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Densities and Viscosities of the Ternary Mixtures Water + Butyl Acetate + Methanol and Water + Ethyl Propionate + Methanol at 303.15 K

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The excess molar volumes, V^E, and viscosity deviations, $\Delta\eta$, were calculated from the measured density and viscosity values over the whole miscibility composition ranges for the ternary systems water + butyl acetate + methanol and water + ethyl propionate + methanol and their constituent binaries, at 303.15 K and atmospheric pressure. A Redlich−Kister type equation was used to correlate binary V^E and $\Delta\eta$ data, as well as the ternary data. This equation was used to calculate the above referred properties along the binodal curve.

Introduction

Rao and Rao determined the solubility curves and tie-line data for liquid systems of the type water + ester + methanol[1] and water + ester + propan-1-ol[2] at 303.15 K. The aim of this research was to find a suitable solvent for the extraction of the alcohols from their aqueous solutions. Indeed, for a conventional liquid−liquid extraction (i.e. not supercritical) the right selection of the solvent is the key to a successful separation. On the other hand, the knowledge of the density and the viscosity of multicomponent systems is essential in many industrial applications.

The mixture functions, such as the excess molar volume, V^E, and viscosity deviations, $\Delta\eta$, are often used to describe the intermolecular forces in mixtures, helping us to understand their real behavior and develop models for its description.

The cited references have suggested to us a systematic study of densities and excess volumes, viscosities, and viscosity deviations, involving the ternary mixtures mentioned above. In a previous paper,[3] we have reported densities and V^E values for the system water + propyl acetate + propan-1-ol at 303.15 K. In the present work we have determined densities, excess molar volumes, viscosities, and viscosity deviations for the ternaries water + butyl acetate + methanol and water + ethyl propionate + methanol, at the same temperature.

Experimental Section

Materials. Tridistilled water was used. Methanol was supplied by Fluka AG and Lab-Scan with a purity > 99.8 mass % (HPLC grade). Ethyl propionate was supplied by Riedel de Haen, while butyl acetate was from Aldrich, both with purity > 99 mass %. Table 1 lists the measured densities and viscosities of the alcohol and of the two esters together with the values found in the literature. Since the agreement is good, and having in mind that small concentrations of impurities have little influence on the excess molar volumes,[13] all the compounds were used without further purification. Mixtures were prepared by mass using a Mettler AT 200 balance with a precision of $\pm 10^{-5}$g.

Table 1. Densities, ρ/(g cm^{-3}), and Viscosities, η/(mPa s), of the Pure Components at 303.15 K

	ρ		η	
component	exptl	lit.	exptl	lit.
water		0.995 70[4]		0.797[8]
methanol	0.781 99	0.781 96[5] 0.781 82[6] 0.782 00[1]	0.516	0.510[9] 0.503[10]
butyl acetate	0.871 20	0.871 23[7] 0.871 00[1]	0.631	0.636[11] 0.623[12]
ethyl propionate	0.878 87	0.879 00[1]	0.494	0.474[11]

Measurements. Densities were measured in an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 602 measuring cell. Air and tridistilled water were used for the calibration of the densimeter. Viscosities were obtained with a Haake Falling Ball Viscosimeter (Hoppler design), calibrated with tridistilled water. The electronic digital stopwatch, with the uncertainty ±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 the Haake D8-G thermostatic water bath, which has a temperature precision of ±0.01 K. In the case of density measurements, the Pt resistance thermometer (calibrated against a precision mercury thermometer, graduated in 0.01 °C, certified by NPL, U.K.) was placed inside the vibrating tube densimeter to find the actual temperature of the measurements. The temperature was maintained at (303.15 ± 0.01) K.

Uncertainties. Densities were measured to a precision of 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 law of errors is 5×10^{-3} cm^3 mol^{-1}. Using a similar methodology and taking into consideration the uncertainties in the measured time and in the density, the experimental uncertainty in the viscosity is ±0.001 mPa s.

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Table 2. Densities, ρ/(g cm^{-3}), and Excess Molar Volumes, V^E/(cm^3 mol^{-1}), for the System Water (1) + Butyl Acetate (2) + Methanol (3) and Its Binary Constituents, at 303.15 K and Atmospheric Pressure

