Relationship of Structure to Properties in Surfactants: II. Efficiency in Surface or Interfacial Tension Reduction[1]

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ABSTRACT

The concept of a quantitative measure for the efficiency with which surfactants depress surface or interfacial tension is introduced. It is shown that the quantity, $\log(1/C)_{\pi=20}$, where C is the bulk concentration or surfactant required to reduce the surface or interfacial tension by 20 dynes/cm (surface pressure, π=20), is a suitable measure of the efficiency. This quantity is a linear function of the free energy of transfer of the surfactant molecule from the interior of the bulk phase to the interface. The effect upon the efficiency of various structural groupings in both the hydrophobic and hydrophilic portions of the molecule is calculated and the results discussed. From surface and interfacial tension data, it is shown that the free energy decrease involved in the transfer of a $-CH_2-$ group at π=20 to the aqueous solution-air interface is 450-500 cal $mole^{-1}$ at 25 C; for the aqueous solution-heptane interface, the free energy decrease/ $-CH_2-$ group transferred is greater than 427 cal $mole^{-1}$ at 50 C.

INTRODUCTION

In a previous publication (1) it was pointed out that in any discussion of the relationship between the structure of surfactants and their reduction of surface tension, it is necessary to distinguish between the efficiency of a surfactant, indicated by the concentration required to produce some significant reduction in the surface tension of the solvent, and its effectiveness, measured by the maximum value to which it can depress the tension, since these two often run counter to each other. This discussion will attempt to define the term efficiency in quantitative fashion and will explore more deeply into its relationship to molecular structure in surfactants.

It is proposed here that the log of the reciprocal of the bulk concentration of surfactant necessary to produce a surface or interfacial pressure of 20 dynes/cm, i.e. a 20 dyne/cm reduction in the surface or interfacial tension, $\log(1/C)_{\pi=20}$, where C is the bulk concentration in moles/ liter, be considered as a measure of the efficiency of a surfactant in reducing interfacial tension. This quantity can be related to the free energy change involved in the transfer of a surfactant from the interior of a bulk phase to the interface and to the various structural groups present in the surface-active molecule.

The free energy of transfer, ΔG, of a surfactant molecule from the interior of a bulk phase to an interface is related to the concentrations of surfactant at the interface, C_I, and in the bulk phase by the expression:

$$C_I/C = \exp(-\Delta G/RT)$$

where R = 1.99 cal $degree^{-1}$ $mole^{-1}$, T = absolute temperature, and C_I and C are expressed in the same units (moles/ liter). The concentration of surfactant at the interface, C_I, is related to the surface excess concentration, Γ, in moles/ cm^2 of the Gibbs adsorption equation, by the equation $C_I = (1000\Gamma/d) + C$, where d is the thickness of the interfacial region, in cm. For solutes, such as surfactants, which are highly surface-active, $1000\,\Gamma/d$ is 1M or more, while C is usually <0.01M, thus $C_I/C = 1000\,\Gamma/dC$ without significant error. The value of Γ can be obtained from a plot of surface tension, γ, or interfactial tension, γ_I, vs log C of the surfactant, since from the Gibbs adsorption isotherm,

$$\Gamma = -(\partial\gamma_{[I]}/\partial\log C)_T/2.3nRT,$$

where n=1 for nonionics, and 1 or 2 for univalent ionic surfactants in the presence or absence of electrolyte containing a common counterion, respectively.

When the interfacial tension has been reduced by 20 dynes/cm, i.e. the interfacial pressure, $\pi = \gamma_o - \gamma = 20$ dynes/ cm, the value of Γ is usually close to its maximum value and falls in the range of 1-5 x 10^{-10} moles/cm^2. The cross-sectional area, A, of a molecule at the interface equals $\frac{1}{N\Gamma}$, where N = Avogadro's number. Calculations at π=20 indicate that most surfactants are lying slightly tilted to the interface at this interfacial pressure. A larger value of A generally indicates a smaller angle of the surfactant with respect to the interface; a smaller value of A indicates that the surfactant is oriented closer to the normal to the interface. If we assume that the thickness, d, of the interfacial layer is determined by the ht of the surfactant normal to the interface, then d is inversely proportional to A, from which $A = \frac{1}{N\Gamma} \alpha \frac{1}{d}$ or $\Gamma/d \cong$ constant. At an interfacial pressure of 20 dynes/cm, then $C_I/C = \exp(-\Delta G/RT) = 1000\Gamma/dC \cong (K_1/C)_{\pi=20}$ and $\log(1/C)_{\pi=20} = -\Delta G/2.303\,RT + K_2$, where K_1 and K_2 are constants.

