

Study of the Surface Thermal Coefficient, b_{TP} : Evidence of Phase Transition at Low Surfactant Concentrations. Example of Solutions of Triton X100 in Water and in Water–Ethylammonium Nitrate Media

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The surface tension–concentration (γ – c) isotherms of soluble surfactants, unlike those of insoluble surfactants, are not sufficient to show whether gas–liquid-phase transitions occur. However, thermodynamic parameters (such as thermal coefficients) can be used to prove the existence of such transitions. The surface thermal coefficient corresponding to $(\partial\gamma/\partial \ln T)_{A,P}$ was described by Defay and named b_{TP} . We determined this surface coefficient for a nonionic surfactant, Triton X100 (TX100), both in water and in a salt solution. We used the Wilhelmy plate method to measure the surface tension of TX100 at between 279 and 303 K. The $b_{TP} = f(\log [TX100])$ plot showed a clear peak, which could be attributed to a surface gas–liquid transition. Temperature and salt concentrations did not affect this transition.

Introduction

The Gibbs equation is usually used to study the physico-chemical surface properties of surfactant solutions. This equation links variations in surface tension with the amphiphile concentration of the solution. It can be used to determine the relative surface excess of the solute according to the Gibbs plane and to deduce the “area of the polar head” value of the surfactant. The main drawback of this approach is that it masks the effect of the solvent in surface tension variations as the solvent is always used as the reference.

Defay¹ showed that the relationships between surface tension and solution composition can be formalized in other ways. We have shown that cross-differentiation properties allow the solvent and the solute to modify the surface tension without having to divide the thermodynamic magnitudes into surface and adjacent phases.² This property has been used to interpret the changes in the wetting properties of drops of surfactant solution on solid hydrophilic and hydrophobic surfaces.

We assessed the use of these relationships for the study of liquid–vapor interfaces in aqueous solutions of nonionic surfactants. A molecular dynamics model recently showed that the behavior of a soluble surfactant at a surface is related to the behavior of insoluble amphiphiles. Thus, adsorbed films of soluble surfactants may also shift from the gaseous to the expanded state.^{3,4}

We showed that thermodynamic relationships can be used to formalize such changes and to determine the magnitudes required for their characterization. To illustrate our theoretical approach, we measured the surface tension of a solution of Triton X100, at various temperatures, in water and in salt media containing ethylammonium nitrate. Ethylammonium nitrate is an ionic liquid that is miscible with water in all proportions at room temperature.^{5–7}

Experimental Procedures

1. Chemicals. Triton X100 (TX100) was purchased from Aldrich (99%) and used without further purification. Its critical micelle concentration (cmc) was 2.2×10^{-4} mol L⁻¹ at 25 °C in pure water. Distilled water was filtered by an Elga UHQ II system ($\kappa = 18$ M Ω).

Ethylammonium nitrate (EAN) was prepared by adding nitric acid (69%, Prolabo, RP) to a cooled solution of ethylamine (70 wt % in water, Aldrich).⁶ Water was removed first with a rotary evaporator and then by freeze-drying.

2. Techniques. Surface tension curves were constructed by using a tensiometer (Krüss K10T) and the Wilhelmy plate method; the probe was a 20 mm wide standard platinum plate. The temperature of the solutions was maintained constant (± 0.1 °C) in a circulating water bath. A tensiometer was used to take repeated measurements of the surface tension at a range of temperatures. The thermostat chamber was filled with a solution at surfactant molality m , and maintained at about 6 °C. The platinum plate was put into the solution, and the first measurement was taken. The temperature was increased by about 1 °C every 2 min. We ensured that the surface tension measurements were reproducible to ± 0.1 mN m⁻¹. The surface tension was measured at between 279 and 303 K.

Thermodynamics of Surface Tension

Let us consider a liquid system, at equilibrium, in contact with atmospheric air, containing n_1 moles of solvent 1 and n_2 moles of an amphiphilic solute 2.

Let us assume that the masses of 1 and 2 in the vapor phase are negligible in comparison to the quantities in the solution and that the interface is planar.

If interfacial energy is considered to be a component of the internal energy, we can write

$$dU = TdS - PdV + \sum \mu_i dn_i + \gamma dA \quad (1)$$

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and

$$U = TS - PV + \sum \mu_i n_i + \gamma A \quad (1')$$

where γ is the interfacial tension associated with area A .

