Thermodynamic and Related Studies of Amphiphile + Water Systems

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1 Introduction

The family of alkyl poly(ethylene glycol) monoethers has the generic formula $C_mH_{2m+1}.(OC_2H_4)_n.OH$; conventionally and conveniently abbreviated to C_mE_n. The alkanols form the subfamily C_mE_0.

The members of this family of non-ionic amphiphiles, with $m \geqslant 6$ and $n \geqslant 3$, have been classified as detergents and shown to be capable of forming micelles. An extensive account of the investigations that have been made of the aqueous mixtures of these species, and the conclusions that have been drawn, from those investigations, can be found in reference 1. The binary aqueous systems are characterized by three important features: (i) critical micelle concentrations (cmc), (ii) miscibility gaps with lower critical solution temperatures (LCST), and (iii) formation of one or more liquid crystalline mesophases.

For species with a common alkyl chain, the cmc values are found to be insensitive to variation in the number of oxyethylene groups in the polar head. They are, however, highly sensitive to the length of the alkyl chain. The cmc values (moles^{-1}), at 25 °C, are well approximated by equation 1.

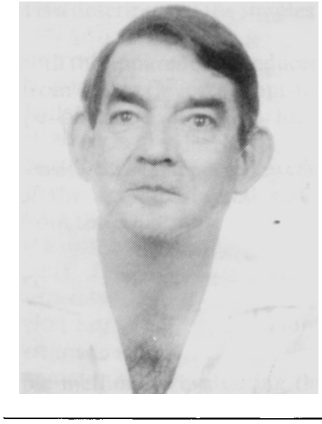
$$\log(\text{cmc}) = (2 - m/2) \qquad (1)$$

Studies of the C_6E_3 + water system have shown that its cmc decreases significantly as the temperature increases. The same trend is presumed to exist for the other systems.

The lower critical solution temperatures increase significantly with the number of oxyethylene groups, for species with a common alkyl chain, and decrease with the length of the alkyl chain for species with the same polar head group. The miscibility gaps are asymmetric, with the critical solution concentrations being only slightly higher than the cmc values. At temperatures just above the LCST, both phases are micellar. The more amphiphile-rich phases contain a substantial mole fraction of water.

Five types of liquid crystalline mesophase have been reported for C_mE_n + water systems, but rarely are more than two or three found in any given system. The lattice symmetries of these mesophases reveal a progression of micellar shapes as the amphiphile mole fraction increases. The first mesophase is of cubic symmetry. It is a close-packed lattice of spherical micelles, with the interstices filled by water. This mesophase is only found for species in which the polar head group is relatively large compared to the alkyl chain. At somewhat higher amphiphile concentrations, a hexagonal mesophase frequently exists. It consists of cylindrical micelles, with water again filling the interstices. The third mesophase is also of cubic symmetry, its proposed bicontinuous structure is described as a rather complicated three-dimensional network of interwoven ribbon shaped micelles. The fourth mesophase is that of the most general interest. Described as lamellar, it consists of membrane-like amphiphile bilayers that are separated by layers of water. The fifth, most amphiphile-rich, mesophase is hexagonal and consists of cylindrical inverted micelles with water filling the central channels.

Born in London in 1936, Michael Davis was educated at Latymer Upper School and University College London. His post-graduate studies, in the area of gas phase electron diffraction, were carried out at the University of Oslo under the direction of Odd Hassel. He joined the faculty of the University of Texas at Austin in 1961 and has been a professor of chemistry at the University of Texas at El Paso since 1971. His current research activities are focused upon the measurement, analysis, and interpretation of the thermodynamic properties of amphiphile + water mixtures.



The liquid crystalline mesophases 'melt' to form micellar mixtures. It is assumed that the geometries of the micelles thus formed are related to those of the mesophase. Thus cylindrical micelles are expected to break up into rods and the lamellar sheets into disks.

Thermodynamic investigations appear to have been restricted to the aqueous mixtures of species with $m \leqslant 6$ and $n \leqslant 3$. This is largely because it is difficult to differentiate between the thermodynamic properties of the very dilute premicellar solutions of the larger amphiphiles and those of pure water. There is a further problem with the substantial cost of the larger detergent species.

C_mE_n + water systems with $m > 6$ and $n < 3$ or with $m < 6$ and $n > 3$ may be of interest but have not been widely studied, with the exception of the higher alcohol + water systems.

Thermodynamic studies of the aqueous mixtures of ionic detergents reveal sharp changes in the slope dQ_m/dx_A at the critical micelle concentration,[2] (where Q_m is a molar or excess molar thermodynamic property of the system and x_A is the amphiphile mole fraction). Graphical evidence for such changes of slope is particularly striking in plots of the excess apparent molar properties Φ_Q^E (= Q^E/x_A) or Φ_Q (= $\Phi_Q^E + Q^*_{m\,A}$, where $Q^*_{m\,A}$ is the molar property of the pure amphiphile).

A major change in the approach to the analysis and interpretation of the thermodynamic properties of smaller amphiphile + water mixtures resulted from the publication of the apparent molar isobaric heat capacities of the 2-butoxyethanol (C_4E_1) + water system.[3] Although there is no evidence that C_4E_1 is capable of forming stable micelles, the profile of this data is essentially identical to that found for the 'true' detergent + water systems. A plot of that data is shown in Figure 1. The change in slope occurs at $x_A = 0.019$, which is very close to the composition predicted for the critical micelle concentration of an alkyl poly(ethylene glycol) monether with $m = 4$.

Since the appearance of reference 3, the results have been published of a variety of studies of the C_4E_1 + water and other related systems. This review will attempt to summarize the information that has been accumulated, from those studies, and to present some possible interpretations. Most of the evidence that will be examined will come from thermodynamic sources.

