

Association models for alcohol-water mixtures

A H ROUX^a and J E DESNOYERS^{b*}

^a Laboratoire de Thermodynamique et Cinétique Chimique, Université de Clermont-Ferrand 2, 63170 Aubière, France.

^b Institut National de la Recherche Scientifique, C.P. 7500, Ste FOY, Québec G1V4C7, Canada.

Abstract. Alcohol-water mixtures are often used as model systems for the study of hydrophobic interactions. In this respect, their thermodynamic properties are of particular interest since precise data are available over the whole miscibility range and they lend themselves readily to theoretical modelling. Three association models have been used to fit the volume data taken from the literature for aqueous methanol, ethanol and n-propanol at various temperatures. A simple micellization equilibrium explains the general trends but fails to fit the reduced excess volumes at both ends of the mole fraction scale. Better fits are obtained if interaction parameters are introduced, but these two parameters cannot easily be rationalized. A double association model (one for the alcohol and one for the water) gives the best fit and all the parameters have a physical significance. However, the parameters extracted, e.g. aggregation numbers, and their trends with temperature are not always realistic. Despite their limitations, these models illustrate well with the kind of avenues that can be explored to fit and interpret the experimental data of these complex systems.

Keywords. Chemical equilibrium model; water-alcohol mixtures; double association; aggregation number; binary mixtures.

1. Introduction

Alcohols are probably the most well-known solutes used for the study of hydrophobic effects, in view of their simple molecular structure, increasing hydrophobic character with chain length and high solubility in water. Most of their physical properties have been studied extensively over the years (Franks and Desnoyers 1985). Near infinite dilution, authors generally agree on the existence of a hydrophobic cosphere around the aliphatic chain which has some resemblance to clathrate hydrates, and this hydrophobic hydration increases with chain length. As the concentration increases, hydrophobic pair and higher order interactions occur between two or more alcohol molecules, and there is strong evidence that, in these complexes, the alcohol molecules are separated by a water molecule, somewhat as suggested by Iwasaki and coworkers (Iwasaki *et al* 1976; Iwasaki and Fujiyama 1977, 1979). As still higher concentrations, these structures collapse and clusters of alcohol molecules are formed which largely have the properties of pure alcohols.

Thermodynamic properties are of particular interest for the study of hydrophobic effects since they lend themselves readily to theoretical modelling (Desnoyers and Jolicœur 1982). The infinite dilution partial molar quantities are functions only of the intrinsic properties of the alcohol and of the solute-solvent interactions. The

*To whom all correspondence should be addressed.

initial slope in the concentration dependence of the partial or apparent molar quantities can be interpreted in terms of hydrophobic interactions between pairs of solutes (Kozak *et al* 1968; Okasaki *et al* 1984; Tanaka *et al* 1984). The high concentration data are more difficult to model in view of the complexity of the system. Eventually, theoretical models based on molecular dynamics or Monte Carlo calculations should succeed in reproducing the thermodynamic properties over the whole miscibility range, but at present the Kirkwood-Buff theory is about the only one that has been applied with some success (Donkersloot 1979). However, at our present state of knowledge, it is difficult to interpret the Kirkwood-Buff integral in terms of molecular interactions. To gain some understanding of the prevailing structures in these high concentration alcohol solutions therefore, simple chemical models, which are easy to treat mathematically, must be used. From these models, some information can in principle be gained from the magnitude of the parameters used to fit the data. The present paper will be concerned with some of these models which are analogous to a micellization process. The application will be limited to volumes since this where more accurate data exist, especially in the dilute regions.

2. Chemical models

The thermodynamic properties of liquid mixtures are often fitted with a polynomial equation. This approach is not satisfactory for strong interacting systems such as alcohol-water mixtures. For example, Benson and Kiyohara (1980) required up to 11 parameters of a power series to reproduce the thermodynamic functions of mixing of lower alcohol and water over the whole mole fraction range, and these parameters had no physical significance. It is therefore necessary to use models that are sufficiently simple to be handled mathematically and at the same time have some resemblance to the actual structure of the system. Such approaches have been proposed by many authors and in particular by Andrae *et al* (1965), Mikhailov (1968), Mikhailov and Ponomareva (1968), Iwasaki *et al* (1976), Iwasaki and Fujiyama (1977, 1979), Hvidt (1978), and Dethlefsen *et al* (1984). None of these models are at present entirely satisfactory.

A clue to the structure of alcohol-water mixtures is provided by the concentration trends of the thermodynamic properties. All properties undergo large changes over a relatively narrow concentration range. The sharpness of the transition region increases and the concentration domain for the change decreases as the chain length of the alcohol increases. The limited solubility in water prevents us from examining these trends beyond *n*-propanol for the linear alcohols and *t*-butanol for the branched ones. *n*-butanol can be made completely miscible with water by the addition of a small quantity of surfactant (Roux-Desgranges *et al* 1982). The miscibility barrier can also be overcome by increasing the hydrophilic character of the polar group. This can be done by the addition of ethoxy groups on the chain or by replacing the $-OH$ group by an amine or a phosphine oxide. In such cases, the thermodynamic properties of the solutes change gradually with chain length. For example, in the case of alkyldimethylamine oxides (Desnoyers *et al* 1982), the lower members of the series are quite similar to alcohols while the long-chain homologs are typical nonionic surfactants. Also, the study of ternary systems of

water-alcohol-hydrocarbon (Smith *et al* 1977; Keiser *et al* 1979; Lara *et al* 1981) strongly suggests that alcohols exist as microaggregates into which the hydrocarbons dissolve preferentially. Therefore, in these organic-water mixtures, microphases of alcohols or of other similar solutes exist in a form that has similarities with micelles. In fact, a mass-action model (Desnoyers *et al* 1983), which was developed for non-ionic surfactants, can be applied to alcohol-water mixtures (Roux *et al* 1984), and the aggregation numbers extracted are of the order of 4 to 7 which is not unreasonable. Unfortunately, this model, which had been developed with the dilute solution approximation, cannot be applied as such to high concentration data. This model will presently be extended to cover the whole mole fraction range.

3. Single equilibrium ideal model

Successful models should apply to all properties, involve a minimum number of adjustable parameters which have some physical significance and reproduce precisely the experimental data. The simplest approach is therefore to identify the equilibrium processes best-suited for alcohol-water mixtures.

