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Excess Gibbs Energies of the Ternary System 2-Methoxyethanol + Tetrahydrofuran + Cyclohexane and Other Relevant Binaries at 298.15 K[†]

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Vapor−liquid equilibria for the ternary system 2-methoxyethanol + tetrahydrofuran + cyclohexane and for the constituent binary mixtures containing 2-methoxyethanol have been determined at 298.15 K. In addition, for a better understanding of the phenomenology, the binary mixtures 2-methoxyethanol + ethanol and 2-ethoxyethanol + cyclohexane were also investigated. Vapor−liquid equilibrium data were collected by headspace gas chromatographic analysis of the vapor phase directly withdrawn from an equilibrium apparatus. Molar excess Gibbs energies G^E and activity coefficients were calculated therefrom. All binaries display positive G^E deviations from ideality, the largest being observed for the binary 2-methoxyethanol + cyclohexane, as well as the ternary mixtures over the whole mole fraction range, indicating that interactions in the pure liquids are not compensated for by new interactions in the mixtures. A positive sign is also displayed by H^E and V^E of the ternary system, while the entropy contribution to G^E, $-TS^E$, is positive in the region rich in the binary 2-methoxyethanol + cyclohexane and negative in the region rich in tetrahydrofuran + cyclohexane. The analysis of activity coefficients allows us to point out the role of hydrogen bonds in the cross-association of alcohols with polar molecules and the self-association both in pure liquid alcohol and in mixtures with hydrocarbons.

Introduction

In our laboratory, we have undertaken a research project on the excess thermodynamic properties 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 were concerned with ternary systems made up of a hydrocarbon (cyclohexane), an ether (tetrahydrofuran), and one of the following compounds with different polarity: ethanol, 2-methoxyethanol, or chloroform. Excess Gibbs energies G^E have already been measured for the ternary systems involving ethanol[1] or chloroform.[2] These latter papers also provide references to the measurements of excess enthalpies H^E, excess heat capacities C_p^E, and excess volumes V^E, which have already been determined as well.

In the present investigation, vapor−liquid equilibria (VLE) of the ternary system 2-methoxyethanol + tetrahydrofuran + cyclohexane, as well as of the binary mixtures 2-methoxyethanol + tetrahydrofuran and 2-methoxyethanol + cyclohexane, have been determined. The binary mixtures 2-methoxyethanol + ethanol and 2-ethoxyethanol + cyclohexane have also been investigated to obtain more information on alcohol−alcohol interactions and on the effect of alkoxy−alcohol chain lengthening. Excess Gibbs energies G^E have been obtained from these data together with activity coefficients, γ_i, of the components. Other excess quantities (H^E, C_p^E, V^E) relative to the ternary system here investigated have already been reported.[3,4]

The experimental G^E data were described with an empirical (Redlich−Kister) and a predictive (Wilson) fitting equation. The results have been discussed in terms of activity coefficients.

Table 1. Vapor Pressures *p, Molar Volumes *V**, and Second Virial Coefficients B_{ii} for Pure Compound (*i*) and Cross Virial Coefficients B_{ij} at 298.15 K**

		*p**[a]	*V**[b]	$-B_{ii}$	$-B_{ij}$[c]
i	compound	kPa	$cm^3 \cdot mol^{-1}$	$dm^3 \cdot mol^{-1}$	$dm^3 \cdot mol^{-1}$
1	2-methoxyethanol	1.33	79.26	6.4[d]	0.77 (1-2)
2	tetrahydrofuran	21.62	81.74	1.2[d]	1.13 (2-3)
3	cyclohexane	13.01	108.75	1.7[d]	1.09 (1-3)
4	ethanol	7.87	58.66	2.7[d]	0.64 (1-4)
5	2-ethoxyethanol	0.77	97.42	7.1[e]	1.35 (3-5)
6	nitrogen	−	−	0.0[d]	0.1[f] (*i*-6)

[a] Taken from Boublik et al.[9] [b] Data from our laboratory. [c] Estimated according to Scatchard and Ticknor.[11] In parentheses are *i* and *j* values. [d] Dymond and Smith.[10] [e] Estimated according to McCann and Danner.[12] [f] Ref 10. This value has been applied to all mixtures of air with the listed substances.

Experimental Section

Materials. All products were high purity Fluka reagents (mass fraction ≥ 0.995) and were used without further purification: 2-methoxyethanol, ethanol, 2-ethoxyethanol, tetrahydrofuran, cyclohexane. Their purity was checked by gas chromatography and their water content by Karl Fischer analysis. The water mass fraction content of the alcohols was $\leq 7 \cdot 10^{-4}$, and that of tetrahydrofuran, maintained over molecular sieves, was 0.01 %. The densities of the pure liquids (see molar volumes, *V**, of Table 1) were in good agreement with literature values.[5]

Apparatus and Experimental Procedure. Vapor−liquid equilibria of mixtures were determined by headspace gas chromatographic analysis[6] of the vapor phase equilibrated with liquid mixture in the presence of air. The apparatus, assembled in our laboratory, composed of an equilibration cell and a gas chromatograph has already been described in detail elsewhere and also extensively used.[7,8] Thermostatting of the equilibration

