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Partial excess molar properties of water in amphiphile + water systems

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Abstract

An account is given of the manner in which plots, against mole fraction, of the partial excess molar properties of water in amphiphile + water systems provide a sensitive means of identifying composition ranges over which significant variations take place in the prevalent modes of molecular aggregation. Examples are provided of instances where one may explore the effects of varying the alkyl chain lengths and polar head group sizes in the aqueous mixtures of alkyl poly(ethylene glycol) monoethers.

INTRODUCTION

Thermodynamic studies of relatively low molecular weight amphiphile + water systems have been carried out, and their results recorded in the literature, for over a century. For much of that time, the authors were content to draw attention to such intriguing aspects of the composition dependence of the thermodynamic properties of these systems as they might happen to possess, without concerning themselves with any consideration of the possible nature of the molecular scale origins of such properties. It is only relatively recently that attempts have been made to correlate the composition dependence of thermodynamic data with other sources of information about these systems, in order to try to gain further insight into the nature of their various schemes of molecular aggregation.

Of the research activities that have provided an impetus to the provision of new interpretations of the composition dependence of the thermodynamic properties of amphiphile + water mixtures, investigations of the phase and microphase characteristics of detergent + water systems have been of special significance. If one were obliged to pick out one particular observation that particularly polarised the interpretive aspects of the thermodynamic studies of simple amphiphile + water systems, it would probably be that the apparent molar isobaric heat capacities of 2-butoxyethanol

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in its aqueous mixtures bear a striking similarity, in their composition dependence at relatively low concentrations, to those of surfactant species in the vicinity of their critical micelle concentrations [1]. The observation is intriguing because there was, and still remains, no evidence that 2-butoxyethanol is capable of forming stable micellar aggregates.

That observation motivated quite a number of laboratories to look for other types of evidence of parallels between the modes of molecular aggregation in the simpler amphiphile + water systems and those which have been fairly well characterised for detergent (or surfactant) + water systems. Thermodynamic studies do not directly address questions related to molecular scale features. What they and other investigations of bulk properties may furnish are striking features of composition dependence that might reasonably be associated with important changes in the patterns of molecular aggregation. It has been demonstrated that several of the macroscopic properties of detergent + water systems exhibit substantial changes in their composition dependence at the critical micelle concentrations [2].

Detergent + water systems have been found to exhibit significant changes in their patterns of molecular aggregation as their compositions change other than that which occurs at the critical micelle concentration [3]. The question may legitimately be posed as to whether any of the simpler amphiphile + water systems also furnish evidence of more than the one significant variation in their patterns of aggregation. Such evidence would have to be derived directly from the data in some appropriate graphical format, as opposed to merely satisfying some type of statistical test of a conceptual model. Obviously, any model that is employed to account for such variations in the scheme of aggregation must then be able to match the graphical evidence for them.

One of the difficulties that faces the solution thermodynamicist is that of finding appropriate ways to reduce the data to a form which clearly and reliably displays, for visual appraisal, the details of composition dependence. Typically, the experiment will yield values for some molar quantity Q_{m} at a number of different amphiphile mole fractions X_{A}. A plot of Q_{m} against X_{A} may well have relatively little visual impact, particularly when there is a substantial difference between the molar properties of the two pure components. That situation can be alleviated to some extent by converting Q_{m} to its excess molar counterpart Q^{E} if the amphiphile is a liquid.

Somewhat more revealing are the plots of the excess apparent molar properties of the amphiphile $\Phi_{Q^{\mathrm{E}}}(=Q^{\mathrm{E}}/X_{\mathrm{A}})$, or the apparent molar property itself $\Phi_{Q}(=\Phi_{Q^{\mathrm{E}}}+Q^{*}_{\mathrm{m.A}}$ where $Q^{*}_{\mathrm{m.A}}$ is the molar property of the pure amphiphile). Such plots are useful for picking out details of the composition dependence of Q_{m} in water rich mixtures. An alternative strategy is to generate plots of the reduced excess molar properties $Q^{\mathrm{E}}_{\mathrm{red}}(=Q^{\mathrm{E}}/X_{\mathrm{A}}X_{\mathrm{W}})$.

The profiles of the reduced and apparent excess molar properties are virtually indistinguishable at low amphiphile mole fractions, but the Q^E_{red} curves possess far more character at higher amphiphile mole fractions. In both of these cases, the data reduction deals with each data entry individually and provides a means of checking on the internal consistency of the data at the extremes of the total composition range.

A more adventurous strategy involves the generation of plots of the excess partial molar quantities. This cannot be achieved on a point by point basis, in view of the need to determine values for dQ^E/dX_A.

