

## **THERMODYNAMIC CHARACTERIZATION OF THE WATER + METHANOL SYSTEM, AT 298.15K**

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(Received 31 May 1988)

### **ABSTRACT**

Thermodynamic characterization of the water + methanol system, at 298.15 K, has been achieved through study of the composition dependence of excess differential coefficients, related to the  $pVT$  dependence of free energies and free enthalpies. For this purpose, density, heat capacity per unit volume of solution, and ultrasonic velocity were measured over the whole composition range. Results suggest that weak hydrophobic effects might develop in the water-rich region; then, the organic molecules are incorporated into the aqueous network by a substitutional association.

### **INTRODUCTION**

The aim of the present work is to study the composition dependence in the water + methanol system, at 298.15 K, of 'differential coefficients'. These are thermodynamic properties related to the temperature or pressure dependence of some of the generalized extensive quantities, which seem able to give a thermodynamic characterization of the system under consideration.

For this purpose, measurements of density, heat capacity per unit volume of solution, and ultrasonic velocity were performed over the entire composition range, at 298.15 K.

The changes of these properties with changing concentration are studied through their deviations from the behaviour of an ideal solution model, defined within the concept of the widely accepted generalization of Raoult's law.

Finally, a special emphasis is placed on rigorous methods for the calculation of ideal and excess ultrasonic velocity in this model system.

## THEORY

The aim of this work is to present a method for the thermodynamic characterization of binary liquid mixtures which is an extension of the basic set of quantities  $H^E$ ,  $pV^E$  and  $TS^E$ . In a previous work [1], we classified thermodynamic quantities into three main categories: generalized extensive quantities, generalized specific quantities, and derived quantities or differential coefficients. A differential coefficient is defined by an equation which is, or which contains, a partial derivative. In the present work we have considered the following differential coefficients, which are  $pVT$ -dependent quantities of the thermodynamic extensive quantities  $G$  and  $F$

isobaric and isochoric molar heat capacity,  $C_X$   
 isothermal and isentropic compressibilities,  $\kappa_X$  and  $K_X$   
 isobaric and isentropic expansibilities,  $\alpha_X$  and  $A_X$   
 isentropic and isochoric pressure coefficient,  $\beta_X$

These are listed in Table 1, together with their definitions and mutual relationships; they are also expressed in terms of the experimental properties which must be known in order to generate the complete set: the density  $\rho$ , the isobaric heat capacity per unit volume of solution  $\sigma$ , and the ultrasonic velocity  $u$  of the binary system under consideration. The differential coefficients are expressed as functions of  $u$  and three derived quantities of  $\rho$  and  $\sigma$ : the molar volume  $v$ , and the two differential coefficients  $\alpha_p$  (the isobaric coefficient of thermal expansion) and  $C_p$  (the isobaric molar heat capacity).

A common approach to describing the composition dependence of thermodynamic properties is to express these quantities as excess functions, i.e. deviations from the behaviour of an ideal mixture. From a thermodynamic point of view, a mixture is said to be ideal when it obeys a generalized form of Raoult's law in which the original statement in terms of vapour pressure is replaced by one in terms of fugacities, as emphasized by Bertrand and Treiner [2]. The excess quantity  $z^E$  relative to the thermodynamic variable  $z$  is given by the general equation

$$z^E = z - z^{\text{id}} \quad (1)$$

representing the difference between observed and ideal quantities. As has been shown by Douhéret et al. [1],  $z^{\text{id}}$  may be written in the shortened form:

$$z^{\text{id}} = \sum_i [\phi_i f_{i(z)}] z_i^+ \quad (2)$$

Except for the case of the pressure coefficients  $\beta_x$ ,  $\phi_i$  is either  $x_i$  or  $\phi_i^v$ , depending on whether  $z$  is a molar property or not.  $x_i$  and  $\phi_i^v$  are, respectively, the mole fraction of component  $i$  of the system, and its volume

TABLE 1

Some thermodynamic differential coefficients: definitions,  $pVT$  dependence, mutual relationships and methods of calculation

Variable	Definition and $pVT$ dependence	Other relationships	Calculation from experiment	
$C_p$	$\left(\frac{\partial H}{\partial T}\right)_p$	$-T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$	$Tv\alpha_p\beta_S$	Calculated from $\rho$ and $\sigma$
$\alpha_p$	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$	—	$\frac{C_p}{Tv\beta_S}$	Calculated from $\rho$ determined at different temperatures
$A_p$	$\left(\frac{\partial V}{\partial T}\right)_p$	$\left(\frac{\partial^2 G}{\partial p\partial T}\right)$	$\frac{C_p}{T\beta_S}$	$v\alpha_p$
$\beta_S$	$\left(\frac{\partial p}{\partial T}\right)_S$	$-\left(\frac{\partial^2 G}{\partial V\partial T}\right)$	$\frac{C_p}{Tv\alpha_p}$	$\frac{C_p}{Tv\alpha_p}$
$\kappa_T$	$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$	—	$\frac{C_p}{Tv\beta_S\beta_V}$	$\frac{[C_p + T\rho v(\alpha_p)^2 u^2]}{\rho C_p u^2}$
$K_T$	$-\left(\frac{\partial V}{\partial p}\right)_T$	$-\left(\frac{\partial^2 G}{\partial p^2}\right)$	$\frac{C_p}{T\beta_S\beta_V}$	$\frac{[vC_p + T\rho(v\alpha_p)^2 u^2]}{\rho C_p u^2}$
$C_V$	$\left(\frac{\partial U}{\partial T}\right)_V$	$-T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$	$-Tv\alpha_S\beta_V$	$\frac{(C_p)^2}{[C_p + T\rho v(\alpha_p)^2 u^2]}$
$\alpha_S$	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$	—	$-\frac{C_V}{Tv\beta_V}$	$-\frac{C_p}{T\rho v\alpha_p u^2}$
$A_S$	$\left(\frac{\partial V}{\partial T}\right)_S$	$\left(\frac{\partial^2 F}{\partial p\partial T}\right)$	$-\frac{C_V}{T\beta_V}$	$-\frac{C_p}{T\rho\alpha_p u^2}$
$\beta_V$	$\left(\frac{\partial p}{\partial T}\right)_V$	$-\left(\frac{\partial^2 F}{\partial V\partial T}\right)$	$-\frac{C_V}{Tv\alpha_S}$	$\frac{\rho\alpha_p C_p u^2}{[C_p + T\rho v(\alpha_p)^2 u^2]}$
$\kappa_S$	$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$	—	$\frac{C_V}{Tv\beta_S\beta_V}$	$\frac{1}{\rho u^2}$
$K_S$	$-\left(\frac{\partial V}{\partial p}\right)_S$	$-\left(\frac{\partial^2 F}{\partial p^2}\right)$	$\frac{C_V}{T\beta_S\beta_V}$	$\frac{v}{\rho u^2}$

fraction, stated in terms of the unmixed components at the temperature and pressure under consideration. For  $\beta_x$ , it has been shown that

$$\phi_i = \phi_i^z = \frac{x_i z_i^+}{\sum_i x_i z_i^+} \quad (3)$$

where the superscript  $+$  refers to the pure component  $i$ . For  $\beta_V$  and  $\beta_S$ , the isochoric and isentropic pressure coefficients,  $z$  is respectively equal to  $K_T$ ,

the molar isothermal compressibility, and  $A_p$ , the molar isobaric expansibility.

$f_{i(z)}$  is a 'multiplying term' [1]. It is equal to 1, over the whole concentration range, for pressure coefficients, isobaric molar heat capacity, isobaric expansibilities and isothermal compressibilities. Otherwise, it is a function of  $(\beta_X)^{id}$  and of some properties of the pure component of the system. Consequently, it is dependent on the composition of the system under consideration, and differs from 1: the corresponding ideal mixing laws are no longer linear in terms of  $\phi_i$ .

It may happen that pseudo-excess quantities  $z^{nE(\phi)}$  are needed. These represent the difference between the observed quantities and the additive quantities  $z^{ad(\phi)}$ , and are calculated from the equation

$$z^{nE(\phi)} = z - z^{ad(\phi)} \quad (4)$$

where  $z^{ad(\phi)}$  is calculated by averaging over the weighting coefficient  $\phi$ , i.e.

$$z^{ad(\phi)} = \sum_i \phi_i z_i^+ \quad (5)$$

## EXPERIMENTAL

### *Experimental techniques*

#### *Densities of solutions*

These were measured using a flow type oscillating tube densimeter Sodev model 02D, thermostatted to within  $\pm 0.002$  K with a Setaram temperature controller. The temperature was checked using a calibrated quartz thermometer Hewlett-Packard model 2801 A. A linear relationship was assumed between the density  $\rho$  of the liquid under consideration and the square of the oscillator period  $\tau_p$

$$\rho = A + B\tau_p^2 \quad (6)$$

Measurements of  $\tau_p$  were performed using a timer-counter Hewlett-Packard model 5308 A, and recorded using a thermal printer Hewlett-Packard model 5150 A.

