Densities, Viscosities, and Surface and Interfacial Tensions of the Ternary Mixture Water + Ethyl Butyrate + Methanol at 303.15 K

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The excess molar volumes, $V^{\rm E}$, viscosity deviations, $\Delta \eta$, and excess surface tensions were calculated from the measured density, viscosity, and surface tension values, σ , over the whole miscibility composition range for the ternary system water + ethyl butyrate + methanol and their constituent binaries, at 303.15 K and atmospheric pressure. The liquid interfacial tension was measured in the liquid–liquid equilibrium range at the same conditions of temperature and pressure. A Redlich–Kister type equation was used to correlate binary and ternary $V^{\rm E}$ and $\Delta \eta$ data. For the correlation of the surface tension of binary and ternary data, the Santos et al. equation was used. The interfacial tension was correlated with the Li and Fu equation.

Introduction

Thermodynamic and transport properties are fundamental in the design of process units that involve fluid flow, interface heat, and mass transfer. In the past few years we have been developed a research program that consists of the experimental determination of densities, viscosities, and surface and interfacial tensions of binary and ternary mixtures.^{1–4}

In the present work we have measured densities, viscosities, and surface and interfacial tensions for the ternary system water + ethyl butyrate + methanol, at 303.15 K and atmospheric pressure. The related properties excess molar volume, viscosity deviation, and excess surface tension were derived from the measured data. This ternary system shows liquid–liquid immiscibility in a wide composition range. The compositions of the liquid phases in equilibrium were measured by Rao and Rao.⁵

The excess molar volume, V^{E} , and viscosity deviations, $\Delta \eta$, are often used to study qualitatively the intermolecular forces in mixtures, helping us to understand their real behavior and develop models for its description. On the other hand, the surface tension, σ , and the interfacial tension, σ' , of liquid mixtures are essential properties in process design, but the available experimental data are relatively scarce.⁶

The V^{E} and $\Delta \eta$ of binary and ternary data were correlated using Redlich–Kister type equations. However, the correlation of the binary surface tension data has been made using the Santos et al.⁴ expression, since the best results are obtained using this simple equation, as was shown in our previous paper.⁴ The liquid interfacial tension was correlated using the equation of Li and Fu.⁷

Experimental Section

Materials. The pure water (water G Chromasolv) was supplied by Riedel de Häen. Methanol (Panreac) was supplied with a purity > 99.8 mass %, while the ethyl butyrate (Riedel de Häen and Acros) was supplied with a

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Table 1. Densities, ρ , Viscosities, η , and Surface	
Tensions, σ , of the Pure Components at 303.15 K and	ł
Atmospheric Pressure	

		-				
	ρ/g	$ ho/g\cdot cm^{-3}$		ıPa∙s	$\sigma/mN\cdot m^{-1}$	
component	exptl	lit.	exptl	lit.	exptl	lit.
water		0.995 70 ⁸		0.79713		71.404,6
ethyl butyrate	0.868 21	0.868 50 ⁹	0.591	0.577^{14}	23.40	23.41^{17}
		0.868 83 ¹⁰				
methanol	0.781 91	0.781 9611	0.504	0.510^{15}	21.68	21.71^{6}
		0.781 82 ¹²		0.503^{16}		
		0.782 00 ⁹		0.516^{2}		
		0 781 992				

purity > 99%. Table 1 lists the measured densities, viscosities, and surface tensions of ethyl butyrate and methanol together with the values found in the literature. Since the agreement is very good, all the compounds were used without further purification. Mixtures were prepared by mass using a Mettler AT 200 balance with an uncertainty of $\pm 10^{-5}$ g. The uncertainty of the mole fraction compositions of the mixtures for which we have determined the densities and viscosities is estimated to be of the order $\pm 10^{-4}$. For the mixtures for which surface and interfacial tensions were measured, the uncertainty of the mole fraction compositions is $\pm 10^{-3},$ since these measurements took place in an open vessel. This value was obtained by weighing the prepared binary solutions at the beginning and at the end of the experiences, which allows us to determine the evaporated mass of liquid.