For a straight chain surfactant of structure, $CH_3(CH_2)_nW$, where W is the hydrophilic portion of the molecule, ΔG can be broken (2,3) into the free energy changes associated with the transfer of the hydrophilic portion of the molecule, ΔG (-W), the terminal methyl group, and the $-CH_2-$ groups of the hydrocarbon chain, from the interior of the bulk phase to the interface, i.e. $\Delta G = \Delta G(-W) + m \times \Delta G(-CH_2-) + K_3$, where m = the total number of carbon atoms (n + 1) in the hydrocarbon chain, and K_3 = the difference in free energy of transfer between the terminal $-CH_3$ group and a $-CH_2-$ group. Thus,

$$\log(1/C)_{\pi=20} = (-\Delta G[-CH_2-]/2.3RT)m + (-\Delta G[-W]/2.3RT) + K_4 \qquad \text{(I)}$$

Under conditions where ΔG(-W) is independent of the length of the hydrophobic group, for a homologous series of straight chain surfactants with the same hydrophilic group at some specified temperature,

$$\log(1/C)_{\pi=20} = (-\Delta G[-CH_2-]/2.3RT)m + K_5, \qquad \text{(II)}$$

where K_4 and K_5 are constants.

EFFECT OF HYDROPHOBIC GROUP UPON EFFICIENCY

Equation II indicates that the efficiency factor, $\log(1/C)_{\pi=20}$, should increase linearly with increase in the number of carbon atoms in a straight chain hydrophobic group. Table I and Figure 1 show data for several homologous series of surfactants, indicating that this is indeed the case. If the hydrophobic group of an ionic surfactant is increased by 2 $-CH_2-$ groups, $\log(1/C)_{\pi=20}$ is increased by 0.55-0.6 for the aqueous solution-air or aqueous solution-heptane interface, meaning that the same 20 dyne/cm reduction in interfacial tension can be obtained with a bulk concentration only 25-30% of that required of the homolo-

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[1] Presented at the AOCS Meeting, Philadelphia, September 1974.

TABLE I

Effect of Length of Hydrophobic Group upon Efficiency of Interfacial Tension Reduction

