Measurement, Analysis, and Utility of Excess Molar − $(\partial V/\partial p)_S$

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1 Introduction

The composition dependence of thermodynamic properties of binary liquid mixtures has proved to be a useful indicator of the existence of significant effects resulting from intermolecular interactions. This review is concerned with the manner in which compressibility measurements are being used in the quest for an improved understanding of the nature of the patterns of molecular aggregation which exist in aqueous mixtures.

It is helpful to identify the place occupied by compressibilities in the hierarchy of thermodynamic properties of liquid mixtures. Since the mixing process takes place under isothermal and isobaric conditions, the potential is the Gibbs free energy (free enthalpy). The excess molar Gibbs function, G^{E}, can be determined experimentally from vapour pressure measurements. Its composition dependence is generally relatively smooth and, from the standpoint of visual appraisal, lacking in interest.

More informative are plots of the first derivatives of the Gibbs function. Excess molar volumes, enthalpies, and entropies may exhibit interesting composition dependence originating from variations in the modes of molecular aggregation. The excess chemical potentials and activity coefficients of the individual components are also first derivative properties.

At the second derivative level are the molar heat capacities and the molar quantities A_p [$= (\partial V_m/\partial T)_p$] and K_Z [$= (\partial V_m/\partial p)_Z$], where Z may be either T or S. These properties appear to exhibit particularly interesting composition dependence and thus have been used as indicators of the existence of significant sensitivity of the patterns of molecular aggregation to changes in composition. It is claimed that the first derivative properties are dominated primarily by chemical and intramolecular effects, while lower energy intermolecular and packing phenomena are generally better evidenced through the second derivative properties.

This review is primarily concerned with the property designated by the symbol K_S. It is both amusing and frustrating to find that it has no 'correct' name. The term compressibility is reserved for the intensive property $\kappa_Z = V_m^{-1}K_Z$, where V_m is the molar volume. The isothermal compressibility, κ_T, is a key thermodynamic property for which accurate data are needed in various areas of physics, chemistry, and chemical engineering. For liquid mixtures, there are few precise data. Traditionally, isothermal compressibilities are determined by direct *PVT*-measurements, at fairly high pressures. More common is the indirect determination of the isentropic compressibility, κ_S. In addition to their own utility, κ_S values, in conjunction with the isobaric expansivity α_p and the isobaric heat capacity, C_p, provide a means of calculating κ_T, the molar quantity K_T and other isentropic and isochoric excess molar properties which exhibit very high sensitivity to composition.

The isentropic quantities κ_S and K_S have been determined for pure substances, electrolyte solutions, and a variety of mixtures of non-electrolytes. Most measurements have been performed at 298.15 K and the nominal pressure of 0.1 MPa. Volumetric and compressibility measurements have also proved to be useful in the study of ternary and quaternary systems, including microemulsions, in which one of the components is an electrolyte. Isentropic compressibility studies have proved to be particularly useful for (amphiphile + water) systems, where hydrophobic effects lead to a variety of patterns of molecular aggregation. Much of the research has been directed towards a better understanding of the nature and extent of these patterns and their sensitivities to changes in composition, temperature, pressure, and the molecular structure of the amphiphile.

It is our contention that, in an aqueous environment, even small amphiphiles tend to possess patterns of aggregation which are labile analogues of those identified in (detergent + water) systems and that the manner in which such patterns vary with composition is reflected by the variations of the macroscopic properties.

We have chosen to focus upon the family of compounds with the formula $C_mE_{2m+1}.(OC_2H_4)_n.OH$, which is conveniently abbreviated to C_mE_n. This family is particularly attractive, since it spans the range from the simple amphiphilic alkanols C_mE_0 to fairly high molar mass detergents.

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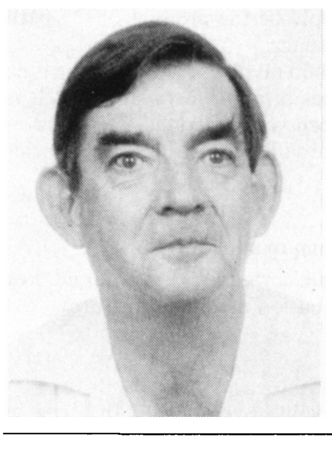

Born in London in 1936, Michael Davis was educated at Latymer Upper School and University College London. His postgraduate studies were carried out at the University of Oslo under the mentorship of Odd Hassel. He has been a Professor of Chemistry at the University of Texas at El Paso since 1971. His current research activities are focused upon the measurement, analysis, and interpretation of the thermodynamic properties of amphiphile + water mixtures.

2 Significance and Role of K_S

In appraising the significance of the compressibilities of pure liquid, one needs to take into account both molecular packing and intermolecular attractions Liquids with low densities and substantial 'free' volumes tend to be more compressible than others, but molecular shape is also a significant factor Propan-2-ol, which is only slightly less dense than propan-1-ol, is far more compressible We note that, for the C_mE_n family, the intensive compressibility κ_S decreases with both alkyl chain length and polar head group size

It has been suggested that the excess property K_S^E might be associated with differences in the size of the molecules and the relative strength of the interactions between them The dependence of K_S^E upon composition tends to resemble to that of the excess molar volumes, V^E Both quantities are negative over the entire composition range for (amphiphile + water) systems We note that K_S^E proves to be one of the most reproducible of the excess molar properties While its composition dependence, in the vicinity of a cmc analogue, may not be quite as dramatic as that of C_p^E, its greater internal consistency makes it amenable to more detailed analysis

3 Experimental Techniques

Before embarking upon a consideration of the available data, it is appropriate to make some mention, albeit brief, of the nature of the experiments that are available for the determination of compressibilities

