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Effect of Hard River Water on the Surface Properties of Surfactants

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The surface properties [effectiveness of surface tension reduction (γ_{CMC}), critical micelle concentration (CMC), efficiency of surface tension reduction ($\mathrm{p}C_{20}$), maximum surface excess concentration ($\Gamma_{\max}$), minimum area/molecule at the interface ($A_{\min}$), and the (CMC/C_{20}) ratio] of well-purified anionic, nonionic, and cationic surfactants, some of which are widely used in daily chemical and industrial products, were investigated at 25 °C in hard river water. The studied surfactants show somewhat greater surface activity in hard river water than in distilled water, but in particular, for anionic surfactants a marked effect of hard river water on surface active properties was observed. The effect of hard river water on surface active properties is, in decreasing order, anionics > cationics > nonionics. For alkyl poly(oxyethylene) glycols, the effect on surface properties is interpreted in terms of complex formation between the ether oxygen atoms of the poly(oxyethylene) group and divalent hardness ions. The linear relationship between the $\mathrm{p}C_{20}$ or CMC values and the number of carbon atoms in the alkyl chain observed in distilled water was confirmed in hard river water. For alkyl poly(oxyethylene) sulfates, the slope of the plot indicates an effect of the alkyl chain on adsorption at the air/water interface or on micellization similar to that observed for nonionic surfactants in distilled water.

Introduction

Surfactants have been widely used in every field from household products to industrial products. The great utility of surfactants is manifested by the growth in the scale of commercial production of all types of surfactants (anionics, cationics, nonionics, and zwitterionics), which has currently reached 100 million tons per year (Hauthal, 1992). Obviously, the impact of surfactants is an important part of the general environmental pollution problem (Cain, 1977; Swisher, 1987). There are limited reports published which attempt to relate the impact of surfactants on the environment to surface properties, such as the critical micelle concentration (CMC) (Tolls et al., 1994). In most cases, however, the surface properties of surfactants are generally measured in distilled water and are therefore different from those in the actual environment. As a result, using such surface activity parameters determined in distilled water to analyze the impact of surfactants in the environment may lead to incorrect conclusions, causing some confusion in understanding the structural effect of surfactants on their environmental impact. Data on the characteristics of surfactants under environmental conditions are sparse and as a result we have no certain knowledge of how these will change under those conditions. For example, alkylbenzenesulfonates in distilled water and tap water have been studied by Bohm-Gossl and Kruger (1965). Critical micellar concentrations were considerably lower in tap water than in distilled water. Japanese researchers studied the behavior of linear alkylbenzenesulfonate in hard water by solubilization, and reported that the solubilizing ability of linear alkylbenzenesulfonate was markedly affected by the water hardness (Arai and Yoshizaki, 1969). These results suggest that studies in pure water cannot always be extended to biological situations. To avoid these problems in an investigation of the environmental impact of surfactants (Rosen et al., 1996), the surface properties of surfactants in river water that mimics the actual environment were measured. In addition, highly purified surfactants were used in this study to assist in understanding the environmental impact of surfactants at the molecular level. Here, we report various surface properties in river water of the studied compounds (anionics, cationics, and nonionics) and compare these properties to those in distilled water, in order to rationalize the effect of river water on these properties.

Experimental Section

Materials. The following materials were studied: $C_{10}H_{21}SO_3K$, $C_{12}H_{25}SO_3Na$, $C_{12}H_{25}SO_4Na$, $C_{12}H_{25}OC_2H_4SO_4Na$ ($C_{12}H_{25}EOSO_4Na$), $C_{12}H_{25}(OC_2H_4)_2SO_4Na$ ($C_{12}H_{25}EO_2SO_4Na$), $C_{12}H_{25}(OC_2H_4)_4SO_4Na$ ($C_{12}H_{25}EO_4SO_4Na$), $C_{14}H_{29}SO_4Na$, $C_{14}H_{29}OC_2H_4SO_4Na$ ($C_{14}H_{29}EOSO_4Na$), $C_{14}H_{29}(OC_2H_4)_2SO_4Na$ ($C_{14}H_{29}EO_2SO_4Na$), $C_{14}H_{29}(OC_2H_4)_4SO_4Na$ ($C_{14}H_{29}EO_4SO_4Na$), $C_{15}H_{31}SO_4Na$, $C_{15}H_{31}OC_2H_4SO_4Na$ ($C_{15}H_{31}EOSO_4Na$), $C_{15}H_{31}(OC_2H_4)_4SO_4Na$ ($C_{15}H_{31}EO_4SO_4Na$), sodium bis(ethylhexyl) sulfosuccinate (DESS), $C_{10}H_{21}N(CH_3)_3Br$, $C_{12}H_{25}N(CH_3)_3Br$, $C_{14}H_{29}N(CH_3)_3Br$, *N*-decylpyridinium bromide ($C_{10}H_{21}PyBr$), dodecane-1,3-diol, *N*-(2-ethylhexyl)pyrrolidinone ($C_{2,6}P$), *N*-octylpyrrolidinone (C_8P), *N*-decylpyrrolidinone ($C_{10}P$), *N*-dodecylpyrrolidinone ($C_{12}P$), $C_9H_{19}P(O)(CH_3)_2$, $C_{10}H_{21}P(O)(CH_3)_2$, $C_{12}H_{25}P(O)(CH_3)_2$, $C_{10}H_{21}(OC_2H_4)_6OH$ ($C_{10}H_{21}EO_6$), $C_{12}H_{25}(OC_2H_4)_4OH$ ($C_{12}H_{25}EO_4$), $C_{12}H_{25}(OC_2H_4)_6OH$ ($C_{12}H_{25}EO_6$), $C_{14}H_{29}(OC_2H_4)_4OH$ ($C_{14}H_{29}EO_4$), $C_{14}H_{29}(OC_2H_4)_6OH$ ($C_{14}H_{29}EO_6$), $C_{14}H_{29}(OC_2H_4)_8OH$ ($C_{14}H_{29}EO_8$), and $C_{16}H_{33}(OC_2H_4)_6OH$ ($C_{16}H_{33}EO_6$). All the surfactants, except the *N*-alkylpyrrolidinones, which were obtained from ISP, were provided by the Procter & Gamble Co. The ionic surfactants were purified by passage of the solution of the surfactants in distilled water below their CMCs at least four times through SEP-PAK (high-density chromatographic columns of octadecylsilanized silica gel) C_{18} cartridges (Water Associates, Milford, MA) to remove any traces of impurities more surface active than the corresponding parent surfactants. The concentration of the surfactant solution in the effluent was determined

