

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/238129359>

^1H NMR and thermodynamic study of self-association and complex formation equilibria by hydrogen bonding. Methanol with chloroform or halothane

ARTICLE in PHYSICAL CHEMISTRY CHEMICAL PHYSICS · APRIL 1999

Impact Factor: 4.49 · DOI: 10.1039/a809545k

CITATIONS

22

READS

16

3 AUTHORS:



Marcela Tkadlecová

University of Chemistry and Technology, Pr...

43 PUBLICATIONS 361 CITATIONS

SEE PROFILE



Vladimír Dohnal

University of Chemistry and Technology, Pr...

98 PUBLICATIONS 986 CITATIONS

SEE PROFILE



Miguel Costas

Universidad Nacional Autónoma de México

105 PUBLICATIONS 2,064 CITATIONS

SEE PROFILE

^1H NMR and thermodynamic study of self-association and complex formation equilibria by hydrogen bonding. Methanol with chloroform or halothane

Marcela Tkadlecová,^a Vladimír Dohnal^{*b} and Miguel Costas^c

^a Department of Analytical Chemistry, Institute of Chemical Technology, 166 28 Prague 6, Czech Republic

^b Department of Physical Chemistry, Institute of Chemical Technology, 166 28 Prague 6, Czech Republic. E-mail: dohnalv@vscht.cz

^c Laboratorio de Termofísica, Departamento de Física y Química Teórica, Facultad de Química, Universidad Nacional Autónoma de México, México D. F. 04510, México

Received 7th December 1998, Accepted 1st February 1999

Mixtures of methanol with two strong proton donors, chloroform and halothane (2-bromo-2-chloro-1,1,1-trifluoroethane), were studied. The behaviour of these systems is governed by aggregate formation through H-bonding, where methanol self-association and its complex formation with the proton donors compete. In order to obtain information about these aggregate formation equilibria, ^1H NMR chemical shifts of the chloroform or halothane proton and of the hydroxy proton of methanol were measured as a function of concentration and temperature. The NMR data are expressed in the form of a new quantity, defined in this work, the relative change of the chemical shift. This quantity is convenient because it gives directly the extent of H-bonding without containing any NMR-specific parameter. The NMR data and the excess thermodynamic functions from the literature (G^E or $\ln \gamma_i$, H^E and C_p^E) were analysed using simple models of athermal association, amended by physical or thermal terms estimated on the basis of coupled homomorph and solution-of-groups approaches. Three particular models were tested, two of continuous methanol association (from tetramers to infinite size species) and one model that considers only methanol tetramerization. For the three models, methanol self-association parameters were previously obtained from independent data. Using enthalpy of solvation values obtained from quantum mechanical calculations, the equilibrium constant for the formation of methanol–chloroform and methanol–halothane complexes was the only fitted parameter. The continuous association models failed to fit the present data even qualitatively, whereas the tetramerization model gave reasonable agreement with experiment both for NMR and the excess thermodynamic functions. In accordance with previously studied mixtures of chloroform and halothane with oxygenated compounds, the methanol–halothane complex is found to be stronger than the methanol–chloroform complex; this is due to a more acidic hydrogen atom in halothane than in chloroform.

Introduction

Liquid mixtures where aggregate formation, through H-bonding, is present have been studied using a variety of thermodynamic properties and spectroscopic techniques. These data have been analysed through the application of chemical equilibria models, providing a better understanding of the behaviour of these systems. Mixtures of alcohols with inert solvents, where aggregate formation occurs only between molecules of the same kind, *i.e.*, self-association equilibria, have been extensively studied. On the other hand, mixtures where both pure components are unable to self-associate but are able to form complexes or cross-associated species in solution have also been the subject of detailed studies; for example, we have recently examined mixtures of chloroform or 2-bromo-2-chloro-1,1,1-trifluoroethane (halothane) with several oxygenated solvents through the measurement and simultaneous correlation of several thermodynamic properties^{1–3} and using ^1H NMR spectroscopy.⁴ When both complex formation and self-association are simultaneously present, the number of

chemical equilibria in the solution increases and the analysis of the data is further complicated. The present work is devoted to the study of this kind of mixture. We have measured the ^1H NMR signals for mixtures of methanol with halothane and with chloroform as a function of concentration and temperature. These NMR data, together with the published thermodynamic properties (G^E , H^E and C_p^E),^{5–9} were analysed using several association models. Other efforts to correlate ^1H NMR measurements with thermodynamic data have been reported in the literature;^{10,11} these studies were aimed at obtaining from the NMR data the equilibrium constants for alcohol self-association in alcohol–hydrocarbon mixtures.

This paper is divided into two sections. The first section contains a brief description of the association models used, the NMR data treatment and the relationship between them; in this section, we introduce a new NMR-derived quantity, which is useful and convenient for the treatment of the NMR data with association models since it provides explicit information on the formation of aggregates. The results are pre-

sented in the second section, together with a discussion of the performance of the association models and an interpretation in physical terms of the solution's behaviour.

Theory

Athermal association models

Simple models of athermal association were tested to calculate the effects of molecular association on thermodynamic excess functions and NMR. Let A represent the monomer of the alcohol and B the monomer of a non-associating proton donor that is capable of forming complexes with the alcohol. The assumptions upon which the models used are based can be summarized as follows.

(1) The alcohol forms linear multimers by consecutive reactions:



and these multimers and component B may further form complexes according to the solvation reactions (single solvation mechanism):



(2) The volume change upon mixing is neglected. Thus, geometric parameters of multimer complexes can be expressed as a sum of the respective parameters of the monomeric units forming a complex:

$$r_{A_i B} = i r_A + r_B \quad (3)$$

(3) The change in the combinatorial entropy caused by mixing the associates of different chain lengths is described by the Flory–Huggins equation. This assumption, together with assumption (2), allows us to work with the classical volumetric association constants given by

$$K_{A_i, A_{i+1}}^{(\phi)} = \frac{\phi_{A_{i+1}}}{\phi_{A_i} \phi_A} \quad (4)$$

$$K_{A_i, A_i B}^{(\phi)} = \frac{\phi_{A_i B}}{\phi_{A_i} \phi_B} \quad (5)$$

(4) The enthalpies of consecutive association $\Delta H_{A_i, A_{i+1}}^\circ = \Delta H_{AA}^\circ$ and the enthalpies of solvation $\Delta H_{A_i, A_i B}^\circ = \Delta H_{AB}^\circ$ are independent of the degree of multimerization and temperature.

