

Polymer Polarity and Surfactant Adsorption

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Synopsis

The effect of polymer polarity on surfactant adsorption from aqueous solution is discussed. The analysis assumes that surfactant adsorption at the polymer-water interface follows a Langmuir-type adsorption isotherm and the free energy of adsorption is controlled by the interfacial tension of the interface. Saturation adsorption given by the area per molecule of surfactant at the critical micelle concentration (CMC) of the surfactant is related to the polymer-water interfacial tension and the polarity of the polymer surface, calculated from the polar and dispersion contributions to the polymer surface energy. Available data on the area per molecule of sodium lauryl sulfate on various polymer surfaces have been used to test satisfactorily the above analysis. The analysis is used to interpret some of the observations relating to surfactant adsorption encountered in the emulsion polymerization of polar monomers and particle size determination of latexes by the soap titration method. Further, potential utility of such area per molecule data to characterize the nature of polymer surfaces is also discussed.

INTRODUCTION

The nature of the interface has been shown to exert a considerable influence on various interfacial phenomena such as interfacial tension,^{1,2} micellization and solubilization,³ free energy for the transfer of a methylene group from water to organic liquids,⁴ surfactant adsorption,^{5,6} formation and stability of polar emulsion particles,⁷⁻⁹ etc.

One area wherein polarity of the interface plays a significant role is in the emulsion polymerization of polar monomers. The effects of polarity on surfactant adsorption and the emulsion polymerization kinetics of polar monomers have received much attention in recent year.¹⁰⁻¹³ The polarities of the monomer-water and polymer-water interfaces are believed to govern surfactant adsorption and particle stabilization,⁷⁻⁹ monomer swelling of growing particles and morphology,^{7,14,15} and other significant features of emulsion polymerization.

Due to the central role of interfacial polarity on the emulsion polymerization of polar monomers, several workers have attempted to correlate the polarity of monomer (polymer)-water interface to monomer water solubility⁹⁻¹¹ and monomer/water interfacial tension.^{8,10} Paxton⁶ suggested that the area per molecule of a surfactant on a polymer surface can give some useful information as to the polarity of the polymer surface. Use of monomer water solubility to estimate polarity is simple and convenient but does not provide any insight into the factors responsible for the various interfacial phenomena mentioned above. Use of monomer-water interfacial tension to estimate polarity is probably a step in the right direction. However, the polar interactions at the monomer-water interface are probably different from those at the corresponding polymer-water interface due to the polarity associated with the unsaturation in the monomer

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molecule. Further, interactions such as surfactant adsorption at a fluid monomer–water interface may be more labile than at a solid polymer–water interface. Hence, we thought it would be worthwhile to expand on Paxton's suggestion and relate the observed differences in the adsorption of a surfactant molecule on various polymer surfaces to the characteristics of the polymer surface, namely, the polar and dispersion forces acting at the polymer–water interface. In such an approach the surfactant molecule is used as a probe to investigate the nature of the polymer surface.

In this paper we plan to discuss the energetics involved in the adsorption of a surfactant molecule from an aqueous medium at a polymer–water interface and to relate the saturation adsorption of the surfactant molecule to the polarity of the polymer surface. Polarity of various polymer surfaces and polymer–water interfacial tensions are calculated from Wu's data.¹⁶ Theoretical predictions relating the area per molecule of a surfactant to interfacial tensions of polymer–water interfaces and polarity of polymer surfaces are tested using the available area per molecule data for sodium lauryl sulfate on various polymer surfaces. In limited cases, adsorption of sodium lauryl sulfate on various polymer surfaces is related to the measured interfacial tension of corresponding monomer–water interfaces.

THEORETICAL CONSIDERATIONS

In this section we develop equations to relate the saturation adsorption of a surfactant molecule on various polymer surfaces to the polymer–water interfacial tension and the polarity of the polymer surface.