3.1 Principle of Measurement

Most of the recent compressibility studies involve the determination of K_S rather than K_T It should be borne in mind that the compressibilities of liquids are very small Both K_S and K_T for water are roughly 9 mm^3 MPa ^{1} mol ^{1} [1] A very high degree of precision is called for in their measurement

The isothermal compressibility κ_T can be determined by static methods the most widely used technique involves the use of a piezometer, which gives directly the volume changes that result from varying the pressure at constant temperature Extreme care is needed in handling the equipment and it is difficult to obtain accurate results [2] The isentropic compressibility κ_S can be determined indirectly from measurements of the density, ρ, and the speed of sound, u It is possible to obtain a high degree of accuracy and is generally preferred to the direct method, despite the fact that it calls for two separate measurements

The speed of propagation of ultrasonic waves through liquids was first determined by interferometry Difficulties were encountered, in dealing with standing waves, that were overcome by using pulse techniques

The 'sing-around' method involves an acoustic pulse passing from a transmitter through the liquid to a receiving transducer [3] After amplification and reshaping, the signal is fed back to the transmitting crystal The pulse frequency is determined for a specific path length If the electronic delay time τ were negligible, the ultrasonic speed would simply be the product of the path length, l, and the recorded frequency, f

The 'pulse-echo-overlap' method involves measuring the time interval between a pair of echoes of an ultrasonic wave [4] It is possible to operate in multiple-echo or in through-transmission mode, and in either case with broadband or radio-frequencies pulses

3.2 Calculation of Isentropic Compressibilities

Whichever method is used, certain corrections are required For the sing-around method, the equation used is of the form

$$u = fl/[n - \tau f] \quad ^1 \qquad (1)$$

where n is a constant, whose value is related to the type of ultrasonic generator and is taken to be 1, unless stated otherwise by the manufacturer Values of the path length and τ are determined using a calibrant liquid for which the ultrasonic speed has been reliably determined Water is invariably chosen as the standard Many attempts have been made to obtain very precise data for the ultrasonic speeds in water over a wide range of temperatures There are some fairly large discrepancies among the reported values Currently, the most widely accepted values are those of Del Grosso and Mader [5]

κ_S and K_S are calculated from the Newton–Laplace equation

$$\kappa_S = 1/(\rho u^2) = V_m/(M_m u^2) \qquad (2)$$

where ρ is the density and M_m the molar mass of the mixture Further

$$K_{S\,m} = V_m^2/(M_m u^2) \qquad (3)$$

Equation 2 is found to be valid, provided that there is a negligible amount of dispersion of the acoustic wave, in which case, the ultrasonic speed may be regarded as a thermodynamic quantity [6]

There are two major sources of error in the measurement of the ultrasonic speed

(i) The signals, which are viewed on an oscilloscope, may be distorted due to diffraction effects in the liquid, reflections from the walls of the cell and inside the transducers These effects are likely to make the largest contribution to the statistical error

(ii) Ultrasonic absorption phenomena can cause large perturbations to the shape and amplitude of the signal for specific ranges of frequency and amplitude It is possible to make corrections for such systematic errors as they introduce

It is appropriate to comment that the investigation of ultrasonic absorption phenomena provides a different perspective of the nature of binary liquid mixtures The subject has been thoroughly reviewed [7]

Densities measured by the vibrating tube technique are generally of adequate accuracy

4 Excess Molar K_S

The basic way of examining the composition dependence of the macroscopic properties is to generate curves which can be subjected to visual scrutiny Raw data curves frequently appear to have no obviously dramatic features There exist, however, several data reduction procedures which have the merit of leading to graphs with enhanced visual impact They are discussed, at some length, in a concurrent review [8]

4.1 The Deviations from Additivity, ΔQ

Really, departures of a given property from additivity, calculated on a mole fraction or volume fraction average of those of the pure components, are somewhat arbitrary quantities They represent deviations from linear dependence upon an often arbitrarily chosen weighting coefficient

4.2 The Excess Molar Properties, Q^E

What is desirable here is to define a reference state for a binary mixture so that we may correlate the deviations of all thermodynamic properties of real mixtures from those of a common model One may define the reference state by generating a thermodynamically consistent set of mixing rules The choice of solution model is not as important as the internal consistency, so that real mixture behaviour relative to one acceptable model may be translated to give deviations from any other existing or future model [9]

The most common reference state is that of the 'ideal' liquid mixture, with properties, Q^{id} The deviations of the molar properties of a real mixture from those of the ideal mixture of the same composition are the excess molar properties, Q^E We may write

$$Q^{E}_{m} = Q_{m} - Q^{id}_{m} = \Delta_{mix}Q_{m} - \Delta_{mix}Q^{id}_{m} \qquad (4)$$

4 2 1 *Defining the Ideal Mixture*

From a thermodynamic point of view, a mixture may be said to be ideal if it obeys a generalized form of Raoult's law in which the original statement in terms of vapour pressures is replaced by one in terms of fugacities [10] Consideration of the liquid–vapour equilibrium leads to the following expressions

$$G^{id}_{m} = x_{A}[G^{*}_{m\,A} + RT\ln x_{A}] + x_{B}[G^{*}_{m\,B} + RT\ln x_{B}] \qquad (5a)$$

$$\Delta_{mix}G^{id}_{m} = RT[x_{A}\ln x_{A} + x_{B}\ln x_{B}] \qquad (5b)$$

The general approach to obtaining expressions for other ideal molar quantities is to state that Q^{id}_{m} can be defined if $\Delta_{mix}Q^{id}_{m}$ can be obtained by differentiating equation 5b either with respect to temperature at constant pressure or with respect to pressure at constant temperature This traditional approach provides a definition for $K^{id}_{T\,m}$, but not for $K^{id}_{S\,m}$