(5) To reduce the number of association constants implied by eqns. (1) and (2) to one for each reaction, either of the following assumptions was adopted:

(a) the Mecke-Kempton type model (MK):

$$K_{A_i, A_{i+1}}^{(\phi)} = K_{AA}^{(\phi)} \quad (6)$$

$$K_{A_i, A_i B}^{(\phi)} = K_{AB}^{(\phi)} \quad (7)$$

(b) the Kretschmer–Wiebe type model (KW):

$$K_{A_i, A_{i+1}}^{(\phi)} = K_{AA}^{(\phi)} \frac{i+1}{i} \quad (8)$$

$$K_{A_i, A_i B}^{(\phi)} = K_{AB}^{(\phi)} \frac{i r_A + r_B}{i r_A r_B} \quad (9)$$

where $K_{AA}^{(\phi)}$ and $K_{AB}^{(\phi)}$ are independent of the degree of multimerization.

Excess thermodynamic functions

Excess thermodynamic functions ($Y^E = G^E$, H^E , C_p^E) are assumed to be a sum of independent chemical and physical contributions:

$$Y^E = Y_{\text{chem}}^E + Y_{\text{phys}}^E \quad (10)$$

The chemical contribution is expressed by means of the athermal association models. In order to estimate the physical con-

tribution, the homomorph concept is adopted as described in the last part of the Theory section (see below). The relationships that allow the calculation of the chemical contributions to the excess functions are as follows. The excess Gibbs energy and activity coefficients are given by

$$G_{\text{chem}}^E = RT(x_1 \ln \gamma_{1, \text{chem}} + x_2 \ln \gamma_{2, \text{chem}}) \quad (11)$$

$$\ln \gamma_{1, \text{chem}} = \ln \frac{\phi_A}{x_1 \phi_A^\circ} + \frac{\phi_A^\circ}{x_A^\circ} - \frac{\phi_A}{x_A} \quad (12)$$

$$\ln \gamma_{2, \text{chem}} = \ln \frac{\phi_B}{x_2} + 1 - \frac{\phi_B}{x_B} \quad (13)$$

where ϕ_A , x_A , ϕ_A° and x_A° are the volume and mole fractions of monomeric alcohol in the solution and in the pure state, respectively. The chemical contribution to the excess enthalpy is calculated as

$$H_{\text{chem}}^E = H_{\text{chem}} - x_1 H_{1, \text{chem}}^\circ \quad (14)$$

where H_{chem} is the molar enthalpy of the mixture, given by

$$H_{\text{chem}} = \frac{\Delta H_{AA}^\circ \sum_i (i-1)(x_{A_i} + x_{A_i B}) + \Delta H_{AB}^\circ \sum_i x_{A_i B}}{1 + \sum_i (i-1)x_{A_i} + \sum_i i x_{A_i B}} \quad (15)$$

and x_{A_i} and $x_{A_i B}$ are the mole fractions of the corresponding multimers; $H_{1, \text{chem}}^\circ$ in eqn. (14) is the molar enthalpy of pure alcohol calculated using eqn. (15) with $x_{A_i B} = 0$ and $x_{A_i} = x_{A_i}^\circ$. The multimer mole fractions in eqn. (15) are conveniently expressed in terms of monomer volume fractions whose calculation is described below. The chemical contribution to the excess heat capacity is calculated by differentiation of eqns. (14) and (15), and is given by

$$\begin{aligned} C_{p, \text{chem}}^E &\equiv \left(\frac{\partial H_{\text{chem}}^E}{\partial T} \right)_p = \left(\frac{\partial H_{\text{chem}}^E}{\partial K_{AA}^{(\phi)}} \right) \left(\frac{\partial K_{AA}^{(\phi)}}{\partial T} \right) + \left(\frac{\partial H_{\text{chem}}^E}{\partial K_{AB}^{(\phi)}} \right) \left(\frac{\partial K_{AB}^{(\phi)}}{\partial T} \right) \\ &+ \left(\frac{\partial H_{\text{chem}}^E}{\partial \phi_A} \right) \left[\left(\frac{\partial \phi_A}{\partial K_{AA}^{(\phi)}} \right) \left(\frac{\partial K_{AA}^{(\phi)}}{\partial T} \right) + \left(\frac{\partial \phi_A}{\partial K_{AB}^{(\phi)}} \right) \left(\frac{\partial K_{AB}^{(\phi)}}{\partial T} \right) \right] \\ &+ \left(\frac{\partial H_{\text{chem}}^E}{\partial \phi_B} \right) \left[\left(\frac{\partial \phi_B}{\partial K_{AA}^{(\phi)}} \right) \left(\frac{\partial K_{AA}^{(\phi)}}{\partial T} \right) + \left(\frac{\partial \phi_B}{\partial K_{AB}^{(\phi)}} \right) \left(\frac{\partial K_{AB}^{(\phi)}}{\partial T} \right) \right] \end{aligned} \quad (16)$$

Here, the partial derivatives of the volume fractions with respect to the association constants are performed numerically, whereas all others are evaluated analytically. The monomer volume and mole fractions involved in the relationships given above are obtained by solving simultaneously equilibrium and balance equations. In particular, the monomer volume fractions ϕ_A and ϕ_B are calculated from

$$\phi_1 = \sum_i \phi_{A_i} + \sum_i \phi_{A_i B} i / (i + r) \quad (17)$$

$$\phi_2 = \phi_B + \sum_i \phi_{A_i B} r / (i + r) \quad (18)$$

where $\phi_{A_i} = \phi_A^i K_{AA}^{(\phi)}$ and $\phi_{A_i B} = \phi_A^i \phi_B K_{AB}^{(\phi)}$ with $K_{AA}^{(\phi)}$ and $K_{AB}^{(\phi)}$ being related to the consecutive association constants $K_{A_j, A_{j+1}}^{(\phi)}$ and $K_{A_j, A_j B}^{(\phi)}$ through

$$K_{A_i}^{(\phi)} = \prod_{j=1}^{i-1} K_{A_j, A_{j+1}}^{(\phi)} \quad (19)$$

$$K_{A_i B}^{(\phi)} = K_{A_i, A_i B}^{(\phi)} \prod_{j=1}^{i-1} K_{A_j, A_{j+1}}^{(\phi)} \quad (20)$$

In eqns. (17) and (18), $r = r_B/r_A$, where r_i are the relative van der Waals volumes scaled according to Abrams and Praus-

nitz.¹² Finally, the monomer and multimer mole fractions are given by

$$x_A = \phi_A V/r_A \quad x_B = \phi_B V/r_B \quad (21)$$

$$x_{Ai} = \phi_{Ai} V/(ir_A) \quad x_{A;B} = \phi_{A;B} V/[r_A(i+r)] \quad (22)$$

where V , the microscopic solution molar volume, is given by

$$1/V = \phi_B/r_B + \sum_i \phi_{Ai}/(ir_A) + \sum_i \phi_{A;B}/[r_A(i+r)] \quad (23)$$

Note that in ref. 13, where the present eqns. (21) and (22) were also used, there is an error in eqn. (A7).