2 Thermodynamic Experiments

Descriptions of the experimental techniques that are most widely used for measuring excess Gibbs free energies, excess enthalpies, and excess volumes, with appropriate references, are to be found in reference 4. That review also discusses some results of the thermodynamic investigations of non-aqueous binary liquid systems.

Most of the recent published data for the isobaric heat

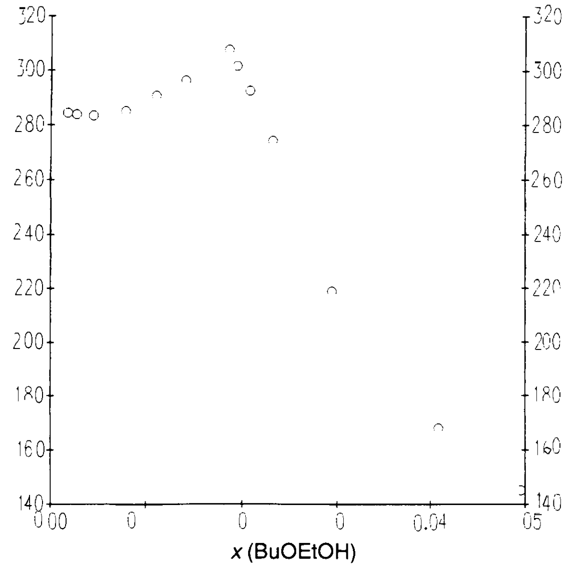


Figure 1 Apparent excess molar isobaric heat capacities of butoxyethanol in its aqueous mixtures Units J K ^{1} mol ^{1}

capacities of binary aqueous mixtures have been measured using Picker-type flow microcalorimeters [5]

Isobaric expansivities can be obtained from density measurements at several different temperatures Molar volumes of aqueous mixtures appear to be fairly well approximated by quadratic temperature dependence Consequently, densities, or excess molar volumes, are needed for at least three, but preferably more, different temperatures

In recent years, there has been an increased interest in the determination of either isothermal or isentropic compressibilities The role that isentropic compressabilities play in the thermodynamic characterization of binary aqueous mixtures is the subject of a recent review [6]

3 Graphical Presentation of Data

The thermodynamic properties of binary liquid mixtures are measured, as a function of composition, in order to identify regions over which significant changes occur in the patterns of molecular aggregation It is clearly desirable to generate visually sensitive graphical representations of the data

Plots of a directly measured variable, such as density or ultrasonic speed, may be interesting, but it is usually preferable to work with molar quantities A given data set, Q_m, can contain important information about its composition dependence that is not evident, from a plot against mole fraction, because of a substantial difference between the values for the two pure components That problem can be alleviated by converting the molar quantities into their excess molar counterparts

An excess molar property is defined by the expression

$$Q^E = Q_m - Q_m^{id} \qquad (2)$$

where Q_m^{id} is the molar property of an 'ideal' mixture of the same composition

The thermodynamic definition of ideality for a binary liquid mixture, A + B, formed under the conditions of constant temperature and pressure, is

$$G_m^{id} = x_A(G^*_{m\,A} + RT\ln x_A) + x_B(G^*_{m\,B} + RT\ln x_B) \qquad (3)$$

where $G^*_{m\,A}$ and $G^*_{m\,B}$ are the respective molar Gibbs free energies (chemical potentials) of the two pure liquid components

Equation 3 is equivalent to Raoult's law provided that the vapours of the two liquids can be treated as ideal gases

Expressions for other ideal molar properties can be derived by assuming that such relationships as exist between the properties of pure substances (or of real mixtures) also hold true for ideal mixtures Thus

$$S_m^{id} = x_A(S^*_{m\,A} - R\ln x_A) + x_B(S^*_{m\,B} - R\ln x_B) \qquad (4)$$

The ideal molar values of the volume, enthalpy, isobaric heat capacity (C_p) and the quantities $A_p = (\delta V/\delta T)_p$ and $K_T = -(\delta V/\delta T)_p$ are given by the mixing rule

$$Q_m^{id} = x_A Q^*_{m\,A} + x_B Q^*_{m\,B} \qquad (5)$$

It should be observed that this is not the approach to defining ideal, and thus excess, molar properties found in most textbooks That approach suffers from an inability to define ideal values for isochoric and isentropic properties like C_V and K_S That inability resulted in the appearance in the literature of a variety of different definitions of $K_S{}^E$, which are inconsistent with equation 3 [6] The problem was resolved by Benson and Kiyohara[7] who adopted the logical approach that, if a thermodynamic quantity, such as C_V, can be evaluated from other properties for which the ideal molar values are unambiguously defined, then the ideal molar values of that property are similarly accessible Thus, since

$$C_{V\,m} = C_{p\,m} - TA^2_{p\,m}/K_{T\,m} \qquad (6)$$

it follows that

$$C^{id}_{V\,m} = C^{id}_{p\,m} - T(A^{id}_{p\,m})^2/K^{id}_{T\,m} \qquad (7)$$

Benson's approach provides access to the ideal and excess molar values of a substantial number of different molar properties of binary liquid mixtures, some of which have very interesting composition dependence [8]

Plots of excess molar properties frequently fail to reveal all of the important features of their composition dependence A number of different strategies are available to project out some of the more subtle features

It is sometimes useful to generate plots of the apparent (or excess apparent) molar properties of the amphiphilic components $\Phi_{Q\,A}$ and $\Phi^E_{Q\,A}$ tend to exhibit interesting composition dependence at low amphiphile concentrations That makes them particularly useful when one is seeking information about critical micelle concentrations or their analogues $\Phi_{Q\,A}$ is also useful when dealing with the thermodynamic properties of aqueous solutions of solids and sparingly soluble liquids

An alternative to the excess apparent molar properties, that are more informative about the composition dependence at higher amphiphile concentrations, are the reduced excess molar properties

$$Q^E_{red} = Q^E/x_A x_B \qquad (8)$$

One notes that Q^E_{red} = a constant is a descriptor of the simplest type of non-ideal mixing

