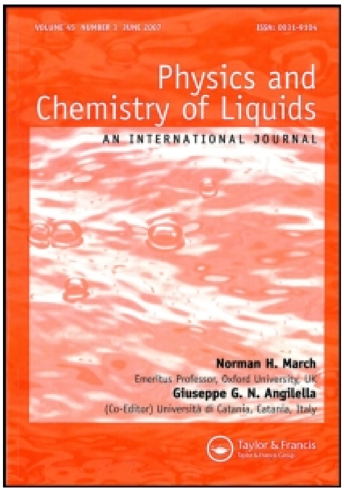

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Liquid-Liquid Equilibria, and Thermodynamic Properties of the System Methyl Acetate Methanol Water at 298.15 K

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LIQUID–LIQUID EQUILIBRIA, AND THERMODYNAMIC PROPERTIES OF THE SYSTEM METHYL ACETATE + METHANOL + WATER AT 298.15 K

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This paper reports the results of experimental measurements of ternary liquid–liquid equilibria (LLE), densities, and refractive indices of the system methyl acetate + methanol + water, and the binary system methyl acetate + water at 298.15 K, and atmospheric pressure. Values of densities, and refractive indices are measured, and compared by different methods, and mixing rules. Excess molar volumes, and changes of refractive index on mixing were computed from experimental data, a set of empirical equations which are dependent of binary derived contributions being applied. A comparative analysis was performed by application of different group contribution methods to predict experimental LLE behaviour of this ternary mixture.

Keywords: Liquid–liquid equilibria; refractive indices; methyl acetate; methanol; water

1. INTRODUCTION

Fluid phase equilibria, and mixing properties, and their corresponding derived values are of primary interest for theoretical purposes (model development, estimation of parameters, etc), and the proper design of

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separating processes. The optimization of the extractive, and azeotropic heterogeneous rectification processes require knowledge of the liquid – liquid equilibria of the system, which can be determined either experimentally or by prediction based on an appropriate model, and a small set of data. With the purpose of identifying more useful entrainers for binary azeotropic mixtures by extractive rectification separation processes, and of testing recently liquid – liquid predictive group contribution methods, water, short chain alcohols, and different high polar co-solvents are being studied in our laboratory.

In what is referred to this paper, the presented contribution is related to the study of thermophysical properties of potential effective separation agents by means of modified distillation processes (extractive or azeotropic homogeneous or heterogeneous distillation), which are in accordance with any phase topological conditions (Tojo and Iglesias, 1995). The minimum binary azeotropic involved in this ternary mixture are related to the industrial production of polyvinyl alcohol (Kirk and Ohtmer, 1983). This article reports experimental values of isothermal LLE, densities, refractive indices, excess molar volumes, and changes of refractive index on mixing for the mixtures methyl acetate + methanol + water, and methyl acetate + water measured at 298.15 K, over the entire mole fraction range at atmospheric pressure. Comparison between the experimental measured values, and those predicted by different methods was then analysed. Binary derived contribution equations were applied in order to estimate the ternary derived values of this mixture. By means of calculated Redlich – Kister (Redlich and Kister, 1948) fitting parameters, the partial excess molar volumes are obtained as a function of molar fraction, the shape of these curves, and corresponding limiting values being evaluated.

Binodal curve, and tie lines phase compositions were determined in samples prepared by mass, by measurement of physical properties, the corresponding fitting polynomials being applied. The prediction of liquid – liquid equilibria data of this mixture requires a knowledge of the activity coefficients as a function of composition. The functional group contribution methods UNIFAC, UNIFAC-Lyngby, and UNIFAC-Dortmund (Fredenslund *et al.*, 1977; Larsen *et al.*, 1987; Weidlich and Gmehling, 1987) are a reliable path for prediction of liquid phase activity coefficients, availability of interaction parameters as a function of temperature being necessary. These methods were applied in order to reproduce experimental measured values, the best agreement being obtained for the UNIFAC-Larsen at this temperature.

2. EXPERIMENTAL SECTION

Merck Lichrosolv quality chemicals were employed in samples preparation. The pure components were recently acquired and kept in inert argon atmosphere as soon as bottles were opened. Ultrasonical degassing, and molecular sieves Type 4a or 3a, 1/16 inch (Aldrich cat. n° 20,860-4 or 20,858-2, respectively) were used for drying. Precautions were taken such as cooling chemicals before samples preparation or reducing to a minimum the vapor space in the vessels, to avoid losses by evaporation during manipulation, and possible errors in fraction calculations. Chromatographic (GLC) tests of the solvents showed purities which fulfilled purchaser specifications. Their mass fraction purities were more than 0.998 for methyl acetate, methanol (maxima water contents of 6.8 10^{-3}, and 1.5 10^{-2} mass percent, respectively) (Metrohm 737 KF coulometer), and water. Further verification was performed ascertaining the constancy of the values in densities, and refractive indices at 298.15 K, which were in accordance with recommended, and recent published values (Tab. I).

A PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K was used to thermostatize the samples, that stayed at the measure temperature at least 30 minutes. Samples were

TABLE I Comparison of data with literature data for pure liquids at 298.15 K

	$\rho/(g\cdot cm^{-3})$		n_D	
component	*exptl.*	*lit.*	*exptl.*	*lit.*
Methyl Acetate	0.92674	0.9273[a] 0.9279[b]	1.35850	1.3589[a]
Methanol	0.78665	0.78664[a] 0.78664[b]	1.32645	1.32652[a] 1.32652[b]
Water	0.9970	0.99705[b]	1.33250	1.33250[b]

[a] Ref. 7.

[b] Ref. 8.

prepared by mass using a Mettler AE-240 Delta Range balance with an accuracy of $\pm 10^{-4}$ g, covering the whole composition ranges of the mixture. The densities of mixtures and pure liquids were measured with an Anton Paar DMA-146 densimeter with an accuracy of $\pm 10^{-4}\,\mathrm{g \cdot cm^{-3}}$ and the refractive indices by the automatic refractometer ABBEMAT-HP Dr Kernchen with an accuracy of $\pm 10^{-5}$. Apparatus calibration was performed periodically, testing values of known densities and refractive indices. Double liquid reference was used for the densimeter calibration (Millipore quality water and degassed and dried Fluka quality *n*-heptane). The accuracy in the calculation of excess molar volumes and changes of refractive indices was estimated as better than 8.6 10^{-3} for excess molar volumes and 2 10^{-5} for changes of refractive index on mixing. The experimental technique and mode of operation has been described previously (Iglesias *et al.*, 1995).