¹H NMR spectroscopy

The formation of a hydrogen bond lowers the local electron density and causes a change in the electromagnetic shielding of the proton involved. In ¹H NMR spectroscopy, the resonance signal of a “free” proton, expressed by the value of its chemical shift $\delta^{(f)}$, is thereby altered to a considerably higher value, $\delta^{(b)}$, for the “bound” proton. As the time for a resonance measurement is much longer than the exchange rate for hydrogen bond formation, these individual signals cannot be observed and instead the signal observed corresponds to their weighted average:

$$\delta_{\text{obs}} = (n^{(f)}/n)\delta^{(f)} + (n^{(b)}/n)\delta^{(b)} \quad (24)$$

the weights being the relative sizes of the respective populations¹⁴ ($n = n^{(f)} + n^{(b)}$). Each of the components in the binary systems under study, *viz.*, methanol (1) + chloroform (2) or + haloethane (2), possesses one active hydrogen atom capable of hydrogen bond formation. Hence two ¹H NMR signals, $\delta_{1,\text{obs}}$ and $\delta_{2,\text{obs}}$ can be monitored as a function of system composition in order to obtain information on the association phenomena. Specifically, at methanol infinite dilution ($x_1 \rightarrow 0$), the self-association of methanol is precluded, the observed signal of the OH proton thus being equal to that of the “free” OH proton:

$$\lim_{x_1 \rightarrow 0} \delta_{1,\text{obs}} \equiv \delta_{1,\text{obs}}^\infty = \delta_1^{(f)} \quad (25)$$

For pure component 2, where there is no aggregate formation, the observed chemical shift for its active hydrogen corresponds to the “free” form:

$$\delta_{2,\text{obs}}(x_2 = 1) \equiv \delta_{2,\text{obs}}^\circ = \delta_2^{(f)} \quad (26)$$

If the chemical shift corresponding to the “free” proton $\delta^{(f)}$ is subtracted from the chemical shift $\delta_{i,\text{obs}}$ observed at a given system composition, the net change in the chemical shift $\Delta\delta_{i,\text{obs}}$ due to hydrogen bonding of the respective proton is obtained:

$$\Delta\delta_{i,\text{obs}} = \delta_{i,\text{obs}} - \delta_i^{(f)} = (n_i^{(b)}/n_i)D = [1 - (n_i^{(f)}/n_i)]D \quad (27)$$

$$D \equiv \delta_i^{(b)} - \delta_i^{(f)}$$

As can be seen from eqn. (27), the change in chemical shift $\Delta\delta_{i,\text{obs}}$ is proportional to the relative size of the “bound” proton population, the proportionality constant D being the difference of chemical shifts of the “bound” and the “free” protons. Unlike $\delta_i^{(f)}$, $\delta_i^{(b)}$ cannot be directly measured so that D remains an unknown parameter. However, upon scaling $\Delta\delta_{i,\text{obs}}$ by the span of its values, this unknown parameter can be eliminated. Note that for the OH proton of methanol, $\Delta\delta_{1,\text{obs}}$ ranges from $\Delta\delta_{1,\text{obs}}(x_1 = 0) = \Delta\delta_{1,\text{obs}}^\infty = 0$ to $\Delta\delta_{1,\text{obs}}(x_1 = 1) = \Delta\delta_{1,\text{obs}}^0$ and, for the proton of component 2, from $\Delta\delta_{2,\text{obs}}(x_2 = 1) = \Delta\delta_{2,\text{obs}}^0 = 0$ to $\Delta\delta_{2,\text{obs}}(x_2 = 0) = \Delta\delta_{2,\text{obs}}^\infty$. Thus, a new quantity, termed the *relative change of the chemical shift*, $\eta_{i,\text{rel}}$, can be defined for the two protons as follows:

$$\eta_{1,\text{rel}} \equiv \frac{\Delta\delta_{1,\text{obs}}}{\Delta\delta_{1,\text{obs}}^\infty} = \frac{\delta_{1,\text{obs}} - \delta_{1,\text{obs}}^\infty}{\delta_{1,\text{obs}}^\circ - \delta_{1,\text{obs}}^\infty} \quad (28)$$

and

$$\eta_{2,\text{rel}} \equiv \frac{\Delta\delta_{2,\text{obs}}}{\Delta\delta_{2,\text{obs}}^\infty} = \frac{\delta_{2,\text{obs}} - \delta_{2,\text{obs}}^\circ}{\delta_{2,\text{obs}}^\infty - \delta_{2,\text{obs}}^\circ} \quad (29)$$

The relative change of the chemical shift is a dimensionless quantity normalized to the $\langle 0, 1 \rangle$ interval and can be directly evaluated from the observed chemical shifts. On combining eqn. (28), (27) and (25), one obtains

$$\eta_{1,\text{rel}} = \frac{1 - (n_1^{(f)}/n_1)}{1 - (n_1^{(f)}/n_1)^\circ} \quad (30)$$

and using eqn. (29), (27) and (26)

$$\eta_{2,\text{rel}} = \frac{1 - (n_2^{(f)}/n_2)}{1 - (n_2^{(f)}/n_2)^\circ} \quad (31)$$

Eqn. (30) and (31) indicate that $\eta_{i,\text{rel}}$ expresses the relative extent of hydrogen bonding compared with its maximum value occurring for proton 1 in the state of pure self-associated component 1, and for proton 2 in the state of infinitely dilute component 2. The major advantage of defining $\eta_{i,\text{rel}}$ is that this quantity does not contain any NMR-specific parameter and therefore can be directly calculated from a solution association model. For the athermal association models outlined above, the relative sizes of the “free” proton populations can be expressed as follows:

$$\begin{aligned} \frac{n_1^{(f)}}{n_1} &= \frac{\sum_i (\phi_{Ai}/i) + \sum_i [\phi_{A;B}/(i+r)]}{\phi_1} \\ &= (\phi_A/x_A - \phi_B/r)/\phi_1 \end{aligned} \quad (32)$$

and

$$n_2^{(f)}/n_2 = \phi_B/\phi_2 \quad (33)$$

which upon substitution into eqn. (30) and (31) gives

$$\eta_{1,\text{rel}} = \frac{1 - (\phi_A/x_A - \phi_B/r)/\phi_1}{1 - (\phi_A^\circ/x_A^\circ)} \quad (34)$$

and

$$\eta_{2,\text{rel}} = \frac{1 - \phi_B/\phi_2}{1 - (\phi_B/\phi_2)^\circ} \quad (35)$$

Note that the definitions and further equations given above for the relative change in chemical shift are quite general, and hence can be applied to systems other than those studied in this work. Eqn. (28) and (34) are still valid and applicable even if component 2 does not have any active hydrogen to cause a complex formation, *i.e.*, it behaves as an inert component, such as an alkane. On the other hand, eqn. (29) and (35) are still valid and applicable even if component 1 does not have any active hydrogen to cause its self-association, *i.e.*, behaves as a non-self-associated proton acceptor, such as an ether.