In an aqueous solution, the driving force for the adsorption of a surfactant molecule such as sodium lauryl sulfate at the monomer–water or polymer–water interface is the favorable free-energy change associated with the transfer of the hydrocarbon portion of the surfactant molecule from the aqueous phase to the interface.¹⁷ The free-energy change for such a process will depend on the nature of the surfactant and the organic phase (monomer or polymer). If one is concerned with the adsorption characteristics of a given surfactant at various interfaces, as in our case, then one can make the reasonable assumption that the observed differences in the adsorption characteristics of the chosen surfactant at various interfaces are due to the differences in the energy of interaction of the surfactant molecule with the surfaces in question.

The free-energy change, ΔG_{CH_2} , associated with transferring a methylene group from water to an organic phase is a complex function of various physical parameters such as miscibility, interfacial tension, dielectric constant of the organic liquid, etc.⁴ However, it is seen that in some cases the interfacial tension controls surfactant adsorption, as shown by van Voorst Vader.⁵ Figure 1 shows that such a relationship is obeyed in the adsorption of hydrocarbon surfactants at various monomer–water interfaces. Approximate ΔG_{CH_2} values for the various acrylate monomers were calculated from the data of Yeliseyeva and Zhui-kov¹⁰ on the energy of adsorption of sodium lauryl sulfate at the respective monomer–water interfaces, and that for the styrene–water interface was estimated from the data of Sieglaff and Mazur.²⁹ Monomer–water interfacial tensions were measured as described in the next section. It is clearly seen that the free energy of adsorption of a surfactant molecule such as sodium lauryl sulfate at monomer–water interfaces is a linear function of the monomer–water

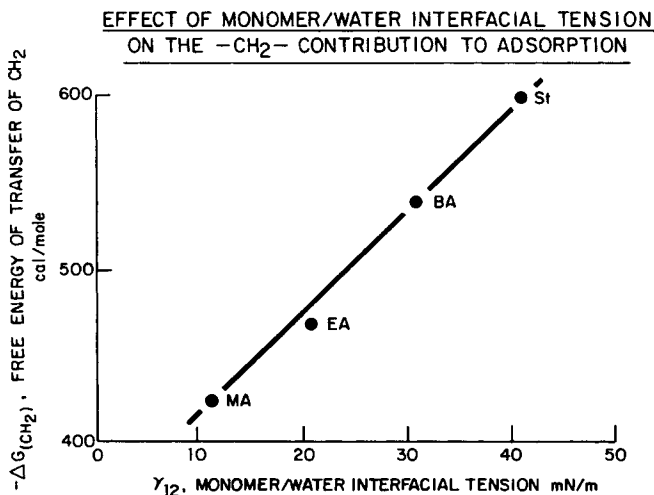


Fig. 1. Plot of free energy of transfer ($-\Delta G_{\text{CH}_2}$) of a CH_2 group from water to monomer-water interface against monomer-water interfacial tension (γ_{12}). See Table I for explanation of monomer symbols.

interfacial tension. A linear relationship between ΔG_{CH_2} and interfacial tension as observed here in the long-chain alkyl sulfate monomer-water system is probably not universal. If one assumes that such a linear relationship is valid for the corresponding polymer-water interface also, we can substitute the free energy of adsorption of the surfactant molecule at various polymer-water interfaces by a linear function of the respective interfacial tensions in our analysis.

Surfactant adsorption at various interfaces is adequately described by Langmuir adsorption isotherms.^{6,17,18,24} Using such an adsorption isotherm in our case and substituting the energy of adsorption of a surfactant molecule at various polymer(monomer)-water interfaces by a function of the respective interfacial tensions (γ_{12}), as discussed above, we obtain a simplified adsorption isotherm given by

$$n = BC \exp f(\gamma_{12})/kT \quad (1)$$

where n = saturation adsorption of surfactant (in number of molecules/unit area of the surface); C = concentration of surfactant (in moles/dm³); B = constant, depending on the hydrodynamics of the adsorption process; k = Boltzmann's constant; T = temperature; and γ_{12} = polymer(monomer)-water interfacial tension.