The chemical models for micellar systems fall into two main groups (Desnoyers *et al* 1986). The pseudo-phase models assume that the surfactant exists as monomers up to a critical micellar concentration which is equivalent to a monomer solubility. Beyond this CMC, the added surfactant will aggregate to form micelles. These simple models are appropriate for long-chain-surfactants that have a relatively sharp CMC region. With shorter-chain surfactants, the mass-action models, which assume an equilibrium between monomers and aggregates of a finite size, are preferable. In the simpler case, micellization is assumed to occur in a single step, i.e., for monodispersed micelles:



where a is the aggregation number of the micelles M in equilibrium with the monomers. Since the properties of the surfactant in the monomeric and micellar regions are different, these species will be identified as A and A' .

In the most simple micellar model, alcohols in water are assumed to form an ideal associated solution (Prigogine and Defay 1950). The solution is thus considered a mixture of monomers, association complexes and water, each species behaving ideally. The chemical potential of each species is given in the mole fraction scale by:

$$\mu_i = \mu_i^0 + RT \ln X_i, \quad (2)$$

where the standard state is the pure liquid of each species. Following the usual convention, the solvent is denoted as component 1, while the solute is the component 2, which can exist in the form A or A' . If n_i is the number of particles of each species, then the fraction of alcohol in the monomeric form is given by:

$$\alpha = n_A/n_2. \quad (3)$$

The number of aggregates in solution are then:

$$n_M = n_2(1 - \alpha)/a. \quad (4)$$

To simplify the notation, the fraction D is defined as:

$$D = \sum_i n_i / (n_1 + n_2) = X_2[\alpha + (1 - \alpha)/a] + X_1. \quad (5)$$

Under these conditions, the total Gibbs free energy of the system is given by:

$$\begin{aligned} G/RT &= \sum_i n_i \mu_i / RT = n_2 \alpha [\mu_A^0 / RT + \ln((\alpha X_2 / D))] + \\ & (n_2 (1 - \alpha) / a) \{ \mu_M^0 / RT + \ln[(1 - \alpha) X_2 / aD] \} + \\ & n_1 [\mu_1^0 / RT + \ln(X_1 / D)]. \end{aligned} \quad (6)$$

The equilibrium condition for this system is:

$$\begin{aligned} [\partial(G/RT) / \partial \alpha]_{T, P, n_1, n_2} &= 0 \\ &= n_2 \{ [\mu_A^0 / RT + \ln(\alpha X_2 / D)] - (1/a) [\mu_M^0 / RT + \ln((1 - \alpha) X_2 / aD)] \}, \end{aligned} \quad (7)$$

which can be rewritten as:

$$\begin{aligned} (\mu_A^0 - \mu_M^0 / a) / RT &= (\mu_A^0 - \mu_A^0) / RT = -\Delta \mu_A / RT \\ &= (1/a) \ln((1 - \alpha) X_2 / aD) - \ln(\alpha X_2 / D). \end{aligned} \quad (8)$$

It is possible to apply this model to any thermodynamic property. For example, the total volume of such a system can readily be expressed in terms of the partial molar volumes of each species:

$$V = n_2 \alpha V_A^0 + n_2 (1 - \alpha) V_A^0 / a + n_1 V_1^0. \quad (9)$$

In this ideal model all the partial molar volumes and the aggregation number a are by definition constants. Equation (9) can now be expressed in any convenient form which corresponds to the measurable data. In the present case, the most convenient quantity is the excess volume defined by:

$$V^E = (V - n_2 V_2^0 - n_1 V_1^0) / (n_1 + n_2) \quad (10)$$

where the standard state for the two components is the pure liquid, i.e., $V_i^0 = V_i^*$. If the fraction of monomers in the pure alcohol ($X_2 = 1$) is denoted by α^* , it then follows that the reduced excess volume is given by:

$$V^E / X_1 X_2 = (\alpha^* - \alpha) (V_A^0 - V_A^0 / a) / X_1. \quad (11)$$

This function is proportional to apparent molar volumes at both ends of the concentration scale. It is therefore a function which remains sensitive to the various types of interactions over the whole mole fraction range. Equations (8) and (11) can readily be solved simultaneously if $\Delta \mu_A$, ΔV_A and a are known. This function was simulated and compared with typical data for alcohol-water mixtures in figure 1. As it stands, this "ideal" model accounts for the increase in volume that is generally observed with these systems but fails to explain the initial decrease in volume in the water-rich end. There are also noticeable differences in the alcohol-rich end. Extra parameters were therefore required to simulate the correct experimental data.

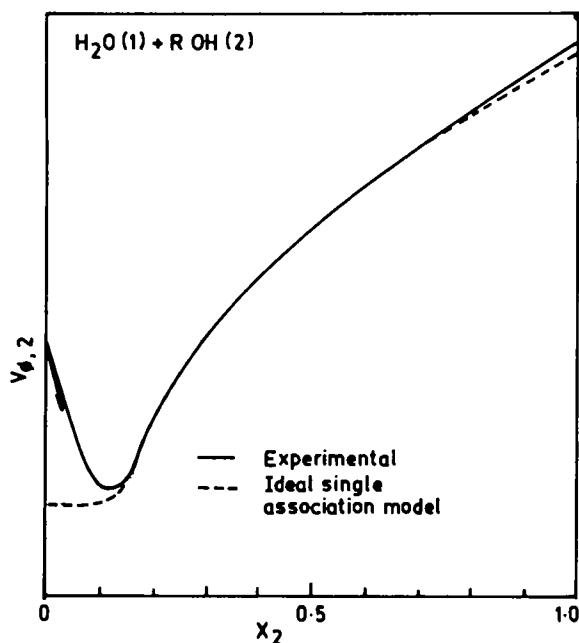


Figure 1. Dependence on the solute mole fraction of the apparent molar volume of alcohols in water, based on the ideal single association model.