The right hand side of eqn. (34) and (35) can be written in terms of the association model parameters, opening up in principle, the possibility of obtaining these parameters using only the NMR data. In turn, these parameters could then be used to predict the excess thermodynamic quantities. In practice, however, this attractive goal is difficult to achieve successfully owing to several factors, mainly due to association model imperfections and the limited information content of the NMR data.

Physical contributions to excess functions

Attempts to take into account physical thermal effects on excess functions usually imply the inconvenience of increasing the number of adjustable parameters, which in turn lose their physical significance, thus causing the model to become a mere correlation scheme. However, using the homomorph

concept, it is possible to account for physical thermal effects without introducing new adjustable parameters. According to this concept, Y_{phys}^E for the systems under study is given by the respective Y^E of a mixture formed and an equal-structure hydrocarbon of methanol, i.e., ethane (1), with chloroform (2) or halothane (2). Here, only the residual (non-combinatorial) part of G^E is to be considered, as the combinatorial effects are already accounted for (at the real species level) by the athermal association model in Y_{chem}^E . Although there are no direct experimental data available in the literature on excess functions of ethane + chloroform or + halothane, they can be estimated on the basis of those for closely related mixtures using the solution-of-groups approach (SGC).¹⁵ Hexane + chloroform or + halothane can well serve as these bases, because for these mixtures reliable data are available for all three excess functions (G^E from ref. 16 and 17, H^E from ref. 18 and 19 and C_p^E from ref. 7 and 20) at (or close to) the temperature of interest. Employing the SGC method of combination of excess functions described previously,²¹ the residual excess functions $Y_{\text{res}}^E(x_1)$ for ethane (1) + chloroform (2) or + halothane (2) were calculated in a very straightforward way from those $\hat{Y}_{\text{res}}^E(\hat{x}_1)$ for the basal system hexane (1) + chloroform (2) or + halothane (2) as follows:

$$Y_{\text{phys}}^E(x_1) = Y_{\text{res}}^E(x_1) = [(1 - x_1/1 - \hat{x}_1)] \hat{Y}_{\text{res}}^E(\hat{x}_1) \quad (36)$$

where \hat{x}_1 , the corresponding composition of the basal system (hexane mole fraction), is given by

$$\hat{x}_1 = \frac{x_1}{\hat{q}_1/q_1 + x_1(1 - \hat{q}_1/q_1)} \quad (37)$$

with \hat{q}_1 and q_1 being the surface parameters of hexane and ethane, respectively. The combinatorial part of G^E for the basal systems was estimated by the Flory–Huggins expression. The values of geometric parameters needed for the outlined calculation of Y_{phys}^E are dimensionless van der Waals surfaces and volumes as given in ref. 22 and scaled according to ref. 12: $q(\text{ethane}) = 1.696$, $q(\text{hexane}) = 3.856$, $r(\text{hexane}) = 4.4998$, further r_i values being given below.

Experimental

Materials

Methanol of analytical-reagent grade (Lachema, Brno, Czech Republic) was refluxed with iodine-activated magnesium and then fractionally distilled on a 1 m column filled with stainless-steel helices. Chloroform of analytical-reagent grade (Lachema) stabilized with 1% ethanol was first washed with water to remove the stabilizer and then dried with calcium chloride. The substance was further refluxed with a small portion of 2,4-dinitrophenylhydrazine acidified with hydrogen chloride and then fractionally distilled under nitrogen twice, on 1 and 1.5 m columns packed with ceramic saddles. Halothane, stabilized with 0.01 mass-% of thymol (Léčiva, Prague, Czech Republic), was distilled on a 1 m packed column filled with ceramic saddles to remove the stabilizing agent. All products were finally dried with 4 Å molecular sieves. Methanol and halothane were stored in the dark in sealed ampoules, while chloroform was purified immediately before measurements because of its rapid decomposition. The purity of each substance, as checked by gas–liquid chromatography with a Carbowax 20M column and a flame ionization detector, was better than 99.9%. The water content determined by Fischer titration did not exceed 0.03 mol-%.

Sample preparation

For each system under study, 18 samples covering the whole composition range were prepared by weighing pure components. In addition, some samples very dilute in methanol ($0.0003 < x_1 < 0.0025$) were prepared in order to determine

accurate values of methanol monomer chemical shifts. For the preparation of the very dilute samples, first a dilute stock standard solution of methanol in component 2 solvent (chloroform or halothane) was prepared and then it was mixed with the pure component 2 solvent to obtain the final samples. Relatively large sample volumes (1 ml) were used in order to minimize the volume of the vapour phase and to decrease the influence of inaccuracy in weighing. A small volume (0.001 v/v) of tetramethylsilane (TMS) was added to the pure components from which the samples were prepared. For dilute methanol samples much lower concentrations of TMS were satisfactory, because for equal molar concentrations of methanol and TMS the intensity of the TMS signal is an order of magnitude higher than that of the OH proton signal. During the preparation and subsequent manipulation of samples, precautions were taken to avoid contamination by moisture and changes of composition due to evaporation.

Instrumentation

Measurements of chemical shifts were carried out using a Bruker AMX spectrometer, the working frequency being 400.136 MHz. The magnetic field homogeneity was adjusted on a sample tube with deuterated chloroform or methanol and then the measurements were performed without lock. All samples had similar volumes of about 1 ml to keep the field homogeneity. Each sample was measured three times with one scan after 20 min of temperature equilibration. The temperature was stable to within ± 0.1 K and was calibrated using the low temperature calibration sample (methanol). The uncertainty of the measurement of the chemical shift was within 0.5 Hz. The signals of halothane or chloroform and of the OH proton of methanol were traced in the NMR spectra, TMS being used as an internal standard. The ^1H NMR signal of halothane is a quartet due to the ^1H – ^{19}F coupling (coupling constant 5.2 Hz). The signals of methanol are a quartet (OH) and a doublet (CH_3) with a coupling constant of 5.5 Hz for low concentrations or singlets for higher concentrations. The signals of chloroform and TMS are singlets. For the measurement of the samples with very low methanol mole fractions ($x_1 < 0.003$), a Bruker Avance DRX spectrometer operating at a frequency of 500.132 MHz was used to improve the measurement sensitivity and the accuracy of the determination of the OH “free” proton chemical shift.

