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## Surface Activity of Fatty Acid Salts in Aqueous Solutions

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**Abstract**—The surface activity of sodium, potassium and, ammonium salts of fatty acids [stearic, oleic, synthetic fatty acids ( $C_{13}$ – $C_{15}$  fractions), higher fatty acids contained in bottoms after separation of volatile fatty acids from cotton oil] in aqueous solutions was studied and analyzed.

Surfactants are widely used in various branches of economy, mostly for improvement of materials and development of their new kinds.

In production of anionic surfactants, narrow fractions of synthetic fatty acids (SFA) ( $C_{13}$ – $C_{15}$  and  $C_{10}$ – $C_{16}$ ) and also individual stearic and oleic acids are used as raw materials. This raw material is expensive and its production is complicated. Therefore, attempts have been made to find alternative sources of fatty acids and their mixtures. For example, anionic surfactant prepared from products recovered from tall oil (one of products of cellulose processing) has been used in emulsion polymerization [1, 2]. It is known also [3, 4] that sodium or potassium salts of higher fatty acids recovered from cotton oil efficiently stabilize bituminous emulsions [3, 4].

In this study, we prepared anionic surfactants from bottoms formed after separation of volatile fatty acids from cotton oil (FACB). These bottoms contain a fairly large amount of fatty acids and are an inexpensive natural raw materials for preparing surfactants. The surface activities of the new and commercial anionic surfactants are compared.

### EXPERIMENTAL

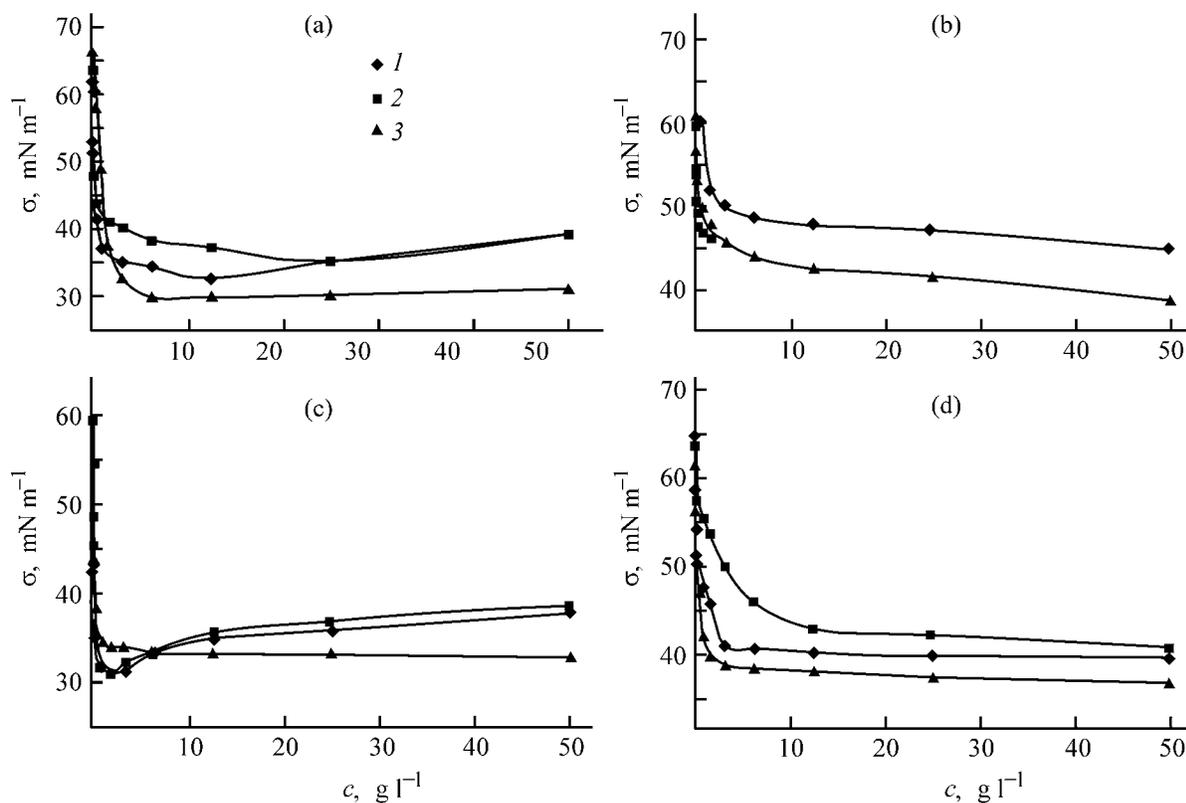
The surface activity of fatty acid salts was studied by common technique [GOST (State Standard 20216–74) [5–9]. The physicochemical features and chemical composition of FACB were determined by the standard method [GOST 5474–5478] [10]. FACB is a dark brown oily liquid with a specific odor, which contains 30 wt % monomeric (stearic, oleic, palmitic, linoleic) and 70 wt % oligomeric fatty acids. The mois-

