STRUCTURAL EFFECTS IN AQUEOUS SOLUTIONS: A THERMODYNAMIC APPROACH

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Abstract – The thermodynamic properties of aqueous solutions have been studied systematically over the years in our laboratory to gain insight on solute–solvent and solute–solute interactions, in particular those related to structural effects. Recently, our efforts have been largely concentrated on complex systems which show microheterogeneity beyond a certain concentration, e.g. micellar systems, some organic–water mixtures, mixed micelles and microemulsions. The concentration dependence of the thermodynamic properties of surfactants can be accounted for quantitatively with a mass-action model. The approach is similar to that of the two-state water model often used to understand the thermodynamic properties of liquid water. From the analysis of the data, it is possible to extract quantitatively the thermodynamic functions of micellization and the aggregation number. Properties of alcohol–water and amine–water mixtures, which also exist as microphases at high concentration, can be interpreted in a similar way. The same model can be extended to ternary systems such as electrolyte–surfactant–water in a way similar to the effect of a solute on the two-state equilibrium of water. It is also possible to consider cases where the solute not only shifts the equilibrium between monomers and micelles but also forms mixed micelles, e.g. mixtures of surfactants and alcohols. Finally, it is possible to account, at least qualitatively, for the thermodynamic properties of microemulsions which are mixtures of water, hydrocarbon, surfactant and alcohol.

INTRODUCTION

Aqueous solutions have been systematically studied over the years in our laboratory primarily with the aim of obtaining information on solute–solvent and solute–solute interactions through thermodynamic properties (1). These interactions are particularly interesting in view of the high degree of structure in aqueous solutions, both in the solvent itself and in the aggregates that can exist as a result of the structure of water. Water is highly associated through hydrogen bonding and various solutes can increase or decrease the distribution of hydrogen bonds (see Fig. 1). Of particular importance are the hydrophobic solutes around which the water molecules tend to organize in a way similar to clathrate hydrates. These time-average complexes have a strong tendency to cluster leading to the
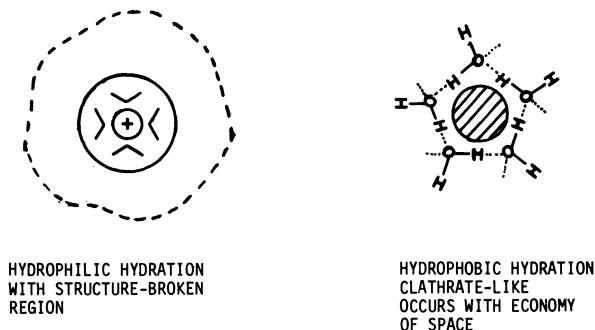

HYDROPHILIC HYDRATION
WITH STRUCTURE-BROKEN
REGION

HYDROPHOBIC HYDRATION
CLATHRATE-LIKE
OCCURS WITH ECONOMY
OF SPACE

Fig. 1. Models for solute–solvent interactions in water.

well-known hydrophobic bonds and to micellization (see Fig. 2). In recent years, we have been extending our studies to more complex systems which show microheterogeneity such as mixed micelles, some organic–water mixtures and microemulsions. The thermodynamics of these systems can be handled with models which are often similar to two-state models for liquid water and for aqueous solutions.

COSPHERE OVERLAP   HYDROPHOBIC BONDING

MICELLE   MIXED MICELLE   MICROEMULSION
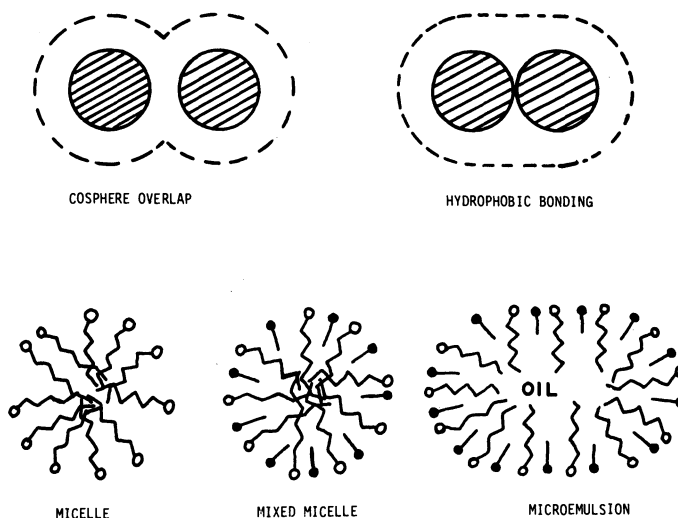
Fig. 2. Models for various types of solute-solute interactions between hydrophobic solutes.