4 2 2 *Ideal and Excess Compressibilities*

In order to extend the range of ideal molar quantities to include isentropic and isochoric properties, Benson and Kiyohara proposed that κ^{id}_{S} should be calculated by rewriting the defining equation for κ_{S}

$$\kappa_{S} = \kappa_{T} - TV\,a^{2}_{p}/C_{p\,m} \qquad (6)$$

in terms of the ideal quantities [11] This approach leads to

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

By contrast to $K^{id}_{T\,m}$, $A^{id}_{p\,m}$ and $C^{id}_{p\,m}$, $K^{id}_{S\,m}$ is not the mole-fraction weighted average of the values for the two pure components The excess molar quantity, $K^{E}_{S\,m}$ is obtained from equation 4

The Benson–Kiyohara approach to defining the properties of ideal mixtures has been widely accepted by those who work with isentropic compressibilities It assumes that the thermodynamic properties of an ideal mixture are mutually related in the same manner as those of pure substances and real mixtures [12] It also permits one to evaluate a wide variety of ideal and excess differential thermodynamic properties [13]

4 2 3 *Approximate Ideal Mixing Rules*

Numerous approximate ideal mixing rules have been proposed to estimate ideal isentropic compressibilities, a thorough study of which is to be found in reference 9

The most frequently encountered error has been the assumption that $K^{id}_{S\,m}$ is the mole fraction weighted average of the values of its pure components There have also been several examples involving the defining equation

$$K^{id}_{S\,m} = K^{id}_{T\,m}\,C^{id}_{V\,m}/C^{id}_{p\,m} \qquad (8)$$

The equation is correct but $C^{id}_{V\,m}$ was erroneously assumed to be the mole fraction weighted average of the value of its pure components

We note the existence of another way of expressing ideal mixing rules, which are typified by

$$K^{id}_{S\,m} = \sum_{i} x_{i}\,f_{i}(K^{*}_{S\,m})_{i} \qquad (9)$$

where x_{i} is an explicit weighting coefficient, such as the mole or the volume fraction, and f_{i} a so-called 'multiplying' coefficient, which is a function of A_{p} and C_{p} This approach, which is a generalization of that of Benson and Kiyohara, helps to identify the origin of other flawed ideal mixing rules

4 2 4 *Deviations of the Ultrasonic Speeds from Ideality*

Insofar as the Newton–Laplace equation is valid, the ultrasonic speed may be expressed solely in terms of thermodynamic quantities

$$u = V_{m}(M_{m}K_{S\,m})^{\frac{1}{2}} \qquad (10)$$

Within the extended framework of ideality, it is possible to evaluate the ultrasonic speed, u^{id}, in an ideal mixture

$$u^{id} = V^{id}_{m}[M_{m}K^{id}_{S\,m}]^{\frac{1}{2}} \qquad (11)$$

Deviations, u^{D}, of the ultrasonic speed from the ideal values are thus accessible from

$$u^{D} = u - u^{id} \qquad (12)$$

This quantity was referred to earlier as an 'excess' ultrasonic speed, but it is not deemed to be appropriate to speak of an excess intensive property [14 15] The term 'deviation' is preferable The term 'excess ultrasonic speed' has sometimes been erroneously identified with the quantity

$$\Delta u(x) = u - \sum x_{i}u_{i}^{+} \qquad (13)$$

5 The Data Base

While our primary concern is with aqueous systems, it is appropriate to mention some of the more interesting aspects of the studies of non-aqueous systems

5.1 Non-Aqueous Systems

A substantial number of compressibility studies of non-aqueous binary systems are to be found in the literature The general aim has been to use the composition dependence of the excess quantities as a means of understanding the nature of the molecular scale processes within those mixtures

Until the late 1970s there was such a diversity in the nature of investigations that it is difficult to discern any type of systematic approach Many of the reports, until a few years ago, dealt with a quantity that was referred to as κ^{E}_{S}, based upon the erroneous assumption that κ^{id}_{S} varies linearly with volume fraction The extent of the error is not, however, so substantial that the qualitative aspects of the composition dependence are totally misleading

Benson and his co-workers have made a systematic study of κ^{E}_{S} and $K^{E}_{S\,m}$ for (an alkane + an alkanol) systems, where molecules of similar and significantly different geometry were involved [16] They concluded that several factors may contribute to the appearance of their data (i) Variation in the extent of strength of the hydrogen bonding in alkanol self-association, with alkyl chain length (ii) Dependence of the orientational order in the n-alkanes upon chain length (iii) Accommodation of the alkane within the alkanol clusters and ultimate cluster disruption (iv) Compatibility of alkane and alkanol alkyl chain lengths (v) The relative sizes of the component molecules Each factor is assigned either a positive or negative contribution to the excess function, the magnitude of which varies with composition

There have been some interesting recent investigations of (amphiphile + an organic solvent) systems designed to provide information about the nature of the amphiphile aggregates A comparative study of the excess compressibilities of (2-butoxyethanol + an organic solvent) provides evidence of the disruption of the butoxyethanol aggregates when the organic component is substituted for water [17]

Quantitative interpretations of isothermal compressibility data are generally based upon concepts of correlations of molecular orientations [18]

5.2 Binary Aqueous Systems

We shall concentrate upon ten data sets of the types (C_mE_0 + ,C_mE_1 +, and C_mE_2 + water). We shall examine the effects of varying the polar head group size among amphiphiles with a common alkyl chain and varying the alkyl chain length for amphiphiles with a common polar head group.

