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THERMODYNAMIC PROPERTIES OF ALKANEDIOLS+ ACETATES AT 298.15 K

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Abstract

In this work we present experimental values of the density, refractive index, speed of sound, isentropic compressibility and liquid-liquid equilibria of the binary mixtures (methyl acetate, ethyl acetate, propyl acetate, and butyl acetate) with (1,2-ethanediol, 1,2-propanediol, or 1,3-propanediol) at 298.15 K and atmospheric pressure, as a function of mole fraction. From the experimental values, the corresponding excess and deviation values were computed (excess molar volumes, changes of refractive index on mixing, and changes of isentropic compressibility), variable-degree polynomials being fitted to the results. The validity of different estimation methods for predicting the experimental values of physical properties was tested. The limiting partial excess molar volume of the components in each binary mixture was determined by means of predetermined Redlich-Kister parameters. Group contribution method (UNIFAC-Dortmund) was applied in order to compare their capability in predicting the experimental equilibria values.

Keywords: binary mixtures,butyl acetate, 1,2-ethanediol, ethyl acetate, experimental, liquid-liquid equilibria, methyl acetate, prediction, 1,2-propanediol, 1,3-propanediol, propyl acetate, thermodynamic properties

Introduction

The capability of alcohol or polyol + ester mixtures are being studied in recent years as alternative separation agent/coagent in modified rectification processes for binary azeotropes. The type and nature of the molecular interactions are investigated in terms of the derived properties (excess molar volumes, changes of refractive index on mixing, etc.) and non-ideality of phase equilibria, an important information about mixture interaction and structure being provided with the variation of these properties with composition and temperature. As a continuation of our programme on thermodynamic properties and phase equili-

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bria of binary and ternary non-electrolyte systems related to homogeneous and heterogeneous extractive distillation, we report experimental data on densities, refractive indices and speeds of sound of the mixtures of (methyl acetate, ethyl acetate, propyl acetate, and butyl acetate) + (1,2-ethanediol, 1,2-propanediol, or 1,3-propanediol), which were measured at 298.15 K and atmospheric pressure, over the entire range of composition, and liquid-liquid equilibria data for these mixtures in the range 273.15 to 298.15 K. From the experimental values, the corresponding excess and deviation values were computed (excess molar volumes, changes of refractive index on mixing, and changes of isentropic compressibility), variable-degree polynomials being fitted to the results. Prediction of properties values was performed applying different methods (Narsimham (Narsimham [1]), Newton (Kurtz and Ward [2]), and Nomoto (Nomoto [3])). The binodal tie lines for each binary mixture and temperature were calculated by the measurement of the different physical properties, which were measured and fitted previously, the procedure being proved to be consistent. UNIFAC-Dortmund group contribution method (Weidlich and Gmehling [4], Gmehling *et al.* [5]) was applied in order to test their validity to predict experimental binary values of these mixtures.

Experimental

All the chemicals were obtained from Merck (LiChrosolv quality), which were recently acquired and kept in an argon atmosphere (N-55, 2 ppmv), as soon as the bottles were opened. They were degassed ultrasonically (at least 3 h) and dried over molecular sieves Type 4A or 3A, 1/16 inch (Aldrich cat. n^o 20,860-4 or 20,858-2, respectively). Precautions were taken, such as cooling the chemicals before preparation of samples and reducing to a minimum the vapor space in the vessels, in order to avoid losses by evaporation during laboratory manipulation and possible errors in composition calculations. Chromatographic (GLC) tests of the solvents showed purities which fulfilled vendor specifications. Their mole fraction purities were compiled in Table 1. A CA-06 Mitsubishi coulometer was used to determine their maximum water content and are showed in Table 1. The purity of the solvents was ascertained by comparing their physical properties with literature findings (Table 1). A PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K was used to thermostat the samples which stayed at the measured temperature for at least 30 min. Samples were prepared by mass using a Mettler At 261 Delta Range balance with a precision of $\pm 10^{-5}$ g. The densities were measured with an Anton Paar DMA-60/602 densimeter with an accuracy of $\pm 10^{-5}$ g cm^{-3}. Speeds of sound of mixtures and pure liquids were measured with an Anton Paar DSA-48 densimeter and sound analyzer with a pre-

Table 1 Purity, maximum water content and comparison of data with literature for pure liquids at 298.15 K