An important characteristic of both the apparent and reduced properties is that they are derived from Q_m, or Q^E, on a point-to-point basis, and require no type of curve fitting or local smoothing of the data

Somewhat more composition-sensitive are the partial excess molar properties Q^E_A and Q^E_W, of the amphiphile and water respectively, which are obtained from the equations

$$Q^E_A = Q^E + (1 - x_A)dQ^E/dx_A \qquad (9)$$

and

$$Q^E_W = Q^E - x_A dQ^E/dx_A \qquad (10)$$

It is necessary to have a reliable method of evaluating the derivatives dQ^E/dx_A at each datum point The method should involve local, rather than global, scrutiny of the form of the data In this laboratory, we have chosen to use a modified cubic splines approach The conventional cubic splines procedure requires that the fitted curve pass exactly through all of the experimental Q^E datum points This means that all of the errors in the data set are retained and, as a consequence, the first derivative curve is likely to be quite erratic The modification that has been adopted involves two cubic splines arranged asymmetrically about each datum point Each spline spans at least five, and up to ten datum entries, if the point density is sufficient Both splines are required to have the same values of Q^E and of dQ^E/dx_A at the mole fraction of interest but can have differing second and third derivatives This approach provides a modest level of smoothing of the original data The first derivative curves that it provides generally appear to be satisfactory The major shortcoming that we have encountered has been a tendency to smooth out some of the more dramatic 'real' features of the data

A comparison of some different ways of providing graphic displays of the composition dependence of thermodynamic data sets is provided by Figure 2 These curves were derived from the isobaric excess molar heat capacity data of Benson *et al* for the 1-PrOH + water system [9] It is seen that dC_p^E/dx_A and C_{pA}^E exhibit more dramatic composition-dependence than do either Φ_C^E or $C_{p\,\mathrm{red}}^E$

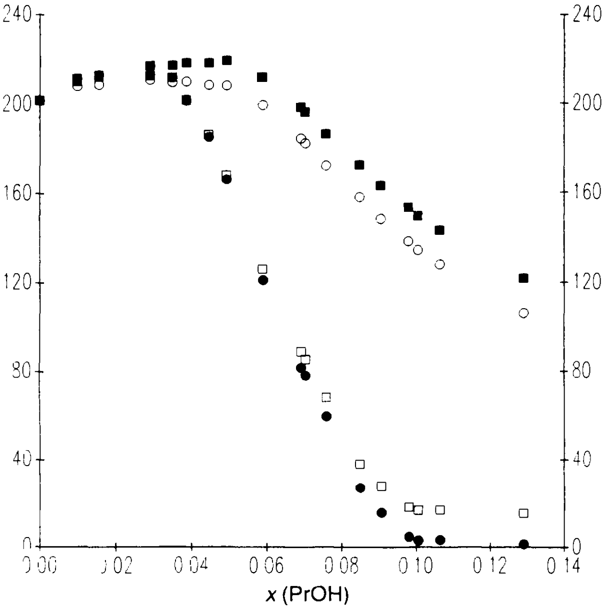


Figure 2 Excess molar isobaric heat capacities of 1-PrOH + water Open circles excess apparent molar C_p of 1-PrOH Closed circles dC_p^E/dX_A Open squares excess partial molar C_p of 1-PrOH Closed squares reduced excess molar C_p Units J K^{-1} mol^{-1}

4 Curve Fitting Strategies

The conventional strategy for fitting smooth curves to the excess molar property data of binary liquid mixtures involves the use of the Redlich–Kister equation [10]

$$Q^E = \sum_{i=1}^{n} C_i x_A x_B (1 - 2x_A)^{i-1} \qquad (11)$$

The coefficients C_i are evaluated by least squares analysis and the optimum number of terms, n, is determined by standard regression criteria Equation 11 serves well for non-aqueous systems but has been found to be ill-suited for fitting the data of most C_mE_n + water systems

A substantial fraction of the investigations of binary aqueous systems has been devoted to water-rich mixtures The most common approach has been to represent the apparent molar properties of the solute species by a polynomial function of its molal concentration This is the McMillan–Mayer equation [11]

$$\Phi_{Q\,A} = \Phi^0_{Q\,A} + b_q m_A + c_q m_A + \text{etc} \qquad (12)$$

$\Phi^0_{Q\,A}$ is the apparent, and also the partial, molar property of the solute at infinite dilution Several authors have devised group additivity rules which do a reasonable job of correlating the values for a substantial number of structurally related solutes [12 13] The explanation for the success of the additivity rules for $Q = V$ and C_p is that each atomic group produces a characteristic modification to the pattern of self aggression of the solvent water molecules in their immediate vicinity

The effects of the interactions between pairs of solute molecules is represented by b_q Wood and his co-workers have made extensive studies of b_q values for a large number of binary aqueous systems, leading to the establishment of the Savage–Wood group–pair additivity rule [14] That rule is consistent with random mutual orientation of the solute pairs and indicates that b_q is more likely to be associated with overlap of the hydration co-spheres than with direct solute–solute contact

The $\Phi_{Q\,A}$ curves for C_mE_n + water systems appear to possess quadratic dependence upon molality (or mole fraction) over a modest composition range The quadratic coefficient c_q is described as being related to cooperative association of the amphiphilic solutes What is being considered here is a 'hydrophobic effect' where the solute species tend to cluster in such a way as to minimize direct contact between their alkyl tails and water [15] That results in enhanced contact between pairs of non-polar groups

There have been two major approaches to extending the curve fitting process beyond the extreme water-rich concentration range Each is based upon a distinct concept of the significance of the cmc

The 'mass action' approach treats a micellar aggregate as a polymeric species and thus deals with the equilibrium

$$nA \longleftrightarrow A_n \qquad (13)$$

It is argued that the equilibrium stays well over towards the monomer side at concentrations up to just below the cmc, at which point it swings rapidly over to the polymer side This concept has been incorporated into an analytical model, by Desnoyers and Roux [16]

