Speeds of Sound and Dynamic Viscosities of the Ternary Mixtures Methyl Acetate + Methanol + 1-Butanol or 1-Pentanol and Their Corresponding Binary Mixtures at 298.15 K

J. Canosa, A. Rodríguez, and J. Tojo*

Department of Chemical Engineering, Vigo University, 36200 Vigo, Spain

Speeds of sound and dynamic viscosities of the ternary mixtures methyl acetate + methanol + 1-butanol and methyl acetate + methanol + 1-pentanol at 298.15 K and atmospheric pressure have been measured over the whole range of mixture compositions. Viscosity deviations and deviations in isentropic compressibilities for the binary and ternary systems were calculated and fitted to Redlich−Kister and Cibulka equations, respectively, to estimate the fitting parameters and the root-mean-square deviations between calculated and experimental data. To correlate viscosities of ternary systems from binary data, different equations have been used, and their parameters are shown. To predict the viscosity of ternary mixtures, two methods based on contribution groups have been proposed and the root-mean-square deviations are gathered. To predict the speed of sound of binary and ternary mixtures, a method has been used, and the results were compared with the experimental data.

1. Introduction

As a continuation of our study of speeds of sound and dynamic viscosities of the ternary liquid mixtures (Canosa et al., 1998a), we present here experimental results of these physical properties at 298.15 K over the whole composition range and atmospheric pressure, for the ternary mixtures methyl acetate + methanol + 1-butanol and methyl acetate + methanol + 1-pentanol and the binaries methyl acetate + 1-butanol, methanol + 1-butanol, methyl acetate + 1-pentanol, and methanol + 1-pentanol.

Viscosity deviations and deviations in isentropic compressibilities for binary mixtures were correlated using the Redlich−Kister equation (1948). Once these parameters are obtained, they are applied to the Cibulka equation (1982), where ternary excess values are correlated. The computed obtained parameters are gathered.

After these viscosities have been measured, the correlation equations (Canosa et al., 1998a) of Katti-Chaudhri (1964), Nissan-Grunberg (1949), Hind et al. (1960), Frenkel (1946), and McAllister (1960) for ternary systems have been applied, using their own binary parameters of correlation, and a comparison between theoretical and experimental values is made. The fitting parameters for binary and ternary systems and the root-mean-square deviations are gathered.

Two predictive equations (UNIFAC−VISCO (Gaston-Bonhomme et al., 1994) and GC−UNIMOD (Cao et al., 1993)) have been applied to compare in terms of root-mean-square deviations the difference between predictive and experimental viscosities using the pure components and group interaction parameters to estimate the viscosity.

To predict the speed of sound of the binary and ternary mixtures, a model developed by Schaaffs (1963) has been applied in the present work. The relative error percent for binary and ternary systems is gathered.

* To whom correspondence should be addressed. E-mail: jtojo@uvigo.es.

Table 1. Comparison of Data with Literature Data for Pure Liquids at 298.15 K

	ρ/(g·cm^{-3})	
component	exptl	lit.
methyl acetate	0.926 74	0.927 90[a]
		0.926 83[b]
methanol	0.786 65	0.786 64[a]
		0.786 67[c]
1-butanol	0.805 89	0.805 75[a]
		0.806 00[d]
1-pentanol	0.810 93	0.810 80[a]
		0.810 92[e]

[a] Riddick and Bunger (1986). [b] Lorenzi et al. (1995). [c] Nagata and Tamura (1996). [d] Das et al. (1994). [e] Linek (1995).

2. Experimental Section

Chemicals are supplied by Merck, and all of them have LiChrosolv quality except methyl acetate, which is synthesis quality. They were recently acquired and kept in an inert argon (N-55, with a maximum content of water of 2 ppmv) atmosphere, degassed in an ultrasound bath, and stored over freshly actived molecular sieves Type 4 Å or 3 Å, for several days before use. Chromatographic (GLC) tests of the solvents showed purities which fulfilled purchaser specifications. Their mass fraction purities were >99.8 mass % for methanol and 1-butanol and >99 mass % for methyl acetate and 1-pentanol with maximum water contents of 1.5×10^{-2}, 1.6×10^{-2}, 6.8×10^{-3}, and 5.7×10^{-3} %, respectively, determined using a Metrohm 737 KF coulometer. The densities of the pure solvents were compared with recently published values in Table 1.

The mixtures were prepared by syringing weighed amounts of the pure liquids into stoppered bottles to prevent preferential evaporation and reduce possible errors in mole fraction calculations, using a Mettler AT-261 Delta Range balance with a precision of $\pm 10^{-5}$ g, covering the whole composition range of the mixture.

10.1021/je9903000 CCC: $19.00
Published on Web 04/26/2000

Table 2. Viscosities η and Viscosity Deviations $\Delta\eta$ for Binary Mixtures at 298.15 K

x_1	η/ (mPa·s)	$\Delta\eta$/ (mPa·s)	x_1	η/ (mPa·s)	$\Delta\eta$/ (mPa·s)
Methyl Acetate (1) + 1-Pentanol (3)					
0	3.505	0	0.5766	0.690	−1.013
0.1014	2.381	−0.807	0.6788	0.575	−0.809
0.2082	1.640	−1.214	0.7517	0.505	−0.651
0.2879	1.292	−1.313	0.8460	0.425	−0.436
0.3821	1.011	−1.300	1	0.380	0
0.4786	0.823	−1.186			
Methanol (1) + 1-Pentanol (3)					
0.1748	2.710	−0.279	0.5951	1.372	−0.376
0.2198	2.528	−0.328	0.6520	1.236	−0.344
0.3270	2.143	−0.397	0.7911	0.932	−0.238
0.4302	1.813	−0.422	0.8761	0.770	−0.149
0.5186	1.570	−0.404	1	0.553	0