Component	Purity/ mol%	Max. water content/mass%	ρ(298.15 K)/g cm^{-3}		n_D(298.15 K)	
			exptl.	lit.[a]	exptl.	lit.[a]
Methyl acetate	>99.0	$6.8\cdot10^{-3}$	0.92674	0.9273	1.35850	1.3589
Ethyl acetate	>99.8	$7.2\cdot10^{-2}$	0.89436	0.8940	1.36939	1.3704
Propyl acetate	>99.0	$4.8\cdot10^{-1}$	0.88313	0.8826	1.38171	1.3828
Butyl acetate	>99.7	$2.9\cdot10^{-2}$	0.87617	0.8766	1.39163	1.3918
1,2-ethanediol	>99.5	$1.4\cdot10^{-1}$	1.10987	1.1100	1.43028	1.4306
1,2-propanediol	>99.5	$1.2\cdot10^{-1}$	1.03274	1.0328	1.43122	1.4314
1,3-propanediol	>99.0	$9.1\cdot10^{-2}$	1.05007	1.0500	1.43830	1.4386

[a] TRC Thermodynamic Table (1994)

cision of ±0.1 m s^{-1}. Refractive indices were measured using an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of $\pm10^{-5}$, calibration checks of the refractometer are done routinely with the help of tridistilled water (Millipore quality) and ambient air. Double liquid reference was used for the densimeter calibration (Millipore quality water and degassed and dried Merck quality *n*-heptane). Accuracy in the calculated excess molar quantities and changes on mixing was estimated as better than 10^{-3} cm^3 mol^{-1} for excess molar volumes, $5\cdot10^{-5}$ for changes of refractive index on mixing, and 2 TPa^{-1} for changes of isentropic compressibility. The experimental technique and mode of operation have been described previously (Iglesias *et al.* [7]). The equilibrium runs were performed in a glass extraction cell surrounded by a water jacket in order to maintain a constant temperature. This jacket were thermostatically controlled ($\pm5\cdot10^{-2}$ K inside the cell) using a bath Polyscience model 9010, with a stability of $\pm10^{-2}$ K. The cell constituents were prepared by volume and stirred for several minutes and allowed to settle at least for 6 h. Longer mixing and settling periods did not result in any change in the phase mole fractions. Temperature in the cell was measured with a Yokogawa 7563 digital thermometer with a precision of $\pm10^{-2}$ K, which was calibrated with an Anton Paar MKT-100 digital thermometer (precision $\pm10^{-3}$ K, temperature scale ITS-90) over the entire range of experimental temperatures. Samples were taken by a couple of syringe from the upper and lower phases, through a needle. A series of LLE measurements were made by changing the temperature. Phase compositions were determined by measurement of physical properties and application of the corresponding fitting polynomials.

Table 2 Physical properties of binary systems at 298.15 K

x_1	ρ/ g cm^{-3}	V^E_m/ cm^3 mol^{-1}	n_D	Δn_D	u/ m s^{-1}	$\Delta\kappa_S$/ TPa^{-1}
			Methyl acetate(1) + 1,2-ethanediol(2)			
0.1008	1.08851	−0.210	1.42221	−0.0008	1574.6	−7
0.1998	1.06783	−0.348	1.41425	−0.0017	1493.9	−6
0.2975	1.04788	−0.425	1.40650	−0.0024	1419.0	1
0.3958	1.02835	−0.447	1.39895	−0.0029	1351.0	12
0.4935	1.00991	−0.444	1.39180	−0.0031	1296.4	21
0.5888	0.99281	−0.420	1.38506	−0.0030	1254.0	26
0.6845	0.97640	−0.371	1.37845	−0.0027	1223.0	23
0.7798	0.96089	−0.306	1.37224	−0.0021	1200.1	15
0.8868	0.94408	−0.190	1.36558	−0.0010	1178.4	3
			Methyl acetate(1) + 1,2-propanediol(2)			
0.1074	1.02095	−0.033	1.42327	−0.0001	1451.3	−2
0.1964	1.01114	−0.045	1.41667	−0.0003	1406.0	−1
0.3017	0.99961	−0.053	1.40891	−0.0004	1356.6	1
0.4031	0.98858	−0.051	1.40150	−0.0004	1314.0	4
0.5027	0.97788	−0.046	1.39424	−0.0004	1275.7	7
0.5964	0.96795	−0.039	1.38745	−0.0004	1244.9	9
0.6931	0.95783	−0.030	1.38047	−0.0003	1217.5	9
0.7888	0.94796	−0.019	1.37361	−0.0002	1193.8	8
0.8883	0.93787	−0.010	1.36648	−0.0001	1172.9	4
			Methyl acetate(1) + 1,3-propanediol(2)			
0.1088	1.03901	0.252	1.43095	0.0013	1567.1	18
0.2267	1.02580	−0.424	1.42204	0.0018	1494.6	−27
0.3087	1.01611	−0.495	1.41550	0.0018	1442.5	−28
0.4193	1.00243	−0.530	1.40641	0.0016	1375.5	−24
0.7557	0.95918	−0.365	1.37880	0.0008	1224.3	−8
0.8010	0.95331	−0.321	1.37509	0.0007	1209.8	−8
0.8324	0.94914	−0.278	1.37250	0.0006	1199.8	−7
0.9259	0.93676	−0.141	1.36476	0.0003	1173.2	−5