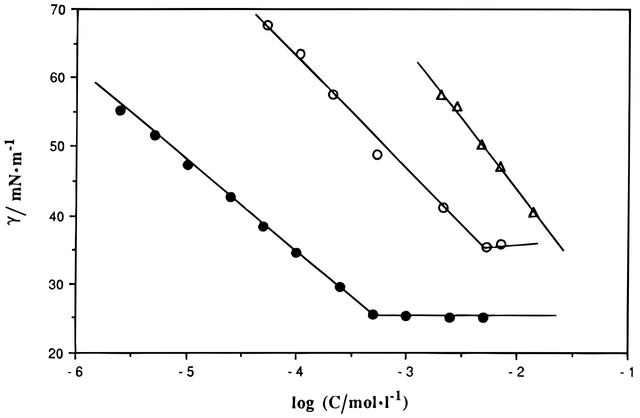

Figure 1. Surface tension vs log molar concentration of surfactant in hard river water at 25 °C: (○) $C_{12}H_{25}SO_3Na$; (●) DESS; (△) $C_{10}H_{21}SO_3K$.

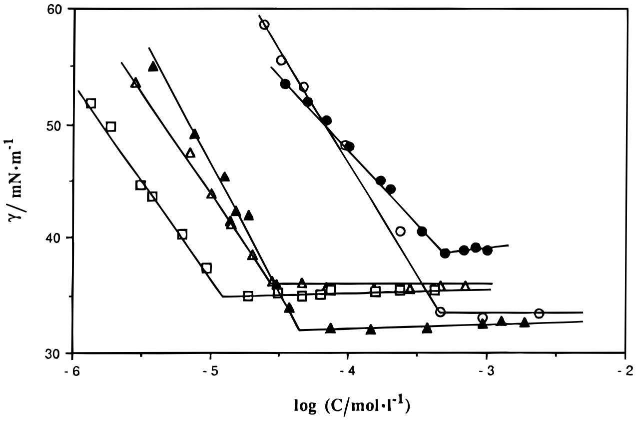

Figure 2. Surface tension vs log molar concentration of surfactant in hard river water at 25 °C: (○) $C_{12}H_{25}EO_2SO_4Na$; (●) $C_{12}H_{25}EO_4SO_4Na$; (▲) $C_{14}H_{29}EO_2SO_4Na$; (△) $C_{14}H_{29}EO_4SO_4Na$; (□) $C_{15}H_{31}EO_4SO_4Na$.

by two-phase mixed indicator titration with a standardized solution of Hyamine (Reid et al., 1967).

"Hard river water" was prepared by the following formula: $CaCl_2{\cdot}2H_2O$, 110.28 mg/L; $MgSO_4{\cdot}7H_2O$, 112.91 mg/L; $NaHCO_3$, 126.0 mg/L; KH_2PO_4, 4.35 mg/L; $NaNO_3$, 85.01 mg/L. The pH of the river water was adjusted to ca. 7.5. This "hard river water" was used to prepare the solutions of surfactants. If the solution of the surfactant was made by using a stock solution of the surfactant in distilled water, its hardness was adjusted to the same as shown in the river water formula by addition of concentrated "hard river water".

Surface Tension Measurements. Measurements were performed with a Kruss K-10T tensiometer by the Wilhelmy vertical plate technique at 25 °C. The instrument was calibrated against quartz condensed water equilibrated against atmospheric CO_2 each time measurements were made. Values were taken until the surface tension was constant for a period of 0.5 h. For solutions of the surfactants at very low concentrations, it usually took several hours to reach equilibrium. Reproducibility of the surface tension measurements is <0.2 mN/m.

Results and Discussion

Surface tension (γ) values at various log molar surfactant concentrations (log C) in the "hard river water" at 25 °C are listed in Table 1. Plots of γ vs log C are shown in Figures 1−7. The plots show no minima in the vicinity of the CMC, indicating no surface-active impurities. The slopes of the plots for some distance below the CMC are linear, indicating maximum surface excess concentration has been reached (eq 1, below). CMC (critical micellar concentration) values are taken as the molar concentration at the intersection of the two linear portions of the curve of surface tension γ vs log molar concentration (C) above and below the discontinuity. The effectiveness of surface tension reduction (γ_{cmc}) is the surface tension value at the CMC.

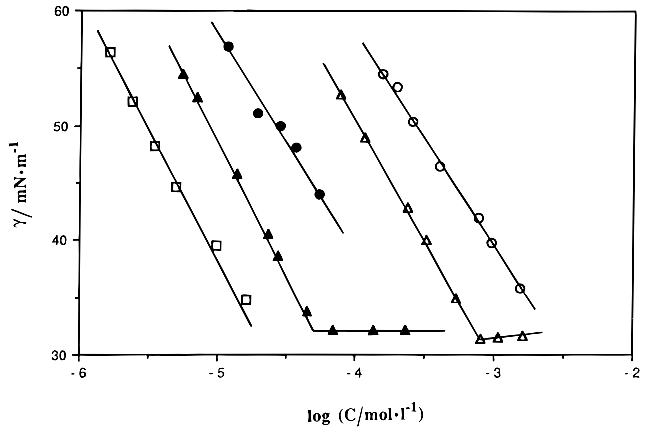

Figure 3. Surface tension vs log molar concentration of surfactant in hard river water at 25 °C: (○) $C_{12}H_{25}SO_4Na$; (●) $C_{14}H_{29}SO_4Na$; (△) $C_{12}H_{25}EOSO_4Na$; (▲) $C_{14}H_{29}EOSO_4Na$; (□) $C_{15}H_{31}EOSO_4Na$.

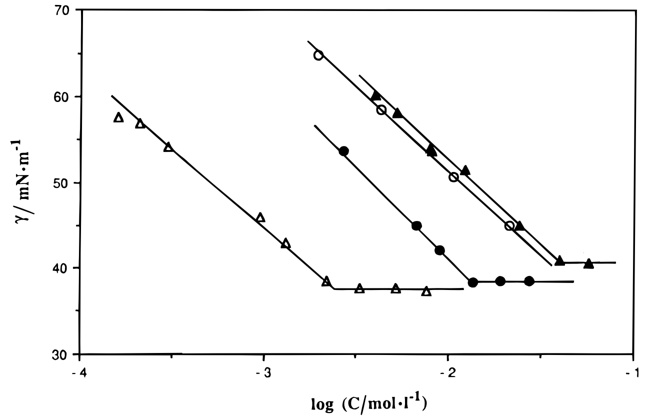

Figure 4. Surface tension vs log molar concentration of surfactant in hard river water at 25 °C: (○) $C_{10}H_{21}N^+(CH_3)_3Br^-$; (●) $C_{12}H_{25}N^+(CH_3)_3Br^-$; (△) $C_{14}H_{29}N^+(CH_3)_3Br^-$; (▲) $C_{10}H_{21}PyBr^-$.