The solutions were passed through the densimeter by gravity. Each sample measurement was bracketed by two water measurements, water serving as a reference fluid to determine the density of the samples. No significant drift of  $\tau_p$  vs. time was observed, after the thermal equilibrium was reached (within 15 min); values of  $(\tau_p)_w$  also exhibited a fairly good constancy throughout. The density of water  $\rho_w$  was calculated by means of the equation proposed by Kell [3], and found to be equal to  $997.048 \text{ kg m}^{-3}$  at 298.15 K. Water and air at very low pressure were used as standards to fix the values of the calibration constant  $K_p$ . No significant change of  $K_p$

occurred during a period of several months. In such conditions, differences between the densities of the sample and of the reference fluid ( $\rho - \rho_r$ ) can be determined with a reproducibility of  $5.10^{-3} \text{ kg m}^{-3}$ .

#### *Isobaric heat capacities per unit volume of solutions*

These were determined using a Picker flow calorimeter equipped with gold cells, manufactured by Setaram. The calorimeter was thermostatted to within 0.001 K. The temperature was measured using a calibrated quartz thermometer Hewlett–Packard model 2801 A. Heat capacities per unit volume of solution  $\sigma$  were measured according to a step-wise procedure. The liquids were sucked up through the calorimeter by means of a peristaltic pump, using a separator as an interface between the calorimetric unit and the pumping system. For all measurements a temperature increment of approximately 1.2 K, centered on 298.15 K, was used. The overall precision of the measurements of  $\sigma$  is  $70 \text{ J K}^{-1} \text{ m}^{-3}$ .

#### *Ultrasonic velocity of solutions*

These measurements were performed with a Mapco sonic solution monitor model 6105, using the “sing-around” method. The electronic processing circuit was coupled to a solution cell designed by McKent (Bergen, Norway). The room temperature was kept constant at  $298 \pm 1 \text{ K}$  throughout the measurements, since Tamura et al. [4] have argued that the electronic delay time of answer  $\tau$  of the sing-around process depends on the surrounding temperature, in relation to the difference between the temperature of the sing-around circuit and that of the bath. The ultrasonic pulse repetition rate (frequency) was determined by a frequency counter Hewlett–Packard model 82905 B.

The cell was submerged in a thermostated water-bath, the temperature of which was monitored using a quartz thermometer Hewlett–Packard Model 2804 A. This was estimated to be accurate to within 0.01 K, with a long term stability of  $\pm 0.002 \text{ K}$ . All the measurements were carried out at 298.15 K. No more than  $10 \text{ cm}^3$  were needed to fill the cell, so the thermal equilibrium was reached quickly. Measurements of the frequency  $f$  were performed 20 min after the cell was dipped into the water-bath, and repeated 10 min later. No significant drift of  $f$  in terms of time  $t$  was observed. Each sample measurement was bracketed by two water measurements, since here again water served as a reference fluid, this time to determine the ultrasonic velocity of the samples. The speed of sound  $u$  is related to the measured frequency  $f$  by the general equation

$$u = \frac{lf(1 + \alpha T)}{(n - \tau f)} \quad (7)$$

where  $n$  is a parameter whose value is dependent on the ultrasonic genera-

TABLE 2

Coefficients relative to the experimental uncertainty on values of frequency and temperature

$z$	$ \delta f $ (s <sup>-1</sup> )	$ \delta T $ (K)	$a_f$ ( $\tau, -$ ) (l, m s <sup>-1</sup> )	$a_T$ ( $\tau, s$ K <sup>-1</sup> ) (l, m K <sup>-1</sup> )	$b_f$ (s <sup>-1</sup> )	$b_T$ (K <sup>-1</sup> )
$\tau$ (s)	0.5 —	— 1.0 E-3	4.6 E-7 —	— 1.1 E-4	4.4 E-1 —	— 1.1 E+2
$l$ (m)	0.5 —	— 1.0 E-3	1.4 E-3 —	— 1.6 E-1	1.7 E-2 —	— 2.1

tor,  $l$  is the path length, and  $\alpha$  is the coefficient of thermal expansion of the material of the probe. Use of the Mapco apparatus implies  $n = 7$ .

Calibration of the cell was carried out by measuring the frequency of water samples at two temperatures  $T_1$  and  $T_2$ , symmetrical in relation to 298.15 K. The calibration was based on the absolute values of the velocity for pure water reported by Del Grosso and Mader [5]. The absolute and relative errors on  $z$ , standing successively for  $\tau$  and  $l$ , are given by the following equations

$$|\delta z| = [a_f |\delta f| + a_T |\delta T|] / \Delta T \quad (8)$$

$$\left| \frac{\delta z}{z} \right| = [b_f |\delta f| + b_T |\delta T|] / \Delta T \quad (9)$$

$|\delta f|$  and  $|\delta T|$  represent the absolute values of the uncertainty on the experimental values of  $f$  and  $T$ , respectively.  $\Delta T$  symbolizes the difference ( $T_2 - T_1$ ) between the temperatures  $T_1$  and  $T_2$  considered for the calibration. The coefficients  $a_f$ ,  $a_T$ ,  $b_f$  and  $b_T$  have been collected together in Table 2. It has been observed that rather small values of  $|\delta f|$  and  $|\delta T|$  give rise to larger changes of  $\tau$  and  $l$  with decreasing  $\Delta T$ .

The accuracy relative to the speed of sound in a sample  $x$ , for which water served as a reference fluid  $r$ , has been calculated for the difference of the respective velocities in  $x$  and  $r$ ,  ${}^{r,x}\Delta u$

$${}^{r,x}\Delta u = u_x - u_r = u_r \left[ \left( \frac{f_x}{f_r} \right) \frac{(n - \tau_f)}{(n - \tau_r)} - 1 \right] \quad (10)$$

Figure 1 shows the changes in the magnitude of the absolute error,  $|\delta u_x|$ , as in

$${}^{r,x}\Delta u = [{}^{r,x}\overline{\Delta u} \pm |\delta u_x|] \quad (11)$$

These have been plotted vs.  $[{}^{r,x}\Delta f]$  for several possible values of  $[\bar{\tau} \pm |\delta \tau|]$ . The difference curves clearly demonstrate that  $|\delta u_x|$  cannot be assumed to be constant over the entire concentration range of a given binary system.

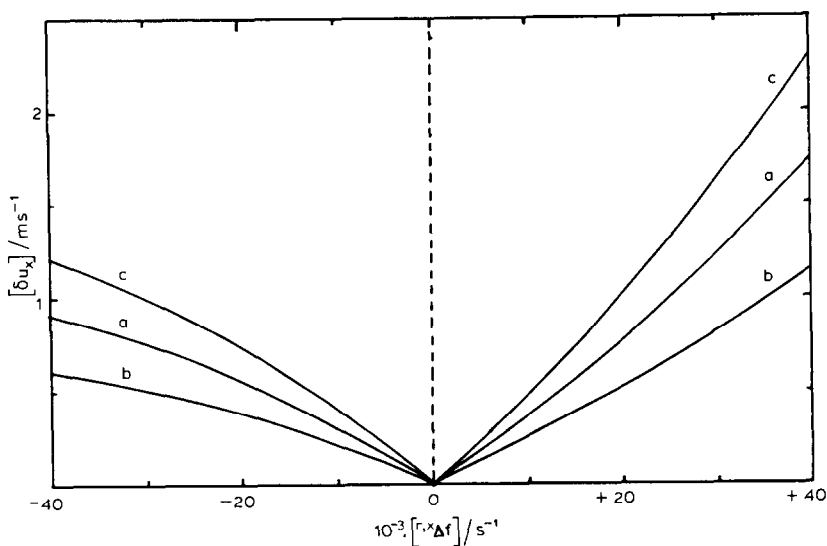


Fig. 1. Changes in  $|\delta u_x|$  as a function of the difference between the frequencies  $f_x$  and  $f_r$ , measured respectively for the sample  $x$  and water serving as reference fluid  $r$ , with:  $\Delta T = 2$  K;  $T_c = 298.15$  K;  $\Delta f = [f_{r(T_2)} - f_{r(T_1)}] = 461$  s $^{-1}$ ;  $f_{r(\tau_c)} = 131854$  s $^{-1}$ ;  $\bar{\tau}_c = 1.05$  E-6 s. a,  $\tau = \bar{\tau}_c \pm 0.15$  E-6 s; b,  $\tau = \bar{\tau}_c \pm 0.10$  E-6 s; c,  $\tau = \bar{\tau}_c \pm 0.20$  E-6 s.