Figure 1 shows the ultrasonic speed data for (alkanol + water) systems. The data for (MeOH + water) is a combination of two sets of data and serves as a testimony to the reproducibility of the ultrasonic speeds from one laboratory to another.[19,20] The data for (EtOH + water) and (1-PrOH + water) are taken from reference 19 and that for (2-PrOH + water) from recent unpublished results.[21]

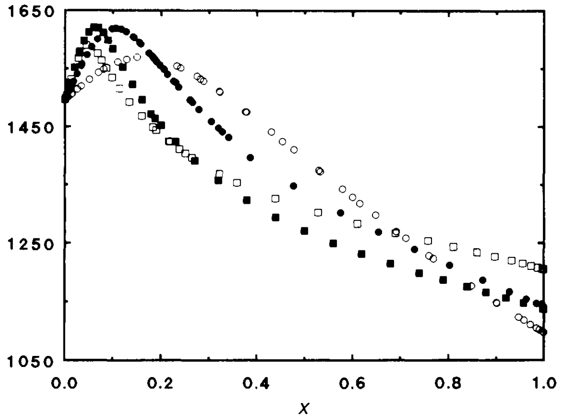

Figure 1 Ultrasonic speeds in [alkanol + water], at 298.15 K and mole fraction x of alkanol. ○, [methanol (C_1E_0) + water]; ●, [ethanol (C_2E_0) + water]; □, [propan-1-ol (C_3E_0) + water]; ■, [propan-2-ol + water]. Units: m s^{-1}.

There are several noteworthy features to this Figure. The initial increase in the ultrasonic speeds with alkanol concentration is common to all (amphiphile + water) systems. The maxima occur at lower alkanol mole fractions as the alkyl chain length increases. There is a substantial difference between the mole fractions of the maxima for the propanol isomers. The u values of the sequence MeOH–EtOH–2-PrOH appear to follow a more logical progression than those of MeOH–EtOH–1-PrOH.

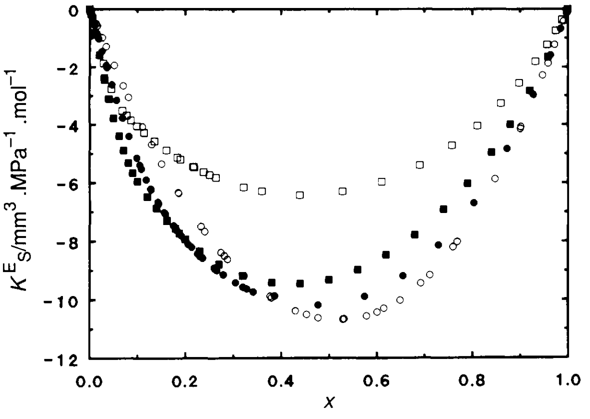

Figure 2 Excess molar quantity $K^E_{S,m}$ for [alkanol + water], at 298.15 K and mole fraction x of alkanol. ○, [methanol (C_1E_0) + water]; ●, [ethanol (C_2E_0) + water]; □, [propan-1-ol (C_3E_0) + water]; ■, [propan-2-ol + water]. Units: mm^3 MPa^{-1} mol^{-1}.

Figure 2 shows the excess molar isentropic compressibilities for the (alkanol + water) systems. One notes that the $K^E_{S,m}$ values are negative across the entire composition ranges, a feature they share with the excess molar volumes of the same systems. The shift from ideality is in the direction of greater density and greater resistance to compression. The limiting slope at $x_A = 0$ becomes more negative with increasing alkyl chain length, while the converse appears to be the case at $x_A = 1$. There is a marked difference in profiles of the two (PrOH + water) curves. There is some feature of (1-PrOH + water) that leads to its $K^E_{S,m}$ values, in roughly equimolar mixtures, being substantially less negative than those of the other systems. There appears to be a fairly abrupt change of slope for $K^E_{S,m}$ of (1-PrOH + water) (Figure 3), in the vicinity of $x_A = 0.07$ that is only weakly mimicked by (2-PrOH + water).

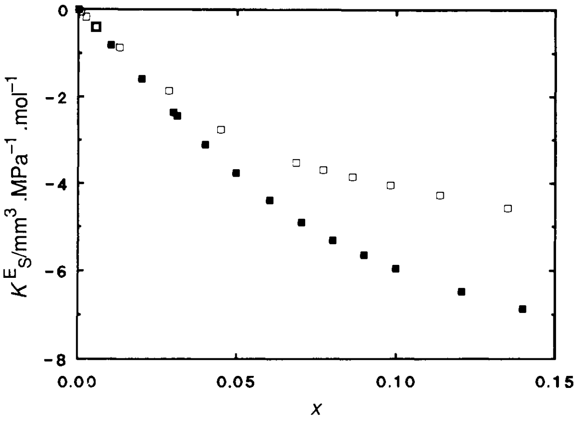

Figure 3 Excess molar quantity $K^E_{S,m}$ for [propanol isomer + water], at 298.15 K and mole fraction x of propanol isomer: □, [propan-1-ol (C_3E_0) + water]; ■, [propan-2-ol + water]. Units: mm^3 MPa^{-1} mol^{-1}.

