Influence of the structure of amphiphilic anions on the Krafft temperature of micellar solutions of anionic surfactants

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The influence of the structure of surfactants on the Krafft temperature T_k was studied for aqueous solutions of anionic surfactants containing the sulfate and sulfonate head groups, the hydrophilic (H) and lipophilic (L) fragments in amphiphilic anions, and various polar and C_8—C_{18} hydrocarbon groups. The best statistical quality was obtained for the model with separate account of the effect of the H and L structural fragments on the T_k value.

Key words: surfactants, alkyl sulfates, alkyl sulfonates, anionic micelles, Krafft temperature, structure—property relationships, regression models.

Solubility of surfactants in water depends strongly on their capability of associating to form micelles. In surfactant—water systems, the lower temperature boundary of micelle existence is determined by the Krafft temperature (T_k), above which the solubility of surfactants (in the form of micelles) increases sharply. However, the monomolecular form and complexes of several surfactant molecules are poorly soluble.[1] The technical application of micellar solutions of surfactants is restricted by the temperature interval from the T_k value to the cloud temperature, *viz.*, the upper boundary of existence of micellar solutions. The temperature effect on the solubility of the surfactants has been studied,[2,3] and the T_k values of aqueous solutions have been determined.

The T_k value varies widely with a change in the structure of ionic surfactants. An increase in the number of oxyethylene groups in the sodium alkylpoly(oxyethylene) sulfate anions has been established[4—6] to successively decrease the T_k values. For the surfactants with the sulfate or sulfonate head groups, T_k increases with an increase in the number of methylene groups in the lipophilic hydrocarbon tail of micelles (with the increment 5.5° per carbon atom).[5]

A study of the dependence of T_k on the surfactant structure is of interest for revealing the internal structure of micelles, for the synthesis of new surfactants, and the development of the related technologies. In this work, we searched for the quantitative structure—property relationships (QSPR), which make it possible to predict the T_k values for the anionic surfactants containing the sulfate and sulfonate head groups and various polar groups, using the available published data.[4—13]

Calculation procedure

The T_k values for aqueous solutions of anionic surfactants were taken from the published works.[4—13] The V_L and V_H descriptors (10^{-2} cm^{3}mol^{-1}) calculated from the atomic increments by the additive method[14,15] were used for the characterization of the volumes of the hydrophilic and lipophilic fragments in the surfactant anions. The V_L and V_H values for anions **1**—**57** are presented in Table 1. The search for QSPR was based on the regression analysis of the T_k values using the subset of descriptors calculated from the surfactant structure (Table 2).

Multiple regressions were calculated by the least-squares method using the STATGRAPHICS *Plus* (Version 2.1) program. The statistical characteristics of the regressions obtained reflect the number of compounds in the subset n, the standard deviation for the subset s, the multiple correlation coefficient (calculated taking into account the number of degrees of freedom), and the Fischer statistical criterion F.

Results and Discussion

The internal structure of ionic micelles in aqueous solutions includes a hydrophobic core surrounded by a hydrophilic polar shell.[1,3] The latter is restricted from the outside by charged head groups of amphiphilic ions, which interact with counterions and water molecules. The micelle core consists of hydrocarbon tails of the amphiphilic ions attached either to the head group, or to the polar group in the ion structure.

The properties of the core are similar to those of liquid alkanes.[1] According to the current data,[16,17] the polar shell can contain from two to four methylene groups of the hydrocarbon tail adjacent to the head or polar group of the amphiphile. Thus, the shell is formed by the polar

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Table 1. The T_k values for sodium salts of amphiphilic anions **1—57** and desciptors V_L and V_H