x_1	x_2	ρ	V^E	x_1	x_2	ρ	V^E
0.0273	0.1466	0.817 83	−0. 101	0.1998	0	0.817 41	−0.637
0.0288	0.6193	0.859 37	−0.079	0.2055	0	0.818 52	−0.651
0.0358	0.7744	0.866 23	−0.067	0.2273	0	0.822 48	−0.691
0.0498	0.2836	0.837 91	−0.151	0.2526	0	0.827 32	−0.746
0.0499	0.3445	0.843 52	−0.140	0.2777	0	0.832 33	−0.802
0.0522	0.0545	0.804 05	−0.172	0.2985	0	0.836 42	−0.840
0.0550	0.4728	0.853 15	−0.114	0.3014	0	0.836 97	−0.849
0.0632	0.7524	0.867 14	−0.103	0.3532	0	0.847 00	−0.905
0.0893	0.5807	0.861 94	−0.172	0.4013	0	0.857 06	−0.977
0.1204	0.4400	0.856 76	−0.230	0.4042	0	0.857 32	−0.964
0.1353	0.1303	0.829 88	−0.383	0.4303	0	0.862 72	−0.983
0.1409	0.3115	0.850 03	−0.325	0.4824	0	0.873 61	−1.004
0.1460	0.5445	0.864 68	−0.265	0.4994	0	0.877 48	−1.017
0.1513	0.0488	0.818 67	−0.460	0.5521	0	0.888 57	−0.997
0.1601	0.2507	0.846 97	−0.388	0.5997	0	0.899 12	−0.971
0.1742	0.5266	0.866 07	−0.303	0.6500	0	0.910 79	−0.932
0.1801	0.2973	0.853 05	−0.396	0.6956	0	0.920 56	−0.853
0.2063	0.3971	0.862 06	−0.370	0.7182	0	0.925 87	−0.815
0.2269	0.2804	0.856 89	−0.476	0.7501	0	0.933 24	−0.752
0.2439	0.1139	0.843 27	−0.612	0.7729	0	0.938 46	−0.701
0.2489	0.0432	0.834 12	−0.685	0.7734	0	0.938 58	−0.698
0.2504	0.2719	0.858 93	−0.515	0.8108	0	0.947 14	−0.600
0.2524	0.3741	0.865 15	−0.434	0.8500	0	0.956 13	−0.484
0.2561	0.2220	0.855 85	−0.558	0.8999	0	0.967 86	−0.321
0.2794	0.2614	0.861 45	−0.554	0.9198	0	0.972 78	−0.253
0.2988	0.3509	0.868 44	−0.489	0	0.0575	0.796 97	−0.012
0.3123	0.2495	0.864 48	−0.598	0	0.1507	0.814 91	−0.018
0.3497	0.0374	0.851 12	−0.849	0	0.2530	0.829 07	−0.024
0.3509	0.2354	0.868 16	−0.641	0	0.2984	0.834 13	−0.028
0.3511	0.0978	0.857 92	−0.778	0	0.3625	0.840 21	−0.032
0.3795	0.2250	0.870 99	−0.667	0	0.5002	0.850 61	−0.037
0.4505	0.0316	0.869 36	−0.940	0	0.6335	0.858 01	−0.032
0.4524	0.0825	0.873 06	−0.863	0	0.7230	0.862 01	−0.026
0.5425	0.0690	0.887 89	−0.882	0	0.8032	0.865 11	−0.021
0.5485	0.0260	0.888 35	−0.956	0	0.9201	0.869 88	−0.014
0.6301	0.0213	0.905 29	−0.915				
0.0435	0	0.789 47	−0.170				
0.1031	0	0.799 72	−0.362				
0.1482	0	0.807 88	−0.500				
0.1722	0	0.812 23	−0.563				

Results and Discussion

The excess molar volumes, V^E, were calculated from the equation

$$V^E = \rho^{-1}(\sum x_i M_i) - \sum x_i M_i \rho_i^{-1} \qquad (1)$$

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

$$\eta = K(\rho_b - \rho)t \qquad (2)$$

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.

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

$$\Delta\eta = \eta - \sum x_i \eta_i \qquad (3)$$

where η is the measured mixture viscosity and η_i represents the pure component viscosity. The viscosity measurements were made for different compositions than those for the density measurements, since they were not performed simultaneously. For that reason, the density value needed to obtain the viscosity by eq 2 was calculated with eq 1.