Table 3. Speed of Sound u, Isentropic Compressibility κ_S, and Deviation in Isentropic Compressibility $\Delta\kappa_S$ for Binary Mixtures at 298.15 K

x_1	u/ (m·s^{-1})	κ_S/ (TPa^{-1})	$\Delta\kappa_S$/ (TPa^{-1})	x_1	u/ (m·s^{-1})	κ_S/ (TPa^{-1})	$\Delta\kappa_S$/ (TPa^{-1})
Methyl Acetate (1) + 1-Butanol (3)				Methanol (2) + 1-Butanol (3)			
0	1239.5	808.0	0	0.0658	1235.1	814.1	−9.6
0.0546	1230.5	814.6	6.2	0.1148	1231.4	819.5	−15.9
0.0530	1230.9	814.2	5.8	0.2056	1223.3	831.5	−25.6
0.1662	1213.8	826.4	17.2	0.2975	1213.9	845.8	−33.2
0.2189	1206.5	831.0	21.5	0.4230	1199.9	867.9	−41.0
0.3037	1195.7	836.7	26.5	0.4929	1191.1	882.1	−43.5
0.4499	1180.4	842.5	31.3	0.6073	1174.7	909.0	−43.9
0.5694	1170.5	842.8	30.7	0.6892	1162.2	931.1	−41.4
0.6655	1163.7	840.5	27.7	0.7893	1145.0	962.1	−34.3
0.8103	1156.5	832.4	18.6	0.9092	1121.9	1006.0	−18.9
0.8850	1153.9	826.3	12.0	0.9519	1113.0	1023.9	−11.2
0.9404	1152.3	820.9	6.2	1	1102.1	1046.6	0
1	1150.6	815.6	0				
Methyl Acetate (1) + 1-Pentanol (3)				Methanol (2) + 1-Pentanol (3)			
0	1275.5	758.0	0	0.0697	1269.9	765.2	−12.9
0.0423	1268.0	764.0	3.6	0.1681	1261.2	776.9	−29.6
0.0870	1259.9	770.7	7.8	0.3201	1244.5	800.3	−50.1
0.1971	1240.9	786.0	16.8	0.3395	1242.1	803.8	−52.2
0.3682	1214.3	805.5	26.5	0.4140	1232.1	818.2	−59.3
0.4538	1202.2	813.5	29.5	0.4792	1222.7	832.1	−64.2
0.5240	1193.2	818.1	30.2	0.5793	1205.7	858.3	−66.9
0.6216	1181.9	823.0	29.5	0.6931	1183.6	893.9	−64.1
0.7205	1171.9	824.7	25.6	0.8021	1158.2	937.9	−51.6
0.8225	1163.2	823.5	18.5	0.9096	1129.6	991.2	−29.3
0.9075	1156.7	820.6	10.8	0.9594	1114.7	1020.6	−14.2
0.9602	1153.3	817.8	4.9				

The densities of the mixtures and the pure liquids were measured with an Anton Paar DMA-60/602 densimeter with a precision of $\pm 10^{-5}$ g·cm^{-3}, and calibrated with Millipore quality water and degassed and dried Fluka quality heptane as reference liquids. Viscosities were measured with an automated AMV 200 Anton Paar microviscosimeter and a precision better than 1% mPa·s. The viscosimeter is based on the rolling-ball principle; a gold-covered steel ball rolls down inside an inclined, sample-filled glass capillary. The apparatus is equipped with an automatic timer (±0.01 s), and the time taken for the ball to roll a fixed distance between two magnetic sensors allows one to evaluate the viscosity of the fluid mixture. The time-measuring range is from 12 to 250 s; the accuracy and the precision of these measurements are ±0.01 s and ±0.1 s, respectively. The capillary was placed in a block, thermostated with a PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K. Apparatus calibration was made periodically, testing three fluids of known viscosity. The viscosimeter was calibrated with Millipore quality water and degassed and dried Fluka quality octane and 1-pentanol. The speeds of sound of the pure liquids and mixtures were measured with an Anton Paar DSA-48 density and sound analyzer with a precision of ±1 m·s^{-1}. Before each series of measurements, this instrument was calibrated in accordance with the use instructions.

The reference fluids, which were used for calibration, have mass fraction purities > 99.5 mass %. The accuracies of the calculations of the viscosity deviation, the mole fraction, and the deviation in the isentropic compressibili-

Table 4. Viscosities η and Viscosity Deviations $\Delta\eta$ for the Ternary Mixture Methyl Acetate (1) + Methanol (2) + 1-Butanol (3) at 298.15 K