Substance	Interface	Temperature (C)	Bulk concentration for 20 dyne/cm reduction (moles/liter)	$\mathrm{Log}\left(\frac{1}{C}\right)_{\pi=20}$	Reference
$C_{10}H_{21}SO_4^-Na^+$	Aqueous solution-air	27	1.29×10^{-2}	1.88_9	4
$C_{12}H_{25}SO_4^-Na^+$	Aqueous solution-air	25	4.1×10^{-3}	2.38_7	5
$C_{12}H_{25}SO_4^-Na^+$	Aqueous solution-air	25	2.7×10^{-3}	2.56_8	6
$C_{12}H_{25}SO_4^-Na^+$	Aqueous solution-air	60	5.75×10^{-3}	2.24_1	7
$C_{16}H_{33}SO_4^-Na^+$	Aqueous solution-air	25	2.0×10^{-4}	3.69_9	8
$C_{12}H_{25}SO_3^-Na^+$	Aqueous solution-air	40	4.95×10^{-3}	2.30_5	9
$C_{12}H_{25}SO_3^-K^+$	Aqueous solution-air	25	3.7×10^{-3}	2.43_1	a
$C_{16}H_{33}SO_3^-K^+$	Aqueous solution-air	40	3.8×10^{-4}	3.42_0	a
$C_{16}H_{33}SO_3^-K^+$	Aqueous solution-air	60	3.9×10^{-4}	3.40_8	7
$C_8H_{17}SO_4^-Na^+$	Aqueous solution-heptane	50	2.45×10^{-2}	1.61_1	10
$C_{10}H_{21}SO_4^-Na^+$	Aqueous solution-heptane	50	7.7×10^{-3}	2.11_4	10
$C_{12}H_{25}SO_4^-Na^+$	Aqueous solution-heptane	50	1.9×10^{-3}	2.72_1	10
$C_{14}H_{29}SO_4^-Na^+$	Aqueous solution-heptane	50	4.9×10^{-4}	3.31_0	10
$C_{16}H_{33}SO_4^-Na^+$	Aqueous solution-heptane	50	1.3×10^{-4}	3.88_6	10
$C_{18}H_{37}SO_4^-Na^+$	Aqueous solution-heptane	50	3.8×10^{-5}	4.42_0	10
$C_8\phi SO_3^-Na^+$	Aqueous solution-air	70	1.1×10^{-2}	1.95_9	11
$C_{10}\phi SO_3^-Na^+$	Aqueous solution-air	70	3.0×10^{-3}	2.52_2	11
$C_{12}\phi SO_3^-Na^+$	Aqueous solution-air	70	7.9×10^{-4}	3.10_2	11
$C_{14}\phi SO_3^-Na^+$	Aqueous solution-air	70	2.3×10^{-4}	3.63_9	11
$C_{16}\phi SO_3^-Na^+$	Aqueous solution-air	70	6.2×10^{-5}	4.20_8	11
$C_9H_{19}COO(CH_2)_2SO_3^-Na^+$	Aqueous solution-air	30	9.5×10^{-3}	2.02_2	12
$C_{11}H_{23}COO(CH_2)_2SO_3^-Na^+$	Aqueous solution air	30	1.87×10^{-3}	2.72_8	12
$C_9H_{19}COO(CH_2)_3SO_3^-Na^+$	Aqueous solution-air	30	8.4×10^{-3}	2.07_6	12
$C_{10}H_{21}COO(CH_2)_3SO_3^-Na^+$	Aqueous solution-air	30	3.5×10^{-3}	2.45_6	12
$C_{11}H_{23}C))(CH_2)_3SO_3^-Na^+$	Aqueous solution-air	30	1.7×10^{-3}	2.76_9	12
$C_9H_{19}COO(CH_2)_4SO_3^-Na^+$	Aqueous solution-air	30	4.9×10^{-3}	2.31_0	12
$C_{11}H_{23}COO(CH_2)_4SO_3^-Na+$	Aqueous solution-air	30	1.15×10^{-3}	2.94_0	12
$C_{14}H_{29}OC_2H_4SO_4^-Na^+$	Aqueous solution-air	25	1.5×10^{-4}	3.82_4	8
$C_{16}H_{33}OC_2H_4SO_4^-Na^+$	Aqueous solution-air	25	3.1×10^{-5}	4.50_8	15
$C_{16}H_{33}(OC_2H_4)_2SO_4^-Na^+$	Aqueous solution-air	25	2.1×10^{-5}	4.67_8	15
$C_{16}H_{33}(OC_2H_4)_3SO_4^-Na^+$	Aqueous solution-air	25	2.1×10^{-5}	4.67_8	15
$C_{18}H_{37}OC_2H_4SO_4^-Na^+$	Aqueous solution-air	25	1.1×10^{-5}	4.96_0	15
$C_{18}H_{37}(OC_2H_4)_2SO_4^-Na^+$	Aqueous solution-air	25	8.3×10^{-6}	5.08_1	15
$C_{18}H_{37}(OC_2H_4)_3SO_4^-Na^+$	Aqueous solution-air	25	1.15×10^{-5}	4.94_0	15
$C_{12}H_{25}SO_4^-Na^+$	0.1M NaCl-air	25	1.6×10^{-4}	3.79_6	16
$C_{16}H_{33}SO_4^-Na^+$	0.1M NaCl-air	25	5.8×10^{-6}	5.23_7	16
$C_{12}H_{25}N(CH_3)_3^+Cl^-$	0.1M NaCl-air	25	2.1×10^{-4}	3.67_8	16
$C_{16}H_{33}N(CH_3)_3^+Cl^-$	0.1M NaCl-air	25	1.0×10^{-5}	5.00_0	16
$C_8H_{17}C_5H_5N^+Br^-$	Aqueous solution-air	20	5.3×10^{-2}	1.27_7	17
$C_{12}H_{25}C_5H_5N^+Br^-$	Aqueous solution-air	30	5.4×10^{-3}	2.26_7	18
$C_{14}H_{29}C_5H_5N^+Br^-$	Aqueous solution-air	30	1.15×10^{-3}	2.94_0	18
$C_{12}H_{25}N(CH_3)_20$	Aqueous solution-air	25	2.4×10^{-4}	3.62_0	a
$C_{18}H_{37}N(CH_3)_2O$	Aqueous solution-air	25	3.8×10^{-6}	5.42_0	a
$C_6H_{13}(OC_2H_4)_6OH$	Aqueous solution-air	20	1.1×10^{-3}	2.95_9	19
$C_{10}H_{21}(OC_2H_4)_6OH$	Aqueous solution-air	23.5	4.9×10^{-5}	4.31_0	20
$C_{12}H_{25}(OC_2H_4)_6OH$	Aqueous solution-air	20	9.2×10^{-6}	5.03_6	20
$C_{11}H_{23}CON(C_2H_4OH)_2$	Aqueous solution-air	25	4.2×10^{-5}	4.37_7	a
$C_{12}H_{25}NH_3^+Cl^-$	Aqueous solution-air	25	3.35×10^{-3}	2.47_5	a

