

Excess thermodynamic properties of asymmetric multicomponent mixtures: Predictive models and microscopic insight for the system ethanol + tetrahydrofuran + cyclohexane at 25 °C

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Abstract: A general picture of the excess thermodynamic properties G_m^E , H_m^E , S_m^E , $C_{p,m}^E$, and V_m^E , for the ternary mixture ethanol + tetrahydrofuran + cyclohexane is presented and discussed. Emphasis is placed on the advantages for interpretation inherent in the contemporaneous observation of all these properties. The trend of the excess entropy and heat capacity reveals the nearly competitive behaviour of the two polar compounds with respect to the hydrocarbon in terms of order-disorder creation. Partial molar quantities of ethanol illustrate the phenomena associated with the presence of hydrogen bonds, while calculation of the Kirkwood-Buff integrals allows quantitative estimation of the local compositions. Lastly, some methods for predicting the thermodynamic properties of multicomponent mixtures are considered.

INTRODUCTION

The thermodynamic properties of multicomponent liquid mixtures and their analysis in terms of interpretative or predictive models constitute a very interesting subject from several standpoints, ranging from the practical need for thermodynamic data for the design and set-up of industrial processes to the increasingly exacting search for models able to focus and interpret the correlations between the molecular structure and macroscopic properties of the liquids. However, in spite of the numerous papers in the literature, few studies provide a general thermodynamic picture of some multicomponent mixture, i.e. contain a coordinated analysis of almost all the main excess thermodynamic quantities pertinent to the system.

Research in our laboratory aiming at the determination of all these thermodynamic quantities for asymmetric multicomponent mixtures (1-4) is based on the comprehensive analysis of the data to look for some consistent clue to the type of interactions between the components and how they change in the composition areas, as well as to test the ability of some of the more commonly used descriptive models to predict the thermodynamic behaviour of complex mixtures. A further step will be to apply the fluctuation theory of Kirkwood and Buff (5), which allows calculation of the integral of the radial distribution function of the components and thus gives a clue as to how their solvation depends on the composition.

Of the possible ternary systems formed of ethanol (EtOH), dimethylformamide (DMF), tetrahydrofuran (THF) and cyclohexane (cyHex), we can now provide a nearly complete thermodynamic picture for the mixture EtOH + THF + cyHex. This includes published data for excess enthalpies (H_m^E) and excess heat

capacities ($C_{p,m}^E$) (1) as well as a preliminary analysis of excess Gibbs energy (G_m^E) and excess volume (V_m^E) data (6). These properties, plus excess entropies (S_m^E), which can be derived, should allow a more objective analysis of the correlations between the macroscopic phenomena and the structure of the components.

DESCRIPTION OF THE DATA

The experimental data (1,6) for the G_m^E , H_m^E , $C_{p,m}^E$, V_m^E of the EtOH (1) + THF (2) + cyHex (3) ternary mixture were described through the equation:

$$Y_{123,m}^E = x_1 x_2 x_3 \sum_{m=0}^3 \sum_{n=0}^m B_{mn} x_1^{m-n} x_2^n + \sum_{i=1}^2 \sum_{j=i+1}^3 Y_{ij,m}^E \quad (1)$$

where $Y = G, H, V, C_p$ and x_i is the molar fraction of component i . The quantities $Y_{ij,m}^E$ on the r.h.s. represent the properties of the binary mixtures EtOH + THF, THF + cyHex and EtOH + cyHex pertinent to the ternary system, which were expressed through Redlich-Kister rational polynomials:

$$Y_{ij,m}^E = \frac{x_i x_j \sum_{k=1}^{k=5} A_k (x_i - x_j)^{k-1}}{1 + A_0 (x_i - x_j)} \quad (2)$$

Values for the binary (A_k) and ternary (B_{mn}) parameters may be found in ref. 1 for H_m^E and $C_{p,m}^E$; those for G_m^E and V_m^E will be supplied by the authors on request.

The behaviour of G_m^E , H_m^E , $C_{p,m}^E$, V_m^E and TS_m^E calculated from eqn.1 is illustrated in Fig. 1. The information available indicates the effect of the two polar components on the properties of the ternary mixtures. G_m^E and H_m^E values are always positive. The entropy term displays remarkably negative values for the binary mixture alcohol + hydrocarbon that gradually decrease in magnitude as the ether is added until they invert their sign and reach a positive maximum in the vicinity of the equimolar ternary mixture. This behaviour evidently illustrates the unfavourable ($TS_m^E < 0$) and favourable ($TS_m^E > 0$) entropy contributions to the mixing process by EtOH and THF, respectively.