The 'pseudophase' approach treats the micellar aggregates as constituting a distinct dispersed microphase In that context, the critical micelle concentration is the solubility of the micellar microphase This carries with it the implication of some type of discontinuity in the partial molar properties, other than the chemical potentials, at the cmc The pseudophase approach has been incorporated into the semi-empirical four-segment composition model [17]

Referring to the excess molar enthalpies of ethanol + water, Franks and Ives[18] wrote of 'the necessity for separate consideration of at least two composition ranges, for they may involve quite separate problems ' Many authors, in their interpretations of the physical properties of binary hydro-organic systems, have drawn attention to what they regard as evidence for the existence of several discrete composition ranges

As its name suggests, the four segment model treats the total composition range of a binary non-ionic amphiphile + water system as being made up of four-separate parts (segments) Across each of the segments, the excess molar properties are assumed to possess a distinct and relatively simple mole fraction dependence Q^E must be continuous at each of the three segment junctions The version of the model, described in reference 17, also requires continuity of dQ^E/dx_A at two of the three junctions That version provides an acceptable quality of fit for the available data sets closer scrutiny indicates it to be maybe more flexible than is necessary for many of the data sets, and, in such cases, it has been found that further constraints can be introduced into the model without serious detriment to its curve fitting ability

5 Composition Dependence of the Patterns of Molecular Aggregation

Before considering the algebraic details of the four-segment model, it is proper to examine some of the conceptual aspects of treating these binary systems as having partitioned composition ranges Some justification for this approach may be found in the appearance of dH^E/dx_A for ethanol + water (Figure 3), as obtained from the data of reference 19

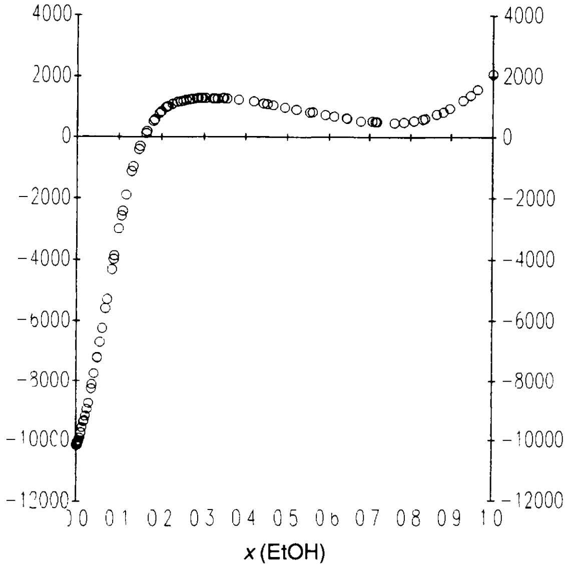


Figure 3 Excess molar dH/dX_A for EtOH + water Units J mol^{-1}

A water-rich segment extends up to the inflexion point in the vicinity of $x_A = 0\ 1$ There is a central segment, that extends from roughly $x_A = 35$ to 65, where dH^E/dx_A is very nearly linear A similar linear feature is present in the dV^E/dx_A data of 1-PrOH + water [20] Three segment junctions may thus be assigned, in the vicinities of $x_1 = 0\ 1$, $x_2 = 0\ 35$, and $x_3 = 0\ 65$, splitting the total composition range into four parts

5.1 The Water-rich Segment $0 \leqslant x_A \leqslant x_1$

Over the past twenty years, our ideas about the structure of liquid water have been strongly influenced by the results of computer simulations While there are some differences between the conclusions drawn from molecular dynamics[21a] and Monte Carlo[21b] simulations, the basic picture appears to be much the same

One may view a water sample as a continuous network of relatively short-lived hydrogen bonds Both types of simulation indicate that the fraction of water molecules with no hydrogen bonds at all is, at any given instant, very small and that the majority are involved in two or more The water molecules are capable of participating in a wide variety of local schemes of self aggregation, of which the ice-like pattern is the lowest in energy and the least compact A dynamic equilibrium may be envisaged between molecules in ice-like sites, on the one hand, and in a multitude of higher energy more compact alternative sites, on the other The equilibrium shifts to occupancy of the alternative sites as either the temperature, or the pressure, is increased This model provides a plausible rationale for the unusual temperature-dependence of both the isobaric expansivity and the isothermal compressibility

The presence of an amphiphilic solute has the effect of disrupting the structural equilibrium of the water molecules in its immediate vicinity The alkyl groups, in common with completely non-polar solutes, are described as being structure making, implying that their presence induces enhanced ice-like aggregation There is evidence for this in the positive values found for V^E_W, in combination with negative values for H^E_W, at very low amphiphile concentrations

The polar head groups are generally capable of forming hydrogen bonds to the solvent water molecules The thermodynamic data indicate that this favours the more compact types of aqueous self aggregation but, at the same time, may bring about enhancement of hydrogen bonding efficiency among their neighbouring water molecules

There appear to be two distinct types of solute–solute interaction Hydrogen co-sphere overlap is thought to dominate at very low amphiphile concentrations but cluster formation becomes progressively more important as the amphiphile concentration increases That situation seems to account for the appearance of the V^E_W curves Figure 4 shows the water-rich V^E_W curve for 1-propanol + water at 25 °C, generated from the data of reference 22