Table 2 Continued

x_1	ρ/ g cm^{-3}	V_m^E/ cm^3 mol^{-1}	n_D	Δn_D	u/ m s^{-1}	$\Delta\kappa_S$/ TPa^{-1}
Ethyl acetate(1) + 1,2-ethanediol(2)						
0.0306	1.10022	–0.088	1.42790	–0.0005	1623.3	0
0.0663	1.08917	–0.176	1.42508	–0.0012	1585.8	1
0.0949	1.08047	–0.233	1.42280	–0.0017	1557.7	2
0.1211	1.07272	–0.281	1.42085	–0.0021	1530.3	5
0.8759	0.91215	–0.179	1.37505	–0.0019	1163.0	16
0.9027	0.90819	–0.145	1.37369	–0.0016	1159.2	10
0.9363	0.90333	–0.101	1.37223	–0.0010	1154.0	4
0.9621	0.89965	–0.062	1.37108	–0.0006	1149.2	1
Ethyl acetate(1) + 1,2-propanediol(2)						
0.0892	1.01722	–0.037	1.42440	–0.0013	1449.6	4
0.2019	0.99853	–0.060	1.41617	–0.0026	1382.5	11
0.3106	0.98150	–0.065	1.40863	–0.0034	1327.5	18
0.4347	0.96323	–0.056	1.40054	–0.0038	1274.0	25
0.5031	0.95367	–0.046	1.39630	–0.0038	1249.7	27
0.6183	0.93841	–0.032	1.38949	–0.0035	1215.1	27
0.7029	0.92782	–0.021	1.38465	–0.0031	1194.1	25
0.7982	0.91642	–0.005	1.37951	–0.0024	1175.2	17
0.8986	0.90508	0.005	1.37432	–0.0013	1157.7	8
Ethyl acetate(1) + 1,3-propanediol(2)						
0.0542	1.04125	–0.172	1.43435	–0.0002	1588.8	–7
0.1256	1.02944	–0.354	1.42930	–0.0003	1540.1	–14
0.1986	1.01728	–0.491	1.42409	–0.0005	1489.4	–17
0.2231	1.01314	–0.524	1.42228	–0.0006	1472.2	–17
0.8799	0.91082	–0.235	1.37685	–0.0008	1172.4	2
0.9030	0.90757	–0.191	1.37537	–0.0007	1166.7	–3
0.9335	0.90333	–0.130	1.37345	–0.0005	1159.3	–4
0.9676	0.89872	–0.067	1.37133	–0.0003	1150.0	–3

Table 2 Continued

x_1	ρ/ g cm^{-3}	V_m^E/ cm^3 mol^{-1}	n_D	Δn_D	u/ m s^{-1}	$\Delta\kappa_S$/ TPa^{-1}
Propyl acetate(1) + 1,2-ethanediol(2)						
0.0082	1.10660	–0.027	1.42963	–0.0002	1645.4	1
0.0212	1.10134	–0.062	1.42867	–0.0006	1629.7	3
0.0308	1.09755	–0.087	1.42799	–0.0008	1618.5	4
0.0400	1.09385	–0.105	1.42730	–0.0010	1607.6	5
0.0477	1.09087	–0.123	1.42676	–0.0012	1597.9	7
0.9504	0.88902	–0.041	1.38301	–0.0011	1175.6	9
0.9583	0.88811	–0.040	1.38270	–0.0010	1174.6	7
0.9706	0.88663	–0.029	1.38242	–0.0007	1172.9	5
0.9812	0.88535	–0.019	1.38216	–0.0005	1171.3	3
Propyl acetate(1) + 1,2-propanediol(2)						
0.1039	1.00979	–0.007	1.42377	–0.0023	1434.5	14
0.2012	0.99036	–0.001	1.41730	–0.0040	1375.4	27
0.2970	0.97295	0.012	1.41155	–0.0050	1327.6	38
0.3997	0.95604	0.023	1.40585	–0.0056	1286.5	45
0.5000	0.94098	0.037	1.40081	–0.0057	1254.4	48
0.5919	0.92835	0.046	1.39663	–0.0053	1230.7	46
0.7040	0.91424	0.056	1.39192	–0.0044	1207.5	40
0.8071	0.90243	0.055	1.38802	–0.0032	1191.2	29
0.8972	0.89296	0.043	1.38493	–0.0019	1180.2	16
Propyl acetate(1) + 1,3-propanediol(2)						
0.0414	1.04122	–0.136	1.43553	–0.0004	1593.9	–2
0.0686	1.03549	–0.217	1.43368	–0.0007	1574.1	–3
0.0838	1.03226	–0.254	1.43263	–0.0009	1563.2	–4
0.1051	1.02776	–0.303	1.43125	–0.0011	1549.3	–5
0.9363	0.89053	–0.073	1.38430	–0.0010	1181.6	4
0.9532	0.88856	–0.057	1.38356	–0.0008	1178.5	2
0.9683	0.88682	–0.044	1.38294	–0.0006	1175.4	1