TWO-STATE WATER MODEL AND SOLUTE-SOLVENT INTERACTIONS

A good starting point for the study of structural effects in water is the two-state model for liquid water. This model has been used by many authors and in particular by Benson (2) and by Hvidt (3). Water molecules are assumed to exist in two states: a hydrogen-bonded state, $H_2O(b)$ and a denser more normal unbonded or free state, $H_2O(f)$. If x represents the fraction of molecule in the free state, the equilibrium constant is given by

$$K = x/(1-x) \tag{1}$$

The sign of the principal thermodynamic changes of this equilibrium reaction is easily deduced from the melting of ice: $\Delta S^o > 0$, $\Delta H^o > 0$, $\Delta V^o < 0$. The other thermodynamic functions are   subtler   since account must be taken of the shift in equilibrium during a unit change in temperature or pressure. To illustrate this let us consider the expression for the total enthalpy of the system per mole of water neglecting interactions between the species.

$$H = \Sigma \ x_i H^o_i$$
$$= xH^o(f) + (1-x) \ H^o(b) \tag{2}$$

Differentiating with respect to temperature at constant pressure, the molar heat capacity of water is obtained as

$$C_p = xC^o_p(f) + (1-x) \ C^o_p(b) + \Delta H^o(\partial x/\partial T)_P \tag{3}$$

From Eq (1)

$$(\partial x/\partial T)_P = \frac{K}{(1+K)^2} \frac{\partial \ln K}{\partial T} = \frac{K \ \Delta H^o}{(1+K)^2 RT^2} \tag{4}$$

Substituting in Eq (3)

$$C_p = xC^o_p(f) + (1-x) \ C^o_p(b) + \frac{K}{(1+K)^2} \frac{(\Delta H^o)^2}{RT^2} \tag{5}$$

Starting from volumes, the following equations can also be derived

$$\left(\frac{\partial V}{\partial T}\right)_P = x \ \frac{\partial V^o(f)}{\partial T} + (1-x) \ \frac{\partial V^o(b)}{\partial T} + \frac{K}{(1+K)^2} \frac{\Delta H^o \Delta V^o}{RT^2} \tag{6}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = x \ \frac{\partial V^o(f)}{\partial P} + (1-x) \ \frac{\partial V^o(b)}{\partial P} - \frac{K}{(1+K)^2} \frac{(\Delta V^o)^2}{RT} \tag{7}$$

The first two terms of Eq (5) to Eq (7) are the static contributions to heat capacities, expansibilities and compressibilities. The last terms are the relaxational or equilibrium displacement contributions. These latter terms are considered responsible for the high heat capacity, low expansibility and high compressibility of liquid water.

The structural contribution to hydration is often discussed in terms of a displacement in the above equilibrium in the vicinity of a solute. For the basic thermodynamic functions H, S and V, we can write for the total function of a solution containing 1 kg of water

$$F = mF_2(in) + n_1F_1^O(f) + (55.51 - n_1) \ F_1^O(b) + \text{interaction terms} \qquad (8)$$

where m is the molality of solute 2, $F_2(in)$ is the intrinsic value, i.e. the molar value for the pure solute in the liquid state, and n_1 is the number of moles of free water molecules. Differentiating with respect to m gives directly the corresponding standard partial molar quantity of the solute if m is sufficiently low to neglect all solute-solute interactions,

$$\bar{F}_2^O = F_2(in) + \Delta F_1^O(\partial n_1/\partial m)_{T,P} + \text{solute-solvent interaction terms} \qquad (9)$$