Anion	V_L	V_H	T_k/°C		
	10^{-2} cm^3 mol^{-1}		Calculation*	Experiment	
				Value**	Refs.
$C_{10}H_{21}OSO_3^-$ (**1**)	1.182	0.713	7.3	8	5
$C_{12}H_{25}OSO_3^-$ (**2**)	1.463	0.713	19.6	21, 16	5 7
$C_{14}H_{29}OSO_3^-$ (**3**)	1.745	0.713	31.9	35.8, 30	5 7
$C_{16}H_{33}OSO_3^-$ (**4**)	2.027	0.713	44.2	43.0, 45	5 7
$C_{18}H_{37}OSO_3^-$ (**5**)	2.309	0.713	56.5	57.5, 56	5 7
$Me_2C_{12}H_{24}OSO_3^-$ (**6**)	1.745	0.713	9.7	11	8
$Me_2C_{14}H_{28}OSO_3^-$ (**7**)	2.027	0.713	22.0	25	8
$Me_2C_{16}H_{32}OSO_3^-$ (**8**)	2.309	0.713	33.3	30	8
$C_{16}H_{33}(OCH_2CHMe)_2OSO_3^-$ (**9**)	2.027	1.676	16.8	19	5
$C_{18}H_{37}(OCH_2CHMe)_2OSO_3^-$ (**10**)	2.309	1.676	29.1	31	5
$C_{14}H_{29}OCH_2CH(Me)OSO_3^-$ (**11**)	1.745	1.194	18.2	14	9
$C_{16}H_{33}OCH_2CH(Me)OSO_3^-$ (**12**)	2.027	1.194	30.5	27	9
$C_{18}H_{37}OCH_2CH(Me)OSO_3^-$ (**13**)	2.309	1.194	42.8	43	9
$C_{16}H_{33}OC_2H_4OSO_3^-$ (**14**)	2.027	1.053	34.7	36	4
$C_{18}H_{37}OC_2H_4OSO_3^-$ (**15**)	2.309	1.053	47.0	46	4
$C_{16}H_{33}(OC_2H_4)_2OSO_3^-$ (**16**)	2.027	1.394	25.1	24	4
$C_{18}H_{37}(OC_2H_4)_2OSO_3^-$ (**17**)	2.309	1.394	37.4	40	4
$C_{16}H_{33}(OC_2H_4)_3OSO_3^-$ (**18**)	2.027	1.735	15.6	19	4
$C_{18}H_{37}(OC_2H_4)_3OSO_3^-$ (**19**)	2.309	1.735	27.9	32	4
$C_{16}H_{33}(OC_2H_4)_4OSO_3^-$ (**20**)	2.027	2.075	6.1	1	4
$C_{18}H_{37}(OC_2H_4)_4OSO_3^-$ (**21**)	2.309	2.075	18.4	18	4
$C_{12}H_{25}OC_2H_4OSO_3^-$ (**22**)	1.463	1.054	10.0	8.5, 9.0	10
$C_{12}H_{25}(OC_2H_4)_2OSO_3^-$ (**23**)	1.463	1.394	0.5	−1	6
$C_{12}H_{25}SO_3^-$ (**24**)	1.463	0.654	32.7	38	7
$C_{13}H_{27}SO_3^-$ (**25**)	1.604	0.654	38.9	35.5	7
$C_{14}H_{29}SO_3^-$ (**26**)	1.745	0.654	45.0	48	7
$C_{15}H_{31}SO_3^-$ (**27**)	1.886	0.654	51.2	48	7
$C_{16}H_{33}SO_3^-$ (**28**)	2.027	0.654	57.3	57	7
$C_{17}H_{35}SO_3^-$ (**29**)	2.168	0.654	63.5	62	7
$C_{18}H_{37}SO_3^-$ (**30**)	2.309	0.654	69.7	70	7
$C_8H_{17}C(O)OC_2H_4SO_3^-$ (**31**)	0.900	1.151	−0.3	0	11
$C_{10}H_{21}C(O)OC_2H_4SO_3^-$ (**32**)	1.182	1.151	12.0	8.1	11
$C_{12}H_{25}C(O)OC_2H_4SO_3^-$ (**33**)	1.463	1.151	24.3	24.2	11
$C_{14}H_{29}C(O)OC_2H_4SO_3^-$ (**34**)	1.745	1.151	36.6	36.2	11
$C_8H_{17}OC(O)C_2H_4SO_3^-$ (**35**)	0.900	1.151	−0.3	0	11
$C_{10}H_{21}OC(O)C_2H_4SO_3^-$ (**36**)	1.182	1.151	12.0	12.5	11
$C_{12}H_{25}OC(O)C_2H_4SO_3^-$ (**37**)	1.463	1.151	24.3	26.5	11
$C_{14}H_{29}OC(O)C_2H_4SO_3^-$ (**38**)	1.745	1.151	36.6	39	11
$C_{10}H_{21}CH(Me)C_6H_4SO_3^-$ (**39**)	1.322	1.403	32.2	31.5	12
$C_{12}H_{25}CH(Me)C_6H_4SO_3^-$ (**40**)	1.604	1.403	44.6	46	12
$C_{14}H_{29}CH(Me)C_6H_4SO_3^-$ (**41**)	1.886	1.403	56.9	54.2	12
$C_{16}H_{33}CH(Me)C_6H_4SO_3^-$ (**42**)	2.168	1.403	69.2	60.8	12
$C_8H_{17}C_6H_4SO_3^-$ (**43**)	0.900	1.262	17.9	25.5, 26	10
$C_{12}H_{25}CH{=}CHCH_2SO_3^-$ (**44**)	1.463	1.034	35.7	40.0, 35.5	10
$C_{12}H_{25}CH(OH)C_2H_4SO_3^-$ (**45**)	1.604	0.995	21.0	21.5, 20.2	10
$C_{10}H_{21}CH(CH_2OH)SO_3^-$ (**46**)	1.322	0.854	57.0	59	7
$C_{12}H_{25}CH(CH_2OH)SO_3^-$ (**47**)	1.604	0.854	69.4	73	7
$C_{14}H_{29}CH(CH_2OH)SO_3^-$ (**48**)	1.886	0.854	81.7	84	7