[a] M.J. Rosen, unpublished results.

gous surfactant with two less carbon atoms. For polyoxyethylenated nonionics at the aqueous solution-air interface and for ionics at the 0.1M NaCl-air interface, $\log(1/C)_{\pi=20}$ is increased by ca. 0.7, when the chain length is increased by 2 $-CH_2-$ groups, with a consequent decrease in the required bulk concentration to one-fifth of that originally required.

Figure 1 also indicates that, in its effect upon the efficiency of interfacial tension reduction, a phenyl group in the hydrophobic portion is equivalent to ca. 3.5 carbons in a straight alkyl chain. This same equivalency has been noted in the solubility behavior of polar organic molecules, in measurements of relative adsorptivity at the air-aqueous solution interface, and in the effect of a phenyl group upon the critical micelle concentration of surfactants in aqueous solution (13,14). For the series, $RCOO(CH_2)_xSO_3^-Na^+$, where x = 2, 3, or 4, the $-CH_2-$ groups between the $-COO-$ and $-SO_3^-Na^+$ groups are equivalent to ca. 0.5 carbons in a straight alkyl chain. In compounds of structure $R(OC_2H_4)_xSO_4^-Na^+$, where x = 1, 2, or 3, or $RCONH(C_2H_4OH)_2$, the first oxyethylene group appears to be equivalent to ca. 2.5 carbon atoms in a straight alkyl chain, with the additional oxyethylene groups having little or no effect. Short alkyl groups (<4 carbon atoms), including the pyridine nucleus, which are part of a quaternary nitrogen or amine oxide hydrophilic group appear to have little effect. In these cases, the efficiency is determined almost exclusively by the length of the long alkyl chain attached to the nitrogen atom. This is again similar to the effect upon the critical micelle concentration (14).

The increased efficiency of the surfactant in reducing interfacial tension as the length of the hydrophobic group is increased is a reflection of the greater free energy decrease involved in the transfer of the molecule from the interior of the bulk phase to the interface. The value of this free energy decrease/methylene group, $-\Delta G\ (-CH_2-)$, can be determined from the slope of the plot of $\log(1/C)_{\pi=20}$ vs m (Fig. 1), since $-\Delta G = 2.3RT \times \text{slope}$. Values calculated in this manner for the various homologous series listed in Table I are given in Table II.