Measurements. Densities were measured in an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 602 measuring cell. Air and pure water were used for the calibration of the densimeter. Viscosities were obtained with a Haake falling ball viscosimeter (Hoppler design), calibrated with pure water. An electronic digital stopwatch, with an uncertainty of ± 0.01 s, was used to measure the falling time of the ball. In all the measurements, the temperature maintenance and control were performed using a Haake D8-G thermostatic water bath, which has a temperature uncertainty of ± 0.01 K. In the case of density measurements, the Pt resistance thermometer (calibrated against a precision mercury thermometer, graduated in 0.01 K, certified by NPL, U.K.) was placed

Table 2. Densities, ρ , and Excess Molar Volumes, V^{E} , for the System Water (1) + Ethyl Butyrate (2) + Methanol (3) and Its Binary Constituents, at 303.15 K and Atmospheric Pressure

		ρ	$V^{\rm E}$			ρ	$V^{\rm E}$
<i>X</i> 1	<i>X</i> 2	g·cm ⁻³	$\overline{\mathrm{cm}^3\cdot\mathrm{mol}^{-1}}$	<i>X</i> 1	<i>X</i> 2	g·cm ⁻³	cm ³ ·mol ⁻¹
0	0.1993	0.820 83	-0.017	0.1061	0.3576	0.848 61	-0.289
0	0.3000	0.832 61	-0.030	0.1111	0.4408	0.854 43	-0.275
0	0.4000	0.841 45	-0.037	0.1207	0.6186	0.863 16	-0.186
0	0.4995	0.848 30	-0.037	0.1317	0.3093	0.847 66	-0.357
0	0.5997	0.853 94	-0.042	0.1434	0.5910	0.864 21	-0.275
0	0.9001	0.865 54	-0.025	0.1537	0.2483	0.845 07	-0.426
0	0.4490	0.845 03	-0.038	0.1572	0.3371	0.852 41	-0.400
0	0.4740	0.846 71	-0.039	0.1586	0.1677	0.837 46	-0.465
0	0.6500	0.856 33	-0.040	0.1705	0.4976	0.861 37	-0.245
0	0.7495	0.860 43	-0.030	0.1850	0.0994	0.832 29	-0.544
0	0.8990	0.865 48	-0.019	0.1952	0.0499	0.826 27	-0.598
0	0.9465	0.866 88	-0.020	0.2023	0.3191	0.856 16	-0.503
0.0560	0.9440	0.868 98	0.036	0.2055	0.0000	0.818 52	-0.651
0.0390	0.9610	0.868 71	0.029	0.2099	0.1575	0.843 39	-0.584
0.0330	0.9670	0.868 46	0.050	0.2250	0.3389	0.860 17	-0.561
0.0190	0.9810	0.868 19	0.054	0.2503	0.2999	0.860 14	-0.586
0.0471	0.3999	0.846 12	-0.172	0.2561	0.1504	0.848 89	-0.660
0.0507	0.7903	0.865 11	-0.109	0.2709	0.1012	0.845 68	-0.710
0.0514	0.4738	0.851 21	-0.160	0.2866	0.0491	0.841 71	-0.779
0.0521	0.1889	0.826 26	-0.193	0.3014	0.0000	0.836 97	-0.849
0.0523	0.0962	0.811 92	-0.183	0.3021	0.2473	0.862 37	-0.654
0.0531	0.5679	0.856 49	-0.156	0.3218	0.1982	0.861 55	-0.707
0.0563	0.6639	0.860 99	-0.149	0.3415	0.1490	0.859 74	-0.717
0.0847	0.7201	0.865 02	-0.181	0.3516	0.1995	0.865 13	-0.714
0.0900	0.2763	0.840 10	-0.260	0.3613	0.0997	0.859 74	-0.835
0.0980	0.0499	0.810 07	-0.328	0.3813	0.0500	0.858 53	-0.902
0.1030	0.0911	0.818 81	-0.351	0.4013	0.0000	0.857 06	-0.977
0.1031	0.0000	0.799 74	-0.362	0.4495	0.0997	0.873 58	-0.884
0.1032	0.4705	0.855 13	-0.226	0.4744	0.0500	0.875 34	-0.955
0.1032	0.5378	0.858 55	-0.205	0.4994	0.0000	0.877 48	-1.017
0.1034	0.1787	0.831 37	-0.321				

inside the vibrating tube densimeter to find the actual temperature of the measurements. The temperature was maintained at (303.15 \pm 0.01) K.