(*to be continued*)

Table 1 (*continued*)

Anion	V_L	V_H	T_k/°C		
	10^{-2} cm^3 mol^{-1}		Calculation*	Experiment	
				Value**	Refs.
$C_{16}H_{33}CH(CH_2OH)SO_3^-$ (**49**)	2.168	0.854	94.0	93	7
$C_{10}H_{21}CH(COOH)SO_3^-$ (**50**)	1.322	0.870	57.5	52	7
$C_{12}H_{25}CH(COOH)SO_3^-$ (**51**)	1.604	0.870	69.8	68	7
$C_{14}H_{29}CH(COOH)SO_3^-$ (**52**)	1.886	0.870	82.1	83	7
$C_{16}H_{33}CH(COOH)SO_3^-$ (**53**)	2.168	0.870	94.5	94	7
$(SO_3^-)OC_{12}H_{24}OSO_3^-$ (**54**)	1.160	1.393	11.7	12	13
$(SO_3^-)OC_{14}H_{28}OSO_3^-$ (**55**)	1.442	1.393	24.0	24.8	13
$(SO_3^-)OC_{16}H_{32}OSO_3^-$ (**56**)	1.724	1.393	36.3	39.1	13
$(SO_3^-)OC_{18}H_{36}OSO_3^-$ (**57**)	2.005	1.393	48.6	44.9	13

* Performed in this work.