x_1	x_2	η mPa·s	$\Delta\eta$ mPa·s	x_1	x_2	η mPa·s	$\Delta\eta$ mPa·s
0.7288	0.1899	0.401	−0.194	0.0706	0.7641	0.694	−0.188
0.5833	0.3389	0.420	−0.193	0.4813	0.2151	0.564	−0.533
0.7968	0.1181	0.397	−0.194	0.3563	0.3621	0.597	−0.476
0.4776	0.4499	0.431	−0.189	0.2401	0.4752	0.670	−0.430
0.3616	0.5722	0.451	−0.176	0.3435	0.3669	0.609	−0.483
0.2690	0.6577	0.485	−0.173	0.3572	0.1279	0.774	−0.782
0.1875	0.7544	0.505	−0.136	0.2925	0.2200	0.808	−0.702
0.1234	0.8189	0.535	−0.116	0.1731	0.3607	0.931	−0.556
0.0581	0.8811	0.583	−0.086	0.0920	0.4724	1.024	−0.413
0.6245	0.2022	0.456	−0.347	0.1475	0.5955	0.722	−0.337
0.5072	0.3318	0.473	−0.325	0.4515	0.1170	0.657	−0.710
0.7183	0.0914	0.444	−0.378	0.3746	0.2057	0.691	−0.665
0.4171	0.4392	0.485	−0.293	0.2630	0.3480	0.747	−0.565
0.2898	0.5743	0.519	−0.265	0.1765	0.4704	0.796	−0.646
0.1975	0.6816	0.553	−0.216	0.0710	0.6028	0.906	−0.309
0.1274	0.7602	0.589	−0.174	0.2648	0.0922	0.994	−0.842
0.0613	0.8212	0.647	−0.138	0.1748	0.2419	1.077	−0.651
0.6219	0.1318	0.493	−0.462	0.0984	0.3586	1.175	−0.483
0.5145	0.2287	0.525	−0.470	0.1619	0.1503	1.245	−0.702
0.4227	0.3558	0.532	−0.406	0.1047	0.2167	1.378	−0.560
0.3255	0.4652	0.559	−0.370	0.0569	0.1333	1.800	−0.417
0.2230	0.5896	0.595	−0.307	0.3767	0.2562	0.650	−0.597
0.1306	0.6812	0.664	−0.255	0.1339	0.1254	1.403	−0.658
0.0983	0.6744	0.740	−0.266	0.2670	0.1724	0.906	−0.760
0.5581	0.1082	0.557	−0.589	0.6198	0.2742	0.425	−0.240

Table 5. Viscosities η and Viscosity Deviations $\Delta\eta$ for the Ternary Mixture Methyl Acetate (1) + Methanol (2) + 1-Pentanol (3) at 298.15 K

x_1	x_2	η mPa·s	$\Delta\eta$ mPa·s	x_1	x_2	η mPa·s	$\Delta\eta$ mPa·s
0.1314	0.1142	1.851	−0.906	0.3669	0.5209	0.515	−0.306
0.3253	0.1143	1.042	−1.109	0.4330	0.5083	0.456	−0.195
0.4118	0.1153	0.853	−1.025	0.0745	0.6524	0.944	−0.402
0.5061	0.1121	0.706	−0.887	0.1320	0.6513	0.775	−0.395
0.5993	0.1030	0.600	−0.728	0.2064	0.6336	0.637	−0.353
0.6837	0.0985	0.510	−0.568	0.2665	0.6281	0.540	−0.278
0.7603	0.0966	0.459	−0.385	0.3293	0.6100	0.477	−0.198
0.8442	0.0943	0.398	−0.191	0.0655	0.7334	0.840	−0.295
0.1147	0.2813	1.546	−0.770	0.1241	0.7221	0.695	−0.291
0.2128	0.2769	1.140	−0.883	0.1918	0.7077	0.573	−0.243
0.2831	0.2818	0.936	−0.852	0.2463	0.7095	0.497	−0.144
0.3708	0.2766	0.750	−0.780	0.0657	0.7950	0.735	−0.218
0.4539	0.2691	0.631	−0.661	0.1132	0.7949	0.611	−0.194
0.5306	0.2641	0.538	−0.529	0.1811	0.7676	0.528	−0.145
0.6114	0.2586	0.471	−0.360	0.0676	0.8384	0.663	−0.156
0.6982	0.2511	0.417	−0.165	0.1040	0.8519	0.561	−0.104
0.0910	0.4507	1.277	−0.613	0.0574	0.9015	0.583	−0.081
0.1701	0.4450	0.997	−0.663	0.1074	0.2135	1.739	−0.800
0.2452	0.4383	0.804	−0.641	0.1004	0.3696	1.414	−0.686
0.3253	0.4268	0.661	−0.568	0.0867	0.5047	1.183	−0.561
0.3967	0.4174	0.565	−0.468	0.0723	0.6071	1.041	−0.446
0.4762	0.4037	0.485	−0.340	0.0755	0.6864	0.882	−0.361
0.5383	0.3965	0.439	−0.213	0.0671	0.7666	0.771	−0.261
0.0836	0.5522	1.109	−0.505	0.0638	0.8226	0.693	−0.184
0.1464	0.5574	0.887	−0.515	0.0573	0.8805	0.615	−0.112
0.2209	0.5461	0.714	−0.489	0.0500	0.9259	0.562	−0.053
0.2984	0.5311	0.593	−0.412				