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

x_1	x_2	ρ	V^E	x_1	x_2	ρ	V^E
0.0428	0.6726	0.868 59	−0.124	0.3110	0.1031	0.855 24	−0.802
0.0476	0.3750	0.848 80	−0.169	0.3322	0.3309	0.878 28	−0.685
0.0497	0.1422	0.820 60	−0.192	0.3490	0.2556	0.875 44	−0.746
0.0509	0.4703	0.857 02	−0.175	0.3507	0.0972	0.861 17	−0.857
0.0510	0.0476	0.802 31	−0.186	0.3514	0.0657	0.857 05	−0.870
0.0511	0.2861	0.840 35	−0.192	0.3516	0.0322	0.852 14	−0.890
0.0512	0.0962	0.812 39	−0.183	0.3547	0.1452	0.866 93	−0.820
0.0550	0.2126	0.831 67	−0.194	0.3997	0.1809	0.876 94	−0.836
0.0976	0.7219	0.875 31	−0.205	0.4002	0.1349	0.873 22	−0.874
0.0986	0.0452	0.809 64	−0.340	0.4009	0.0298	0.861 23	−0.944
0.0988	0.2028	0.836 22	−0.313	0.4011	0.0896	0.868 94	−0.911
0.0997	0.3545	0.852 76	−0.293	0.4012	0.0607	0.865 40	−0.924
0.1003	0.1346	0.826 66	−0.335	0.4015	0.2350	0.880 98	−0.796
0.1003	0.2712	0.844 80	−0.320	0.4237	0.2263	0.883 44	−0.810
0.1017	0.0911	0.819 31	−0.341	0.4499	0.1237	0.880 35	−0.910
0.1034	0.4443	0.860 48	−0.293	0.4500	0.0274	0.870 57	−0.979
0.1080	0.5389	0.867 25	−0.295	0.4500	0.0558	0.873 87	−0.960
0.1086	0.6264	0.871 83	−0.253	0.4502	0.0823	0.876 56	−0.936
0.1444	0.6012	0.873 75	−0.321	0.4526	0.1650	0.883 73	−0.873
0.1491	0.2565	0.849 44	−0.437	0.5000	0.0249	0.880 37	−0.997
0.1500	0.1272	0.833 05	−0.472	0.5000	0.0507	0.882 98	−0.979
0.1501	0.0862	0.826 16	−0.477	0.5000	0.0748	0.885 01	−0.958
0.1503	0.3346	0.856 90	−0.408	0.5012	0.1122	0.888 08	−0.930
0.1504	0.1912	0.841 88	−0.446	0.5053	0.1491	0.890 82	−0.887
0.1531	0.5116	0.869 95	−0.380	0.5497	0.0224	0.890 45	−0.995
0.1539	0.0424	0.818 42	−0.500	0.5503	0.0673	0.893 89	−0.960
0.1556	0.4185	0.864 17	−0.404	0.6002	0.0598	0.903 11	−0.943
0.1777	0.5778	0.875 58	−0.378	0.6012	0.0198	0.901 27	−0.974
0.1944	0.4866	0.872 63	−0.457	0.6258	0.0184	0.906 80	−0.964
0.1998	0.0400	0.825 96	−0.618	0.6259	0.0560	0.908 03	−0.926
0.1999	0.2412	0.854 54	−0.550	0.6499	0.0172	0.912 04	−0.940
0.2002	0.1800	0.847 59	−0.561	0.6750	0.0160	0.917 53	−0.910
0.2002	0.3149	0.861 18	−0.510	0	0.0503	0.794 74	−0.006
0.2004	0.0811	0.833 44	−0.598	0	0.0703	0.799 32	−0.012
0.2005	0.1197	0.839 76	−0.595	0	0.1001	0.805 51	−0.017
0.2272	0.3830	0.869 50	−0.532	0	0.1203	0.809 40	−0.021
0.2464	0.4553	0.876 13	−0.540	0	0.1479	0.814 31	−0.023
0.2495	0.1689	0.853 46	−0.660	0	0.1734	0.818 60	−0.031
0.2505	0.2259	0.859 81	−0.644	0	0.2505	0.829 75	−0.040
0.2511	0.2949	0.865 84	−0.605	0	0.4031	0.846 34	−0.055
0.2513	0.0759	0.841 09	−0.706	0	0.5006	0.854 27	−0.056
0.2516	0.1120	0.846 73	−0.699	0	0.6063	0.861 27	−0.045
0.2554	0.0373	0.835 27	−0.735	0	0.6513	0.863 84	−0.037
0.2753	0.3592	0.873 43	−0.611	0	0.7085	0.866 89	−0.032
0.2998	0.1576	0.859 74	−0.747	0	0.7384	0.868 37	−0.029
0.3001	0.0348	0.842 88	−0.808	0	0.7722	0.869 74	−0.022
0.3028	0.2738	0.870 74	−0.686	0	0.8510	0.873 35	−0.013
0.3099	0.0700	0.850 29	−0.811				