The two excess partial molar properties are obtained from the equations

$$Q^E_A = Q^E + (1 - X_A)\, dQ^E/dX_A \tag{1}$$

and

$$Q^E_W = Q^E - X_A\, dQ^E/dX_A \tag{2}$$

The evaluation of the excess partial molar properties calls for objective and reliable estimation of the derivatives of the excess molar quantities with respect to the mole fraction. For most nonaqueous systems this can be accomplished using the Redlich–Kister equation to fit Q^E [4]. For many of the amphiphile + water systems for which thermodynamic data is available, the Redlich–Kister equation has proved to be a rather poor curve-fitting tool and, as a consequence, little faith can be placed in the estimates that it provides of the derivative function. A more objective approach that has been used in this laboratory involves the use of a modified cubic splines approach. The conventional cubic splines procedure furnishes a continuous curve which passes through each of the data points. That is to say, it retains all of the errors of the measurement process. Even if those errors are relatively small, the derivatives of that cubic splines fitted curve are likely to possess substantial irregularities. A modification that appears to be reasonably satisfactory is to have only two cubic splines, which span assymmetrically the composition range around each specific mole fraction value. The splines each cover the range of at least five, and up to 10, data points if the point density is judged to be high enough. They are required to have common values of Q^E and dQ^E/dX_A at the selected mole fraction value, but may have different values for their second and third derivatives. The advantage is that this procedure provides an objective means for estimating the derivatives from local, rather than global, considerations of the composition dependence. It also provides a modest degree of smoothing of the original data. We are by no means confident that the algorithm that we have introduced into the computer program that generates these derivatives is as efficient as it could be, but we do claim that it is reasonably effective. It is appropriate to add that any scheme to generate derivatives requires that the data should have not only a good level of internal consistency but also an adequate point density in those mole fraction

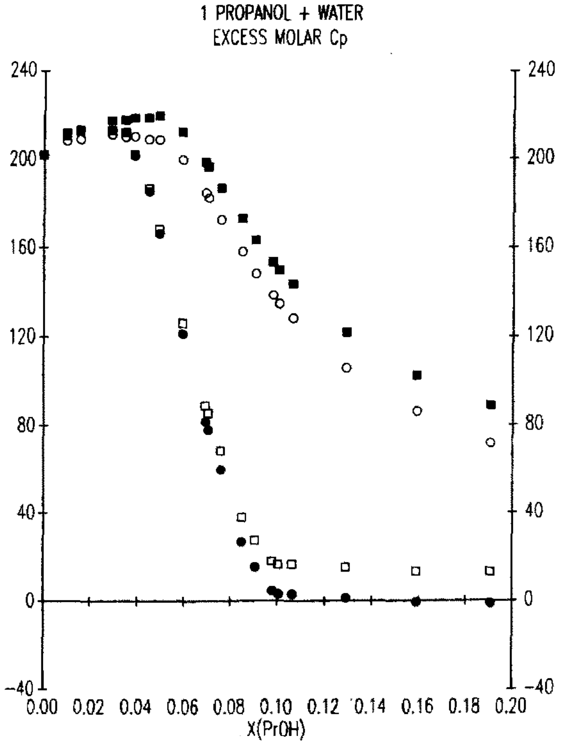

Fig. 1. Properties derived from the excess molar isobaric heat capacities of the 1-PrOH + water system. Units, J K^{-1} mol^{-1}. Key: ○, apparent excess molar C_p; ■, reduced excess molar C_p; ●, dC_p^E/dX_A; □, partial excess molar C_p of 1-PrOH.

ranges where important changes in composition dependence are taking place.

It is interesting to compare the graphical patterns of the partial excess molar properties Q_A^E of the amphiphile, at low amphiphile concentration, with those of the apparent and reduced excess molar properties and also of dQ^E/dX_A. As can be seen in Fig. 1, C_p^E and dC_p^E/dX_A for the 1-PrOH + water system (derived from the data of ref. 5) show substantially more dramatic composition dependence than do either of the other two quantities. At higher amphiphile mole fractions, Q_A^E values tend to vary monotonically to zero. From a purely graphical standpoint, the partial excess molar properties of water are perhaps the more interesting of the two. They have distinctive features at amphiphile rich mixtures, where Q_W^E is particularly sensitive to composition, and also in the water rich region.

In this article, attention will be focussed upon some representative comparative plots of Q_W^E versus X_A for species with common polar head groups and varying alkyl chain lengths, for species with common alkyl chain lengths and varying head group size, and also for isomeric amphiphiles.

The amphiphiles dealt with here are all members of the family of alkoxypoly(ethylene glycol)monoethers. The convenient abbreviation C_mE_n is used for their generic formula $C_mH_{2m+1}(OC_2H_4)_nOH$. The available thermodynamic data span the range from C_1E_0(MeOH) to C_6E_3(HexOEtOEtOEtOH).

The Q_W^E curves have also provided a means of making a critical evaluation of the four segment curve fitting model that was developed in this laboratory. It was found that the most recent set of model equations [6], while appearing to be quite satisfactory for replicating the excess molar property Q^E values, were in many instances too flexible and thus apt to introduce unfortunate artefacts into the dQ^E/dX_A curves and, as a consequence, the plots of the excess partial molar properties of water. It was found that the model could be subjected to additional constraints which had the effect of removing most of those artefacts without serious worsening of the quality of fit.