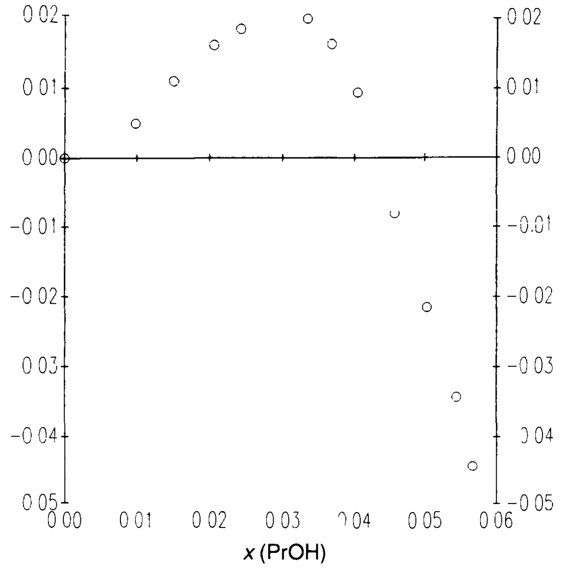


Figure 4 Excess partial molar volumes of water in 1-PrOH + water Units cm^3 mol^{-1}

It has been found that a satisfactory fit of water-rich excess molar property data can be obtained with a cubic function of x_A The segment junction, $x_A = x_1$, is the mole fraction above which that cubic equation is no longer satisfactory The water-rich segment may be limited for any one of several reasons (i) In the case that the amphiphile is truly capable of forming micelles, the water-rich segment is limited by the cmc (ii) Where, as appears to be the case for 2-butoxyethanol, one is obliged to talk of micelle-like or pseudomicellar aggregates then x_1 might be termed a cmc analogue (iii) There are systems, like 1-BuOH + water, in which the amphiphile has limited solubility and the water-rich segment terminates with the formation of a bulk phase separation The amphiphile-rich phase may contain a substantial amount of water At temperatures up to 10 K above its lower critical solution temperature, 2-butoxyethanol + water shows evidence of a cmc analogue at a lower amphiphile concentration than the onset of the miscibility gap [4a] (iv) It is improper to talk in terms of a cmc analogue for methyl or ethyl amphiphiles Nevertheless, the composition dependence of some of the excess molar properties of their binary aqueous systems possess features which are similar to, but much less pronounced than, those of their more hydrophobic homologues [16,17] A possible explanation for the termination of the water-rich segment for the aqueous mixtures of these species is that the volume fraction of the amphiphile has risen to a level where all of the water is directly involved in solvation

Some years ago, Hvidt[23] introduced a mass-action approach, somewhat different from that of Roux and Desnoyers Her analysis addressed the question of the relative amounts of water involved in hydrophobic and hydrophilic hydration The conclusion reached was that the fraction of water molecules engaged in hydrophobic hydration falls off fairly sharply with increasing amphiphile mole fraction whereas hydrophilic hydration persists up to high amphiphile concentrations.

5.2 The Central Segment $x_2 \leqslant x_A \leqslant x_3$

This is the segment across which dQ^E/dx_A appears to maintain linear dependence upon mole fraction. This observation led to the proposal of the original segmented composition model.[24] Such simple composition dependence suggests the existence of a fairly uniform scheme of molecular aggregation spanning the entire segment. It is pointed out in reference 1 that, in detergent + water systems, roughly equivolumar mixtures frequently give rise to a lamellar liquid crystalline mesophase. The question may then be posed as to whether it is possible that what one observes in the central segments of the somewhat smaller amphiphile + water systems is a manifestation of the existence of some type of labile pseudolamellar analogue, consisting of metastable disks.

5.3 The Amphiphile-rich Segment $x_3 \leqslant x_A \leqslant 1.0$

Figure 5 shows the partial excess molar volumes of water in the three systems EtOH + water,[22] EtOEtOH + water,[25] and EtOEtOEtOH + water.[26] The profiles of the three sets of data are very similar up to an amphiphile mole fraction of 0.5. Above that point the form of the EtOH + water data differs very markedly from the other two. This probably reflects significant differences between the modes of aggregation of the pure alkanols, on the one hand, and the ethoxylated ethanols, on the other.

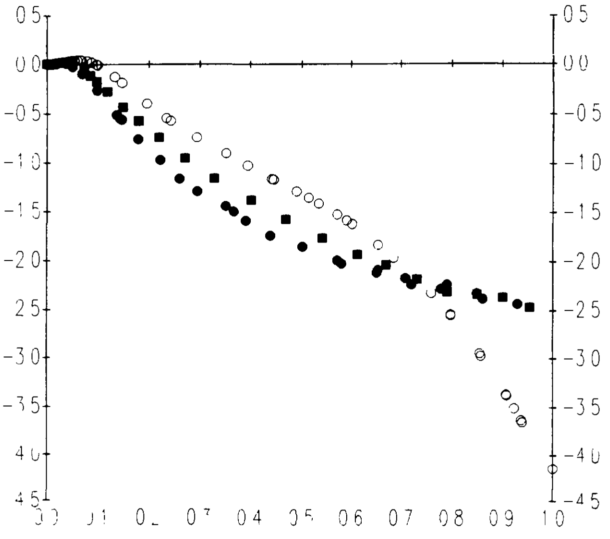


Figure 5 Excess partial molar volumes of water in C_2E_n + water. Open circles: EtOH + water. Closed squares - EtOEtOH + water. Closed circles: EtOEtOEtOH + water. Units $cm^3\ mol^{-1}$

Alkanols tend to self-associate through the agency of hydrogen bonding to produce relatively small labile clusters. In solutions of alkanols in non-polar solvents, there appears to be a tendency towards the formation of cyclic oligamers made up of four hydrogen-bonded monomers.[27] It is probable that such oligomers play a significant role in the structure of the pure alkanols. Solute water molecules would tend to be incorporated into the polar regions of such structures. The significant changes in V_W^E with increasing water content may be an indication of significant variations in the mode of alkanol self-aggregation as the composition changes from pure alkanol to the limit of the central segment. That no such significant changes occur in the V_W^E values for the other two systems might be taken as an indication that the self aggregative schemes of the pure ethers already resemble that of the central segment.