The Gibbs free energy, G , is then written as

$$G = \sum \mu_i n_i + \gamma A \quad (2)$$

whose derivative is

$$dG = VdP - SdT + \sum \mu_i dn_i + \gamma dA \quad (3)$$

It is noteworthy that surface energy is taken into account in the expression of the internal energy, i.e., a magnitude associated with the extensivity of the second dimension because the extensivity of the third dimension, represented by the volume, is not sufficient to describe the behavior of the system. In this approach, the area is introduced as the variable of extensivity of the second dimension and is not necessarily associated with a geometrically defined surface.

In the case of the previous system, we can write

$$dG = VdP - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \gamma dA \quad (4)$$

If the surface variables and the magnitudes characteristic of the amphiphilic surfactant are favored, the cross-differentiation properties allow us to write

$$\left(\frac{\partial \gamma}{\partial \mu_2} \right)_{T,P,n_1,A} = - \left(\frac{\partial n_2}{\partial A} \right)_{T,P,n_1,\mu_2} \quad (5)$$

Thus, the observation that compound 2 has a surface active effect (variation of γ with μ_2), implies that the solution of the right-hand term is different from zero. If this is the case, at controlled T and P , the variation of the area value involves a change in the system content for a constant number of moles of solvent and at fixed surfactant chemical potential. This transformation can only occur if there is a change of the quantity of compound 2 in the system. This implies that a certain number of moles of solute 2 (n_2^σ) is associated with the area variations. In the same way, n_1^σ moles of solvent 1 will be associated with the area. Thus, n_1^σ and n_2^σ define the "surface content" of the system.

The mass assessments can be written as

$$n_1 = n_1^\sigma + n_1^b \quad (6)$$

$$n_2 = n_2^\sigma + n_2^b \quad (6')$$

Thus, n_1^b and n_2^b are the numbers of moles of 1 and 2 associated with the extensivity of the third dimension (volume). These numbers define the "bulk content" of the system.

The right-hand term of eq 5 can be clarified by introducing the molality of solute 2, as defined from the bulk content

$$m = \frac{n_2^b}{n_1^b M_1} \quad (7)$$

The value of the molality (m) fixes the chemical potential of 2, described in the infinitely dilute solute model. In practice, as the surface content is negligible in comparison to the bulk content, the value of this molality can be calculated by

considering the total numbers of moles (n_1 and n_2). The total quantity of solute 2 is linked to the surface contents by

$$n_2 = n_2^\sigma + m(n_1 - n_1^\sigma)M_1 \quad (8)$$

The right-hand term of eq 5, can therefore be written as

$$\left(\frac{\partial n_2}{\partial A} \right)_{T,P,n_1,\mu_2} = \left(\frac{\partial n_2^\sigma}{\partial A} \right)_{T,P,n_1,\mu_2} - mM_1 \left(\frac{\partial n_1^\sigma}{\partial A} \right)_{T,P,n_1,\mu_2} \quad (9)$$

Thus, a rule for the variation in surface tension according to the chemical potential of 2 can be deduced. This relationship simultaneously involves the number of moles of the solute and of the solvent linked to the area:

$$\left(\frac{\partial \gamma}{\partial \mu_2} \right)_{T,P,n_1,A} = - \left(\frac{\partial n_2^\sigma}{\partial A} \right)_{T,P,n_1,\mu_2} + mM_1 \left(\frac{\partial n_1^\sigma}{\partial A} \right)_{T,P,n_1,\mu_2} \quad (10)$$

This means that, for a given system, an area modification, when the chemical potential of the solute is constant, involves a change in the content of the solution, modifying the two components. Formally, eq 10 can be written as

$$\left(\frac{\partial \gamma}{\partial \mu_2} \right)_{T,P,n_1,A} = -D_{2(A)} + mM_1 D_{1(A)} \quad (10')$$

The right-hand term of this equation is thus identical to Gibbs relative surface excess, Γ_2 .

It is important to note two things about the partial derivatives, $D_{1(A)}$ and $D_{2(A)}$. First, if n_1^σ and n_2^σ are supposed to be associated to the area, A , these magnitudes increase with the area, so, $D_{1(A)}$ and $D_{2(A)}$ must be positive. Second, the partial derivatives, $D_{1(A)}$ and $D_{2(A)}$ are equal to n_1^σ/A and n_2^σ/A , respectively, when the area is a homogeneous function of the first order of n_1^σ and n_2^σ . This property of the area cannot be established as a general rule. For this reason, we will keep the significance of the partial derivative to the terms $D_{1(A)}$ and $D_{2(A)}$. Equation 10 can be used to determine the thermodynamic results of variations to the surface tension according to the content of the solution.

