(CH_3)_2CH_2CHOHCH_2SO_3^-$	4	60	47	44	30	31	89
	3	$C_{16}H_{33}N^+(CH_3)_2C_2H_4SO_3^-$	5	60	50	42	89	91	>90
	4	$C_{16}H_{33}N^+(CH_3)_2C_4H_8OSO_3^-$	5	60	50	49	70	>90	>90
	5	$C_{14}H_{29}N^+(CH_3)_2C_2H_4OSO_3^-$	5	60	46	39	53	64	>90
	6	$C_{14}H_{29}CH(CO_2CH_3)SO_3^-Na^+$	6	60	56	49	27	23	<20
	7	$C_{17}H_3CONHCH_2CH(CH_3)OSO_3^-Na^+$	7	60	56	53	40	39	31
Sodium oleate	2	$C_{16}H_{33}N^+(CH_3)_2CH_2CHOHCH_2SO_3^-$	4	<20	<20	<20	39	46	89
	3	$C_{16}H_{33}N^+(CH_3)_2C_2H_4SO_3^-$	5	<20	<20	51	88	91.5	>90
	5	$C_{14}H_{29}N^+(CH_3)_2C_2H_4OSO_3^-$	5	<20	<20	<20	46	67	>90
Sodium tallowate	2	$C_{16}H_{33}N^+(CH_3)_2CH_2CHOHCH_2SO_3^-$	4	41.5	33	33	29	40	89

acids, respectively. Syntheses of lime soap dispersing agents have been reported elsewhere as indicated in the reference column of Table I.

Each intimate mixture of soap and LSDA was prepared by dissolving both together in 80% ethanol and subsequently drying the solution to constant weight in the vacuum oven at 30 C. One percent solutions of the dried mixtures were prepared in deionized water, and Krafft points of the solutions were determined in the same manner as that used for pure surfactants. The test solutions were initially heated until they became clear, then they were cooled until they became cloudy, and finally they were reheated slowly. The process was repeated until two or more determinations checked within 1 C. The temperatures at which the solutions became clear were read and recorded as the Krafft points. Figures 1 and 2 and Table I show Krafft points for various binary mixtures of soap and LSDA.

Figure 3 shows the Krafft points for a ternary system, consisting of sodium palmitate, a sulfobetaine, and sodium metasilicate pentahydrate.

DISCUSSION AND RESULTS

While there is a certain parallelism between Krafft points and melting points, the precise mechanism of the mutual depression of Krafft points is not clearly understood. M. Raison (8) studied Krafft points of several binary mixtures of surfactants. Some of these binary mixtures showed a mutual Krafft point depression but others did not. Since the mechanism of interaction between soap and an LSDA is not clearly understood, this discussion is confined to the experimental data of this study and is primarily focused on the solubilization of high Krafft point LSDA by up to 20% soap and the solubilization of high Krafft point soap with up to 20% LSDA.

Table I indicates that addition of 10% or more of any of the seven LSDA of this study to sodium palmitate brought about depression of the Krafft point of the soap. Similarly, the addition of 10% of any of the three soaps of this study to amphoteric LSDA 2, which has a high Krafft point, brought about a considerable depression of the Krafft point of the LSDA.

Even a 5% addition of soap to the LSDA resulted in a dramatic Krafft point depression except in the case of LSDA #4 whose Krafft point was not in a measurable range. The Krafft point of the soap itself does not appear to affect the extent of Krafft point depression of a high Krafft point LSDA such as compound 2.

The data of Table I show the amphoteric LSDAs differ from the anionic ones with respect to the degree of Krafft point depression. The results of a more detailed study of the mutual solubilization of amphoteric LSDA 1 and 3, and two soaps are shown graphically in Figure 1. Here curves **b** and **c** depict the solubilization of sodium palmitate, a high Krafft point soap, with a high Krafft point amphoteric compound 3 (curve **b**), and a low Krafft point amphoteric compound 1 (curve **c**). Since the two curves are almost identical up to a 60:40 ratio of LSDA:soap it is obvious that the Krafft point of the LSDA used has no effect in this region. Curve **a** shows the Krafft point behavior of mixtures of sodium oleate, a low Krafft point soap, and amphoteric compound 3 possessing a high Krafft point. Curve **a** shows an essentially linear relationship, and in the 70-100% LSDA range, it is almost identical with curve **b**. Obviously, the Krafft point of mixtures in this range is affected by the nature of the LSDA and not that of the soap used.

Anionic LSDA, such as compounds 6 and 7, exert less of a depressing effect on the Krafft point of sodium palmitate as shown in Figure 2. Here the Krafft point of the LSDA does have an effect on the degree of Krafft point depression achieved, with the more soluble compound 6 having a greater effect on Krafft point depression than does compound 7.

Since sodium silicates have been shown to be good detergent builders for soap-LSDA combinations (1,2) it was of interest to determine the extent to which Krafft points of ternary mixtures would be affected by the builder. The Krafft points of the system sodium palmitate, amphoteric LSDA 3, sodium metasilicate pentahydrate are shown in the triangular diagram of Figure 3, which indicates that the builder essentially does not affect the Krafft points of the mixtures.

Thus it can be concluded that the addition of lime soap dispersing agents improves the water solubility of soap (lowers the Krafft point) in addition to improving its hard water performance.

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