## Materials

Water was first deionized by means of ion-exchange resins, then distilled. Its conductivity was always less than  $1.0 \times 10^{-6}$   $\Omega^{-1}$  cm $^{-1}$ . The methanol used was a Prolabo RP Normapur guaranteed reagent, used as received. The manufacturer estimate of purity for the methanol was greater than 99.8 mass %. The main impurity was water, whose content was ca. 0.2 mass %. The methanol was stored, protected as far as possible from atmospheric moisture and CO $_2$ .

## Preparation of solutions

All solutions were prepared by weight with a precision of 0.1 mg from thoroughly degassed samples of deionized and distilled water and of methanol; then corrected for buoyancy. A correction for the water content of the methanol was included in the calculation of the mole fraction. The mole fraction values are therefore reliable to within  $1 \times 10^{-4}$ .

## RESULTS AND DISCUSSION

### Experimental results

The density, isobaric heat capacity per unit volume of solution, and ultrasonic velocity of the water (1) + methanol (2) mixtures were measured

TABLE 3

Density, heat capacity per unit volume and ultrasonic velocity in water + methanol mixtures, at 298.15 K

$x_2$	$\rho$ (g cm <sup>-3</sup> )	$\sigma$ (J K <sup>-1</sup> cm <sup>-3</sup> )	$u$ (ms <sup>-1</sup> )	$x_2$	$\rho$ (g cm <sup>-3</sup> )	$\sigma$ (J K <sup>-1</sup> cm <sup>-3</sup> )	$u$ (ms <sup>-1</sup> )
0	0.997048	4.1670	1496.687	0.4018		3.1593	
0.0151	0.99220		1507.00	0.4304	0.89620		1441.31
0.0200		4.1606		0.4486		3.0344	
0.0304		4.1567		0.4771	0.88595		1409.98
0.0339	0.98658		1520.07	0.4916		2.9344	
0.0499		4.1395		0.5291	0.87503		1374.57
0.0700	0.97711		1543.32	0.5501		2.7898	
0.0804		4.0972		0.5793	0.86455		1342.14
0.1003		4.0609		0.6005	0.86020		1328.58
0.1105	0.96743		1561.48	0.6011		2.6876	
0.1507	0.95827		1569.52	0.6485	0.85056		1297.71
0.1513		3.9304		0.6496		2.5848	
0.1822		3.8388		0.7021		2.4787	
0.1851	0.95065		1568.14	0.7114	0.83821		1258.51
0.1999		3.7808		0.7688	0.82725		1223.64
0.2313		3.6840		0.8002		2.2999	
0.2327	0.94005		1554.58	0.8151			1195.83
0.2517		3.6125		0.8498		2.2194	
0.2707	0.93156			0.8697		2.1891	
0.2749	0.93064		1537.34	0.9004	0.80326		1148.59
0.3008		3.4631		0.9424		2.0774	
0.3216	0.92017		1511.54	0.9582	0.79331		1118.43
0.3497		3.3166		0.9982	0.78663		1098.28
0.3796	0.90724		1475.23	1	0.78635	1.9930	1097.48

over the whole composition range, at 298.15 K. The number of experimental points was chosen to give an adequate point density, allowing a precise numerical treatment of the data; the mixtures were also chosen so as to fill the gaps observed in previously published data sets in the range of composition  $0.5 < x_2 < 1$  [6–12]. The properties of pure methanol were obtained by extrapolating to unit mole or volume fraction,  $x_2$  and  $\phi_2^v$ , respectively, by means of a simple polynomial expansion. The relevant results are presented in Table 3.

In view of further numerical treatment of the data sets, the values of the molar volume  $v$ , and those of the isobaric molar heat capacity  $C_p$  were calculated from the values of the density  $\rho$ , and the isobaric heat capacity per unit volume of solution  $\sigma$ , respectively.

The molar volume  $v$  is easily derived from the density  $\rho$ , using the following equation

$$v = \frac{M}{\rho} = \sum_{i=1}^2 \frac{x_i M_i}{\rho} \quad (12)$$

where  $M_i$  denotes the molar mass of the component  $i$ .



As for  $\sigma$ , this is converted in a first step to the specific heat  $c_p$ , by means of the relationship

$$c_p = \frac{\sigma}{\rho} \quad (13)$$

Then the isobaric molar heat capacity  $C_p$  is obtained from the equation

$$C_p = \sum_{i=1}^2 [x_i M_i] c_p \quad (14)$$

The respective values of  $c_p$  and  $C_p$  for water were taken to be  $4.1793 \text{ J K}^{-1} \text{ g}^{-1}$  and  $75.292 \text{ J K}^{-1} \text{ mol}^{-1}$ , after Kell [3].

### *Numerical treatment*

The following excess and non-excess quantities were calculated using experimental values

$$v^E = \sum_{i=1}^2 x_i M_i \left( \frac{1}{\rho} - \frac{1}{\rho_i^+} \right) \quad (15)$$

$$C_p^E = \sum_{i=1}^2 x_i M_i \left( \frac{\sigma}{\rho} - \frac{\sigma_i^+}{\rho_i^+} \right) \quad (16)$$

$$u^{nE(x_i)} = u - \sum_{i=1}^2 x_i u_i^+ \quad (17)$$

Curve-fitting procedures are needed in order to estimate the level of internal consistency of our data sets, and to compare this level with those of corresponding data sets taken from the literature [6–12]. Here we would emphasize the distinction between curve-fitting techniques designed solely to provide an algebraic summary of a specific set, together with an estimate of the level of internal consistency, by means of the value of the standard deviation  $\sigma_i$ ; and those which provide the same kind of information, but are parameterized in such a way as to attempt to interpret the data in the context of a model.

The subsequent equation is one of the former techniques. Redlich and Kister [13] have introduced a simple and empirical representation for the excess properties, which can be extended to multicomponent systems. For a binary system, a simplified form of their equation is:

$$z^E = \phi_1 \phi_2 \sum_{i=0}^n a_i (1 - 2\phi_2)^i \quad (18)$$

The  $\phi_i$  elements represent the weighting coefficients relative to components 1 and 2 of the system. The number of coefficients  $a_i$  which are needed to describe the experimental results depends on the number of points available, on their density throughout the whole concentration range, on their quality, and on the molecular complexity of the system.

TABLE 4

Standard deviations of the Redlich–Kister and the four-segment model analyses of the excess molar volumes [9] and excess isobaric molar heat capacities [7] of the water + methanol system, at 298.15 K

$z^E$		Weighting coefficients	Number of parameters		
			5	6	7
$10^6 v^E$ ( $\text{m}^3 \text{mol}^{-1}$ )	Redlich–Kister [13]	$x_2$	0.0019	0.0007	0.0006
		$\phi_2^v$	0.0007	0.0007	0.0007
	Davis [15]	$x_2$	—	—	0.0009
$C_p^E$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	Redlich–Kister [13]	$x_2$	0.067	0.059	0.048
		$\phi_2^v$	0.052	0.047	0.047
	Davis [15]	$x_2$	—	—	0.045

The model recently devised by Davis [14] for the analysis of excess property data for aqueous binary systems is one of the latter techniques. It embodies the concept of the segmentation of the total composition range into four distinct regions; the values of the mole fractions at the three segment junctions are determined in order to obtain the best overall optimization. Seven parameters are needed in this treatment, which deals primarily with molar quantities. Some excess properties of the water + methanol system, taken from the literature, including the excess molar volume  $v^E$  [7], and the excess isobaric molar heat capacity  $C_p^E$  [9], have been analysed previously by Davis [15], using the four-segment model. A comparison of the accuracy of the two curve-fitting procedures suggested that we should analyse these data sets using the Redlich–Kister eqn. (18). The values of the standard deviations  $\sigma_r$  obtained using these two different approaches are reported in Table 4. Taking into account the respective symmetry and dissymmetry of the plots of  $v^E$  and  $C_p^E$  against  $x_2$ , the Redlich–Kister analysis appears to require, at equal values of  $\sigma_r$ , an equal or smaller number of coefficients than the four-segment model, *for the system considered*. Also, the Redlich–Kister procedure allows us to analyse the excess quantities vs. different weighting coefficients; those giving rise to the more symmetrical plots require a lower number of coefficients and, for a given data set, a lower value of  $\sigma_r$  is obtained. Owing to this versatility, the Redlich–Kister eqn. (18) was preferred to the four-segment model. However, we are aware of the vast superiority of the model devised by Davis [14] for the great majority of binary aqueous systems, especially for those where strong hydrophobic effects are observed in the water-rich region. We are also convinced that, even in its first form of development, a modest degree of physical significance may be attributed to some of the parameters of this model. This is not the case for the coefficients of the Redlich–Kister eqn. (18), which have no interpretive use.