Table 4. Viscosities, η/(mPa s), and Viscosity Deviations, $\Delta\eta$/(mPa s), for the System Water (1) + Butyl Acetate (2) + Methanol (3) and Its Binary Constituents, at 303.15 K and Atmospheric Pressure

x_1	x_2	η	$\Delta\eta$	x_1	x_2	η	$\Delta\eta$
0.1081	0.2745	0.649	0.071	0.1232	0	0.625	0.074
0.1853	0.2501	0.709	0.112	0.1599	0	0.679	0.118
0.2411	0.2336	0.776	0.165	0.2168	0	0.765	0.188
0.3114	0.2119	0.845	0.217	0.2992	0	0.874	0.274
0.4010	0.1843	0.921	0.271	0.3639	0	0.972	0.354
0.0936	0.4363	0.657	0.061	0.3948	0	1.021	0.394
0.1699	0.4305	0.698	0.110	0.4567	0	1.129	0.485
0.2025	0.3839	0.711	0.128	0.5837	0	1.310	0.630
0.2732	0.3770	0.776	0.140	0.8272	0	1.319	0.571
0.0200	0.1967	0.563	0.019	0.8782	0	1.213	0.450
0.0785	0.1850	0.628	0.069	0.8860	0	1.185	0.420
0.0511	0.0752	0.574	0.035	0.9125	0	1.110	0.349
0.0806	0.0728	0.602	0.055	0	0.0963	0.528	0.001
0.2189	0.0619	0.735	0.150	0	0.1331	0.533	0.002
0.3238	0.0536	0.855	0.242	0	0.1759	0.539	0.003
0.0673	0.1624	0.608	0.054	0	0.2825	0.552	0.004
0.1631	0.1457	0.704	0.125	0	0.3931	0.566	0.005
0.3747	0.1089	0.978	0.344	0	0.4804	0.577	0.006
0.0773	0.1859	0.621	0.062	0	0.5458	0.585	0.006
0.1672	0.1678	0.699	0.117	0	0.6116	0.592	0.006
0.1519	0.3474	0.725	0.126	0	0.6478	0.596	0.006
0.2511	0.3068	0.784	0.162	0	0.7391	0.606	0.005
0.0892	0.3823	0.667	0.082	0	0.8007	0.612	0.004
0.1313	0.3646	0.705	0.110	0	0.8409	0.616	0.003
0.1242	0.5228	0.634	0.095	0	0.8858	0.621	0.003
0.1510	0.5067	0.665	0.118	0	0.9240	0.624	0.002
0.0804	0.6256	0.591	0.066				

Table 5. Viscosities, η/(mPa s), and Viscosity Deviations, $\Delta\eta$/(mPa s), for the System Water (1) + Ethyl Propionate (2) + Methanol (3) and Its Binary Constituents, at 303.15 K and Atmospheric Pressure

x_1	x_2	η	$\Delta\eta$	x_1	x_2	η	$\Delta\eta$
0.2875	0.1830	0.769	0.176	0	0.1102	0.524	0.010
0.4750	0.1649	1.016	0.370	0	0.1551	0.525	0.012
0.0830	0.2343	0.560	0.026	0	0.2735	0.526	0.016
0.1337	0.2329	0.589	0.041	0	0.3189	0.527	0.018
0.0650	0.1491	0.568	0.037	0	0.3721	0.528	0.020
0.1094	0.1447	0.608	0.064	0	0.4967	0.527	0.022
0.1512	0.1301	0.652	0.096	0	0.5395	0.524	0.020
0.2028	0.1265	0.727	0.157	0	0.6130	0.521	0.019
0.2551	0.1160	0.758	0.173	0	0.6625	0.518	0.017
0.2242	0.3689	0.629	0.058	0	0.7231	0.514	0.014
0.1118	0.4561	0.565	0.028	0	0.8087	0.508	0.010
0.1403	0.3921	0.601	0.054	0	0.9141	0.501	0.005
0.0911	0.3734	0.590	0.057				
0.1302	0.3507	0.606	0.061				
0.1248	0.5418	0.622	0.083				
0.0531	0.5918	0.553	0.035				
0.1152	0.6309	0.594	0.060				
0.0531	0.6649	0.565	0.049				
0.0587	0.7049	0.568	0.115				
0.2542	0.3066	0.736	0.155				

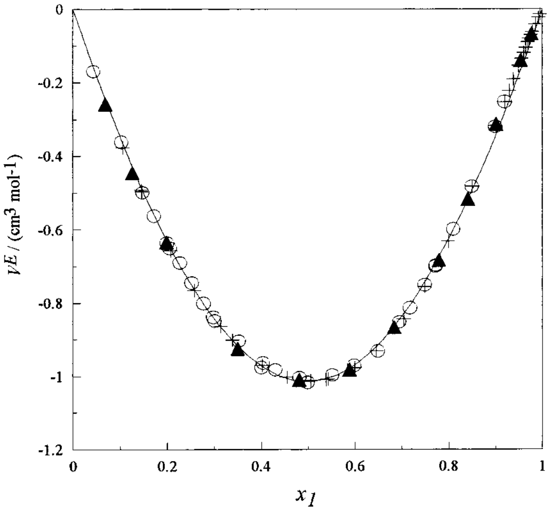


Figure 1. V^E of water (1) + methanol (3) as a function of mole fraction of water: (○) this work; (+) Benson and Kiyohara;[14] (▲) Dizechi and Marschall.[4]