The binodal curve was determined by the cloud point method in a magnetically stirred glass cell, where temperature was controlled with a stability of 10^{-2} K. The tie lines phase compositions were computed from samples prepared by mass, by measurement of density, and refractive index on mixing. The estimated accuracy in phase composition was better than 2 10^{-3}.

3. RESULTS AND DATA CORRELATION

3.1. Thermodynamic Properties

The excess molar volumes and changes of refractive indices on mixing of binary, and ternary mixtures have been computed applying, respectively, equations (1) and (2).

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{1}$$

$$\Delta_{\mathrm{mix}} n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{2}$$

In these equations, ρ is the density of the mixture, n_D is the refractive index of the mixture, and ρ_i and n_{Di} are the properties of pure components. Value of N represents the number of components in the mixture. Figures 1a, and 1b show, excess molar volumes and changes of refractive indices on mixing of the binary mixture methyl acetate + water. Densities, and refractive indices of the mixture are given in Tables II and III. The ternary, and binary properties have been fitted to a polynomial (Eq. 3), where data corresponding to methyl acetate + methanol, and methanol + water were obtained from our previous papers (Rodríguez *et al.*, 1996, Iglesias *et al.*, 1995):

$$Q = \sum_{i=1}^{N} A_i x_i + \sum_{i<j}^{N} B_{ij} x_i x_j + \sum_{k=2}^{N} \sum_{i \neq j}^{N} C_{ijk} x_i^k x_j \tag{3}$$

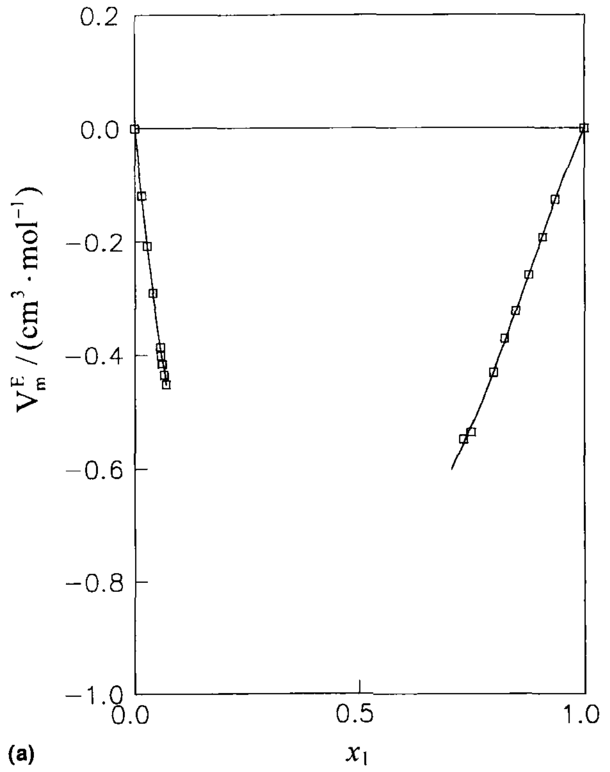

FIGURE 1 Variation of the (a) excess molar volumes and (b) changes in refractive index on mixing for methyl acetate(1) + water (3) (□) with mole fraction at 298.15 K.

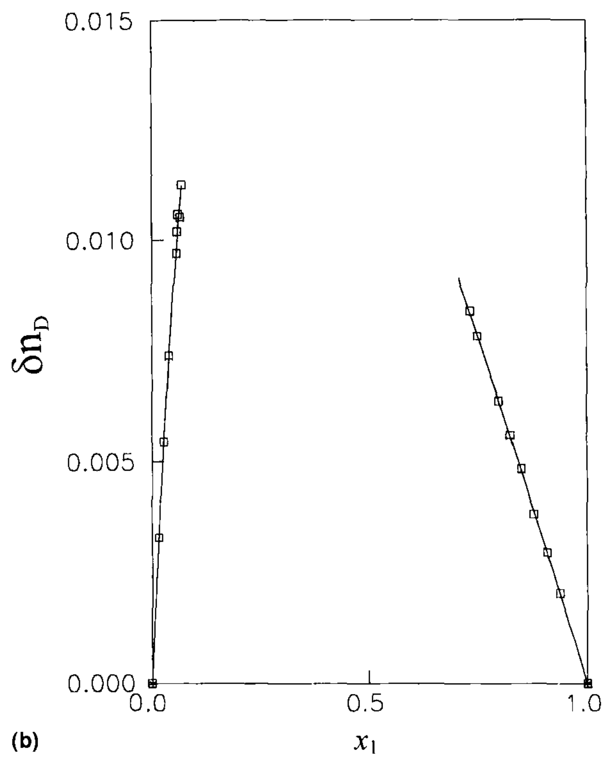

FIGURE 1 (Continued).

TABLE II Densities, refractive indices, excess molar volumes, and changes of refractive index on mixing for binary mixture at 298.15 K

x	$\rho/(g\cdot cm^{-3})$	n_D	$V_m^E/(cm \cdot mol^{-1})$	δn_D
		methyl acetate(1) + water(3)		
0.0154	0.9987	1.3362	−0.1190	0.003290
0.0275	0.9997	1.3387	−0.2080	0.005455
0.0398	1.0003	1.3409	−0.2913	0.007396
0.0572	1.0000	1.3437	−0.3863	0.009703
0.0591	1.0002	1.3442	−0.4016	0.010200
0.0616	1.0002	1.3447	−0.4161	0.010600
0.0661	0.9999	1.3448	−0.4358	0.010500
0.0697	0.9997	1.3456	−0.4523	0.011300
0.7326	0.9402	1.3599	−0.5490	0.008390
0.7485	0.9395	1.3598	−0.5371	0.007836
0.7985	0.9365	1.3596	−0.4327	0.006357
0.8234	0.9350	1.3595	−0.3727	0.005600
0.8482	0.9337	1.3594	−0.3224	0.004845
0.8777	0.9322	1.3591	−0.2603	0.003809
0.9078	0.9307	1.3590	−0.1932	0.002946
0.9364	0.9293	1.3589	−0.1257	0.002033