Plots of excess molar properties do not always do justice to all of the significant features of the composition dependence of the data. Such features can often be projected out of the data in the form of plots of apparent or partial molar properties. Evaluation of the excess partial molar compressibilities requires determination of the derivatives dK^E_S/dx_A. Reliable determination of the derivatives requires not only an objective procedure, but also data with a high level of internal consistency and an adequate point density.[8] Figure 4 shows the derivative curve for (1-PrOH + water). This curve shows very nicely the change of curvature at $x_A = 0.07$. It also clearly exhibits a linear region from $x_A = 0.3$ to 0.7, similar to that noted earlier for V^E_m.[22]

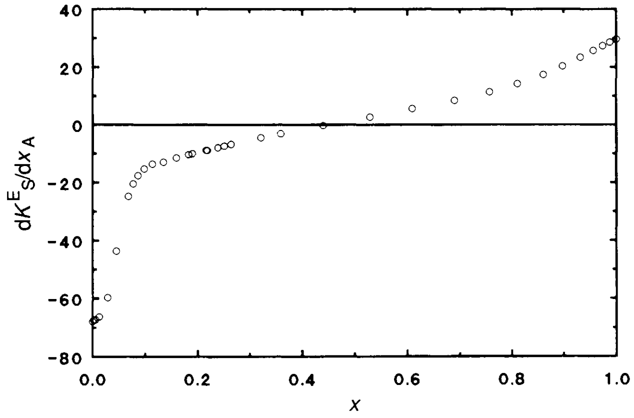

Figure 4 Derivative (dK^E_S/dX_A) for [propan-1-ol (C_3E_0) + water], at 298.15 K and mole fraction x of propan-1-ol. Units: mm^3 MPa^{-1} mol^{-1}.

Figure 5 shows $K^E_{S,w}$ for the two (PrOH + water) systems. At very low propanol concentrations, $K^E_{S,w}$ remains virtually unchanged from $K^*_{S,w}$. Above $x_A = 0.02$, there is a fairly rapid drop in $K^E_{S,w}$ until, in the vicinity of $x_A = 0.08$, it flattens out again.

Figure 6 shows (dK^E_S/dx_A) for (2-butoxyethanol + water).

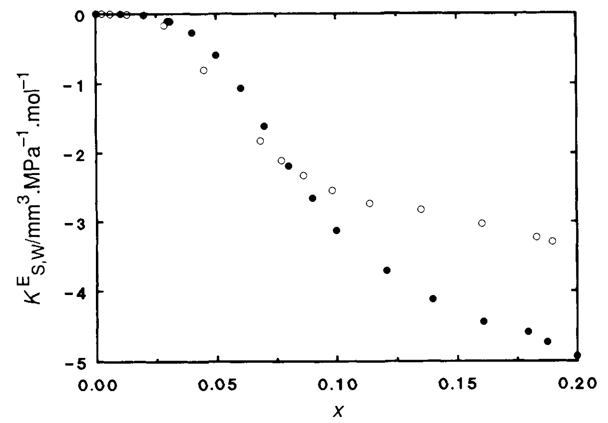

Figure 5 Excess partial molar quantity $K^{E}_{S,w}$ for water in [propanol isomer + water], at 298.15 K and mole fraction x of propanol isomer. ○, [propan-1-ol (C_3E_0) + water]; ●, [propan-2-ol + water]. Units: mm^3 MPa^{-1} mol^{-1}.

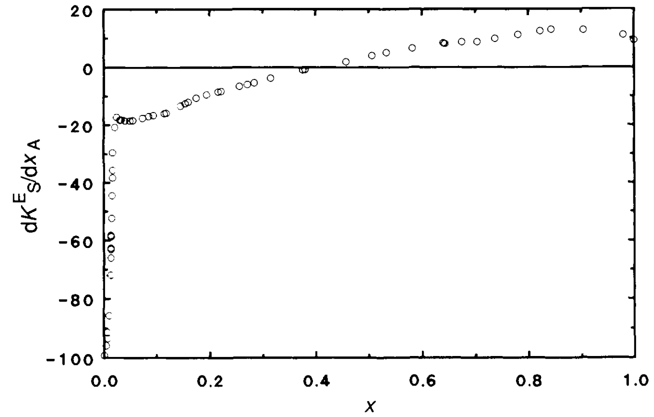

Figure 6 Derivative (dK^{E}_{S}/dX_A) for [2-butoxyethanol (C_4E_1) + water], at 298.15 K and mole fraction x of 2-butoxyethanol. Units: mm^3 MPa^{-1} mol^{-1}.

This is based upon a combination of two sets of ultrasonic speeds with a high level of mutual consistency.[17,23] It is interesting to compare this plot with Figure 4, the abrupt change of slope has shifted to a much lower mole fraction range in the (BuOEtOH + water) case. The linear region, in Figure 5, also appears at a lower mole fraction range. In the amphiphile-rich regions, (dK^{E}_{S}/dx_A) for (1-PrOH + water) shows a pronounced increase in slope as x_A increases, while it appears to diminish for (BuOEtOH + water).

Abrupt changes of the slope dQ^E/dx_A are known to be symptomatic of the existence of critical micelle concentrations.[24] Whether or not butoxyethanol is capable of forming micellar aggregates has been a matter of speculation for over a decade. Investigations of a wide variety of properties of the (C_4E_1 + water) system were prompted by the appearance of apparent molar isobaric heat capacity data.[25] There remains no direct evidence of stable micelle formation, but the data strongly indicate the formation of some type of micelle-like aggregates at $x_A = 0.02$. Significantly that is the composition predicted for the cmc of species of the type C_4E_n by an equation that is derived from the cmc values for species in which the alkyl chain has six or more carbons.[26]

One of us has recently measured, at 5 °C, the ultrasonic speeds in (C_6E_2 + water).[27] This system has a lower critical solution temperature of 11 °C.[28] To the best of our knowledge, there has been no cmc value reported, but C_6E_3 has a cmc at $x_A = 0.002$ at 25 °C. Figure 7 shows the water-rich values of (dK^{E}_{S}/dx_A). It clearly exhibits a pronounced change in slope in the vicinity of $x_A = 0.004$.

