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Patterns of molecular aggregation in aqueous mixtures of species of the type $C_mE_{2m+1} \cdot (OC_2H_4)_n \cdot OH$
Part 1. Applications of an empirical model to some C_mE_0 plus water systems

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Abstract

A rationale is given for the four-segment composition approach to the analysis and interpretation of the thermodynamic properties of binary amphiphile plus water systems. The hypothesis is introduced that there exist, within isotropic binary water plus amphiphile mixtures, labile patterns of molecular aggregation which resemble the more stable schemes that are observed in water plus non-ionic detergent systems. The nature of such patterns of molecular aggregation varies from one composition range to another in a manner which is reflected by changes in the composition dependence of the macroscopic properties.

A new version of the four-segment model equations was devised to explore, in more detail, the nature of the composition dependence of thermodynamic properties in that composition segment which corresponds to a range of varying micellar geometries.

INTRODUCTION

There exists a substantial and growing literature dealing with the physicochemical properties of the aqueous mixtures of alkyl poly(ethylene glycol) monoethers. The members of this family possess the generic formula $C_mH_{2m+1} \cdot (OC_2H_4)_n \cdot OH$, which is frequently and conveniently abbreviated to C_mE_n. We note that the alkanols (C_mE_0) are, in a sense, members of this family. The polyethylene glycols themselves can be represented by the formula C_0E_n.

The higher molecular weight members of this family, those with $m \geqslant 6$ and $n \geqslant 3$, are classified as non-ionic detergents. Reference 1 contains a number of articles that describe the results of various methods of studying the aqueous mixtures. Many of the investigations have been concerned with establishing the nature of the phase diagrams of the binary aqueous systems and the manner in which those phase diagrams vary with the molecular structures of the amphiphile. Light scattering and various relaxation techniques have been employed to determine the nature of the composition dependence of the size and shape of the micellar aggregates that are formed in ostensibly isotropic liquid mixtures.

Thermodynamic studies have been largely limited to aqueous mixtures of the smaller members of the family; those with $m \leqslant 6$ and $n \leqslant 3$. This is partly due to the fact that, over the relatively narrow ranges of premicellar concentrations of the species with longer alkyl chains, the macroscopic properties of the solutions differ to only a modest extent from those of the pure solvent. The cost of pure samples of the larger members of the family has also tended to be a deterrent to carrying out experiments which require fairly large amounts of material.

The aqueous mixtures of family members with $m > 6$ and $n < 3$ or with $m < 6$ and $n > 3$ are not necessarily without interest but they do not appear to have been widely studied.

We have been interested in trying to correlate the results of the two sets of investigations. In particular, we have been concerned with testing the hypothesis that the thermodynamic data, for the aqueous mixtures of the smaller amphiphiles, might be interpreted in terms of the existence of patterns of molecular aggregation that are similar, at least to some extent, to those found in the detergent plus water systems. In this paper, we examine the basis for that hypothesis and an empirical model for analysing thermodynamic data.

DETERGENT PLUS WATER SYSTEMS

Investigations of the detergent plus water systems have revealed the existence of three interesting characteristics [1].

(1) They are capable of forming micellar solutions.

(2) Many of the systems have been found to possess lower critical solution temperatures. Some are known to have closed immiscibility loops.

(3) Many of the systems have been observed to form one or more of a number of different liquid crystalline mesophases.

Critical micelle concentrations

It has been found that for a series of amphiphiles with a common alkyl chain length, the critical micelle concentration (c.m.c.) is virtually independent of the number of (OC_2H_4) groups. By contrast, the c.m.c. is very strongly dependent upon the alkyl chain length m.

Reference 2 presents the following formula, which very nicely fits the available data at 25 °C:

$$\log_{10} (\text{c.m.c}) = 2.0 - \tfrac{1}{2}m \qquad (1)$$

where c.m.c. is in moles per liter. It is also noted that the c.m.c. of a specific amphiphile tends to decrease as the temperature is increased [2].

Lower critical solution temperatures

For a series of amphiphiles with a common alkyl chain length, the lower critical solution temperature (LCST) values of their binary aqueous systems increase with increasing numbers of (OC_2H_4) groups. Thus, at a given temperature, increasing the hydrophilic character of the amphiphile enhances miscibility. For a series with a common polar head group, the LCST values decrease with increasing alkyl chain length. These trends persist for both $m < 6$ and $n < 3$.

The more dense of the two phases that are formed within the miscibility gap has a concentration of the same order of magnitude as the c.m.c. and may be regarded as a saturated solution of the amphiphile in water. The less dense phase is another solution in which there is still a substantial mole fraction of water.

It is of interest to compare the temperature dependence of the amphiphile solubility with that of the c.m.c. It is stated in ref. 2 that at temperatures just above the LCST the aqueous phase is micellar. However, the solubility decreases more rapidly with increasing temperature than does the c.m.c. and the two curves ultimately converge. Above that convergence temperature, the saturated solution is presumed to be non-micellar.

Liquid-crystal mesophases

Five different types of liquid-crystal mesophase have been observed and characterised in C_mE_n plus water mixtures [2]. Of these, three are of particular interest. They are, in the order of increasing amphiphile content, cubic, hexagonal and lamellar.