Qualitative criteria correlating the sign and magnitude of thermodynamic mixing quantities with the creation or disruption of structural order in mixtures of non-electrolytes (see Table 1), show that the entropy term is much more sensitive to this kind of information than the separate G_m^E and H_m^E trends. A consistent phenomenology is observed for $C_{p,m}^E$. Its large positive values in the binary mixture ethanol + hydrocarbon decrease monotonously following addition of the ether.

The peculiar thermodynamic behaviour exhibited by alcohol + hydrocarbon mixtures has been extensively discussed by many authors (7) and attributed to the self-association of the alcohol molecules. To emphasize this specific phenomenon, Fig. 2 shows the trends of the ethanol excess partial molar quantities for Gibbs energy (\bar{G}_1), enthalpy (\bar{H}_1), entropy (\bar{TS}_1), volume (\bar{V}_1) and heat capacity ($\bar{C}_{p,1}$). In the limit of infinite dilution in cyHex, these quantities always display very large positive values. It should be noted that, while the positive entropy term is in agreement with a situation of presumably completely dissociated alcohol, the positive $\bar{C}_{p,1}$ values appear to be inconsistent with it. Negative $\bar{C}_{p,1}$ values, in fact, have been observed (8) at very low alcohol concentrations ($x_1 < 0.01$), and considered typical of alcohol + inert compound mixtures. This phenomenon is not revealed by the present measurements, which were not extended to EtOH mole fractions lower than 0.02.