4. Single equilibrium non-ideal model

The initial negative slope that is observed with the apparent volumes of hydrophobic solutions in water is generally attributed to the overlap of hydrophobic hydration cospheres when two solutes approach each other (Desnoyers and Jolicoeur 1982). With dilute solutions this effect can be accounted for by the addition of the pair interaction term between monomers (Desnoyers *et al* 1983). With liquid mixtures, this type of non-ideality can be introduced in a form similar to the regular solution theory by introducing two extra terms to (11):

$$V^E/X_1X_2 = (\alpha^* - \alpha)(V_A^0 - V_A^0)/X_1 + B_{v,A}\alpha X_1 + B_{v,A'}(1 - \alpha)X_1, \quad (12)$$

To be consistent, two extra terms of the type $B_{G,A} \alpha X_1$ should also be added to (8). However, with four extra adjustable parameters of this type, the model becomes of questionable use. Therefore, interaction terms were added only to the volume expression as it was done with surfactant systems (Desnoyers *et al* 1983).

Equations (8) and (12) were solved simultaneously and the parameters were optimized using an appropriate non-linear least-squares. For this purpose, the data of Benson and Kiyohara (1980) were used. These simulations are compared with the actual experimental data for the three lower normal alcohols in figures 2 to 4. The parameters derived from these fits are given for different temperatures in table 1 and plotted against temperature in figures 5 and 6.

The general trends for the volumes of the alcohol-water mixtures are accounted for reasonably well with this non-ideal model. However, the deviations between

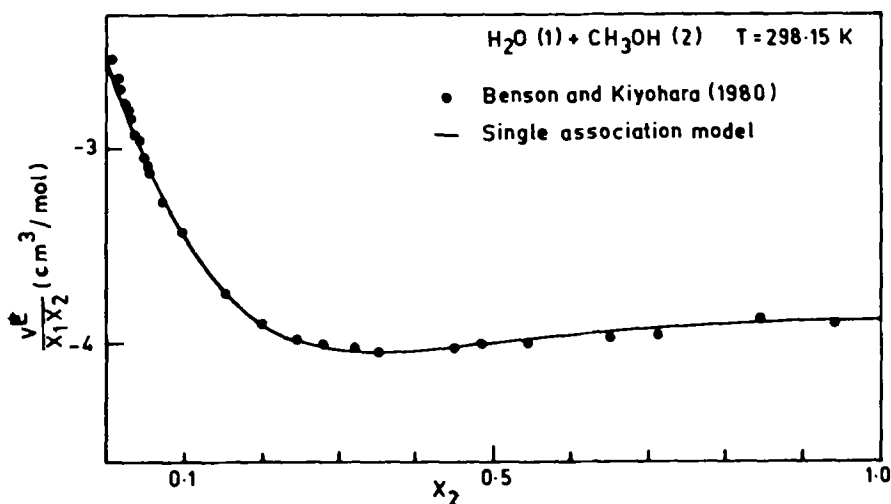


Figure 2. Simulation of the reduced excess volume of methanol-water mixtures with the non-ideal single association model.

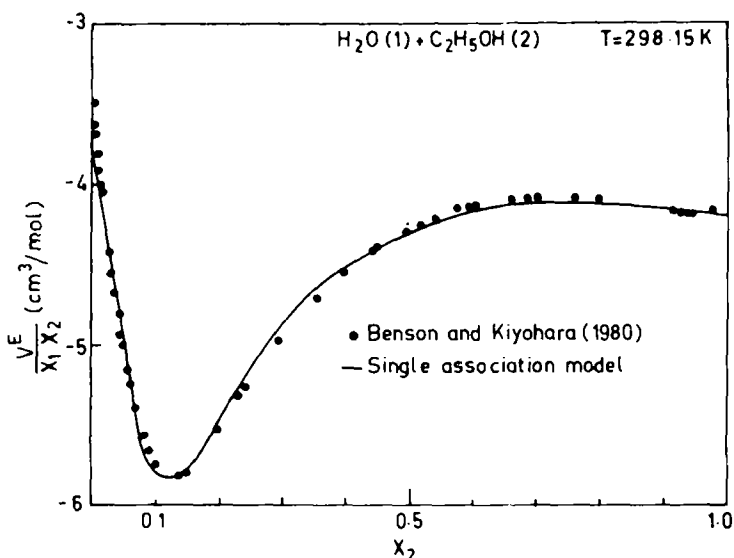


Figure 3. Simulation of the reduced excess volume of ethanol-water mixtures with the non-ideal single association model.

the simulations are the experimental data are definitely larger than the experimental scatter of points. The magnitude of the parameters, especially V_A and a , are not unreasonable. The aggregation number, on the other hand, is assumed to be independent of temperature and pressure in the model, but figure 6 shows that this is not so. With surfactants, the aggregation numbers are also generally found to decrease with temperature as observed here with alcohols. This non-ideal association model can reproduce the experimental reduced excess volumes and at least three of the adjustable parameters have magnitudes that are as expected. On the other hand, the two interaction parameters cannot easily be rationalized. But

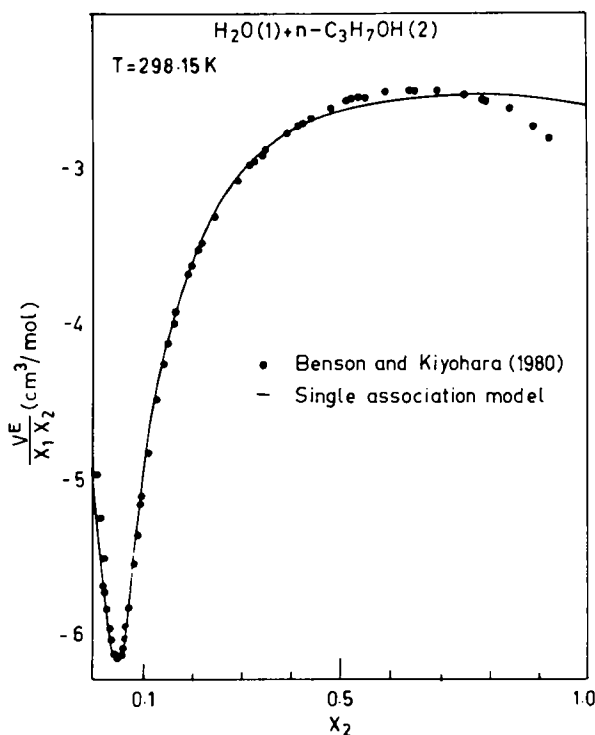


Figure 4. Simulation of the reduced excess volume of *n*-propanol-water mixtures with the non-ideal single association model.

the main failure of this model is that it does not explicitly take into account the high degree of structure of liquid water which should be quite different at both ends of the concentration scale.