Results and discussion

For methanol + chloroform and + halothane, the ^1H NMR chemical shifts of the methanol hydroxy proton and of the chloroform and halothane proton, and their relative changes as given by eqns. (28) and (29), have been deposited as supplementary data,[‡] as a function of methanol concentration and at two temperatures. The chemical shifts for methanol at infinite dilution were obtained by extrapolation of the data measured for very dilute solutions which have also been deposited as supplementary data and are displayed in Fig. 1. For the chloroform and halothane protons, the chemical shifts at infinite dilution were obtained by a second-order polynomial extrapolation of the data. The new NMR-derived quantity $\eta_{i,\text{rel}}$ is useful for the treatment of the NMR data since it is independent of any NMR-specific parameter; as such, it can be calculated directly from association models, providing specific information on aggregate formation, through H-bonding, in the solution.

The experimental thermodynamic data of the studied mixtures (G^E or $\ln \gamma_i$ at 40 and 35 °C for chloroform and halo-

[‡] Available as supplementary material (SUP 57494, pp. 6) deposited with the British Library. Details are available from the Editorial Office. For direct electronic access see <http://www.rsc.org/suppdata/pccp/1999/1479>.

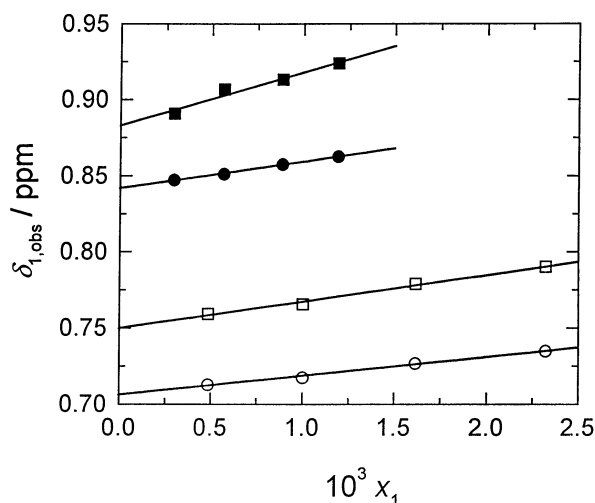


Fig. 1 $\delta_{1,\text{obs}}$ for very dilute solutions of methanol (1) in chloroform (2) at (■) 24.7 and (●) 43.0 °C or in halothane at (□) 23.3 and (○) 41.8 °C. Extrapolation to methanol infinite dilution.

thane, respectively, and H^E and C_P^E at 25 °C) are displayed in Fig. 2–5. For methanol + chloroform, reliable data exist in the literature on VLE⁵ and excess enthalpy;⁶ missing data for C_P^E have been recently measured.⁷ For methanol + halothane, all the thermodynamic properties were obtained previously.^{8,9} Several association models, with varying degrees of complexity and number of adjustable parameters, can be fitted to this experimental information and to the NMR $\eta_{1,\text{rel}}$ and $\eta_{2,\text{rel}}$ data shown in Fig. 6 and 7. We tested three of the simple athermal association models described above, namely those that exclude lower multimers and for which the alcohol self-association parameters are known. These models were successful in interpreting the thermodynamic data of methanol + hexane and of methanol + 1,1,2-trichlorotrifluoroethane (Freon 113), where for the latter system it was found that there is a weak specific interaction between the alcohol and the Freon 113.¹³ These three models are the Mecke–Kempter [MK(4 → ∞)] and Kretschmer–Wiebe [KW(4 → ∞)] models of continuous association of the alcohol starting with the tetramerization, and a model considering only tetramerization (KW4). Note that considering only tetramerization or that tetramers are the smallest alcohol self-associated species is consistent with the fact that dimerization and trimerization equilibrium constants for alcohols are substantially smaller than the subsequent consecutive association constants.²³ As given by eqn. (2), the single solvation mecha-

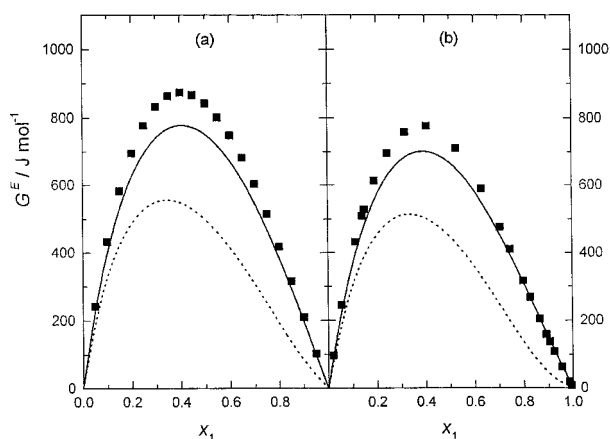


Fig. 2 G^E for (a) methanol (1) + chloroform (2) at 313.15 K and (b) methanol (1) + halothane (2) at 308.15 K. Points are experimental data from ref. 5 and 8, respectively, and lines were calculated using the KW4 model: chemical term only (dotted line) and with physical contribution added (full line).

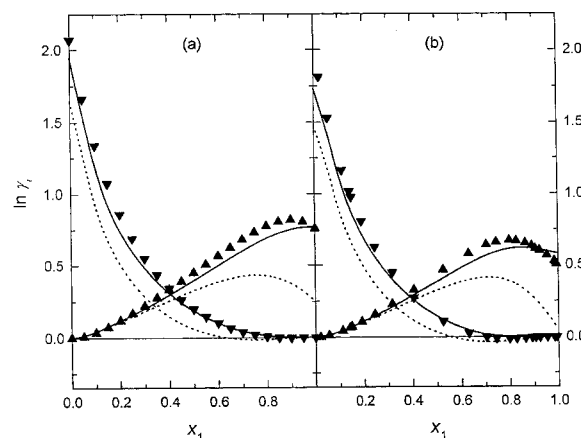


Fig. 3 $\ln \gamma_i$ for (a) methanol (1) + chloroform (2) at 313.15 K and (b) methanol (1) + halothane (2) at 308.15 K. Points are experimental data from ref. 5 and 8, respectively, and lines were calculated using the KW4 model: chemical term only (dotted line) and with physical contribution added (full line).

nism is considered in these models, *i.e.*, every alcohol species present in solution forms a complex with just one molecule of the other compound. In testing the models, we have taken the approach of minimizing the number of adjustable parameters.