From the equilibrium constant, $K = n_1/(55.51 - n_1)$,

$$\partial n_1/\partial m = \frac{55.51}{(1+K)^2} \frac{\partial K}{\partial m} \qquad (10)$$

and

$$\bar{F}_2^O = F_2(in) + \frac{55.51 \ \Delta F_1^O}{(1+K)^2} \frac{\partial K}{\partial m} + \text{solute-solvent interaction terms} \qquad (11)$$

For a structure breaker $\partial K/\partial m > 0$ and for a structure maker $\partial K/\partial m < 0$. Since the signs of ΔH_1^O, ΔS_1^O and ΔV_1^O are well known from the melting of ice, it is easy to predict the sign of the structural hydration on these thermodynamic functions. The situation is more complex with free energies since $\Delta G_1^O = - RTlnK$ and the magnitude of K is not known *à priori*. With these functions the interaction terms are usually large and it is difficult to evaluate the importance of the structural effects.

One way of largely eliminating the intrinsic function and interaction terms is to measure transfer functions from one solvent to another. Of particular interest are the transfer function from water to heavy water or from water to urea-water systems since structural effects are usually considered larger in D_2O and smaller in urea-water mixtures while coulombic interactions are nearly the same. These transfer functions generally have the sign predicted by the simple model. As seen for example from Fig. 3, the enthalpies of transfer from propylene carbonate to water are more positive with structure breakers and more negative with structure makers than the transfers to non-aqueous solvents.
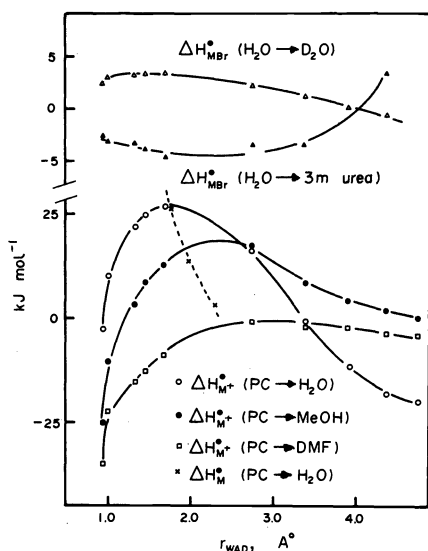

Fig. 3. Enthalpies of transfer of 1:1 electrolytes at 25°C from propylene carbonate to various solvents ploted against the ionic radii of Waddington. From ref. 1 with permission.

There are notable exceptions to the success of this simple two-state model. With heat capacities, expansibilities and compressibilities, an equilibrium displacement contribution

must be added. For example, for heat capacities

$$\bar{C}_{P,2}^{o} = C_p(in) + \frac{55.51}{(1+K)^2} \Delta C_{P,1}^{o} + \frac{55.51 (\Delta H_1^o)^2}{(1+K)^3 RT^2} (1-K) \frac{\partial K}{\partial m} + \text{interaction terms (12)}$$

As noted by Ben-Naim (4), it is not possible to predict the sign of the equilibrium displacement term since it is not known *à priori* if K is larger or smaller than unity. To be consistent with the experimental data, it is necessary to postulate that K > 1 (see Fig. 4). A second difficulty is found for the volumetric properties of hydrophobic solutes. In these cases $V_2(in)$ should be the molar volume of the pure liquid V_2^o. For most organic liquids $\bar{V}_2^o < V_2^o$ while the structural contribution would predict the opposite sign. The explanation comes from the cavity effect. Hydrophobic hydration occurs with an economy of space since the hydrophobic solute tends to occupy natural cavities in the water network as in the case of clathrate hydrates. This cavity effect supercedes any increase in volume due to the structure-making effect. The sign of $\bar{E}_2^o$ and $\bar{K}_2^o$ of hydrophobic solutes is consistent with a decrease in magnitude of the cavity effect as the temperature or pressure increases. This is well illustrated in Fig. 5 where $\bar{K}_2^o$ of tetraalkylammonium halides are negative in water and positive in acetonitrile.
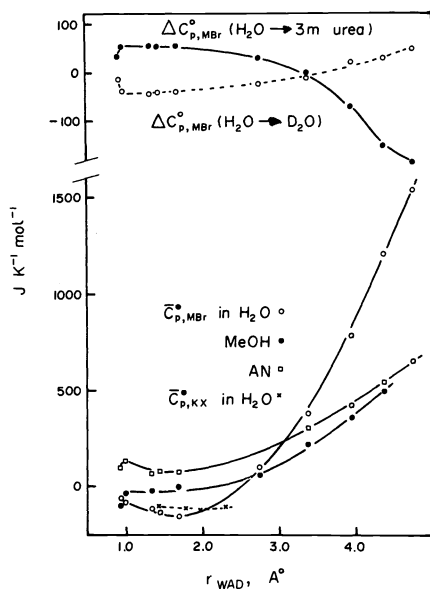