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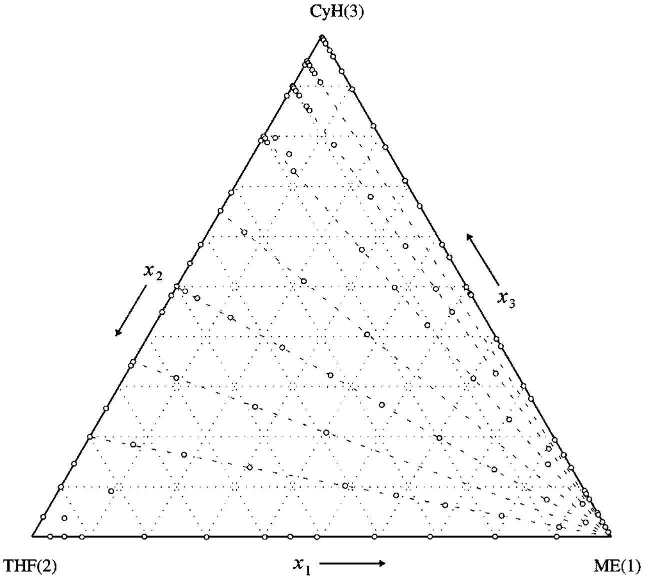

Figure 1. Map of the experimental measurements for the ternary system 2-methoxyethanol (ME) + tetrahydrofuran (THF) + cyclohexane (CyH).

cell allows us to keep temperature within ± 0.02 K with an accuracy of 0.05 K. Further details of the apparatus used for the present measurements have also been previously reported.[1]

All mixtures were prepared by weighing. The uncertainty in the liquid mole fraction x, after correction for buoyancy and for evaporation of components in the vapor space of the container cell, was estimated to be less than 0.1 %, though becoming 10 times larger at extreme dilutions.[4] In the case of the ternary system, the solutions were made by adding different amounts of 2-methoxyethanol to a binary mixture of the other two at fixed composition. The extent of coverage of the ternary composition diagram by experimental points is depicted in Figure 1. At least three vapor samples were analyzed for each given composition. All measurements were carried out at 298.15 K.

The values of vapor mole fraction y_i of component i were obtained from

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

with S_i being the measured peak surface area of the ith component in the vapor 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 constant of proportionality between the measured area ratio and the corresponding ratio of moles present in the vapor phase. It can be determined by calibration experiments with the pure liquids. Thanks to our previous experience,[1,2] we preferred to determine it as an adjustable parameter in the least-squares fitting of experimental data. The overall uncertainty in y, resulting mostly from the uncertainty in S_j/S_i, was typically less than 1 %, though doubling for very diluted solutions.

Treatment of Data. The experimental values of vapor-phase mole fraction y given by eq 1 were used in a nonlinear least-squares procedure in which the sum of the squares of residuals or objective function (eq 2), extended over all n constituents and over all N experimental points, is minimized, thus leading

$$\mathrm{OF} = \sum_{k=1}^{N}\sum_{i=1}^{n}[\ln y_{ik}^{\mathrm{exptl}} - \ln y_{ik}^{\mathrm{calcd}}]^2 \qquad (2)$$

to the determination of the parameters of the function representing the dependence of the excess Gibbs energy, G^{E}, on mixture composition.

As functions describing G^{E} for binary systems, we used the Redlich−Kister (eq 3) and Wilson (eq 4) equations

$$G_{ij}^{\mathrm{E}}/RT = x_i x_j \sum_{m=0}^{m=2} A_m(x_i - x_j)^m/[1 + B(x_i - x_j)] \qquad (i < j) \qquad (3)$$

$$G_{ij}^{\mathrm{E}}/RT = -x_i \ln(x_i + \Lambda_{ij}x_j) - x_j \ln(x_j + \Lambda_{ji}x_i) \qquad (4)$$

For each experimental point, y_i^{exptl} is given by eq 1, and y_i^{calcd} for component i is obtained from

$$y_i^{\mathrm{calcd}} = (\gamma_i^{\mathrm{calcd}} x_i p_i^*/\Phi_i)/\sum_{j=1}^{n}(\gamma_j^{\mathrm{calcd}} x_j p_j^*/\Phi_j) \qquad (5)$$

where p^* is the vapor pressure of the pure component and γ is the activity coefficient obtained by differentiation of the equations for G^{E}.

The correction terms Φ_i account for the nonideality of the vapor phase which, our experiments being carried out at room pressure, also contains air; they are related to the fugacity coefficients and are readily evaluated from second virial coefficients as described in a preceding work.[1] For air we assumed a virial coefficient equal to that of nitrogen. In the objective function (eq 2), the residuals of ln y, instead of y, were used to give a constant weight to all y measurements which are affected by an almost constant relative uncertainty. This treatment has the advantage of resulting in a better representation of the behavior of all components in the dilute regions.

The excess Gibbs energies of ternary mixtures, G_{123}^{E}, have been calculated as the sum of a binary and a ternary term

$$G_{123}^{\mathrm{E}} = G_{\mathrm{B}}^{\mathrm{E}} + G_{\mathrm{T}}^{\mathrm{E}} \qquad (6)$$

The binary contribution $G_{\mathrm{B}}^{\mathrm{E}}$ has been evaluated using only binary coefficients, i.e., parameters determined from binary data. When the Redlich−Kister equation is employed, the $G_{\mathrm{B}}^{\mathrm{E}}$ term is calculated through

$$G_{\mathrm{B}}^{\mathrm{E}} = \sum G_{ij}^{\mathrm{E}}(x_i, x_j) \qquad (7)$$

where the G_{ij}^{E} values were obtained by inserting into the correlation equation for binary $i + j$ (eq 3) the mole fractions of the ternary mixtures.