Surface and interfacial tensions were measured using a PC controlled KSV Sigma 70 tension balance which employs the Du Noüy ring-detachment method. The platinum ring was thoroughly cleaned by immersion in a concentrated solution of nitric acid during several hours. Then it was rinsed with distilled water and flame dried before each measurement. The measurements were automatically corrected by means of the Huh and Mason compensation for interface distortion. The temperature inside the surface tension measurement vessel was maintained and controlled at (303.15 \pm 0.10) K using a Julabo FP50 bath.

For the liquid interfacial tension measurements, the mixture with a known global composition was kept at 303.15 K in a thermostated vessel and shaken several times during a period of at least 24 h to reach the equilibrium. The surface tension of each liquid phase was also measured separately.

Uncertainties. Densities were measured with an uncertainty of $\pm 10^{-5}$ g·cm⁻³. Having in mind that the error in the excess molar volume, V^E , is determined by the uncertainties in mole fraction and density, the maximum error in V^E resulting from the propagation of errors is 5×10^{-3} cm³·mol⁻¹. Taking into account the uncertainties in the measured time and in the density, the experimental uncertainty in the viscosity is ± 0.001 mPa·s. The uncertainty of the surface and interfacial tensions is indicated by the instruction manual of the tension balance to be of the order of ± 0.01 mN·m⁻¹.

Results and Discussion

The excess molar volumes, $V^{\rm E}$, were calculated from the densities by the equation

$$V^{E} = \rho^{-1} (\sum x_{i} M_{j}) - \sum x_{i} M_{j} \rho_{j}^{-1}$$
(1)

where x_i is the mole fraction of component *i* in the mixture, M_i is its molecular weight, and ρ and ρ_i are the measured densities of the mixture and the pure component, respectively.

The calculation of the dynamic viscosity is done according to the formula

$$\eta = K(\rho_{\rm b} - \rho)t \tag{2}$$

where *t* is the falling time of the ball measured with the stopwatch. *K* is a calibration constant, and ρ_b and ρ represent the densities of the ball and the liquid, respectively. ρ was calculated through eq 1. The V^E values are obtained by eqs 5 and 7 for binary and ternary systems, respectively.

The viscosity deviations, $\Delta \eta$, were obtained using the expression

$$\Delta \eta = \eta - \sum x_i \eta_i \tag{3}$$

where η is the measured mixture viscosity and η_i represents the pure component viscosity.

The composition dependence of the surface tensions of mixtures can be represented in terms of the excess surface tension, σ^{E} , defined as

$$\sigma^{\rm E} = \sigma - \sum x_i \sigma_i \tag{4}$$

where σ is the surface tension of the mixture and σ_i is the surface tension of the *i*th component of mole fraction x_i .

Table 2 lists the measured densities, ρ , and the corresponding values of V^{E} , Table 3 presents the measured viscosities, η , and the corresponding $\Delta \eta$ values, and the measured surface tensions and the corresponding excess surface tensions as a function of the composition are shown in Table 4, for the ternary system and its constituent binary systems. Experimental results for the binary water (1) +

Table 3. Viscosities, η , and Viscosity Deviations, $\Delta \eta$, for the System Water (1) + Ethyl Butyrate (2) + Methanol (3) and Its Binary Constituents, at 303.15 K and Atmospheric Pressure

		η	$\Delta \eta$			η	$\Delta \eta$
<i>X</i> ₁	<i>X</i> ₂	mPa∙s	mPa∙s	<i>X</i> ₁	<i>X</i> ₂	mPa∙s	mPa∙s
0	0.9004	0.577	-0.005	0.1205	0.1369	0.633	0.082
0	0.8054	0.565	-0.009	0.1326	0.6091	0.600	0.004
0	0.6976	0.551	-0.014	0.1415	0.2059	0.650	0.086
0	0.6226	0.543	-0.015	0.1432	0.0639	0.669	0.117
0	0.5064	0.535	-0.013	0.1564	0.5272	0.626	0.030
0	0.4147	0.529	-0.011	0.1603	0.3344	0.645	0.065
0	0.3147	0.522	-0.009	0.1785	0.4458	0.651	0.056
0	0.2036	0.517	-0.005	0.1808	0.3865	0.662	0.071
0	0.1040	0.511	-0.002	0.2060	0.2205	0.706	0.122
0.0128	0.9872	0.587	-0.007	0.2127	0.3726	0.688	0.089
0.0319	0.9681	0.584	-0.014	0.2214	0.0473	0.768	0.195
0.0390	0.9610	0.586	-0.013	0.2333	0.1315	0.763	0.179
0.0488	0.9512	0.584	-0.017	0.2567	0.2398	0.751	0.151
0.0588	0.9412	0.597	-0.006	0.2582	0.3038	0.740	0.134
0.0394	0.0430	0.560	0.041	0.2769	0.0633	0.839	0.249
0.0408	0.7249	0.565	-0.014	0.3167	0.2313	0.826	0.209
0.0423	0.1607	0.558	0.028	0.3189	0.0820	0.894	0.289
0.0579	0.2522	0.567	0.024	0.3219	0.1412	0.865	0.255
0.0813	0.0635	0.601	0.068	0.3825	0.0672	0.989	0.367
0.0946	0.3198	0.598	0.038	0.4097	0.1400	1.022	0.386
0.0950	0.6997	0.585	-0.008	0.4597	0.0640	1.120	0.475