5. Double association model

In the non-ideal single association model, all changes in the structure of water are included in the two interaction parameters. A more satisfactory approach would be to take water as an associated liquid, somewhat in the way suggested by Mikhailov (1968) and Hvidt (1978). Again, for simplicity, a two-state model is used for liquid water. To the relations for the alcohol, (1), (3) and (4), similar ones must now be added for water. If the clusters of water *L* are made up of *b* water molecules *B'*,



where *B* represents water in the monomeric form. As with the alcohol, we define the fraction of monomers of water by

$$\beta = n_B/n_1 \quad (14)$$

and the number of clusters by

$$n_L = n_1(1 - \beta)/b. \quad (15)$$

Table 1. Parameters for the "non-ideal single association model".

	$T(^{\circ}\text{C})$	ΔV_A (cm^3/mol)	B_A (cm^3/mol)	B'_A (cm^3/mol)	$\Delta\mu_A$ (J/mol)	a	$\sigma(V^E/x_1x_2)$ (cm^3/mol)	X_2 range
MeOH	15	9.090 (0.141)	5.653 (0.131)	-0.757 (0.095)	1802 (26)	4.25 (0.09)	0.022	0.00136 0.97751
	20	8.661 (0.092)	4.858 (0.088)	-0.645 (0.077)	1574 (20)	4.05 (0.05)	0.014	0.00246 0.89691
	25	8.320 (0.080)	4.059 (0.075)	-0.365 (0.075)	1273 (18)	3.83 (0.04)	0.012	0.00293 0.94059
	30	8.327 (0.086)	3.633 (0.080)	-0.325 (0.064)	1072 (20)	3.61 (0.04)	0.009	0.00503 0.89421
	35	8.387 (0.082)	3.253 (0.074)	-0.177 (0.070)	874 (19)	3.44 (0.04)	0.008	0.00299 0.88414
	EtOH	15	14.778 (0.367)	10.642 (0.426)	1.507 (0.252)	3118 (76)	7.87 (0.29)	0.069
20		13.600 (0.332)	9.061 (0.387)	1.769 (0.158)	2903 (70)	6.72 (0.17)	0.050	0.02395 0.93869
25		13.430 (0.243)	8.680 (0.280)	1.889 (0.099)	2852 (50)	6.17 (0.11)	0.048	0.01477 0.97325
30		12.350 (0.190)	7.237 (0.224)	1.809 (0.073)	2650 (46)	5.53 (0.08)	0.031	0.02032 0.97151
35		11.888 (0.198)	6.486 (0.236)	1.853 (0.083)	2517 (53)	5.06 (0.08)	0.028	0.02034 0.96956
nPrOH		15	19.861 (0.487)	14.728 (0.545)	1.757 (0.100)	4653 (77)	8.85 (0.41)	0.041
	20	18.884 (0.519)	13.616 (0.577)	1.763 (0.096)	4577 (87)	7.60 (0.33)	0.048	0.02046 0.88124
	25	17.723 (0.245)	12.310 (0.275)	1.396 (0.053)	4604 (48)	6.92 (0.16)	0.031	0.02053 0.84634
	30	16.242 (0.438)	10.661 (0.495)	1.499 (0.081)	4428 (92)	6.03 (0.24)	0.043	0.02018 0.92674
	35	15.659 (0.558)	10.017 (0.623)	1.342 (0.095)	4496 (123)	5.74 (0.26)	0.051	0.01363 0.96426

Equation 5 becomes:

$$D = X_2[\alpha + (1 - \alpha)/a] + X_1[\beta + (1 - \beta)/b]. \quad (16)$$

The total Gibbs free energy is now given by

$$\begin{aligned} G/RT = & n_2\alpha[\mu_A^0/RT + \ln(\alpha X_2/D)] + \\ & [n_2(1 - \alpha)a]\{\mu_M^0/RT + \ln[(1 - \alpha)X_2/aD]\} + n_1\beta[\mu_B^0/RT + \ln(\beta X_1/D)] \\ & + [n_1(1 - \beta)/b]\{\mu_L^0 + \ln[(1 - \beta)X_1/bD]\}. \end{aligned} \quad (17)$$

If a and b are independent of the composition, the double stability of the system implies that we have simultaneously:

$$\begin{aligned} & [\partial(G/RT)/\partial\alpha]_{T,P,n_1,n_2,\beta} = 0 \\ & = n_2\{\mu_A^0/RT + \ln(\alpha X_2/D)\} - (1/a)[\mu_M^0/RT + \ln((1 - \alpha)X_2/aD)], \end{aligned} \quad (18a)$$

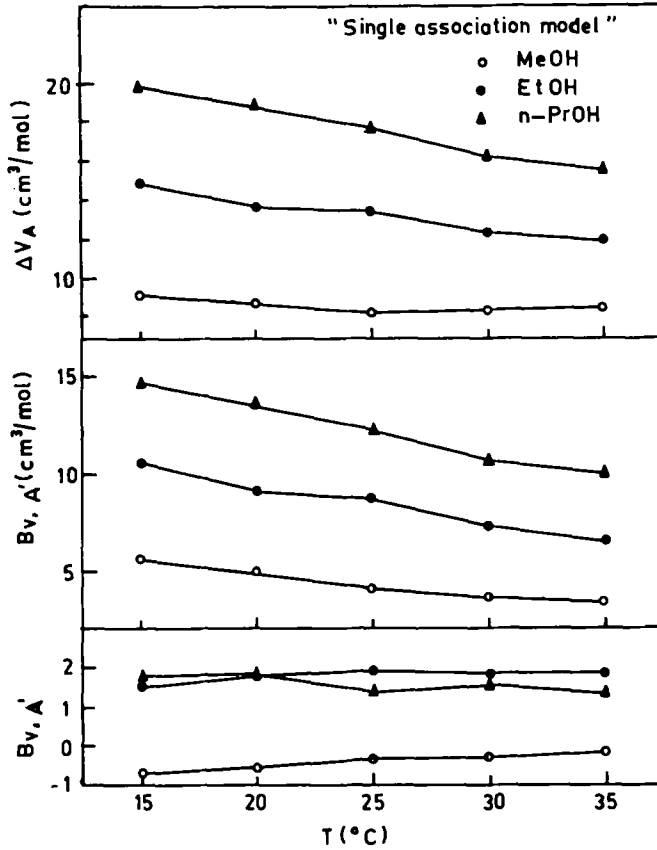


Figure 5. Temperature dependence of the parameters ΔV_A , and $B_{V,A}$ and $B_{V,A}'$ of alcohol-water mixtures extracted from the non-ideal single association model.