RESULTS AND DISCUSSION

Figure 2 shows the excess partial molar volumes of water in MeOH +, EtOH + and 1-PrOH + water. One may note that the curve for MeOH + water varies more or less monotonically across the entire composition range. The EtOH + water curve shows somewhat more character but less than does that for 1-PrOH + water. These curves have been derived from the V^E data of Benson and Kiyohara [7].

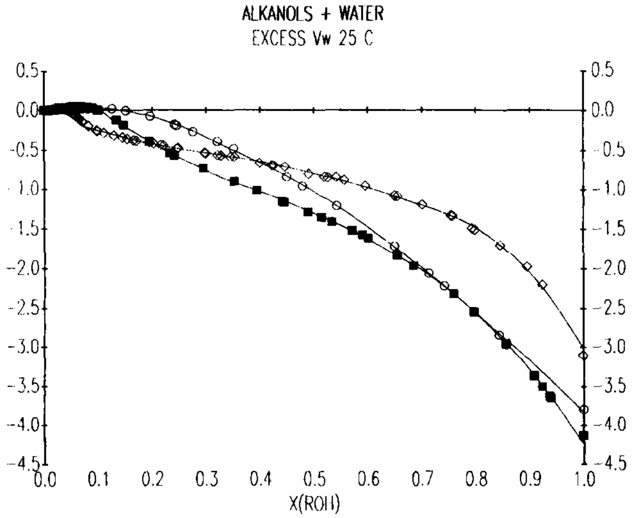

Fig. 2. Partial excess molar volumes of water in alkanol + water systems. Units, $cm^3\ mol^{-1}$. Key: ○, MeOH; ■, EtOH; ◇, 1-PrOH. ———, four segment model versions.

Of substantial interest is the observation that all three systems exhibit positive excess partial molar volumes for water at very low amphiphile concentrations. Some care needs to be exercised in attempting to interpret this phenomenon. It is generally held that, at low amphiphile concentrations, the dominant type of solute–solute interaction involves the overlap of the hydration cospheres of randomly oriented solute pairs. The excess partial molar volumes of water are presumed to reflect the effects of inserting water molecules between such pairs and thus restoring the individual hydration cospheres. Since the increases are more pronounced as the alkyl chain length increases, it appears that the water molecules in that part of the hydration cosphere that is in contact with the hydrophobic tail of the amphiphile are in a less dense state of self-aggregation. This is entirely consistent with the idea that hydrophobic groups promote ice-like self-aggregation of the water molecules with which they are in contact. This is widely referred to as a structure-making, or iceberg, effect. The range of compositions over which V_W^E is positive is limited. The values decrease quite precipitously for PrOH + water and progressively less so as the alkyl chain length decreases. The transition to negative values is presumed to be associated with the existence of some type of amphiphile aggregation which tends to minimise direct contact between the hydrophobic alkyl chains and water. The rate of growth of such aggregates with increasing amphiphile mole fraction is clearly more pronounced for the longer alkyl chain lengths.

There are other features of the PrOH + water curve that are worthy of comment. There is an inflexion point in the neighborhood of $X_A = 0.3$ and a relatively abrupt change of slope around $X_A = 0.75$. Attention has been drawn to the fact that dV^E/dX_A is virtually linear over that composition range, and that one might entertain the possibility that the amphiphiles are tending to adopt some type of labile lamellar scheme of self-aggregation [6]. It is noted that the V_W^E values for all three systems change very rapidly with mole fraction at extreme amphiphile rich compositions.

Figure 3 compares the excess partial molar volumes of water for the sequence EtOH + [7], EtOEtOH + [8] and EtOEtOEtOH + water [9]. There is clearly a substantial similarity between the profiles of the three curves up to $X_A = 0.5$. The mole fraction in the water rich composition region at which the curves begin to dip downwards decreases as the size of the polar head group increases. It is interesting to note that there is a significant difference in the profiles at the higher amphiphile mole fractions between the EtOH + water data on the one hand and that for the other two systems on the other. This is presumed to result from a difference between the types of aggregative schemes which exist in the two cases. That distinction is not apparent in a comparative plot of the V^E values. It is highly probable that, at very low concentrations, water, in the role of solute, tends to favor occupancy of sites close to the polar head groups. The distinction that we observe in the shapes of the V_W curves may well