In the case of the Wilson equation, the binary contribution to G^{E} is given by eq 8

$$G_{\mathrm{B}}^{\mathrm{E}} = -RT\sum_{i=1}^{n} x_i \ln(\sum_{j=1}^{n} x_j\Lambda_{ij}), \qquad (\Lambda_{ii} = \Lambda_{jj} = 1) \qquad (8)$$

Table 2. Experimental VLE Data (x,y) for Binary Mixtures at 298.15 K

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
2-Methoxyethanol (1) + Tetrahydrofuran (2)							
0.0319	0.0043	0.1941	0.0229	0.4464	0.0493	0.6874	0.0913
0.0560	0.0074	0.3018	0.0336	0.4923	0.0527	0.7994	0.1364
0.0861	0.0110	0.4026	0.0437	0.5917	0.0685	0.9066	0.2577
2-Methoxyethanol (1) + Cyclohexane (3)							
0.0019	0.0147	0.0695	0.0718	0.5143	0.0786	0.9080	0.1336
0.0031	0.0203	0.1062	0.0764	0.5172	0.0775	0.9144	0.1493
0.0040	0.0222	0.1791	0.0790	0.6044	0.0857	0.9248	0.1569
0.0044	0.0264	0.2212	0.0806	0.6194	0.0887	0.9520	0.2082
0.0076	0.0398	0.2880	0.0804	0.6984	0.0880	0.9559	0.2290
0.0134	0.0512	0.3393	0.0817	0.7239	0.0879	0.9703	0.2779
0.0146	0.0571	0.4163	0.0801	0.8064	0.0963	0.9807	0.3807
0.0281	0.0744	0.4416	0.0824	0.8368	0.1068	0.9905	0.5395
0.0408	0.0653	0.5010	0.0786	0.8620	0.1145		
2-Methoxyethanol (1) + Ethanol (2)							
0.0724	0.0159	0.2694	0.0626	0.4542	0.1231	0.8476	0.4552
0.1100	0.0223	0.3015	0.0704	0.5711	0.1821	0.9112	0.6015
0.1278	0.0282	0.3682	0.0916	0.6925	0.2584	0.9219	0.6215
0.1787	0.0392	0.4251	0.1164	0.7431	0.3173	0.9432	0.7044
0.1842	0.0405						
2-Ethoxyethanol (1) + Cyclohexane (2)							
0.0012	0.0031	0.0891	0.0302	0.4973	0.0390	0.8944	0.0934
0.0032	0.0061	0.1355	0.0331	0.5114	0.0413	0.9641	0.2044
0.0052	0.0085	0.1889	0.0351	0.6036	0.0449	0.9815	0.3388
0.0065	0.0096	0.2987	0.0366	0.6584	0.0478	0.9844	0.3807
0.0132	0.0150	0.4014	0.0388	0.7668	0.0570	0.9871	0.4275
0.0288	0.0213	0.4862	0.0413	0.8396	0.0713	0.9916	0.5200
0.0464	0.0248						

where parameters Λ_{ij} are those obtained from binary data (eq 4), and x are the mole fractions in the ternary mixture.

The ternary contribution G^E_T in eq 6 contains a few adjustable ternary parameters, which are obtained from ternary data through fitting of an equation of the type

$$G^E_T = G^E_{123} - G^E_B = RTx_1x_2x_3(c_0 + c_1x_1 + c_2x_2)/[1 + D(2x_1 - 1)] \quad (9)$$

When the ternary term is omitted, eq 6 is a predictive equation, and when the ternary term is included, eq 6 is to be considered a descriptive or correlation equation.

A detailed description of the procedure adopted to calculate r_{ij}, γ_i, and G^E is reported in ref 1.

Results

Table 1 collects the values of molar volume V^*, vapor pressure p^* of the pure compounds, and second virial coefficients B_{ii} and B_{ij} used in the calculation[1] of the correction terms Φ_i in eq 5. Most B_{ii} and B_{ij} are affected by a large uncertainty; however, for all our mixtures, the values of Φ_i were found to differ from 1 by less than 5 % and usually in the same sense for all compounds, so that their ratio in eq 5 is even less different from unity. As a result, the y and G^E values obtained by taking into account vapor nonideality ($\Phi_i \neq 1$) differ by less than 2 % from those obtainable neglecting this correction ($\Phi_i = 1$).

Binary Mixtures. The experimental x,y data for all binary mixtures investigated in this work are given in Table 2. Figure 2 illustrates the plot of excess Gibbs energy functions for the same binaries. The curve relative to the binary tetrahydrofuran + cyclohexane, previously studied,[1] is also reported for comparison. All these binary mixtures display practically symmetrical positive deviations, which are quite large for the binaries 2-methoxyethanol + cyclohexane and 2-ethoxyethanol + cyclohexane. For these mixtures, our data are slightly lower than those measured by Campbell at 303.15 K,[13,14] consistently with the negative molar excess entropy which can be calculated for these binaries from G^E and H^E (refs 3 and 15). Other literature VLE data for the systems 2-methoxyethanol + cyclohexane[16,17] and for 2-methoxyethanol + ethanol[18] cannot be directly compared with ours having been measured at constant total pressure. No literature data were found for the binary 2-methoxyethanol + tetrahydrofuran.

Figure 3 compares the trend of the functions $y_1 = f(x_1)$ for all the above binaries. The figure indicates that binary mixtures 2-methoxyethanol (1) + cyclohexane and 2-ethoxyethanol (1) + cyclohexane exhibit an azeotrope at $x_1 \cong 0.075$ and $x_1 \cong 0.01$, respectively. The much larger steepness of the y curve