Table 6. Speed of Sound u, Isentropic Compressibility κ_S, and Deviation in Isentropic Compressibility $\Delta\kappa_S$ for the Ternary Mixture Methyl Acetate (1) + Methanol (2) + 1-Butanol (3) at 298.15 K

x_1	x_2	u/(m·s^{-1})	κ_S/(TPa^{-1})	$\Delta\kappa_S$/(TPa^{-1})	x_1	x_2	u/(m·s^{-1})	κ_S/(TPa^{-1})	$\Delta\kappa_S$/(TPa^{-1})
0.0197	0.1916	1220.8	832.9	−20.9	0.5281	0.3269	1146.9	868.8	−21.2
0.0209	0.2057	1219.1	834.9	−22.3	0.6095	0.3236	1142.5	862.1	−27.7
0.1461	0.1981	1200.6	846.7	−9.7	0.1188	0.4674	1175.2	887.6	−32.8
0.2473	0.1946	1187.1	853.7	−2.7	0.1835	0.4709	1165.5	891.7	−30.1
0.3427	0.1910	1176.5	856.9	0.7	0.2604	0.4635	1156.5	893.2	−27.4
0.4447	0.1545	1169.6	854.7	6.4	0.3359	0.4572	1149.1	891.8	−27.8
0.5210	0.1907	1159.3	858.0	0.5	0.4065	0.4553	1142.4	889.9	−29.8
0.5897	0.1977	1154.3	855.1	−4.5	0.4821	0.4526	1137.3	884.2	−35.5
0.6994	0.1885	1149.4	846.8	−11.5	0.0994	0.5790	1163.0	909.8	−37.1
0.7776	0.1774	1147.6	838.2	−18.0	0.1737	0.5529	1153.0	907.6	−33.6
0.0199	0.2031	1219.8	834.3	−22.3	0.2354	0.5728	1145.3	912.7	−33.7
0.1138	0.1890	1206.2	842.5	−11.5	0.3017	0.5714	1138.2	911.4	−35.2
0.2216	0.1886	1191.3	850.7	−4.0	0.3751	0.5675	1131.9	906.9	−39.3
0.3138	0.1883	1179.5	856.0	0.7	0.0959	0.6691	1150.2	931.2	−37.1
0.4110	0.1789	1169.9	857.6	3.8	0.1504	0.6735	1141.6	934.1	−35.7
0.4970	0.1795	1162.2	857.3	2.7	0.2183	0.6620	1135.3	930.4	−37.2
0.5824	0.1787	1155.8	854.7	−0.4	0.2942	0.6518	1128.3	925.9	−39.8
0.6798	0.1616	1151.8	847.4	−4.3	0.0931	0.7447	1138.8	950.9	−35.5
0.7472	0.1762	1148.3	841.8	−14.0	0.1414	0.7480	1130.9	953.2	−34.3
0.7836	0.1728	1147.6	837.3	−17.9	0.2051	0.7431	1123.9	950.2	−36.7
0.0920	0.3373	1194.6	862.2	−27.0	0.5796	0.1371	1159.5	851.5	6.4
0.1361	0.3365	1188.2	865.6	−23.7	0.7224	0.1708	1149.8	843.5	−10.8
0.2152	0.3123	1179.6	867.4	−16.7	0.0798	0.8759	1116.4	993.5	−24.1
0.2858	0.3377	1168.2	873.7	−17.0	0.2178	0.1804	1192.4	849.5	−3.2
0.3755	0.3306	1159.3	873.9	−15.8	0.3827	0.1778	1173.2	856.5	3.1
0.4522	0.3261	1152.7	872.2	−17.1					

Table 7. Speed of Sound u, Isentropic Compressibility κ_S, and Deviation in Isentropic Compressibility $\Delta\kappa_S$ for the Ternary Mixture Methyl Acetate (1) + Methanol (2) + 1-Pentanol (3) at 298.15 K

x_1	x_2	u/(m·s^{-1})	κ_S/(TPa^{-1})	$\Delta\kappa_S$/(TPa^{-1})	x_1	x_2	u/(m·s^{-1})	κ_S/(TPa^{-1})	$\Delta\kappa_S$/(TPa^{-1})
0.0779	0.0660	1255.4	777.6	−3.9	0.3777	0.4474	1155.9	876.0	−32.7
0.0625	0.9058	1116.2	998.5	−24.5	0.3996	0.5127	1142.0	890.0	−38.8
0.1341	0.1143	1241.1	791.4	−7.2	0.5241	0.0988	1182.9	829.4	13.0
0.2171	0.1653	1221.0	809.9	−8.2	0.5220	0.2017	1171.2	842.1	−3.9
0.1920	0.2857	1211.2	825.3	−26.1	0.5040	0.2986	1160.8	855.4	−17.6
0.1892	0.3335	1205.3	833.5	−31.5	0.5048	0.3968	1146.8	870.4	−30.9
0.1202	0.5173	1190.4	863.4	−50.7	0.6420	0.0789	1171.2	831.8	14.3
0.1285	0.5957	1174.4	886.1	−51.1	0.6017	0.2020	1162.0	844.0	−6.7
0.0979	0.7146	1156.1	920.6	−49.3	0.6001	0.3033	1149.5	856.2	−23.7
0.0969	0.8050	1134.8	956.4	−39.5	0.7154	0.1044	1161.93	833.5	4.5
0.2289	0.0772	1228.6	799.1	5.7	0.6770	0.2163	1153.4	843.9	−15.2
0.1954	0.2042	1220.7	812.1	−15.9	0.8004	0.1024	1155.8	829.9	−3.4
0.1940	0.2960	1209.6	827.0	−27.5	0.8839	0.0632	1153.8	822.9	−3.8
0.2384	0.3093	1199.7	835.4	−25.4	0.1116	0.3094	1223.4	817.2	−36.5
0.2251	0.4883	1174.8	871.2	−40.6	0.0907	0.4105	1213.4	833.7	−47.9
0.2075	0.5953	1158.5	897.3	−44.4	0.1880	0.4098	1194.4	848.5	−38.5
0.2282	0.6462	1144.3	914.6	−42.9	0.1322	0.8204	1123.6	966.73	−35.6
0.2895	0.0981	1216.7	809.0	6.2	0.2180	0.7472	1124.2	946.4	−39.7
0.2954	0.2077	1203.3	825.2	−9.6	0.7664	0.1605	1151.9	836.1	−12.1
0.3009	0.2941	1191.4	839.8	−20.3	0.4842	0.4623	1139.3	880.9	−38.2
0.3175	0.3670	1178.1	855.1	−26.9	0.0823	0.2003	1242.2	794.6	−25.9
0.2956	0.4998	1160.3	881.3	−37.8	0.0781	0.3563	1224.4	819.6	−45.7
0.3038	0.6129	1138.0	910.5	−41.7	0.0700	0.4884	1206.6	846.2	−56.7
0.3892	0.1050	1200.6	820.2	9.7	0.0605	0.6707	1174.8	897.0	−58.0
0.4139	0.1922	1186.9	834.4	−2.7	0.0563	0.7501	1158.1	925.7	−52.0
0.3985	0.3189	1172.5	853.1	−19.7					