Surface excess concentrations (Γ_{max}) in mol/cm² and minimum area/molecule (A_{min}) in Å² at the interface of water and air were calculated from the following equations (Rosen, 1989 (a)),

$$\Gamma = -\frac{1}{n2.303RT}\left(\frac{\partial \gamma}{\partial \log C}\right)_{\max,T} \qquad (1)$$

and

$$A_{\min} = \frac{10^{14}}{N\Gamma_{\max}} \qquad (2)$$

where $(\partial\gamma/\partial \log C)_{\max,T}$ is the maximum slope in each case; T is absolute temperature, $R = 8.31$ J·mol⁻¹·K⁻¹, and N is Avogadro's number. The ionic strength of the hard river water is 6.58×10^{-3} M. The value of n (the number of species into which the surfactant dissociates) is taken as 1 for nonionics and for 1:1 electrolyte surfactants when the concentrations used to calculate A_{min} are less than one-tenth of the ionic strength (i.e., $<6.6 \times 10^{-4}$ M). When the concentrations are greater than 6.6×10^{-4} M for a 1:1

Table 1. Surface Tension vs −log C Data for Surfactants in Hard River Water at 25 °C

−log(*C*/mol/L)	*γ*/(mN/m)	−log(*C*/mol/L)	*γ*/(mN/m)	−log(*C*/mol/L)	*γ*/(mN/m)	−log(*C*/mol/L)	*γ*/(mN/m)
$C_{10}H_{21}SO_3K$		$C_{12}H_{25}SO_3Na$		$C_{10}H_{21}N(CH_3)_3Br$		$C_{12}H_{25}N(CH_3)_3Br$	
1.86	40.60	2.15	35.97	1.67	45.00	1.56	38.40
2.16	47.20	2.28	35.54	1.98	50.70	1.72	38.40
2.33	50.30	2.67	41.20	2.37	58.40	1.87	38.30
2.55	55.75	3.28	48.82	2.71	64.80	2.05	42.00
2.70	57.50	3.67	57.60			2.17	44.90
		3.98	63.41			2.57	53.70
		4.28	67.76				
$C_{12}H_{25}SO_4Na$		$C_{12}H_{25}EOSO_4Na$		$C_{14}H_{29}N(CH_3)_3Br$		$C_{10}H_{21}PyBr$	
2.81	35.90	2.79	31.60	2.12	37.30	1.24	40.50
3.02	39.80	2.97	31.50	2.28	37.70	1.40	40.90
3.11	42.00	3.09	31.40	2.48	37.60	1.61	44.90
3.40	46.50	3.27	35.00	2.66	38.40	1.92	51.50
3.59	50.20	3.49	40.00	2.88	42.80	2.10	54.00
3.71	53.40	3.63	42.90	3.02	45.95	2.09	53.80
3.81	54.55	3.94	48.90	3.52	54.30	2.28	58.10
		4.11	52.70	3.68	57.00	2.40	60.25
				3.80	57.60		
$C_{12}H_{25}EO_2SO_4Na$		$C_{12}H_{25}EO_4SO_4Na$		Dodecane-1,2-diol			
2.63	33.40	3.00	38.95	3.81	30.40		
3.03	33.10	3.08	39.10	4.12	36.30		
3.33	33.60	3.17	38.85	3.64	30.10		
3.63	40.60	3.30	38.70	4.51	49.00		
4.03	48.20	3.47	40.55	4.81	59.65		
4.33	53.20	3.70	44.25	5.12	67.15		
4.50	55.60	3.77	44.95				
4.63	58.60	4.00	48.05				
		4.17	50.35				
		4.30	52.00				
		4.47	53.55				
$C_{14}H_{29}SO_4Na$		$C_{14}H_{29}EOSO_4Na$		$C_{2,6}P$		C_8P	
4.26	44.00	3.64	32.20	2.11	33.75	2.25	28.10
4.44	48.00	3.86	32.20	2.41	40.00	2.55	35.10
4.55	49.90	4.16	32.20	2.50	41.45	2.72	39.20
4.72	51.10	4.34	33.80	2.80	47.60	2.95	43.70
4.94	56.90	4.56	38.70	2.95	50.10	3.09	47.10
		4.64	40.60	3.11	53.20	3.29	51.90
		4.86	45.80	3.28	56.00		
		5.16	52.50				
		5.26	54.50				
$C_{14}H_{29}EO_2SO_4Na$		$C_{14}H_{29}EO_4SO_4Na$		$C_{10}P$		$C_{12}P$	
2.73	32.70	3.16	35.80	3.10	26.20	3.50	25.95
2.90	32.80	3.33	35.80	3.33	26.80	3.67	25.90
3.03	32.50	3.55	35.60	3.47	31.60	3.89	25.90
3.43	32.20	3.81	35.55	3.63	34.50	4.19	26.40
3.83	32.00	4.16	35.70	3.80	38.90	4.37	26.40
4.13	32.20	4.33	36.10	4.03	44.30	4.59	30.10
4.43	33.95	4.55	36.25	4.17	47.60	4.74	33.90
4.52	35.95	4.70	38.55			4.89	39.60
4.83	42.35	4.85	41.20			5.19	46.75
4.73	42.00	5.00	43.85			5.59	56.00
4.91	45.35	5.16	47.50			5.37	53.20
5.13	49.25	5.55	53.60				
5.43	55.00	4.86	41.40				
$C_{15}H_{31}SO_4Na$		$C_{15}H_{31}EOSO_4Na$		$C_9H_{19}P(O)(CH_3)_2$		$C_{10}H_{21}P(O)(CH_3)_2$	
3.97	51.20	4.79	34.80	2.00	31.40	2.29	29.80
4.09	52.70	5.01	39.50	2.13	34.10	2.59	32.80
4.27	54.30	5.30	44.60	2.23	36.20	2.77	36.60
4.67	55.50	5.46	48.20	2.31	37.70	2.99	41.90
5.01	56.90	5.62	52.10	2.70	46.30	3.29	48.15
4.50	54.80	5.79	56.40	3.05	53.70	3.47	50.90
				3.21	55.80	3.69	54.45
						2.39	30.00
$C_{15}H_{31}EO_4SO_4Na$		DESS		$C_{12}H_{25}P(O)(CH_3)_2$		$C_{10}H_{21}EO_6$	
3.38	35.50	2.30	25.10	2.83	28.40	2.54	32.80
3.63	35.50	2.60	25.00	3.00	28.40	2.83	32.90
3.81	35.40	3.00	25.20	3.23	28.40	3.02	32.00
4.13	35.50	3.30	25.60	3.40	28.60	3.24	36.00
4.20	35.10	3.60	29.50	3.92	38.70	3.39	38.00
4.33	35.00	4.00	34.70	3.53	29.40	3.55	41.10
4.51	35.15	4.30	38.45	4.10	42.55	3.72	43.80
4.73	35.00	4.60	42.60	4.62	53.00	4.02	48.30
5.03	37.40	5.00	47.25	4.77	55.40		
5.21	40.35	5.30	51.55	4.40	49.00		
5.43	43.60	5.60	55.10				
5.51	44.65						
5.73	49.80						
5.87	51.90						