Table 4. Surface Tension, σ , and Excess Surface Tension, σ^E , for the System Water (1) + Ethyl Butyrate (2) + Methanol (3) and Its Binary Constituents, at 303.15 K and Atmospheric Pressure

		σ	σ^{E}			σ	σ^{E}
<i>X</i> 1	<i>X</i> 2	$\overline{mN{\boldsymbol{\cdot}}m^{-1}}$	$\overline{mN{\boldsymbol{\cdot}}m^{-1}}$	<i>X</i> 1	<i>X</i> 2	$\overline{mN{\boldsymbol{\cdot}}m^{-1}}$	$\overline{mN \cdot m^{-1}}$
0	0.050	21.86	0.09	0.021	0.837	23.56	-0.60
0	0.101	22.03	0.18	0.190	0.050	24.08	-7.13
0	0.150	22.22	0.28	0.170	0.149	23.86	-6.53
0	0.200	22.36	0.34	0.149	0.250	23.78	-5.74
0	0.299	22.65	0.46	0.131	0.350	23.76	-5.04
0	0.400	22.85	0.48	0.111	0.450	23.74	-4.23
0	0.496	22.99	0.46	0.091	0.550	23.62	-3.53
0	0.605	23.12	0.40	0.070	0.646	23.50	-2.77
0	0.700	23.18	0.30	0.053	0.747	23.56	-2.05
0	0.800	23.29	0.23	0.279	0.050	25.10	-10.54
0	0.883	23.35	0.15	0.250	0.150	24.39	-9.98
0.055	0.945	23.60	-2.44	0.220	0.249	23.83	-9.22
0.041	0.959	23.53	-1.84	0.192	0.350	23.73	-8.10
0.018	0.982	23.46	-0.80	0.161	0.450	23.64	-6.82
0.101	0.050	23.08	-3.71	0.130	0.550	23.61	-5.48
0.090	0.150	23.18	-3.23	0.101	0.650	23.34	-4.48
0.077	0.250	23.05	-2.89	0.380	0.050	25.36	-15.30
0.069	0.345	23.19	-2.51	0.341	0.150	24.04	-14.85
0.059	0.453	23.34	-2.05	0.301	0.249	23.50	-13.57
0.051	0.549	23.42	-1.74	0.480	0.050	25.58	-20.05
0.037	0.675	23.48	-1.20	0.450	0.100	24.48	-19.75
0.033	0.745	23.58	-1.02				

methanol (3) system are presented in previous papers.^{2–4} All types of measurements were made for different compositions, since they were not performed simultaneously.

The experimental liquid interfacial tension and the values of the surface tensions of the aqueous and organic phases of the system water + ethyl butyrate + methanol are listed in Table 5.

The V^{E} and $\Delta \eta$ binary data were correlated using a Redlich–Kister type equation for the binary systems:¹⁸

$$Y_{ij} = x_i x_j \sum A_k (x_i - x_j)^k \qquad k = 0, 1, 2, ..., n$$
 (5)

where Y_{ij} represents $V^{\mathbb{E}}$ and $\Delta \eta$.

For the correlation of surface tensions of binary systems, a simple equation, proposed by Santos et al.,⁴ was used to describe the behavior of the observed systems:

$$\frac{\sigma^{\rm E}}{x_i x_i} = A + B[1 - (x_i - x_j)]^C$$
(6)

where A, B, and C are adjustable parameters.