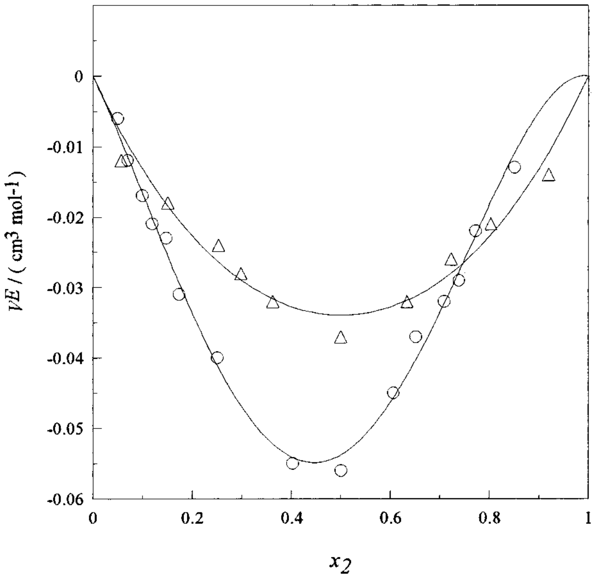


Figure 2. Excess molar volumes, V^E, of methanol + ester as a function of mole fraction of the ester, x_2, at 303.15 K and atmospheric pressure: (△) butyl acetate; (○) ethyl propionate.

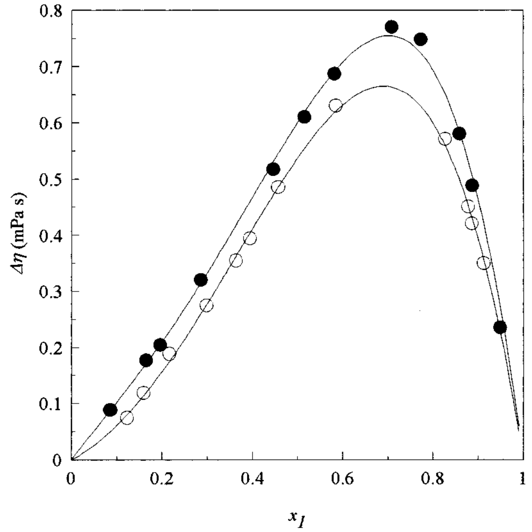


Figure 3. Viscosity departures, $\Delta\eta$, of water + methanol as a function of mole fraction of water, x_1, at atmospheric pressure: (○) this work, at 303.15 K; (●) Noda et al.,[16] at 298.15 K.