TABLE III Densities, refractive indices, excess molar volumes, and changes of refractive index on mixing for methyl acetate(1) + methanol(2) + water(3) at 298.15 K

x_1	x_2	$\rho/(g \cdot cm^{-3})$	n_D	$V_m^E/(cm^3 \cdot mol^{-1})$	δn_D
0.0096	0.6021	0.8608	1.33836	−0.95461	0.00907
0.0217	0.0276	0.9907	1.33824	−0.23487	0.00533
0.0329	0.3281	0.9200	1.34387	−0.95752	0.01240
0.0359	0.9031	0.8065	1.33062	−0.23369	0.00237
0.0429	0.6926	0.8448	1.33742	−0.76090	0.00778
0.0455	0.3752	0.9094	1.34431	−0.99216	0.01278
0.0498	0.5760	0.8675	1.34040	−0.91603	0.00991
0.0507	0.1562	0.9596	1.34530	−0.72995	0.01238
0.0560	0.8251	0.8219	1.33394	−0.42785	0.00472
0.0561	0.2324	0.9418	1.34590	−0.88203	0.01328
0.0570	0.4848	0.8865	1.34291	−0.99435	0.01171
0.0728	0.5322	0.8770	1.34244	−0.93652	0.01110
0.0746	0.8098	0.8253	1.33456	−0.39216	0.00477
0.0787	0.0293	0.9912	1.34737	−0.56189	0.01299
0.0815	0.1268	0.9657	1.34801	−0.75936	0.01412
0.0854	0.1097	0.9696	1.34805	−0.73615	0.01396
0.0861	0.7921	0.8292	1.33540	−0.41532	0.00521
0.0886	0.1877	0.9512	1.34857	−0.87879	0.01484
0.0888	0.6984	0.8458	1.33838	−0.63575	0.00758
0.0940	0.6141	0.8616	1.34082	−0.79043	0.00940
0.0945	0.0865	0.9752	1.34895	−0.72767	0.01449
0.1150	0.4181	0.9005	1.34644	−0.98915	0.01335
0.1202	0.4805	0.8877	1.34481	−0.92614	0.01194
0.1253	0.1274	0.9626	1.35085	−0.84184	0.01582
0.1335	0.6496	0.8562	1.34056	−0.63790	0.00832
0.1402	0.1870	0.9483	1.35111	−0.93275	0.01604
0.1421	0.7370	0.8413	1.33832	−0.40604	0.00636
0.1461	0.4511	0.8932	1.34644	−0.91621	0.01273
0.1498	0.8064	0.8300	1.33630	−0.17578	0.00454
0.1529	0.3153	0.9205	1.34971	−0.99228	0.01505
0.1686	0.4138	0.9007	1.34783	−0.94593	0.01332
0.1768	0.1100	0.9626	1.35345	−0.88753	0.01699
0.1812	0.4842	0.8868	1.34637	−0.83309	0.01194
0.1816	0.1105	0.9621	1.35330	−0.89294	0.01671
0.1890	0.5600	0.8729	1.34431	−0.68800	0.01011
0.1975	0.3961	0.9030	1.34888	−0.90724	0.01352
0.2002	0.2205	0.9376	1.35248	−0.97288	0.01604
0.2031	0.6656	0.8549	1.34135	−0.41856	0.00739
0.2317	0.1281	0.9545	1.35480	−0.94426	0.01701
0.2459	0.6882	0.8522	1.34137	−0.24790	0.00643
0.2550	0.4902	0.8851	1.34727	−0.68968	0.01096
0.2606	0.3255	0.9145	1.35175	−0.90686	0.01435
0.2626	0.1150	0.9542	1.35560	−0.92513	0.01694
0.2737	0.1407	0.9485	1.35562	−0.94228	0.01681
0.2763	0.5896	0.8682	1.34454	−0.41878	0.00824
0.2772	0.3916	0.9019	1.35023	−0.80503	0.01277
0.2802	0.2541	0.9267	1.35324	−0.93043	0.01492
0.3313	0.1656	0.9398	1.35592	−0.91808	0.01576
0.3409	0.0937	0.9519	1.35710	−0.90165	0.01628
0.3431	0.2823	0.9187	1.35354	−0.84217	0.01374

TABLE III (Continued)

x_1	x_2	$\rho/(g \cdot cm^{-3})$	n_D	$V_m^E/(cm^3 \cdot mol^{-1})$	δn_D
0.3531	0.4126	0.8963	1.35031	−0.63047	0.01100
0.3572	0.5008	0.8820	1.34776	−0.43264	0.00885
0.3666	0.5683	0.8716	1.34584	−0.24458	0.00707
0.3919	0.2145	0.9277	1.35549	−0.83479	0.01404
0.4088	0.4795	0.8849	1.34871	−0.37788	0.00834
0.4191	0.0979	0.9455	1.35797	−0.86251	0.01514
0.4289	0.2974	0.9124	1.35347	−0.67903	0.01153
0.4457	0.3934	0.8968	1.35096	−0.46257	0.00913
0.5019	0.4270	0.8906	1.35030	−0.25803	0.00721
0.5068	0.1809	0.9271	1.35645	−0.71157	0.01182
0.5369	0.0912	0.9391	1.35849	−0.75709	0.01256
0.5430	0.2886	0.9092	1.35377	−0.46040	0.00881
0.5619	0.1650	0.9269	1.35690	−0.65642	0.01074
0.5797	0.2551	0.9127	1.35457	−0.45314	0.00847
0.6079	0.0677	0.9382	1.35892	−0.67495	0.01101
0.6249	0.3123	0.9031	1.35318	−0.22254	0.00623
0.6595	0.1554	0.9231	1.35684	−0.46511	0.00809
0.6611	0.1192	0.9281	1.35796	−0.52715	0.00896
0.6634	0.2256	0.9134	1.35529	−0.32349	0.00684
0.6690	0.0971	0.9307	1.35825	−0.54268	0.00892
0.7418	0.1479	0.9203	1.35667	−0.29907	0.00574
0.7460	0.0640	0.9311	1.35852	−0.44441	0.00700
0.8358	0.0960	0.9226	1.35751	−0.18165	0.00384
0.9249	0.0538	0.9238	1.35787	−0.06372	0.00164

Where Q is $\rho/(\mathrm{g \cdot cm^{-3}})$ or n_D, ρ the density, n_D the refractive index, x_i the mole fraction of the component i, and A_i, B_{ij} and C_{ijk} are the corresponding fitting parameters. No values of these properties for the investigated ternary system have been published, as far as we know, in open literature.