and

$$\begin{aligned}
 & [\partial(G/RT)/\partial\beta]_{T,P,n_1,n_2,\alpha} = 0 \\
 & = n_1\{[\mu_B^0/RT + \ln(\beta X_1/D)] - (1/b)[\mu_L^0/RT + \ln((1-\beta)X_1/bD)]\}. \quad (18b)
 \end{aligned}$$

The solution of these two equations will give $\Delta\mu_A$ and $\Delta\mu_B$ in terms of α , β , a and b .

The total volume of the system is given by

$$V = n_2\alpha V_A^0 + n_2(1-\alpha)V_A^0 + n_1\beta V_B^0 + n_1(1-\beta)V_B^0. \quad (19)$$

If, as in the case of the single equilibrium model, the fraction of monomers in the pure water ($X_1 = 1$) to given by β^* , then the reduced excess volume is given by

$$V^E/X_1X_2 = (\alpha^* - \alpha)\Delta V_A/X_1 + (\beta^* - \beta)\Delta V_B/X_2. \quad (20)$$

The excess volume is now a function of six parameters all of which have a physical significance: $\Delta\mu_A$, $\Delta\mu_B$, a , b , ΔV_A and ΔV_B . These experimental points from other authors are also included in these figures to give some idea of the scatter of the data when plotted in this fashion but were not used in the least-squares. The derived parameters for various temperatures are summarized in table 2.

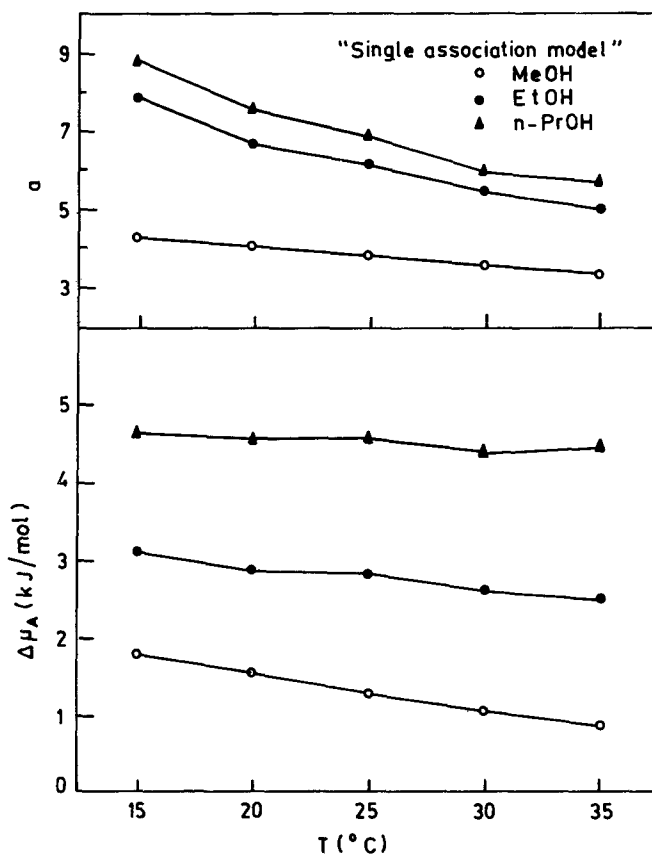


Figure 6. Temperature dependence of the parameters $\Delta\mu_A$ and a of alcohol-water mixtures extracted from the non-ideal single association model.

The fit between the simulations and experimental data is excellent in all cases for intermediate mole fractions. Therefore, only the water-rich and alcohol-rich regions are shown in figures 7 to 9. The fit is essentially quantitative over the whole mole fraction range in the case of MeOH and EtOH. The agreement is also excellent in the water-rich region with *n*-PrOH but less good in the alcohol-rich region. This kind of plot and simulation illustrates very well the necessity of obtaining precise data over the whole mole fraction region, especially to very low and very high mole fraction. For example, we were unable to simulate enthalpy data from the literature since the dilute region and concentrated one were not measured by the same authors and the disagreement between the different sets of data were too large.

The various parameters obtained from the model are plotted against temperature in figures 10 to 13. The trends of V_A (figure 10) are not unexpected but their magnitudes, especially with the higher homologs, seem high. The aggregation numbers a of the alcohols (figure 12) do not change in a regular way, their magnitude seem high, especially with *n*-PrOH, and vary with temperature while the model assumes a to be independent of temperature. The trends and magnitudes of $\Delta\mu_B$, ΔV_B and b should also have been independent of the alcohol if the role of

Table 2. Parameters for the "ideal double association model".