Table 2 Continued

x_1	ρ/ g cm^{-3}	V^E_m/ cm^3 mol^{-1}	n_D	Δn_D	u/ m s^{-1}	$\Delta\kappa_S$/ TPa^{-1}
		Butyl acetate(1) + 1,2-ethanediol(2)				
0.0128	1.10361	–0.036	1.42935	–0.0004	1638.0	3
0.0217	1.09938	–0.062	1.42875	–0.0007	1625.0	6
0.0324	1.09440	–0.092	1.42802	–0.0010	1610.9	8
0.9354	0.88271	0.012	1.39273	–0.0014	1198.5	14
0.9554	0.88068	0.001	1.39236	–0.0010	1196.8	9
0.9632	0.87994	–0.008	1.39224	–0.0008	1195.9	7
		Butyl acetate(1) + 1,2-propanediol(2)				
0.1059	1.00473	0.040	1.42417	–0.0029	1427.1	23
0.2028	0.98267	0.079	1.41859	–0.0046	1368.8	41
0.3115	0.96118	0.124	1.41316	–0.0057	1319.0	55
0.4182	0.94299	0.151	1.40842	–0.0062	1282.4	61
0.5112	0.92906	0.162	1.40487	–0.0061	1257.7	61
0.6123	0.91549	0.173	1.40136	–0.0056	1237.0	56
0.7037	0.90458	0.164	1.39856	–0.0048	1222.1	48
0.7912	0.89509	0.149	1.39621	–0.0037	1211.1	36
0.8993	0.88463	0.103	1.39363	–0.0020	1200.2	18
		Butyl acetate(1) + 1,3-propanediol(2)				
0.0235	1.04393	–0.084	1.43668	–0.0005	1605.8	0
0.0420	1.03914	–0.143	1.43545	–0.0009	1590.8	1
0.0769	1.03035	–0.245	1.43318	–0.0015	1563.0	2
0.9436	0.88202	–0.051	1.39320	–0.0011	1201.3	6
0.9614	0.88016	–0.037	1.39266	–0.0008	1198.4	3
0.9747	0.87879	–0.027	1.39229	–0.0005	1195.8	2

Results and discussion

The experimental results of density, ρ, refractive index, n_D, and speed of sound, u, at 298.15 K, for all binary mixtures are reported in Table 2. The excess molar volumes, changes of refractive index on mixing, and changes of isentropic compressibility were evaluated for each composition point, using the following equations:

Table 3 Parameter of the Eq. (4) and root mean square deviation σ

			Methyl acetate(1) + 1,2-ethanediol(2)			
$V_m^E/(cm^3\ mol^{-1})$	B_0=–1.7790	B_1=0.3918	B_2=–0.5617	B_3=–0.2084		σ=0.0023
Δn_D	B_0=–0.0124	B_1=–0.0009	B_2=0.0036			σ=0.00004
$\Delta\kappa_S/(TPa^{-1})$	B_0=8576	B_1=147.62	B_2=–179.34	B_3=–136.22		σ=0.22
			Methyl acetate(1) + 1,2-propanediol(2)			
$V_m^E/(cm^3\ mol^{-1})$	B_0=–0.1850	B_1=0.1444	B_2=–0.0520			σ=0.0006
Δn_D	B_0=–0.0017	B_1=0.0001	B_2=0.0003			σ=0.00001
$\Delta\kappa_S/(TPa^{-1})$	B_0=28.74	B_1=55.75	B_2=–27.78	B_3=–30.41		σ=0.22
			Methyl acetate(1) + 1,3-propanediol(2)			
$V_m^E/(cm^3\ mol^{-1})$	B_0=–2.0999	B_1=0.4438	B_2=–0.3569	B_3=–0.1429		σ=0.0017
Δn_D	B_0=0.0055	B_1=–0.0056	B_2=0.0064			σ=0.00001
$\Delta\kappa_S/(TPa^{-1})$	B_0=–75.83	B_1=123.89	B_2=–82.37	B_3=–73.31		σ=0.23
			Ethyl acetate(1) + 1,2-ethanediol(2)			
$V_m^E/(cm^3\ mol^{-1})$	B_0=–1.7669	B_1=0.6568	B_2=–0.6510			σ=0.0007
Δn_D	B_0=–0.0185	B_1=0.0010				σ=0.00004
$\Delta\kappa_S/(TPa^{-1})$	B_0=248.34	B_1=163.24	B_2=–267.19	B_3=–172.62		σ=0.22
			Ethyl acetate(1) + 1,2-propanediol(2)			
$V_m^E/(cm^3\ mol^{-1})$	B_0=–0.1922	B_1=0.2400	B_2=–0.1014	B_3=0.1251	B_4=0.1542	σ=0.0010
Δn_D	B_0=–0.0153	B_1=0.0012				σ=0.00002
$\Delta\kappa_S/(TPa^{-1})$	B_0=109.08	B_1=49.59	B_2=–62.09	B_3=–44.60		σ=0.23

Table 3 Continued

		Ethyl acetate(1) + 1,3-propanediol(2)			
$V_m^E/(\mathrm{cm^3\ mol^{-1}})$	B_0=–2.6079	B_1=0.6737	B_2=–0.1820		σ=0.0020
Δn_D	B_0=–0.0054	B_1=–0.0032			σ=0.00003
$\Delta\kappa_S/(\mathrm{TPa^{-1}})$	B_0=16.64	B_1=169.74	B_2=–157.58	B_3=–165.26	σ=0.15
		Propyl acetate(1) + 1,2-ethanediol(2)			
$V_m^E/(\mathrm{cm^3\ mol^{-1}})$	B_0=0.2572	B_1=0.9883	B_2=–2.5086		σ=0.0016
Δn_D	B_0=–0.0079	B_1=0.0009	B_2=–0.0209		σ=0.00003
$\Delta\kappa_S/(\mathrm{TPa^{-1}})$	B_0=356.47	B_1=17.62	B_2=–237.11		σ=0.17
		Propyl acetate(1) + 1,2-propanediol(2)			
$V_m^E/(\mathrm{cm^3\ mol^{-1}})$	B_0=0.1467	B_1=0.2329	B_2=0.0761	B_3=0.1725	σ=0.0007
Δn_D	B_0=–0.0022	B_1=0.0003			σ=0.00002
$\Delta\kappa_S/(\mathrm{TPa^{-1}})$	B_0=192.44	B_1=12.69	B_2=–43.85		σ=0.30
		Propyl acetate(1) + 1,3-propanediol(2)			
$V_m^E/(\mathrm{cm^3\ mol^{-1}})$	B_0=–1.2860	B_1=2.1299	B_2=–1.3285	B_3=–1.1581	σ=0.0012
Δn_D	B_0=–0.0145	B_1=–0.0034			σ=0.00002
$\Delta\kappa_S/(\mathrm{TPa^{-1}})$	B_0=1.1299	B_1=62.82			σ=0.47
		Butyl acetate(1) + 1,2-ethanediol(2)			
$V_m^E/(\mathrm{cm^3\ mol^{-1}})$	B_0=1.9477	B_1=1.4173	B_2=–3.9441		σ=0.0030
Δn_D	B_0=–0.0277	B_1=0.0051			σ=0.00001
$\Delta\kappa_S/(\mathrm{TPa^{-1}})$	B_0=553.82	B_1=–42.17	B_2=–371.70		σ=0.16

Table 3 Continued

		Butyl acetate(1) + 1,2-propanediol(2)			
$V_m^E/(\mathrm{cm}^3\ \mathrm{mol}^{-1})$	B_0=0.6514	B_1=0.2188	B_2=0.1733	B_3=0.3710	σ=0.0023
Δn_D	B_0=–0.0247	B_1=0.0051	B_2=–0.0021		σ=0.00002
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	B_0=245.86	B_1=–32.05	B_2=–33.18		σ=0.21
		Butyl acetate(1) + 1,3-propanediol(2)			
$V_m^E/(\mathrm{cm}^3\ \mathrm{mol}^{-1})$	B_0=–2.2620	B_1=1.4103			σ=0.0024
Δn_D	B_0=–0.0146	B_1=0.0040	B_2=–0.0081	B_3=–0.0037	σ=0.00001
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	B_0=214.51	B_1=136.00	B_2=–191.86	B_3=–115.79	σ=0.09