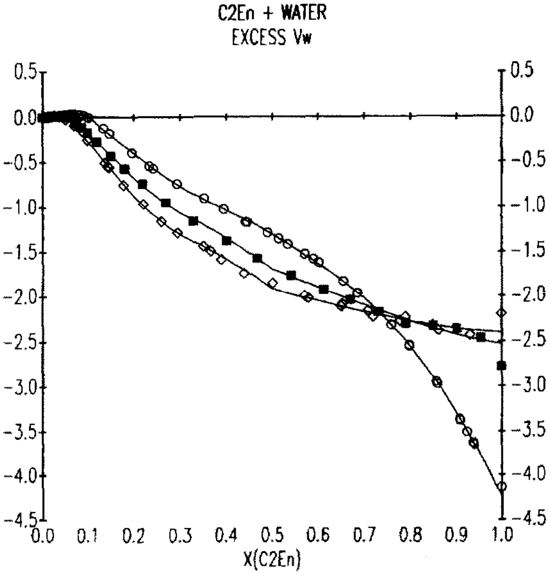

Fig. 3. Partial excess molar volumes of water in C_2E_n + water systems. Units, cm^3 mol^{-1}. Key: ○, EtOH; ■, EtOEtOH; ◇, EtOEtOEtOH; ——, four segment model versions.

arise from differences in the modes of self-aggregation of the pure amphiphiles and their sensitivities to the presence of the aqueous solute.

We have been interested in investigating the difference between the excess molar properties of the aqueous mixtures of pairs of isomeric amphiphiles, notably 1-PrOH [7] and 2-PrOH [10]. The profiles of V_W^E for the two aqueous systems are quite similar over most of the total mole fraction range. Where they differ is at low amphiphile mole fractions (Fig. 4). The precipitous change of the slope noted earlier for the 1-PrOH + water system is somewhat less pronounced for the 2-PrOH + water system, and occurs at a higher amphiphile mole fraction. It should be noted that the cubic spline procedure that was employed in the determination of the partial excess molar properties tends to smooth out abrupt changes of slope, whereas the nature of the model is such as to tend to exaggerate them.

Much of the interest in these C_mE_n + water systems is in their respective abilities to form micellar aggregates or metastable analogs. Of the systems for which we have access to data, only C_6E_3 + water has been reported as possessing a critical micelle concentration (cmc) [3]. It is of interest to compare the excess partial molar volumes of water in the vicinity of the cmc for this system with those of other systems. C_6E_2 + water has a lower critical solution temperature at 11°C [11]. The excess molar volumes of the C_6E_2 + water system were measured at 5°C [12]. The C_6E_3 + water data with which they are compared is that measured at 15°C [13]. Figure 5 shows

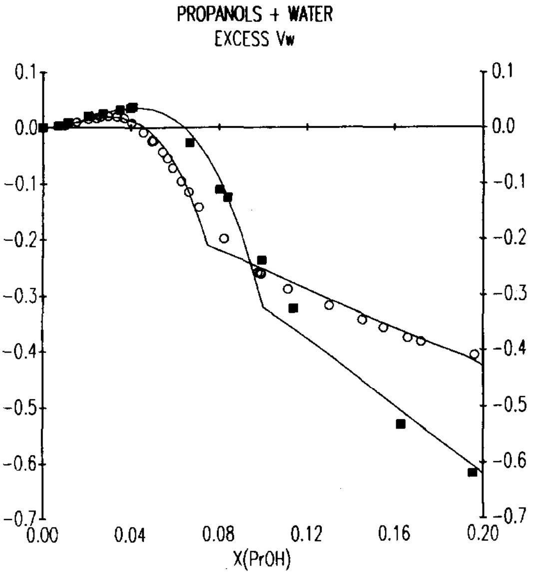

Fig. 4. Partial excess molar volumes of water in the propanol + water systems. Units, cm^3 mol^{-1}. Key: ○, 1-PrOH; ■, 2-PrOH; ———, four segment model versions.

the V_W^E curves for C_6E_3 + and C_6E_2 + water at low amphiphile concentrations. The profiles of the two curves are quite similar. Both systems show precipitous changes of slope at what is, for C_6E_3, very close to its reported

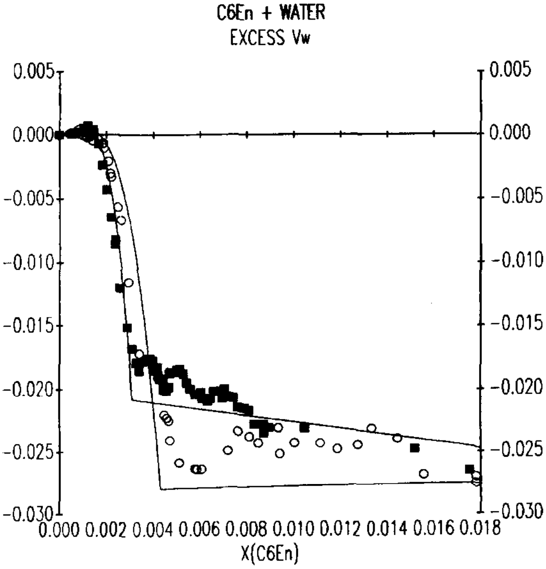

Fig. 5. Partial excess molar volumes of water in C_6E_n + water systems. Units, cm^3 mol^{-1}. Key: ○, C_6E_2; ■, C_6E_3; ———, four segment model versions.