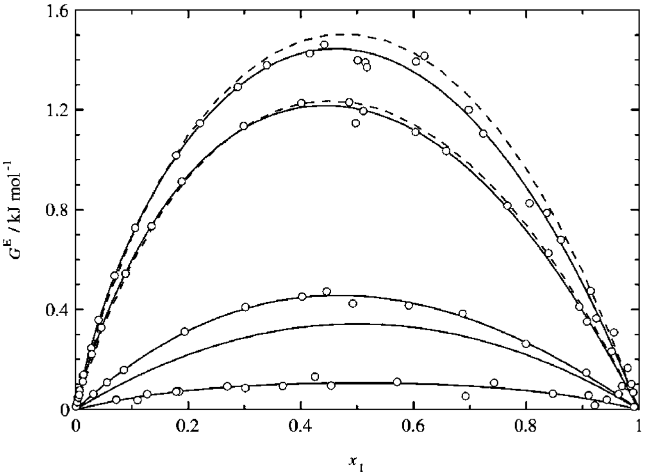

Figure 2. Excess Gibbs energies for the investigated binary systems: ○, exptl points; ——, Redlich−Kister fitting function, this work at 298.15 K; - - -, literature data at 303.15 K. From top to bottom: $x_1$2-methoxyethanol + (1 − x_1)cyclohexane (- - -, ref 13); $x_1$2-ethoxyethanol + (1 − x_1)cyclohexane (- - -, ref 14); $x_1$2-methoxyethanol + (1 − x_1)tetrahydrofuran, $x_1$tetrahydrofuran + (1 − x_1)cyclohexane (ref 1), and $x_1$2-methoxyethanol + (1−x_1)ethanol.

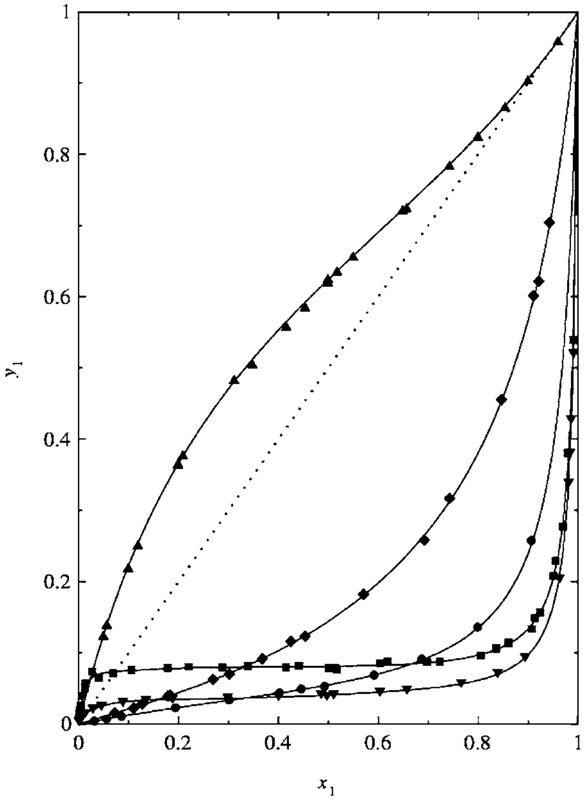

Figure 3. Plot of vapor phase mole fraction, y_1, against liquid mole fraction, x_1, for binary systems at 298.15 K: ●, 2-methoxyethanol (1) + tetrahydrofuran; ■, 2-methoxyethanol (1) + cyclohexane; ▲, tetrahydrofuran (1) + cyclohexane; ▼, 2-ethoxyethanol (1) + cyclohexane; ♦, 2-methoxyethanol (1) + ethanol. Solid lines are best-fitting Redlich−Kister equations (parameters in Table 3); dotted line is the $x_1 = y_1$ line.

observed for 2-methoxyethanol + cyclohexane at high dilution of the alcohol is due to the weaker interaction with cyclohexane of the shorter hydrocarbon chain of this alcohol. No azeotrope is shown by the systems 2-methoxyethanol (1) + tetrahydrofuran and 2-methoxyethanol (1) + ethanol. The binary tetrahydrofuran + cyclohexane was found to form an azeotropic mixture at high tetrahydrofuran mole fractions ($x_2 = 0.95$).[1]

Values of the adjustable parameters of eqs 3 and 4, employed for describing G^E of all investigated binary mixtures, are collected in Table 3.

Ternary Mixtures. Table 4 collects the experimental (x_1,x_2,y_1,y_2) data for the ternary mixture 2-methoxyethanol + tetrahydrofuran + cyclohexane at 298.15 K. Treatment of these data through eqs 6 to 9 allowed us to obtain the adjustable ternary parameters reported in Table 5. In the same table are also reported values of standard deviation of the fit, the calculated values of the property at the center of the composition triangle ($x = 1/3$), and the values of the activity coefficient ($\ln \gamma^\infty$) of each component at infinite dilution in the equimolar mixture of the other two components.

Analysis of the σ values of Table 5 shows that the predictive Wilson equation (no ternary and six binary parameters) is able to predict the G^E values of the ternary mixtures with practically the same uncertainty as that obtained through the empirical Redlich−Kister equation including two ternary and eight binary parameters.

Discussion

A graphical representation of calculated excess Gibbs energies over the whole composition domain of the ternary system here investigated is given in Figure 4. The curves on the triangle base represent contour lines at constant values of each excess thermodynamic property. Positive G^E values are exhibited not only by all binaries but also by the ternary mixtures over the whole concentration domain. The shape of the G^E surface is regular, with no extreme inside the triangle, and appears strongly influenced by the behavior of the 2-methoxyethanol + cyclohexane binary.

In Figure 4 are also illustrated the surfaces of excess molar enthalpies, H^E, and volumes, V^E, previously determined,[3,4] and the entropic contribution ($-TS^E$) to G^E, obtained from the Gibbs equation. The H^E surface is always positive but, unlike G^E and V^E presents a maximum about at the center of the concentration domain. The $-TS^E$ surface is positive near the binary 2-methoxyethanol + cyclohexane, nearly zero in the region of the binary 2-methoxyethanol + tetrahydrofuran and negative near the binary tetrahydrofuran + cyclohexane. Throughout the triangle surface, the magnitude of $-TS^E$ is lower than that of H^E. This clearly indicates that the thermodynamics of the mixing process is dominated by enthalpy which overcomes either favorable or unfavorable entropic effects.