ties were estimated as better than 2 × 10^{-2} mPa·s, 5 × 10^{-5}, and 2 TPa^{-1}, respectively.

3. Results and Discussion

The viscosities of the binary mixtures methyl acetate + 1-pentanol and methanol + 1-pentanol, the speeds of sound of the binary mixtures methyl acetate + 1-butanol, methyl acetate + 1-pentanol, methanol + 1-butanol, and methanol + 1-pentanol, and the viscosities and speeds of sound of the ternary mixtures methyl acetate + methanol + 1-butanol and methyl acetate + methanol + 1-pentanol were measured at 298.15 K and atmospheric pressure and given in Tables 2−7. In previous papers, we have measured the densities of the ternary liquid mixtures (Iglesias et al., 1998; Rodríguez et al., 1998a) and the viscosities of the binaries methyl acetate + 1-butanol and methanol + 1-butanol (Canosa et al., 1998b). The viscosity deviations are calculated from dynamic viscosities with eq 1,

$$\Delta\eta = \eta - \sum_{i=1}^{N}(\eta_i^{o}\cdot x_i) \qquad (1)$$

where η and η_i^{o} are the dynamic viscosities of the mixture and the pure component, respectively, and x_i represents the mole fraction of the pure component. Isentropic compressibilities (determined by means of the Laplace equation, $\kappa_S = \rho^{-1}u^{-2}$) and deviations in the isentropic compressibilities $\Delta\kappa_S$ of the binary and ternary mixtures

Table 8. Parameters of Eqs 3 and 4, and Root Mean Square Deviations σ

		Methyl Acetate (1) + 1-Butanol (3)			
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	$B_0 = 126.33 \pm 0.36$	$B_1 = -2.99 \pm 0.64$	$B_2 = -10.98 \pm 1.40$		$\sigma = 0.15$
		Methyl Acetate (1) + 1-Pentanol (3)			
$\Delta\eta/(\mathrm{mPa\cdot s})$	$B_0 = -4.60 \pm 0.01$	$B_1 = 3.26 \pm 0.02$	$B_2 = -2.31 \pm 0.02$	$B_3 = 0.35 \pm 0.06$	$\sigma = 0.002$
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	$B_0 = 120.66 \pm 0.31$	$B_1 = 18.71 \pm 0.68$	$B_2 = -11.60 \pm 1.37$		$\sigma = 0.14$
		Methanol (2) + 1-Butanol (3)			
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	$B_0 = -173.56 \pm 0.55$	$B_1 = -43.78 \pm 1.09$	$B_2 = -26.90 \pm 2.35$		$\sigma = 0.25$
		Methanol (2) + 1-Pentanol (3)			
$\Delta\eta/(\mathrm{mPa\cdot s})$	$B_0 = -1.64 \pm 0.01$	$B_1 = 0.42 \pm 0.01$	$B_2 = -0.08 \pm 0.02$		$\sigma = 0.002$
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	$B_0 = -259.96 \pm 0.37$	$B_1 = -92.85 \pm 0.81$	$B_2 = -28.01 \pm 1.79$		$\sigma = 0.18$
		Methyl Acetate (1) + Methanol (2) + 1-Butanol (3)			
$\Delta\eta/(\mathrm{mPa\cdot s})$	$C_1 = -1.72 \pm 0.15$	$C_2 = 3.02 \pm 0.25$	$C_3 = -0.45 \pm 0.23$		$\sigma = 0.005$
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	$C_1 = 97.71 \pm 15.23$	$C_2 = 118.99 \pm 25.68$	$C_3 = 346.53 \pm 25.24$		$\sigma = 0.52$
		Methyl Acetate (1) + Methanol (2) + 1-Pentanol (3)			
$\Delta\eta/(\mathrm{mPa\cdot s})$	$C_1 = 1.10 \pm 0.19$	$C_2 = 0.02 \pm 0.32$	$C_3 = -2.72 \pm 0.29$		$\sigma = 0.005$
$\Delta\kappa_S/(\mathrm{TPa}^{-1})$	$C_1 = 89.99 \pm 17.32$	$C_2 = 253.31 \pm 30.01$	$C_3 = 482.21 \pm 31.07$		$\sigma = 0.61$

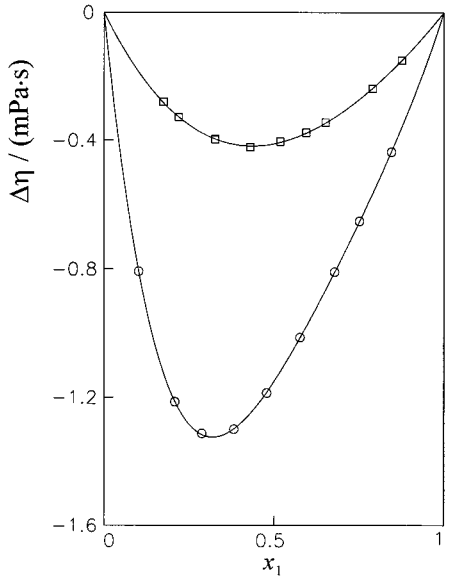


Figure 1. Curves of viscosity deviations ($\Delta\eta$/mPa·s) from the Redlich−Kister equation, eq 3, for the binary mixtures (○) methyl acetate (1) + 1-pentanol (3) and (□) methanol (2) + 1-pentanol (3) at 298.15 K.