The results indicate a value of $-\Delta G$ ($-CH_2-$) at $\pi=20$ of slightly more than 400 cal/mole of $-CH_2-$, perhaps increasing slightly with increase in temperature for both the aqueous solution-air and aqueous solution-heptane interfaces in the absence of added electrolyte. For the polyoxyethylenated nonionics at the aqueous solution-air interface and for the ionics at the 0.1M NaCl-air interface, the value is ca. 50 cal/mole higher. One reason for this may be the dependence of $-\Delta G(-W)$ for ionizing surfactants upon the ionic strength of the solution. Lin and Somasundaran (21) have pointed out that, in micellization, $\Delta G(-W)$ is a function of the length of the alkyl chain of an ionizing surfactant in the absence of added electrolyte, since the concentration of an ionizing surfactant at its critical micelle concentration, and hence the ionic strength of the solution, varies with the length of the chain of the surfactant. The same may be expected to be true in this case, since the concentration to produce a reduction in interfacial tension of 20 dynes/cm varies with the length of the alkyl/chain. Following their line of reasoning, the linearity of the plots of $\log (1/C)_{\pi=20}$ vs m implies that $\Delta G(-W)$ is a first order function of m, i.e. $-\Delta G(-W) = W_e m$, where W_e is the free energy of transfer of the hydrophilic group/carbon atom in the chain. Thus,

$$\log (1/C)_{\pi=20} = (-\Delta G[-CH_2-]/2.3RT)m + (W_e/2.3RT)m + K_4,$$

or (III)

$$\log (1/C)_{\pi=20} = \left\{ (-\Delta G[-CH_2-]+W_e)/2.3RT \right\} m + K_4.$$

The slope of the plot of $\log(1/C)_{\pi=20}$ vs m is then the sum of $-\Delta G(-CH_2-)$ and $-\Delta G(-W)/m$. Since $-\Delta G(-CH_2-)$ and $-\Delta G(-W)$ have opposite signs, this would account for the smaller absolute values of $\Delta G(-CH_2-)$ in the case of ionizing surfactants in the absence of electrolyte. The higher energies of transfer of the polyoxyethylenated nonionics and the ionics at the 0.1M NaCl-air interface also may reflect the higher position in the interface of the hydrophobic groups in these compounds. The hydrophobic groups of polyoxyethylenated nonionics have been shown to be somewhat elevated above the interface (22), and the slope of the γ-log C curves for ionics in 0.1M NaCl (16) indicates that the molecules at the interface are much more vertically oriented in this solvent than in pure water. At very sparse surface coverage ($\pi \rightarrow 0$), the value for the free energy decrease involved in the transfer of a $-CH_2-$ group from aqueous solution to air has been calculated as ca. 600 cal mole^{-1} (23).

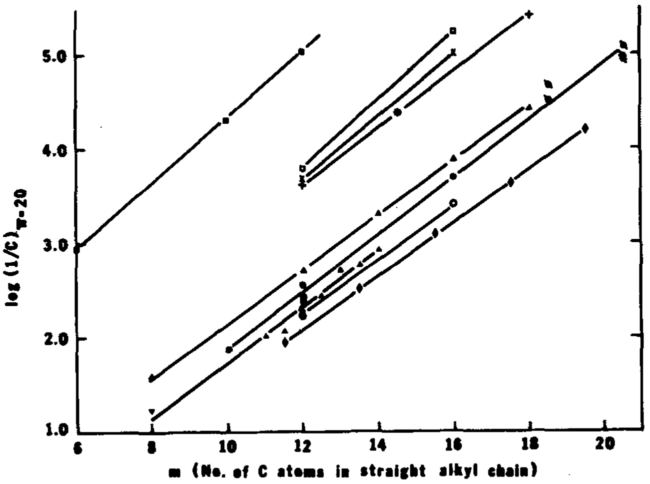
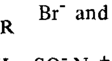


FIG. 1. Effect of length of the hydrophobic group upon efficiency of surface or interfacial tension reduction. ■ = $R(OC_2H_4)_6OH$ at 20 C. □ = $RSO_4^-Na^+$ in 0.1M NaCl at 25 C. + = $RN(CH_3)_2O$ at 25 C. * = $C_{11}H_{25}CON(C_2H_4OH)_2$ at 25 C. △ = $RSO_4^-Na^+$ at heptane-water interface at 50 C. ● = RSO_3^- and RSO_4^- at 25 C. ◣ = $R(OC_2H_4)_xSO_4^-Na^+$ at 25 C (x=1,2,3). ▼ =  Br^- and ▲ = $RCOO(CH_2)_xSO_3^-Na^+$ (x=2,3,4) at 30 C. ○ = $C_{12}H_{25}SO_3^-Na^+$ and $C_{16}H_{33}SO_3^-K^+$ at 60 C. ◆ = $R\phi SO_3^-Na^+$ at 70 C. x = $RN(CH_3)_3^+Cl^-$ in 0.1M NaCl at 25 C.