### Comparison with published data

It seemed useful to define clearly the conditions under which the best overall fit of the excess quantities previously defined in eqns. (15–17) may be obtained. Therefore,  $\sigma_r$  was determined for  $v^E$ ,  $C_p^E$  and  $u^{nE(x_i)}$  from the Redlich–Kister analysis of our results and other data sets taken from the literature [6–12]. Two different weighting coefficients,  $x_i$  and  $\phi_i^v$ , were used successively in eqn. (18), while  $n$ , the number of  $a_i$  coefficients, was allowed to vary. The values of the standard deviations  $\sigma_{r(x_i)}$  and  $\sigma_{r(\phi_i^v)}$  for  $n = 6–8$  are summarized in Table 5. It is clear that, for a given data set, values of  $\sigma_{r(x_i)}$  are weakly dependent on  $\phi_i$  and  $n$ , for both  $v^E$  and  $C_p^E$ ; on the other hand, the best overall fit of  $u^{nE(x_i)}$  is obtained with  $\phi_i^v$ .

Values of the  $a_i$  coefficients from the Redlich–Kister analysis of  $v^E$  and  $C_p^E$  against  $x_i$  and of  $u^{nE(x_i)}$  against  $\phi_i^v$  are reported in Table 6, along with  $\sigma_{r(x_i)}$  for the two first excess quantities and  $\sigma_{r(\phi_i^v)}$  for  $u^{nE(x_i)}$ ;  $N$  is the number of experimental points. It should be emphasized that  $n$  has been taken to be equal to 6, in order to preclude overparameterization which might provide meaningless coefficients. The level of the internal consistency of our results appears to be in reasonable agreement with that of most of the previously published data sets.

The following graphical method for comparing the levels of internal consistency of various data sets is undoubtedly more illustrative. The

TABLE 5

Values of standard deviation as a function of the weighting coefficient  $\phi_i$  and of the number of parameters  $n$  of the Redlich–Kister eqn. (18), for some excess and pseudo-excess properties of the water + methanol system, at 298.15 K

Property	Ref.	$\sigma_{r(x_i)}$			$\sigma_{r(\phi_i^v)}$		
		$n$			$n$		
		6	7	8	6	7	8
$10^6 v^E$ ( $\text{m}^3 \text{mol}^{-1}$ )	This work	0.0012	0.0011	0.0011'	0.0013	0.0011	0.0012
	6	0.0055	0.0047	0.0045	0.0050	0.0053	0.0054
	7	0.0007	0.0006	0.0007	0.0007	0.0007	0.0007
$C_p^E$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	This work	0.08	0.09	0.09	0.09	0.09	0.09
	8	0.10	0.09	0.10	0.09	0.09	0.10
	9	0.06	0.05	0.05	0.05	0.05	0.05
	10	0.05	0.03	0.01	0.02	0.02	0.01
$u^{nE(x_i)}$ ( $\text{m s}^{-1}$ )	This work	0.77	0.44	0.35	0.35	0.36	0.36
	11	0.67	0.19	0.18	0.23	0.19	0.20
	12	0.59	0.30	0.29	0.23	0.21	0.21

TABLE 6

Coefficients  $a_i$  and standard deviations  $\sigma_r$  for the least-squares analysis by the Redlich-Kister eqn. (18) of some excess and pseudo-excess properties of the water + methanol system, at 298.15 K

$a_i$	$C_p^E$ (J K <sup>-1</sup> mol <sup>-1</sup> )							$u^{\mu E}(x_r)$ (m s <sup>-1</sup> )				
	$10^6 v^E$ (m <sup>3</sup> mol <sup>-1</sup> )	7	8	9	10	11	12	Ref.				
	This work <sup>a</sup>	This work <sup>b</sup>	This work <sup>c</sup>	9	10	11	12	This work <sup>c</sup>				
$a_0$	-4.0095	-4.1110	-4.0115	17.666	20.017	18.065	19.138	582.674	578.408	589.531		
$a_1$	-0.1742	-0.2099	-0.1427	14.453	14.370	16.595	15.536	290.358	292.672	298.710		
$a_2$	0.0248	0.1566	-0.0245	21.835	18.926	21.706	19.039	-179.821	-182.658	-190.310		
$a_3$	0.1582	0.0839	0.1677	35.546	28.526	30.266	32.172	-295.611	-323.190	-330.028		
$a_4$	0.8761	0.7930	0.8381	9.372	11.332	5.394	12.439	-72.192	-66.374	-43.056		
$a_5$	0.5950	0.7987	0.7012	-17.704	-12.727	-9.380	-15.684	145.428	193.401	194.210		
$\sigma_r$	0.0011	0.0055	0.0007	0.08	0.10	0.06	0.05	0.35	0.23	0.23		
$N$	22	15	44	23	18	42	19	22	24	29		

<sup>a</sup>  $v_1^+ = 1.80687 \text{ E-}5 \text{ m}^3 \text{ mol}^{-1}$  [3];  $v_2^+ = 4.07483 \text{ E-}5 \text{ m}^3 \text{ mol}^{-1}$ . The ideal volume fractions  $\phi_i^v$ , when taken into account in the smoothing eqn. (19), have been calculated using these values of  $v_i^+$ .

<sup>b</sup>  $(C_p)_1^+ = 75.292 \text{ J K}^{-1} \text{ mol}^{-1}$  [3];  $(C_p)_2^+ = 81.21 \text{ J K}^{-1} \text{ mol}^{-1}$ .

<sup>c</sup> A "pulse-echo-overlap" method was used, not a "sing-around" technique.

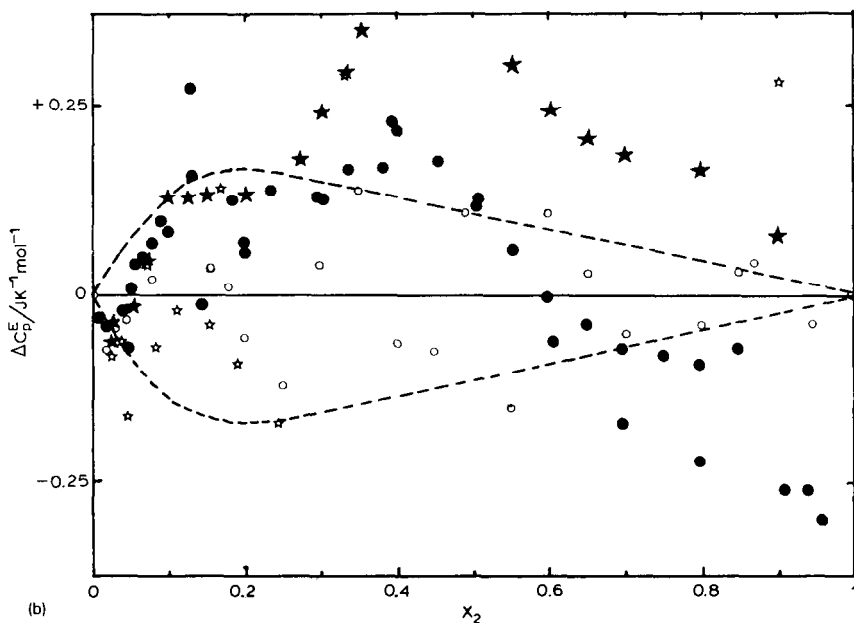
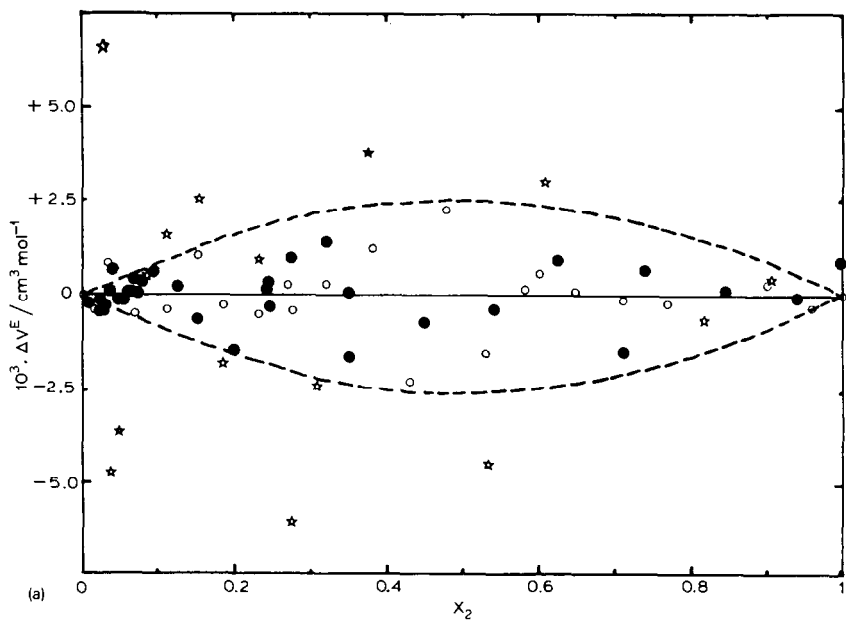


Fig. 2-a. Differences  $\Delta v^E$  (calculated from eqn. (19)) for the water (1) + methanol (2) system, at 298.15 K, as a function of the mole fraction of methanol  $x_2$ .  $\circ$ , Our results;  $\bullet$ , Benson and Kiyohara (1980);  $\star$ , Grolier et al. (1978); ---,  $\pm 0.25\%$  deviation.