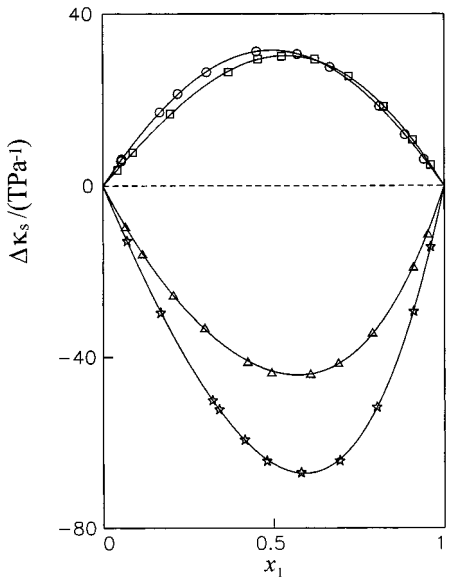


Figure 2. Curves of the deviation in isentropic compressibility ($\Delta\kappa_S/\mathrm{TPa}^{-1}$) from the Redlich−Kister equation, eq 3, for the binary mixtures (○) methyl acetate (1) + 1-butanol (3), (□) methyl acetate (1) + 1-pentanol (3), (△) methanol (2) + 1-butanol (3), and (☆) methanol (2) + 1-pentanol (3) at 298.15 K.

are given in the last columns of Tables 3, 6, and 7. The deviations in isentropic compressibility values were calculated as

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

where κ_S is the isentropic compressibility of the mixture and $\kappa_{S,i}$ is the isentropic compressibility of the pure component.

The binary viscosity deviations and the deviations in the isentropic compressibilities were fitted to a Redlich−Kister type equation

$$\Delta Q_{ij} = x_i x_j \sum_{\rho=0}^{M} B_p (x_i - x_j)^p \tag{3}$$

where ΔQ_{ij} is the excess property, x is the mole fraction, B_p is the fitting parameter, and M is the degree of the polynomic expansion, which was optimized using the F-test (Bevington, 1969). Viscosity deviations and deviations in the isentropic compressibilities of the ternary systems were correlated with the Cibulka equation:

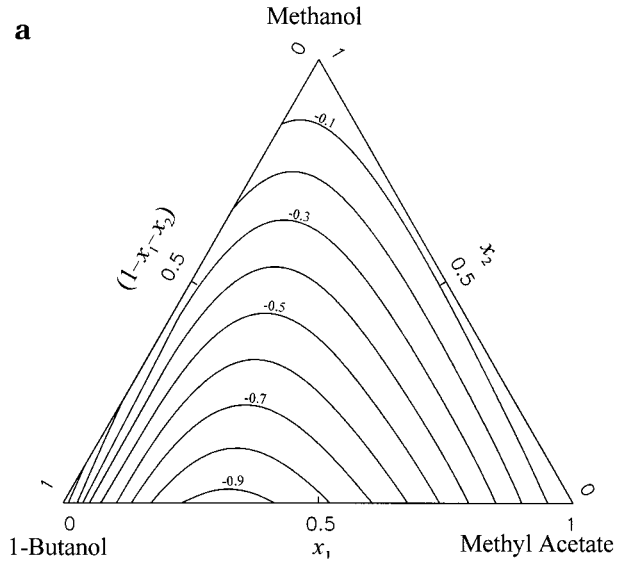
$$\Delta Q_{123} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} + x_1 x_2 (1 - x_1 - x_2)(C_1 + C_2 x_1 + C_3 x_2) \tag{4}$$

where ΔQ_{12}, ΔQ_{13}, and ΔQ_{23} are the binary contributions expressed by the Redlich−Kister expression. The fitting parameters are shown in Table 8, for binary and ternary mixtures, together with the root-mean-square deviations (σ). This deviation is calculated with eq 5,

$$\sigma = \left(\frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \tag{5}$$

where the value of the property and the number of experimental data are represented by z and n_{DAT}, respectively.

Figure 1 shows viscosity deviation values for the binary mixtures methyl acetate + 1-pentanol and methanol + 1-pentanol, respectively, plotted against mole fraction, together with the fitted curve. The viscosity deviations for the systems are negative over the entire composition range; that is to say, there is a decrease in the viscosity of the mixture with regard to ideal behavior.