** In the case of two T_k values, the average value is used in calculations.

groups (including small hydrocarbon chains), charged head groups, and several C atoms of the hydrocarbon tail. The polar groups are absent from some simplest surfactants. The physicochemical properties of the shell are close to those of aqueous-alcohol mixtures.[1,3]

Taking into account a great difference in the properties of the hydrophobic core and hydrophilic shell, it seems reasonable in studies of the influence of the surfactant structure on the T_k value (and on other properties of micellar solutions) to use a model in which two fragments of the amphiphile structure, *viz.*, lipophilic L (corresponding to the core) and hydrophilic H (corresponding to the shell), are characterized by separate subsets of descriptors. Due to the differences in the properties of the L and H fragments, one can expect that the additivity of the effects of different structural groups in the amphiphilic ions on the T_k value (and on other properties) is better fulfilled as applied to the L and H fragments rather than to the whole anion. The equation of linear multiple regression for the model proposed can be written, in the general case, in the form

$$P = \Sigma k_{L,i}D_{L,i} + \Sigma k_{H,i}D_{H,i} + \text{const}, \qquad (1)$$

where $P = T_k$ (or another property); $D_{L,i}$ and $D_{H,i}$ are the descriptors for the L and H fragments; and $k_{L,i}$ and $k_{H,i}$ are the coefficients at the descriptors, respectively.

Table 2. Optimal subset of descriptors for the series of anionic surfactants with sulfate and sulfonate head groups

Descriptor	Characteristic	Value
V_L	Volume of the L fragment of amphiphilic anion	V_L values (calculated for N_{sh} = 2) are presented in Table 1
N_L	Number of ramifications (CH groups) in the L fragment	For anions **6**—**8** N_L = 1, for other anions N_L = 0
V_H	Volume of the H fragment of amphiphilic anion	V_H values (calculated for N_{sh} = 2) are presented in Table 1
N_H	Number of ramifications in the H fragment	For anions **9** and **10** N_H = 2, for anions **11**—**13**, **31**—**42**, and **45**—**53** N_H = 1, for others N_H = 0. For anions **31**—**38** and **50**—**53** N_H = 1, because in the model used ramification of the COO groups should be taken into account
N_{Ph}	Number of benzene cycles and alkene groups in the H fragment	For anions **39**—**44** N_{Ph} = 1, for other anions N_{Ph} = 0
N_O	Number of O atoms in ether groups and hydroxyl groups, which do not form hydrogen bonds with the head group, in the H fragment	For anions **11**—**15**, **22**, and **45** N_O = 1, for anions **9**, **10**, **16**, **17** and **23** N_O = 2, for anions **18** and **19** N_O = 3, for anions **20** and **21** N_O = 4, for others N_O = 0
N_{es}	Number of COO and SOO groups in the H fragment	For anions **1**—**23** and **32**—**37** N_{es} = 1, for anions **54**—**57** both sulfate groups are taken into account, N_{es} = 2, for others N_{es} = 0
N_{OH}	Number of OH groups of the H fragment capable of forming a hydrogen bond with the head group of the amphiphilic anions	For anions **46**—**53** N_{OH} = 1, for other anions N_{OH} = 0

Our calculations showed that the model tested is statistically appropriate and corresponds to the regression

$$T_k = (-50.7\pm3.3) + (43.7\pm1.1)V_L + (29.8\pm3.6)V_H - (22.2\pm1.8)N_L - (8.35\pm0.91)N_H - (8.3\pm1.7)N_{Ph} - (19.7\pm1.1)N_O - (14.9\pm1.4)N_{es} + (32.9\pm1.4)N_{OH} \quad (2)$$

$(n = 55, s = 2.6, r = 0.994, F = 533)$,

obtained using the optimum subset of descriptors (their characteristics are given in Table 2). Equation (2) describes ~99% of the total change in the T_k values (determination coefficient $r^2 = 0.987$) for the series of 57 anionic surfactants examined (see Table 1), except for anions **42** and **43** (see below).

Using the additive model, which does not include the isolation of the L and H fragments from the structure of the amphiphilic anions, we obtained the following regression:

$$T_k = (-57.1\pm3.7) + (42.9\pm1.5)V_{an} - (11.46\pm0.93)N_i - (15.5\pm2.2)N_{Ph} - (22.60\pm0.80)N_O - (19.7\pm1.1)N_{es} + (32.5\pm1.8)N_{OH} \quad (3)$$

$(n = 55, s = 3.6, r = 0.988, F = 380)$,

The descriptors for the whole anions were used in the calculation of this regression (in particular, $V_{an} = V_L + V_H$ and $N_i = N_L + N_H$; other descriptors did not require recalculation but in this model they refer to the whole anions).