Fig. 2-b. Differences  $\Delta C_p^E$  (calculated from eqn. (19)) for the water (1) + methanol (2) system, at 298.15 K, as a function of the mole fraction of methanol  $x_2$ .  $\circ$ , Our results;  $\bullet$ , Benson et al. (1980);  $\star$ , Grolier et al. (1978);  $\star$ , Ogawa and Murakami (1986); ---,  $\pm 0.25\%$  deviation.

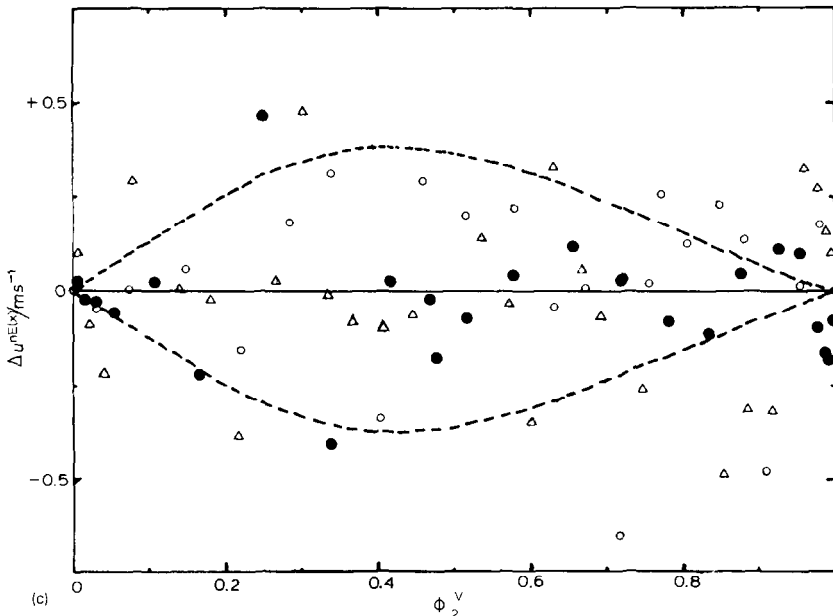


Fig. 2-c. Differences  $\Delta u^{nE(x_i)}$  (calculated from eqn. (19)) for the water (1)+methanol (2) system, at 298.15 K, as a function of the ideal volume fraction of methanol  $\phi_2^v$ . ○, Our results; ●, Benson et al. (1981); △, Lara and Desnoyers (1981); — — —,  $\pm 0.25\%$  deviation.

method consists in drawing a deviation plot of  $z^E$  or  $z^{nE(\phi_i)}$  against  $\phi_2$ . Figures 2-a–c show the deviation plots of  $\Delta v^E$  and  $\Delta C_p^E$  against  $x_2$  (Figs. 2-a and 2-b, respectively), and that of  $u^{nE(x_i)}$  against  $\phi_2^v$  (Fig. 2-c).  $\Delta z^E$ , where  $z^E$  holds for  $v^E$ ,  $C_p^E$  and  $u^{nE(x_i)}$  is equal to

$$\Delta z^{(n)E} = z_{\text{obs}}^{(n)E} - z_{\text{calc}}^{(n)E} \quad (19)$$

$z_{\text{obs}}^{(n)E}$  represents the non-smoothed values of  $z^E$ , as defined in eqns. (15–17);  $z_{\text{calc}}^{(n)E}$  represents the smoothed values obtained in the present work by means of eqn. (18).  $\Delta z^E$  is calculated first with  $z_{\text{obs}}^E$  as obtained in the present work, and then with the various data sets taken from the literature. Figure 2-a shows clearly that our results are in good agreement with those of Benson and Kiyohara [7]. The results obtained for  $\Delta C_p^E$  are more scattered; some of them even exhibit positive or negative drifts, particularly in the methanol-rich region, as shown in Fig. 2-b. A better consistency is observed for  $\Delta u^{nE(x_i)}$ ; except for a few extra points, no systematic drift is observed in Fig. 2-c.

### Differential coefficients

#### Isobaric coefficient of thermal expansion

$\alpha_p$  was derived from precise values of the excess molar volume  $v^E$  computed from density measurements performed at 15–35°C by Benson

and Kiyohara [7] by two separate methods, since these authors did not publish explicit values of  $\alpha_p$ . On first attempts at using their method we could not reproduce the smoothed values of  $v^E$  and got only approximate values of  $\alpha_p$ . Finally, sound values were obtained after a misprint was deleted from the smoothing equation, a modified form of the Redlich–Kister eqn. (18). This expression should be written in the following form

$$v^E = \phi_1^v \phi_2^v \sum_{i=1}^n [a_{i1} + a_{i2}(t - 25)](1 - 2\phi_1^v)^{i-1} \quad (20)$$

where  $t$  is the temperature in degrees Celsius, and  $a_{i1}$  and  $a_{i2}$  are the coefficients of the polynomial expansion. The values of  $\alpha_p$  were converted to  $A_p$ , according to the equation given in Table 1.

We also decided to use a separate method proposed by Davis [16], where a modified cubic splines procedure is used to interpolate the same values of  $v^E$  at rounded mole fraction. Assuming  $v^E$  to be a quadratic function of  $(t - 25)$ ,  $v_{25}^E$  (temperature smoothed) and  $(\partial v^E / \partial T)_p$  were calculated. These quantities are readily convertible to  $v$  and  $(\partial v / \partial T)_p$ , i.e.  $A_p$ . Deriving  $\alpha_p$  from these results is straightforward.

The values of  $A_p$  were found to be in excellent agreement with those obtained according to the method used by Benson and Kiyohara [7]. It is clear that the Redlich–Kister eqns. (18) and (20) are purely empirical, but one should also be aware that the cubic splines procedures have some limitations. However, the fact that these two methods give very similar results is a supplementary argument for their being reasonably accurate.

The  $a_i$  coefficients of the smoothing equation for  $A_p^E$ , the excess molar expansibility, are collected in Table 7.

#### *Other differential coefficients*

The values of the other differential coefficients listed in Table 1 are readily obtained according to the equations given therein, where the coefficients are given as functions of  $\rho$ ,  $v$ ,  $\alpha_p$ ,  $C_p$  and  $u$ . The excess quantities have been calculated from these values by means of eqn. (1). The corresponding ideal quantities have been estimated from the ideal mixing laws proposed recently by Douhéret et al. [17]. The coefficients of the Redlich–Kister analysis are reported in Table 7, together with the weighting coefficients used and the values of both standard deviations,  $(\sigma_r)_{\phi_1^v}$  and  $(\sigma_r)_{x_r}$ .

#### *Composition dependence of the excess differential coefficients*

As shown in Table 1, the differential coefficients are related to the second derivatives of either the free enthalpy  $G$  or the free energy  $F$ . The composition dependence of the corresponding excess quantities is discussed in the next section.