When $(\partial \gamma / \partial \mu_2)_{T,P,n_1,A} = 0$, then $D_{2(A)} / D_{1(A)} = mM_1$ which can be also written as $\delta n_2^\sigma / \delta n_1^\sigma = n_2^b / n_1^b$.

The surface composition varies with the bulk composition. Accordingly, if γ decreases as the molality of 2 increases

$$\frac{D_{2(A)}}{D_{1(A)}} > mM_1 \quad (11)$$

Thus

$$\frac{\delta n_2^\sigma}{\delta n_1^\sigma} > \frac{n_2^b}{n_1^b} \quad (12)$$

The surface content is more enriched with component 2 than the bulk content. This behavior is observed with amphiphilic compounds.

Thus, in the studied case, enriching the solution with 2 enriches the surface content with 2, thus decreasing the surface content of 1, which corresponds to an increase in $D_{2(A)}$ and a decrease in $D_{1(A)}$. The opposite situation occurs when the molality, m , increases with the surface tension (e.g., with mineral salts).

Thus, eq 10 enables us to formalize the contributions of the solute and the solvent to the variations in surface tension that

occur as the content of the solution changes. However, we still need to determine how a possible “surface transition” can be expressed. Numerous authors^{8,9} have reported behavioral changes, appearing plateaus or cusps, in the surface tension isotherms for low concentrations of some surfactants. More recently, an ellipsometry study demonstrated the existence of a 2D first-order liquid–gas-phase transition at the surface of decanol solutions.¹⁰ Other authors used a calculation model to show that, for soluble surfactants as for insoluble surfactants, a gas/liquid expanded transition exists in some conditions.^{3,4,11}

With our approach, the only way of determining whether a surface transition exists is to use a thermodynamic method. The difficulty is to show sudden changes in variations of the system content with the area, for a given surfactant molality in the range of low molalities.

For high molalities, this type of behavior is observed at the critical micelle concentration, cmc. Equation 3 shows that, beyond the cmc, if the chemical potential is independent of surfactant molality (pseudophase model), a change in the system area does not necessarily modify the solution content. Thus, at the cmc, there is a sudden variation in the system response. This phenomenon may be explained if $D_{1(A)}$ and $D_{2(A)}$ are both equal to zero at the cmc. It is not easy to understand the spatial organization of this condition.

In the same way, we can assume that this type of phenomenon could occur in the presence of low solute concentrations and thus could cancel or strongly decrease the positive component of the surface tension variation, $(D_{1(A)})$, while keeping a finite value for $D_{2(A)}$. This “transition” phenomenon should be translated into a change in slope at the critical concentration of transition (cct) on the $\gamma = f(\ln m)$ curve, which should be in agreement with the described behaviors of some surfactants.^{8,9}

To understand the molecular significance of this property, it is possible that the change from a gaseous surface state, with randomly distributed solvent and solute molecules, to a liquid surface state, in which the solute molecules interact with each other, is translated into a partial or total release of solvent molecules from the surface. Therefore, the application of a surface constraint to this kind of system should lead to alter the amount of solute. If $D_{1(A)}$ is considered to be equal to zero, beyond the cct, eq 10' can be simplified as follows:

$$\left(\frac{\partial \gamma}{\partial \mu_2}\right)_{T,P,n_1,A} = -D_{2(A)} \quad (13)$$

Thus, $D_{2(A)}$ becomes identical to the Gibbs relative surface excess.

With this approach, the behavior of the surfactant in solution can be characterized by two critical concentrations, corresponding to the cct when $D_{1(A)} = 0$ and the cmc when $D_{1(A)} = D_{2(A)} = 0$.

It is difficult to obtain unequivocal experimental evidence for this phenomenon because the surface tension variations for diluted surfactant solutions are very weak and it is difficult to prove the existence of a cusp (a change in slope) on the adsorption isotherm. To determine the validity of this assumption, it is necessary to include other thermodynamic variables, more suited to the description of possible changes in state. Thermal coefficients are usually suitable for this kind of description because they can show discontinuities that occur at the time of phase change.

Thus, Defay (12) introduced the notion of the heat of the reversible extension of the surface at constant T and P , b_{TP} ,

defined as the reversible heat that explicitly contains the area variable:

$$\delta Q_{\text{rev}} = C_p dT + h dP + b_{TP} dA \quad (14)$$

where C_p , h , and b_{TP} are thermal coefficients.