The significant differences in coefficients for the pair descriptors (V_L and V_H), (N_L and N_H) in regression (2) and better statistical characteristics of Eq. (2) compared to (3) confirm that the model with separate account of the structures of the L and H fragments is preferential.

The T_k values for anions **42** and **43** (see Table 1) were excluded from the calculations of regressions (2) and (3). Their deviations from Eq. (2) were several times higher than those for other anions and exceeded the criterion 3*s*. Probably, the T_k values for anions **42** and **43** contain high experimental errors (8—9 K).

The calculations of regression (2) are performed in several variants, which made it possible to estimate the number of the CH_2 (or CH) groups N_{sh} in the hydrocarbon tail, which penetrate into the polar shell of micelles and, correspondingly, are included into the composition of the H fragment. In the calculation of the variants, the V_L and V_H descriptors were calculated in the N_{sh} interval from 0 to 4, and then the statistical characteristics of all five variants of regression (2) were determined. The minimum s value and maximum r and F values were obtained under the condition $N_{sh} = 2$ corresponding to regression (2). Several calculations of regression (2) were performed at variation of 1) the N_{sh} values in the [0,4] interval for the anions without polar groups and under the condition $N_{sh} = 2$ for other anions and 2) N_{sh} values for the anions with polar groups under the condition that $N_{sh} = 2$ for other anions. In both cases, the quality of regression (2) did not improve. Thus, the statistical estimation makes it possible to accept $N_{sh} = 2$ for all amphiphilic anions (see Table 1). This value was used in the calculations of the regressions in this work. Regression (2) describes well the T_k values for symmetrical bolamorphic amphiphiles (anions **54**—**57**, see Table 1) when $N_{sh} = 2$ is used for each end of the hydrocarbon chain.

The coefficients at these descriptors in Eq. (2) show that an increase in the volumes of the V_L and V_H fragments increases the T_k value to different extent. The ramification of the L and H fragments also has different effects on T_k, decreasing the latter. In both cases, the lower absolute values of the coefficients correspond to the H fragment. Probably, the smaller influence of the volume and ramification of the H fragment on T_k can be explained by the fact that its group-components exist in the partially hydrated state in the crystalline phase,[1] and changes in their solvation on transferring to micelles are not great.

The coefficients at the descriptots for the polar groups in the H fragment are negative in most cases. They reflect their influence on the hydrophile-lipophile balance[18] of the amphiphile. The ramification of the anionic surfactants results in loosening of the internal structure of micelles and facilitating water to penetrate into the polar shell.[19] This agrees with the negative coefficients at the N_L and N_H descriptors. The positive coefficient at the N_{OH} descriptor shows that the formation of an intramolecular hydrogen bond between the polar and head group decreases the hydration of the latter. The equilibrium between micelles and crystal hydrates should shift toward the crystal hydrates, increasing the T_k value.

The differences between the calculated (using Eq. (2)) and observed T_k values (see Table 1) correspond to the level of reproducibility of the latter in different works. Eight descriptors were needed for the considered series of anionic surfactants, whose structures contain the sulfate and sulfonate head groups, the ramifications of the L and H fragments, and various polar groups. The number of these descriptors could be greater, but for three pairs of polar groups (C_6H_4 and CH=CH, C(O)O and S(O)O, OH and COOH involved in the hydrogen bond) their influence on T_k was the same within the pairs, which made it possible to use three instead of six descriptors.