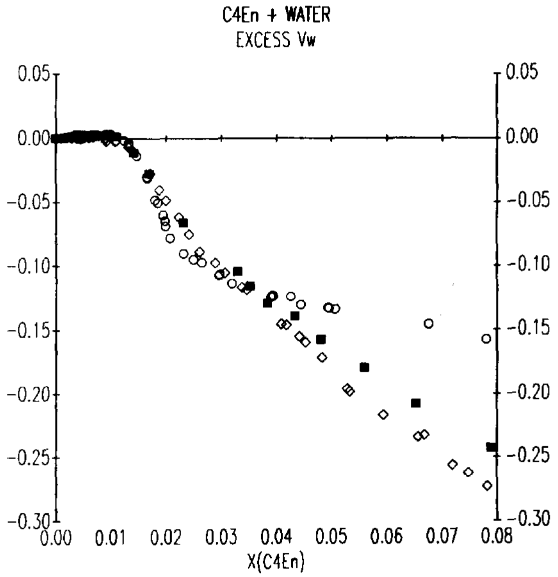

Fig. 6. Partial excess molar volumes of water in C_4E_n + water systems. Units, $cm^3\ mol^{-1}$. Key: ○, C_4E_1; ■, C_4E_2; ◇, C_4E_3.

critical micelle concentration. It should be noted that the demands upon the data and upon the model are particularly severe in this instance.

Figure 6 shows the excess partial molar volumes of water in C_4E_1 + [14–16]. C_4E_2 + [9] and C_4E_3 + water [17] at low amphiphile mole fractions. C_4E_1 + water shows a marked change of slope at $X_A = 0.025$, leading to much the same type of profile as seen in Fig. 5 at the substantially lower critical micelle concentrations of C_6E_2 and C_6E_3. The change of slope at that composition appears to become less marked as the polar head group increases in size.

Excess molar volumes are available for a larger number of systems than are any other type of data. There are, however, a sufficient number of other types of excess molar property data to provide other perspectives of the nature of the binary systems.

Figure 7 shows the excess partial molar enthalpies of water in MeOH + [18,19], EtOH + [20] and 1-PrOH + water [10] systems. These curves possess more overall character than their partial molar volume counterparts (Fig. 2). The profiles at low amphiphile mole fractions are quite similar to those of the excess partial molar volumes. There is, however, one significant difference and that is that, at very low alkanol concentrations, the H_W^E values are negative while the V_W^E values are positive. This would be consistent with the tendency towards ice-like aggregation of the hydration cosphere of the alkyl group that was mentioned above.

Figure 8 shows the excess partial molar enthalpies of water in MeOEtOH + water, EtOEtOH + water [21] and BuOEtOH + water [16]. At

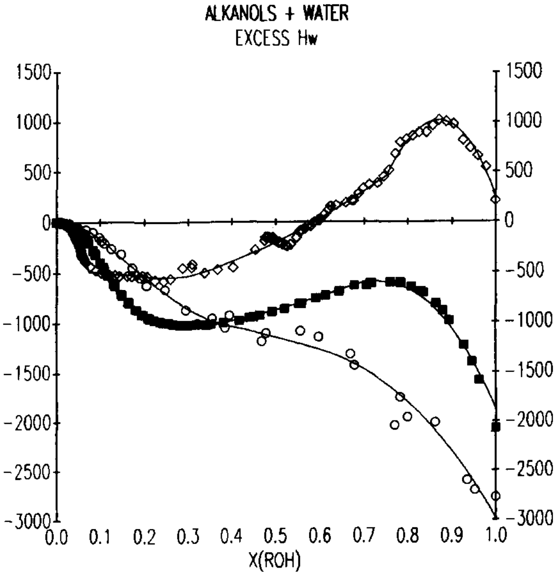

Fig. 7. Partial excess molar enthalpies of water in alkanol + water systems. Units, J mol^{-1}. Key: ○, MeOH; ■, EtOH; ◇, 1-PrOH; ———, four segment model versions.

relatively low amphiphile mole fraction, the trends that are observed with increasing alkyl chain length are similar to those seen in Fig. 7. At higher amphiphile mole fraction, the H_W^E values are again progressively less negative as the alkyl chain length increases. There is, however, a very substantial difference in the shapes of the ROEtOH + water H_W^E curves above $X_A = 0.5$, on the one hand, and the ROH + water curves, on the other, as there was with the V_W^E curves.

Figure 9 shows the excess partial molar isobaric heat capacities of water in MeOH + , EtOH + and 1-PrOH + water [5]. At very low concentrations, C_{pW}^E is very close to zero. Above $X_A = 0.05$ the values increase quite significantly, with the increase becoming steeper as the alkyl chain is extended. In all three systems, there are extensive ranges of mole fractions where C_{pW}^E remains fairly constant. In MeOH + water, this situation persists up to $X_A = 1$, whereas in the other two systems there are significant increases over the amphiphile rich range.