TABLE 7

Polynomial coefficients and standard deviations of the Redlich-Kister eqn. (18), applied to the least-squares analysis of some excess differential coefficients, in the water + methanol system, at 298.15 K

$z^E$	$\phi_i$	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	$(\sigma_i)_{\phi_i}$	$(\sigma_i)_{x_i}$
$10^9 A_P^E$ ( $\text{m}^3 \text{K}^{-1} \text{mol}^{-1}$ )	$x_i$	-6.0986	7.6006	-7.5994	3.0671	-5.6095	-20.844	-11.883	0.0070	0.0037
$10^{-6} \beta_S^E$ ( $\text{Pa K}^{-1}$ )	$\phi_i^y$	7.8646	12.829	24.860	33.445	60.680	73.656	34.449	0.0205	0.5605
$10^{12} \kappa_T^E$ ( $\text{Pa}^{-1}$ )	$\phi_i^y$	-1395.2	531.61	-308.10	338.99	-160.22	71.201	1.4448	0.27	0.34
$10^{15} K_T^E$ ( $\text{m}^3 \text{Pa}^{-1} \text{mol}^{-1}$ )	$\phi_i^y$	-36.695	29.193	-20.188	16.578	10.987	7.9801	-3.1035	0.007	0.008
$C_V^E$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$x_i$	5.9640	8.8559	24.763	44.836	39.213	-12.617	-19.398	0.02	0.03
$10^3 \alpha_S^E$ ( $\text{K}^{-1}$ )	$\phi_i^y$	15.678	7.6832	-2.4329	-9.5755	-24.485	-32.151	-17.722	0.0106	0.2378
$10^6 A_S^E$ ( $\text{m}^3 \text{K}^{-1} \text{mol}^{-1}$ )	$\phi_i^y$	0.41873	0.04002	-0.06861	-0.24903	-0.48025	-0.49085	-0.29554	0.0002	0.0041
$10^{-6} \beta_V^E$ ( $\text{Pa K}^{-1}$ )	$\phi_i^y$	2.1944	0.27822	-1.9900	-1.7383	-0.36684	0.88843	0.34575	0.0006	0.0009
$10^{12} \kappa_S^E$ ( $\text{Pa}^{-1}$ )	$\phi_i^y$	-1367.0	504.66	-220.19	292.42	-134.53	-51.540	99.122	0.26	0.31
$10^{15} K_S^E$ ( $\text{m}^3 \text{Pa}^{-1} \text{mol}^{-1}$ )	$\phi_i^y$	-35.841	27.790	-17.057	14.997	-10.276	1.8837	2.3503	0.0070	0.0070



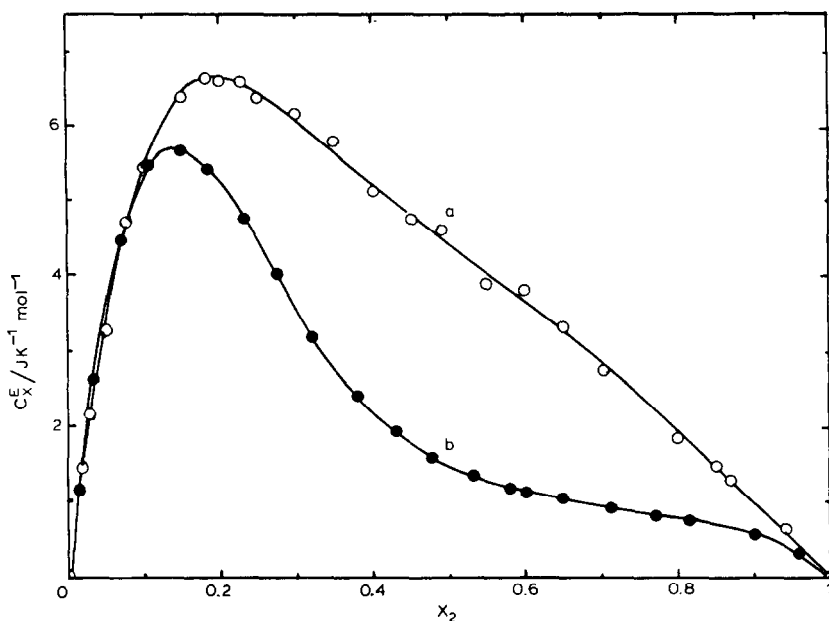


Fig. 3. Variations of excess molar heat capacities  $C_X^E$ , as a function of the mole fraction of methanol  $x_2$ , at 298.15 K: a,  $C_p^E$ ; b,  $C_V^E$ .

#### *Isobaric and isochoric molar heat capacities*

These properties are necessary for predicting the temperature dependence of various equilibrium properties;  $C_p$  and  $C_V$  are related, respectively, to the second derivatives of  $G$  and  $F$  with regard to the temperature  $T$ . As has been pointed out by Ogawa and Murakami [10], "of the excess thermodynamic functions,  $C_p^E$  is related the most closely to the behavior of component molecules in the solution state". More difficult is the interpretation of  $C_V^E$ , since  $C_V$  is a key thermophysical variable, depending on the various external and internal degrees of freedom of the molecules [18].

Our results support the foregoing conclusions of Kiyohara and Benson [9]. The deviations of  $C_X^E$  ( $X$  standing successively for  $p$  and  $V$ ) from ideality are positive over the whole composition range. A maximum occurs in the water-rich region. The magnitude of this maximum is larger for  $C_p^E$ ; for  $C_V^E$  it is sharper and shifted towards the water-rich region [ $x_2 \approx 0.20(C_p^E)$ ;  $x_2 \approx 0.14(C_V^E)$ ], as shown in Fig. 3.

#### *Isothermal and isentropic compressibilities*

As shown in Table 1, the compressibilities  $K_X$  are the second derivatives of  $G$  and  $F$  with regard to the pressure  $p$ . Isothermal or isentropic quantities correspond respectively to  $X = T$  or  $S$ . The compressibilities may be considered to be the sum of the instantaneous compressibility due to compression of the molecules and intermolecular distance, and the structural

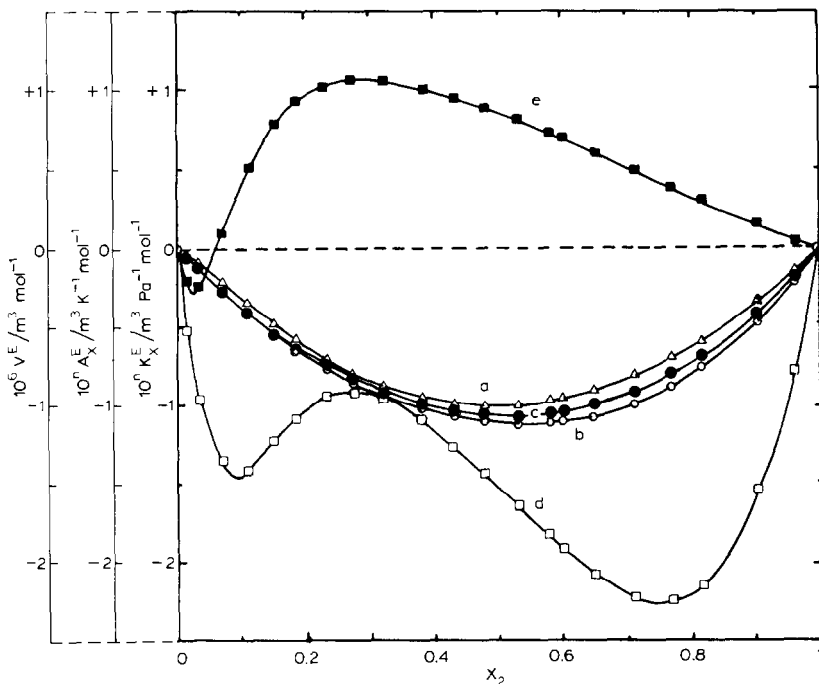


Fig. 4. Changes in excess molar volume  $v^E$ , excess molar compressibilities  $K_X^E$  and excess molar expansibilities  $A_X^E$ , as a function of the mole fraction of methanol  $x_2$ , at 298.15 K: a  $10^6 v^E$ ; b  $10^{14} K_T^E$ ; c  $10^{14} K_S^E$ ; d  $10^9 A_p^E$ ; e  $10^7 A_S^E$ .

compressibility due to breakdown of the intermolecular bonds accompanying the open structure of water. The excess coefficients  $\kappa_X^E$  and excess molar quantities  $K_X^E$  are both negative over the whole composition range. The changes of  $K_T^E$  and  $K_S^E$  have been plotted vs.  $x_2$ , as shown in Fig. 4 (curves (b) and (c), respectively). The composition dependence of these two excess quantities is very similar, especially in the water-rich region, where the two curves (b) and (c) are almost indistinguishable; in both cases, a minimum is observed close to the equimolar mixture. These changes look like those of the excess molar volume  $v^E$  (curve (a)), for which a minimum occurs at  $x_2 \approx 0.50$ . As has been pointed out by Fort and Moore [19], the excess isentropic compressibility is approximately proportional to the strength of the interactions between unlike molecules in a mixture. This means that deviations from ideality arise not only from differences in molecular size but also from changes in hydrogen bonding.