Table 1 (Continued)

$-\log(C/\text{mol/L})$	$\gamma/(\text{mN/m})$	$-\log(C/\text{mol/L})$	$\gamma/(\text{mN/m})$	$-\log(C/\text{mol/L})$	$\gamma/(\text{mN/m})$	$-\log(C/\text{mol/L})$	$\gamma/(\text{mN/m})$
$C_{12}H_{25}EO_4$		$C_{12}H_{25}EO_6$		$C_{14}H_{29}EO_8$		$C_{16}H_{33}EO_6$	
3.72	28.80	2.75	32.00	4.43	35.10	3.83	31.20
4.10	28.80	3.05	32.00	4.60	35.20	4.45	31.20
4.23	29.00	3.35	32.00	4.92	35.10	4.96	31.50
4.53	33.40	3.75	32.00	5.12	37.00	5.13	31.60
4.63	35.90	4.05	32.00	5.29	39.50	5.35	32.20
4.80	39.60	4.35	35.70	5.52	42.90	5.65	31.95
4.93	42.30	4.53	38.90	5.70	45.50	5.96	37.60
5.24	49.40	4.65	41.50	5.80	47.60	6.13	41.15
		4.95	46.50			6.26	43.00
						5.45	32.20
						5.75	33.55
						6.05	38.70
$C_{14}H_{29}EO_4$		$C_{14}H_{29}EO_6$					
4.15	28.60	4.18	31.30				
4.30	28.80	4.48	31.40				
4.60	29.00	4.78	32.00				
5.00	29.10	5.05	32.40				
5.15	29.20	5.18	33.20				
5.25	30.00	5.28	34.40				
5.34	31.40	5.42	37.40				
5.44	34.20	5.56	40.40				
5.50	35.50	5.75	44.00				
5.55	37.20						
5.70	41.70						

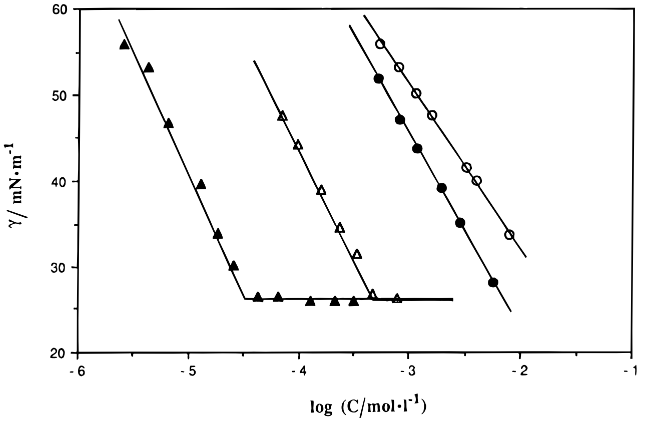

Figure 5. Surface tension vs log molar concentration of surfactant in hard river water at 25 °C: (○) $C_{2,6}P$; (●) C_8P; (△) $C_{10}P$; (▲) $C_{12}P$.

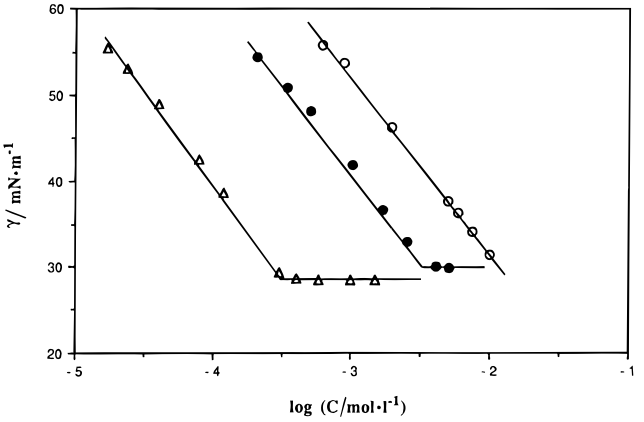

Figure 6. Surface tension vs log molar concentration of surfactant in hard river water at 25 °C: (○) $C_9H_{19}P(O)(CH_3)_2$; (●) $C_{10}H_{21}P(O)(CH_3)_2$; (△) $C_{12}H_{25}P(O)(CH_3)_2$.

electrolyte surfactant, then the value of n can be obtained by use of the relationship: $n = 1 + (C_{surf}/C_{surf} + IS)$ (Matijevic and Pethica, 1958), where IS is the ionic strength of the added electrolyte. Using this relationship, values of 1.5, 1.3, 1.5, 1.5, 1.0, and 1.7 were used for n in the case of $C_{10}H_{21}SO_3K$, $C_{12}H_{25}SO_3Na$, $C_{10}H_{21}N^+(CH_3)_3Br^-$, $C_{12}H_{25}N^+(CH_3)_3Br^-$, $C_{14}H_{29}N^+(CH_3)_3Br^-$, and $C_{10}H_{21}PyBr^-$, respectively. In distilled water, n is taken as 2 for 1:1 electrolyte surfactants. Tables 2 and 3 list the values of γ_{CMC}, CMC, pC_{20} (the efficiency of surface adsorption, the negative log of the bulk surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m), Γ_{max}, A_{min}, and the CMC/C_{20} ratio. The CMC/C_{20} ratio is a measure of the tendency of the surfactant to adsorb at the aqueous/air interface relative to its tendency to form micelles (Rosen, 1989 (b)).