The cubic mesophase is described as being a close-packed array of spherical micelles with water filling the interstices. The hexagonal mesophase is described as being formed by a close-packed array of cylindrical (extended rod) micelles with interstitial water. The lamellar mesophase consists of membrane-like amphiphile bilayers alternating with layers of water.

A given amphiphile plus water system may exhibit all three mesophases or only one or two. Each of the mesophases "melts" to form an isotropic liquid mixture. Such mixtures typically contain micellar aggregates. It seems probable that those micellar aggregates bear some structural resemblance to those of the corresponding mesophase. Thus the cylindrical mesophase would give rise, on melting, to rod shaped micelles while the lamellar phase would give rise to disks. The micellar shape, like the symmetry of the mesophase, is largely dictated by the relative proportions of water and the amphiphile. Paralleling the sequence of liquid-crystal mesophases, one thus anticipates the sequence of micellar geometries: spherical, rod and disk.

It is noted that amphiphiles that possess a polar head group that is small relative to the alkyl chain length tend to be incapable of forming spherical micelles presumably due to their inability to provide a complete hydrophilic outer layer.

Isotropic liquid mixtures

Premicellar mixtures

At infinite dilution, an amphiphilic solute disrupts the normal pattern of self-aggregation of the water molecules in its immediate vicinity to form an aqueous solvent cosphere. The respective effects of the two parts of the amphiphile are significantly different. The non-polar alkyl group is generally described as promoting ice-like aggregation, with significant decreases in both the partial molar enthalpy and entropy of the solvent. The ether groups and the hydroxyl group are capable of hydrogen bonding with the solvating water. Thus, it is considered that the interactions between the polar head group and water are less disruptive of the solvent structure and may even diminish the extent of ice-like aggregation in its vicinity.

Solute–solute interactions can be separated into two types, aggregative and non-aggregative. At very low amphiphile concentrations, the dominant interactions are those between the aqueous cospheres of monomeric solutes. At higher concentrations, the phenomenon of hydrophobic aggregation is presumed to become important. This results in the formation of labile clusters in which there is a tendency towards enhanced contact between pairs of alkyl groups and diminished contact between the alkyl groups and water.

Critical micelle concentrations

Two different theoretical approaches have been used to explain the significance of a c.m.c.

In the mass action approach [3] the micelle is treated rather like a polymeric species. A monomer–polymer equilibrium is envisaged:

$$n\mathrm{A} \leftrightarrow \mathrm{A}_n$$

The nature of this type of equilibrium is such that the fraction of the amphiphile molecules, to be found in micellar aggregates, remains quite small until the total amphiphile concentration approaches the c.m.c. At that point, the equilibrium swings rapidly to the micelle side over a very narrow concentration range. This approach does not preclude the transition, with increasing amphiphile concentration, from monomer to micelle taking place by some type of stepwise aggregation process. Such a process would necessarily lead smoothly to micelle formation. At concentrations in excess of the c.m.c., the conversion to micellar aggregates is considered to be essentially complete.

The pseudophase approach [4] treats the micellar aggregates as constituting a separate dispersed phase. In that sense, the c.m.c. is the solubility, in water, of that dispersed phase. At concentrations in excess of the c.m.c., an equilibrium exists between the dispersed phase and its saturated solution. As the mole fraction of water diminishes, the equilibrium would be expected to shift fairly quickly, but not precipitously, to the micellar side. The saturated solution may well be considered to contain labile amphiphile clusters.

Micellar transformations

Light scattering and several types of relaxation study have been employed to investigate the sensitivity of micellar geometry to both amphiphile concentration and temperature. It is evident that some significant variations in shape and size do exist. Interpretation of the data is made difficult by an apparent tendency for some micelles to cluster together without fusion.

Thus, above the c.m.c. there is both a transfer to amphiphile molecules from the saturated solution to the micellar dispersed phase and a modification of the micellar geometry. Even if the volume fraction of the dispersed phase is small, there may also be micelle clustering taking place. As the concentration increases, the dominant micellar geometry becomes that which is described as disk-shaped (pseudolamellar). Dominance by pseudolamellar aggregation appears to persist over fairly extensive ranges of composition.

Organic-rich mixtures

A few of the amphiphile plus water systems have been observed to form an additional organic-rich hexagonal liquid-crystal mesophase. This is described as consisting of cylinders of water encased by the amphiphiles in an inverted micellar arrangement. The ability of the amphiphile to engage in this type of aggregation is presumed to depend upon the relative sizes of the polar head group and the alkyl chain. A relatively small polar group would appear to be favorable.

In the pure liquid amphiphiles, there is presumably some tendency towards labile cluster formation with adhesion between the polar head groups, particularly when hydrogen bonding is possible. As a solute species, water would be expected to exhibit a marked tendency towards preferential occupation of the sites closest to the polar heads, thereby enhancing the stability of the clusters.

As the water content increases, aqueous self-aggregation must inevitably become an important factor and introduce a tendency towards some type of stable or metastable pattern of inverse micellar aggregation. As the water mole fraction rises, the geometry of such aggregates would be expected to vary in much the same way as does that of the micellar aggregates with increasing amphiphile mole fraction. Ultimately, the water content would be high enough for a lamellar or pseudolamellar mode of aggregation to be dominant.