Most of the comparative studies of the thermodynamic properties of (C_mE_n + water) systems have been focused upon the effects of varying the alkyl chain length. Figure 8 shows the $K^{E}_{S,w}$ values for the sequence (EtOH + water),[19] (EtOEtOH + water),[23] and (EtOEtOEtOH + water).[12] On this scale, there are no obvious difference between the three curves up to $x_A = 0.05$. Above that mole fraction there is a major difference between the (EtOH + water) curve, on the one hand, and the two others. It is possible that the solute water molecules are more readily incorporated into the pure liquid structures of the ethoxylated alkanols than they are with the alkanols. Alkanols appear to form cyclic oligomers, which may be broken up by the inclusion of water. The ethoxylated species may tend to possess a more laminar type of pure liquid structure. Figure 9 shows the more water-rich composition range for the same three systems. It is evident that the downward trend starts at lower amphiphile mole fractions, as the size of the polar head group increases. That is consistent with the notion that the polar head groups help to promote a less compressible scheme of aggregation than that of pure water and that hydrophobic clustering reduces the level of direct contact between the alkyl tails and water.

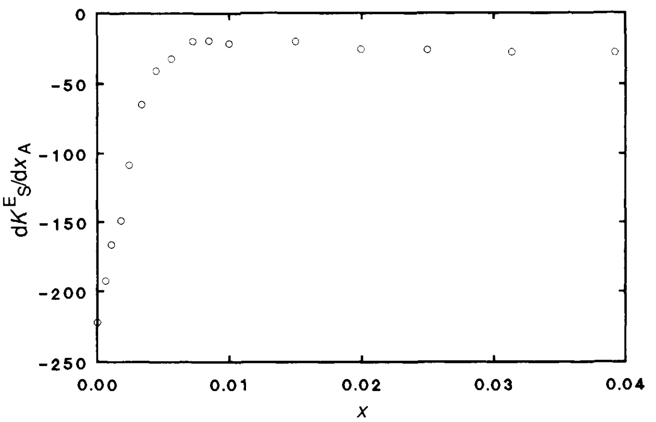

Figure 7 Derivative (dK^{E}_{S}/dX_A) for [2-(hexyloxyethoxy)ethanol (C_6E_2) + water], at 278.15 K and mole fraction x of 2-(hexyloxyethoxy)ethanol. Units: mm^3 MPa^{-1} mol^{-1}.

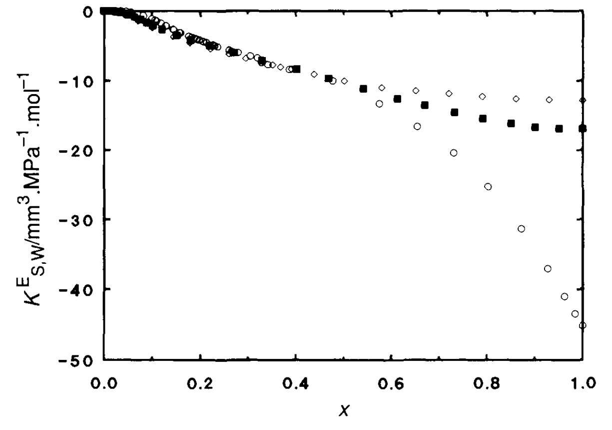

Figure 8 Excess partial molar quantity $K^{E}_{S,w}$ for water in [2-ethoxy)$_{n-1}$ ethanol (C_2E_n) + water)], at 298.15 K and mole fraction x of [2-(ethoxy)$_{n-1}$ethanol]. ○, [ethanol (C_2E_0) + water]; ■, [2-(ethoxy)-ethanol (C_2E_1) + water]; ◇, [2-(ethoxy)$_2$ethanol (C_2E_2) + water]. Unit: mm^3 MPa^{-1} mol^{-1}.

6 Curve-fitting Techniques

In the foregoing section, we made some qualitative assessments of the molecular scale origins of some of the more graphically interesting features of the isentropic compressibility data. It is clearly desirable to attempt to quantify the trends to which we have drawn attention. Numerical analysis of excess thermodynamic property data and the segmented composition model

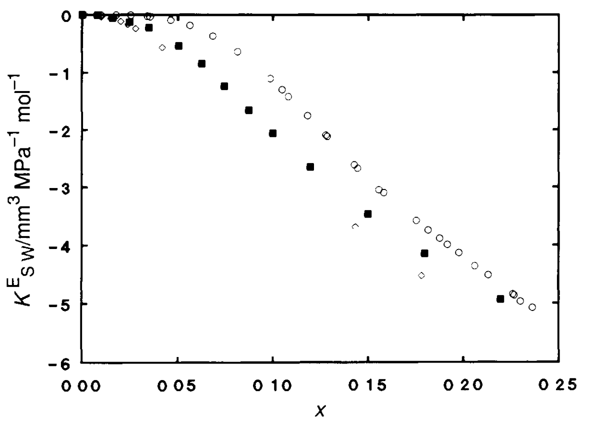

Figure 9 Excess partial molar quantity K^E_S for water in the water-rich region of [2-(ethoxy)$_{n-1}$ethanol (C_2E_n) + water)], at 298 15 K and mole fraction x of [2-(ethoxy)$_{n-1}$ethanol] ○, [ethanol (C_2E_0) + water], ■,[2-(ethoxy)ethanol(C_2E_1) + water], ◇,[2-(ethoxy)$_2$ethanol (C_2E_2) + water] Units mm^3 MPa^{-1} mol^{-1}

approach that we employ are discussed at length in a concurrent review and will be summarized only briefly here [8]

6.1 Conventional Techniques

The conventional approach to analysing the excess molar properties of binary liquid mixtures, proposed by Redlich and Kister, suffers from two disadvantages for the (C_mE_n + water) systems [29] It is ill-suited to fitting curves with sharp changes of slope and its optimizable coefficients have no recognizable physical significance Attempts to modify the Redlich–Kister formulation to cater to the more complex data curves have been only modestly successful Much better quality of fit is obtained by procedures which are designed to accomodate the variations of excess molar properties in the vicinity of a cmc or its analogue