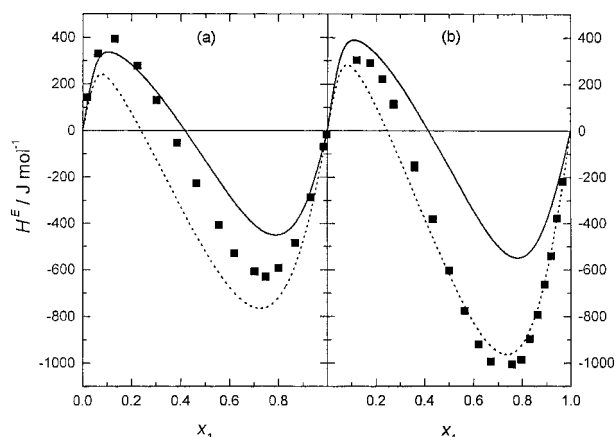


Fig. 4 H^E at 298.15 K for (a) methanol (1) + chloroform (2) and (b) methanol (1) + halothane (2). Points are experimental data from ref. 6 and 9, respectively, and lines were calculated using the KW4 model: chemical term only (dotted line) and with physical contribution added (full line).

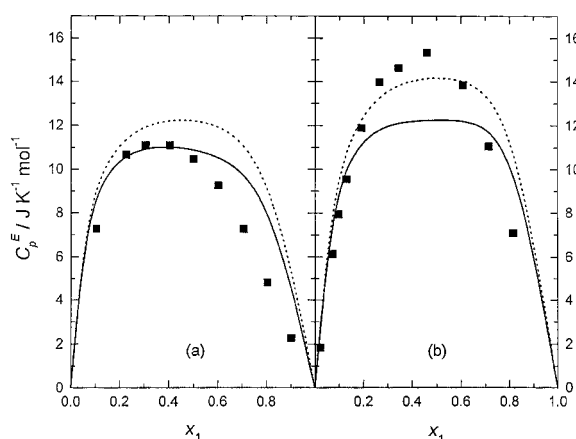


Fig. 5 C_P^E at 298.15 K for (a) methanol (1) + chloroform (2) and (b) methanol (1) + halothane (2). Points are experimental data from ref. 7 and 9, respectively, and lines were calculated using the KW4 model: chemical term only (dotted line) and with physical contribution added (full line). Note that in ref. 9 (p. 158), x_1 refers to methanol mole fraction and not to halothane mole fraction as wrongly stated there.

We have therefore (i) taken the self-association parameters, $K_{AA}^{(\phi)}$ and ΔH_{AA}^0 , as fixed and equal to those obtained from fitting the experimental pure alcohol vapour pressures [for MK(4 \rightarrow ∞) and KW(4 \rightarrow ∞) models] or the apparent heat capacities of dilute solutions of methanol in hexane (KW4 model)^{13,23} and (ii) used the enthalpy of complex formation ΔH_{AB}^0 calculated with the AM1 quantum mechanical method;²⁴ this method has been used previously for other complexes to obtain formation enthalpies which correlate very well with the values obtained by fitting the thermodynamic quantities.^{1–3} With this approach, the only adjustable parameter is $K_{AB}^{(\phi)}$, the equilibrium constant for the formation of cross-associated species. We have found that the MK(4 \rightarrow ∞) and KW(4 \rightarrow ∞) models systematically overestimate the chemical part of H^E and underestimate C_p^E , failing to reproduce some of the essential features of the data; these deficiencies are not overcome if different, within a reasonable range, ΔH_{AB}^0 values are used. In contrast, a reasonably good simultaneous fit of the thermodynamic and NMR data was obtained with the KW4 model. The performance of this model is discussed in detail below.

The performance of the KW4 model for G^E and $\ln \gamma_i$, with and without physical contributions considered, is shown in Fig. 2 and 3. These calculations were made using the KW4 model equations given above with $K_{Ai}^{(\phi)} = 0$ in eqn. (19) for all i values except $i = 4$ and with $K_{AB}^{(\phi)}$ being the only fitted parameter; the values of $K_{AB}^{(\phi)}$ for both chloroform and halothane are given in Table 1, together with the values of the other model parameters. Fig. 2 and 3 indicate that the asymmetry of G^E and $\ln \gamma_i$ with alcohol concentration, the existence of the inflection point in G^E and the corresponding extrema in $\ln \gamma_i$ are well reproduced. The chemical contribution underestimates G^E , which was also observed when using the same model for the mixtures methanol + hexane ($K_{AB}^{(\phi)} = 0$) and + Freon 113. The inclusion of the physical contributions is clearly of importance to fit the experimental G^E or $\ln \gamma_i$ data, as has been found on numerous occasions.^{13,25,26} Note also that the relative magnitude of the deviations from ideality for both mixtures is well reflected by the model. The experimental H^E values for both methanol + chloroform and + halothane are S-shaped curves, with the positive part occurring at low methanol concentrations. As can be seen in Fig. 4, these concentration dependences are well reproduced by the KW4 model. For methanol + chloroform H_{chem}^E is more negative than the experimental curve whereas for methanol + halothane H_{chem}^E matches the experimental results almost perfectly. For both mixtures, H_{phys}^E is positive, as expected, but its magnitude appears to be too large so that the total H^E is less negative at high x_1 and more positive at low x_1 than the experimental data, except for the chloroform case, where for $x_1 < 0.3$ the agreement with experiment is almost perfect. In Fig. 5, the KW4 model reflects correctly the large observed C_p^E values for these systems. However, the shape of the calculated curves does not match the experimental behaviour very well, the KW4 curves being markedly flatter. As