SMALLER AMPHIPHILE PLUS WATER SYSTEMS

In discussing the aggregative tendencies of smaller amphiphiles in their aqueous mixtures we shall focus upon the nature of the evidence that is furnished by the composition dependence of their thermodynamic properties. Other types of physicochemical study have been carried out and we shall mention some of the findings in the ensuing discussion.

In the foregoing section, we mentioned the plausible assumption that there is a parallel between the variation in micellar geometry with increasing amphiphile concentration and the sequence of liquid-crystal structures. We believe that the composition dependence of the properties of the smaller amphiphile plus water systems can be accounted for in terms of the existence of a sequence of metastable patterns of molecular aggregation which bear varying levels of resemblance to those encountered in both the micelles and the liquid crystals.

While little is known of the thermodynamic properties of the aqueous mixtures of the C_mE_n series with $m \geqslant 6$ and $n \geqslant 3$, there have been numerous published reports of those of micellar ionic amphiphile plus water systems, which are easier to study since their c.m.c. values are somewhat higher. These studies have largely been devoted to water-rich mixtures, rarely extending far above the c.m.c. Particular attention has been paid to the apparent molar isobaric heat capacities of the amphiphile, as a function of molar concentration. A dramatic change in the slope $(\delta(C_p^E/X_A)/\delta m_A)_T$ is observed at the c.m.c. [5]. Similar observations have been made for other apparent molar properties of the amphiphile.

Some years ago, attention was drawn to the fact that the apparent molar isobaric heat capacities of 2-butoxyethanol plus water exhibit the same type of composition dependence as do the micellar systems [6]. Since that time there have been a number of surface property and relaxation studies of the C_4E_1 plus water system, which were designed to explore the extent to which the amphiphile exhibits typical surfactant characteristics [7]. While none of the investigators has gone so far as to claim that C_4E_1 is capable of forming stable micelles, in the accepted sense of the word, there is a general concensus that it does form highly structured aggregates that warrant the use of terms such as "borderline surfactant" and "pseudomicellar".

It is evident that the C_4E_1 plus water system possesses some type of analog of a c.m.c. Like a c.m.c., its value decreases with increasing temperature [8]. Its value, at 25 °C, is in the vicinity of 1.0 M which is the value predicted by eqn. (1) for $m = 4$.

Pseudomicellar systems appear to be characterised by abrupt changes, if not outright discontinuities, in the mole fraction derivatives of the excess molar properties (dQ^E/dX_A) at their c.m.c. analogs. This type of behavior has also been noted for the 1-propanol plus water [9], 2-propanol plus water and *t*-butanol plus water systems [10]. It is interesting to note that the c.m.c. analog of the 1-propanol plus water system is not greatly in excess of the 3.1 M predicted from eqn. (1) for $m = 3$.

There are other features of the composition dependence of the thermodynamic properties of amphiphile plus water systems that are worthy of attention and may be presumed to be indicative of the nature of the varying patterns of molecular aggregation.

In ref. 9, attention was drawn to the fact that a plot of $(\mathrm{d}V^{\mathrm{E}}/\mathrm{d}X_{\mathrm{A}})$ for the 1-propanol plus water system appears to possess four fairly distinct composition segments. A similar situation is found for the derivative curves of other excess molar properties for a number of other binary aqueous systems.

We have demonstrated that it is a relatively simple matter to devise a set of model equations, one for each composition segment, that collectively do an acceptable job of fitting excess molar property data [11]. Since the four-segment composition model was first introduced [12], several different versions of its sets of equations have been proposed [13].

The model is essentially empirical. Our primary objective was to find a set of equations which can provide faithful replicas of the data sets that they are used to analyze. Some of the changes that we have made to the individual equations have been prompted by the desire to improve the quality of fit for data sets which exhibit a dramatically varying composition dependence. In that context, the major concern is with finding the appropriate level of flexibility for each segment. Other changes have been motivated by the intention of formulating the equations in a manner that permits us to designate some kind of physical significance to each of the independent variables.

Our efforts have led us to explore the use of both trigonometric and exponential functions. Closer scrutiny has led us to the conclusion that we can do as well or better with polynomial functions. One advantage of using polynomial functions is that the flexibility of the individual equations can easily be varied. The data sets for some of the systems can be reasonably well reproduced with relatively inflexible equations; those for other systems require greater model flexibility.

In the following sections, we shall discuss the rationale behind the manner in which we have chosen to reformulate our model equations and offer some suggestions as to the significance of the parameters.

SELECTION OF MODEL EQUATIONS

The equations to be presented here are those that are designed to fit excess molar property data. It is a relatively simple matter to adapt them for use with apparent molar quantities.

The water-rich (premicellar) segment, $0 \leqslant X_A \leqslant X_1$

The segment junction X_1 is an analog of the c.m.c. For most of the data sets, excess molar property data, Q^E, can be adequately represented by a cubic function of the mole fraction of the amphiphile, X_A. For a few others, it appeared that a quartic function might be capable of furnishing a better quality of fit. We were interested in exploring the relative merits of those two alternatives.

Cubic dependence upon the amphiphile mole fraction may be expressed in the general form

$$Q^E = a_w X_A + b_w X_A^2 + c_w X_A^3 \tag{2}$$

We have chosen to rearrange this equation to the form

$$Q^E = a_w X_A(1 - y^2) + b_w X_A^2(1 - y) + a_1 X_A y^2 \tag{3a}$$

where $y = X_A/X_1$ and a_1 is the apparent excess molar property of the amphiphile at $X_A = X_1$; a_w is the apparent excess molar property of the amphiphile at infinite dilution and b_w is a pair interaction contribution for very low amphiphile concentrations.