The above equation is an approximate one, as it does not take into account electrostatic interactions of the ionic groups of the surfactant, increased van der Waals attraction of the hydrocarbon tail groups due to close packing, counterion adsorption in the Stern layer, and other effects.^{17,18} However, it appears that since we are concerned only with the adsorption behavior of a given surfactant at various interfaces, it is reasonable to make the assumption that these interactions are constant at the various interfaces and that the dominant factor controlling surfactant adsorption, at least in the first order analysis is the interfacial tension.

In the soap titration method of Maron,¹⁹ the source of our adsorption data on

sodium lauryl sulfate, the saturation adsorption is determined at the critical micelle concentration (CMC) of the surfactant, and hence the value of C in eq. (1) is a constant in our analysis. Substituting $A_m = 10^{16}/n$ and converting eq. (1) to logarithmic form we have

$$\log A_m = K_1 + \log (1/n) = K_2 - f(\gamma_{12}) \quad (2)$$

where A_m = area per molecule of surfactant at saturation adsorption (nm^2) and K_1, K_2 = constants.

The next step in the analysis is to relate γ_{12} to the polarity of the polymer surface. This is done by using the extended geometric mean approximation with the polar terms included as shown below in eq. (3).²⁰ Use of the geometric mean approach to estimate polar interactions at an interface has been criticized and it has been shown that the harmonic mean equation of Wu¹⁶ often fits the experimental data better. In our first-order analysis, the approximate geometric mean equation is used for simplicity to estimate the relationship between polymer polarity and interfacial tension:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^P \gamma_2^P)^{1/2} \quad (3)$$

where γ_1 = surface tension of water phase; γ_2 = surface tension of polymer phase; γ_1^d, γ_2^d = dispersion contribution to water and polymer surface tension; and γ_1^P, γ_2^P = polar contributions to water and polymer surface tension.

Further, we define polarity (X^P)* following Wu's method¹⁶ as

$$X^P = \gamma^P/\gamma, \quad X^d = \gamma^d/\gamma, \quad \text{and } X^P + X^d = 1 \quad (4)$$

where X^d = nonpolar contribution to surface tension. Substituting eq. (4) into (3) and using the numerical values for γ_1, γ_1^P , and γ_1^d (1 = water phase) of 72.8, 50.7, and 22.1 mN/m, respectively,^{16,20} we have

$$\gamma_{12} = 72.8 + \gamma_2 - [(4 \times 22.1 \gamma_2^d)^{1/2} + (4 \times 50.7 \gamma_2^P)^{1/2}] \quad (5)$$

Multiplying and dividing the factors within the brackets by $\gamma_2^{1/2}$

$$\gamma_{12} = 72.8 + \gamma_2 - [(88.4(1 - X^P))^{1/2} + (202.8X^P)^{1/2}] \gamma_2^{1/2} \quad (6)$$

Expanding $(1 - X^P)^{1/2}$ as a power series and retaining the first two terms, we have $(1 - X^P)^{1/2} \simeq 1 - X^P/2$; and substituting in eq. (6), we have

$$\gamma_{12} = 72.8 + \gamma_2 - [9.4 - 4.6X^P + 14.2(X^P)^{1/2}] \gamma_2^{1/2} \quad (7)$$

Equation (7) relates the interfacial tension between a polymer-water interface and the polarity of the polymer surface. The expression still contains γ_2 , the surface tension of the polymer, and is not convenient to use. However, the data calculated from Wu's results (see Table II) show that γ_2 values do not change as drastically as the polarity values. For a 20–30% change in γ_2 , it is seen that X^P values change by as much as 100%. Further, eq. (7) shows that the effect of γ_2 may be somewhat compensating due to its additive and subtractive contributions to γ_{12} . Due to these considerations, we further simplify eq. (7) to

$$\gamma_{12} = k^1 - f^1(X^P) \quad (8)$$

where k^1 = constant.