Fig. 4. Standard partial molar heat capacities in water, acetonitrile and methanol and heat capacities of transfer of 1:1 electrolytes at 25°C. From ref. 1 with permission.
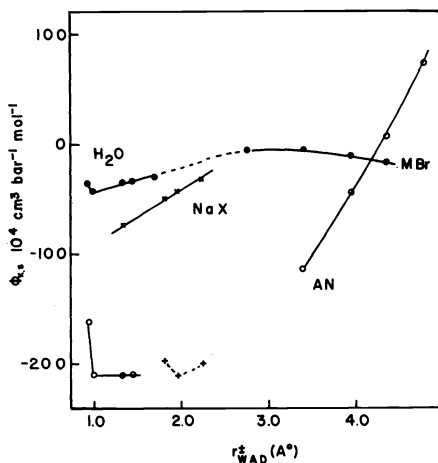

Fig. 5. Standard partial molar isentropic compressibilities of 1:1 electrolytes in water and acetonitrile at 25°C. From ref. 5 with permission.

SOLUTE-SOLUTE INTERACTIONS

The above relations were all derived for standard functions, i.e. for cases where solute-solute interactions could be considered negligible. When the concentration is varied in a binary or ternary system the structural effects will be changed. To express this in a formal way, the MacMillan-Mayer approach is often the simplest to visualize. In a binary system containing 1 kg of water the total function is given by

$$F(1,2) = 55.51 \, F_1^O + m\bar{F}_2^O + m^2 f_{22} + m^3 f_{222} + \ldots \tag{13}$$

where f_{22}, f_{222}, ... are pair, triplet and higher order interaction parameters between solute molecules. The apparent molar quantity of the solute is then

$$F_{\phi,2} = \frac{F(1,2) - 55.51 \, F_1^O}{m} = \bar{F}_2^O + mf_{22} + m^2 f_{222} + \ldots \tag{14}$$

The parameter f_{22} is then equivalent to a second virial coefficient. In many cases the sign of the structural contribution to f_{22} can be predicted from the concept of the overlap of the hydration cosphere (6). Difficulties arise with functions like heat capacities since it is not easy to evaluate the importance of the equilibrium displacement contribution.

This treatment can readily be extended to ternary systems in which the two solutes are identified by the subscripts 2 and 3.

$$F(1,2,3) = 55.51 \, F_1^O + m_2 \bar{F}_2^O + m_3 \bar{F}_3^O + m_2^2 f_{22} + \ldots$$
$$+ 2 \, m_2 m_3 f_{23} + 3 \, m_2^2 m_3 f_{223} + \ldots \tag{15}$$

where the cross terms f_{23}, f_{223}, ... are pair, triplet and higher-order interaction parameters between the solutes 2 and 3. The transfer thermodynamic function of solute 3 from the binary to the ternary solution is simply

$$\Delta F_3(1 \rightarrow 1 + 2) = \frac{F(1,2,3) - F(1,2)}{m_3} - F_{\phi,3} \tag{16}$$

If m_3 tends to zero, the standard transfer function becomes

$$\Delta F_3^O(1 \rightarrow 1 + 2) = 2 \, m_2 f_{23} + 3 \, m_2^2 f_{223} + \ldots \tag{17}$$

An interesting consequence of this treatment is that the same parameter f_{23} can be obtained from the converse transfer function

$$\Delta F_2^O(1 \rightarrow 1 + 3) = 2 \, m_3 f_{23} + 3 \, m_3^2 f_{233} + \ldots \tag{18}$$