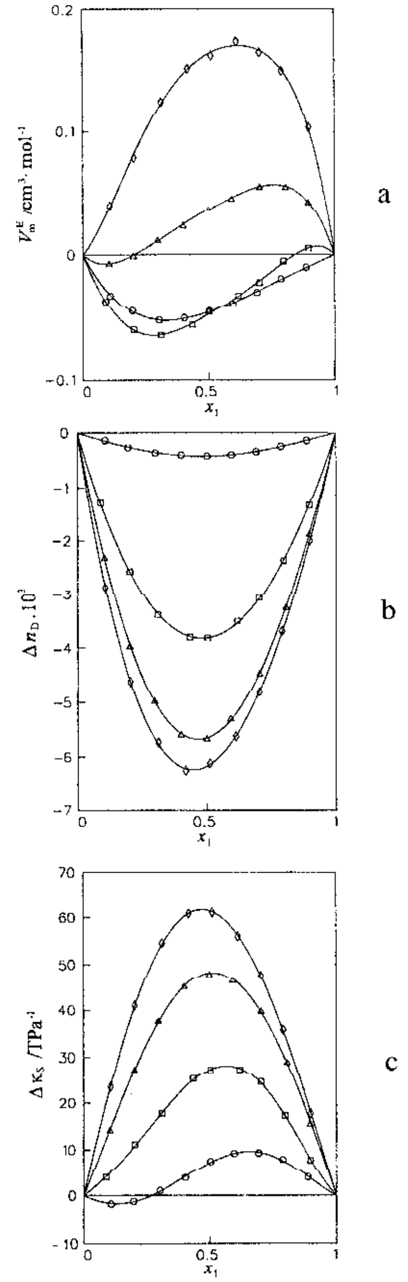

Fig. 2 a) Excess molar volumes, b) changes of refractive index on mixing, and c) changes of isentropic compressibility on mixing with mole fraction of ○ – methyl acetate, □– ethyl acetate, △– propyl acetate and ◇ – butyl acetate with 1,2-propanediol at 298.15 K

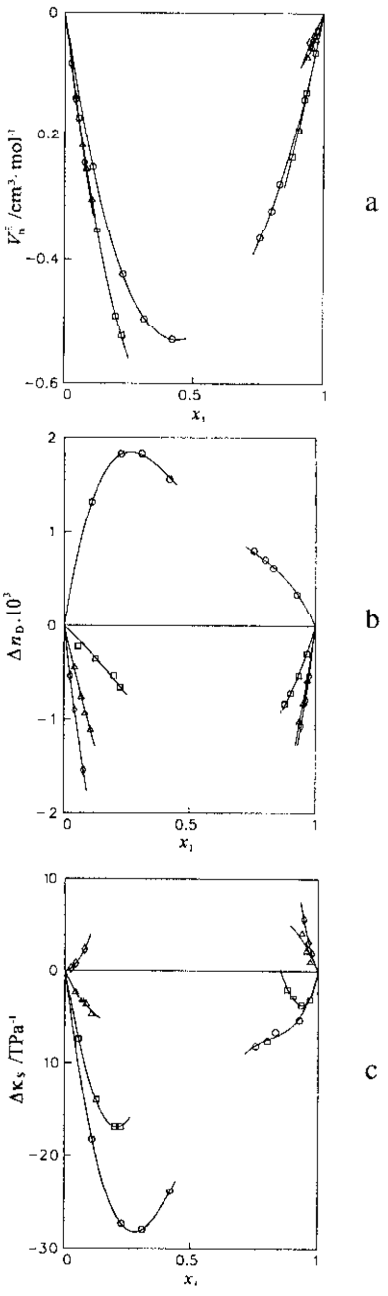

Fig. 3 a) Excess molar volumes, b) changes of refractive index on mixing, and c) changes of isentropic compressibility on mixing with mole fraction ○ – methyl acetate, □– ethyl acetate, △ – propyl acetate, and ◇ – butyl acetate with 1,3-propanediol, at 298.15 K