When excluded the anions with some polar groups from the subset, the regressions with a smaller number of descriptors can easily be obtained. In particular, when the subset does not contain anions with any polar groups in the H fragment and the L and H fragments are not

Table 3. Structure of the L and H fragments and their contributions to Eq. (2)

Anion	L	H	$\Sigma a_{L,i}D_{L,i}$	$\Sigma a_{H,i}D_{H,i}$
1	C_8H_{17}	$(CH_2)_2OSO_3^-$	51.63	6.35
2	$C_{10}H_{21}$	$(CH_2)_2OSO_3^-$	63.95	6.35
3	$C_{12}H_{25}$	$(CH_2)_2OSO_3^-$	76.26	6.35
4	$C_{14}H_{29}$	$(CH_2)_2OSO_3^-$	88.58	6.35
5	$C_{16}H_{33}$	$(CH_2)_2OSO_3^-$	100.89	6.35
6	$(Me)_2C_{10}H_{20}$	$(CH_2)_2OSO_3^-$	54.06	6.35
7	$(Me)_2C_{12}H_{24}$	$(CH_2)_2OSO_3^-$	66.38	6.35
8	$(Me)_2C_{14}H_{28}$	$(CH_2)_2OSO_3^-$	78.69	6.35
9	$C_{14}H_{29}$	$(CH_2)_2(OCH_2CHMe)_2OSO_3^-$	88.58	−21.02
10	$C_{16}H_{33}$	$(CH_2)_2(OCH_2CHMe)_2OSO_3^-$	100.89	−21.02
11	$C_{12}H_{25}$	$(CH_2)_2OCH_2CH(Me)OSO_3^-$	76.26	−7.34
12	$C_{14}H_{29}$	$(CH_2)_2OCH_2CH(Me)OSO_3^-$	88.58	−7.34
13	$C_{16}H_{33}$	$(CH_2)_2OCH_2CH(Me)OSO_3^-$	100.89	−7.34
14	$C_{14}H_{29}$	$(CH_2)_2OC_2H_4OSO_3^-$	88.58	−3.19
15	$C_{16}H_{33}$	$(CH_2)_2OC_2H_4OSO_3^-$	100.89	−3.19
16	$C_{14}H_{29}$	$(CH_2)_2(OC_2H_4)_2OSO_3^-$	88.58	−12.72
17	$C_{16}H_{33}$	$(CH_2)_2(OC_2H_4)_2OSO_3^-$	100.89	−12.72
18	$C_{14}H_{29}$	$(CH_2)_2(OC_2H_4)_3OSO_3^-$	88.58	−22.25
19	$C_{16}H_{33}$	$(CH_2)_2(OC_2H_4)_3OSO_3^-$	100.89	−22.25
20	$C_{14}H_{29}$	$(CH_2)_2(OC_2H_4)_4OSO_3^-$	88.58	−31.78
21	$C_{16}H_{33}$	$(CH_2)_2(OC_2H_4)_4OSO_3^-$	100.89	−31.78
22	$C_{10}H_{21}$	$(CH_2)_2OC_2H_4OSO_3^-$	63.95	−3.19
23	$C_{10}H_{21}$	$(CH_2)_2(OC_2H_4)_2OSO_3^-$	63.95	−12.72
24	$C_{10}H_{21}$	$(CH_2)_2SO_3^-$	63.95	19.50