The question might be raised as to whether there is any evidence for the formation of inverse micelles in these systems. If there were, one might expect to observe some type of critical concentration, analogous to the cmc of the water-rich region. Such does not appear to be the case. However, it is possible that, in some of the systems, the central (pseudolamellar) segment contains either micellar aggregates or some type of metastable analogues. If so, one might expect to encounter some type of discontinuity in the thermodynamic data at the composition $x_A = x_3$.

Some of the recent attempts to improve the four-segment model have revealed that, while the constraint that $d^2Q^E/dx_A{}^2$ should be continuous at $x_A = x_3$ has relatively little effect upon the curve fitting attributes of the model for most of the alkanol + water data sets, its imposition is detrimental for the data of the alkoxylated ethanols + water.

5.4 The Intermediate (Transitional) Segment $x_1 \leqslant x_A \leqslant x_2$

While it is possible to make some plausible suggestions as to the nature of the schemes of molecular aggregation which exist in the water-rich (premicellar), central (pseudolamellar), and amphiphile-rich segments, it has proved to be more difficult to describe this intermediate or transitional segment.

For amphiphilic species which are capable of forming stable micellar aggregates, $x_A = x_1$ is the concentration at which they first appear. As the mole fraction of the amphiphile increases, so the population of micellar aggregates rises and some type of equilibrium must exist between them and their saturated solution. There are several points that need to be kept in mind. The phase diagrams and other studies of the detergent + water systems indicate that there are progressive changes in the micellar geometries. Further, the amphiphile concentration is not likely to rise very far above the cmc before all of the water present is directly involved in solvation making it inappropriate to talk in terms of a solution in the normal sense of the word.

Some help in gaining an appreciation of the nature of the aqueous mixtures of the more hydrophobic amphiphiles, within this segment, may be gained from a consideration of Figure 6. This shows the partial excess molar volumes of water in the C_6E_2 + water at 5 °C[28] and C_6E_3 + water at 15 °C.[29] Above what is recorded as the cmc for C_6E_3 and what is presumably also that for C_6E_2, the V_W^E values remain virtually constant before beginning a fairly significant decrease. That the cmc is lower in the case of C_6E_3 is thought to be due to the temperature difference, rather than the size of its polar head group.

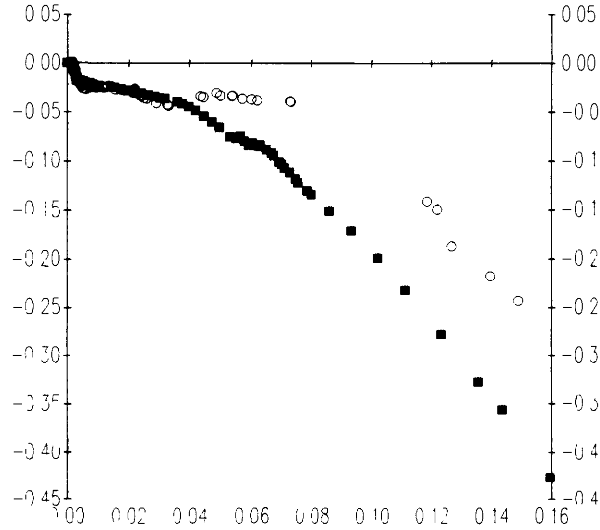


Figure 6 Excess partial molar volumes of water in C_6E_n + water. Open circles: C_6E_2 + water. Closed squares - C_6E_3 + water. Units $cm^3\ mol^{-1}$

It may well be that, in those systems, there exists, above the cmc, a range of compositions where the water can maintain something approximating to bulk characteristics. The addition of water would then result in some of the amphiphile going back into 'solution'. Constant partial molar properties are attributes of phase, or microphase, separations.

5.5 The Four-segment Model Equations

In the foregoing sections, some comments have been made about the trends in the composition dependence of the thermodynamic properties of C_mE_n + water systems as either the alkyl chain length or the polar head group size is increased. The four-segment composition model provides a reasonably effective tool for exploring the nature of such trends.

The excess molar properties of the water-rich mixtures appear to possess cubic mole fraction dependence. This is equivalent to a quadratic version of the McMillan–Mayer equation (equation 13). There are several different ways in which a cubic function of the amphiphile mole fraction might be formulated. For the purpose of this review, the following form has been adopted:

$$Q^E(W) = a_W(x_A - x_A^3) + b_W(x_A^2 - x_A^3) + c_W x_A^3 \qquad (14)$$

a_W is the excess apparent (and also partial) molar property of the amphiphile at infinite dilution, and is easily converted into $\Phi^0_{Q\,A}$, by the addition of $Q^*_{m\,A}$, b_W plays much the same role as does b_q of equation 13, and may be converted into b_q by multiplying by $M_{m\,W}/1000$, c_W is regarded as representing the effects of cluster formation.

dQ^E/dx_A appears to possess linear dependence upon mole fraction across the central (pseudolamellar) segment, so that Q^E can be assigned quadratic dependence. The following quadratic equation has been adopted:

$$Q^E(L) = q_W(1 - x_A) + q_A x_A + b_L x_A(1 - x_A) \qquad (15)$$

In this context, q_W represents an excess molar property of some type of hypothetical standard state of water and, as such, may be regarded as a measure of the effects of the changes in the nature of aqueous self-aggregation. q_A plays a similar role for the amphiphile. b_L must then represent the effects of the interactions between the two hypothetical states. If there were a true phase-separation, or a uniform microphase separation, b_L would be zero.

The six optimizable parameters of equations 14 and 15 form a minimum set. For a few alkanol + water data sets this is an adequate curve fitting model but for most of the alkanol + water sets at least seven parameters are required.

The excess molar properties of the intermediate (transitional) segment appear to require an equation with quartic dependence upon mole fraction. However, for many data sets, it is possible to require that both Q^E and dQ^E/dx_A are single valued (continuous) at both $x_A = x_1$ and x_2, and also that d^2Q^E/dx_A^2 is single valued at $x_A = x_2$. This eliminates all five of the coefficients of the quartic equation as independent model parameters.