The excess ternary magnitudes which are presented in Table III, were correlated with the Nagata equation (Nagata and Tamura 1990):

$$\begin{aligned} \Delta Q_{123} = {} & \Delta Q_{12} + Q_{13} + \Delta Q_{23} + \\ & x_1 x_2 x_3 \mathrm{RT}(B_0 - B_1 x_1 - B_2 x_2 \\ & - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2) \end{aligned} \tag{4}$$

where ΔQ_{12}, ΔQ_{13}, and ΔQ_{23} are the binary contribution expressed by the Redlich-Kister expression for every binary mixture:

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{M} B_p (x_i - x_j)^p \tag{5}$$

In this equation ΔQ_{ij} is the excess property, x is the molar fraction, B is a fitting parameter, and p is the degree of the polynomial expansion. The unweighted least-squares method was used to fit the polynomials to the data. The degree of eq. 5 was optimized by applying the F-test (Bevington, 1969). Curves of constant excess molar volumes and changes of refractive index on mixing have been plotted in Figures 2a and 2b, respectively. The system presents contractive character in the whole composition diagram, the lowest value of excess molar volume being gathered for approximately equimolar methanol + water composition mixtures. A sharp contraction could be observed in Figure 2a towards mixtures of 0.6 molar fraction in water, low concentration values of methanol causing inmiscibility near of methyl acetate + water binary. In changes of refractive index on mixing, the same effect could be observed, the maximum value being showed near inmiscibility zone. Different molecular volume between hydroxil compounds, and ester, as well as the different polar behaviour motivate high contractive effects by hydrogen bounds, and an important steric hyndrance phenomena leading to liquid phase splitting. In Figures 3a and 3b, the ternary contributions to the excess molar volumes, and changes of refractive index on mixing are shown. Positives values are shown by ternary contribution of the excess molar volumes with a maximum appearing at equimolar composition of hydroxil compounds (0.07421 $\text{cm}^3\cdot\text{mol}^{-1}$ at $x_1 = 0.26$, $x_2 = 0.5$). For ternary contribution to the changes of refractive index on mixing, both positive and negative contribution regions occur at higher and lower concentrations of water respectively (max. 0.00060, at $x_1 = 0.27$, $x_2 = 0.12$; min. -0.00037, at $x_1 = 0.51$, $x_2 = 0.32$).

The parameters of fitting equations (Eqs. 4 and 5 for excess values, and eq. 3 for physical properties), and corresponding standard deviations are given in Table IV. No significantly better standard deviations were obtained by trying different fitting models to correlate excess values as well as physical properties, because of high non-ideality of the mixture.

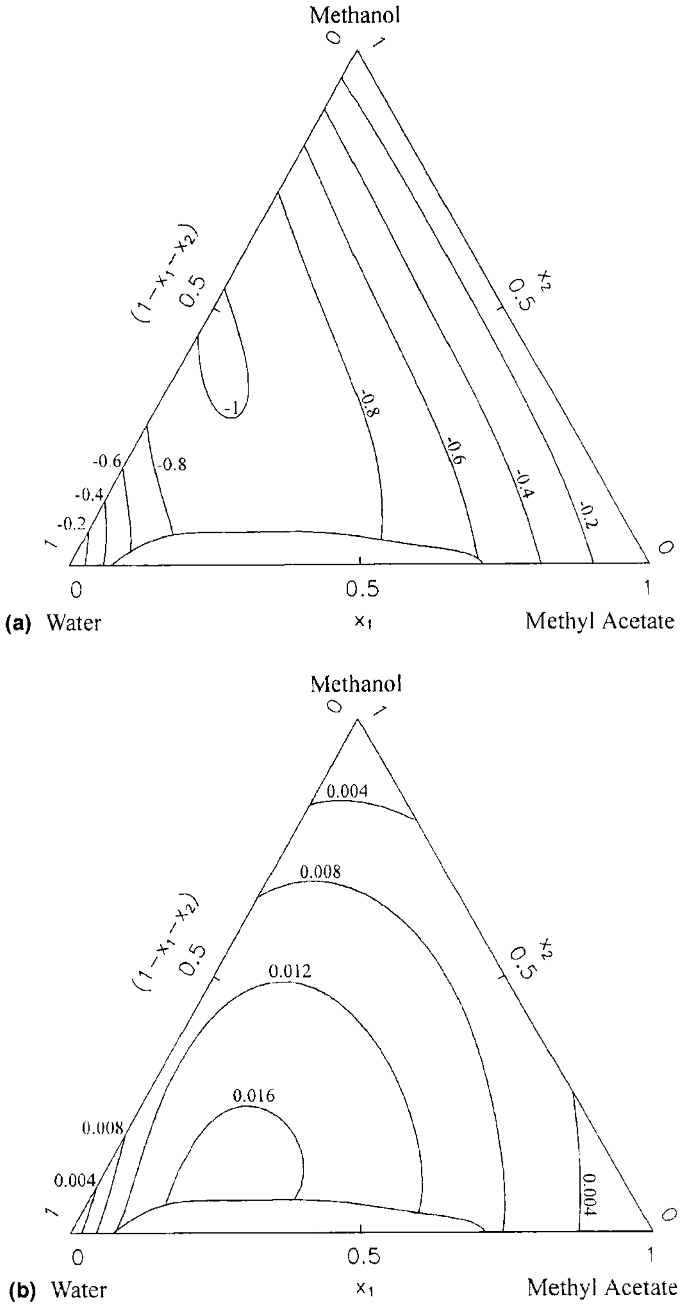

FIGURE 2 Curves of (a) constant excess molar volumes and (b) and constant changes in refractive index on mixing at 298.15 K for methyl acetate(1) + methanol(2) + water(3).