25	$C_{11}H_{23}$	$(CH_2)_2SO_3^-$	70.10	19.50
26	$C_{12}H_{25}$	$(CH_2)_2SO_3^-$	76.26	19.50
27	$C_{13}H_{27}$	$(CH_2)_2SO_3^-$	82.42	19.50
28	$C_{14}H_{29}$	$(CH_2)_2SO_3^-$	88.58	19.50
29	$C_{15}H_{31}$	$(CH_2)_2SO_3^-$	94.73	19.50
30	$C_{16}H_{33}$	$(CH_2)_2SO_3^-$	100.89	19.50
31	C_6H_{13}	$(CH_2)_2C(O)OC_2H_4SO_3^-$	39.32	11.06
32	C_8H_{17}	$(CH_2)_2C(O)OC_2H_4SO_3^-$	51.63	11.06
33	$C_{10}H_{21}$	$(CH_2)_2C(O)OC_2H_4SO_3^-$	63.95	11.06
34	$C_{12}H_{25}$	$(CH_2)_2C(O)OC_2H_4SO_3^-$	76.26	11.06
35	C_6H_{13}	$(CH_2)_2OC(O)C_2H_4SO_3^-$	39.32	11.06
36	C_8H_{17}	$(CH_2)_2OC(O)C_2H_4SO_3^-$	51.63	11.06
37	$C_{10}H_{21}$	$(CH_2)_2OC(O)C_2H_4SO_3^-$	63.95	11.06
38	$C_{12}H_{25}$	$(CH_2)_2OC(O)C_2H_4SO_3^-$	76.26	11.06
39	C_9H_{19}	$CH_2CH(Me)C_6H_4SO_3^-$	57.79	25.16
40	$C_{11}H_{23}$	$CH_2CH(Me)C_6H_4SO_3^-$	70.10	25.16
41	$C_{13}H_{27}$	$CH_2CH(Me)C_6H_4SO_3^-$	82.42	25.16
42	$C_{15}H_{31}$	$CH_2CH(Me)C_6H_4SO_3^-$	94.73	25.16
43	C_6H_{13}	$(CH_2)_2C_6H_4SO_3^-$	39.32	29.31
44	$C_{10}H_{21}$	$(CH_2)_2CH{=}CHCH_2SO_3^-$	63.95	22.51
45	$C_{11}H_{21}$	$CH_2CH(OH)C_2H_4SO_3^-$	70.10	1.62
46	C_9H_{19}	$CH_2CH(CH_2OH)SO_3^-$	57.79	50.00
47	$C_{11}H_{23}$	$CH_2CH(CH_2OH)SO_3^-$	70.10	50.00
48	$C_{13}H_{27}$	$CH_2CH(CH_2OH)SO_3^-$	82.42	50.00
49	$C_{15}H_{31}$	$CH_2CH(CH_2OH)SO_3^-$	94.73	50.00
50	C_9H_{19}	$CH_2CH(COOH)SO_3^-$	57.79	50.46
51	$C_{11}H_{23}$	$CH_2CH(COOH)SO_3^-$	70.10	50.46
52	$C_{13}H_{27}$	$CH_2CH(COOH)SO_3^-$	82.42	50.46
53	$C_{15}H_{31}$	$CH_2CH(COOH)SO_3^-$	94.73	50.46
54	C_8H_{16}	$[(CH_2)_2OSO_3^-]_2$	50.69	11.72
55	$C_{10}H_{20}$	$[(CH_2)_2OSO_3^-]_2$	63.01	11.72
56	$C_{12}H_{24}$	$[(CH_2)_2OSO_3^-]_2$	75.32	11.72
57	$C_{14}H_{28}$	$[(CH_2)_2OSO_3^-]_2$	87.64	11.72