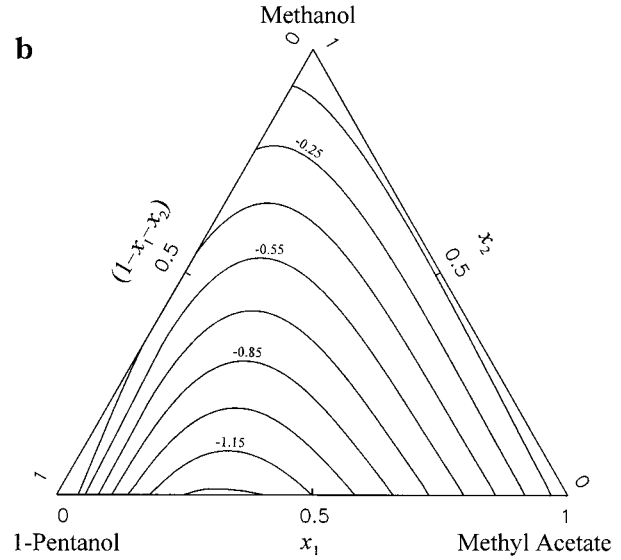
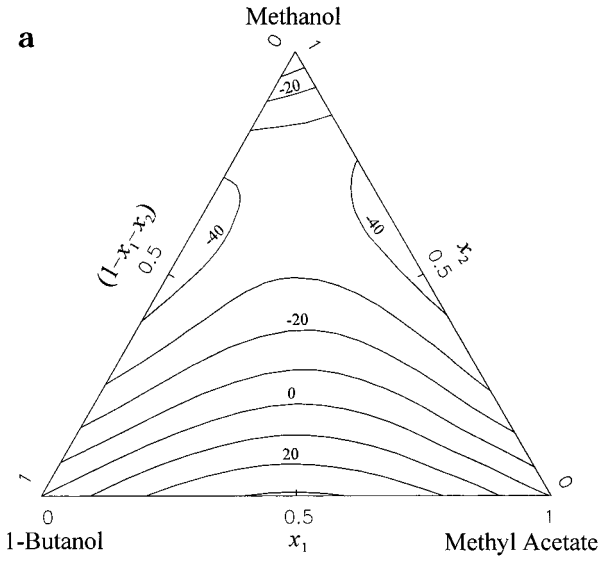


Figure 3. Curves of constant viscosity deviations ($\Delta\eta$/mPa·s) from the Cibulka equation, eq 4, for the ternary systems (a) methyl acetate (1) + methanol (2) + 1-butanol (3) and (b) methyl acetate (1) + methanol (2) + 1-pentanol (3) at 298.15 K.



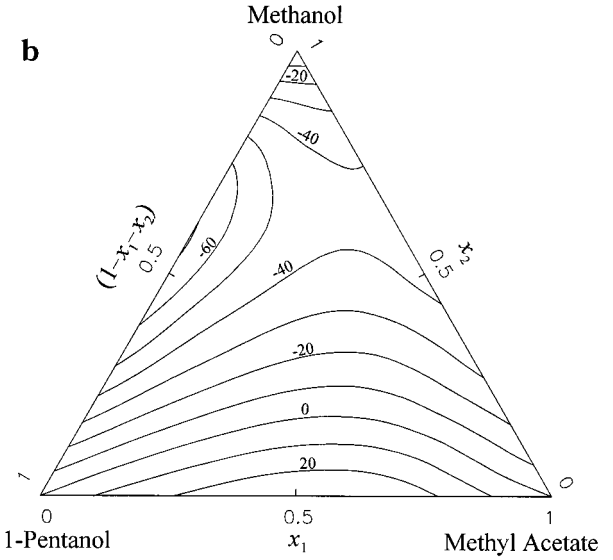


Figure 4. Curves of constant deviation in isentropic compressibility ($\Delta\kappa_S$/TPa^{-1}) from the Cibulka equation, eq 4, for the ternary systems (a) methyl acetate (1) + methanol (2) + 1-butanol (3) and (b) methyl acetate (1) + methanol (2) + 1-pentanol (3) at 298.15 K.

Figure 2 shows a deviation in isentropic compressibility values for the binary mixtures methyl acetate + 1-butanol, methyl acetate + 1-pentanol, methanol + 1-butanol, and methanol + 1-pentanol, plotted against mole fraction, together with the fitted curves. In this figure it is observed that positive values of the deviation in isentropic compressibility are obtained for the binary mixtures methyl acetate + *n*-alcohols and negative values are obtained for the binary mixtures methanol + *n*-alcohols.

Parts a and b of Figure 3 show curves of constant viscosity deviations obtained from Cibulka's equation, plotted against mole fraction, for the ternary systems methyl acetate + methanol + 1-butanol and methyl acetate + methanol + 1-pentanol, respectively. The ternary viscosity deviations of the systems are also negative over the whole composition range.

Parts a and b of Figure 4 show graphically the curves of constant deviation in isentropic compressibilities for the ternary systems at 298.15 K. In this figure two zones with different signs are observed. Positive values of the constant curves indicate that the isentropic compressibility of the mixture is bigger than the isentropic compressibilities of the pure components. An examination of this effect suggests that the presence of a large amount of methanol has the effect of changing the expansive behavior of the deviation in isentropic compressibilities for the ternary systems.

Parts a and b of Figure 5 show the variation of the viscosity deviations and deviations in isentropic compressibility for the binary sytems methyl acetate + *n*-alcohols and methanol + *n*-alcohols when the composition is equimolar, respectively. Some information about these binaries has been published previously (Canosa et al., 1998b; Rodríguez et al., 1999). In these figures it is observed that the viscosity deviations decrease when the binary is methyl acetate + *n*-alcohols; however, the deviations in isentropic compressibility are positive when the length of the alkanol is growing. The same behavior is observed for the binary mixtures methanol + *n*-alcohols for the two derived properties: the derived values decrease with the length of the alkanol.