6.2 Segmented Composition Techniques

6 2 1 *The Four-Segment Model*

Numerous authors have drawn attention to what they perceive as several distinct composition ranges in a variety of physical properties of binary hydroorganic mixtures The four-segment model represents an attempt to formalize and quantify that approach to data interpretation

The model is based upon the assumption that even (small amphiphile + water) systems tend, to varying extents, to mimic the patterns of molecular aggregation of (non-ionic surfactant + water) systems A rationale for partitioning the total composition range into four separate regions (segments) is given elsewhere and is based upon a scrutiny of curves like those shown in Figures 4 and 6 [8,22]

The Q^E values for each segment are assigned a distinct simple polynomial function of mole fraction, the order of which has been determined by examination of data plots and by testing different possibilities The analysis requires the location of three segment junctions In order of increasing amphiphile mole fraction, they are x_1, which corresponds to the location of sharp changes of slope seen in Figures 4, 6, and 7 In the case of Figure 7, x_1 is presumably a cmc For the other systems, it is more appropriate to refer to it as a cmc analogue x_2 and x_3 are the limiting mole fractions of the linear range of dQ^E/dx_A values, seen in Figures 4 and 6

The ranges, names, and polynomial functions for the four segments are (i) $0 \leqslant x_A \leqslant 1$, water-rich, cubic, (ii) $x_1 \leqslant x_A \leqslant x_2$, transitional, quartic, (iii) $x_2 \leqslant x_A \leqslant x_3$, pseudolamellar, quadratic, and (iv) $x_3 \leqslant x_A \leqslant 1$, amphiphile-rich, cubic

It is necessary to introduce a number of constraints upon the degree of discontinuity permitted at each of the three segment junctions $x_a = x_1, x_2$, and x_3 For the $K^E_{S\,m}$ data, we found that we could require both $K^E_{S\,m}$ and dK^E_S/dx_A to be single valued (continuous) at all three segment junctions We could also require that $d^2K^E_S/dx^2_A$ is single valued at x_2 We found that $d^2K^E_S/dx^2_A$ could be required to be single valued at x_3 for the (alkanol + water) data, without impairing the quality of fit, but not for the (ethoxylated + water) data These constraints limited the number of independent model parameters to six for the (C_mE_0 + water) systems and seven for the (C_mE_1 + water) and (C_mE_2 + water) systems

At the minimum set of six parameters, we have chosen the three which describe Q^E for the water-rich segment plus the three which describe Q^E in the central (pseudolamellar) segment The seventh parameter is the excess partial molar K^E_S of water at infinite dilution in the amphiphilic solvent

The form of the cubic equation for the water-rich segment is

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

where a_W is the excess partial (and apparent) molar property of the amphiphile at infinite dilution, b_W is related to the effects of solute pair interactions, and c_W is regarded as being a measure of the effects of hydrophobic cluster formation

For the pseudolamellar segment, the form adopted for the quadratic equation is

$$Q^E(L) = q_W(1 - x_A) + q_A x_A + b_L x_A x_W \tag{15}$$

where q_W is the excess molar property of water in some type of hypothetical standard state that is characteristic of this segment, q_A plays the same role for the amphiphile Were there a true microphase separation, b_L would be zero As it is, it is regarded as a measure of the magnitude of the departure from either microphase formation or from ideal mixing of two complexes with stoichiometries corresponding to x_2 and x_3

6 2 2 *Results*

In the following Tables, we show the values obtained for the six major four-segment model parameters, for the $K^E_{S\,m}$ data

Table 1a The a_w values for the $K^E_{S\,m}$ data for (C_mE_n + water) systems, at the temperature 25 °C Units mm^3 MPa^{-1} mol^{-1}

n m → ↓	1	2	3	4	6
0	− 36 3	− 57 5	− 67 4		
1	− 45 6	− 67 6		− 90 2	
2		− 78 9		− 114 5	− 176 6^a
3				− 129 6^b	

Value obtained at 5 °C [27] ^{b} Value obtained at 25 °C [27] The value for (2 PrOH + water) is − 84 2 mm^3 MPa^{-1} mol^{-1} [21]

Table 1b The apparent molar compressibilities of C_mE_n species at infinite aqueous dilution

n m → ↓	1	2	3	4	6
0	4 7	− 0 1	− 2 6		
1	0 2	− 5 3		− 3 8	
2		− 5 8		− 16 5	− 73 5^a
3				− 19·3^b	

Value obtained at 5 °C Value obtained at 25 °C The value for (2 PrOH + water) is − 8 0 mm^3 MPa^{-1} mol^{-1}

The a_W values of Table 1a can be converted into the apparent molar K_S values at infinite dilution by adding the molar K_S values of the pure amphiphiles (Table 1b) That the apparent molar K_S values are mostly negative is very interesting and implies that the presence of the amphiphile promotes extra rigidity to the pattern of self-aggregation of the solvating water molecules

Table 2 The b_{w} values for the $K^{\mathrm{E}}_{S\,m}$ data of ($\mathrm{C}_m\mathrm{E}_n$ + water) systems, at the temperature 25 °C Units mm^3 MPa^{-1} mol ^{1}

n $m\rightarrow$ ↓	1	2	3	4	6
0	2 8	1 6	− 50 6		
1	192 1	102 3		− 1805	
2		276 1		1223	− 6130^a
3				1863^b	

Value obtained at 5 °C [27] [b] Value obtained at 25 °C [27] The value for (2 PrOH + water) is − 10 1 mm^3 MPa ^{1} mol ^{1} [21]