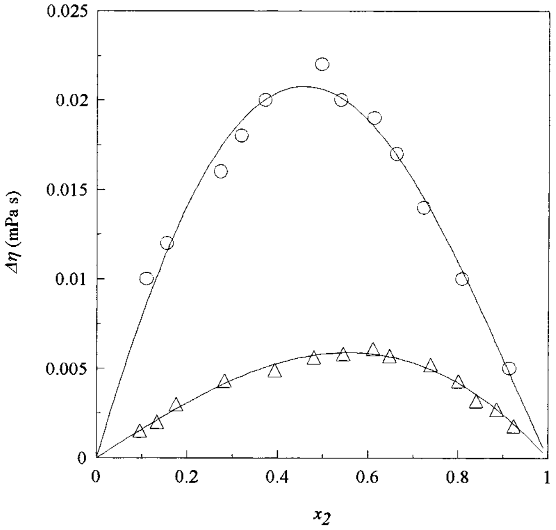
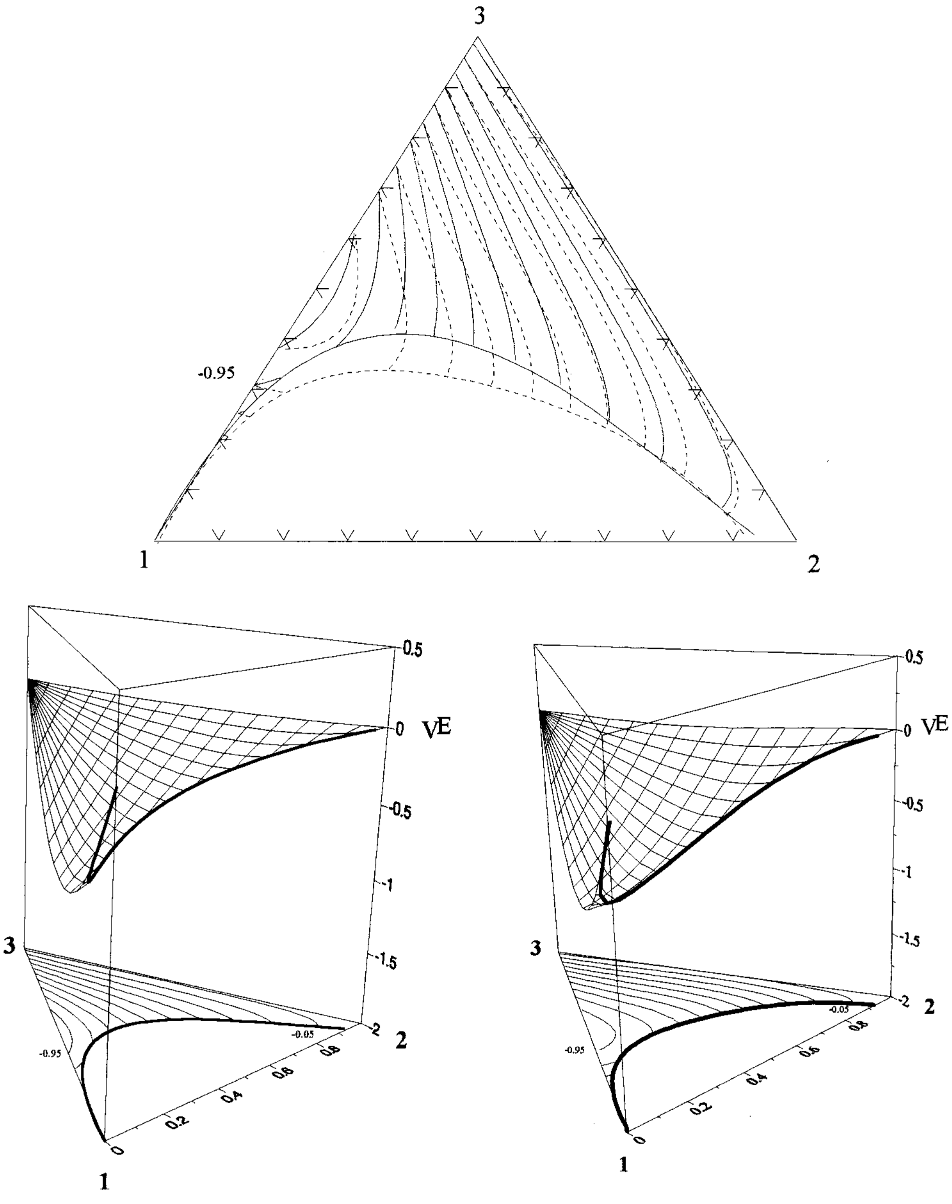


Figure 4. Viscosity departures, $\Delta\eta$, of ester + methanol as a function of mole fraction of the ester, x_2, at 303.15 K and atmospheric pressure: (△) butyl acetate; (○) ethyl propionate.

Tables 2 and 3 list the measured densities, ρ, and the corresponding values of V^E for the two ternary systems, whereas Tables 4 and 5 present the measured viscosities, η, and the corresponding $\Delta\eta$ values for the same ternaries. Results for the constituent binaries water (1) + methanol (3) and ester (2) + methanol (3) are also included.

In Figure 1 we have plotted the experimental V^E values for the binary water (1) + methanol (3) measured by several authors together with our own, which shows a good agreement. The experimental V^E values for the binaries ester (2) + methanol (3) are represented against the mole fraction of the ester in Figure 2. As far as we know, these values have not been published before.

We have not found in the literature any binary viscosity data at 303.15 K for the system water (1) + methanol (3). The only values available in the literature are for 298.15 K. In Figure 3 we compare our measured $\Delta\eta$ values at 303.15 K with the data from the literature at 298.15 K. As we can see, both sets of points show the same trend. In Figure 4 we have presented the experimental $\Delta\eta$ values for the binaries ester (2) + methanol (3) as a function of the mole fraction of the ester. We have not found



water(1)+butyl acetate(2) +methanol(3)

water(1) + ethyl propionate(2) + methanol(3)

Figure 5. Excess molar volume isolines and perspective views of V^E (cm^3 mol^{-1}) for water (1) + butyl actate (2) + methanol (3) (—) and water (1) + ethyl propionate (2) + methanol (3) (- - -) at 303.15 K and atmospheric pressure. The increment of V^E is 0.1 cm^3 mol^{-1}.

in the literature any $\Delta\eta$ experimental values for these systems.