ture content is 10.2 wt %, ash content 0.6 wt %, the number-average molecular weight 1130, acid number 156.7 mg KOH  $g^{-1}$ , saponification number 192.0 mg KOH  $g^{-1}$ , and iodine number 76.1 g  $I_2/100$  g.

The fatty acids were converted into their salts by saponification with 30% aqueous sodium, potassium and ammonium hydroxides at 90–100 °C for 2 h. Aqueous solutions of these surfactants have pH 10.0–11.4.

It is known that surfactant molecules have a large excess free energy at the interface between the aqueous solution and air. The specific interfacial excess free energy ( $\sigma$ ) (surface tension) of a surfactant is a function of its molecular weight, molecular configuration, and intermolecular interaction features. In order to characterize the surface activity of surfactants based on FACB, we studied their surface tension isotherms ( Figs. 1a–1b). The surface tension in these systems was measured by the Du Nouy technique.

The surface tension of aqueous anionic surfactants is dependent on both the molecular structure of the surfactants and the cation type. It is known that branched anionic surfactants exhibit a higher surface tension. As can be seen from the table, the lowest surface tension is exhibited by paraffinates (fraction  $C_{13}$ – $C_{15}$ ) used as emulsifiers in production of commercial butadiene-vinylidene-chloride latexes. The highest surface tension is exhibited by sodium stearate. We found that the surface activity of salts prepared from FACB containing a mixture of fatty acids is intermediate between the surface activities of particular fatty acid salts, i.e., the multicomponent FACB salt does not show synergism in the surface activity.



**Fig. 1.** Surface tension isotherms of aqueous solutions of (a) SFA ( $C_{13-15}$  fraction), (b) stearic acid, (c) oleic acid, and (d) FACB salts. ( $\sigma$ ) Surface tension and (c) surfactant concentration. (1)  $K^+$ , (2)  $Na^+$ , and (3)  $NH_4^+$ .

Along with the surface tension, the surface activity of surfactant can be characterized by the parameter  $pc_{20}$  (negative logarithm of the surfactant concentration at which the surface tension decreases by  $20 \text{ mN m}^{-1}$ ). The table shows that this parameter is sensitive to the molecular structure of the hydrocarbon moiety in the surfactant molecule. The sodium SFA salt and sodium oleate have comparable  $pc_{20}$  values. In going

to sodium stearate and then to FACB salts, this parameter appreciably increases. These data show that, although the multicomponent surfactants based on FACB do not exhibit synergism in surface tension, they are synergistic with respect to the  $pc_{20}$  value.

Both dispersing and stabilizing effects of surfactants are due to their interfacial sorption. Therefore,

#### Characteristics of aqueous surfactants

Surfactant	Cation	$\sigma$ , $\text{mN m}^{-1}$	$pc_{20}$ , $\text{g dm}^{-3}$	$\Gamma_{\infty} \times 10^6$ , $\text{g m}^{-2}$	$n$	CMC, $\text{g dm}^{-3}$
SFA $C_{13-C_{15}}$	$K^+$	32.8	0.25	5.6	0.59	0.6
	$Na^+$	35.3	0.03	4.8	1.52	0.1
	$NH_4^+$	29.7	0.78	6.9	1.36	5.0
Stearic acid	$K^+$	43.2	3.98	3.3	2.18	6.3
	$Na^+$	47.2	0.32	3.8	1.38	0.8
	$NH_4^+$	38.7	0.32	2.5	1.76	6.3
Oleic acid	$K^+$	31.1	–	0.5	4.28	2.6
	$Na^+$	30.9	0.04	6.0	1.75	0.6
	$NH_4^+$	32.7	–	7.1	1.76	0.4
FACB	$K^+$	39.8	0.40	3.0	0.57	0.4, 4.2
	$Na^+$	41.0	3.16	2.5	1.19	7.9
	$NH_4^+$	36.9	0.25	2.8	2.54	1.8