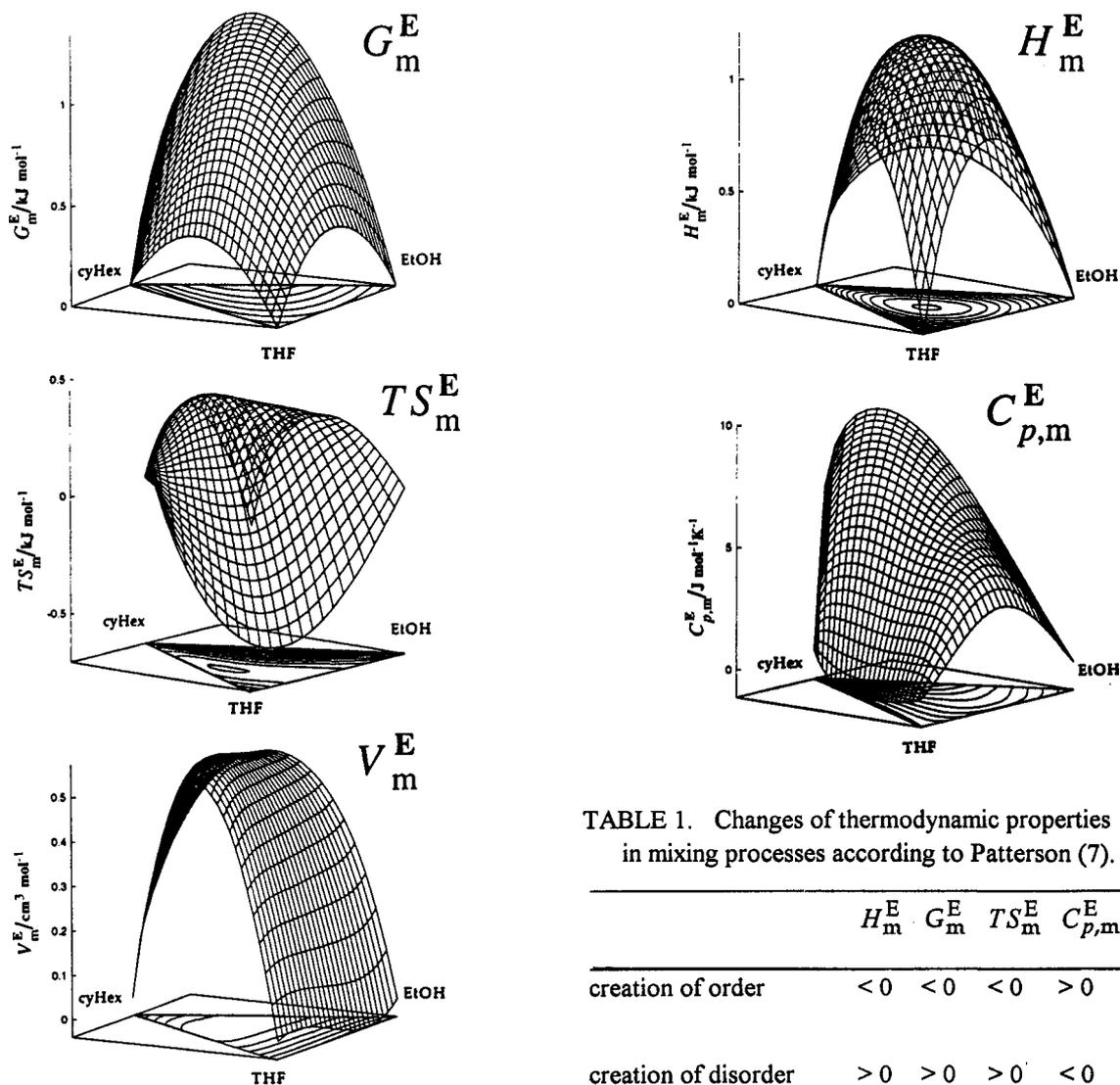


Fig. 1. Excess thermodynamic properties for the EtOH+THF+cyHex mixture.

TABLE 1. Changes of thermodynamic properties in mixing processes according to Patterson (7).

	H_m^E	G_m^E	TS_m^E	$C_{p,m}^E$
creation of order	< 0	< 0	< 0	> 0
creation of disorder	> 0	> 0	> 0	< 0

The enthalpy and liquid-vapour equilibria measurements are less critical. They indicate the characteristic trend of the TS_1 term, which abruptly inverts its negative sign in the vicinity of the highly diluted solutions. The steep increase of the partial molar volume of EtOH as it approaches zero concentration can also be regarded as due to the disruption of hydrogen bonds.

A less qualitative interpretation of the thermodynamic data can be given by using Gibbs energy and volume data for the calculation of Kirkwood-Buff integrals, G_{ij} , (5):

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 dr = f \left(G_m^E, V_m^E, \kappa_T^E \right) \quad (3)$$

where $g_{ij}(r)$ is the pair radial distribution function and κ_T^E is the excess isothermal compressibility (this latter quantity plays a negligible role and can be ignored). The G_{ij} values yield information on the local environment of molecules. Positive values indicate a tendency of *i* and *j* molecules to gather together, negative ones suggest repulsion. The G_{ij} values can also be used to calculate local compositions.

G_{11} is shown as an example in Fig. 3. If we focus our attention on its trend along the binary EtOH (1) + cyHex (3), we find a relative maximum around $x_1 \sim 0.50$ ($c_1 = 5.97 \text{ mol dm}^{-3}$) and a large maximum