Equation 6 correlates well the surface tensions of these systems even for the system water + methanol, which is highly nonsymmetrical with large values of $\sigma^{\text{E}.4}$

In Figures 1–3 we have plotted the experimental V^{E} , $\Delta \eta$, and σ^{E} , respectively, for the binary system ethyl butyrate (2) + methanol (3) as a function of composition of the ester. As can be seen, the agreements between experimental and correlated values are reasonable, although the V^{E} and $\Delta \eta$ values show some dispersion which is a consequence of the small absolute values of these properties.

The ternary data (V^{E} and $\Delta \eta$) were correlated by a Redlich–Kister type equation:¹⁸

$$Y_{123} = Y_{12} + Y_{13} + Y_{23} + x_1 x_2 x_3 [A_1 + B_1 (x_1 - x_2) + B_2 (x_2 - x_3)]$$
(7)

where Y_{123} represents V_{123}^E and $\Delta \eta_{123}$, the excess molar volume and the viscosity deviation data for the ternary system, and Y_{ij} are the values of the Redlich–Kister polynomial for the same properties of the binary systems, obtained by fitting eq 5.

The excess surface tension for the ternary mixtures, $\sigma^{\rm E}_{123}$, has been fitted to the equation

$$\sigma_{123}^{\rm E} = \sigma_{12}^{\rm E} + \sigma_{13}^{\rm E} + \sigma_{23}^{\rm E} + \sigma_{\rm T}^{\rm E}$$
(8)

where the ternary term, $\sigma_{\rm T}^{\rm E}$, is given by

$$\sigma_{\rm T}^{\rm E} = x_1 x_2 x_3 \frac{D_1 + D_2 (x_1 - x_2) + D_3 (x_2 - x_3)}{1 + D_4 (x_1 - x_2)} \tag{9}$$

and $\sigma^{\rm E}_{ij}$ represents the excess surface tension for the binaries, which is given by eq 6.

The Li and Fu expression⁷

$$\sigma' = \sigma'_0 \left(\frac{X}{X_0}\right)^k \tag{10}$$

where

$$X = -\ln(x_1^{\alpha} + x_2^{\beta} + x_{3p}) \tag{11}$$

was fitted to the interfacial tension σ' between the two immiscible liquid phases α and β in the ternary system. σ'_0

Table 5. Experimental Liquid Interfacial Tension, σ' , for the System Water (1) + Ethyl Butyrate (2) + Methanol (3), at 303.15 K and Atmospheric Pressure^{*a*}

overall c	overall composition		water layer		organic layer			
X1	X3	<i>X</i> 1	<i>X</i> 3	$\sigma/mN\cdot m^{-1}$	<i>X</i> 1	X3	$\sigma/mN\cdot m^{-1}$	$\sigma'/mN \cdot m^{-1}$
0.850	0	0.999	0		0.067	0		15.3
0.813	0.043	0.955	0.044	50.43	0.076	0.039	23.63	12.2
0.754	0.112	0.892	0.107	45.29	0.101	0.123	23.58	8.4
0.691	0.186	0.819	0.177	38.85	0.124	0.215	23.77	5.9
0.613	0.279	0.722	0.269	28.87	0.185	0.319	23.80	2.7

^{*a*} The surface tension, σ , and the compositions of the liquid phases at equilibrium are also indicated.

Table 6. Coefficients of Eqs 5 and 6 Fitted to the Excess Molar Volume, V^{E} , the Viscosity Deviation, $\Delta \eta$, and the Excess Surface Tension, σ^{E} , Respectively^{*a*}

system	property	A_0	A_1	A_2	S
water + ethyl butyrate ethyl butyrate+methanol	V ^E ∕cm ³ ·mol ^{−1}	1.003 - 0.159	-0.069		0.026
water + ethyl butyrate ethyl butyrate +methanol	$\Delta \eta / mPa \cdot s$	4.718 - 0.055	5.524 -0.028	0.023	0.003 0.001
water + ethyl butyrate ethyl butyrate +methanol	$\sigma^{E\ b}/mN\cdot m^{-1}$	-46.805 1.195	0.613	1.000	0.030 0.020

^{*a*} The values of the standard deviation, *S*, and the parameters are expressed in the units of the related property. ^{*b*} The coefficients A_0 , A_1 , and A_2 correspond to *A*, *B*, and *C*, respectively, in eq 6.