EFFECT OF HYDROPHILIC GROUP UPON EFFICIENCY

Equation I indicates that the efficiency factor, $\log (1/C)_{\pi=20}$, also should reflect the effect of the hydrophilic group, -W, in the surfactant molecule; the greater the free energy decrease in transferring -W from interior to interface, $-\Delta G(-W)$, the greater the efficiency should be. Absolute values for $\Delta G(-W)$ cannot be determined, since data are not available to evaluate the constant K_4, which depends upon the quantities Γ/d and $\Delta G(-CH_3)$-$\Delta G(-CH_2-)$. However, since these quantities are functions of the hydrophobic group, rather than the hydrophilic group, we may assume that K_4 does not vary significantly with change in the hydrophilic group. We then can evaluate the difference in free energies of transfer of two hydrophilic groups, $\Delta G(-W_1)$-$\Delta G(-W_2)$, and determine the relative effect of these two groups upon the efficiency of surface or interfacial tension reduction. For straight chain surfactants with similar values of $\Delta G(-CH_2-)$ at the same temperature containing the same number of carbon atoms in a straight alkyl chain but different hydrophilic groups, the difference in $\log (1/C)_{\pi=20}$ should reflect the difference in the free energies

TABLE II

Free Energies of Transfer of $-CH_2-$ @ $\pi=20$

Structure	Temperature (C)	Interface	$\Delta G(-CH_2-)$ Cal/mole
$RSO_4^-Na^+$ or $RSO_3^-K^+$	25	Aqueous solution-air	-410
$RN(CH_3)_2O$	25	Aqueous solution-air	-410
$RCOO(CH_2)_xSO_3^-Na^+$ (x=2,3,4)	30	Aqueous solution-air	-425
$RC_5H_5N^+Br^-$	30	Aqueous solution-air	-407
$RSO_3^-Na^+(K^+)$	40	Aqueous solution-air	-400
$RSO_4^-Na^+$	50	Aqueous solution-heptane	-427
$RSO_4^-Na^+$ or $RSO_3^-K^+$	60	Aqueous solution-air	-445
$R\phi SO_3^-Na^+$	70	Aqueous solution-air	-442
$RSO_4^-Na^+$	25	0.1M NaCl-air	-492
$RN(CH_3)_3^+Cl^-$	25	0.1M NaCl-air	-454
$R(OC_2H_4)_6OH$	20	Aqueous solution-air	-459
$R(OC_2H_4)_5OH$[a]	20	Aqueous solution-air	-475

[a] From data, references 19 and 20.

TABLE III

Effect of Hydrophilic Group upon Efficiency of Surface and Interfacial Tension Reduction

Hydrophilic group	Temperature (C)	Log (1/C) - log ($1/C_{SO_4^-}$) (π=20; m=12)	ΔG(-W)-ΔG(-SO_4^-) (kcal/mole)
-$(OC_2H_4)_4OH$[a]	55	3.35	--
-$(OC_2H_4)_7OH$[a]	55	3.35	--
-$(OC_2H_4)_{14}OH$[a]	55	3.27	--
-$(OC_2H_4)_{23}OH$[a]	55	3.15	--
-$(OC_2H_4)_{30}OH$[a]	55	3.12	--
-$(OC_2H_4)_6OH$	20	2.53	-2.7$_5$
-$(OC_2H_4)_5OH$[b]	20	2.52	-2.5$_5$
-$N(CH_3)_2O$	25	1.14	-1.5$_6$
–$N(CH_3)_3^+Cl^-$ in 0.1M NaCl	25	1.20	-1.1$_5$
-$SO_4^-Na^+$ in 0.1M NaCl	25	1.32	-0.8$_5$
-$SO_4^-Na^+$ at heptane-aqueous solution interface	50	0.41	-0.7$_1$
-SO_3^-	25	-0.05	+0.0$_7$
 N^+–Br^-	30	-0.18	+0.1$_3$
-$NH_3^+Cl^-$	25	0.00	--

[a] From data, reference 22. ΔG(-W)-ΔG(-SO_4^-) values not determinable since data for log $(1/C)_{\pi=20}$ vs m not available.