We note that the significance placed upon estimates of a_1 depends upon whether one adheres to the mass-action or pseudophase concept of c.m.c.s.

If Q^E is chosen to have quartic mole fraction dependence, one possible analog to eqn. (3a) is

$$Q^E = a_w X_A(1 - y^2) + b_w X_A^2(1 - y^2) + a_1 X_A y^2 + b_1 X_A^2 y^2 \tag{3b}$$

where it is now $a_1 = b_1 X_1$ which is the apparent excess molar property at $X_A = X_1$.

The pseudolamellar segment, $X_2 \leqslant X_A \leqslant X_3$

It is across this composition range that dQ^E/dX_A has been observed in many instances to possess an obviously linear dependence on X_A. This implies that Q^E may be represented by a quadratic function.

We have chosen to express that quadratic dependence by

$$Q^E = q_w(1 - X_A) + q_A X_A + b_L X_A(1 - X_A) \tag{4}$$

where q_w is the excess molar property of water in some kind of hypothetical standard state and is presumed to reflect the effects of the differences between the self-aggregative patterns of water in pseudolamellar aggregation and those of the pure bulk liquid; q_A is the analogous property of the amphiphile; b_L evidently reflects, in some way, the effects of varying the composition upon the nature of the interactions between aggregates of the two species.

The organic-rich segment, $X_3 \leqslant X_A \leqslant 1$

The excess molar properties of mixtures that fall within this range of compositions appear to be adequately represented by a cubic function of the water mole fraction X_w:

$$Q^E = a_A X_w + b_A X_w^2 + c_A X_w^3 \tag{5}$$

The requirement that Q^E must be continuous at $X_A = X_3$ enables us to eliminate c_A as an independent variable. It was found to be appropriate to impose the additional constraint that dQ^E/dX_w is continuous at X_3, which permits us to eliminate b_A. This leads to the equation

$$\begin{aligned} Q^E = {} & q_w X_w (2y - y^2) + q_A [y^2(1 + 2X_3) - y^3(1 + X_3)] \\ & + b_L X_w [y(1 + X_3) - y^2] + a_A X_w (1 - y)^2 \end{aligned} \tag{6}$$

where, on this occasion, $y = X_w/(1 - X_3)$. The quantity a_A is the excess apparent molar volume of water at infinite dilution in the organic solvent.

The secondary (transitional) segment, $X_1 \leqslant X_A \leqslant X_2$

This segment spans the range from the c.m.c. (or its analog) to that composition at which pseudolamellar aggregation becomes dominant. It is this segment that has given us the most difficulty in terms of assigning a satisfactory mole fraction dependence to its excess molar properties.

Cubic dependence appeared to provide a reasonable representation for the excess molar properties of the aqueous mixtures of methyl and ethyl species, but greater flexibility seemed to be required to obtain a satisfactory fit for those of amphiphilic species with longer alkyl chains.

Obviously Q^E must be continuous at $X_A = X_2$. From eqn. (4) we can set its value, at that segment junction, equal to

$$Z_2 = q_w(1 - X_2) + q_A X_2 + b_L (X_2 - X_2^2) \tag{7}$$

For the secondary segment, we have chosen to write the cubic equation in the form

$$Q^E = Z_2 + a_s f_s + b_s f_s^2 + c_s f_s^3 \tag{8}$$

where $f_s = (X_2 - X_A)/(X_2 - X_1)$.

Q^E must also be continuous at $X_A = X_1$. From eqns. (3a) and (3b), we can set its value, at that composition, equal to either

$$Z_1 = a_1 X_1 \tag{9a}$$

or

$$Z_1 = a_1 X_1 + b_1 X_1^2 \tag{9b}$$

Thus

$$Z_1 = Z_2 + a_s + b_s + c_s \tag{10}$$

which permits us to eliminate c_s as an independent variable.

Equation (8) thus becomes

$$Q^E = Z_1 f_s^3 + Z_2(1 - f_s^3) + a_s(f_s - f_s^3) + b_s(f_s^2 - f_s^3) \tag{11a}$$

The analogous equation, when Q^E is assigned quartic mole fraction dependence is

$$Q^E = Z_1 f_s^4 + Z_2(1 - f_s^4) + a_s(f_s - f_s^4) + b_s(f_s^2 - f_s^4) + c_s(f_s^3 - f_s^4) \tag{11b}$$

We note that the first two terms, of either eqn. (11a) or (11b), suggest a fairly quick transition from the saturated solution, as represented by $Q^E = Z_1$, to the pseudolamellar aggregation, represented by $Q^E = Z_2$.

Equations (11a) and (11b) do not require $\mathrm{d}Q^E/\mathrm{d}X_A$ to be continuous at either $X_A = X_1$ or $X_A = X_2$. It has been our experience that to constrain that derivative function to be continuous at $X_A = X_1$ makes the model far too inflexible and adversely affects the quality of fit. However, that same constraint at $X_A = X_2$ is certainly worthy of consideration.