According to the simple interpretative scheme proposed by Patterson,[19] positive values of Y^E ($Y = G$, H, S, and V) for both

Table 3. Parameters *k* (Dimensionless) of the Different Best-Fitting Equations, Standard Deviation *σ* for the Representation of ln *y*, Excess Gibbs Energy at *x* = 0.5, and Logarithm of Activity Coefficients at Infinite Dilution γ_i^∞ of the Components for the Binary Systems at 298.15 K

equation	k_1	k_2	k_3	k_4	k_5	k_6	$\sigma(\ln y)$	$G^E(x = 0.5)$ J·mol^{-1}	$\ln \gamma_i^\infty$	$\ln \gamma_j^\infty$
									$i < j$	
2-Methoxyethanol (1) + Tetrahydrofuran (2)										
Redlich−Kister[a]	0.73519	−0.0985	−	−	−	−	0.009	456	0.83	0.64
Wilson[b]	0.49895	0.84846	−	−	−	−	0.011	455	0.85	0.67
2-Methoxyethanol (1) + Cyclohexane (3)										
Redlich−Kister[a]	2.3211	1.6755	0.11914	0.12021	−	0.8522	0.031	1438	4.36	2.29
Wilson[b]	0.02569	0.2474	−	−	−	−	0.036	1413	4.41	2.37
Tetrahydrofuran (2) + Cyclohexane (3)[c]										
Redlich−Kister[a]	0.5533	0	0	−	−	−	0.005	343	0.55	0.55
Wilson[b]	0.7295	0.75171	−	−	−	−	0.005	344	0.56	0.56
2-Methoxyethanol (1) + Ethanol (2)										
Redlich−Kister[a]	0.1713	−	0.05772	−	−	−	0.016	106	0.30	0.30
Wilson[b]	0.8339	0.994	−	−	−	−	0.018	111	0.19	0.17
2-Ethoxyethanol (1) + Cyclohexane (2)										
Redlich−Kister[a]	1.9437	1.4974	0.02223	0.09976	−0.1981	0.9572	0.018	1204	3.98	1.72
Wilson[b]	0.04053	0.4653	−	−	−	−	0.048	1195	3.74	1.72

[a] $k_m = A_{m-1}$ ($m = 1-5$), $k_6 = B$ (eq 3). [b] $k_1 = \Lambda_{ij}$; $k_2 = \Lambda_{ji}$ ($i < j$) (eq 4). [c] Ref 1.

Table 4. Experimental VLE Data (x,y) for the Ternary Mixture 2-Methoxyethanol (1) + Tetrahydrofuran (2) + Cyclohexane (3) at 298.15 K

x_1	x_2	y_1	y_2	x_1	x_2	y_1	y_2
			2-Methoxyethanol + (0.050 Tetrahydrofuran + 0.950 Cyclohexane)				
0.0033	0.0499	0.0108	0.1447	0.0253	0.0488	0.0430	0.1204
0.0087	0.0496	0.0227	0.1358	0.0446	0.0478	0.0544	0.1108
0.0180	0.0491	0.0359	0.1270				
			2-Methoxyethanol + (0.100 Tetrahydrofuran + 0.900 Cyclohexane)				
0.0013	0.0995	0.0029	0.2295	0.2454	0.0752	0.0675	0.1301
0.0045	0.0992	0.0099	0.2206	0.3549	0.0643	0.0708	0.1094
0.0101	0.0985	0.0189	0.2276	0.4497	0.0548	0.0726	0.0921
0.0206	0.0975	0.0310	0.2142	0.5009	0.0497	0.0844	0.0888
0.0443	0.0951	0.0453	0.1958	0.6378	0.0361	0.0897	0.0691
0.0539	0.0943	0.0471	0.1883	0.8046	0.0195	0.1033	0.0461
0.1305	0.0866	0.0602	0.1576				
			2-Methoxyethanol + (0.200 Tetrahydrofuran + 0.800 Cyclohexane)				
0.0045	0.1990	0.0055	0.3848	0.4715	0.1060	0.0698	0.1742
0.0123	0.2000	0.0126	0.3737	0.6042	0.0791	0.0763	0.1394
0.0864	0.1830	0.0433	0.3118	0.7072	0.0586	0.0834	0.1152
0.2826	0.1430	0.0625	0.2301	0.8183	0.0363	0.1002	0.0897
0.3772	0.1250	0.0673	0.2018	0.9181	0.0164	0.1519	0.0671
			2-Methoxyethanol + (0.350 Tetrahydrofuran + 0.650 Cyclohexane)				
0.0625	0.3290	0.0250	0.4741	0.3769	0.2180	0.0571	0.3249
0.2142	0.2750	0.0456	0.3925				
			2-Methoxyethanol + (0.500 Tetrahydrofuran + 0.500 Cyclohexane)				
0.0194	0.4900	0.0075	0.6249	0.4726	0.2640	0.0596	0.3958
0.0473	0.4760	0.0150	0.5998	0.6047	0.1980	0.0670	0.3413
0.1242	0.4380	0.0285	0.5537	0.7310	0.1350	0.0829	0.2877
0.2432	0.3780	0.0413	0.4960	0.8519	0.0741	0.1170	0.2303
0.3539	0.3230	0.0503	0.4457	0.9415	0.0293	0.2187	0.1770
			2-Methoxyethanol + (0.650 Tetrahydrofuran + 0.350 Cyclohexane)				
0.0910	0.5920	0.0204	0.6934	0.4041	0.3880	0.0517	0.5624
0.2553	0.4850	0.0392	0.6222				
			2-Methoxyethanol + (0.800 Tetrahydrofuran + 0.200 Cyclohexane)				
0.0825	0.7330	0.0135	0.8003	0.5877	0.3300	0.0663	0.6272
0.1807	0.6550	0.0245	0.7668	0.6820	0.2540	0.0838	0.5903
0.3069	0.5540	0.0362	0.7246	0.7898	0.1680	0.1158	0.5268
0.4898	0.4080	0.0556	0.6624	0.9002	0.0798	0.2081	0.4389
			Miscellaneous				
0.0219	0.1810	0.0206	0.3589	0.0617	0.1730	0.0419	0.3188
0.0377	0.9250	0.0060	0.9513	0.0914	0.8170	0.0126	0.8822