For the amphiphile-rich segment, the excess molar property data can be fitted to a cubic function of mole fraction. For most of the alkanol + water systems, it is possible to constrain Q^E, dQ^E/dx_A, and d^2Q^E/dx_A^2 to be continuous at x_3, which eliminates all three of the coefficients of the cubic equation as independent parameters. It is interesting to note that, for the C_mE_n + water systems with $n > 0$, the constraint on d^2Q^E/dx_A^2 is no longer conducive to an acceptable quality of fit. In such cases, one must add, to the parameter set, the excess apparent molar property of water at infinite dilution in the amphiphilic solvent.

The parameters of the four-segment model equations can be optimized using a linear least squares procedure, provided that the compositions, corresponding to the three segment junctions, are fixed. The determination of the optimum segment junction compositions forms a critical part of the analysis. A rough idea of the locations of the segment junctions may be gained from visual appraisals of plots of the dQ^E/dx_A curves. Using those estimates as a starting set, one may then proceed to determine optimum values for each data set by means of a 'simplex' procedure. This procedure tends to be vulnerable to blatant errors in the data and requires screening of the more obvious violations of internal consistency. For the most part, the data sets for a given system lead to a reasonably consistent estimate of the locations of the segment junctions.

Some results of four-segment analyses are set out in Tables 1—7.

Table 1a Amphiphile mole fractions for the segment junction x_1 at 25 °C

	$m =$ 1	2	3	4	6
$n = 0$	0.135	0.100	0.070		
1	0.09	0.075	0.050	0.025	
2		0.075		0.025	0.0035[a]
3				0.025	0.0025

[a] The values for C_6E_2 + water correspond to a temperature of 5 °C

These values are all for n-alkyl amphiphiles. The values found for 2-PrOH + water and iso-PrOEtOH + water are both higher than those given in the table. That for t-BuOH + water is 0.050. Values are found to vary slightly from one type of data to another, and with temperature, for the C_4E_n + water and C_6E_n + water systems.

Table 1b Amphiphile mole fractions for the segment junction x_2 at 25 °C

	$m =$ 1	2	3	4	6
$n = 0$	0.400	0.400	0.250		
1	0.333	0.333	0.250	0.250	
2		0.333		0.333	0.250
3				0.333	0.300

Table 1c Amphiphile mole fractions for the segment junction x_3 at 25 °C

	$m =$ 1	2	3	4	6
$n = 0$	0.600	0.667	0.750		
1	0.500	0.500	0.500	0.500	
2	0.500	0.500		0.500	0.500
3				0.400	0.400

The largest number of data sets is for the excess molar volumes. The following tables give the values obtained for the six major four-segment model parameters of the property V^E.

Table 2a Values of the parameter a_W for the excess molar volumes of n-alkyl C_mE_n + water systems at 25 °C (units $cm^3\ mol^{-1}$)

	$m =$ 1	2	3	4	6
$n = 0$	−2.55	−3.62	−4.45		
1	−4.24	−6.36	−8.02	−8.88	
2		−8.44		−10.73	−13.10 (5 °C)
3				−14.03	−15.26

The a_W values may be converted into the apparent molar volumes of the amphiphiles at infinite dilution (Table 2b) by adding the molar volumes of the pure amphiphiles

Table 2b Apparent molar volumes of C_mE_n species at infinite aqueous dilution at 25 °C (units cm^3 mol^{-1})

m =	1	2	3	4	6
n = 0	38 20	55 06	70 73		
1	75 02	91 07	106 56	122 94	
2		127 98		160 39	
3				196 34	228 75

These values correspond to an average increment of 36 5 cm^3 mol^{-1} per OC_2H_4 group and 16 0 cm^3 mol^{-1} per CH_2 group at a β-carbon They conform fairly well to a simple group additivity scheme

The a_W values derived from the excess molar enthalpy data are all negative There are substantial negative shifts as the size of the polar head group increases, due presumably to hydrogen bonding between water and the ether groups There is a modest decrease (− 3 kJ mol^{-1}) on increasing the chain length from 1 to 2 but no significant change thereafter The a_W values for the excess molar isobaric heat capacities are all positive and generally of the same order of magnitude as the absolute molar heat capacities of the amphiphiles They increase with both the length of the alkyl chain and the size of the polar head group The a_W values obtained from the K_S^E data show similar trends to those for V^E[6]

Table 3 Values of b_W for the excess molar volumes data for C_mE_n + water systems at 25 °C (units cm^3 mol^{-1})

m =	1	2	3	4	6
n = 0	− 8 9	− 30 4	− 60 6		
1	− 19 9	− 42 1	− 40 1	− 143 4	
2		− 44 1		− 180 0	− 1225 (5 °C)
3				− 166 6	− 380

There are no clear trends in the b_W values (Table 3) associated with variation of the polar head group size, but a very definite increase as the length of the alkyl chain increases The b_W values for the excess molar enthalpy data are all positive They increase significantly with both the length of the alkyl chain and the size of the polar head group Both hydrophobic and hydrophilic hydration appear to lead to enthalpy decreases As a consequence overlap and disruption of the hydration co-spheres might be expected to be endothermic It is difficult to pick out any reliable trends among the b_W values derived from the limited number of excess molar C_p data sets

Table 4 Values of c_W for the excess molar volumes data for C_mE_n + water systems at 25 °C (units cm^3 mol^{-1})

m =	1	2	3	4	6
n = 0	20	115	589		
1	98	317	702	6760	
2		405		6636	372500 (5 °C)
3				6117	615900

If b_W is an indicator of the effects of hydration co-sphere overlap, the rapid decrease in its V^E values as the alkyl chain length increases indicates that the major effect is to disrupt the pattern of ice-like aggregation Similarly, the trends in the c_W values, which are regarded as being indicators of the effects of amphiphile clustering, also reflect the diminution of the structure-making effects of hydrophobic hydration