Table 3 The c_{w} values for the $K^{\mathrm{E}}_{S\,m}$ data of ($\mathrm{C}_m\mathrm{E}_n$ + water) systems, at the temperature 25 °C Units mm^3 MPa ^{1} mol^{-1}

n $m\rightarrow$ ↓	1	2	3	4	6
0	64 4	476 6	4000		
1	− 123 3	1012		135 000	
2		505		22 980	5 184 000^a
3				2454^b	

Value obtained at 5 °C [27] [b] Value obtained at 25 °C [27] The value for (2 PrOH + water) is 2200 mm^3 MPa ^{1} mol ^{1} [21]

The b_{W} values of Table 2 show significant increase with increasing polar head group The pattern of change with chain length is intriguing as is the nature of the dependence of c_{W} (Table 3) upon molecular structural variation We have no simple explanation for these features, but it is clear that the more dramatic results can be associated with some type of critical hydrophobic–hydrophilic balance

Table 4 The q_{w} values for the $K^{\mathrm{E}}_{S\,m}$ data of ($\mathrm{C}_m\mathrm{E}_n$ + water) systems, at the temperature 25 °C Units mm^3 MPa^{-1} mol ^{1}

n $m\rightarrow$ ↓	1	2	3	4	6
0	0 23	− 3 41	− 2 77		
1	− 3 33	− 4 27		− 1 63	
2		− 4 91		− 2 87	− 2 33^a
3				− 3 21^b	

Value obtained at 5 °C [27] [b] Value obtained at 25 °C [27] The value for (2 PrOH + water) is − 4 85 mm^3 MPa ^{1} mol ^{1} [21]

The q_{W} values of Table 4 become progressively more negative as the size of the polar head group increases Their dependence upon alkyl chain length is an intriguing feature which is also found for the V^{E}_m data [8] It is possible that we are looking at a combination of two factors packing and the formation of disk-shaped (pseudolamellar) aggregates, with the latter factor becoming the more important as the hydrophobic group tends to become the more dominant of the two

The q_{A} values of Table 5 show no clear-cut dependence upon alkyl chain length, but become significantly more positive as the polar head group size increases Evidently the amphiphile aggregates, in this composition range, become progressively more compressible as the polar head group is enlarged

Table 5 The q_{A} values for the $K^{\mathrm{E}}_{S\,m}$ data of ($\mathrm{C}_m\mathrm{E}_n$ + water) systems, at the temperature 25 °C Units mm^3 MPa ^{1} mol ^{1}

n $m\rightarrow$ ↓	1	2	3	4	6
0	− 1 10	− 1 51	− 0 88		
1	1 64	2 92		2 13	
2		4 14		4 00	4 19^a
3				8 02^b	

Value obtained at 5 °C [27] [b] Value obtained at 25 °C [27] The value for (2 PrOH + water) is − 1 04 mm^3 MPa ^{1} mol ^{1} [21]

Table 6 The b_{L} values for the $K^{\mathrm{E}}_{S\,m}$ data of ($\mathrm{C}_m\mathrm{E}_n$ + water) systems, at the temperature 25 °C Units mm^3 MPa^{-1} mol^{-1}

n $m\rightarrow$ ↓	1	2	3	4	6
0	− 41 0	− 30 9	− 18 3		
1	− 10 2	− 24 5		− 20 5	
2		− 21 6		− 21 5	− 21 1^a
3				− 26 9^b	

Value obtained at 5 °C [27] [b] Value obtained at 25 °C [27] The value for (2 PrOH + water) is − 25 4 mm^3 MPa ^{1} mol ^{1} [21]

The b_{L} values of Table 6 are remarkable in that so many of the values are close to each other This suggests a strong similarity between the nature of the interfaces between water and the amphiphile aggregates

7 Conclusion

The measurement of the speed of ultrasonic waves in liquids is one of the most accurate and reproducible of the tools available for the study of liquid mixtures The Newton–Laplace equation permits us to translate their values into reliable estimates of the molar quantity $K_{S\,m} = -(\partial V_m/\partial p)_S$ Since $K_{S\,m}$ is a second derivative of the molar Gibbs free energy function, its values are particularly sensitive to changes in composition

In the context of the Benson–Kiyohara approach to defining ideal molar properties, it is possible to define and evaluate $K^{\mathrm{id}}_{S\,m}$ and hence the excess molar property, $K^{\mathrm{E}}_{S\,m}$ [11] This definition supersedes those based upon a variety of thermodynamically inconsistent definitions, which we have identified within this review The Newton–Laplace equation also permits us to estimate the ultrasonic speed in an ideal mixture and the deviation of the measured speed from the ideal value

The $K^{\mathrm{E}}_{S\,m}$ values are affected by both packing and the patterns of molecular aggregations induced by the intermolecular interactions In common with $K^{\mathrm{E}}_{T\,m}$ and V^{E}_m, the $K^{\mathrm{E}}_{S\,m}$ values for (amphiphile + water) mixtures are negative at all compositions, implying that the mixing promotes enhanced density and rigidity

Plots of $K^{\mathrm{E}}_{S\,m}$, and quantities derived from it, reveal interesting types of composition dependence which, we consider, support the contention that even relatively small amphiphiles tend to adopt patterns of molecular aggregation that mimic those of their detergent homologues

Conventional curve-fitting procedures have been proved to be ill-suited for the $K^{\mathrm{E}}_{S\,m}$ data of all but the very simplest of (amphiphile + water) systems Far more satisfactory is the four-segment model, a version of which has been used to generate results discussed in this review

In the course of discussing the graphs of the $K^{\mathrm{E}}_{S\,m}$ data and the results of our analyses, we have offered some suggestions concerning the nature of the schemes of molecular aggregation that exist within (amphiphile + water) mixtures Such suggestions are inevitably tentative, however plausible What should be stressed is that the accumulated $K^{E}_{S\,m}$ data represent a reliable body of information with which any future model must be consistent

8 References

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