



## Excess Gibbs energies and volumes of the ternary system ethanol + dimethylformamide + tetrahydrofuran at 298.15 K



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### ABSTRACT

Density measurements have been carried out by means of a vibrating tube densimeter for the ternary system ethanol (EtOH) + dimethylformamide (DMF) + tetrahydrofuran (THF) and for the binary mixtures containing DMF. For the same ternary system and for the binary DMF + THF vapour–liquid equilibrium data have been collected by head-space gas-chromatographic analysis of the vapour phase directly withdrawn from an equilibration apparatus. All experiments have been conducted at 298.15 K. Molar excess Gibbs energies  $G^E$  and volumes  $V^E$ , as well as activity coefficients  $\gamma_i$  and excess apparent molar volumes  $\Phi_{V,i}^E$  of the components, have been obtained from the measured quantities. Both binaries involving THF show positive deviations from ideality for  $G^E$ , while slightly negative deviations are exhibited by EtOH + DMF. The  $G^E$ 's and  $\ln \gamma_i$  of the ternary system are positive almost throughout due to destruction upon mixing of H-bonding in EtOH and dipolar interactions in DMF and THF pure liquids. Feeble negative  $V^E$ 's are displayed by the binaries involving DMF, whereas EtOH + THF shows an S-shaped curve with very small  $V^E$  values. As a consequence, the  $V^E$ 's and  $\Phi_{V,i}^E$  of the ternary system, differently from  $G^E$  and  $\ln \gamma_i$ , are negative nearly over the whole composition domain suggesting a more ordered structure in solution, namely that EtOH–DMF association prevails on EtOH and DMF self-association.

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### 1. Introduction

Since long we have undertaken a research project on the excess thermodynamic properties (enthalpies  $H^E$ , heat capacities  $C_p^E$ , volumes  $V^E$  and Gibbs energies  $G^E$ ) of multicomponent liquid mixtures involving polar substances, with the aim of obtaining information on association phenomena and on the local structure in solution. Most of these studies have dealt with ternary systems made up of a hydrocarbon (cyclohexane), and two among the following compounds having different polarity and H-bonding capability: tetrahydrofuran (THF), dimethylformamide (DMF), ethanol (EtOH), 2-methoxyethanol or chloroform [1–6]. The excess properties of such mixtures are governed by the breaking of the hydrogen bonding and/or dipolar interactions in the pure polar components by addition of the non-polar hydrocarbon. We then started to investigate ternary systems made up of all polar compounds, where the excess properties are expected to be a balance of strong interactions between like molecules in the pure liquids and unlike molecules in solution.

In the present investigation we determined vapour–liquid equilibria (VLE) and densities of the ternary system EtOH(1)+DMF(2)+THF(3), as well as of the binary mixtures DMF+THF. We also measured densities of the binary mixtures EtOH+DMF whose  $G^E$  data are already known [5].  $H^E$  and  $C_p^E$  data for all these mixtures, both binary and ternary, have already been reported [6].

Excess Gibbs energies  $G^E$  and volumes  $V^E$  have been obtained from these data together with activity coefficients,  $\gamma_i$ , and excess apparent molar volumes,  $\Phi_{V,i}^E$ , of the components and discussed in terms of formation/destruction of H-bonding and dipolar interactions in the mixing process, following the interpretative scheme by Patterson [7].

### 2. Experimental

#### 2.1. Materials

All chemicals were high purity reagents and were used without further purification. Their purity, in mass%, was checked by gas chromatography and their water content by Karl–Fischer analysis. No significant difference was found with respect to the impurity content declared by the factories. EtOH: RPE 99.9% C. Erba anhydrous reagent, with water content <0.1%; DMF: puriss. absolute

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**List of symbols***Latin symbols*

<i>A</i>	Redlich–Kister binary parameter
<i>B<sub>ij</sub></i>	virial coefficient
<i>c</i>	ternary parameter
<i>g<sup>E</sup></i>	reduced molar excess Gibbs energy
<i>G<sup>E</sup></i>	molar excess Gibbs energy
<i>H<sup>E</sup></i>	molar excess enthalpy
<i>M</i>	molecular weight
<i>N</i>	number of experimental points
<i>n</i>	number of components
<i>n<sub>i</sub></i>	number of moles
<i>p<sup>*</sup></i>	vapour pressure of pure liquid
<i>r<sub>ij</sub></i>	chromatographic response factor
<i>R</i>	gas constant
<i>S</i>	chromatographic peak surface area
<i>S<sup>E</sup></i>	molar excess entropy
<i>T</i>	absolute temperature
<i>V<sup>*</sup></i>	molar volume of pure liquid
<i>V<sup>E</sup></i>	molar excess volume
<i>x</i>	liquid mole fraction
<i>y</i>	vapour mole fraction
<i>z</i>	pseudo-binary mole fraction

*Greek symbols*

$\gamma$	activity coefficient
$\Lambda_{ij}$	Wilson parameter
$\delta_{ij}$	Wilson volume parameter
$\rho$	density
$\sigma$	standard deviation
$\varphi$	correction term for vapour non-ideality
$\Phi_V^E$	excess apparent molar volume

*Subscripts*

123	ternary mixture
<i>i, j, k</i>	component
B	binary contribution
T	ternary contribution

over molecular sieves Fluka reagent, purity > 99.5% water < 0.01%; THF: Fluka reagent, purity 99.5%, water < 0.01%, maintained over molecular sieves. The densities measured at 298.15 K for the air-saturated samples of the liquid components are reported in Table 1 as molar volumes,  $V^*$ .