From eqn. (4), we can set the derivative at $X_A = X_2$ equal to

$$Y_2 = -q_w + q_A + b_L(1 - 2X_2) \tag{12}$$

Differentiating either eqn. (11a) or (11b) leads to

$$Y_2 = -a_s/(X_2 - X_1) \tag{13}$$

Thus a_s ceases to be an independent variable and eqns. (11a) and (11b) become respectively

$$Q^E = Z_1 f_s^3 + Z_2(1 - f_s^3) - Y_2(X_2 - X_1)(f_s - f_s^3) + b_s(f_s^2 - f_s^3) \tag{14a}$$

and

$$Q^E = Z_1 f_s^4 + Z_2(1 - f_s^4) - Y_2(X_2 - X_1)(f_s - f_s^4)$$
$$+ b_s(f_s^2 - f_s^4) + c_s(f_s^3 - f_s^4) \tag{14b}$$

Either eqn. (3a) or (3b) may be combined with any one of the four eqns. (11a), (11b), (14a) or (14b) to give a selection of eight different models. Equations (5) and (6) are common to all eight models. The number of parameters ranges from eight (eqns. (3a) and (14a)) to eleven (eqns. (3b) and (11b)). In addition to the task of optimising the model parameters, it is also necessary to determine optimal values for the segment junction mole fractions X_1, X_2 and X_3.

ANALYTIC STRATEGY

For a given combination of X_1, X_2 and X_3 values, it is a relatively simple matter to write a linear least-squares computer program to optimise the model parameters. Finding the "best" set of segment junction mole fractions is far less straightforward. Of several different approaches that have been tried, a "simplex" procedure appears to be the most satisfactory. This involves parameter optimisation at each of a substantial number of segment junction combinations. The optimum segment junction combination represents a local minimum of the standard deviation, within the space of X_1, X_2 and X_3. For a given data set and a specific model, several such local minima may well exist. By seeking out estimates of the "best" combinations of segment junction values for each of the eight models and for several different data sets for each system, it proved to be possible to arrive at a fairly well-defined representative set for each of the binary systems that we have studied.

In comparing the standard deviations obtained for the different versions of the model, it became apparent that, for the majority of the data sets analysed, substantially better fits were obtained using those versions in which Q^E is represented, in the secondary segment, by a quartic function of X_A than by a cubic function. We note that for the distinction between the two models to be meaningful, there needs to be a sufficient number of data points in that segment.

Analyses were carried out upon a number of data sets taken from the literature, for the three systems: methanol (MeOH) plus water, ethanol (EtOH) plus water and 1-propanol (1-PrOH) plus water. Our results indicate that for these systems there is no significant improvement in the standard deviation σ when a cubic function of X_A is replaced by a quartic function to represent Q^E in the water-rich segment. Such modest improvements, as were found, were largely limited to data sets for the 1-PrOH plus water system.

For the MeOH plus water system, no significant improvements in the standard deviations were discerned when the constraint that dQ^E/dX_A should be continuous at the segment junction X_2 was removed. Somewhat more substantial improvements were obtained when that constraint was removed for the EtOH plus water and, to a lesser extent, the 1-PrOH plus water data sets. The improvements were considered to be too small to be statistically significant and we chose to confine our attention to the constrained model, which we shall refer to as model CQ9.

RESULTS AND DISCUSSION

Excess molar volume data for all three systems were taken from ref. 14. Excess molar isobaric heat capacities were taken from ref. 15. Excess molar $K_s = (-(\delta V^E/\delta p)_s)$ values were obtained from the ultrasonic speed data of refs. 16 (MeOH + H_2O) and 17 (EtOH + H_2O and 1-PrOH + H_2O).

We decided that, of the eight models, that which required a cubic function of X_A for the water-rich segment, a quartic function of X_A for the secondary segment and continuity of (dQ^E/dX_A) at $X_A = X_2$ was the best choice. The

TABLE 1

Best representative segment junction compositions for three alcohol plus water systems

System	X_1	X_2	X_3
MeOH + H_2O	0.130	0.425	0.625
EtOH + H_2O	0.100	0.375	0.705
1-PrOH + H_2O	0.062	0.255	0.735

best representative segment junction compositions for the three systems, using that model, are shown in Table 1. We note that the X_1 values decrease with increasing alkyl chain length. We further note that the value of $X_1 = 0.062$ for the 1-PrOH plus water is quite close to that predicted, by eqn. (1), for the c.m.c. of species of the type C_3E_n. There is no suggestion that either methanol or ethanol could form anything as highly structured as micellar aggregates. That does not rule out, however, non-trivial levels of clustering brought about by hydrophobic aggregation. We are inclined to think of the X_1 values for their binary aqueous systems as being the compositions at which all of the water has become closely involved with the amphiphile and, as such, has ceased to be a solvent in the customary sense of that term.

Both X_2 and X_3 vary systematically with increasing alkyl chain length, giving rise to significant broadening of the mole fraction range of the "pseudolamellar" segment.

In Tables 2–4, we have listed the results of our analyses of the excess molar volume data.

For some of the optimised model parameters estimated for the excess molar volume data, there are systematic variations of their values with temperature. The a_w values, which are negative for all three systems, decrease with increasing temperature. The b_w values, which are also negative for all three systems, increase uniformly with increasing temperature. The a_1 values for MeOH plus water decrease with increasing temperature while those for the EtOH plus water and 1-PrOH plus water systems show systematic increases with increasing temperature.