This reciprocity theorem has been well verified in the literature (see for example Fig. 6).
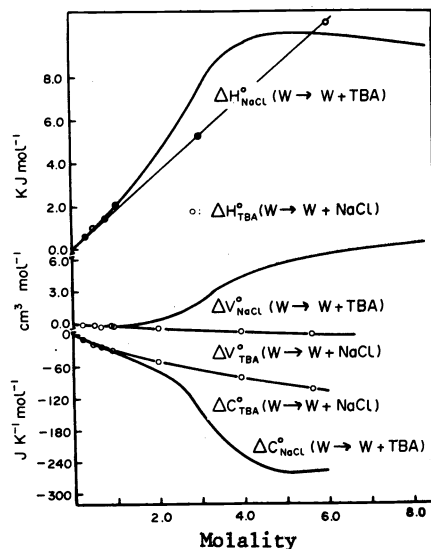

Fig. 6. The standard thermodynamic transfer functions of the system NaCl-*tert*-butanol (TBA)-water (W) at 25°C. From ref. 7.

THERMODYNAMICS OF MICELLAR SYSTEMS

With most solutions of simple systems only the pair interactions parameters of binary or
ternary systems can be interpreted easily. On the other hand, with hydrophobic systems,
higher order terms usually vary in a very systematic fashion since these systems tend to
associate in a cooperative way. A limiting case is the formation of micelles. Beyond a
certain critical concentration, amphiphilic molecules will aggregate, the hydrophobic tails
coming in contact thus losing their hydration cosphere. Thus, as seen in Fig. 7, all the
functions $\bar{F}_2$ in the post-micellar region tend to values approaching F_2^o, the molar values
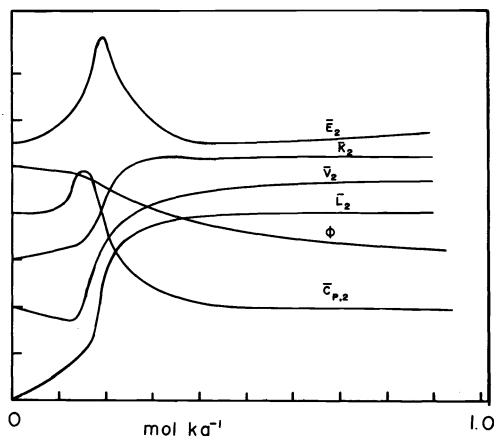of the pure liquid surfactant.

Fig. 7. The thermodynamic properties of octyldimethylamine oxide in water at 25°C.
From ref. 8.

This micellization process for non-ionic surfactants can be treated as a chemical equili-
brium as for the two-state water problem and for the complexation of ion (9). In this mass-
action approach, it is assumed that micelles form an ideal solution with the monomers
although allowance can be made for solute-solute interactions in the pre-micellar region. If
the aggregation number is n, then the equilibrium constant for micellization is

$$K_M = [\text{micelles}]/[\text{monomers}]^n = \frac{1-\alpha}{n\alpha^n m^{n-1}} \qquad (19)$$

where α is the fraction of monomers and m is the surfactant molality. Equations for the
thermodynamic functions can be written in the same way as Eq (2) and (3). Allowing for the
possibility of pair interactions between monomers, the expression for osmotic coefficients,
apparent molar relative enthalpies and heat capacities of the surfactants S are (8)

$$\phi = \alpha (1 + g_S \alpha m) + (1-\alpha)/n \qquad (20)$$

$$\phi_L = h_S \alpha^2 m + (1-\alpha) L_M \qquad (21)$$

$$\phi_C = \alpha(\bar{C}_{P,S}^o + \dot{c}_S \alpha m) + (1-\alpha) C_{P,M} + \frac{\alpha(1-\alpha)}{1-\alpha+\alpha/n} \frac{(\Delta H_M)^2}{RT^2} \qquad (22)$$

where $L_M = H_M - \bar{H}_S^o$ and $C_{P,M}$ are the molar relative enthalpy and heat capacity of the sur-
factant in the micellar form. To solve these equations, it is convenient to introduce an
operational critical micelle concentration m_I from the inflexion point in α.