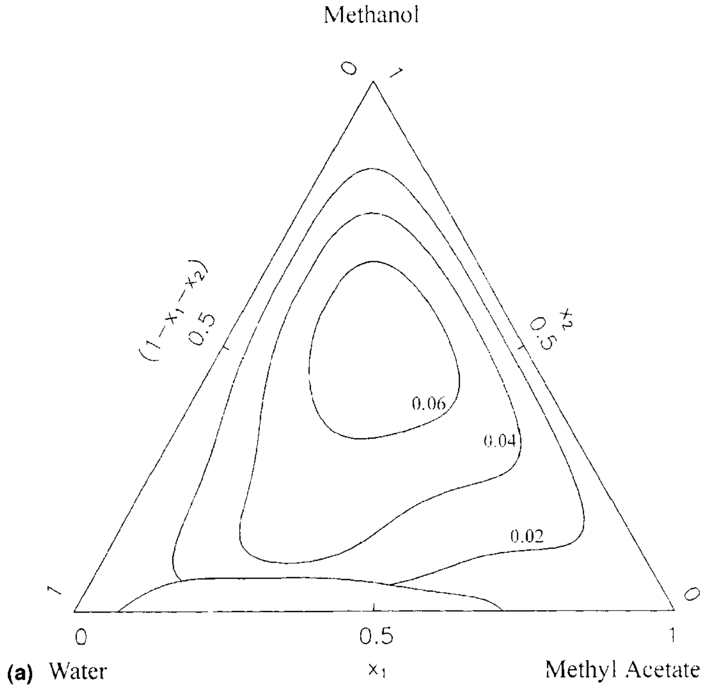

FIGURE 3 Curves of (a), $\delta V^E = V^E_{123} - V^E_{12} - V^E_{13} - V^E_{22}$ and (b), $\delta(\Delta n_{D,123}) = n_{D,123} - n_{D,12} - n_{D,13} - n_{D,23}$ at 298.15 K for methyl acetate(1) +methanol(2)+water(3).

4. DISCUSSION

4.1. Partial Excess Molar Volumes

The partial excess molar volume of a component in a binary mixture can be determined from excess molar volume data by means of the following expression (Iglesias *et al.*, 1997):

$$\overline{V}_i^E = V^E + (1 - x_i)\left(\frac{dV^E}{dx_i}\right) \tag{6}$$

where the differential term is calculated taking into account we have applied the Redlich-Kister expression to correlate the excess values, the parameters enclosed in Table V for eq. 4 being applied. The expressions for the partial excess molar volumes, once the differentiation is performed, should be written as:

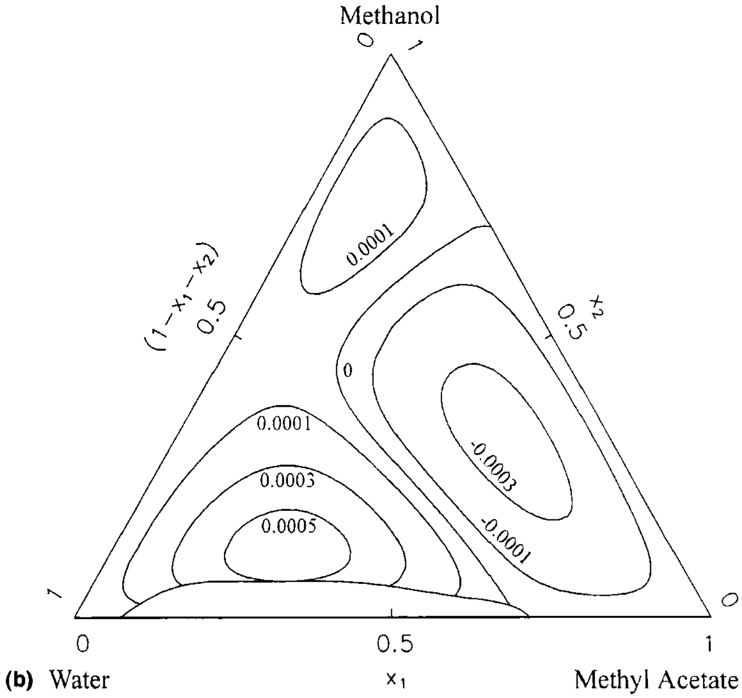

FIGURE 3 (Continued).

$$\overline{V}_1^E = (1 - x_1)^2 \left[\sum_{p=0}^{m} B_p(2x_1 - 1)^p + x_1 \sum_{p=1}^{m} 2pB_p(2x_1 - 1)^{p-1} \right] \quad (7)$$

$$\overline{V}_2^E = (1 - x_2)^2 \left[\sum_{p=0}^{m} B_p(1 - 2x_2)^p + x_2 \sum_{p=1}^{m} (-2)pB_p(1 - 2x_2)^{p-1} \right] \quad (8)$$

where the symbols keep the meaning explained above. From eqs. 7 and 8, the corresponding limiting partial excess molar volumes should be determined by considering x_1 nule in every expression, such limiting values being dependent on the correlation parameters. Figures 4a and 4b show the trends of partial excess molar volumes with the corresponding molar fraction for the binary mixtures, the values of limiting partial excess molar volumes at 298.15 K being enclosed in Table V.