Figure 10 shows the K_{SW}^E values, where $K_S = -(\delta V/\delta p)_S$, for MeOH + , EtOH + and 1-PrOH + water [22,23]. One may note the strong similarities in the profiles of these curves and those of the corresponding excess partial molar volumes (Fig. 2). One can also note that the level of internal consistency in the K_{SW}^E data is generally better than any other type. The measurement of ultrasonic speeds is unusually precise.

Figure 11 shows the K_{SW}^E values for EtOH + water [23], EtOEtOH + water [8] and EtOEtOEtOH + water [9]. The profiles of the three curves

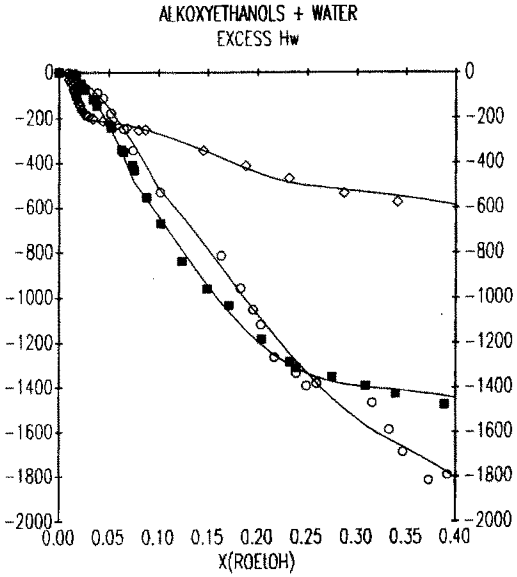

Fig. 8. Partial excess molar enthalpies of water in alkoxyethanol + water systems. Units, J mol^{-1}. Key: ○, MeOEtOH; ■, EtOEtOH; ◇, BuOEtOH; ——, four segment model versions.

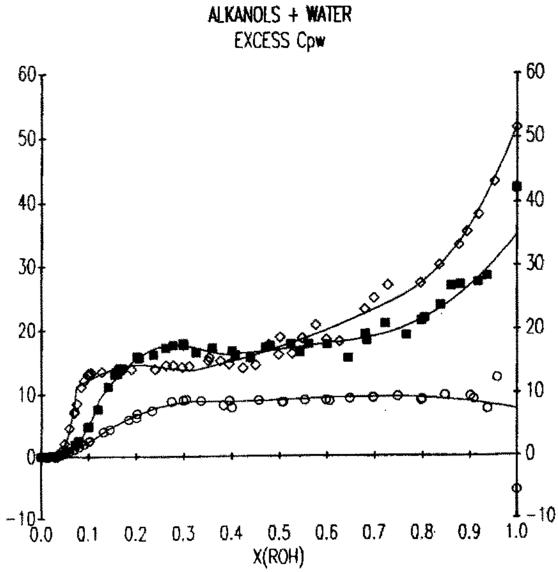

Fig. 9. Partial excess molar isobaric heat capacities of water in alkanol + water systems. Units, J K^{-1} mol^{-1}. Key: ○, MeOH; ■, EtOH; ◇, 1-PrOH; ——, four segment model versions.

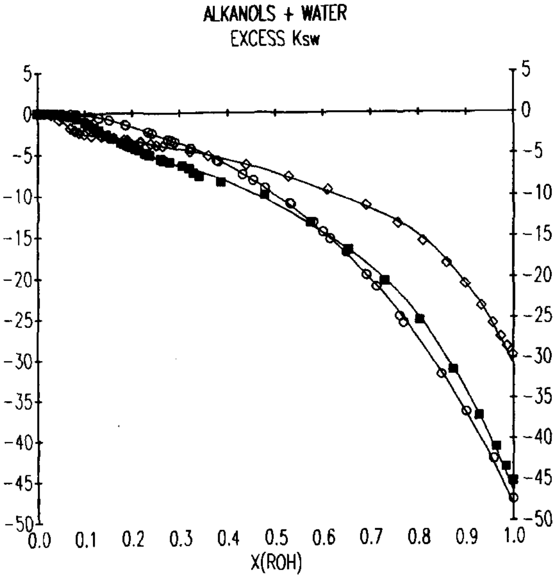

Fig. 10. Partial excess molar isentropic compressibilities of water in alkanol+water mixtures. Units, $mm^3\ MPa^{-1}\ mol^{-1}$. Key: ○, MeOH; ■, EtOH; ◇, 1-PrOH; ——, four segment model versions.