$$(\partial^2 \alpha/\partial m^2)_{m_I} = 0 \qquad (23)$$

which gives

$$\alpha_I = \frac{n}{n-1} (1 - \sqrt{1/2n}) \qquad (24)$$

Thus, the concentration dependence of the osmotic coefficient can be defined completely by
three parameter (B_G, n, m_I), ϕ_L by four (g_S, n, m_I, h_S) and ϕ_C by six $(\bar{C}_{P,S}^o, c_S, n, m_I,$
$C_{P,M}, \Delta H_M)$. These equations can be solved by a non-linear least-squares analysis and the
results are shown for heat capacities in Fig. 8 for octyl(methyl)$_2$NO in water. The equili-
brium displacement contribution to $C_{P,S,\phi}$ is responsible for the observed hump in the
micellar region. The heat of micellization ΔH_M derived from the least-squares analysis of
ϕ_C is close to that derived from enthalpy data. The situation is unfortunately not as
simple with ionic surfactants since we must in addition take into account the Debye-Hückel

coulombic forces in the pre-micellar region and the ionic dissociation of the micelles.
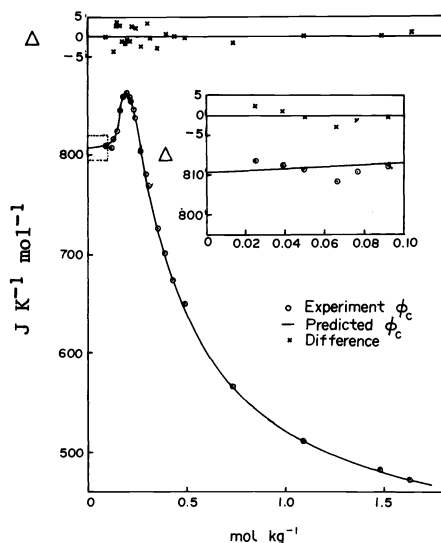

Fig. 8. Mass-action model and the heat capacity of octyldimethylamine oxide in water at 25°C. From ref. 8, with permission.

MICROHETEROGENEITY IN ORGANIC-AQUEOUS MIXTURES.

Our thermodynamic studies on aqueous-organic mixtures show that some systems such as alcohols and amines undergo transitions which resemble micellization. For example, the properties of *tert*-butanol in water (Fig. 9) are remarkably similar to those of surfactants (compare for example with Fig. 7). These systems can be treated with a mass-action model. Eventhough it appears well established that alcohols and amines can exist as microphases in water at high concentration, the analogy with micellization should not be pushed too far since solutes like alcohols will not form well-defined aggregates in water.
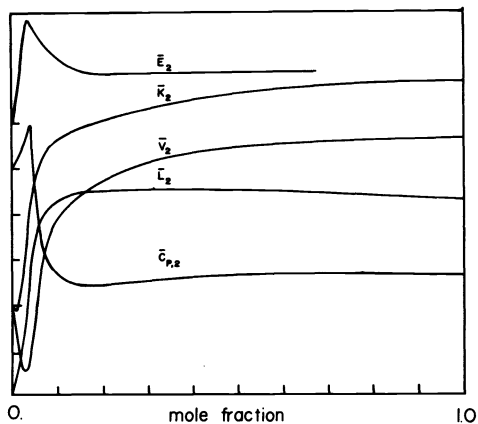

Fig. 9. Thermodynamic properties of *tert*-butanol in water at 25°C. From ref. 10.

TERNARY MICELLAR SOLUTIONS

It is well known that various solutes will shift the critical micelle concentration (CMC) of surfactants. Electrolytes will lower the CMC by salting out the monomers, nonelectrolytes such as urea will raise the CMC by decreasing the structure of water, and hydrophobic solutes such as most alcohols will lower the CMC through the formation of mixed micelles with the surfactant.