expected, the physical contribution is small and negative, and its use results in a slightly better fit for methanol + chloroform, but for methanol + halothane it produces a worse agreement, especially in the middle range of concentrations. Fig. 6 indicates that the general trend of the experimental relative change of the chemical shift for the methanol proton, $\eta_{1,rel}$, is correctly predicted by the KW4 model for both chloroform and halothane mixtures. In particular, the model is able to reproduce the steep increase in $\eta_{1,rel}$ at low methanol concentrations, which gradually slows with increasing x_1 , so that at equimolar concentration the degree of methanol self-association is already close to that in the pure alcohol. The KW4 curves lie above the experimental data, not reflecting fully the effect of complexation of methanol with the proton donors chloroform and halothane which pushes the calculated $\eta_{1,rel}$ values towards the experimental values; in other words, a larger $K_{AB}^{(\phi)}$ value would give better $\eta_{1,rel}$ values but then the thermodynamic quantities would not be well reproduced (for example, G^E would be too small and hence unrealistic). On the other hand, in Fig. 6 the strong effect of temperature on the experimental $\eta_{1,rel}$ values is very well reproduced by the model. The experimental relative changes in the chemical shift for the chloroform and halothane protons, $\eta_{2,rel}$, are seen in Fig. 7 to be very well matched by the KW4 model, except in the range of medium concentrations where the calculated values are slightly lower than the experimental values. Especially noted should be the correctly predicted inflection point of $\eta_{2,rel}$ at low methanol concentrations; this can be well seen for methanol + halothane in Fig. 7(b), where we carried out a number of measurements to identify this inflection clearly. In full accordance with the experiment, the effect of temperature on the calculated $\eta_{2,rel}$ is small. Since according to eqns. (30) and (31) $\eta_{1,rel}$ and $\eta_{2,rel}$ are the reflections of the relative

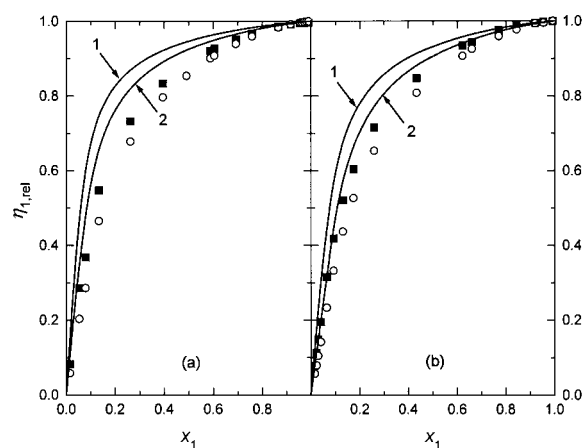


Fig. 6 $\eta_{1,rel}$ for (a) methanol (1) + chloroform (2) at (■, 1) 24.7 and (○, 2) 43.0 °C and (b) methanol (1) + halothane (2) at (■, 1) 23.3 and (○, 2) 41.8 °C. Points are experimental data from this work and lines were calculated using the KW4 model.

Table 1 Parameters of the KW4 model for methanol (A) self-association and complex formation with chloroform (B) or halothane (B)

Self-association		Complex formation			
		With chloroform		With halothane	
$K_{AA}^{(\phi)}$ (25 °C)	H_{AA}^0 / kJ mol ⁻¹	$K_{AB}^{(\phi)}$ (25 °C)	H_{AB}^0 / kJ mol ⁻¹	$K_{AB}^{(\phi)}$ (25 °C)	H_{AB}^0 / kJ mol ⁻¹
198.7 ^a	-27.9 ^a	10 ^b	-11.0 ^c	15 ^b	-12.3 ^c
$r(\text{methanol}) = 1.4311$	$r(\text{chloroform}) = 2.8700$	$r(\text{halothane}) = 3.5682$			

^a From ref. 23. Fitted to experimental chemical apparent heat capacities of dilute solutions of methanol in hexane. The value of $K_{AA}^{(\phi)}$ is related to that of $K_{AA}^{(p)}$ given in ref. 23 through $K_{AA}^{(\phi)} = (K_{AA}^{(p)}/4)^{1/3}$. ^b Adjusted to obtain the best simultaneous fit of thermodynamic (G^E , H^E , C_p^E) and NMR ($\eta_{1,rel}$, $\eta_{2,rel}$) data for the methanol + chloroform or + halothane system. ^c Calculated using the AM1 quantum mechanical method.

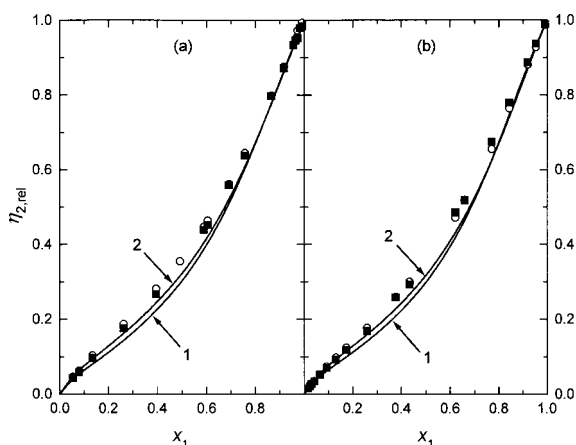


Fig. 7 $\eta_{2,\text{rel}}$ for (a) methanol (1) + chloroform (2) at (■, 1) 24.7 and (○, 2) 43.0 °C and (b) methanol (1) + halothane (2) at (■, 1) 23.3 and (○, 2) 41.8 °C. Points are experimental data from this work and lines were calculated using the KW4 model.

populations of self-associated and complex species in the solution, the results in Fig. 6 and 7 indicate that the KW4 model with single solvation considered is able to reproduce fairly well the distribution of these species and the equilibria between them.

The overall comparison between the experimental behaviour and the KW4 model in Fig. 2–7 shows, however, that the performance of the model is not perfect, and thus a better simultaneous correlation of the NMR and thermodynamic data might be possible. The discrepancies between experiment and theory in Fig. 2–7 can be attributed to several factors, namely (i) other solvation mechanisms are present; (ii) there are more types of bound hydroxy proton than that considered, *e.g.*, the oxygen atom in the hydroxy group can be involved or not in other H-bonds; this may be of different importance for thermodynamics and NMR; (iii) in the solution both linear and cyclic species co-exist; (iv) the inseparability of the chemical and physical contributions to the excess thermodynamic functions; and (v) an insufficiently good approach for the estimation of the physical effects. Consideration of factors (ii) and (iii) requires the introduction of additional adjustable parameters, which, in turn, complicates the interpretation of the behaviour of the solution in physical terms. Since our present models are not sufficiently developed, the influence of factors (iv) and (v) is difficult to evaluate; separability has only been shown to be exact for physical effects following the solution-of-groups approach and considering the interchange energy between the free and bound hydroxy groups to be zero.^{26,27} On the other hand, factor (i) can be partially evaluated through consideration of models which include solvation mechanisms different from single solvation. In this work, we assessed this factor using two other KW4 models: a model that only considers 1:1 complexes (AB species) to be present in the solution and a model which includes multiple solvation, *i.e.*, the AB and A_4B_j ($j = 1-4$) species. The expressions for the thermodynamic quantities in these two models are not given here; these models were tested using a reasonable range of $K_{AB}^{(\phi)}$ and ΔH_{AB}° values. The employment of these two models does not improve the description of the data by the KW4 model seen in Fig. 2–7. For these models the global correlation between the thermodynamic and NMR properties, and also amongst the thermodynamic properties themselves, is broken. In other words, when one or two properties are well represented, the others are not. For example, the model that includes only the 1:1 complex is able to represent adequately G^E and $\ln \gamma_i$, but then H^E is positive at all concentrations and $\eta_{2,\text{rel}}$ is much larger than by experiment; for the model with multiple solvation, when G^E and $\ln \gamma_i$ are well correlated, H^E and C_p^E are much

more negative and positive than by experiment, respectively, and $\eta_{1,\text{rel}}$ and $\eta_{2,\text{rel}}$ are both larger than needed. These results make these two models unacceptable, their performance being markedly poorer than that of the KW4 model with single solvation.