[b] From data, references 19 and 20.

of transfer of the different hydrophilic groups, i.e.:

$$\log (1/C_1)_{\pi=20} - \log (1/C_2)_{\pi=20} = \Delta \log (1/C)_{\pi=20} = (-\Delta G[-W_1] - \{-\Delta G[-W_2]\})/2.3RT$$

and

$$\Delta G(-W_1) - \Delta G(-W_2) = -2.3RT\ \Delta \log (1/C)_{\pi=20}\ . \qquad (IV)$$

For surfactants with differing values of $\Delta G(-CH_2-)$, e.g. ionics in 0.1 M NaCl or polyoxyethylenated nonionics, compared to sulfonates in distilled water at 25 C, $\Delta \log (1/C)_{\pi=20}$ for surfactants with the same number of carbon atoms reflects also the different values of $\Delta G(-CH_2-)$ and thus cannot be used to evaluate $\Delta G(-W_1)$-$\Delta G(-W_2)$. In these cases, $\Delta G(-W)/2.3RT + K_4$ can be evaluated either from the y-intercepts, when m=0, of plots of $\log (1/C)_{\pi=20}$ vs m or from $\log (1/C)_{\pi=20}$ and the slope of the plot, $-\Delta G(-CH_2-)/2.3RT$, by use of equation I. $\Delta G(-W_1)$-$\Delta G(-W_2)$ then can be evaluated from the difference in values of $\Delta G(-W)/2.3RT + K_4$.

$$y_1 - y_2 = -\Delta G(-W_1)/2.3RT + K_4 - (-\Delta G[-W_2]/2.3RT + K_4) = (\Delta G[-W_2] - \Delta G[-W_1])/2.3RT$$

and

$$\Delta G(-W_1) - \Delta G(-W_2) = 2.3RT\,(y_2 - y_1), \qquad (V)$$

where y_1 and y_2 are y-intercepts of the $\log (1/C)_{\pi=20}$ vs m plots at the same temperature. Alternatively,

$$-\Delta G(-W_1)/2.3RT + K_4 = \log (1/C_1)_{\pi=20} - (\text{slope}_1)m$$

and

$$\Delta G(-W_1) - \Delta G(-W_2) = 2.3RT\,(\log[1/C_2]_{\pi=20} - \log[1/C_1]_{\pi=20} + m[\text{slope}_1 - \text{slope}_2]) \qquad (VI)$$

Table III lists the efficiency factor difference, log (1/C) - log ($1/C_{SO_4^-}$) @ π=20 between surfactants, all of which contain 12 carbon straight chain hydrophobic groups but different hydrophilic groups and one containing the same hydrophobic group with -SO_4^- as the hydrophilic group at the same temperature at the aqueous solution-air interface. It also lists the difference between the free energies of transfer of various hydrophilic groups and that for the -SO_4^- group at the aqueous solution-air interface at the same temperature, ΔG(-W)-ΔG(-SO_4^-).

From the results, it is apparent that the efficiency in water is affected slightly, if at all, by changes in the nature of a univalent ionic hydrophilic group, but that the replacement of an ionic hydrophilic group by a nonionic one results in a large increase in efficiency. The depression of the ionization of an ionic hydrophilic group by the addition of electrolyte (NaCl) to the water in which the surfactant is dissolved results in a significant increase in its efficiency.

In polyoxyethylenated nonionics, an increase in the number of oxyethylene units in the hydrophilic group causes very little change in efficiency. This is similar to the effect noted above for other polyoxyethylenated surfactants. An increase in the temperature of the system, however, causes a sharp increase in efficiency toward surface-tension reduction.

The free energy of transfer differences given in Table III indicates that, for the hydrophilic groups listed, the order of increasing -ΔG(-W) is: -SO_4^-, -SO_3^-,  N^+–<-SO_4^- at heptane-aqueous solution interface <-SO_4^-, -$N(CH_3)_3^+$ at 0.1M NaCl-air interface <-$N(CH_3)_2O$<<-$(OC_2H_4)_5OH$, -$(OC_2H_4)_6OH$.

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