The parameter a_s does not appear as an independent variable in model CQ9, but its value can be calculated from eqns. (12) and (13). The b_s values for the three systems are seen to be comparable in magnitude and relatively insensitive to changes in temperature. There is no systematic variation with temperature for the parameter c_s.

The q_w values for the excess molar volumes are negative for all three systems. For MeOH plus water there is no systematic temperature dependence. For EtOH plus water and 1-PrOH plus water the values increase with increasing temperature. The q_A values for MeOH plus water are positive and show a systematic decrease with increasing temperature. The q_A values

TABLE 2

Four-segment model analysis of excess molar volumes [a] for the methanol plus water system using model CQ9

Parameter	15 °C	20 °C	25 °C	30 °C	35 °C
a_w	−2.133	−2.338	−2.527	−2.709	−2.878
b_w	−13.09	−10.99	−9.64	−8.22	−6.98
a_1	−3.080	−3.142	−3.170	−3.228	−3.283
b_s	0.361	0.341	0.427	0.375	0.368
c_s	0.121	0.154	−0.028	0.064	0.067
q_w	−0.028	−0.030	−0.057	−0.032	−0.027
q_A	0.077	0.052	0.017	0.016	0.008
b_L	−4.058	−4.024	−3.930	−4.016	−4.042
a_A	−3.618	−3.718	−3.843	−3.936	−4.037
σ_1	0.287	0.149	0.254	0.129	0.126
σ_2	0.455	0.825	0.619	0.253	0.110
σ_3	1.786	0.533	0.675	0.434	0.164
σ_4	0.584	0.599	1.164	0.744	0.174
σ	0.758	0.561	0.631	0.481	0.166

[a] Units: V^E, cm^3 mol^{-1}; $\sigma(V^E)$, mm^3 mol^{-1}.

TABLE 3

Four-segment model analysis of excess molar volumes [a] for the ethanol plus water system using model CQ9

Parameter	15 °C	20 °C	25 °C	30 °C	35 °C
a_w	−2.993	−3.278	−3.554	−3.825	−4.045
b_w	−41.91	−37.54	−32.83	−28.12	−24.74
a_1	−5.244	−5.191	−5.158	−5.114	−5.079
b_s	0.329	0.300	0.376	0.379	0.363
c_s	−0.069	−0.033	−0.168	−0.181	−0.144
q_w	−0.621	−0.577	−0.575	−0.557	−0.536
q_A	−0.094	−0.085	−0.095	−0.098	−0.091
b_L	−2.962	−3.015	−2.933	−2.903	−2.899
a_a	−4.301	−4.249	−4.225	−4.147	−4.139
σ_1	0.292	0.260	0.264	0.224	0.294
σ_2	0.899	0.580	0.476	0.617	0.365
σ_3	0.365	0.484	0.734	0.545	0.527
σ_4	0.151	0.734	0.388	0.751	0.573
σ	0.516	0.572	0.502	0.589	0.496

[a] Units: V^E, cm^3 mol^{-1}; $\sigma(V^E)$ mm^3 mol^{-1}.

TABLE 4

Four-segment model analysis of excess molar volumes [a] for the 1-propanol plus water using model CQ9

Parameter	15 °C	20 °C	25 °C	30 °C	35 °C
a_w	−3.819	−4.136	−4.371	−4.591	−4.766
b_w	−83.16	−72.15	−65.03	−54.81	−49.11
a_1	−6.072	−5.883	−5.689	−5.401	−5.329
b_s	0.282	0.283	0.250	0.276	0.283
c_s	−0.512	−0.488	−0.393	−0.431	−0.440
q_w	−0.435	−0.415	−0.394	−0.385	−0.371
q_A	−0.105	−0.103	−0.092	−0.076	−0.061
b_L	−1.695	−1.635	−1.633	−1.575	−1.545
a_A	−3.193	−3.077	−2.989	−2.766	−2.628
σ_1	0.285	0.524	0.509	0.489	0.403
σ_2	1.255	1.225	1.207	1.503	1.348
σ_3	0.767	1.300	1.274	1.039	1.286
σ_4	1.878	1.202	1.121	0.878	0.449
σ	1.177	1.181	1.162	1.145	1.081

[a] Units: V^E, cm^3 mol^{-1}; $\sigma(V^E)$, mm^3 mol^{-1}.

for the other two systems are negative. There is little or no variation of q_A with temperature for the EtOH plus water system but an increase with increasing temperature for 1-PrOH plus water. The b_L values for all three systems are negative. The only systematic variation with temperature is the increase with increasing temperature for the 1-PrOH plus water system.

The excess molar volume a_A values for all three systems are negative. Their values decrease with increasing temperature for MeOH plus water but increase with increasing temperature for both EtOH plus water and 1-PrOH plus water.

In order to compare more precisely the temperature dependence of the excess molar volumes of these three systems, we have estimated values of the quantity $(\delta V^E/\delta T)_p$. Since each set of V^E data was reported at a different set of mole fractions, it was necessary to make use of an interpolation scheme to provide estimates at a common set of compositions. We have adopted, for that purpose, two different strategies. The more objective strategy is to use a cubic spline procedure. This provides values for V^E and dV^E/dX_A at each of a set of rounded mole fractions. It has been our experience that this approach works reasonably well except in the vicinity of the segment junction $X_A = X_1$, if there are radical changes in the slope dV^E/dX_A. The alternative strategy is to estimate the interpolated values using optimised four-segment model equations.