If this equation is taken into account for the expression of state functions, the following equation is obtained for the enthalpy:

$$dH = C_p dT + (h + V) dP + (b_{TP} + \gamma) dA \quad (15)$$

and the following equation is obtained for the entropy:

$$dS = \frac{C_p}{T} dT + \frac{h}{T} dP + \frac{b_{TP}}{T} dA \quad (16)$$

The comparison of the cross-differentiations of eqs 15 and 16 leads to

$$T\left(\frac{\partial \gamma}{\partial T}\right)_{A,P} = -b_{TP} = -T\left(\frac{\partial S}{\partial A}\right)_{T,P} = -TS'_A \quad (17)$$

The change in surface tension with the temperature can be used to calculate the “surface entropy” of the system, S'_A .

Equation 17 can also be written as

$$b_{TP} = -\left(\frac{\partial \gamma}{\partial \ln T}\right)_{A,P} \quad (18)$$

b_{TP} is obtained from the variations in interfacial tension with the logarithm of the temperature for a given solute molality. For the different domains defined by the two critical concentrations, the expression of the variation of b_{TP} with the chemical potential of the solute is given by the following equation, which is derived from eq 10', at constant P , n_1 , and A :

$$\frac{d^2 \gamma}{d\mu_2 dT} = -\frac{dS'_A}{d\mu_2} = -\frac{1}{T} \frac{db_{TP}}{d\mu_2} = -\frac{dD_2}{dT} + mM_1 \frac{dD_1}{dT} \quad (19)$$

Thus

$$\frac{db_{TP}}{d\mu_2} = T\left(\frac{dD_2}{dT} - mM_1 \frac{dD_1}{dT}\right) \quad (20')$$

From one domain to the other, the function $b_{TP} = f(\mu_2)$ may become discontinuous.

We have illustrated these properties with a system constituted of water and Triton X100 (TX100), in the presence of an electrolyte, ethylammonium nitrate (EAN).

Illustrations

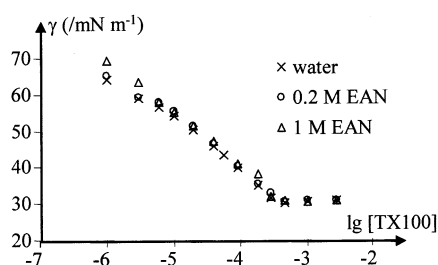
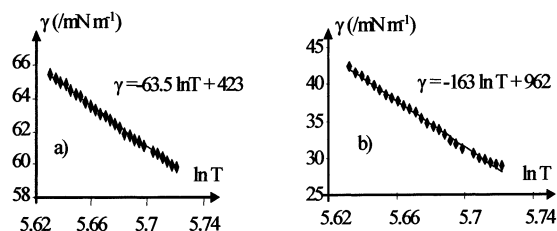
1. Surface Tensions of TX100. The surface tensions of TX100 solutions were plotted against surfactant concentrations for water and several mixtures containing various quantities of EAN, at 298 K (Figure 1). The value of surface tension was accurate to within 0.1 mN m^{-1} .

The surface tension decreased when the surfactant concentration increased. When the micellization occurred, the surface tension was minimal; above the cmc, a plateau was observed. The cmc of TX100 did not vary in the presence of the electrolyte. Although the surfactant was used as received without further purification, these curves (Figure 1) show that the quantity of impurities was sufficiently weak and did not disturb the surface tensions measurements.

TABLE 1: Changes in the Thermal Coefficient, b_{TP} (in mJ m^{-2}), and Surface Entropy (in $\text{N m}^{-1} \text{K}^{-1}$) vs TX100 Molality, m , in Water and in Water–EAN Mixtures (Expressed in mol kg^{-1})

$\log \{m\}$	water		0.2 M EAN		0.5 M EAN		1 M EAN		2 M EAN	
	b_{TP}	$S^s/(10^{-4})$	b_{TP}	$S^s/(10^{-4})$	b_{TP}	$S^s/(10^{-4})$	b_{TP}	$S^s/(10^{-4})$	b_{TP}	$S^s/(10^{-4})$
−7			60	2.05						
−6.7	69	2.35							60	2.05
−6.52	91	3.10	115	3.92	113	3.85	75	2.56	80	2.73
−6.4	107	3.65	121	4.13	135	4.61	130	4.43	83	2.83
−6.35	102	3.48								
−6.3	65	2.22	158	5.39	141	4.81	86	2.93	77	2.63
−6.22			127	4.33	130	4.43				
−6.16			114	3.89						
−6	63	2.15	110	3.75	83	2.83	77	2.63	65	2.22
−5.69	63	2.15	71	2.42						
−5.52							67	2.29		
−5.4	72	2.46	86	2.93	70	2.39			59	2.01
−5	84	2.87	93	3.17	91	3.10	71	2.42	68	2.32
−4.71	103	3.51					87	2.97	87	2.97
−4.41	126	4.30	122	4.16	126	4.30	102	3.48	102	3.48
−4.13							121	4.13	122	4.16
−4.04	158	5.39	133	4.54	137	4.67	120	4.09	127	4.33
−3.87	163	5.56	133	4.54	130	4.43	nl		nl	
−3.56	nl ^a		nl				nl		nl	
−3.2	nl									
−3	15	0.51	11	0.38	10	0.34	10	0.34	12	0.41
−2	29	0.99	28	0.96	27	0.92	28	0.96		
−1.5	30	1.02	28	0.96					27	0.92