Table 5. Comparison of Different Correlation Equations for the Representation of the G^E Behavior of the Ternary System 2-Methoxyethanol (1) + Tetrahydrofuran (2) + Cyclohexane (3) at 298.15 K

correlation equation (eq 6)	no. of binary parameters[a]	no. of ternary parameters (eq 9)	σ[b]	G_m^E ($x_1 = x_2 = 1/3$) J·mol^{-1}	$\ln \gamma_1^\infty$ ($x_2 = x_3 = 0.5$)	$\ln \gamma_2^\infty$ ($x_1 = x_3 = 0.5$)	$\ln \gamma_3^\infty$ ($x_1 = x_2 = 0.5$)
Redlich−Kister	8	2[c]	0.058	1041	1.87	0.14	1.32
	8	0	0.072	994	1.56	0.04	1.22
Wilson	6	1[d]	0.059	1038	1.76	0.20	1.33
	6	0	0.060	1020	1.71	0.15	1.28

[a] Parameters of Table 3 obtained from the fitting of ln y. [b] Standard deviation on ln y. [c] $c_o = 0.39551$, $D = 0.6862$ (dimensionless). [d] $c_o = 0.1989$ (dimensionless).

binary and ternary mixtures here examined can be qualitatively explained with the net destruction in the mixing process of the structural order present in the pure liquids: H-bonds in the alcohols and dipolar interactions in tetrahydrofuran.

A nearly ideal behavior is exhibited by the mixtures 2-methoxyethanol + ethanol (see Figure 2), indicating a substantial compensation of the strong like interactions in the pure alcohols and the equally strong unlike interactions between 2-methoxyethanol and ethanol.

The similar positive values of G^E in the binaries tetrahydrofuran + cyclohexane and 2-methoxyethanol + tetrahydrofuran (see Figure 2) are a mere coincidence and do not reflect similarity in molecular interactions or order in the mixtures. In tetrahydrofuran + cyclohexane, the small G^E values are due to the weakly polar character of tetrahydrofuran, while in 2-methoxyethanol + tetrahydrofuran the similarly small G^E's are caused by a partial compensation of the strong self-association of 2-methoxyethanol in the pure liquid and the strong interaction between 2-methoxyethanol and tetrahydrofuran in the mixture.

The lower G^E values observed for 2-ethoxyethanol + cyclohexane with respect to 2-methoxyethanol + cyclohexane (Figure 2) are probably caused by the more favorable interaction with cyclohexane of the alcohol containing an additional CH_2 group.

For 2-methoxyethanol + cyclohexane and 2-ethoxyethanol + cyclohexane, and in general for alcohols in inert solvents, the large and positive G^E, H^E, and V^E can be ascribed to the net breaking of H-bonds on mixing, while the slightly negative TS^E exhibited by 2-methoxyethanol + cyclohexane and 2-methoxyethanol + tetrahydrofuran as well as by the ternary system in the regions rich in these binaries (see Figure 4) indicates a more