**2.2. Apparatus and experimental procedure for VLE**

Vapour–liquid equilibria of mixtures were determined by head-space gas chromatographic analysis [8] of the vapour-phase equilibrated with liquid mixture in the presence of air. The

apparatus, assembled in our laboratory, composed of a thermostated equilibration cell and a gas chromatograph, has been already described in detail elsewhere and extensively used [9,10]. Further details of the apparatus used for the present measurements have also been previously reported [2].

Each mixture (about 20 g) was prepared by weighing. The uncertainty in the liquid mole fraction  $x$ , after correction for buoyancy and for evaporation of components in the vapour space of the container, was estimated less than 0.1%. In the case of the ternary system, the solutions were obtained by adding different amounts of a compound to a binary mixture of the other two at fixed composition. The extent of coverage of the ternary composition domain by experimental points is depicted in Fig. 1.

At least three vapour samples were analyzed for each mixture at a given composition. All measurements were carried out at 298.15 K. The values of vapour mole fraction  $y_i$  of component  $i$  were obtained from

$$y_i = \frac{1}{\sum_{j=1}^n r_{ij}(S_j/S_i)} \quad (1)$$

$S_i$  being the measured peak surface area of  $i$ th component in the vapour phase and the sum being extended over all  $n$  components of the liquid mixture. The quantity  $r_{ij}$  is the response factor of the chromatograph for the couple  $i$ – $j$ ; it expresses the proportionality constant between the measured area ratio and the corresponding ratio of moles present in the vapour phase [2]. It can be determined from the ratio of peak areas obtained when a liquid or vapor mixture of known composition is injected into the chromatograph under the same conditions as the unknown samples. In the present work we have treated the response factors  $r_{ij}$  as additional adjustable parameters in the least square procedure described in Appendix A.

The overall uncertainty in  $y$ , resulting mostly from the uncertainty in the chromatographic areas, was generally less than 1%.

**2.3. Apparatus and experimental procedure for density**

The density measurements were carried out at  $T = 298.15$  K and atmospheric pressure using a DMA 602 Anton–Paar vibrating-tube densimeter operated in the static mode and capable of a precision better than  $3 \times 10^{-3} \text{ kg m}^{-3}$ . The apparatus was calibrated with deionised degassed water and nitrogen gas. The liquid mixtures were prepared by weight and were not degassed to avoid the uncertainty brought about by the density decrease due to the air dissolution that occurs during the mixing and measurement processes. The uncertainty on  $V^E$  brought about by changes in dissolved air during measurements was estimated to be well within the experimental error from other sources. The liquid mole fraction  $x$  after correction for buoyancy and for evaporation of the components in the space above the liquids was evaluated to better than  $\pm 0.0002$ . The required vapour pressures and activity coefficients of the components were taken from the present VLE measurements. In the case of ternary mixtures, the solutions were obtained by adding

**Table 1**

Vapour pressures  $p^*$ , molar volumes  $V^*$ , second virial coefficients  $B_{ij}$  for pure compound ( $i$ ), and cross virial coefficients  $B_{ij}$  at 298.15 K.

Compound	$p^*$ (kPa) <sup>a</sup>	$V^*$ (cm <sup>3</sup> mol <sup>-1</sup> ) <sup>b</sup>	$B_{ii}$ (dm <sup>3</sup> mol <sup>-1</sup> )	$B_{ij}$ (dm <sup>3</sup> mol <sup>-1</sup> ) <sup>c</sup>
EtOH(1)	7.865	58.68	2.7 <sup>d</sup>	0.51 (1–2)
DMF(2)	0.502	77.43	6 <sup>e</sup>	0.79 (2–3)
THF(3)	21.91	81.74	1.2 <sup>d</sup>	0.52 (1–3)
Nitrogen (4)	–	–	0.0 <sup>d</sup>	0.1 (i–4) <sup>f</sup>

<sup>a</sup> Taken from Boublik et al. [12].

<sup>b</sup> This work.

<sup>c</sup> Computed according to Scatchard and Ticknor [13]. In parentheses are  $i$  and  $j$  values.

<sup>d</sup> Extrapolated from higher temperature data in Dymond and Smith [14].

<sup>e</sup> Estimated according to McDann and Danner [15] using the critical temperature value reported by Riddick [16].

<sup>f</sup> Ref. [14]; this value has been applied to all mixtures of air with the listed substances ( $i = 1, 2, 3$ ).

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