Estimation of the quantity $A_p^E = (\delta V^E/\delta T)_p$ is then based upon the assumption that V^E, at a specific composition, can be represented by a

TABLE 5

Temperature-smoothed excess molar volumes [a]

Parameter	MeOH		EtOH		1-PrOH	
	I [b]	CQ9 [c]	I [b]	CQ9 [c]	I [b]	CQ9 [c]
a_w	−2.529	−2.528	−3.558	−3.558	−4.376	−4.382
b_w	−9.49	−9.55	−32.81	−32.75	−63.81	−63.61
a_1	−3.181	−3.178	−5.144	−5.153	−5.683	−5.686
gb_s	0.387	0.390	0.333	0.356	0.293	0.269
c_s	0.058	0.045	−0.089	−0.137	−0.496	−0.435
q_w	−0.043	−0.044	−0.567	−0.569	−0.397	−0.397
q_A	0.024	−0.093	−0.093	−0.093	−0.092	−0.092
b_L	−3.975	−3.971	−2.957	−2.951	−1.615	−1.616
a_A	−3.832	−3.835	−4.198	−4.206	−2.962	−2.956
σ	0.216	0	0.330	0	0.906	0

[a] Units: V^E, cm^3 mol^{-1}; $\sigma(V^E)$, mm^3 mol^{-1}.
[b] Cubic spline interpolated version.
[c] Model version.

quadratic function of the temperature. It is preferable to have data at more than the minimum requirement of three temperatures. In that case, in addition to the estimates of A_p^E, one obtains temperature smoothed estimates of V^E. Both estimates correspond to a temperature of 25 °C. The results of

TABLE 6

Excess molar $(\delta V/\delta T)_p$ [a]

Parameter	MeOH		EtOH		1-PrOH	
	I [b]	CQ9 [c]	I [b]	CQ9 [c]	I [b]	CQ9 [c]
a_w	−37.16	−37.23	−53.10	−53.01	−57.30	−47.13
b_w	301.2	299.7	883.0	875.0	2437	1718
a_1	−10.10	−9.87	7.74	8.15	31.55	37.59
b_s	0.81	0.96	3.02	2.96	1.75	0.15
c_s	−3.38	−3.97	−6.44	−5.94	0.65	3.40
q_w	−0.11	0.01	3.90	3.81	3.07	3.16
q_A	−3.53	−3.46	−0.03	−0.11	2.20	2.32
b_L	1.14	0.78	4.39	4.75	7.65	7.25
a_A	−21.19	−21.16	7.91	8.52	28.75	28.81
σ	1.17	0	3.12	0	7.05	0

[a] Units: A_p^E, mm^3 K^{-1} mol^{-1}; $\sigma(A_p^E)$, 10^{-2} mm^3 K^{-1} mol^{-1}.
[b] Cubic spline interpolated version.
[c] Model version.

TABLE 7

Excess molar isobaric heat capacities and excess molar K_s $(-(\delta V_m^E/\delta p)_s)$ values obtained using model CQ9

Parameter	C_p^E (J K^{-1} mol^{-1})			K_s^E (mm^3 MPa^{-1} mol^{-1})		
	MeOH	EtOH	1-PrOH	MeOH	EtOH	1-PrOH
a_w	77.51	148.9	202.2	−37.76	−56.85	−66.88
b_w	−220.8	−96.22	615.3	−9.93	−19.01	−76.65
a_1	47.30	121.4	200.3	−36.22	−52.18	−54.70
b_s	0.35	−2.49	−1.23	3.13	1.84	1.27
c_s	0.80	13.12	8.25	0.31	−0.22	−1.02
q_w	8.73	16.06	12.06	−0.10	−3.59	−2.86
q_A	0.06	2.28	2.29	−1.61	−1.74	−1.02
b_L	0.62	32.22	20.81	−39.31	−29.98	−17.76
a_A	6.35	13.12	47.58	−47.14	−45.21	−30.00
$\sigma 1$	1.93	1.86	5.68	0.259	0.451	0.152
$\sigma 2$	4.17	6.63	7.65	0.497	1.397	0.234
$\sigma 3$	1.66	10.27	10.71	0.833	5.542	0.751
$\sigma 4$	6.25	8.83	9.08	0.407	0.773	0.464
$10^2\sigma$	4.66	8.34	9.84	0.695	1.928	0.5

our calculations are set out in Tables 5 and 6. Results are also presented, in Table 7, for the excess molar isobaric heat capacities and for $-(\delta V_m^E/\delta p)_s$.

For the temperature-smoothed excess molar volumes, the three parameters a_w, b_w and a_1 are all negative and become more negative with increasing alkyl chain length. The differences between the cubic spline interpolated and model interpolated versions of V^E are evidently quite small. The apparent molar volumes of the alkanols, at infinite dilution, are respectively 38.22 (MeOH), 55.13 (EtOH) and 70.78 cm^3 mol^{-1} (1-PrOH). The CH_2 increments of 16.91 and 15.65 cm^3 mol^{-1} correspond to substitution of a hydrogen by a CH_3 group at the α and β carbon atoms respectively. That the two increments should be roughly equal is scarcely surprising.