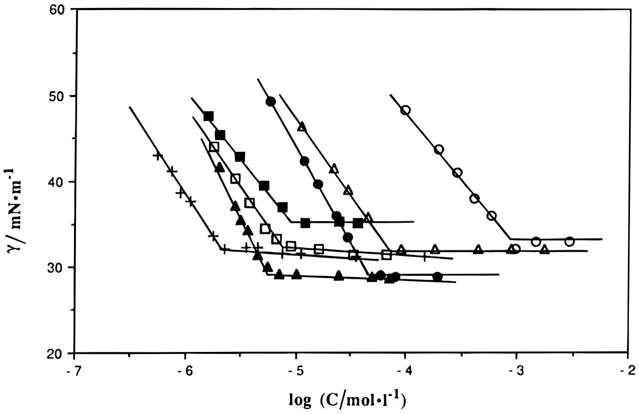

Figure 7. Surface tension vs log molar concentration of surfactant in hard river water at 25 °C: (○) $C_{10}H_{21}EO_6$; (●) $C_{12}H_{25}EO_4$; (△) $C_{12}H_{25}EO_6$; (▲) $C_{14}H_{29}EO_4$; (□) $C_{14}H_{29}EO_6$; (■) $C_{14}H_{29}EO_8$; (+) $C_{16}H_{33}EO_6$.

For comparison, the pC_{20} and CMC values of the surfactants in distilled water and in hard river water are shown in Table 4 to show the effect of hard river water on adsorption at the aqueous/air interface and on the micellization. Table 5 lists the CMC/C_{20} ratio and A_{min} values of the surfactants in distilled water and in hard river water.

Efficiency of Adsorption or Surface Tension Reduction (pC_{20}). The pC_{20} value is an index of the adsorption of the surfactant at the water/air interface (Rosen, 1989 (c)). It is apparent that the pC_{20} value of anionics is greatly affected by the hard river water; anionics showed pC_{20} values higher in hard river water than in distilled water, indicating that anionics are more surface active in hard river water. The pC_{20} values of nonionics is little influenced; only a slight increase in pC_{20} was observed in the hard river water. On the basis of the pC_{20} values listed in Table 4, it is obvious that the pC_{20} values increase when the alkyl chain length increases, indicating that a longer

Table 2. Surface Properties in River Water of Ionic Surfactants Investigated at 25 °C

compd	γ_{CMC}/(mN/m)	CMC/(mol/L)	pC_{20}	Γ_{max}/(mol/cm^2 × 10^{10})	A_{min}/Å^2	CMC/C_{20}
		Anionics				
$C_{10}H_{21}SO_3K$	<40.0[a]	$>1.41 \times 10^{-2}$ [a]	2.44	2.48	66.9	
$C_{12}H_{25}SO_3Na$	36.0	3.46×10^{-3}	3.46	2.34	70.9	9.97
$C_{12}H_{25}SO_4Na$	<36.0[b]	$>1.58 \times 10^{-3}$ [b]	3.68	3.29	50.4	
$C_{12}H_{25}EOSO_4Na$	31.4	8.1×10^{-4}	4.10	3.59	46.2	10.2
$C_{12}H_{25}EO_2SO_4Na$	33.2	5.50×10^{-4}	4.32	3.24	51.23	11.5
$C_{12}H_{25}EO_4SO_4Na$	38.8	4.68×10^{-4}	4.35	2.41	68.8	10.5
$C_{14}H_{29}SO_4Na$	<44.0[b]	$>5.62 \times 10^{-5}$ [b]	4.68	3.42	48.5	
$C_{14}H_{29}EOSO_4Na$	32.2	5.5×10^{-5}	5.16	3.91	42.5	7.9
$C_{14}H_{29}EO_2SO_4Na$	32.3	4.57×10^{-5}	5.24	3.66	45.43	7.95
$C_{14}H_{29}EO_4SO_4Na$	35.8	3.10×10^{-5}	5.51	2.92	56.85	10.0
$C_{15}H_{31}SO_4Na$ (30 °C)	<51.0[b]	$>1.0 \times 10^{-4}$ [b]	4.12	2.02		
$C_{15}H_{31}EOSO_4Na$	<35.0[b]	$>1.58 \times 10^{-5}$ [b]	5.64	3.77	44.0	
$C_{15}H_{31}EO_4SO_4Na$	35.0	1.26×10^{-5}	5.96	2.98	55.7	11.5
DESS	25.2	5.75×10^{-4}	5.42	2.28	72.8	151.3
		Cationics				
$C_{10}H_{21}N(CH_3)_3Br$	<45.0[a]	$>2.0 \times 10^{-2}$ [a]	2.08	2.21	75.0	
$C_{12}H_{25}N(CH_3)_3Br$	38.3	1.26×10^{-2}	2.50	2.72	61.1	3.99
$C_{14}H_{29}N(CH_3)_3Br$	37.6	2.45×10^{-3}	3.42	3.18	52.1	6.45
$C_{10}H_{21}PyBr$	40.5	4.17×10^{-2}	1.98	2.01	82.5	3.97

[a] CMC of the surfactant not reached because of limitation of material available. [b] Solubility of the surfactant in hard river water too low to reach CMC.

Table 3. Surface Properties in River Water of Nonionic Surfactants at 25 °C

compd	γ_{CMC}/(mN/m)	CMC/(mol/L)	pC_{20}	Γ_{max}/(mol/cm^2 × 10^{10})	A_{min}/Å^2	CMC/C_{20}
dodecane-1,2-diol	30.0	1.15×10^{-4}	4.64	5.46	30.4	5.02
		N-Alkyl-2-pyrrolidone				
$C_{2,6}P$	*a*	*a*	3.10	3.42	48.5	
C_8P	*a*	*a*	3.34	4.01	41.4	
$C_{10}P$	*a*	*a*	4.38	4.17	39.8	
$C_{12}P$	26.4	3.47×10^{-5}	5.37	5.11	32.5	8.13
		Dimethylalkylphosphine Oxide				
$C_9H_{19}P(O)(CH_3)_2$	*b*	*b*	3.02	3.72	44.62	
$C_{10}H_{21}P(O)(CH_3)_2$	30.0	3.55×10^{-3}	3.53	3.79	43.80	12.03
$C_{12}H_{25}P(O)(CH_3)_2$	28.4	3.16×10^{-4}	4.60	3.89	42.67	12.59
		Alkyl Poly(oxyethylene) Glycol				
$C_{10}H_{21}EO_6$	32.8	8.7×10^{-4}	4.27	2.83	58.7	16.2
$C_{12}H_{25}EO_4$	28.8	4.8×10^{-5}	5.38	3.88	42.8	11.5
$C_{12}H_{25}EO_6$	32.0	6.9×10^{-5}	5.27	3.19	52.0	12.8
$C_{14}H_{29}EO_4$	29.3	5.5×10^{-6}	6.10	4.89	34.0	6.9
$C_{14}H_{29}EO_6$	32.6	6.9×10^{-6}	6.18	3.34	49.7	10.5
$C_{14}H_{29}EO_8$	35.1	1.0×10^{-5}	6.14	2.67	62.2	13.8
$C_{16}H_{33}EO_6$	32.1	2.1×10^{-6}	6.78	3.23	51.4	12.7