These trends will also be reflected in the thermodynamic functions of transfer. This is best illustrated by examining Fig. 10. If the temperature is increased, the CMC of a non-ionic surfactant is lowered and the heat of micellization is also decreased (less endothermic). The difference between the two ϕ_L defines the excess heat capacity function, the hump being related to the lowering of the CMC and the decrease in ϕ_C^{EX} to the lowering of ΔH_M. Similarly, if the presence of a solute A lowers the CMC, the heat capacity of transfer of that solute A from water to the surfactant solution will reflect this shift in

equilibrium. While the exact shape of the transfer function depends on the nature of the function and of the third component, these equilibrium displacement contributions are observed for ternary systems of electrolyte-surfactant-water (11), surfactant-alcohol-water (12,13), electrolyte-alcohol-water (see Fig. 4) and hydrocarbon-alcohol-water (14). For example, the apparent molar volumes and heat capacities of octylamine hydrobromide in a butoxyethanol solution are shown in Fig. 11.
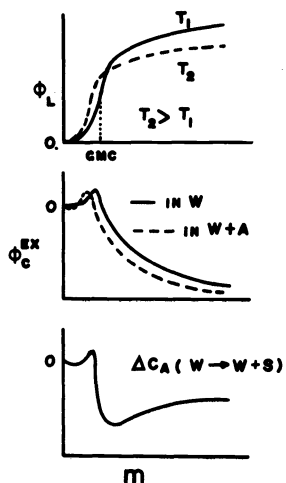

Fig. 10. Origin of the chemical displacement contribution to the heat capacity of surfactants and to the heat capacity of transfer of a solute from water to a surfactant solution in the case where the CMC is lowered by the solute.
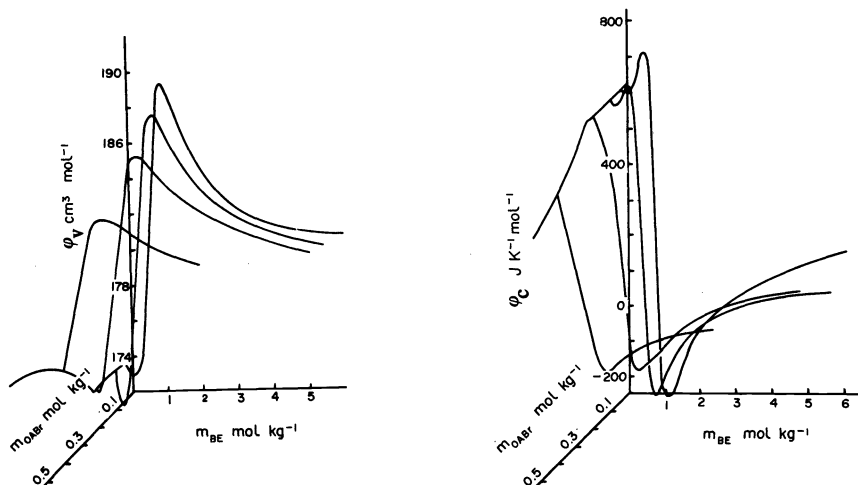

Fig. 11. Apparent molar volumes and heat capacities of octylamine hydrobromide in 2-butoxyethanol-water solutions at 25°C. From ref. 13.

The effect of a solute on the micellization can be predicted readily with a mass-action model, especially in the case where no mixed micelles are formed. For example, the volume of transfer of an electrolyte to a surfactant solution is given by

$$\Delta V_E(W \rightarrow W+S) = 2\ v_{ES} \alpha m_S - \frac{\alpha(1-\alpha)\ (n-1)}{\alpha + n\ (1-\alpha)}\ \frac{\partial\ \ln\ CMC}{\partial m_E}\ \Delta V_M\ m_S \qquad (25)$$

The first term in the relation represents the pair interactions between the electrolyte and the surfactant monomers and is identical to that in Eq (17) or (18). The chemical displacement contribution depends on the lowering of the CMC by the electrolyte and on α, n and ΔV_M, the change in volume during micellization. These parameters can be measured experimentally, for example by analysis of the ϕ_V of the surfactant in water as discussed for the relation 20 to 24. The similarity between the chemical displacement contribution due to temperature (see Eq (22)) and due to an additive should be noted.

The transfer functions of systems that can form mixed micelles such as surfactants and alcohols in water can also be treated by a similar mass-action model, but the relations

become much more complex since multiple equilibria must be considered.

It should be stressed that these chemical displacement contributions arise since the state of equilibrium in the ternary system is not the same as in the reference binary system. These contributions would therefore not be seen if the properties of the ternary system alone are measured, for example by some spectroscopic technique.