TABLE IV Parameters of equations 3, 4 and 5 and standard deviations σ

			Methyl Acetate (1) + Methanol (2)			
$V_m^E/(\mathrm{cm^3 \cdot mol^{-1}})$	$B_0=-0.331443$	$B_1=0.000839$	$B_2=-0.063863$			$\sigma=0.0018$
δn_D	$B_0=0.022717$	$B_1=-0.005778$	$B_2=-0.001794$	$B_3=0.004844$	$B_4=0.002663$	$\sigma=0.000015$
			Methyl Acetate (1) + Water (3)			
$V_m^E/(\mathrm{cm^3 \cdot mol^{-1}})$	$B_0=-3.318166$	$B_1=1.421333$	$B_2=-1.708301$	$B_3=1.883202$		$\sigma=0.0041$
δn_D	$B_0=0.053771$	$B_1=-0.0313178$	$B_2=-0.038315$	$B_3=-0.066499$	$B_4=0.039137$	$\sigma=0.000012$
			Methanol (2) + Water (3)			
$V_m^E/(\mathrm{cm^3 \cdot mol^{-1}})$	$B_0=-4.034707$	$B_1=0.235959$	$B_2=-0.074721$	$B_3=-0.838935$	$B_4=0.822255$	$\sigma=0.0043$
δn_D	$B_0=0.040332$	$B_1=-0.01986$	$B_2=0.009379$	$B_3=-0.006738$	$B_4=-0.0022023$	$\sigma=0.00005$
			Methyl Acetate (1) + Methanol (2) + Water (3)			
$\rho \setminus (\mathrm{g \cdot cm^{-3}})$	$A_1=0.925188$	$A_2=0.787280$	$A_3=0.997561$	$B_{12}=-0.096593$	$B_{13}=-0.017180$	$B_{23}=0.272415$
	$C_{122}=0.048209$	$C_{132}=0.40718$	$C_{212}=0.303239$	$C_{232}=-0.353010$	$C_{312}=-\ 0.235224$	$C_{322}=-\ 0.217028$
	$C_{123}=0.133998$	$C_{133}=-0.006824$	$C_{213}=-0.069899$	$C_{233}=0.012473$	$C_{313}=0.389973$	$C_{323}=-\ 0.127618$
						$\sigma=0.00072$
n_D	$A_1=1.357834$	$A_2=1.326940$	$A_3=1.332914$	$B_{12}=-0.138334$	$B_{13}=-0.008188$	$B_{23}=0.278501$
	$C_{122}=0.058191$	$C_{132}=0.117775$	$C_{212}=0.257590$	$C_{232}=-0.321666$	$C_{312}=-\ 0.101429$	$C_{322}=-\ 0.140144$
	$C_{123}=0.103211$	$C_{133}=-0.055328$	$C_{213}=-0.090957$	$C_{233}=0.059186$	$C_{313}=0.299873$	$C_{323}=-\ 0.087256$
						$\sigma=0.00033$
$V_m^E/(\mathrm{cm^3 \cdot mol^{-1}})$	$B_0=0.000912$	$B_1=-0.006812$	$B_2=0.006434$	$B_3=0.020806$	$B_4=-0.018001$	$B_5=0.009423$
	$B_6=-0.014645$	$B_7=0.011361$	$B_8=-0.023286$			$\sigma=0.0066$
δn_D	$B_0=-0.000019$	$B_1=-0.000071$	$B_2=0.000103$	$B_3=0.000228$	$B_4=-0.000165$	$B_5=0.000136$
	$B_6=-0.000123$	$B_7=0.000060$	$B_8=-0.000265$			$\sigma=0.00014$

TABLE V Partial excess molar volumes at infinite dilution of the binary mixtures at 298.15 K

	$\overline{V}_1^{E,\infty}/(cm^3mol^{-1})$	$\overline{V}_2^{E,\infty}/(cm^3mol^{-1})$
Methyl Acetate (1) + Methanol (2)	−0.396	−0.394
Methyl Acetate (1) + Water (3)	−8.331	−1.722
Methanol (2) + Water (3)	−2.684	−3.890

In these figures it can be observed a high different behaviour against composition for the three binaries. Methyl acetate + water mixture shows the fastest variation of this derived property (slightly positive in rich composition of water), which is related to phase separation while methanol + water presents a change in the trend for low compositions of methanol. Low effect of partial excess molar volumes will be

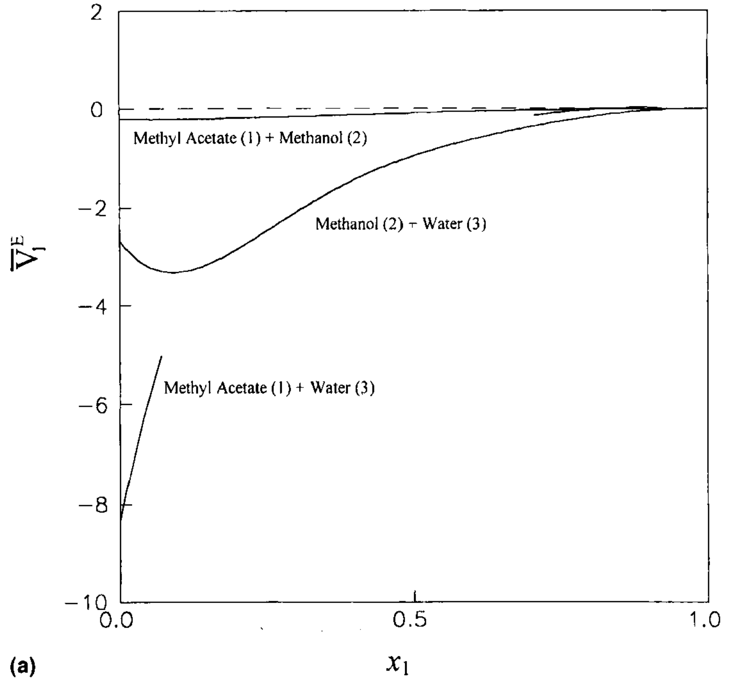

FIGURE 4 Partial excess molar volumes of methyl acetate(1) + methanol(2), methyl acetate(1) + water(3), and methanol(2) + water(3) mixtures at 298.15 K for (a) V_1^E and (b) V_2^E.

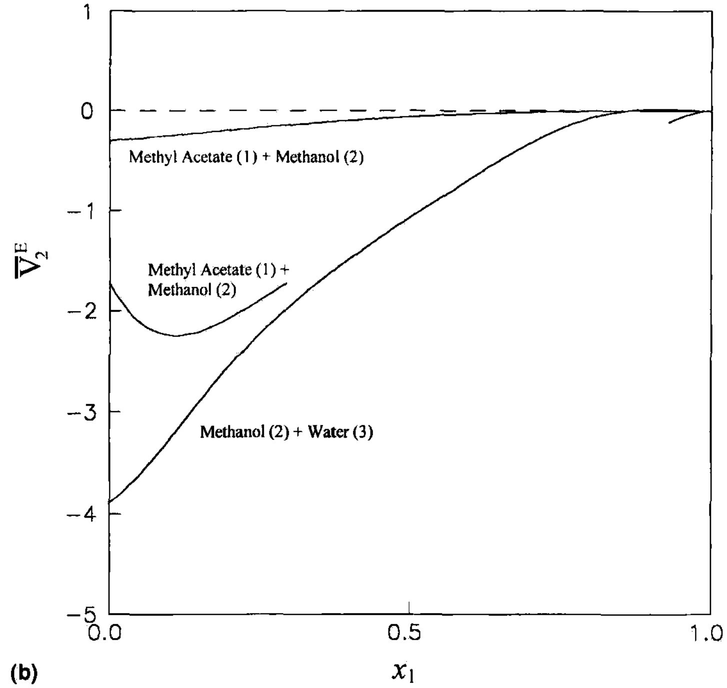

FIGURE 4 (Continued).

produced to ternary values by the binary methyl acetate + methanol due to its negligible contribution.