$$V_m^E = \sum_{i=1}^{2} x_i M_i \left(\rho^{-1} - \rho_i^{-1}\right) \tag{1}$$

$$\Delta n_D = n_D - \sum_{i=1}^{2} x_i n_{D,i} \tag{2}$$

$$\Delta \kappa_S = \kappa_S - \sum_{i=1}^{2} x_i \kappa_{S,i} \tag{3}$$

In these equations, ρ is the density, n_D is the refractive index, and κ_S is the isentropic compressibility (by means Laplace equation, $\kappa_S = \rho^{-1} u^{-2}$) of the mixture, and the corresponding quantities with subscript *i* refer to pure chemicals. The excess values are given in Table 2, too. Excess and derived values were correlated by means of the Redlich-Kister expression (Redlich and Kister [8]) for every binary mixture:

$$\Delta Q_{ij} = x_i x_k \sum_{p=0}^{M} B_p (x_i - x_j)^p \tag{4}$$

In this equation ΔQ_{ij} is the excess property, x is the mole fraction, B is a fitting parameter, and M is the degree of the polynomial expansion. The unweighted least-squares method was used to fit the polynomials to the data, the degree of this

Table 4 Values of limiting partial excess molar volumes at 298.15 K for binary mixtures

System	$V_1^{E,\infty}$	$V_2^{E,\infty}$
Methyl acetate + 1,2-ethanediol	–2.524	–2.157
Methyl acetate + 1,2-propanediol	–0.381	–0.093
Methyl acetate + 1,3-propanediol	–2.758	–2.156
Ethyl acetate + 1,2-ethanediol	–3.075	–1.761
Ethyl acetate + 1,2-propanediol	–0.504	0.226
Ethyl acetate + 1,3-propanediol	–3.464	–2.116
Propyl acetate + 1,2-ethanediol	–3.240	–1.263
Propyl acetate + 1,2-propanediol	–0.183	0.628
Propyl acetate + 1,3-propanediol	–3.586	–1.643
Butyl acetate + 1,2-ethanediol	–3.414	–0.579
Butyl acetate + 1,2-propanediol	0.235	1.415
Butyl acetate + 1,3-propanediol	–3.672	–0.852

Table 5 LLE compositions of the binary systems at different temperatures

T/K	x_1^{I}	x_1^{II}	*T*/K	x_1^{I}	x_1^{II}
Methyl acetate(1) + 1,2-ethanediol(2)			Methyl acetate(1) + 1,3-propanediol(2)		
273.15	0.887	0.212	273.15	0.916	0.252
278.15	0.863	0.234	278.15	0.903	0.270
283.15	0.830	0.260	283.15	0.884	0.294
288.15	0.791	0.299	288.15	0.856	0.323
293.15	0.717	0.370	293.15	0.817	0.373
			298.15	0.757	0.417
Ethyl acetate(1) + 1,2-ethanediol(2)			Ethyl acetate(1) + 1,3-propanediol(2)		
273.15	0.932	0.101	273.15	0.933	0.164
278.15	0.923	0.106	278.15	0.928	0.174
283.15	0.911	0.110	283.15	0.915	0.179
288.15	0.899	0.123	288.15	0.903	0.197
293.15	0.885	0.131	293.15	0.889	0.210
298.15	0.869	0.142	298.15	0.875	0.222
Propyl acetate(1) + 1,2-ethanediol(2)			Propyl acetate(1) + 1,3-propanediol(2)		
273.15	0.961	0.050	273.15	0.956	0.102
278.15	0.954	0.052	278.15	0.951	0.106
283.15	0.943	0.055	283.15	0.944	0.110
288.15	0.941	0.057	288.15	0.937	0.116
293.15	0.932	0.060	293.15	0.927	0.124
298.15	0.924	0.065	298.15	0.919	0.125
Butyl acetate(1) + 1,2-ethanediol(2)			Butyl acetate(1) + 1,3-propanediol(2)		
273.15	0.967	0.024	273.15	0.962	0.063
278.15	0.962	0.026	278.15	0.958	0.065
283.15	0.957	0.028	283.15	0.953	0.069
288.15	0.952	0.028	288.15	0.946	0.070
293.15	0.945	0.030	293.15	0.941	0.073
298.15	0.936	0.032	298.15	0.935	0.075

equation being optimized by application of the F-test (Bevington [9]). The parameters calculated using Eq. (4) are listed in Table 3. The curves fitted, as well as excess and derived properties values are shown from Figs 1–3.

A contractive behaviour is shown for excess molar volumes in acetate+1,2-ethanediol and acetate+1,3-propanediol. Butyl acetate+1,2-ethanediol and ethyl acetate+1,2-propanediol exhibit a small expansive behaviour at high mole fraction of acetate. Butyl acetate+1,2-propanediol and propyl acetate+1,2-propanediol mixtures present an increasing volume for all composition range, apart from low propyl acetate concentration. Changes of refractive index on mixing are positive for methyl acetate+1,3-propanediol and negative for the rest of systems. Methyl acetate+1,3-propanediol and ethyl acetate+1,3-propanediol mixtures present negative values of changes of isentropic compressibility. Propyl acetate+1,3-propanediol, methyl acetate+1,2-propanediol and methyl acetate+1,2-ethanediol show a small negative zone close to polyol pure component.

