

Empirical Relationships between the Krafft Points and the Structural Units in Surfactants

Tiren Gu* and Johan Sjöblom†

Department of Chemistry, University of Bergen, N-5007 Bergen, Norway

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Depending on their structure, surfactants display different behaviour when in contact with water. The simplest case is that they dissolve into water and form micelles above a certain critical concentration (CMC). Other categories of surfactants are insoluble in water and swell into a liquid-crystalline phase (the D phase). At high water concentrations there will be a dispersion of the D phase and almost pure water. A third category of surfactants are insoluble and form crystals when contacted with water. For ionic surfactants there is a temperature, called the Krafft point (KP), below which the solubility is quite low and insufficient for micellization. Above the Krafft temperature, micelle formation evidently becomes possible and there is a rapid increase in the solubility of the surfactant. It has been generally accepted that this behaviour arises from the fact that unassociated surfactant monomer has a limited solubility, whereas the micelles are highly soluble.

Many empirical equations relating the critical micelle concentration to the various structural units in surfactants have been developed.^{1,2} To our knowledge, however, only Raison³ has made a similar attempt for the Krafft point. He plotted the Krafft points of sodium alkyl sulphates against chain length and showed that these points fall very satisfactorily on a straight line. The aim of this short note is further to develop empirical expressions relating the Krafft point to the various structural units in surfactants on a general basis.

Table 1 shows Krafft points of some ionic surfactants taken from the literature. For surfactants with a single straight hydrocarbon chain, the Krafft point seems to be related to the number of carbon atoms in the hydrocarbon chain (n) by eqn. (1), where k_i is a constant for a particular ionic group and k_c is a constant (= 5.5) for surfactants with

$$KP/^\circ\text{C} = K_c n - k_i \quad (1)$$

a single straight hydrocarbon chain. Eqn. (1) can be used to express the experimental Krafft points quite accurately (Table 1), the average error being $< 2^\circ\text{C}$. Moreover, the results show that even for bivalent metal salts (compounds with twin straight hydrocarbon chains) eqn. (1) can also be used reasonably well.

For ionic surfactants containing both a straight hydrocarbon chain and ethylene oxide groups, the Krafft point is related to the number of carbon atoms in the chain (n) and the number of ethylene oxide groups (m) by eqn. (2),

$$KP/^\circ\text{C} = k_c n - k_e m - k_i \quad (2)$$

where again k_i is a constant for a particular ionic end-group, $k_e = 5.5$ and $k_c = 9$.

It should be noted that the values of k_i for even and odd members of sodium alkanesulfonates are somewhat different (Table 1). Weil *et al.*⁴ noted that the sodium alkanesulfonates show a decrease in Krafft point from even to odd members, with increasing chain length, that is similar to the alternation in melting points in the fatty acid series. However, it seems to us that the mechanism of this phenomenon still remains undefined.

All in all, the Krafft point closely follows a linear relationship based on the number of carbon atoms in the hydrocarbon chains, as is shown in Table 1 for a large number of surfactants. This kind of relationship should be expected from a molecular interpretation of the Krafft point, since it refers to the state of the hydrocarbon chain of the micelle-forming compound.

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* On leave from Department of Chemistry, Peking University, Beijing 100871, China.

† To whom correspondence should be addressed.

Table 1. Krafft points of surfactants.