4.2. Physical Properties Estimation

In this paper, the measured experimental properties were compared with those estimated applying several relations. The density of the mixtures were estimated by application of the Hankinson-Brobst-Thompson (HBT), Rackett (R), Spencer and Danner modified Rackett (SDR), Bradford-Thodos (BT), Riedel (RI), Narsimham (N), and Yen-Woods (YW) equations (Iglesias *et al.*, 1995) using expansioned mixing rules proposed by those authors and the Kay (modified Prausnitz-Gunn combination) rule (Reid *et al.*, 1985).

The refractive indices were compared with the predicted results by Lorentz-Lorenz (LL), Gladstone-Dale (GD), Arago-Biot (AB), Eykman (Ey), Newton (N), Oster (O), Eyring-Jhon (EJ), Wiener (W) and Heller (H) mixing rules (Iglesias *et al.*, 1995, Tasic *et al.*, 1992). In Tables VI and VII the mean square deviations of the estimations are gathered. In density prediction, the equation yielding the most accurate predictions varies from one binary mixture to another. For methyl acetate + methanol, Narsimham, and Yen Woods are the best options, while for methyl acetate + water the Riedel equation, and for methanol + water again the Yen-Woods equation offers the lowest deviations. The ternary mixture values are best described using the Narsimham equation. In what is referred to changes of indices on mixture, the equations of Dale-Gladstone and Oster give the most accurate representation of the derived values of the magnitude for both the binaries, and the ternary mixture, considering in every case non additivity on mixing, which improves neatly the results obtained.

4.3. Excess Properties Estimation

The predictive methods applied for excess properties (Iglesias *et al.*, 1995, Piñeiro *et al.*, 1997), determine ternary excess values by means of additive binary contributions, using different rules to determine them. The ternary excess properties of mixtures may be estimated from binary values applying eq. 9:

TABLE VI Standard deviations of the experimental results of densities from those estimated for Hankinson-Brobst-Thompson (HBT), Rackett (R), Spencer and Danner Modified Rackett (SDR), Bradford-Thodos (BT), Riedel (Ri), Narsimham (N), and Yen-Woods (YW)

HBT	*R*	*SDR*	*BT*	*Ri*	*N*	*YW*
		methyl acetate(1) + methanol(2)				
0.0198	0.0553	0.0283	0.0134	0.0180	0.0094	0.0095
		methyl acetate(1) + water(3)				
0.1915	0.074	0.0505	0.0273	0.0052	0.0116	0.0177
		methanol(2) + water(3)				
0.0217	0.0667	0.0339	0.0237	0.0117	0.0102	0.0081
		methyl acetate(1) + methanol(2) + water(3)				
0.0973	0.0644	0.0363	0.0235	0.0144	0.0070	0.0155

TABLE VII Standard deviations of the experimental results of refractive indices from the prediction results for the Lorentz-Lorentz (L-L), Dale-Gladstone (D-G), Arago-Biot (A-B), Eykman (Eyk), Newton (NW), Oster (OS) Eyring-Jhon (E-J), Weiner (W) and Heller (H) Equations

L-L	*D-G*	*A-B*	*Eyk*	*Nw*	*Os*	*E-J*	*W*	*H*
methyl acetate (1) + methanol (2)								
0.00044	0.00039	0.00039	0.00041	0.00035	0.00037	0.00042	0.00050	0.00041
0.00027	0.00028	0.00124	0.00028	0.00030	0.00029	0.00268	0.00049	0.00042
methyl acetate (1) + water (3)								
0.00409	0.00406	0.00406	0.00407	0.00403	0.00405	0.00408	0.00374	0.00410
0.00068	0.00033	0.01272	0.00049	0.00042	0.00028	0.02976	0.00396	0.00433
methanol (2) + water (3)								
0.00816	0.00816	0.00816	0.00816	0.00816	0.00816	0.00816	0.00815	0.00816
0.00122	0.00036	0.02612	0.00079	0.00075	0.00015	0.06145	0.00808	0.00810
methyl acetate (1) + methanol (2) + water (3)								
0.00705	0.00700	0.00700	0.00702	0.00695	0.00698	0.00703		
0.00072	0.00026	0.02050	0.00042	0.00091	0.00036	0.04869		

The second data line indicates mixtures with non aditivity on mixing Wiener and Heller mixing rules and binary applications.

TABLE VIII Standard deviations of the experimental results from the prediction results for different empirical equations

	$\sigma(V_m^E/(cm^3 \cdot mol^{-1}))$	$\sigma(\delta n_D)$
Kohler	0.058	0.0008
Jacob-Fitzner	0.048	0.0003
Colinet	0.046	0.0006
Tsao-Smith[a]	0.175	0.0031
Tsao-Smith[b]	0.147	0.0032
Tsao-Smith[c]	0.073	0.0007
Scatchard[a]	0.058	0.0020
Scatchard[b]	0.049	0.0004
Scatchard[c]	0.079	0.0014
Toop[a]	0.056	0.0020
Toop[b]	0.058	0.0009
Toop[c]	0.079	0.0014
Mathieson-Tynne[a]	1.071	0.0419
Mathieson-Tynne[b]	1.097	0.0121
Mathieson-Tynne[c]	0.530	0.0091
Hillert[a]	0.496	0.0066
Hillert[b]	0.306	0.0069
Hillert[c]	0.060	0.0018
Knobeloch	0.151	0.0030
Lakhanpal	0.430	0.0031