Several predictive methods were applied to test their validity for these mixtures. Density, refractive index and speed of sound were estimated using the Narsimham method, Newton and Nomoto equations, respectively. The root mean square deviation in calculating the densities using the Narsimham method is below 0.08 in all the systems studied. The Newton mixing rule reproduces adequately the refractive index values corresponding to the binary systems, giving deviations less than $5\cdot10^{-4}$. Nomoto's relation gives deviations less than 4% for the calculated speed of sound.

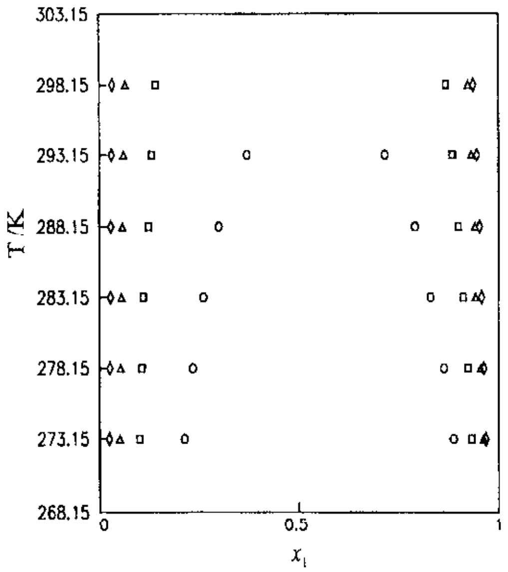

Fig. 4 Experimental tie-lines with mole fraction of ○ – methyl acetate, □ – ethyl acetate, △ – propyl acetate and ◇ – butyl acetate with 1,2-ethanediol

The limiting partial excess molar volume of the components in each binary mixture was determined by means of Eqs [5], and [6], using predetermined Redlich-Kister parameters:

$$V_1^{E,\infty}=\sum_{p=0}^{M}B_p(-1)^p \tag{5}$$

$$V_2^{E,\infty}=\sum_{p=0}^{M}B_p \tag{6}$$

where M and B are the polynomial grade and the fitting parameters, respectively. These ones values are listed in Table 4.

Acetates with 1,2-ethanediol and 1,3-propanediol show an immiscibility zone at temperatures betwen 273.15 and 298.15 K, except for methyl acetate + 1,2-ethanediol which is miscible at 298.15 K. The liquid-liquid equilibria (LLE) in the systems has been determined at temperatures between 273.15 and 298.15 K. Table 5 lists the LLE compositions of both phases at each temperature. Figures 4 and 5 show the experimental tie lines. These figures shows the decreassing in immiscibility when the temperature is increased and the length of the carbon chain of the acetate decreases. The UNIFAC-Dortmund group contribution method was applied in order to predict LLE in these systems. This method

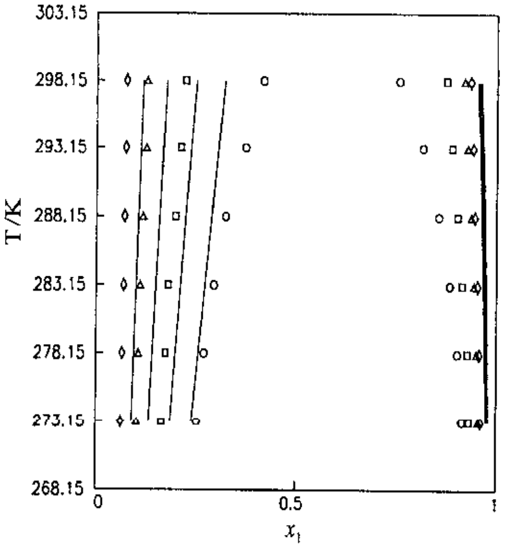

Fig. 5 Experimental tie-lines with mole fraction of o – methyl acetate, □ - ethyl acetate, △– propyl acetate and ◊ – butyl acetate with 1,3-propanediol — UNIFAC-Dortmund predicted values

gives good agreement at high 1,3-propanediol composition, like it is observed in Fig. 5. For acetate + 1,2-ethanediol mixtures the application of this method leads to erroneous results, because it is unable to predict phase separation, due to the model parameters are not appropiate at below temperatures [4].

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