	$T(^{\circ}\text{C})$	ΔV_A (cm^3/mol)	$-\Delta V_B$ (cm^3/mol)	$\Delta\mu_A$ (J/mol)	$\Delta\mu_B$ (J/mol)	a	b	$\sigma(V^E/x_1x_2)$ (cm^3/mol)	X_2 range
MeOH	15	8.893	2.309	1533	185	7.08	14.49	0.010	0.02536 0.86127
	20	8.332	2.160	1422	172	6.79	12.81	0.009	0.02463 0.89691
	25	8.328 (0.018)	2.187 (0.027)	809 (15)	-543 (22)	4.07 (0.05)	7.85 (0.08)	0.007	0.00809 0.94059
	30	7.948	1.912	869	-331	4.48	7.99	0.006	0.02451 0.89421
	35	7.841	1.898	695	-458	4.24	6.96	0.002	0.02882 0.88414
EtOH	15	19.124	6.482	2109	-156	6.17	10.32	0.010	0.02444 0.94196
	20	18.059	5.904	2095	-115	6.13	10.28	0.012	0.01921 0.94698
	25	17.882 (0.013)	6.697 (0.032)	1952 (3)	-391 (6)	4.93 (0.02)	8.22 (0.04)	0.012	0.00089 0.93984
	30	16.002	5.179	1974	-126	5.61	9.37	0.010	0.02032 0.94760
	35	15.694	5.416	1847	-278	4.89	8.07	0.007	0.02034 0.93263
nPrOH	15	45.512	12.241	3210	514	26.01	73.8	0.052	0.00274 0.97225
	20	32.522	7.361	3392	416	18.12	55.73	0.031	0.00830 0.79079
	25	27.402 (1.675)	5.853 (0.510)	3356 (33)	333 (47)	11.6 (1.7)	37.6 (5.6)	0.047	0.02053 0.92388
	30	22.571	4.829	3282	331	10.1	31.8	0.046	0.01442 0.92674
	35	19.434	3.497	3514	231	8.84	29.7	0.027	0.00800 0.79013

the alcohol was simply to perturb the monomer-cluster equilibrium of water. Figures 11 and 13 show that this is certainly not so. We can therefore conclude from these simulations that, although the prediction of the observed trends are, in general, excellent with this double equilibrium model, the parameters extracted and their trends with temperature are not always realistic.

6. Discussion

A mass-action model (Desnoyers *et al* 1983) has been used successfully to fit the thermodynamic properties of non-ionic surfactants in water and extract from these the functions of micellization. The equilibrium constants and aggregation numbers were of the right order of magnitude and, as a first approximation, independent of the property. This model has presently been generalized to include all systems that

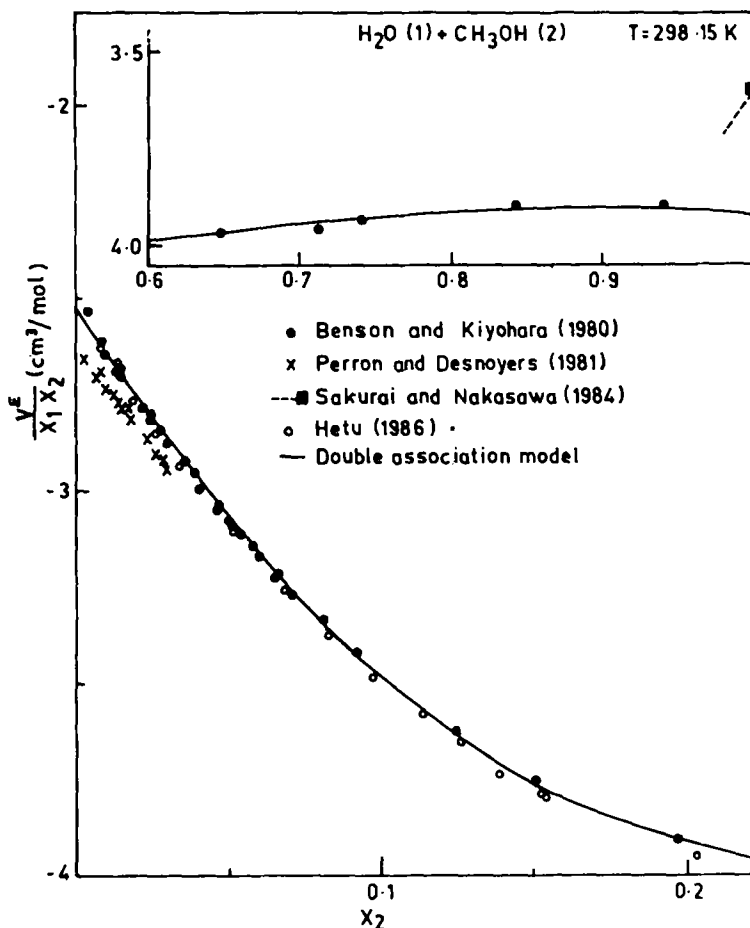


Figure 7. Simulation of the reduced excess volume of methanol-water mixtures with the double association model.

form microaggregation in water. Two variances of this micellar model have been applied to volume data of alcohol-water mixtures.

The main advantage of the present approach is that the models apply equally well to systems which show concentration microheterogeneity and to the micellar systems. The models can also readily be extended to all thermodynamic properties. The non-ideal single equilibrium model fits reasonably well the reduced excess volumes, and the three basic parameters, $\Delta\mu_A$, ΔV_A and a , are of the right order of magnitude and vary as expected with chain length of the alcohol. On the other hand, a varies with temperature, contrary to the basic assumption of the model, and the parameters $B_{V,A}$ and $B_{V,A'}$ have no simple molecular meaning. The double equilibrium model fits the data better, and all the parameters have a physical meaning. However, the magnitude and trends of these parameters are not always as expected. In particular, the parameters for water depend on the alcohol, which is contrary to the basic assumption that the role of the alcohol was simply to shift the monomer-cluster equilibrium of water.