ramificated, the three-parameter regression can be obtained

$$T_k = (-46.6\pm4.6) + (41.7\pm1.9)V_L + (29.4\pm4.5)V_H - (15.0\pm1.8)N_{es} \quad (4)$$

($n = 16$, $s = 2.6$, $r = 0.989$, $F = 235$).

Equation (4) describes the T_k values for *n*-alkyl sulfates, *n*-alkyl sulfonates, and bolaformic sulfates (**1—5**, **24—30**, and **54—57**, see Table 1). Due to the smaller number of the terms in the subset ($n = 16$), the errors of the coefficients in Eq. (4) are higher than those of the corresponding coefficients in Eq. (2). A similar decrease in quality can be expected for other particular regressions, which should not be calculated because Eq. (2) describes possible variants.

It is of interest to compare the influence of the *L* and *H* fragments on the T_k values. The structure of the *L* and *H* fragments for the series of amphiphilic anions (see Table 1) and total effects of the fragments on the T_k values are presented in Table 3. For all anions, the *L* fragment makes the predominant contribution to the T_k value ($\Sigma k_{L,i}D_{L,i} > \Sigma k_{H,i}D_{H,i}$). However, in the series of amphiphiles considered, the $\Sigma k_{L,i}D_{L,i}$ value changes in the interval of 62 K, and the change in $\Sigma k_{H,i}D_{H,i}$ is 82 K. Due to this, when the structure of the amphiphilic anions is varied, the T_k values depend, to a greater extent, on the structure of the *H* fragment. The negative $\Sigma k_{H,i}D_{H,i}$ values were obtained for anions **9—23**. They reflect the most pronounced decrease in the T_k values when the amphiphiles contain the corresponding *H* fragments.

No software is required for the prediction of the T_k values of the anionic surfactants, whose structures correspond to those in Table 2, using Eq. (2). It is not difficult to calculate the necessary descriptors (see Table 2). Qualitative consequences from Eq. (2) can be used in the synthesis of new surfactants. Different polar groups favor the decrease in T_k, and their effect are additive. When the nature of the groups changes, their influence decreases in the series C(O)O > COC ≈ OH > S(O)O > Ph ≈ CH=CH (the OH group, which does not form a hydrogen bond with the head anions, is shown). The T_k values also decrease when the *L* and *H* fragments are ramificated and their volumes decrease.

References

1. A. I. Rusanov, *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* [*Micelle Formation in Solutions of Surfactants*], Khimiya, St. Petersburg, 1992, 280 pp. (in Russian).
2. T. Gu and J. Sjoblom, *Colloids Surf.*, 1992, **64**, 39.
3. M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York, 1994, 448 pp.
4. J. K. Weil, A. J. Stirton, R. G. Bistline, and E. W. Maurer, *J. Am. Oil Chem. Soc.*, 1959, **36**, 241.
5. T. Gu and J. Sjoblom, *Acta Chem. Scand.*, 1991, **45**, 762.
6. M. Hato and K. Shinoda, *J. Phys. Chem.*, 1973, **77**, 378.
7. J. K. Weil, F. S. Smith, A. J. Stirton, and R. G. Bistline, *J. Am. Oil Chem. Soc.*, 1963, **40**, 538.
8. E. Gotte and M. J. Schwuger, *Tenside*, 1969, **6,** 131.
9. J. K. Weil, A. J. Stirton, and E. A. Barr, *J. Am. Oil Chem. Soc.*, 1966, **43**, 157.
10. K. Tsujii, N. Saito, and T. Takeuchi, *J. Phys. Chem.*, 1980, **84**, 2287.
11. T. Hikota, K. Morohara, and K. Meguro, *Bull. Chem. Soc. Jpn.,* 1970, **43**, 3913.
12. F. S. Smith, A. J. Stirton, and M. V. Nunez-Ponzoa, *J. Am. Oil Chem. Soc.*, 1966, **43**, 501.
13. M. Uena, S. Yamamoto, and K. Meguro, *J. Am. Oil Chem. Soc.*, 1974, **51**, 373.
14. M. H. Abraham, *Chem. Soc. Rev.*, 1993, **22**, 73.
15. M. H. Abraham and J. C. McGowan, *Chromatographia,* 1987, **23**, 243.
16. R. Ranganathan, M. Peric, R. Medina, U. Garcia, and B. L. Bales, *Langmuir*, 2001, **17**, 6765.
17. B. L. Bales and R. Zana, *J. Phys. Chem.*, *B*, 2002, **106**, 1926.
18. P. M. Kruglyakov, *Hydrophile-Lipophile Balance of Surfactants and Solid Particles*, Elsevier, Amsterdam, 2000, 391 pp.
19. R. Varadaraj, J. Bock, P. Valint, and N. Brons, *Langmuir,* 1990, **6**, 1376.

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