Table 7. Fitted Coefficients of Eq 7 to the Excess Molar Volume, V^{E} , and to the Viscosity Deviation, $\Delta \eta$, and of Eq 9 to the Excess Surface Tension, σ^{E} , for the System Water (1) + Ethyl Butyrate (2) + Methanol (3)^{*a*}

property	A_1	B_1	B_2		S
V^{E} /cm ³ ·mol ⁻¹ $\Delta \eta$ /mPa·s	$-5.688 \\ -13.393$	-2.769 -13.552	-5.99 -10.5	8 79	0.026 0.011
property	D_1	D_2	D_3	D_4	S
$\sigma^{\rm E}/{\rm mN}\cdot{\rm m}^{-1}$	-53.695	-196.907	-92.456	-1.466	0.17

^{*a*} The values of the standard deviation, *S*, and the parameters are expressed in the units of the related property.

Table 8. Coefficients of Eq 10 Fitted to the Liquid Interfacial Tension, σ' , for the System Water (1) + Ethyl Butyrate (2) + Methanol (3)

			k	
X_0^a	$\sigma_0'/\mathrm{mN}\cdot\mathrm{m}^{-1}$	k_1	k_2	$S/mN \cdot m^{-1}$
2.688	15.3	$1.156 \\ 1.355$	0 -0.157	0.29 0.02

^{*a*} X_0 is defined by eq 11 when $x_3 = 0$.



Figure 1. Excess molar volumes, $V^{\mathbb{E}}$, of ethyl butyrate (2) + methanol (3) as a function of mole fraction of the ester, x_2 , at 303.15 K and atmospheric pressure. The curve represents eq 5.

is the interfacial tension of the partially miscible binary pair, which corresponds to $x_3 = 0$ and $X = X_0$ in eq 11. x_1^{α} is the mole fraction of component 1 in the liquid phase α , which is richer in component 2, x_2^{β} is the mole fraction of component 2 in the phase richer in component 1, and x_{3p} is the mole fraction of component 3 in the phase poor in it. Li and Fu considered the parameter *k* as an adjustable one in eq 10, and they have also used a more general form, $k = k_1 + k_2 X$.

The optimized coefficients, A_k (eq 5), A, B, and C (eq 6), and the standard deviations, S, obtained from the Levenberg–Marquardt method of fitting, are given in Table 6. The coefficients A_1 and B_i of eq 7, D_i of eq 9, and the standard deviations of the corresponding fittings are given in Table 7. The parameter k has been calculated consider-



Figure 2. Viscosity departures, $\Delta \eta$, of ethyl butyrate (2) + methanol (3) as a function of mole fraction of the ester, x_2 , at 303.15 K and atmospheric pressure. The curve represents eq 5.



Figure 3. Excess surface tension, σ^{E} , of ethyl butyrate (2) + methanol (3) as a function of mole fraction of the ester, x_2 , at 303.15 K and atmospheric pressure. The curve represents eq 6.

ing that $k = k_1$ and that $k = k_1 + k_2 X$. The results of the fittings are listed in Table 8.

The standard deviation of the fittings, S, is defined as

$$S = \left[\sum (Z_{\text{exp}} - Z_{\text{calc}})^2 / (M - n)\right]^{1/2}$$
(12)

where *Z* represents V^{E} , $\Delta \eta$, σ^{E} , or σ' and *M* and *n* represent the numbers of the experimental points and parameters, respectively.

The experimental determinations of surface tension for the ternary system were made following lines of constant ratio z (= x_1/x_3). In Figure 4 we have represented experimental σ^{E} values and fitted lines of constant (x_1/x_3) obtained using eq 8.

Conclusions

The densities, viscosities, and surface and interfacial tensions of the system water + ethyl butyrate + methanol



Figure 4. Excess surface tension, $\sigma^{\rm E}$, for the ternary system water (1) + ethyl butyrate (2) + methanol (3), at 303.15 K and atmospheric pressure, along the curves of constant ratio $z = x_1/x_3$ as a function of the ester composition, x_2 . Symbols represent the experimental points. Solid curves were calculated with eq 8. The dashed line is the binodal curve.⁵

have been determined experimentally at 303.15 K and atmospheric pressure.

Binary as well as ternary $V^{\rm E}$ and $\Delta \eta$ data were correlated using only up to three parameters in the Redlich–Kister polynomials. For the binary surface tensions, correlation of the experimental data was made using a threeparameter equation (eq 6), whereas, for the ternary system, a ternary term, $\sigma_{\rm T}^{\rm E}$ (eq 9), with four adjustable constants was used.