#### *Isobaric and isentropic expansibilities*

The expansibilities  $A_X$  are the second derivatives of  $G$  and  $F$  with regard to the pressure  $p$  and the volume  $V$ . Isobaric or isentropic quantities correspond respectively to  $X = p$  or  $S$ . Both excess coefficients  $\alpha_X^E$  and

excess molar quantities  $A_X^E$  have been considered. As stated by Alary et al. [20], "like the other second derivatives of free energy functions ... the thermal expansion coefficient specifies one aspect of thermodynamic fluctuations. While  $\kappa$  ... defines the magnitude of volume fluctuations,  $\alpha$  reflects the co-variance in these fluctuations". The composition dependence of the excess molar expansibilities  $A_p^E$  and  $A_S^E$  is shown in Fig. 4, where the changes of these excess quantities have been plotted vs.  $x_2$  (curves (d) and (e), respectively).  $A_p^E$  is negative over the whole composition range; its changes are quite different from those of  $K_X^E$ , since three extrema are observed: a minimum in the water-rich region ( $x_2 \approx 0.10$ ), followed by a maximum at  $x_2 \approx 0.27$  and a second minimum in the methanol-rich region ( $x_2 \approx 0.75$ ). By contrast,  $A_S^E$  is positive, except in the water-rich region where a minimum occurs at  $x_2 \approx 0.025$ ; then a maximum is observed at  $x_2 \approx 0.27$ , followed by a steady decrease. The molecular significance of the extrema of  $A_p^E$  may be attributable to structural transitions taking place in the mixture [7]. One might also conclude from the quasi-linear changes of  $A_S^E$  and other excess properties that such behaviour is suggestive of a pseudo two-phase system; however, as has been emphasized by Benson et al. [9], the corresponding partial molar excess properties are not constant over the composition ranges concerned, which is not consistent with the proposed assumption.

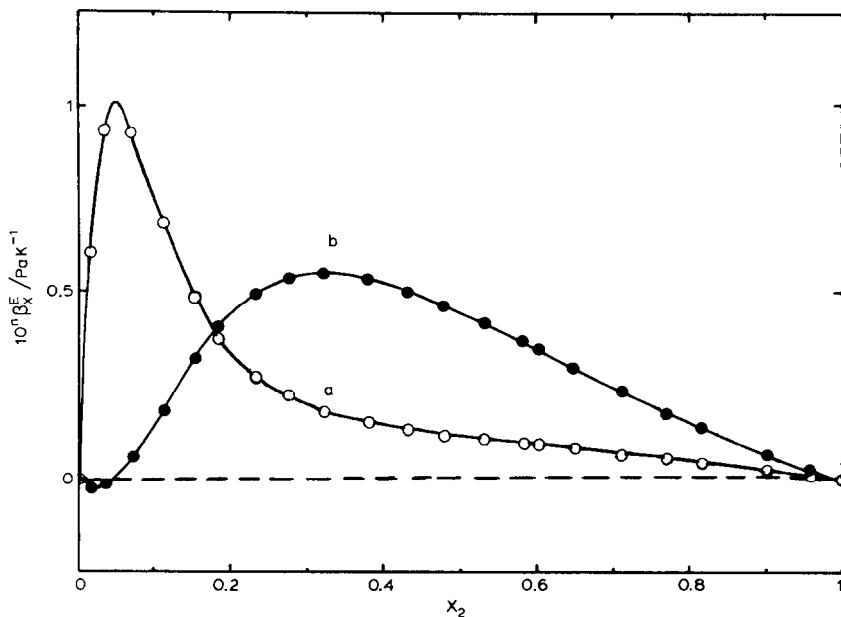


Fig. 5. Variations in excess pressure coefficients  $\beta_X^E$ , as a function of the mole fraction of methanol  $x_2$ , at 298.15 K: a  $10^{-5} \beta_S^E$ ; b  $10^{-6} \beta_V^E$ .

### *Isentropic and isochronic pressure coefficients*

The pressure coefficients  $\beta_X$  are closely related to the second derivatives of  $G$  and  $F$  with regard to the temperature  $T$  and the volume  $V$ . Isentropic or isochoric quantities correspond respectively to  $X=S$  or  $V$ . To our knowledge, no data relative to  $\beta_S$  and  $\beta_S^E$  are available from the literature, although they can be calculated from the recent results of Douhéret et al. [17], relative to the water-acetonitrile system. The changes of  $\beta_S^E$  have been plotted vs.  $x_2$  in Fig. 5 (curve (a)). A sharp maximum is observed at  $x_2 \approx 0.05$ . The composition dependence of this excess quantity would undoubtedly repay further consideration. At the moment it is known for only a limited number of systems, which precludes a detailed discussion here.

Data relative to  $\beta_V$  are also scarce, in spite of the fundamental importance of this property, whose composition dependence is interpreted as being the result of the attractive and repulsive forces between molecules. Macdonald et al. [21] measured  $\beta_V$  at a number of temperatures in the range 20–55°C for several water + alcohol mixtures, but they did not calculate  $\beta_V^E$ . As shown in Fig. 5 (curve (b)),  $(\beta_V)^E$  is positive except in the water-rich region, where a minimum is observed at  $x_2 \approx 0.03$ ; a maximum occurs at  $x_2 \approx 0.33$ . Thus, the sign of  $\beta_V^E$  is opposite to that of  $v^E$ . A similar composition dependence for  $v^E$  has been reported by Griot et al. [22] for binary mixtures of organic solvents, and explained in terms of the creation of disorder in long-chain molecules. A systematic study of aqueous organic solvents would be worthwhile.

### *Ideal and excess ultrasonic velocity*

The ultrasonic velocity  $u$  in a fluid is related to the isentropic bulk compressibility by the equation

$$u = (v/M\kappa_s)^{1/2} \quad (21)$$

As has been emphasized by Rowlinson [23], according to this definition  $u$  is a purely thermodynamic quantity. The experimental velocity is equal to  $u$  under conditions of negligible dispersion; it may therefore be regarded as an equilibrium property.

Various approaches to the determination of ideal and excess ultrasonic velocity have been considered. However, a literature search revealed some misconceptions concerning the calculation of these quantities. This will be discussed in a subsequent section. A more well-founded method, proposed recently by Douhéret et al. [1], was used in the present work. This method consists in rewriting the equation defining the variable under consideration  $z$ , itself a function of other variables  $z_1, z_2, \dots$ , i.e.

$$z = f(z_1, z_2, \dots) \quad (22)$$

in terms of the ideal quantity  $z^{\text{id}}$  using the equation

$$z^{\text{id}} = f(z_1^{\text{id}}, z_2^{\text{id}}, \dots) \quad (23)$$

This requires prior knowledge of the ideal mixing laws of the variables included in the defining equation. Consequently,  $u^{\text{id}}$  may be written in the following way

$$u^{\text{id}} = \left( v^{\text{id}} / \kappa_S^{\text{id}} \sum_i x_i M_i \right) \quad (24)$$

It should be emphasized that such an approach does not allow the weighting coefficients to be made explicit.  $u^{\text{E}}$  is then obtained from the general eqn. (1). Its composition dependence has been determined from the Redlich–Kister analysis. The best overall fit was obtained by using  $\phi_i^{\text{v}}$  as a weighting coefficient, as shown in Table 8, where the values of the standard deviations  $\sigma_{r(x_i)}$  and  $\sigma_{r(\phi_i^{\text{v}})}$  are reported. The changes of  $u^{\text{E}}$  have been plotted vs.  $\phi_2^{\text{v}}$ , as shown in curve (a) of Fig. 6;  $u^{\text{E}}$  is positive over the whole composition range, with a maximum at  $\phi_2^{\text{v}} \approx 0.46$ . When  $u^{\text{E}}$  is plotted vs.  $x_2$ , the maximum at  $x_2 \approx 0.27$  is followed by a quasi-linear decrease beyond the equimolar mixture. A symmetrical behaviour may be taken as indicative of the structure-breaking nature of the methanol molecules. This has been observed for several excess properties:  $v^{\text{E}}$ ,  $K_T^{\text{E}}$ ,  $K_S^{\text{E}}$  and, to a lesser extent,  $\beta_V^{\text{E}}$ .

For other variables, such as  $\beta_S^{\text{E}}$  and, to a lesser extent,  $C_p^{\text{E}}$  and  $C_V^{\text{E}}$ , the extrema are observed in the water-rich region; this unsymmetrical behaviour could be attributable to weak hydrophobic effects, reflecting the occurrence of structural interactions in solution. These phenomena are characterized by their low magnitude and the narrow range of concentrations within which they can develop. It should be emphasized that both water and methanol are extensively associated by hydrogen bonding, but their two types of association are quite dissimilar and mutually incompatible. Franks and Ives [24] have argued that methanol is probably incorporated into the water network by substitutional (and not interstitial) association. Antoniewicz et al. [25] consider that this assumption agrees very well with their quasi-chemical interpretation of the ultrasonic velocity in this system.

TABLE 8

Values of the standard deviation, as a function of the weighting coefficient  $\phi_i$  and of the number of parameters  $n$  of the Redlich–Kister eqn. (18), for the excess ultrasonic velocity

$\phi_i$	$n$			
	5	6	7	8
$x_i$	1.00 <sub>0</sub> ( $a_4$ ) <sup>a</sup>	0.43 <sub>0</sub> ( $a_4$ ) <sup>a</sup>	0.35 <sub>0</sub>	0.33 <sub>4</sub> ( $a_5$ ) <sup>a</sup>
$\phi_i^{\text{v}}$	0.59 <sub>7</sub>	0.32 <sub>4</sub>	0.33 <sub>3</sub> ( $a_4, a_6$ ) <sup>a</sup>	0.33 <sub>7</sub> ( $a_4 - a_7$ ) <sup>a</sup>

<sup>a</sup> The coefficients  $a_i$  mentioned within brackets are meaningless; the uncertainty on their absolute value is larger than or of the same order of magnitude as the value itself.