[a] Solubility in hard river water of the surfactant is too low to reach CMC. [b] CMC not reached because of limitation of material available.

alkyl chain in the surfactant molecule facilitates adsorption of a surfactant at the aqueous/air interface. It is worth noting that DESS with two branched alkyl chains, each equivalent to a seven carbon straight alkyl chain, has a higher pC_{20} than $C_{14}H_{29}SO_4Na$, which has a single C_{14} straight alkyl chain. A similar result was obtained in previous studies on double-chain surfactants with two head groups (Zhu et al., 1991, 1992). For compounds with the same alkyl chain, the pC_{20} value is dependent on the properties of the hydrophilic group. The nonionics showed the highest pC_{20} values even in the hard river water. The alkyl poly(oxyethylene) sulfates showed pC_{20} increases with an increase in the number of oxyethylene units, consistent with the decrease in the CMC shown with the introduction of a few oxyethylene units into the molecule. This is also consistent with previous data in the presence of 0.1 M NaCl (Schwuger, 1984; Dahanayake et al., 1986). Figure 8 shows a linear relationship between pC_{20} and the number of carbon atoms in the alkyl chain of the $C_nH_{2n+1}(OC_2H_4)_4SO_4Na$ series. The slope of the line is 0.543, implying that in hard river water the tendency of these ionic surfactants to adsorb onto the water/air interface is similar to that of nonionics in distilled water.

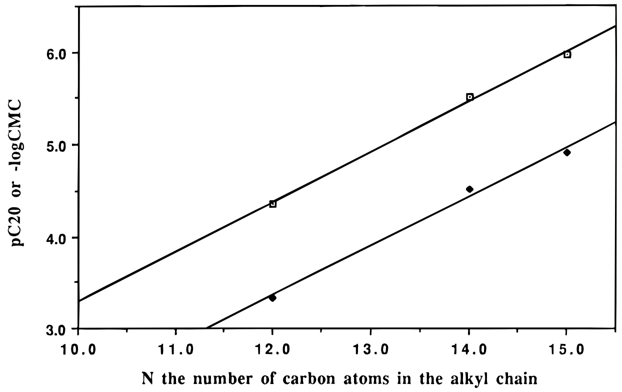

Figure 8. Effect of the length of the alkyl chain in $C_nH_{2n+1}(OC_2H_4)_4SO_4Na$ on pC_{20} and log CMC of hard river water at 25 °C: (⊡) p$C_{20} = 0.543N - 2.14$, $R^2 = 0.997$; (◆) $-\log \mathrm{CMC} = 0.533N - 0.314$, $R^2 = 0.991$.

Critical Micelle Concentration (CMC). From the data listed in Table 4, all the studied compounds, except several poly(oxyethylene) glycol mono *n*-alkyl ethers, show smaller CMC values in hard river water than in distilled water, indicating micellization is facilitated in hard river

Table 4. Comparison of pC_{20} and CMC of Surfactants in Hard River Water and in Distilled Water at 25 °C

	in hard river water		in distilled water	
compd	pC_{20}	CMC/ (mol/L)	pC_{20}	CMC/ (mol/L)
$C_{12}H_{25}SO_3Na$	3.46	3.46×10^{-3}	2.36	1.24×10^{-2} [a]
$C_{12}H_{25}SO_4Na$	3.68		2.51[a]	
$C_{12}H_{25}EOSO_4Na$	4.10	8.1×10^{-4}	2.83	3.9×10^{-3} [a]
$C_{12}H_{25}EO_2SO_4Na$	4.32	5.50×10^{-4}	2.92	2.9×10^{-3} [a]
$C_{12}H_{25}EO_4SO_4Na$	4.35	4.68×10^{-4}	3.02	1.7×10^{-3} [b]
$C_{14}H_{29}SO_4Na$	4.68		3.1	
$C_{14}H_{29}EOSO_4Na$	5.16	5.5×10^{-5}		1.39×10^{-3} [c]
$C_{14}H_{29}EO_2SO_4Na$	5.24	4.57×10^{-5}		1.00×10^{-3} [c]
$C_{14}H_{29}EO_4SO_4Na$	5.51	3.10×10^{-5}		6.92×10^{-4} [c]
DESS	5.42	5.75×10^{-4}	4.05	2.5×10^{-3} [a]
dodecane-1,2-diol	4.64	1.15×10^{-4}	4.55	1.8×10^{-4} [d]
$C_{10}H_{21}P(O)(CH_3)_2$	3.53	3.55×10^{-3}	3.48	3.89×10^{-3}
$C_{12}H_{25}P(O)(CH_3)_2$	4.60	3.16×10^{-4}	4.56	3.31×10^{-4}
$C_{2,6}P$	3.10		3.00[e]	
C_8P	3.34		3.14[e]	
$C_{10}P$	4.38		4.19[e]	
$C_{12}P$	5.37		5.30[e]	
$C_{10}H_{21}EO_6$	4.27	8.7×10^{-4}	4.27	7.1×10^{-4}
$C_{12}H_{25}EO_4$	5.38	4.8×10^{-5}	5.34	6.4×10^{-5} [a]
$C_{12}H_{25}EO_6$	5.27	6.9×10^{-5}	5.33	6.31×10^{-5}
$C_{14}H_{29}EO_4$	6.10	5.5×10^{-6}	5.90	1.2×10^{-5}
$C_{14}H_{29}EO_6$	6.18	6.9×10^{-6}	6.20	6.03×10^{-6}
$C_{14}H_{29}EO_8$	6.14	1.0×10^{-5}	6.02	9.0×10^{-6} [a]
$C_{16}H_{33}EO_6$	6.78	2.1×10^{-6}	6.80	1.66×10^{-6} [c]
$C_{12}H_{25}N^+(CH_3)_3Br^-$	2.50	1.26×10^{-2}		1.6×10^{-2} [a]
$C_{14}H_{29}N^+(CH_3)_3Br^-$	3.42	2.45×10^{-3}		3.6×10^{-3} [a]
$C_{10}H_{21}PyBr^-$	1.98	4.17×10^{-2}	1.82[f]	4.17×10^{-2} [f] (30 °C)