MICROEMULSIONS

Microemulsions are complex mixtures of oil, water, surfactant and cosurfactant. When the components are added in the right proportions these systems are clear and form spontaneously, they are thus thermodynamically stable. A well-known system is that of toluene-water-sodium dodecylsulfate-n-butanol. Recently Roux-Desgranges et al. (15) have measured the apparent molar heat capacities of toluene over the whole miscibility region. Similar experiments were made in our laboratory (16) on the heat capacity of benzene in the ternary system benzene-water-2-propanol. These results are compared in Fig. 12 and 13. The trends are amazingly similar indicating that many of the thermodynamic features of microemulsions are already present in simple hydrocarbon-water-alcohol systems. Similarly, it can also be shown that the thermodynamic properties of water in the hydrocarbon-rich region of hydrocarbon-water-alcohol systems (16) have many of the features of the properties of water in inverse micelles (17).
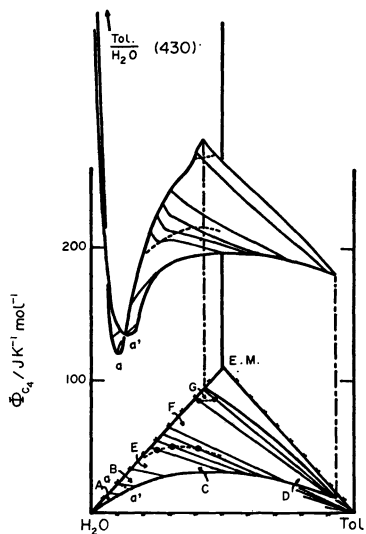

Fig. 12. Apparent molar heat capacities of toluene in the whole pseudo-ternary phase diagram water-toluene-sodium dodecylsulfate-n-butanol at 25°C. From ref. 15, with permission.
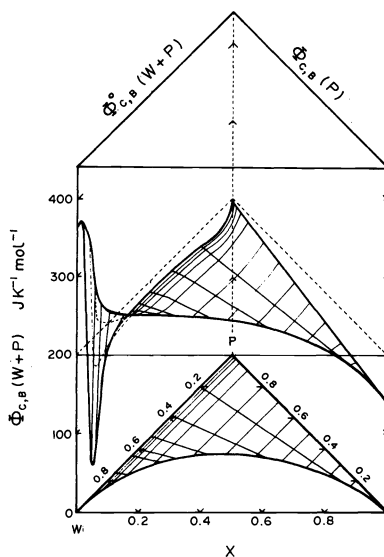
Fig. 13. Apparent molar heat capacities of benzene over the whole miscibility region of the system water-benzene-2-propanol at 25°C. From ref. 16, with permission.

CONCLUSION

Thermodynamic properties measure average interactions over all the species present in the solution and as such cannot give directly information on the structure of the system. On the other hand, these properties can be measured very precisely and lend themselves readily to theoretical analysis. The trends in the concentration dependence of thermodynamic quantities may appear at first sight very complicated with some systems, but very useful information can be derived if the data are analysed systematically with simple models.

LIST OF SYMBOLS

F	:	thermodynamic function
F_i^o	:	molar function of component i
$F^o(f)$, $F^o(b)$	:	molar functions of free and bonded water molecules
$F_2(in)$	:	intrinsic molar function of component 2
$F_{\phi,2}$ or ϕ_F	:	apparent molar function of solute 2
$\bar{F}_2$	:	partial molar function of component 2
$\bar{F}_2^o$	:	standard partial molar function of component 2
$F(12)$, $F(123)$	:	total function of a binary or ternary system
f_{22}, $f_{23}\cdots f_{222}\cdots$	:	pair and triplet interaction parameters
f_S	:	pair interaction parameter between surfactant monomers
G	:	Gibbs free energy
H	:	enthalpy
S	:	entropy
C_p	:	isobaric heat capacity
V	:	volume
E	:	expansibility or electrolyte
K	:	compressibility or equilibrium constant
K_M	:	equilibrium constant for the micellization process
m	:	molality
m_I	:	molality at the inflexion point of α
n	:	agregation number
n_1	:	number of moles of component 1
x	:	fraction of molecules of water in the free state
α	:	fraction of surfactant in the monomeric form
α_I	:	value of α at the inflexion point
ϕ	:	osmotic coefficient.

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