### Approximation in the calculation of the excess quantities

In a recent study [1] Douh ret et al. emphasized that various approaches to the determination of ideal and excess thermodynamic quantities have been considered. A literature search has clearly revealed some misconceptions about the calculation of these quantities. These errors are generally due to incorrect formulation of the ideal mixing laws: either the weighting coefficient is inappropriate; or the multiplying term is erroneous.

The most common error is generally due to  $f_{i(z)}$  being ignored, which amounts to making it equal to 1. The difference  $\delta\phi_{i(z)}$  between the approximate and rigorous values of the weighting coefficients of the ideal mixing laws is then equal to

$$\delta\phi_{i(z)} = \phi_i [1 - f_{i(z)}] \quad (25)$$

The orders of magnitude of errors introduced by such an assumption are shown in Fig. 7. Large discrepancies are observed for some variables, e.g.  $A_S$  and, to a lesser extent  $K_S$ . For  $C_V$  the approximation error appears to be

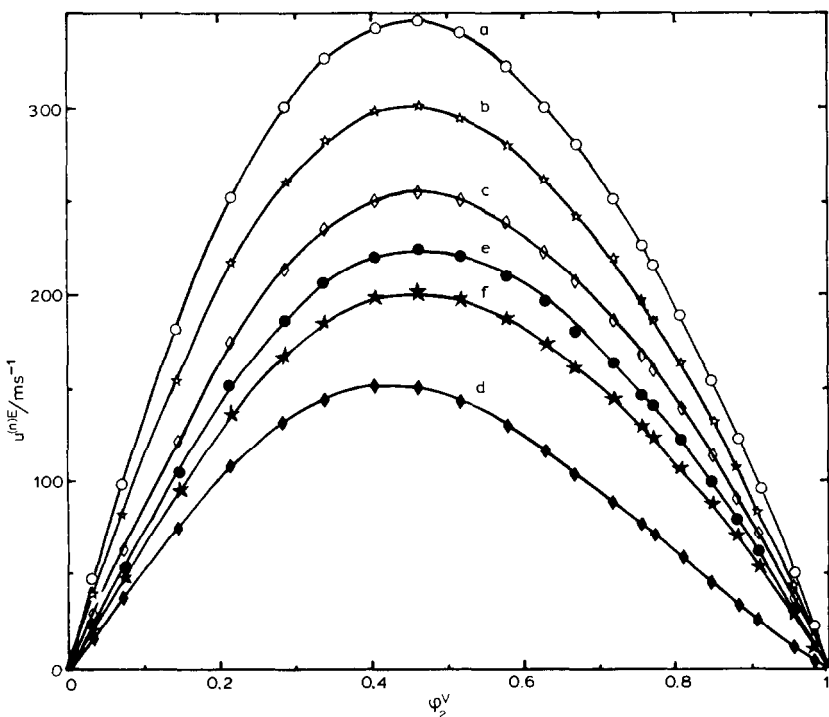


Fig. 6. Changes in excess ultrasonic velocity and in pseudo-excess ultrasonic velocity, as a function of the ideal volume fraction of methanol  $\phi_2^V$ , at 298.15 K: a,  $u^E$ ; b,  $\kappa_S^{id}$  in eqn. (24), approximated by a volume fraction averaging; c,  $u^{(n)E}$ , calculated from the model of Natta and Baccaredda [26]; d,  $u^{nE(x_i)}$ ; e,  $u^{nE(\phi_i^y)}$ ; f,  $u^{nE(w_i)}$ .

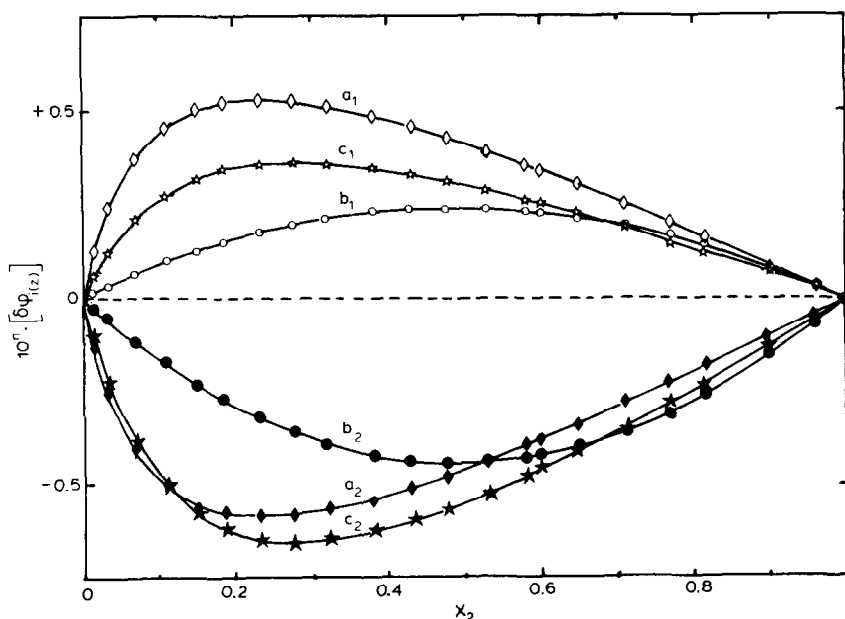


Fig. 7. Differences  $\delta\phi_{i(z)} = [x_i - x_i f_{i(z)}]$  in the values of the weighting coefficients calculated respectively with and without the multiplying term  $f_{i(z)}$ , for the water (1) + methanol (2) system, as a function of the mole fraction of methanol  $x_2$ , at 298.15 K:  $a_i$ ,  $\delta\phi_{i(A_s)}$ ;  $b_i$ ,  $10^2 \delta\phi_{i(K_s)}$ ;  $c_i$ ,  $10^2 \delta\phi_{i(C_s)}$ .

negligible, but this latter case is fortuitous and in no way justifies the multiplying term  $f_{i(z)}$  being ignored, for a quantitative, or even a qualitative interpretation.

The calculation of  $u^{\text{id}}$  and  $u^{\text{E}}$  has given rise to many different and approximate approaches. The use of eqn. (24) implies knowledge of the rigorous ideal law of mixing for  $v$  and  $\kappa_S$ . Sometimes,  $\kappa_S^{\text{id}}$  is approximated by a volume fraction averaging. Introduction of such an expression into the defining equation of  $u^{\text{id}}$  obviously gives rise to erroneous values of  $u^{\text{E}}$ , as shown in Fig. 6 (curve (b)).

Natta and Baccaredda [26] developed an intuitive model from the two basic thermodynamic criteria of ideality. According to these authors, the ideal ultrasonic velocity in a binary mixture is given by the equation

$$u^{\text{id}} = \frac{u_1^+ u_2^+}{\phi_1^v u_2^+ + \phi_2^v u_1^+} \quad (26)$$

The validity of this expression was discussed many years later. The model was supported by Ernst and Glinski [27], but Kiyohara et al. [28], in a reply to these authors, argued against its soundness. Changes in the pseudo-excess quantity calculated from eqns. (1) and (26) plotted vs.  $\phi_2^v$ , are shown in Fig. 6 (curve (c)).

Various authors have obtained a so-called "ideal" ultrasonic velocity from the following equation

$$u^{\text{id}} = \sum_i \phi_i u_i^+ \quad (27)$$

The weighting coefficient  $\phi_i$  has been variously identified with the mass fraction of  $i$ ,  $w_i$  (Schaafs [29]), the volume fraction  $\phi_i^v$  (Utter and Kling [30]), and  $x_i$  (Lara and Desnoyers [12]). Consequently, a number of different pseudo-excess quantities have been calculated from eqns. (1) and (27). The changes of these vs. the composition of the system are shown plotted vs.  $\phi_2^v$  in Fig. 6 (curves (d) to (f)). Such quantities represent nothing more than departures from a given additivity rule.

#### ACKNOWLEDGEMENTS

G.D. wishes to thank Professor M.I. Davis (University of Texas, El Paso, U.S.A.) for the persevering and sympathetic interest he has taken in this work. His pertinent remarks are gratefully acknowledged. Thanks are also due to Professor H. Hoiland and Engineer E. Hogseth (University of Bergen, Norway) for their kind advice on the measurement of ultrasonic velocity with the cell they designed.

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