[a] pC_{20} values and CMC values from pp 70−80 and 122−132, respectively, of Rosen (1989). [b] Calculated value from Schwuger (1984, p 3). [c] Mukerjee and Mysels (1977, p 171). [d] Kwan, C.; Rosen, M. J. *J. Phys. Chem.* **1980**, *84*, 574. [e] Rosen et al. (1988, p 1273). [f] Estimated value from data of R. L. Venable and R. V. Nauman (*J. Phys. Chem.* **1964**, *68*, 3498).

water. The effect of hard river water on the CMC is in the order anionics > cationics > nonionics, which implies the degree of interaction of the hydrophilic group in the surfactant molecule with the ions present in hard river water. As expected, the strongest interaction takes place between the anionic head group and the Ca^{2+} and Mg^{2+} ions of hard river water because of the electrostatic charge interaction. Cationics interact much less strongly with the divalent anions CO_3^{2-} and SO_4^{2-}, presumably because of their smaller charge density, compared to Ca^{2+} and Mg^{2+}. Thus, the CMC of dodecyltrimethylammonium chloride (2.0×10^{-2} mol/L) is almost identical with that of dodecyltrimethylammonium sulfate (1.6×10^{-2} mol/L) at 25 °C (Mukerjee and Mysels, 1977). The unusual CMC increases observed in several nonionic poly(oxyethylene) glycol mono *n*-alkyl ethers may be a consequence of complex formation between the ether oxygen atoms of the oxyethylene units and the cations of hard river water. This would cause the surfactant molecule to acquire a positive charge, inhibiting micellization because of the increased repulsion between the similarly charged surfactant molecules. This appears to depend upon the number of oxyethylene units in the surfactant molecule. When the number of oxyethylene groups in the molecule in six or more, complex formation with the divalent Ca^{2+} and Mg^{2+} ions results in an increase in the CMC value. In the case of a surfactant with few oxyethylene units, a "salting out" effect is usually predominant, resulting in a reduction in the CMC value. For the homologous alkyl poly(oxyethylene) sulfates, the CMC value decreases with an increase in the number of oxyethylene units. This is in good agreement with that obtained previously in distilled water (Dahanayake et al., 1986), where it was suggested that the negative charge of the hydrophilic head group increases the potential of the ether oxygen atoms of the oxyethylene units to interact with metal ions, imparting a partial zwitterionic character to the surfactant molecule. This results in a decrease in the CMC value. For all types of surfactants, the CMCs in hard river water decrease with an increase in the length of the alkyl chain. This also coincides with that reported in distilled water (Dahanayake et al., 1986; Rosen, 1976). From the CMC values of the alkyl tetra(oxyethylene) sulfate homologues, a linear relationship of −log CMC and the number of carbon atoms in the alkyl chain was obtained, shown in Figure 8. The slope of this curve is about 0.5, close to that for nonionics (Rosen, 1989 (d)), indicating that these anionics in hard river water behave like nonionics in distilled water.

Minimum Area per Surfactant Molecule at the Air/Water Interface (A_{min}). The minimum area occupied by the surfactant molecule in the interface between air and hard river water greatly depends upon the hydrophilic head group. Nonionics, in general, show lower A_{min} values than anionics and cationics, attributed to the absence of electrostatic repulsion in the former. Consistent with this, A_{min} values of anionics decreased in the hard river water as compared with those in distilled water. This results from the reduction of electrostatic repulsion between the anionic head groups in the hard river water due to their interaction with Ca^{2+} and Mg^{2+} ions. For the alkyl poly(oxyethylene) sulfates, the introduction of oxyethylene units into the molecule increases A_{min}. This is also consistent with that obtained before (Dahanayake et al., 1986). For the nonionic *N*-alkylpyrrolidinone and dimethylalkylphosphine oxide series, and the polyoxyethylenated nonionics with four oxyethylene groups, the A_{min} value is decreased slightly with an increase in the length of the straight alkyl chain. The A_{min} value is increased for a branched alkyl chain compared to its isomeric straight chain compound. Both these effects are believed to be related to the chain−chain hydrophobic interaction and the steric hindrance of branched alkyl chains. A similar decrease in A_{min} with the increase in the length of the alkyl chain was reported for other homologous series of nonionic surfactants in Meguro et al. (1981) and our previous studies (Rosen, 1989 (e); Rosen et al., 1988).

Among nonionics, *N*-alkylpyrrolidinones hardly showed any difference in A_{min} values in distilled water and in the hard river water. However, it is interesting to note that the polyoxyethylenated nonionics with six or more oxyethylene units have A_{min} values higher in hard river water than in distilled water. This is consistent with their increased CMC values mentioned before, due to the formation of a cationic complex through the interaction of oxyethylene units with Ca^{2+} and Mg^{2+} in the hard river water. Here, the resulting positive charge on the molecule produces intermolecular repulsion and an increase in A_{min}.

Adsorption at the Air/Water Interface Relative to Micellization (CMC/C_{20}). The CMC/C_{20} ratio, an index of adsorption onto the water/air interface relative to micellization in the bulk surfactant concentration, is shown in Table 5. Reduction in the mutual repulsion of hydrophilic head groups (which results in increased adsorption at the interface) and the presence of bulky groups in the surfactant molecule (which inhibits micellization) both increase the CMC/C_{20} ratio. As a result, the CMC/C_{20} ratio of anionics is greatly affected by hard river water, showing a higher value than that in distilled water (due to the interaction with Ca^{2+} and Mg^{2+}). The cationics showed a slight increase in the CMC/C_{20} ratio, consistent with the