There is really too little data for H^E to state more than the c_W values become more endothermic with increasing alkyl chain length

Table 5 Values of q_W for the excess molar volumes of C_mE_n + water systems (units cm^3 mol^{-1})

m =	1	2	3	4	6
n = 0	− 0 019	− 0 559	− 0 386		
1	− 0 458	− 0 731	− 0 453	− 0 214	
2		− 0 958		− 0 536	− 0 264
3				− 0 772	− 0 389

There is a clear tendency for q_W (Table 5) to become more negative as the size of the polar head group increases The greatest decreases in the molar volume, among species with a common polar head group, occur when $m = 2$ It is suggested that this parameter reflects the effect of the changes in the patterns of self aggregation of water, from that of the pure liquid The negative values would then correspond to a decrease in the level of ice-like aggregation

The q_W values that have been derived from the excess molar enthalpy data are all negative They show the same kind of dependence upon alkyl chain length as do the values for V^E and the same tendency to become more negative with increasing polar head group size The values for the excess molar isobaric heat capacity data are all positive and tend to show the same trends as, but are of opposite sign to, the H^E values

Table 6 Values of q_A for the excess molar volumes of C_mE_n + water systems (units cm^3 mol^{-1})

m =	1	2	3	4	6
n = 0	0 037	− 0 088	− 0 088		
1	0 068	0 584	0 507	0 432	
2		0 708		0 613	1 086 (5 °C)
3				1 252	1 149

There is a remarkable difference, between the q_A values (Table 6) for the alkanols and the alkoxyethanols It is not clear whether this reflects differences in the modes of self aggregation of the two families in the mixtures or as pure liquids The values obtained for the H^E data are generally quite small Those for the alkanols are all negative, while those for the alkoxyethanols are positive There are no well-defined trends among the C_p^E values

Table 7 Values of b_L for the excess molar volumes of C_mE_n + water systems (units cm^3 mol^{-1})

m =	1	2	3	4	6
n = 0	− 4 05	− 2 98	− 1 66		
1	− 4 16	− 3 85	− 3 45	− 3 31	
2		− 3 76		− 3 76	− 5 14 (5 °C)
3				− 4 70	− 4 55

There is a sharp increase in the b_L values with increasing alkyl chain length for the alkanol + water systems The values obtained from the H^E data for the alkanols range from − 1 16 kJ mol^{-1} for MeOH + water to 2 12 kJ mol^{-1} for 1-PrOH + water It is this variation which is manifested in the vastly different H^E profiles The value of b_L for the alkoxyethanols is consistently negative

6 Conclusions

In the foregoing sections, an examination has been made of some of the graphical and analytic perspectives of the thermodynamic data that have been accumulated for the aqueous mixtures of the C_mE_n family In conclusion, it is fair to ask whether we are any closer to an understanding of the nature of the patterns of molecular aggregation which exist within such mixtures than we were 25 years ago

The first claim that can be made is that our concepts have been polarized in the right direction by recognizing that the hydrophobic effects, which are responsible for the formation of micelles, vesicles, and membrane bilayers, almost certainly play some role in determining the less dramatic patterns of molecular aggregation that exist in the aqueous mixtures of even quite humble amphiphiles In that context, it is important to recognize the influence of Tanford [30]

One may state, with a fair degree of certainty, that the structures of the aqueous mixtures are dictated by tendencies towards minimization of direct contact between water and the apolar hydrocarbon tails, and by a tendency for water molecules to hydrogen bond to the lone pairs of electrons of the ether and hydroxyl oxygens In the formation of a micelle, the separation of water from the alkyl groups is essentially complete All of the evidence points to 2-butoxyethanol (C_4E_1) forming aggregates which, if not truly micellar, bear considerable resemblance to micelles It is possible that such aggregates have no single well-defined geometry

It is noted that the C_3E_n + water systems show some of the same types of composition dependence features for their thermodynamic properties, as are associated with the existence of critical micelle concentrations Little mention has been made here of the t-butanol + water system but it also shows pseudo-micellar characteristics

There is evidently a fair degree of hydrophobic clustering of the amphiphiles at premicellar concentrations This leads to substantial increases in the viscosities of the amphiphile + water mixtures and corresponding decreases in their diffusion coefficients Equally evident is the fact that such clustering does not necessarily lead to the formation of stable micelles, since many of the features of the composition dependence of the thermodynamic properties that are attributable to clustering are also present, to a more modest extent, for the methyl and ethyl systems

Relatively little attention had been paid to the thermodynamic data at higher amphiphile mole fractions There appears to be evidence for the existence of a range of compositions which corresponds to the lamellar regions of detergent + water systems

Questions concerning the patterns of aggregation in binary aqueous mixtures will not be properly answered until such time as it becomes feasible to carry out large-scale computer simulations That is not something that is anticipated in the immediate future It is possible, however, to examine the stabilities and preferred structures of small clusters using molecular modelling techniques, such as those based upon the Allinger algorithms Some preliminary studies, carried out in this laboratory, reveal the fact that the C_mE_n species are capable of existing in a wide variety of different conformations, many of which are close enough in energy to the most stable of their number that they have significant populations The sequence of conformational energies in the gas-phase is likely to differ from those in the pure liquid states and those existing in aqueous mixtures Significant changes in conformation on going from the pure liquid to an aqueous mixture may well have a significant effect upon the values of the excess molar properties

This review has dealt exclusively with a single family of non-ionic amphiphiles This family has become the object of a great many investigations because of the possibility of varying both the alkyl chain length and the size of the polar head group In that sense, it is believed that the lessons learned from the study of the aqueous mixtures of the members of this family serve to enhance our understanding of amphiphile + water mixtures in general

The continuously increasing data base places progressively greater constraints upon conceptual models that we might invoke We may be able to discuss the structures of amphiphile + water mixtures somewhat more intelligently than before but we obviously still have a long way to go before our understanding of them will have reached a completely satisfactory level

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