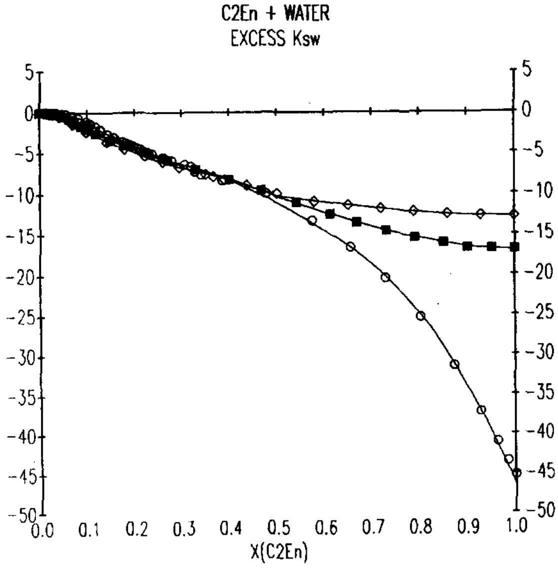

Fig. 11. Partial excess molar isentropic compressibilities of water in C_2E_n +water mixtures. Units, $mm^3\ MPa^{-1}\ mol^{-1}$. Key: ○, EtOH; ■, EtOEtOH; ◇, EtOEtOEtOH; ——, four segment model versions.

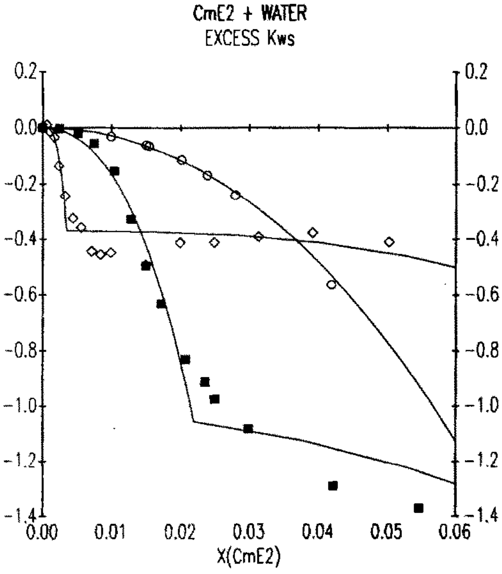

Fig. 12. Partial excess molar isentropic compressibilities of water in C_mE_2 + water mixtures. Units, mm^3 MPa^{-1} mol^{-1}. Key: ○, C_2E_2; ■, C_4E_2; ◇, C_6E_2; ———, four segment model versions.

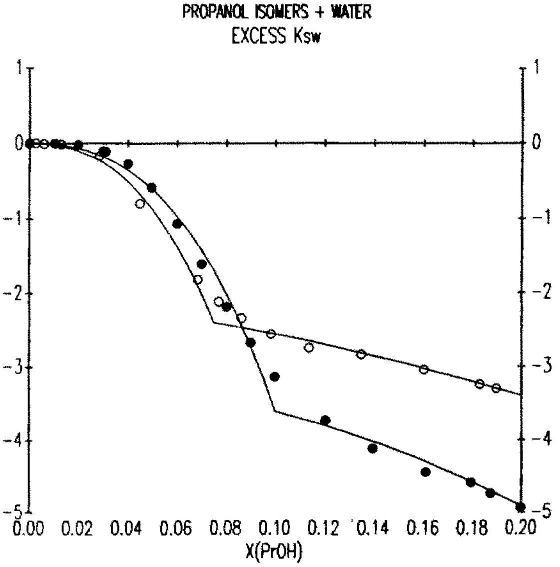

Fig. 13. Partial excess molar isentropic compressibilities of water in the propanol + water systems. Units, mm^3 MPa^{-1} mol^{-1}. Key: ○, 1-PrOH; ■, 2-PrOH; ———, four segment model versions.

are fairly similar at low amphiphile mole fractions. At extreme water rich compositions, the K^E_{SW} values are small and negative. The rapid drop off of the K^E_{SW} values, which parallels that of both V^E_W and H^E_W, begins at lower amphiphile concentrations as the size of the polar head group increases. For $X_A > 0.5$, there is a remarkable difference between the profile for EtOH + water and the other two curves. The inference appears to be that the average aqueous environment changes radically for EtOH + water but remains fairly consistent over that entire composition range for the other two systems.

Figure 12 shows the water rich K^E_{SW} values for the aqueous mixtures of C_2E_2 + water [9], C_4E_2 + water [9] and C_6E_2 + water [24]. The C_6E_2 + water curve, which was generated at 5°C, show the kind of features that might be thought of as being consistent with the existence of a critical micelle concentration in the vicinity of $X_A = 0.0035$.

Figure 13 shows the K^E_{SW} values for the aqueous mixtures of the two propanol isomers [23,25]. The profiles are very similar, but there are again interesting differences in the water rich region. There are significant changes of slope in both curves, but that in 1-PrOH + water, as with V^E_W, appears to occur earlier and to be somewhat more pronounced.

CONCLUSIONS

In their 1966 review of the physical properties of alkanol + water mixtures, Franks and Ives identified as a major incentive, for many solution thermodynamics, the wish to try to tie together the nature of the composition dependence of the macroscopic properties of binary systems with prevailing concepts of molecular scale features; notably molecular aggregation [26]. That situation has not changed, but in the intervening years there has been a substantial increase in the amount of high quality thermodynamic data available for close scrutiny. There has emerged furthermore the appreciation that the alkanols are amphiphilic, and that to some extent they might be found to mimic the schemes of structural aggregation that have been identified in the aqueous mixtures of larger amphiphiles like detergents and surfactants.