[a] Water is the asymmetric component in the equation.
[b] Methanol is the asymmetric component in the equation.
[c] Methyl Acetate is the asymmetric component in the equation.

$$\Delta Q_{ijk} = \sum_{i<j} (x_i x_j / x'_i x'_j) \Delta Q_{ij}(x'_i, x'_j), \tag{9}$$

For each ternary mixture the molar fractions x' may be obtained from a triangular diagram by projecting the point representing the ternary composition onto the corresponding binary axis, using different symmetric or asymmetric criteria of binary contribution to the ternary value. In said rules symmetry is understood to be the contribution of the three binaries to the ternary excess, all three of which contribute equally. Asymmetry is understood to indicate the different individual contribution of one of the binaries, being normally attributed to polar components. In Table VII, the experimental, and estimated excess values are compared showing standard deviations (σ) (eq. 10). The value of the property and the number of experimental data are represented by z, and n_{DAT}, respectively:

$$\sigma = \left(\frac{\sum_i^{n_{\mathrm{DAT}}} (z_{\mathrm{exp}} - z_{\mathrm{pred}})^2}{n_{\mathrm{DAT}}} \right)^{1/2} \tag{10}$$

The best predictions are achieved for both excess volumes, and changes of refractive indices by applying the symmetric equations of Kohler, Jacob-Fitzner and Colinet and also with the asymmetric equation of Scatchard considering the ordering b, which means supposing methanol to be the polar component in the mixtures.

4.4. Phase Equilibria Prediction

Mulitcomponent liquid–liquid equilibria are of interest in extraction or modified heterogeneous distillation, and useful to develop thermodynamic predictive methods, and compute new sets of contribution parameters. The Universal Function-group Activity Coefficients model (Fredenslund *et al.*, 1975), as well as the modified versions (Larsen *et al.*, 1987, Weidlich and Gmehling, 1987) where a modified combinatorial part is introduced, as well as temperature-dependent group interaction parameters, have been successfully applied for the prediction of several liquid–liquid systems. These models depend on the interaction parameters between each pair of main functional groups present in the mixture, which were obtained by regressing the experimental data to the models, and obtaining numerical values for the interaction parameters.

Liquid–liquid equilibrium calculations were performed by solving the isoactivity relation of each component in two liquid phases, as follows:

$$\gamma_i^E x_i^E = \gamma_i^R x_i^R \tag{11}$$

$$N_i = N_i^E + N_i^R \tag{12}$$

where E is the extract (organic phase), and R the raffinatte (aqueous phase), and N_i is the number of moles, γ_i being the corresponding activity coefficients of component i in the different liquid phases, as calculated from the equilibrium model. The interaction parameters between methyl acetate, methanol and water of the group contribution

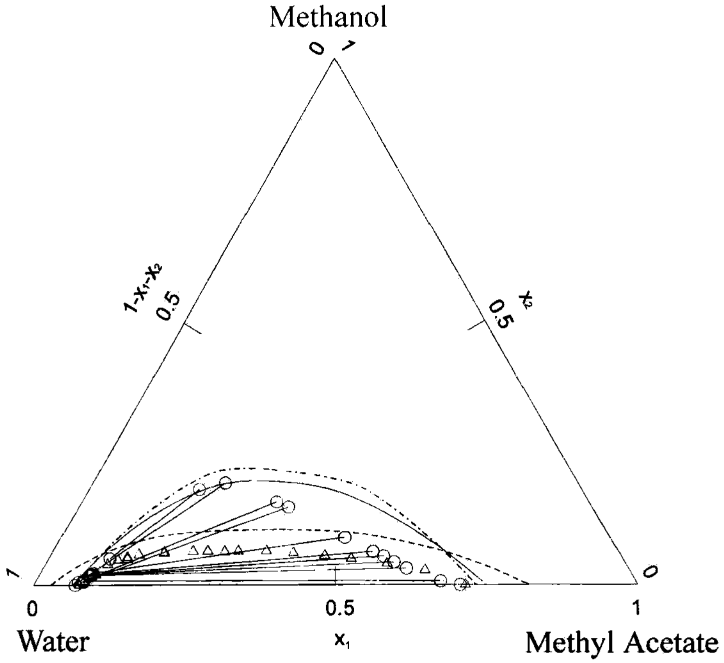

FIGURE 5 (Δ) Cloud points, (o) measured compositions for tie lines, and liquid liquid equilibrium predictions using the model of (— — —)UNIFAC, (- - -)version of Larsen, (— · — · ·) version of Dortmund.

TABLE IX Experimental tie lines compositions

x_1	x_2	x_1	x_2
0.1821	0.1836	0.5521	0.0549
0.1006	0.0504	0.0824	0.0175
0.2195	0.1957	0.5755	0.0436
0.0707	0.0057	0.0828	0.0185
0.3222	0.1597	0.6019	0.0316
0.0788	0.0073	0.0851	0.0186
0.3471	0.1498	0.6698	0.0070
0.0791	0.0056	0.0780	0.0080
0.4696	0.0904	0.7060	0.0000
0.0870	0.0226	0.0678	0.0000
0.5300	0.0635		
0.0868	0.0198		

TABLE X Cloud points compositions

x_1	x_2	x_1	x_2
0.0749	0.0000	0.2318	0.0639
0.0771	0.0076	0.2561	0.0644
0.0806	0.0124	0.2845	0.0634
0.0916	0.0205	0.3064	0.0648
0.1027	0.0395	0.3523	0.0647
0.1157	0.0477	0.3996	0.0609
0.1292	0.0524	0.4542	0.0558
0.1306	0.0495	0.5002	0.0503
0.1457	0.0577	0.5651	0.0405
0.1848	0.0622	0.6348	0.0284
0.1848	0.0607	0.7154	0.0000

models were used to predict the activity coefficients. Equations 11 and 12 are solved to calculate the mole fraction for component i in each liquid phase, a single tie line being obtained by this method of calculation. The applicability of these models was confirmed by comparing, as shown in Figure 5, the calculated phase equilibrium compositions, with the experimental results, which are displayed in Table IX. In this figure the measured cloud points are also plotted, being their compositions enclosed in Table X.

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