The V^E and $\Delta\eta$ binary data were correlated using a Redlich–Kister type equation for the binary systems:[15]

$$X_{ij} = x_i x_j \sum A_k (x_i - x_j)^k \qquad k = 0, 1, 2, ..., n \qquad (4)$$

where X represents V^E and $\Delta\eta$.

The ternary data (V^E and $\Delta\eta$) were correlated by a Redlich–Kister type equation for the ternaries:[15]

$$X_{123} = X_{12} + X_{23} + X_{13} + x_1 x_2 x_3 [A + B_1(x_1 - x_2) + B_2(x_2 - x_3)] \qquad (5)$$

where X_{123} represents the excess molar volume and the viscosity data for the ternary system and X_{ij} are the values of the Redlich–Kister polynomial for the same properties, obtained by fitting eq 4 to the binary data.

Several authors have used the Cibulka's equation,[17]

$$\Delta\eta_{123} = \Delta\eta_{12} + \Delta\eta_{13} + \Delta\eta_{23} + x_1 x_2 x_3 (C_0 + C_1 x_1 + C_2 x_2) \qquad (6)$$

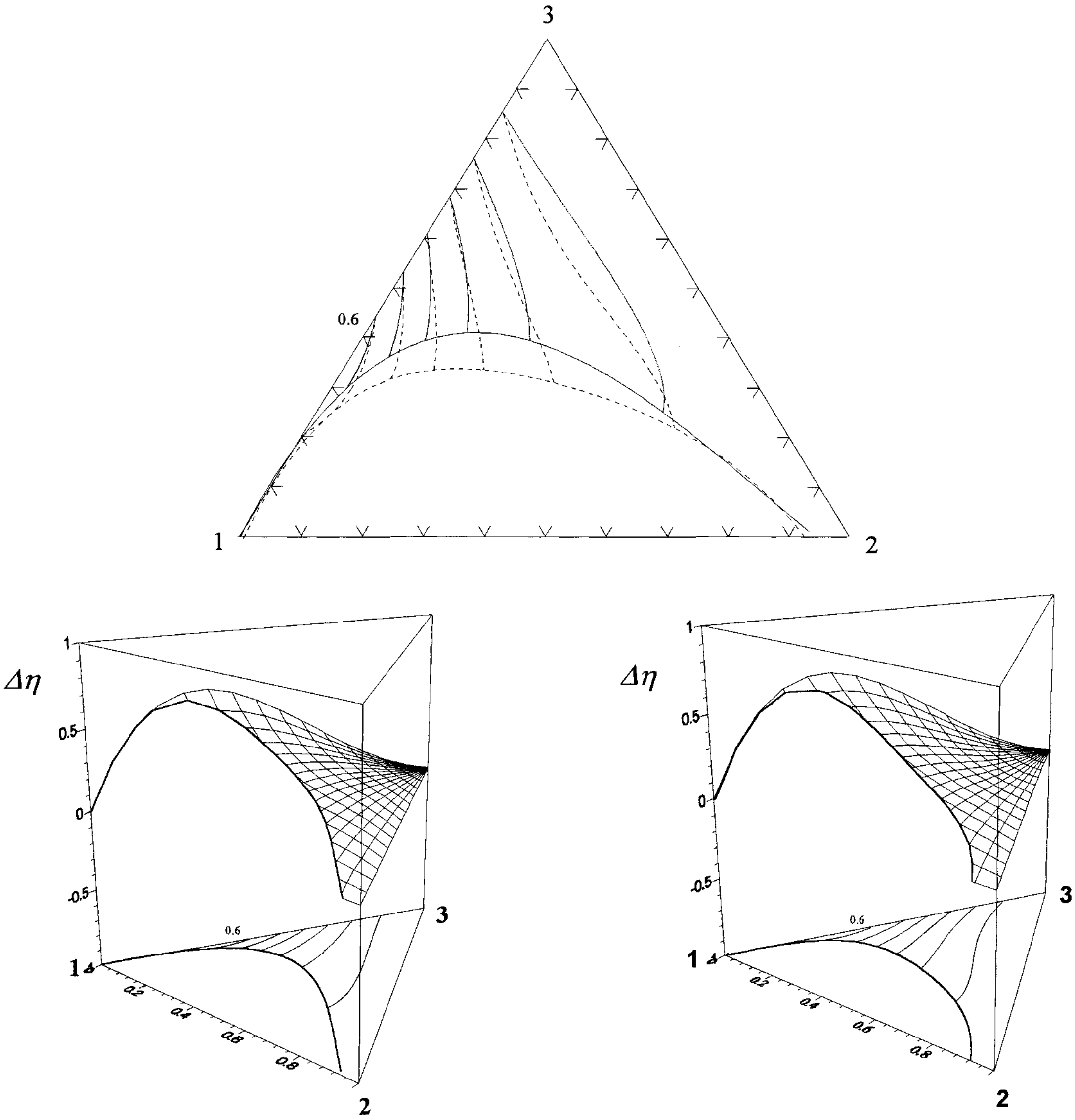
to describe the ternary $\Delta\eta$ data, where the terms have a similar meaning as in eq 5. This equation differs from the Redlich–Kister one in the form of the ternary contribution. However, both forms are equivalent, since their coefficients are related by the following expressions