* Polarity can be estimated based on other parameters as polar contribution to solubility parameter, dipole moment, polarizability, and ionization constant. In general, agreement between polarity values of a compound calculated based on various parameters is not good.³¹ Here, polarity based on surface tension is employed because of its apparent usefulness in estimating wetting, adhesion, etc.

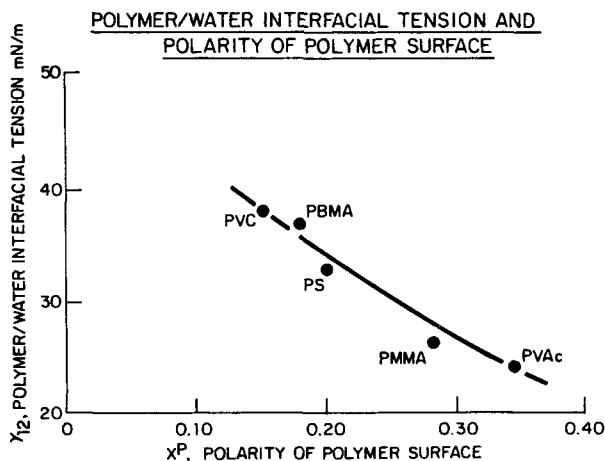


Fig. 2. Plot of calculated polymer-water interfacial tension (γ_{12}) values against polymer polarity (X^P): PVC = poly(vinyl chloride); PBMA = poly(butyl methacrylate); PS = polystyrene; PMMA = poly(methyl methacrylate); PVAc = poly(vinyl acetate).

Figure 2 shows that the calculated interfacial tension of some polymer-water interfaces decreases with increasing polarity of the polymer¹⁶ as predicted by eq. (8). Substituting the expression for γ_{12} from eq. (8) in eq. (2), we have

$$\log A_m = k^{11} + f^{11}(X^P) \quad (9)$$

where $k^{11} = \text{constant}$. This shows that the logarithm of the area per molecule of surfactant increases with the polarity of the polymer surface.

To summarize the theoretical results, we have shown that, as a first approximation, the area occupied by a surfactant molecule on a polymer surface decreases logarithmically with increasing interfacial tension of the polymer-water interface, eq. (2). Further, $\log A_m$ increases with the polarity of the polymer surfaces, eq. (9). In the next section we shall test these predictions using appropriate data from the literature.

RESULTS AND DISCUSSION

Sodium lauryl sulfate is chosen as the surfactant probe, as it has been widely studied and its area per molecule on various polymer surfaces is known from several studies.^{8-10,21-24} The interfacial tension at 20°C of various polymer-water interfaces and polarity of the polymers have been calculated from Wu's data,¹⁶ using the harmonic mean equation. Equating Wu's polarity values obtained from polymer melts with the polarity of corresponding polymer latexes is probably not completely valid, as the latex surface is known to contain ionic and polar groups. However, such an approximation may not be serious in our analysis, as we are only interested in the relative adsorption behavior of sodium lauryl sulfate at various polymer latex-water interfaces. In limited cases, the interfacial tension of monomer-water interface has been measured by the Wilhelmy plate method using a Prolabo automatic tensiometer as described by Lankveld and Lyklema.²⁵ Measurements with the hydrophobic monomers such as methacrylates and 2-ethylhexyl acrylate were not reliable due to poor wetting and hence are not reported. The measured interfacial tension of the monomer-water interfaces is correlated with the water solubility of monomers and