As mentioned in §2, a severe test of these models would be to apply them to

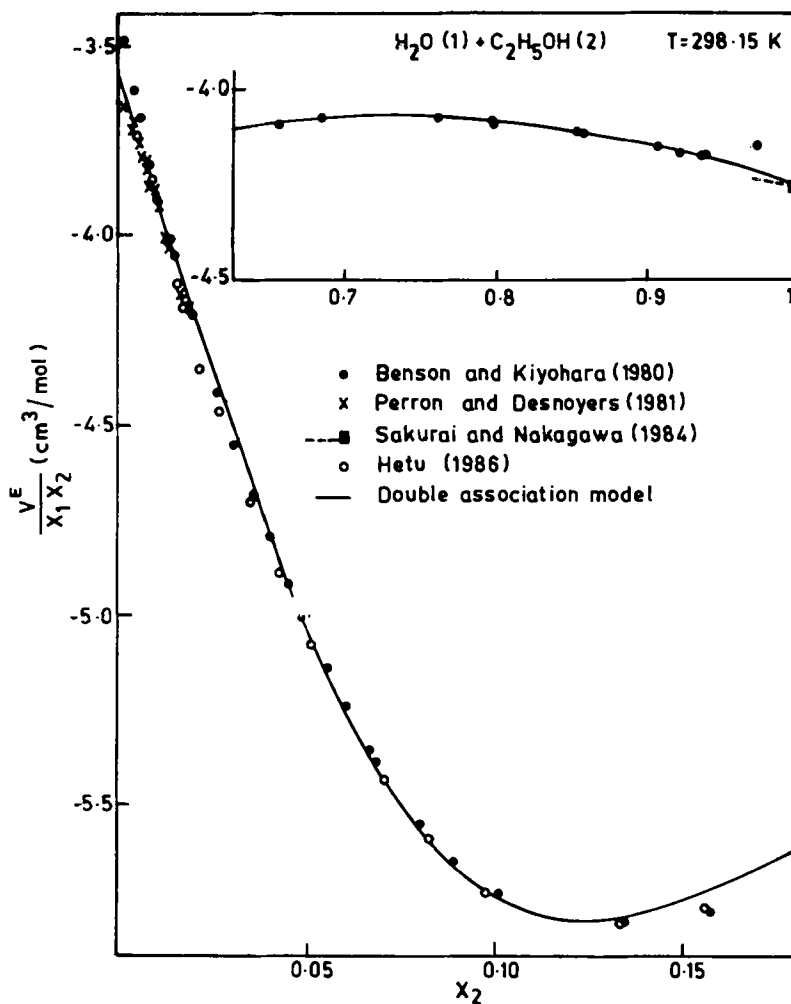


Figure 8. Simulation of the reduced excess volume of ethanol-water mixtures with the double association model.

different properties and check to see if $\Delta\mu_A$, a and the parameters for water remain independent of the properties. Unfortunately, free energies and enthalpies have not been measured with sufficient precision over the whole mole fraction range, including the very dilute regions, to treat the data the way we did with volumes. Reasonably good data exist for heat capacities and compressibilities, but these functions, being second derivatives of the chemical potential with respect to temperature or pressure, must automatically include terms for the displacement of the equilibrium with temperature or pressure, and this will add extra adjustable parameters.

Many of the oversimplified assumptions of these models could be responsible for their weaknesses. The three main ones are:

1. The aggregation numbers are not constants with respect to temperature and pressure.

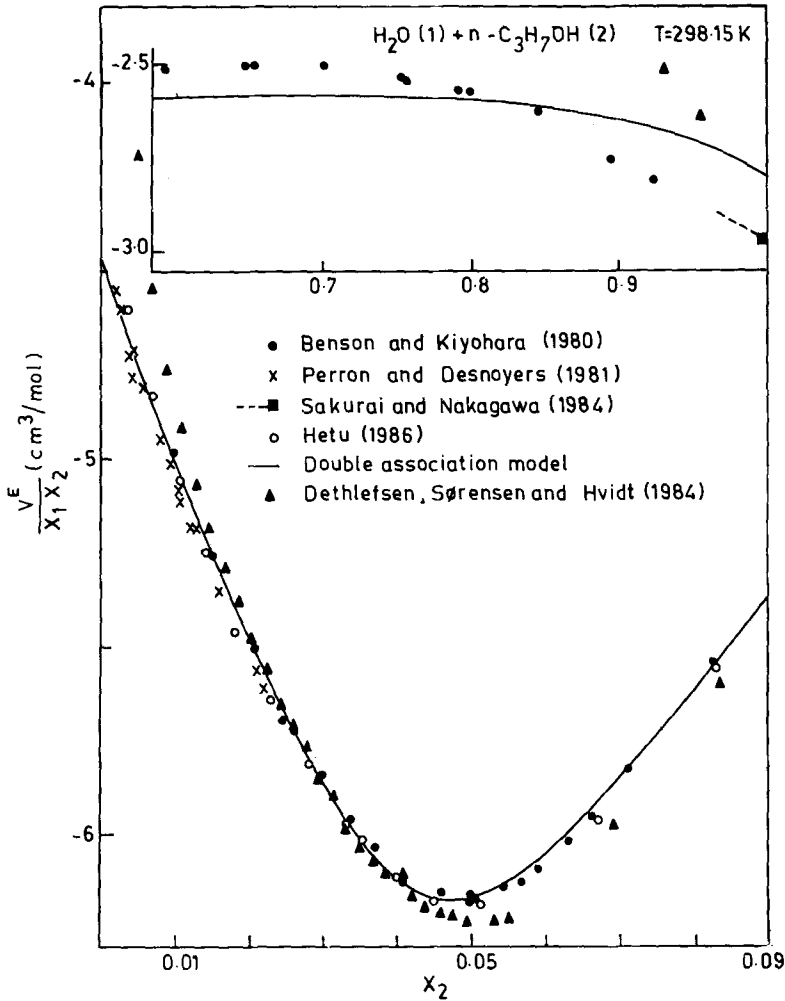


Figure 9. Simulation of the reduced excess volume of *n*-propanol-water mixtures with the double association model.

2. The size of the alcohol aggregates and of water clusters are not independent of alcohol and of water concentration.
3. The aggregates and clusters are not monodispersed.
4. The structure of water in the hydrophobic copheres certainly has some differences with the clusters which exist in pure water.

The models can readily be correlated for all these effects but at the expense of extra parameters. Also, in such cases, the convergence of the least-squares will be much slower.