It would be misleading to claim that we have reached any kind of profound understanding of the nature of the structure of the smaller amphiphile + water mixtures and of the factors that control them. What has been accomplished is a deeper appreciation of the role of the "hydrophobic effect" in dictating what kinds of structural patterns, if any, are likely to be formed.

The extensive work that has been, and continues to be, carried out on the phase and microphase characteristics of C_mE_n + water systems provides us with a sense of the kinds of structural schemes which are possible [3]. Relatively little has been accomplished in the way of thermodynamic characterization of detergent (or surfactant) + water systems, other than the observation that dQ^E/dX_A shows an abrupt change in the vicinity of a critical micelle concentration. What little data is available for the C_6E_n + water systems, which are presumably capable of forming micelles, provides us with an idea of the form that the thermodynamic data takes in the cmc neighborhood. We find that the C_4E_n + water thermodynamic data curves bear a strong similarity to those of the C_6E_n + water systems, despite the fact there is no conclusive evidence that C_4E_n species can form micelles. This suggests that the thermodynamic data for the aqueous mixtures of such species is not a conclusive indicator of the existence of micelles, but that there are strong similarities between their self-aggregative characteristics and those of true micelle forming species.

At higher mole fractions, there are features of the composition dependence of the amphiphile + water systems which suggest that there may well be a sequence of patterns of metastable molecular aggregates that to some extent mimic those of the detergent + water system. What have been sought are reliable graphical means of projecting significant trends in the composition dependence of the thermodynamic properties that may be treated as a sound basis for drawing conclusions (by analogy with the detergent + water systems) about the existence and nature of such schemes of aggregation. Hopefully, it has been demonstrated here that the excess partial molar properties of water represent one such sensitive probe of composition dependence.

In each of the data sets, Q_W^E values remain close to zero over a modest range of water rich compositions before taking off fairly abruptly in one direction or the other. The V_W^E values are invariably positive at the lowest amphiphile mole fractions, which has been described above as being consistent with the so-called structure making effect which results in an increase in the ice-like character of the self-aggregation of water in the vicinity of a hydrophobic group. The precipitous change is invariably towards negative V_W^E values. It is argued that this change is related to the growth of amphiphile aggregates in which there is diminishing contact between the hydrophobic groups and water. Evidently, the hydrophobic surface areas are becoming more and more limited so there is a steady decrease in the extent of "iceberg" formation.

For each type of Q^E data, and for all of the systems that have been studied, it is possible to obtain a satisfactory fit to Q^E of water rich mixtures, using a cubic function of mole fraction, or some other function of equivalent flexibility. For each system, there is an upper limit to the mole fraction range for which that cubic function is valid. For systems with a common polar head group, the upper limit $X_A = X_1$ decreases as the length of the alkyl chain increases. For C_6E_2 and C_6E_3, the values are close to the reported critical micelle concentration of C_6E_3. For C_4E_n (where $n = 1$, 2 or 3), the values are close to those predicted from the extrapolation of a formula given by Digiorgio for cmc values as a function of alkyl chain length, even though no direct evidence has been furnished for the existence of stable micellar entities [3]. For 1-PrOh and 2-(1-PrOH)EtOH, the X_1 values are slightly larger that the cmc values that are predicted by Digiorgio's formula. There is no question of there existing any type of cmc analog for species of the types C_1E_n or C_2E_n.

For C_mE_n, when $m = 3$, 4 or 6, there is a significant change of slope and curvature for Q_W^E in the vicinity of $X_A = X_1$. For C_6E_3, this can be attributed to the presence, above X_1, of stable micelles. For the other systems, where this effect is still very obvious and where no direct evidence has been furnished for the existence of stable micelles, one might conclude that there is present some type of metastable micelle analogs. The significant changes of slope do not appear to exist when the alkyl group is methyl, ethyl or isopropyl. There are, however, obvious changes of curvature for the ethyl and isopropyl species and, in some cases, even for the methyl species.

Attention has been drawn to the fact that for many of the data sets there exists a range of mole fractions ($X_2 \leq X_A \leq X_3$) for which dQ^E/dX_A varies linearly with X_A. This feature is most obvious for the alkanol + water systems, most notably 1-PrOH + water. For Q_W^E, in that same segment, the dependence is quadratic.

One of the more interesting aspects of the Q_W^E curves is their amphiphile rich behavior. There appear to be radical differences between the profiles of the alkanol + water curves, on the one hand, and the ether group containing amphiphile + water curves on the other. Typically, there are large variations in Q_W^E with increasing water content for C_mE_0 + water but far smaller variations for $C_mE_n(n > 0)$ + water. It is not clear why this should be the case, since relatively little is known about the structures of the pure liquid amphiphiles, but it may have to do with significant differences in the ways in which the presence of water as a solute species modifies those structures.

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