TABLE I

Monomer	Mole fraction N_2 of monomer in water (26)	Monomer-water interfacial tension, mN/m	Area per molecule A_m of sodium lauryl sulfate on polymer surface, nm ²
Methyl acrylate (MA)	0.0113	13-14	1.75 (10) ^a 1.46 (9)
Vinyl acetate (VA)	0.0053	18-19	1.1 (24)
Ethyl acrylate (EA)	0.0027	21-22	0.86 (8, 10) 0.98 (9)
Methyl methacrylate (MMA)	0.0027	—	0.79 (9)
Vinyl chloride (VC)	0.003	—	0.38-0.42 (23)
Propyl acrylate (PA)	0.0009	26-27	0.69 (9)
Ethyl methacrylate (EMA)	0.0009	—	0.77 (9)
Butyl acrylate (BA)	0.0003	30-31	0.62 (8, 10) 0.56 (9)
Styrene (St)	0.000054	40-43	0.49 (8, 10) 0.585 (22) 0.45 (9, 24)
2-Ethylhexyl acrylates (2-EHA)	0.0000097	—	0.43 (9)
<i>n</i> -Butyl methacrylate (BMA)	0.000079	—	0.54 (9) 0.585 (9, 22)

^a Figures in parentheses denote reference numbers.

the area per molecule of sodium lauryl sulfate on the respective polymer surfaces.

In Table I are listed the water solubility of the monomers in mole fraction,²⁶ measured monomer-water interfacial tensions, and the area per molecule of sodium lauryl sulfate on various polymer surfaces. It is seen from the table that the area per molecule of sodium lauryl sulfate at the various interfaces increases with the mole fraction N_2 of monomer in water, as observed by others.^{9,10}

It is well known that water solubility of organic liquids (a rough measure of polarity as mentioned earlier) is inversely related to the respective interfacial tensions.^{1,2} Figure 3 shows that such an inverse relationship between interfacial tension and solubility is obeyed by the various monomer-water interfaces

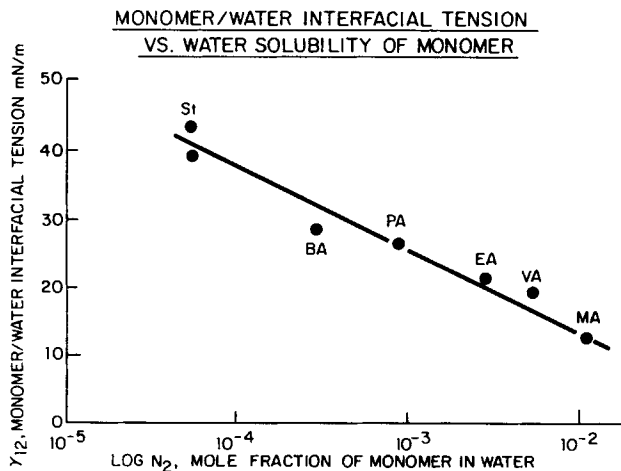


Fig. 3. Plot of measured monomer-water interfacial tension (γ_{12}) against logarithm of monomer solubility in water (N_2).

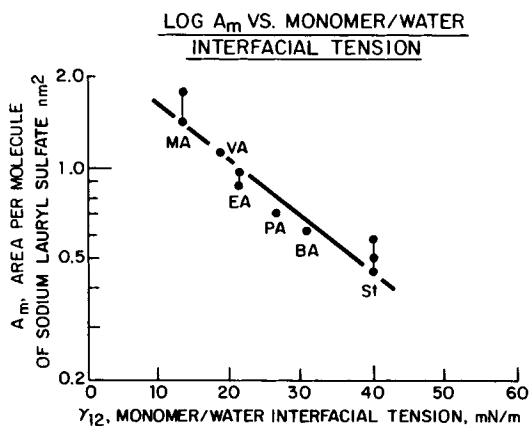


Fig. 4. Plot of logarithm of area per molecule of sodium lauryl sulfate (A_m) against monomer-water interfacial tension (γ_{12}).

studied. This leads to the observation that the area per molecule of sodium lauryl sulfate decreases with increase in γ_{12} of the water-monomer interface as seen in Figure 4. This suggests that the interfacial tension of a monomer-water interface is a good indication of surfactant adsorption on the corresponding polymer-water interface as given by eq. (2), even though there are obvious differences in the nature of the monomer-water and polymer-water interfaces, as mentioned earlier.