the limiting interfacial surfactant sorption (surface concentration of the surfactant, at which its monomolecular surface layer is formed) can be used for characterization of its surface activity. The limiting sorption  $\Gamma_{\infty}$  of surfactants under consideration was determined from their sorption isotherms (see table). The highest sorption is exhibited by ammonium oleate, and the lowest sorption, by ammonium stearate. The surfactants based on FACB salts have  $\Gamma_{\infty}$  value close to that of stearates and are virtually insensitive to cation nature. The water solubility of surfactants is dependent on cation nature. The most soluble are potassium salts. The table shows that, irrespective of the cation kind, the stearates and FACB salts are less soluble than the SFA salts and oleates.

The surface activity of surfactants can be characterized also by the slope  $n$  of the plot of the surface tension against the interfacial sorption. The surfactants belonging to a certain type (water-soluble, nonionic, ionic), have approximately equal colligative parameter  $n$  irrespective of their molecular structure. Depending on the type of a surfactant, the  $n$  values vary as follows: water-soluble 1.5, nonionic 1, and ionic 2. The  $n$  value of ionic surfactants in electrolyte solutions is in the range 1–2. Most part of the surfactants tested by us, apart from their potassium derivatives, belong to the ionic type. Due to weak dissociation of SFA and FACB potassium salts, their  $n$  parameters are less than unity. At the same time, for completely dissociated potassium stearate and oleate, the  $n$  value exceeds 2.

The critical micelle concentration (CMC) is one of the most important characteristics of a surfactant. This parameter is sensitive to both the features of surfactant molecular structure and such factors as temperature, electrolyte content, presence of polar organic impurities, etc. The CMC decreases with lengthening of the hydrocarbon radical,<sup>1</sup> and depends on the number, kind, and position of ionic groups and presence of unsaturated functional groups. The surfactants with branched and, especially, cyclic hydrocarbon chains have lower CMC.

Our results (see table) do not show any relationship between the nature of a surfactant and its surface activity. However, these data show some features of FACB salts.

(1) There are two inflection points in the surface tension isotherm corresponding to two different CMC

<sup>1</sup> Decrease in CMC of SFA (C<sub>13</sub>–C<sub>15</sub> fractions) potassium salts by an order of magnitude in comparison with that of potassium stearate (table) is due to the low water solubility of potassium stearate.

values. We suggest that the appearance of these two CMC values can be caused either by the multicomponent composition of FACB, hindering formation of uniform micelles, or by transformation of the initial spherical micelles into those of another kind. The second CMC can also be due the fact that FACB contains a large amount of oligomeric fatty acids. Their salts are associated at concentrations higher than the first CMC, and this is manifested in the sorption isotherm as the point of critical concentration of association.

(2) The FACB sodium salt has considerably higher CMC than FACB salts with other cations.

(3) The CMC of the FACB ammonium salt is intermediate between those of ammonium stearate (paraffinate) and ammonium oleate.

Thus, our experiments showed that the surface activity of FACB potassium, sodium and ammonium salts is intermediate between the surface activities of unsaturated and saturated acid salts contained in FACB salt. There is a synergistic effect in the slope of the concentration dependence of the surface tension, but the synergism is lacking with respect to other characteristics of surface activity.

## CONCLUSION

Anionic surfactants prepared from higher fatty acids contained in bottoms formed after separation of volatile fatty acids from cotton oil are not inferior to commercial industrial surfactants. These surfactants can be applied as emulsifiers in emulsion polymerization, as plasticizers in production of concretes, and as dispersing agents in preparation of suspensions of solids.

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