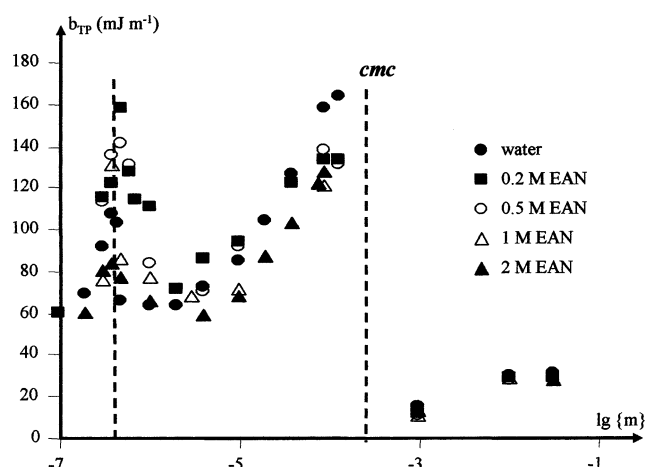
^a “nl” is a non-linear variation of γ vs T or $\ln T$.

**Figure 1.** Changes in the surface tension with surfactant concentrations of TX100 (in units of molality) for different mixtures of water and EAN at 298 K.**Figure 2.** Graphical representations of γ vs $\ln T$ for $\log[\text{TX100}] = -5.7$ (a) and $\log[\text{TX100}] = -3.87$ (b), in aqueous solution. (a) $b_{TP} = 63.5 \text{ mJ m}^{-2}$; (b) $b_{TP} = 163 \text{ mJ m}^{-2}$.

It is clearly not easy to identify possible cusps or plateaus associated with transitions on these curves. Thus, we studied the variations of surface tension with the temperature to determine surface entropies and surface thermal coefficients, b_{TP} .

2. Changes in b_{TP} with the TX100 Concentration in Water and in Water–EAN Solutions. At the temperatures used, the surface tension varied linearly with temperature.^{13–16} The thermal surface coefficient, b_{TP} , was determined graphically; two examples are given in Figure 2.

These examples show that γ varied linearly with $\ln T$. This behavior was observed for nearly all surfactant molalities and for all electrolyte concentrations. The exceptions will be discussed later. Table 1 shows how b_{TP} and surface entropy

**Figure 3.** Variations of the thermal coefficient b_{TP} with the TX100 molality in water and various salt solutions.

change with respect with the molality of TX100, in water and in salt media. The error on b_{TP} was about 5%.

In some experiments, surface tension did not vary linearly with $\ln T$ (Table 1). We also measured how b_{TP} varied with the logarithm of TX100 molality in water and salt solutions (Figure 3).

Two kinks were visible on the curves (Figure 3). The position of these kinks was not modified by the concentration of the salt. The first kink occurred at a molality of about $4 \times 10^{-7} \text{ mol kg}^{-1}$. The surface thermal coefficient seemed to be maximal at this value. This kind of behavior has already been described by Glinski et al.¹⁴ with normal short-chain alcohols. This could be explained by a surface gas/liquid expanded transition at the maximum point, followed by the release of a large number of surface solvent molecules.

The second kink occurred at the cmc of TX100, i.e., $2.2 \times 10^{-4} \text{ mol kg}^{-1}$. As this critical concentration was approached, γ no longer varied linearly with temperature or $\ln T$. We did not study the behavior of the system in this zone in further detail,

because it has already been described in detail in the literature.^{17–19}

Conclusion

The thermal coefficient described by Defay seemed to be a useful tool for showing whether surface transitions occur in soluble surfactants. Classical thermodynamic relationships link this thermal coefficient to the isotherm adsorption of the surfactant at the liquid–vapor interface. In these conditions, the effects of interfacial surfactant molecules and solvent molecules, present at this interface, appeared simultaneously.

However, thermodynamics could not be used to determine the nature of surface aggregation processes. One of the characteristics of the relationships is that they concern the behavior of the system as a whole and not only of the surface of the system.

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