Let us turn our attention to the interfacial tension and polarity data on various polymers which are shown in Table II. In Figure 5, A_m values are plotted against γ_{12} of the various polymer-water interfaces on a semilog scale. It is seen that the adsorption of surfactant decreases with decrease in interfacial tension of the polymer-water interface. The data on hand seem to substantiate the validity of our assumption that the surfactant adsorption from aqueous solution is related to the interfacial tension of the polymer-water interface, as given in eq. (2). In Figure 6, A_m values are plotted against the polarity of the polymer surfaces on a semilog scale. The plot shows that the data obey eq. (9) quite well, considering the various approximations used in the analysis and that the adsorption data were obtained from various sources with apparent differences in the purity of sodium lauryl sulfate and latex preparation.

Thus, it appears we are able to relate satisfactorily the observed differences in the area per molecule of sodium lauryl sulfate at various polymer surfaces to the polarity of the polymer surface and the polymer-water interfacial tension.

TABLE II
Polymer-Water Interfacial Tension and Polarity of Various Polymers at 20°C^a

Polymer	Surface tension γ_2	Interfacial tension γ_{12}	Dispersion contribution γ_2^d	Polar contribution γ_2^P	Polarity $X^P = \gamma_2^P/\gamma_2$
Polystyrene	40.7	32.7	32.5	8.2	0.20
Poly(butyl methacrylate)	31.2	36.7	25.7	5.5	0.18
Poly(methyl methacrylate)	41.1	26.0	29.7	11.4	0.28
Poly(vinyl acetate)	36.5	23.5	24.2	12.3	0.34
Poly(vinyl chloride)	41.9	37.8	35.6	6.3	0.15

^a Calculated from reference 16; all surface tension values are in mN/m.

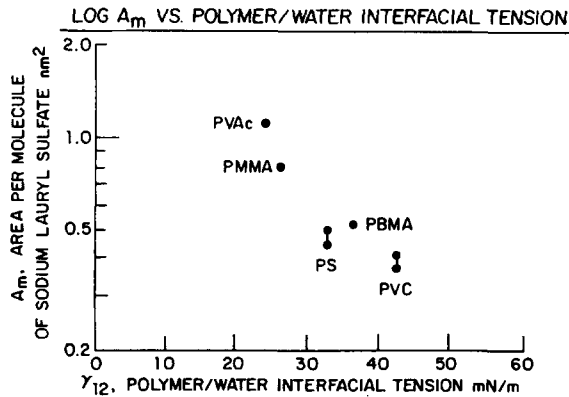


Fig. 5. Plot of $\log A_m$ against calculated polymer-water interfacial tension (γ_{12}).

The A_m values for a given surfactant depend strongly on the nature of the polymer surface. This clearly points out some limitations in using a simple hydrocarbon-water interface such as heptane-water, as has been attempted,²¹ as a model for polymer-water interface of varying polarity. The analysis also points out problems in using the soap titration method to determine the particle size of latexes of diverse polarities. Soap titration method of particle size determination can give satisfactory results only if the actual area occupied by the soap molecules in the saturated adsorption layer at the given surface is known. However, such information is not well known for soap molecules commonly used in soap titration. For instance, A_m values of 0.20 to 0.47 nm² for oleate ions^{19,27} and 0.41 to 0.49 nm² for laureate ions²⁸ have been used in the particle size determination of latexes by the soap titration method.