With the appropriate corrections for temperature differences in the data for G^E and H^E , taken together Fig. 2 and 4 show that the excess entropies are small and positive at very low methanol mole fractions and large and negative at all other concentrations. This indicates the high degree of organization that results from the formation of H-bonded species in solution, *i.e.*, of methanol self-associated species and methanol–chloroform and methanol–halothane complexes. These complexes are formed *via* H-bonding between the acidic hydrogen in halothane or chloroform and the oxygen atom of methanol. The results in Table 1 and the comparison between panels (a) and (b) in Fig. 2–7 show that the methanol–halothane H-bonding is stronger than the methanol–chloroform H-bonding; this is due to the more acidic hydrogen atom in halothane than in chloroform. A similar situation, *i.e.*, stronger complexes with halothane than with chloroform, was also found for mixtures of these two substances with a series of non self-associating oxygenated solvents.^{1–3} In this context, it is interesting to compare the thermodynamic equilibrium constant K_1 for the AB complexes studied here with those obtained for chloroform and halothane mixed with the non self-associating oxygenated solvents. Since $K_1 = K_{AB}^{(\phi)} e^{-1(r_A + r_B)/r_A r_B}$, using the results in Table 1, $K_1 = 5.40$ for methanol + halothane and 3.85 for methanol + chloroform. These values are slightly greater than the largest K_1 values obtained with the oxygenated solvents, *e.g.*, $K_1 = 4.89$ for halothane + 2,5-dioxahexane and 2.76 for chloroform + tetrahydrofuran, indicating that it is more favourable to form the complexes with methanol. On the other hand, in ref. 13 also using the KW4 model it was found that for methanol + Freon 113 $K_1 = 0.14$, reflecting the weakness of the charge transfer complex formation between methanol and the fully halogenated Freon 113. It appears, then, that by using the KW4 model it is possible to characterize a wide range of complexes, from the weak methanol–Freon 113 to the strong methanol–halothane complex.

Acknowledgements

We thank Dr. Michal Bureš for performing the AM1 quantum mechanical calculations. V.D. is grateful for a Catedra Patronal from the Consejo Nacional de Ciencia y Tecnología de México (CONACyT). This work was carried out under a Czech–Mexican scientific cooperation project supported by the Ministry of Education of the Czech Republic (grant ME 237/1998) and CONACyT.

References

- 1 V. Dohnal and M. Costas, *J. Solution Chem.*, 1996, **25**, 635.
- 2 V. Dohnal, D. Fenclová, M. Bureš and M. Costas, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1025.
- 3 V. Dohnal, K. Kratochvilová, M. Bureš and M. Costas, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1877.
- 4 M. Tkadlecová, J. Havlíček and V. Dohnal, *Can. J. Chem.*, 1995, **73**, 1406.
- 5 M. Goral, G. Kolasinska and P. Oracz, *Int. DATA Ser., Sel. Data Mixtures, Ser. A*, 1985, 209.
- 6 I. Nagata and K. Tamura, *Fluid Phase Equilib.*, 1983, **15**, 67.
- 7 D. Fenclová, V. Dohnal, S. Perez-Casas, C. Frigolet and M. Costas, *Int. Electron. J. Phys.-Chem. Data*, 1995, **1**, 217.
- 8 D. Fenclová and V. Dohnal, *Int. DATA Ser., Sel. Data Mixtures, Ser. A*, 1993, **21**, 85.
- 9 M. Costas, *Int. DATA Ser., Sel. Data Mixtures, Ser. A*, 1993, **21**, 154.
- 10 A. M. Karachewski, M. M. McNeil and C. A. Eckert, *Ind. Eng. Chem. Res.*, 1989, **28**, 315.

- 11 A. M. Karachewski, W. J. Howell and C. A. Eckert, *AIChE J.*, 1991, **37**, 65.
- 12 D. S. Abrams and J. M. Prausnitz, *AIChE J.*, 1975, **21**, 116.
- 13 D. Fenclová, V. Dohnal, M. Costas and D. Patterson, *Fluid Phase Equilib.*, 1990, **57**, 119.
- 14 H. A. Gutowsky and A. Saike, *J. Chem. Phys.*, 1953, **21**, 1688.
- 15 G. M. Wilson and C. H. Deal, *Ind. Eng. Chem. Fundam.*, 1962, **1**, 20.
- 16 T. G. Bissell and A. G. Williamson, *J. Chem. Thermodyn.*, 1975, **7**, 131.
- 17 D. Fenclová and V. Dohnal, *J. Chem. Thermodyn.*, 1993, **25**, 689.
- 18 B. R. Sharma, G. S. Pundeer and P. P. Singh, *Thermochim. Acta*, 1975, **11**, 105.
- 19 M. Costas, S. Perez-Casas, V. Dohnal and D. Fenclová, *Thermochim. Acta*, 1993, **213**, 23.
- 20 V. Dohnal, M. Costas and D. Fenclová, *Thermochim. Acta*, 1993, **214**, 183.
- 21 V. Dohnal, R. Holub and J. Pick, *Fluid Phase Equilib.*, 1981, **6**, 61.
- 22 A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Gases*, Wiley, New York, 1968, pp. 450–468.
- 23 L. Andreoli-Ball, D. Patterson, M. Costas and M. Caceres-Alonso, *J. Chem. Soc., Faraday Trans.*, 1988, **84**, 3991.
- 24 M. J. S. Dewar, E. G. Zoebish, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
- 25 I. Prigogine and R. Defay, *Chemical Thermodynamics*, Longmans Green, London, 1962, pp. 432–434.
- 26 A. J. Treszczanowicz and T. Treszczanowicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1981, **29**, 269.
- 27 A. J. Treszczanowicz and T. Treszczanowicz, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1975, **23**, 169.

Paper 8/09545K