The double equilibrium model is therefore a good curve-fitting model since it uses the minimum number of adjustable parameters necessary to fit the observed thermodynamic data, but, as it stands, it does not provide much insight on the structure of these systems. It does suggest however promising paths for the

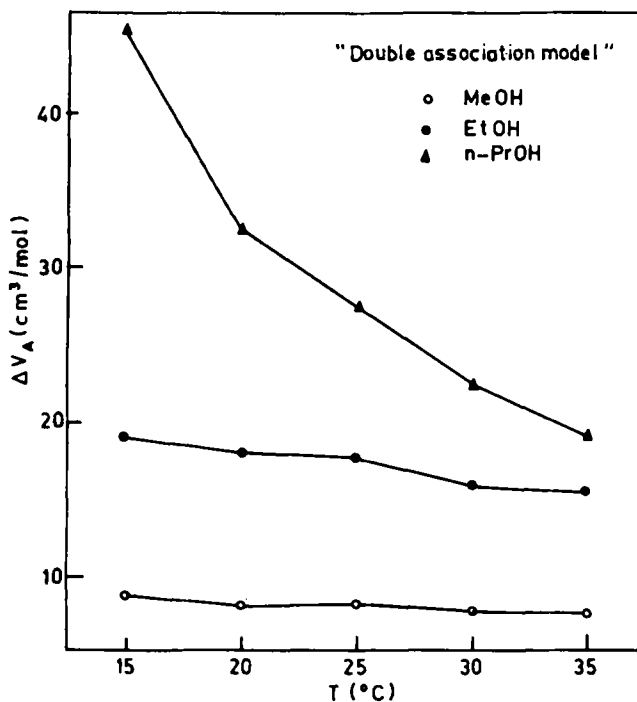


Figure 10. Temperature dependence of the parameter ΔV_A of alcohol-water mixtures extracted from the double association model.

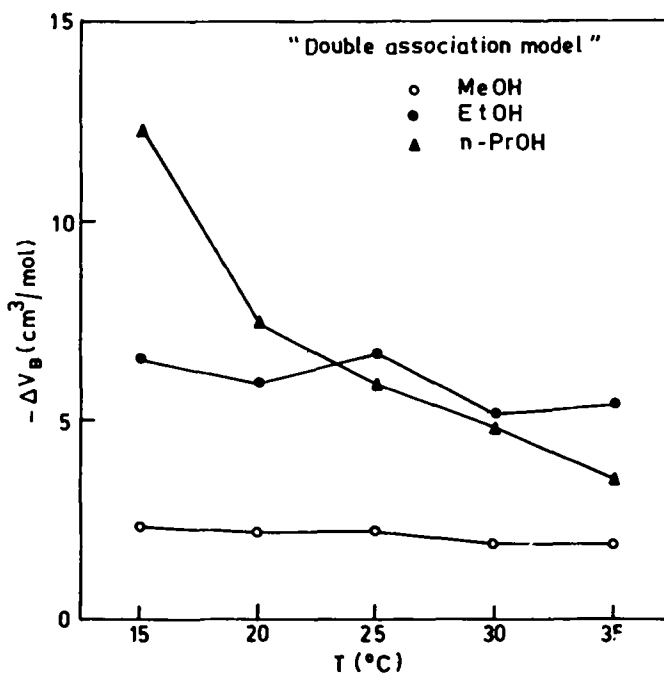


Figure 11. Temperature dependence of the parameters ΔV_B of alcohol-water mixtures extracted from the double association model.

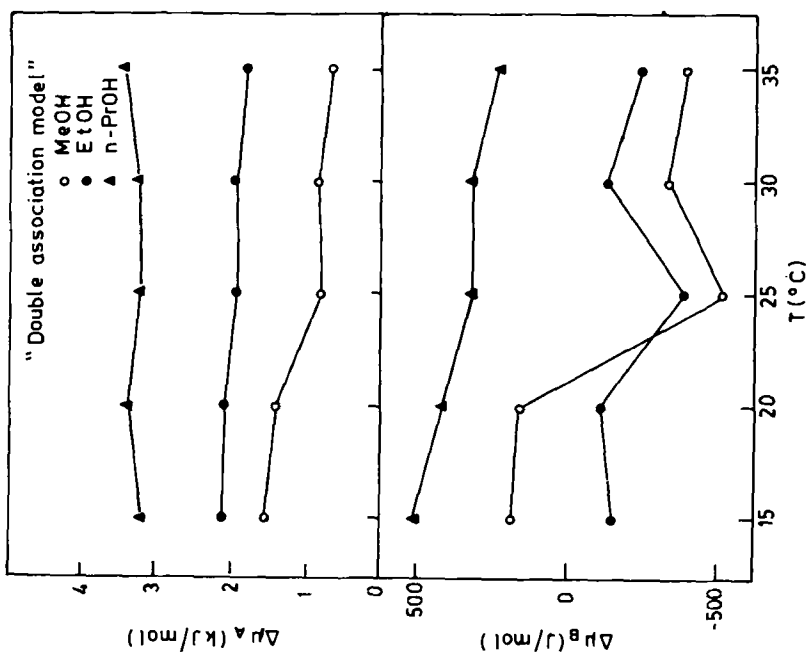


Figure 12. Temperature dependence of the parameters $\Delta\mu_A$ and $\Delta\mu_B$ of alcohol-water mixtures extracted from the double association model.

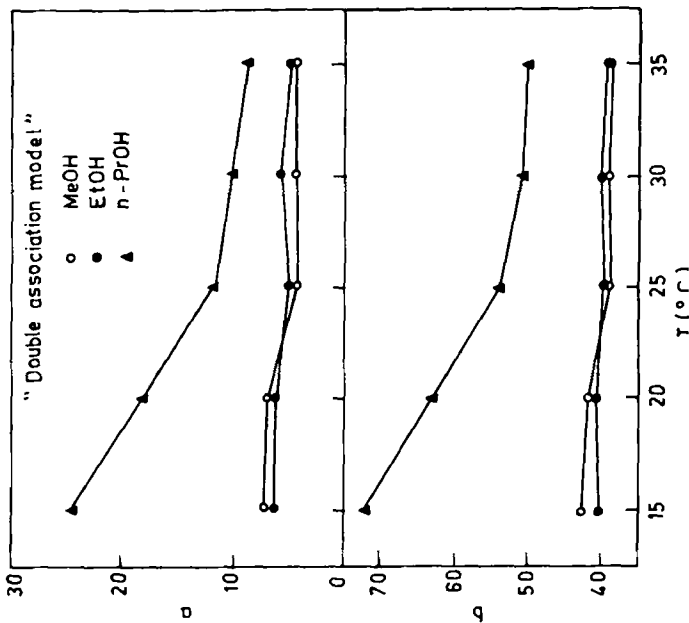


Figure 13. Temperature dependence of the parameters a and b of alcohol-water mixtures extracted from the double association model.

development of successful models for these systems. For example, the mass-action model for the micellar system can be introduced, as it was done here, with a more appropriate theory for liquid water, where all the water parameters would be fixed by the pure liquid.

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