It may be appropriate to mention here the results of Maron,¹⁹ which showed that the molecular areas of a homologous series of soaps in which the hydrocarbon chain varied from C₁₂ to C₁₇ decreased regularly from 0.41 nm² to 0.23 nm² as the length of the hydrocarbon chain increased. This result can readily be explained by the increase in the energy of adsorption of the soap molecules due to increased hydrophobic interactions as the chain length of hydrocarbon increases. Using an adsorption isotherm similar to eq. (1), one can readily calculate the energy of adsorption of a —CH₂— group to be -2.1 kJ/mole (-500 cal/mole)

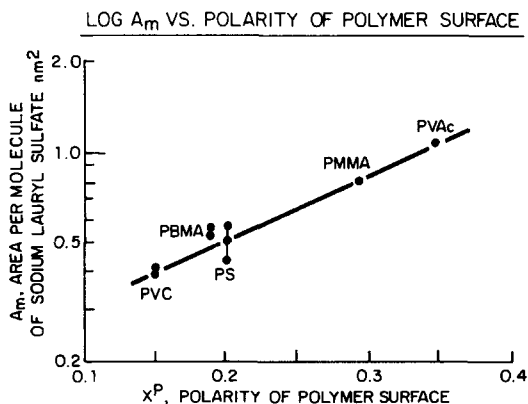


Fig. 6. Plot of $\log A_m$ against calculated polymer polarity (X^P).

from the soap titration data of Maron on C_{12} – C_{17} soaps.¹⁹ The value of -2.1 kJ/mole determined for the transfer of a $-\text{CH}_2-$ group from an aqueous medium to a particle surface agrees quite well with the value of -2.5 kJ/mole (-600 cal/mole) determined from electrophoretic mobilities and adsorption data calculated using a Stern–Langmuir adsorption isotherm in the systems composed of latex and C_8 – C_{16} aliphatic soaps by Sieglaff and Mazur²⁹ and other surfactant adsorption studies on solid surfaces.³⁰

The present analysis accounts for one of the factors controlling the low aggregate stability during the preparation of polar emulsion polymers so commonly encountered in practice. The increase in the area per molecule of surfactant on the more polar polymers results in diminished stability against flocculation of primary particles due to decreased surfactant adsorption under saturation condition. It is therefore reasonable to expect that the stabilizing action of a surfactant will diminish with increase in the polarity of the interface. However, the increased polarity of the monomer may favor self-stabilization due to the orientation of the polar groups of the polymer at the water interface.⁷

The above analysis may have some utility in characterizing the nature of polymer surfaces, especially those composed of monomers of widely diverse polarities. For instance, the area per molecule of sodium lauryl sulfate on a 90:10 poly(vinyl chloride/vinyl acetate) latex has been determined²³ to be 0.66 to 0.68 nm^2 . It is seen from Table I that A_m values for sodium lauryl sulfate on homopolymer PVC and PVAc surfaces are about 0.40 nm^2 and 1.1 nm^2 , respectively. Assuming that the surface composition of the PVC/PVAc copolymer is the same as the bulk and that the polarity of the mixed surface is additive based on mole fractions, then one can readily calculate the polarity of the surface corresponding to the 90/10 composition to be 0.17 from the polarity data in Table II. A_m corresponding to a surface of 0.17 polarity is seen to be about 0.50 nm^2 from Figure 6. However, the A_m value on the 90/10 copolymer has been determined to be about 0.66 to 0.68 nm^2 . This clearly suggests that the surface of the copolymer is richer in the more polar poly(vinyl acetate) segments compared to the bulk. Using Figure 6 and the measured A_m value of 0.66 to 0.68 nm^2 , the copolymer surface polarity is estimated to be about 0.25 , corresponding to a composition of 50/50 (PVC/PVAc). Similar preferential enriching of the polymer surface by the more polar acrylonitrile monomer has been observed in some preliminary work on styrene/acrylonitrile copolymer systems.²⁴

Information on the polarity of polymer surfaces, or more precisely on the polar and dispersion contributions to the surface energy of the polymer surfaces, should be of great value in understanding the various practical aspects of polymer surfaces such as wetting, adhesion, etc.

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