The simple equation of Li and Fu correlates well the liquid ternary interfacial tension data, with a standard deviation of the fitting $< 0.3 \text{ mN} \cdot \text{m}^{-1}$.

Literature Cited

 Natividade, N. A. T.; Ferreira, A. G. M.; Fonseca, I. M. A. Densities and Excess Molar Volumes of Water+Propyl Acetate+Propan-1-ol and Its Constituent Binaries at 303.15 K. J. Chem. Eng. Data 1997, 42, 1232–1234.

- (2) Visak, Z. P.; Ferreira, A. G. M.; Fonseca, I. M. A. Densities and Viscosities of the Ternary Mixtures Water+Butyl Acetate+Methanol and Water+Ethyl Propionate+Methanol at 303.15 K. *J. Chem. Eng. Data* **2000**, *45*, 926–931.
- (3) Giro, F.; Gonçalves, M. F.; Ferreira, A. G. M.; Fonseca, I. M. A. Viscosity and Density Data of the System Water+n-Pentyl Acetate+Methanol. Calculations with a Redlich-Kwong-Soave Equation of State. *Fluid Phase Equilib.* **2002**, *51*, 1–16.
- (4) Santos, B. M. S.; Ferreira, A. G. M.; Fonseca, I. M. A. Surface and Interfacial Tensions of the Systems Water+n-Butyl Acetate+ Methanol and Water+n-Pentyl Acetate+Methanol at 303.15 K. *Fluid Phase Equilib.* 2003, 208, 1–21.
- (5) Rao, R. J.; Rao, C. V. Ternary Liquid Equilibria: Methanol-Water-Esters. J. Appl. Chem. 1957, 7, 435-439.
- (6) Jasper, J. J. The Surface Tension of Pure Liquid Compounds. J. Phys. Chem. Ref. Data 1972, 1, 841–1009.
- (7) Li, B.; Fu, J. Interfacial Tensions of Two-Liquid-Phase Ternary Systems. J. Chem. Eng. Data 1992, 37, 172–174.
- (8) Dizechi, M.; Marschall, E. Viscosity of Some Binary and Ternary Liquid Mixtures. J. Chem. Eng. Data 1982, 27, 358–363.
- (9) Rao, R. J.; Rao, C. V. Ternary Liquid Equilibria Systems: N-Propanol-Water-Esters. J. Appl. Chem. 1959, 9, 69-73.
- (10) Oswald, S. R.; Oswald, P.; Dave, J. P. V^E of Mixtures Containing Alkyl Acetate, or Ethyl Alkanoate, or Ethyl Bromoalkanoate with n-Hexane. *Fluid Phase Equilib.* **1994**, *98*, 225–234.
- (11) Wilhoit, R. C.; Zwolinski, B. J. Physical and Thermodynamic Properties of Aliphatic Alcohols. J. Phys. Chem. Ref. Data 1973, 2, Suppl. 1.
- (12) Pikkarainen, L. Densities and Viscosities of Binary Mixtures of N,N-Dimethylacetamide with Aliphatic Alcohols. J. Chem. Eng. Data 1983, 28, 344–347.
- (13) Kestin, J.; Sokolov, M.; Wakeham, W. A. Viscosity of Liquid Water in the Range -8 °C to 150 °C. J. Phys. Chem. Ref. Data 1978, 7, 941-948.
- (14) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
- (15) Aralaguppi, M. I.; Jadar, C. V.; Aminabhavi, T. M. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Acrylonitrile with Methanol, Ethanol, Propan-1-ol, Butan-1-ol, Pentan-1-ol, Hexan-1-ol, Heptan-1-ol, and Butan-2ol. J. Chem. Eng. Data 1999, 44, 216-221.
- (16) Aminabhavi, T. M.; Patil, V. B. Density, Viscosity, and Speed of Sound in Binary Mixtures of 1-Chloronaphthalene with Methanol, Ethanol, Propan-1-ol, Butan-1-ol, Pentan-1-ol, and Hexan-1-ol in the Temperature Range (298.15–308.15) K. J. Chem. Eng. Data 1998, 43, 504–508.
- (17) Lide, D. R. Handbook of Chemistry and Physics, 76th ed.; CRC Press: New York, 1995.
- (18) Redlich, O.; Kister, A. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, 40, 345–348.

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