Surfactant	<i>n</i>	<i>m</i>	KPI/°C	
			Experimental ^a	Calculated
1. C _n H _{2n+1} SO ₄ ⁻ Na ⁺	10		8(3)	5.5 <i>n</i> - 44 11
	12		21(3), 16(4)	22
	14		35.8(3), 30(4)	33
	16		43.0(3), 45(4)	44
	18		57.5(3), 56(4)	55
2. 2-MeC _n H _{2n} SO ₄ ⁻ Na ⁺	11		< 0(5)	5.5 <i>n</i> - 61 0
	13		11(5)	11
	15		25(5)	22
	17		30(5)	33
3. C _n H _{2n+1} [OCH ₂ CH(CH ₃) ₂ SO ₄ ⁻ Na ⁺	16		19(5)	5.5 <i>n</i> - 69 19
	18		31(5)	30
4. C _n H _{2n+1} OCH ₂ CH(SO ₄ ⁻ Na ⁺)CH ₃	14		14(6)	5.5 <i>n</i> - 60 17
	16		27(6)	28
	18		43(6)	39
5. C _n H _{2n+1} (OC ₂ H ₄) _m SO ₄ ⁻ Na ⁺	16	1	36(7)	5.5 <i>n</i> - 9 <i>m</i> - 44 35
	18	1	46(7)	46
	16	2	24(7)	26
	18	2	40(7)	37
	16	3	19(7)	17
	18	3	32(7)	28
	16	4	1(7)	8
	18	4	18(7)	19
6. Na ⁺ O ₄ ⁻ S(CH ₂) _n SO ₄ ⁻ Na ⁺	12		12(8)	5.5 <i>n</i> - 52 14
	14		24.8(8)	25
	16		39.1(8)	36
	18		44.9(8)	47
7. Li ⁺ O ₄ ⁻ S(CH ₂) _n SO ₄ ⁻ Li ⁺	14		35(8)	5.5 <i>n</i> - 45 32
	16		39(8)	43
8. K ⁺ O ₄ ⁻ S(CH ₂) _n SO ₄ ⁻ K ⁺	16		45(8)	5.5 <i>n</i> - 43 45
	18		55(8)	56
9. C _n H _{2n+1} SO ₃ ⁻ Na ⁺		(even <i>n</i>)		5.5 <i>n</i> - 29
	12		38(4)	37
	14		48(4)	48
	16		57(4)	59
	18		70(4)	70
		(odd <i>n</i>)		5.5 <i>n</i> - 34
	13		35.5(4)	38
15		48(4)	49	
		17	62(4)	60

(contd.)

Table 1 (contd.)

Surfactant	<i>n</i>	<i>m</i>	<i>KP</i> /°C	
			Experimental ^a	Calculated
10. $C_nH_{2n+1}COO(CH_2)_2SO_3^-Na^+$	8		0(9)	$5.5n - 44$ 0
	10		8.1(9)	11
	12		24.2(9)	22
	14		36.2(9)	33
11. $C_nH_{2n+1}OOC(CH_2)_2SO_3^-Na^+$	8		0(9)	$5.5n - 41$ 3
	10		12.5(9)	14
	12		26.5(9)	25
	14		39.0(9)	36
12. $C_nH_{2n+1}CHCH_3C_6H_4SO_3^-Na^+$	10		31.5(10)	$5.5n - 24$ 31
	12		46.0(10)	42
	14		54.2(10)	53
	16		60.8(10)	64
13. $C_nH_{2n+1}CH(SO_3^-Na^+)CH_2OH$	10		59(4)	$5.5n + 6$ 61
	12		73(4)	72
	14		84(4)	83
	16		93(4)	94
14. $C_nH_{2n+1}CH(SO_3^-Na^+)COOH$	10		52(4)	$5.5n + 3$ 58
	12		68(4)	69
	14		83(4)	80
	16		94(4)	91
15. $C_nH_{2n+1}CH(SO_3^-Na^+)COONa$	14		76(4)	$5.5n + 1$ 78
	16		91(4)	89
16. $C_nH_{2n+1}CH(Py^+)COO^-$ ^b	12		23.2(11)	$5.5n - 41$ 25
	14		38(11)	36
17. $(C_nH_{2n+1}SO_4^-)_2Ca^{2+}$	12		50(12, 13)	$11n - 85$ 47
	14		70(12), 71(13)	69
	16		85(13)	91
18. $(C_nH_{2n+1}SO_4^-)_2Mg^{2+}$	12		25(13)	$11n - 115$ 17
	14		38.5(13)	39
	16		52(13)	61
19. $(C_nH_{2n+1}SO_4^-)_2Mn^{2+}$	12		16(12)	$11n - 121$ 11
	14		29(12)	33
20. $(C_nH_{2n+1}SO_4^-)_2Cu^{2+}$	12		19(12)	$11n - 113$ 19
	14		40(12)	41
21. $(C_nH_{2n+1}SO_4^-)_2Zn^{2+}$	12		11(12)	$11n - 121$ 11
	14		32(12)	33

^aFigures in parentheses denote reference numbers. ^bPy⁺ = pyridinium ion.

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