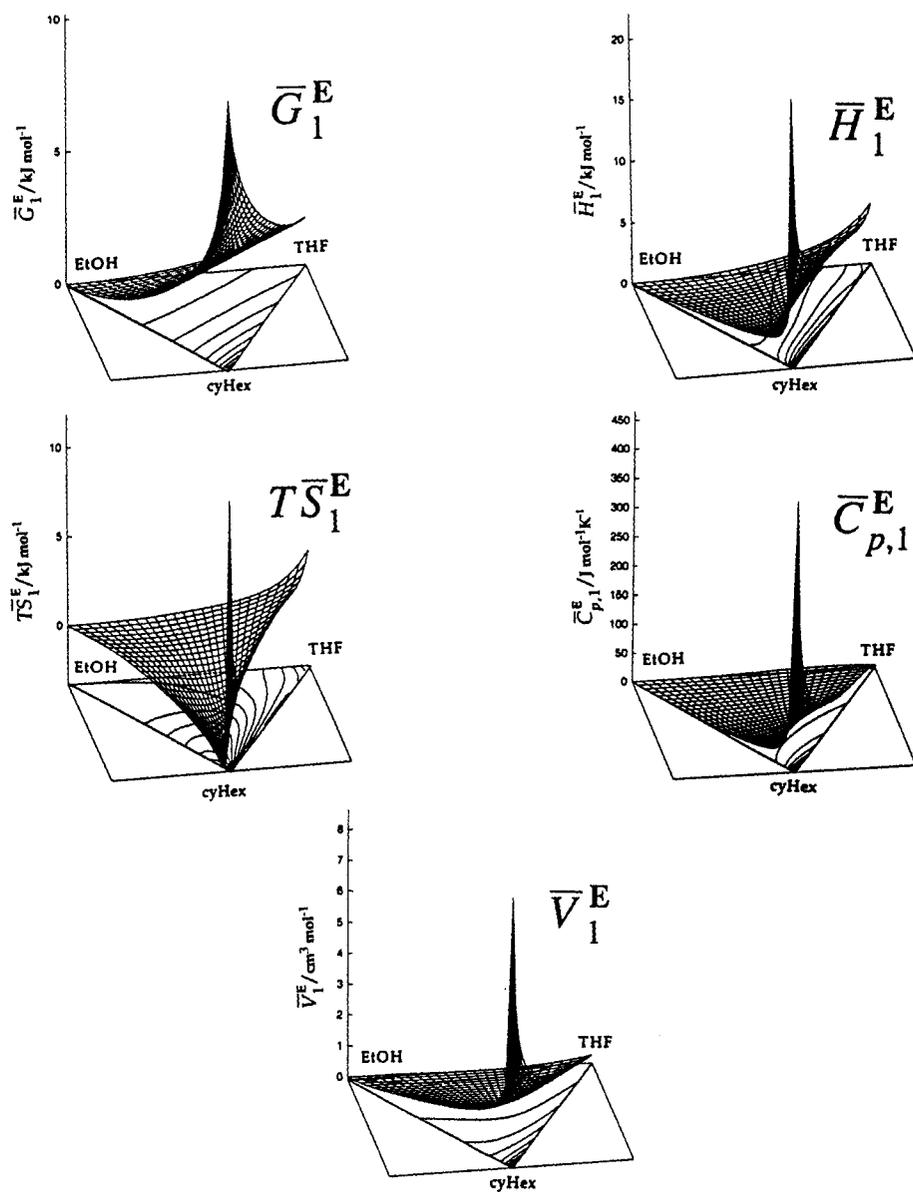


Fig. 2. Partial molar properties of EtOH(1) in the EtOH+THF+cyHex mixture.

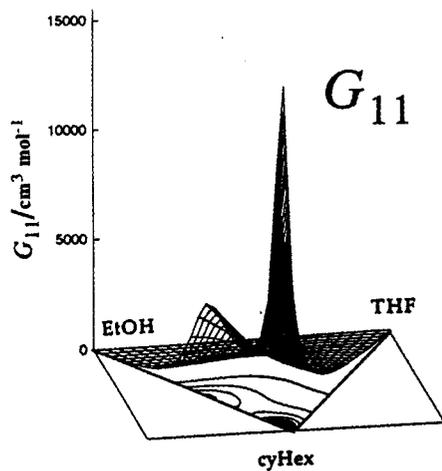


Fig. 3. Kirkwood-Buff integral for EtOH-EtOH correlations in mixtures EtOH+THF+cyHex.

around $x_1 \sim 0.04$ ($c_1 = 0.375 \text{ mol dm}^{-3}$). With the simplifying assumption that the excess surrounding molecules are all located inside a sphere whose radius is four times the molecular diameter of the alcohol molecule (i.e., the correlations do not extend beyond that distance), we calculate a local alcohol concentration of $c_1 = 8.20$ and $c_1 = 0.795 \text{ mol dm}^{-3}$ respectively. These in turn correspond to a $\Delta c_1/c_1$ increase of 112% and 37%, values which point to the strong tendency toward association of alcohol molecules, especially in very dilute solutions. Analogous calculations of the excess local concentrations of the other components will provide information on preferential solvation. This will be dealt with in a future paper.

PREDICTIVE MODELS

Comparison of experimental thermodynamic data of multicomponent (liquid) mixtures with those calculated by means of various predictive methods is very useful from different points of view; it suggests which model is more appropriate to the characteristics of the system, it may indicate which parameters should be improved when the model involves group contributions and also, perhaps more important, it may allow the identification of some model as a convenient "reference" for interpretation of the deviations observed (experimental minus calculated) as departures from the assumptions which constitute its conceptual basis.