$$C_0 = A - B_2, \quad C_1 = B_1 + B_2, \quad \text{and} \quad C_2 = 2B_2 - B_1 \qquad (7)$$

Thus, to be consistent, we decided to treat all the experimental data with the Redlich–Kister equation.

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

$$\sigma = [\sum (X_{\text{exp}} - X_{\text{calc}})^2/(M - n)]^{1/2} \qquad (8)$$



water(1)+butyl acetate(2)+methanol(3)

water(1)+ethyl propionate(2)+methanol(3)

Figure 6. Isolines and perspective views of $\Delta\eta$ (mPa s) for water (1) + butyl acetate (2) + methanol (3) (—) and water (1) + ethyl propionate (2) + methanol (3) (- - -) at 303.15 K and atmospheric pressure. The increment of $\Delta\eta$ is (−0.1) mPa s.

Table 6. Coefficients of Eq 4 Fitted to the Excess Volume, V^E/(cm^3 mol^{-1}), and Viscosity Deviation, $\Delta\eta$/(mPa s), for the Binary Systems[a]

system	property	A_0	A_1	A_2	σ
water + methanol	V^E	−4.053	0.024	0.316	0.012
butyl acetate + methanol		−0.136	−0.001	−0.018	0.003
ethyl propionate + methanol		−0.215	0.080	0.146	0.002
water + methanol	$\Delta\eta$	2.149	2.308	0.578	0.010
butyl acetate + methanol		0.023	0.006		0.001
ethyl propionate + methanol		0.081	−0.016		0.001

[a] The value of the standard deviation, σ, and the parameters are expressed in the units of the related property.

where X is V^E or $\Delta\eta$ and M and n represent the numbers of the experimental points and parameters, respectively.

The optimized coefficients, A_k, and the standard deviations, σ, for binary V^E and $\Delta\eta$ data are listed in Table 6. V_{12}^E and $\Delta\eta_{12}$ are taken to be identically zero, since water and the ester are practically immiscible. The coefficients A and B_i of eq 5 and the standard deviations of the corresponding fittings are given in Table 7.

Table 7. Coefficients of Eq 5 Fitted to the Excess Volume, V^E/(cm^3 mol^{-1}), and Viscosity Deviation, $\Delta\eta$/(mPa s), for the Ternary Systems[a]

ester	property	A	B_1	B_2	σ
butyl acetate	V^E	−1.805	−3.949	−6.801	0.010
ethyl propionate		−5.824	−6.931	−9.537	0.015
butyl acetate	$\Delta\eta$	−1.669	−6.742	−2.302	0.015
ethyl propionate		−1.140	−0.764	3.129	0.024

[a] The value of the standard deviation, σ, and the parameters are expressed in the units of the related property.

In Figures 5 and 6 are shown the isolines and the perspective views of the excess molar volumes and the viscosity deviations for the ternary systems.

Conclusions

The determined values of the excess molar volumes for the binaries and ternaries at 303.15 K and atmospheric pressure are all negative. The minimum V^E value obtained from eq 5 for each ternary system is located on the V^E curve of the binary water + methanol ($x_1 = 0.4980$, $V^E = -1.013$ cm^3 mol^{-1}). The $\Delta\eta$ values are all positive with a maximum on the binary water + methanol ($x_1 = 0.6893$, $\Delta\eta = 0.665$ mPa s).

The binary V^E data as well as the ternary ones were correlated using only three parameters in the Redlich−Kister polynomials, whereas, for the correlation of the binary $\Delta\eta$ data, even two coefficients were enough for a good fitting.

Since we have measured densities in the whole miscibility region including the proximity of the binodal curve, we have calculated the density values for this curve using the eqs 1, 4, and 5. The aim of this procedure was to compare our calculated densities with the experimental data of Rao and Rao.[1] We found that their data are systematically higher than our calculated values, although the mean percentage deviation is 0.5%. In our opinion, this fact is due to the high density of the water used in their experiments, which value is not mentioned in their work.

The viscosity is a very important property in the design of liquid−liquid separation equipments. Equations 3− 5 can be used to calculate the viscosities of the equilibrium phases.

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