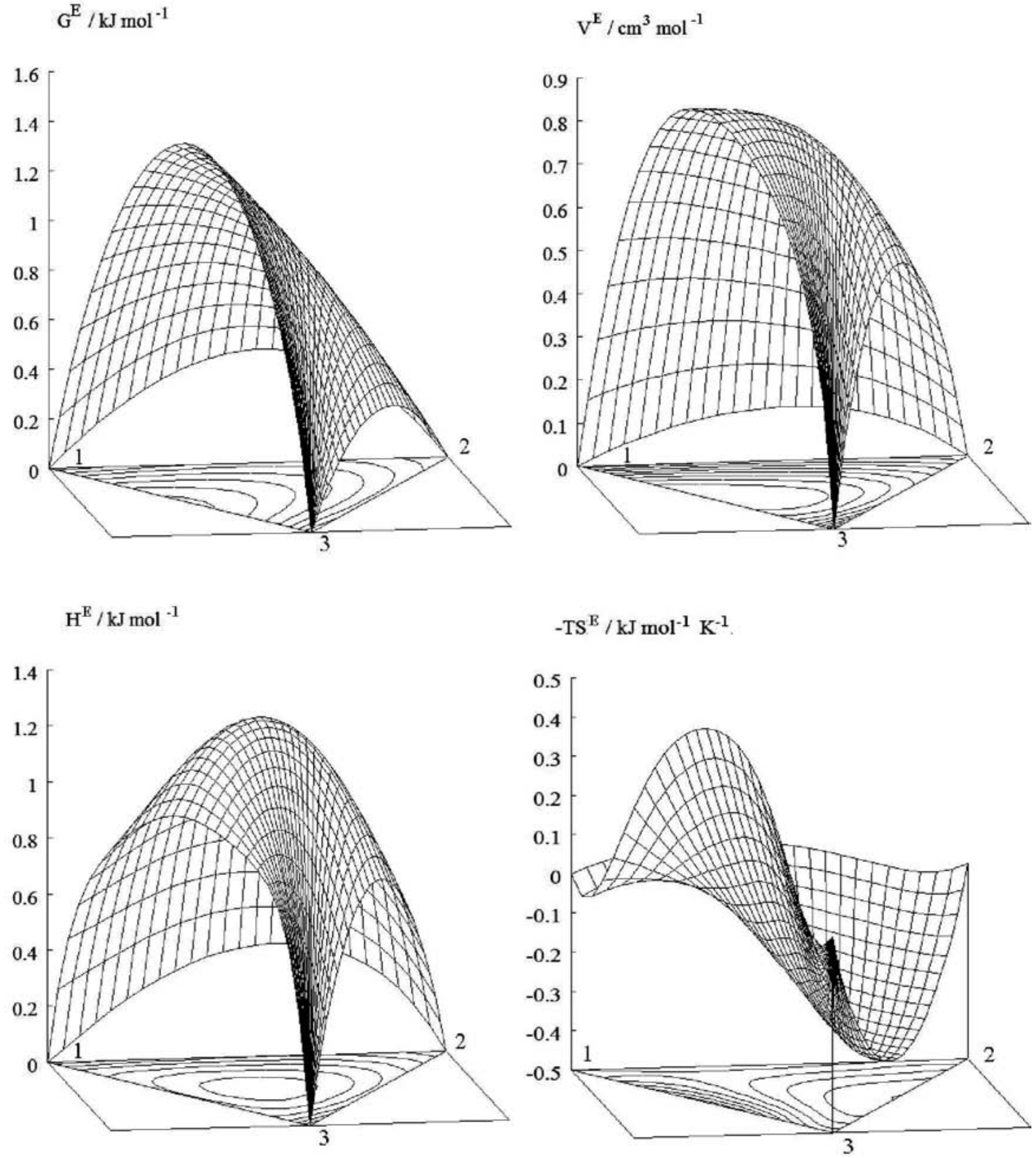

Figure 4. Graphical representation of the surfaces of excess thermodynamic properties (G^E, V^E, H^E, $-TS^E$) for the ternary system 2-methoxyethanol (1) + tetrahydrofuran (2) + cyclohexane (3) at 298.15 K.

ordered structure in solution. These apparently conflicting results are hard to explain. The basic hypothesis that order destruction/formation brings about positive/negative Y^E ($Y = G$, H, S, and V) values is evidently an oversimplification, order not being a well-defined property. The positive C_p^E of alcohol + inert solvent mixtures were explained by assuming that H-bonds are not completely broken on mixing.[20] Likely, the same explanation applies for negative TS^E in 2-methoxyethanol + cyclohexane. An association model due to Kehiaian and Treszczanowicz[21] can predict the C_p^E behavior throughout the concentration range. In highly dilute solution, all the H-bonds are broken, and C_p^E is negative. At higher alcohol concentrations, H-bonds are not completely broken, and positive C_p^E values arise from dissociation of multimers due to the temperature increase involved in the C_p measurements. Insights into the structure of solutions of alcohols in inert solvents may possibly come from the estimation of the local composition by means of the fluctuation theory.[22]

The effect of breaking and/or forming hydrogen bonds, and in general of association phenomena in solution, is emphasized by the partial molar quantities of the single components in solution. Thus, we will focus our attention on the trend of activity coefficients, γ_i, which are a measure of their tendency to escape from the solution.

We will examine first the binary systems alcohol + cyclohexane. In Figure 5 are compared the logarithms of the activity coefficients for the binaries 2-methoxyethanol + cyclohexane and 2-ethoxyethanol + cyclohexane as well as for ethanol + cyclohexane previously investigated.[1] It is immediately apparent the common behavior of these systems, in which all components display a large escaping tendency, with γ^∞ values around 7 for cyclohexane and around 50 for the alcohols. The $\ln \gamma^\infty$ values of cyclohexane indicate that the antipathy of cyclohexane toward the alcohol is in the order 2-methoxyethanol > ethanol > 2-ethoxyethanol or that the strength of the cyclohexane−alcohol interaction is in the opposite order 2-methoxyethanol < ethanol < 2-ethoxyethanol. The same behavior is displayed by $\ln \gamma^\infty$ of the alcohols in cyclohexane. The $\ln \gamma^\infty$ of 2-methoxyethanol is larger than that of 2-ethoxyethanol owing to the stronger

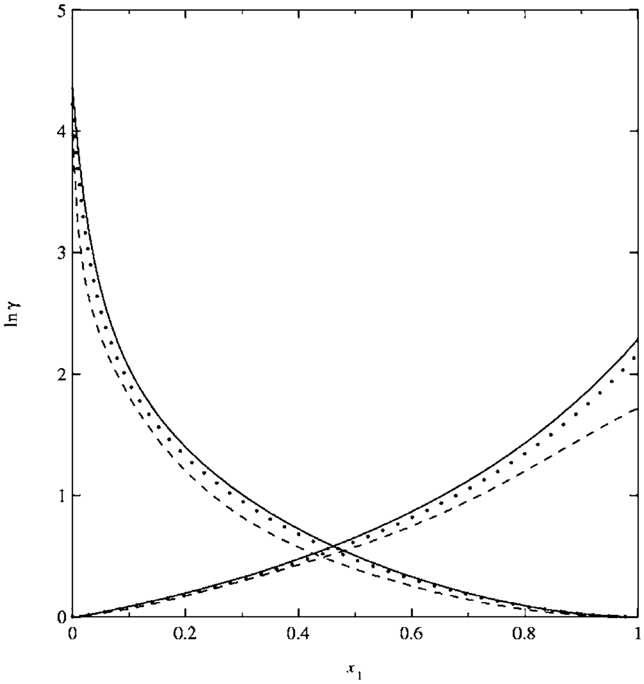

Figure 5. Plot of logarithm of activity coefficients of the components of the binary mixtures: —, 2-methoxyethanol (1) + cyclohexane; ••••, ethanol (1) + cyclohexane; - - -, 2-ethoxyethanol (1) + cyclohexane.