Table 5. CMC/C_{20} Ratios and A_{min} of Surfactants in Hard River Water and in Distilled Water at 25 °C

	in hard river water		in distilled watera	
compd	CMC/C_{20}	A_{min}/Å^2	CMC/C_{20}	A_{min}/Å^2
$C_{12}H_{25}SO_3Na$	10.0	70.9	2.8	57.0
$C_{12}H_{25}SO_4Na$		50.4	2.6	53.0
$C_{12}H_{25}EOSO_4Na$	10.2	46.2	2.6	56.8
$C_{12}H_{25}EO_2SO_4Na$	11.5	51.23	2.5	63.0
$C_{12}H_{25}EO_4SO_4Na$	10.5	68.8	1.8[b]	75.8[b]
$C_{14}H_{29}SO_4Na$		48.5	2.6	45.0
DESS	151.3	72.8	28.0	106
dodecane-1,2-diol	5.0	30.4	6.5[c]	26.0[c]
$C_{10}H_{21}P(O)(CH_3)_2$	12.0	43.8	11.8	46.5
$C_{12}H_{25}P(O)(CH_3)_2$	12.6	42.67	12.1	43.8
$C_{2,6}P$		48.5		46.5[d]
C_8P		41.4		37.9[d]
$C_{10}P$		39.8		36.0[d]
$C_{12}P$		32.5		32.7[d]
$C_{10}H_{21}EO_6$	16.2	58.7	13.2	51.1
$C_{12}H_{25}EO_4$	11.5	42.8	13.7	46.0
$C_{12}H_{25}EO_6$	12.8	52.0	13.4	50.3
$C_{14}H_{29}EO_4$	6.9	34.0	9.5	39.6
$C_{14}H_{29}EO_6$	10.5	49.7	9.57	45.0
$C_{14}H_{29}EO_8$	13.8	62.2	8.4	48.0
$C_{16}H_{33}EO_6$	12.7	51.4	6.3	38.0
$C_{14}H_{29}N^+(CH_3)_3Br^-$	6.45	52.1	2.1	61
$C_{10}H_{21}PyBr^-$	3.97	82.5	2.69[e]	

[a] CMC/C_{20} ratios and A_{min} values from pp 144−147 and 70−80, respectively, of Rosen (1989). [b] Calculated value from Schwuger (1984, p 3). [c] Kwan, C.; Rosen, M. J. *J. Phys. Chem.* **1980**, *84*, 547. [d] Rosen et al. (1988, p 1273). [e] Estimated value from data of R. L. Venable and R. V. Nauman (*J. Phys. Chem.* **1964**, *68*, 3498).

fact that the CMC/C_{20} ratio increases with an increase in the ionic strength of the solution. Nonionics showed a small decrease in the CMC/C_{20} ratio except for the nonionic alkyl poly(oxyethylene) glycols with six or more poly(oxyethylene) in the molecule, which show an increase in the CMC/C_{20} ratio. This result is believed to be linked to the formation of the cationic complex of the poly(oxyethylene) group and divalent Ca^{2+} and Mg^{2+} described above. DESS, an anionic surfactant with two branched alkyl chains shows a large CMC/C_{20} value, compared to other surfactants with a single straight alkyl chain, due to steric inhibition of micellization. This result is in good agreement with the fact that the more bulky the alkyl chain of the surfactant, the higher the CMC/C_{20} ratio value (Rosen, 1989 (f)). In hard river water, the presence of Ca^{2+} and Mg^{2+} increases the CMC/C_{20} even more.

Effectiveness of Surface Tension Reduction (γ_{CMC}). γ_{CMC} values in hard river water and in distilled water are shown in Table 6. For most of the anionic surfactants studied, the γ_{CMC} value in hard water is less than that in distilled water, reflecting the decrease in A_{min} and the increase in the CMC/C_{20} ratio mentioned above, both of which have been shown (Rosen, 1989 (f)) to decrease the value of γ_{CMC}. Since for cationic and nonionic surfactants these two values in hard water are not very different from the values in distilled water, there is little change in values of γ_{CMC} in these two media. For alkyl poly(oxyethylene) glycol ethers with six or more oxyethylene units, the γ_{CMC} value in hard water is slightly higher than that in distilled water, reflecting the increase in A_{min} in the former medium.

Conclusions

1. Surfactants show greater surface activity in hard water than in distilled water; the activity increases in the order nonionics < cationics < anionics. The increased activity is attributed to the presence of the electrolytes in the hard river water, especially the divalent cations Ca^{2+} and Mg^{2+}.

Table 6. Comparison of γ_{CMC} of Surfactants in Hard River Water and in Distilled Water at 25 °C

	γ_{CMC}/mN·m^{-1}	
compd	in hard river water	in DDI H_2O
$C_{12}H_{25}SO_3Na$	36.0	39.0[a]
$C_{12}H_{25}EOSO_4Na$	31.4	39.2[a]
$C_{12}H_{25}EO_2SO_4Na$	33.2	41.4[a]
$C_{12}H_{25}EO_4SO_4Na$	38.8	46.3[b]
$C_{14}H_{29}EOSO_4Na$	32.2	32.0[a]
N-dodecyl-2-pyrrolidone	26.4	26.4[c]
$C_{10}H_{21}P(O)(CH_3)_2$	30.0	30.3
$C_{12}H_{25}P(O)(CH_3)_2$	28.4	28.7
$C_{10}H_{21}EO_6$	32.8	31.3
$C_{12}H_{25}EO_4$	28.8	28.6[a]
$C_{12}H_{25}EO_6$	32.0	32.0
$C_{14}H_{29}EO_6$	32.6	31.6
$C_{14}H_{29}EO_8$	35.1	34.0[a]
$C_{16}H_{33}EO_6$	32.1	32.0[a]
$C_{14}H_{29}N^+(CH)_3Br^-$	40.5	41.0[a]

[a] Rosen (1989, pp 220−225). [b] Calculated value from Schwuger (1984, p 3). [c] Rosen et al. (1988, p 1273).

2. For ionic surfactants, the electrolytes produce reduced electrostatic repulsion between the ionic hydrophilic groups, resulting in decreased values of the CMC and A_{min}, and increased values of the pC_{20} and the CMC/C_{20} ratio.

3. The result of the decrease in A_{min} and increase in the CMC/C_{20} is a decrease in γ_{CMC}.

4. For nonionics, the effect of the electrolytes is different. There is little or no increase in the pC_{20} value. For polyoxyethylenated nonionics with six or more oxyethylene groups, the CMC and A_{min} values show an increase, attributed to complex formation between the ether oxygen of the oxyethylene groups and the divalent ions Ca^{2+} and Mg^{2+}.

5. For anionic surfactants, the γ_{CMC} values in hard water are less than those in distilled water, due to the combined effect of the decrease in A_{min} and the increase in the CMC/C_{20} ratio in hard water. The γ_{CMC} values of cationic and nonionic surfactants are little affected by the hardness of hard water.

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