We applied to the excess Gibbs energy and excess enthalpy functions of the ternary mixture just investigated a few predictive methods that mostly use information collected by studying binary mixtures, namely: (a) the method of Redlich-Kister-Muggianu (9), used above for the description of the present system (second term of the r.h.s. of eqn. 1) and Kohler's method (10), both based on a random behaviour of the liquid mixture; (b) the method of Toop (11), characterized by an asymmetric equation in which one binary (normally that exhibiting the most ideal behaviour) receives a different weight with respect to other two; (c) the UNIQUAC method (12), which overcomes the restriction of random behaviour by introducing the concept of local composition, this possibly being quite different from bulk concentration for asymmetric mixtures; (d) the UNIFAC group contribution method, in the version modified by Gmehling et al. (13); (e) the Nitta-Chao model (14), which adopts group contributions as well, but relies on the rigorous basis of the cell theory.

Table 2 gives the observed G_m^E and H_m^E deviations for all these methods. The deviations were calculated as relative average values (percent with respect to the maximum value observed for the property) and also

TABLE 2. Predictive capability of various models for H_m^E and G_m^E of the ternary mixtures EtOH(1) + THF(2) + cyHex(3).

dev.		Kohler	RKM	Models ^a			UNIQUAC ^c	UNIFAC	Nitta-Chao ^d
				1	2	3			
H_m^E	$\delta\%$ ^e	7.2	8.3	4.7	8.4	8.3	0.5	-0.3	11.3
	σ^f	114	127	82	127	131	25	36	130
G_m^E	$\delta\%$ ^e	-0.5	0.4	-1.6	-0.3	1.2	0.9	-6.6	5.0
	σ^f	15	9	26	15	22	28	109	53

^a For the equations see the following references: Kohler, Redlich-Kister-Muggianu (RKM) and Toop, ref. 15; UNIQUAC, in the form used in this work, ref. 1; UNIFAC, ref. 13; Nitta-Chao, ref. 14. ^b Headings 1, 2 and 3 indicate the compound common to the two binaries with analogous weight. ^c Parameters used: $q_1 = 1.56$ (H^E), 0.92 (G^E); $q_2 = 1.762$; $q_3 = 2.382$.

^d Calculations performed only for compositions obtained by adding cyHex to an equimolar mixture of EtOH + THF.

^e Average deviations, given as percent of the maximum value of the property (1280 J mol⁻¹ for G^E and 1210 J mol⁻¹ for H^E).

^f Root mean square deviation.

as root mean square deviations, in order to emphasize both their possible systematic trend and their magnitude.

The data show that the four predictive methods that use parameters obtained from the related binary mixtures all produce good results for the G_m^E of the ternary system. For H_m^E , only UNIQUAC is able to reproduce the experimental data with very good accuracy; the other three methods produce systematically lower values. In particular, Kohler's and the Redlich-Kister-Muggianu method show similar discrepancies which can be interpreted as due to the deviations of the system examined from the random behaviour, which constitutes the basic principle of these two models, and which can be taken as a useful reference basis for the descriptions of the H_m^E of ternary mixtures. However, the fact that G_m^E data do not deviate from this reference renders this basis unreliable at least for this property, perhaps because of entropy-enthalpy compensation phenomena.

Use of the asymmetric Toop equation implies, as already pointed out (15), the choice of the component common to the two binary mixtures to which an analogous weight is assigned to calculate ternary data, as shown in Table 2. For the present system, the best results are obtained when this compound is EtOH for enthalpy data, whereas THF must be chosen to get the smallest deviations between the experimental and calculated G_m^E data. This indicates the difficulty of finding a univocal criterion for the choice of the component allowing the Toop equation to give the best reproduction of ternary data.

In application of the UNIQUAC method, we have obtained a better fitting of the binary data and a sensibly better reproduction of the ternary G_m^E data by using a value for q_1 , the relative molecular surface area of EtOH, rather lower than that calculated by Bondi's (16) method (see note "c" to Table 2) as recommended by Prausnitz (17). In the case of H_m^E , on the contrary, a very good reproduction of experimental data is obtained with the normal q_1 value.

The two methods based on group contributions, UNIFAC and Nitta-Chao, present larger deviations than the others, except for the good reproduction of H_m^E data by UNIFAC. Even so, they permit predictions acceptable for the practical use of these quantities. It should be mentioned, however, that whereas the Nitta-Chao model is more rigorous than UNIFAC, for the latter a much wider set of reliable group contributions has been made available.

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