2-ethoxyethanol−cyclohexane interaction brought about by the additional CH_2 group in the 2-ethoxyethanol molecule. Similarly, the ln γ^∞ of 2-methoxyethanol is larger than that of ethanol owing to the stronger ethanol−cyclohexane interaction, though the ethanol molecule contains one O atom and one CH_2 group less than 2-methoxyethanol. The formation of a H-bond between the −OH and −O− functional groups of the same alkoxyethanol molecule in solution may be ruled out since this intramolecular H-bond would compete with intermolecular ones leading to sensibly lower γ^∞ and G^E values for alkoxyethanol + cyclohexane with respect to ethanol + cyclohexane, contrary to what is observed.

Let us examine now the trend of activity coefficients in the ternary system investigated. In Figure 6a, the ln γ_1 of 2-methoxyethanol is plotted against x_1 for different mole fractions $z_2 = x_2/(x_2 + x_3)$ of the binary tetrahydrofuran (2) + cyclohexane (3). Each curve represents the ln γ_1 trend along an experimentally investigated diagonal of the triangle (see Figure 1). It appears evident that ln γ_1 steeply increases with increasing alcohol dilution and that both the ln γ_1 magnitude and steepness of the curves strongly decrease with increasing tetrahydrofuran content in the mixture. This behavior is evidence of 2-methoxyethanol self-association, which is the largest in the pure liquid (low escaping tendency) and lowest in infinitely dilute solution (high escaping tendency). The addition of tetrahydrofuran, which due to its polar character interacts more strongly with 2-methoxyethanol than cyclohexane, clearly reduces the alcohol tendency to escape from the solution.

The peculiar behavior of the tetrahydrofuran activity coefficient, γ_2, in the ternary mixture is also worth mentioning. As depicted in Figure 6b, ln γ_2 assumes values that are much lower in the ternary mixture than in the two binaries 2-methoxyethanol + tetrahydrofuran and tetrahydrofuran + cyclohexane, which show very similar positive deviation from ideality. This indicates that, in this particular composition region, tetrahydrofuran behaves as if it were dissolved in an ideal mixture, practically unaffected by what happens in its neighborhood, where both 2-methoxyethanol and cyclohexane are self-associating, the former by cooperative H-bonding and the latter as a consequence of 2-methoxyethanol association. This feature will be thoroughly discussed in a future work where this mixture will be analyzed by the Kirkwood−Buff theory.[22]

Figure 6c shows the plot of ln γ_3 vs x_3 for cyclohexane in the two binaries 2-methoxyethanol + cyclohexane and tetrahydrofuran + cyclohexane and in ternary mixtures obtained by adding cyclohexane to an equimolar mixture of the other two components (0.5 2-methoxyethanol + 0.5 tetrahydrofuran). It is seen that ln γ_3 increases with cyclohexane dilution, and its values increase regularly on going from the binary tetrahydrofuran + cyclohexane to 2-methoxyethanol + tetrahydrofuran.

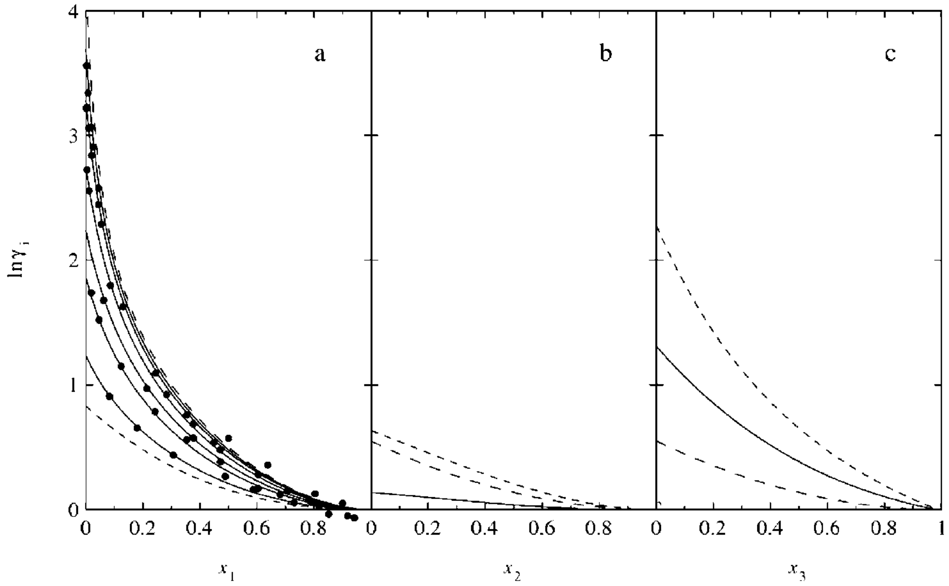

Figure 6. Plot of the logarithm of activity coefficients, γ_i, vs x_i for the ternary system 2-methoxyethanol (1) + tetrahydrofuran (2) + cyclohexane (3) at 298.15 K along specific diagonals. (a) 2-Methoxyethanol + (tetrahydrofuran + cyclohexane) mixtures with different tetrahydrofuran mole fractions $z_2 = x_2/(x_2 + x_3)$, from top to bottom: z_2 = 0, 0.05, 0.1, 0.2, 0.5, 0.8, 1. (b) Tetrahydrofuran + (2-methoxyethanol + cyclohexane) mixtures with different 2-methoxyethanol mole fractions $z_1 = x_1/(x_1 + x_3)$, from top to bottom: z_1 = 0, 1, 0.5. (c) Cyclohexane + (2-methoxyethanol + tetrahydrofuran) mixtures with different 2-methoxyethanol mole fractions $z_1 = x_1/(x_1 + x_2)$, from top to bottom: z_1 = 1, 0.5, 0.

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