The parameter b_w is associated with the effects of aqueous cosphere overlap. One reasonable explanation for the manner in which it varies with alkyl chain length is that the cosphere overlap tends to decrease the extent of the promotion of ice-like aggregation in the solvent cage by the hydrophobic moieties of the amphiphiles.

The apparent molar volumes at $X_A = X_1$ are 37.57 (MeOH), 53.54 (EtOH) and 69.48 cm^3 mol^{-1} (1 − PrOH). In this instance, the CH_2 increments are 15.97 and 15.94 cm^3 mol^{-1}. It is not obvious how one should attempt to appraise the optimised values of the parameter a_1.

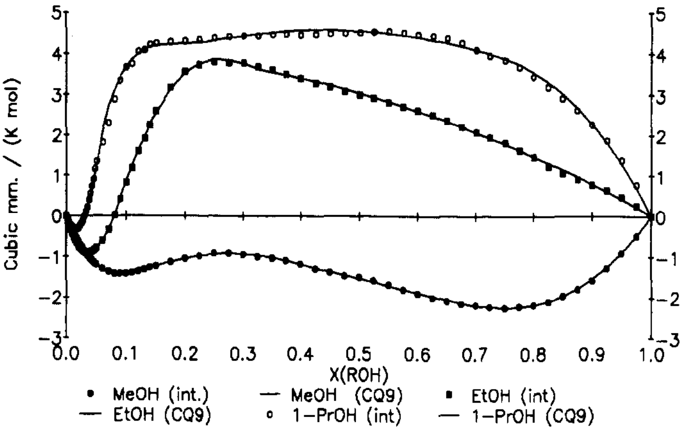

Fig. 1. Excess molar $(\delta V^E/\delta T)_p$ for some alkanol plus water systems at 25 °C (mm^3 K^{-1} mol^{-1}). Values obtained from cubic splines interpolation of excess molar volume data are represented by open circles (MeOH + H_2O), closed squares (EtOH + H_2O) and closed circles (1-PrOH + H_2O). The corresponding values obtained from model equation fitting of the excess molar volume data are represented by continuous curves.

There is a modest decrease in the b_s values with increasing alkyl chain length and a more substantial one for the c_s values. It is gratifying to note that there is a good level of internal consistency in the estimates of those two parameters.

The alkyl chain length dependence of the other parameters follows no logical sequence except for the case of b_L.

There are some substantial differences between the respective optimised model parameters for the cubic spline and model interpolated versions of A_p^E for 1-PrOH plus water. The two versions of A_p^E for each of the three systems are shown in Fig. 1. The cubic spline versions are shown as individual points, while the model versions are shown as continuous curves. Of the two versions of A_p^E for 1-PrOH plus water, we are inclined to have more faith in that derived from the model interpolated excess molar volume data.

We reported earlier [13] that the a_w values of MeOEtOH plus water, EtOEtOH plus water and BuOEtOH plus water follow a similar sequence of an initial decrease and then an increase, as the alkyl chain is extended. Insofar as one can compare the results of the analyses of this paper with those of ref. 13, which made use of a different set of model equations, there are gratifying similarities between the way in which the optimised model parameter values for A_p^E, C_p^E and K_s^E vary with increasing alkyl chain length in the ROH plus water and ROEtOH plus water systems.

There is no question but that the four-segment model is an effective data fitting tool. The version described here is generally more effective than any of its predecessors. What is perhaps questionable is the extent of its utility as an interpretive tool. Some of its parameters have appeared in other models, specifically a_w, b_w and a_A. Their roles are fairly clearly defined. The three parameters that characterise the pseudolamellar segment have been discussed in each of the preceding papers by the current authors. The grey area is the secondary (transitional) segment and the parameters of the equations that are employed to fit the data of that segment. We are inclined to believe that the new way that we have formulated the equations representing the composition dependence of the excess molar properties of mixtures, in that segment, are a significant improvement upon the previous versions.

Before any attempt can be made to interpret the roles played by the parameters b_s and c_s it will be necessary to use the same analytic strategy for data for as many other related systems as possible.

SUMMARY

In the course of this paper we have attempted to justify the segmented composition model approach to the analysis of thermodynamic data for amphiphile plus water systems, on the basis of the existence of labile schemes of molecular aggregation that mimic the well-characterised stable structures of true detergent plus water systems. We have also taken a fresh look at the various options for quantifying the four-segment model.

For the available data for the three systems MeOH plus water, EtOH plus water and 1-PrOH plus water, the model has proved to be a highly satisfactory curve fitting tool. For all of the excess molar property data sets of all three systems, the water-rich segment is adequately represented by a cubic function of alkanol mole fraction. For the data of the secondary (transitional) segment it appears to be necessary to employ a quartic function of mole fraction. In a previous paper [18], a cubic function was employed, for many of the same data sets, with less gratifying results.

It is our intention to carry out similar sequences of analyses upon excess molar property data for other C_mE_n plus water systems with the object of establishing the nature of such trends as exist which can be used to correlate the parameter values of the model equations with molecular structural features. We have started out with the alkanol plus water data because of its excellent quality and the distinct changes which appear in the data profiles as the alkyl chain is extended.

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