Figure 6a shows a comparison of viscosity deviations among the systems methyl acetate + methanol + *n*-alcohol

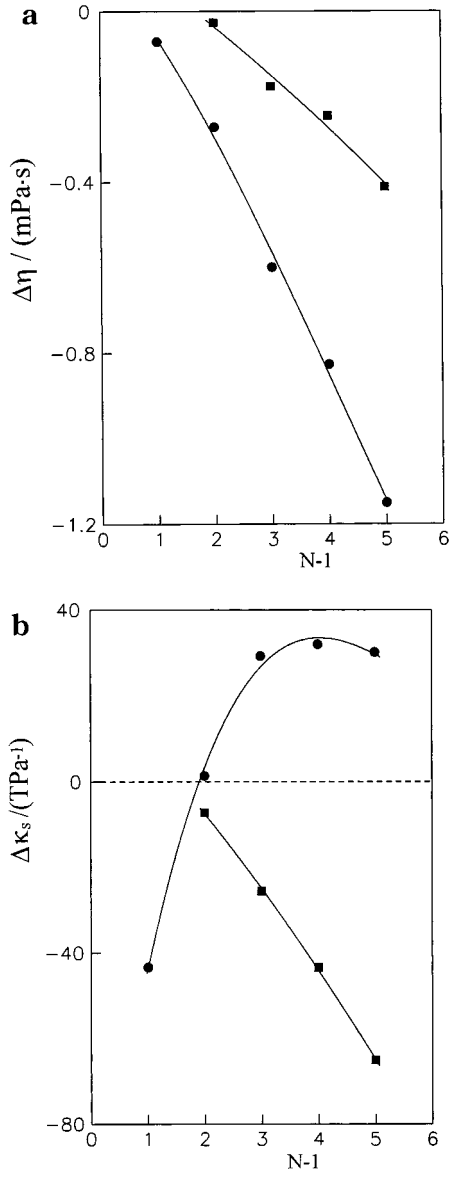


Figure 5. Curves of (a) constant viscosity deviations and (b) deviation in isentropic compressibility when $x_1 = x_2$ for the binary mixtures (○) methyl acetate (1) + $CH_3(CH_2)_{n-1}OH$ (2) from $n = 1$ to $n = 5$ and (□) methanol (1) + $CH_3(CH_2)_{n-1}OH$ (2) from $n = 2$ to $n = 5$, at 298.15 K.

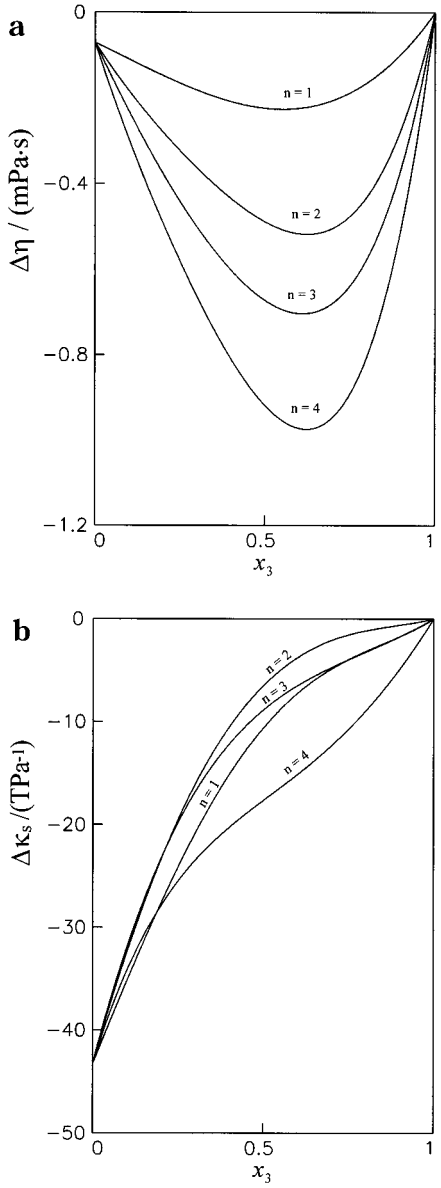


Figure 6. Curves of (a) constant viscosity deviations and (b) deviation in isentropic compressibility when $x_1 = x_2$ for the ternary mixture methyl acetate (1) + methanol (2) + $CH_3(CH_2)_nOH$ (3) from $n = 1$ to $n = 4$ at 298.15 K.

(Canosa et al., 1998a; Rodríguez et al., 1998b) when the mole fraction of methyl acetate is equal to that of methanol in the entire composition range for the third component. It is observed in this figure how negative values of viscosity deviations increase when the length of the chain of the *n*-alcohol is higher, the most negative value being the one corresponding to the viscosity deviations of the system methyl acetate + methanol + 1-pentanol. Figure 6b shows a comparison of deviations in isentropic compressibility among the systems methyl acetate + methanol + *n*-alcohol (Canosa et al., 1998a; Rodríguez et al., 1999) when the mole fraction of methyl acetate is equal to that of methanol in the entire composition range for the third component. In this figure the most negative values of deviations in isentropic compressibility correspond with the ternary mixture methyl acetate + methanol + 1-pentanol; however, the ternary mixture methyl acetate + methanol + 1-propanol shows less negative values.

The correlation equations of Katti-Chaudhri, Nissan-Grunberg, Hind et al., Frenkel, and McAllister are developed, in the literature, for binary mixtures. However, Laddha (Kalidas and Laddha, 1964) introduces a new parameter to correlate ternary systems in the McAllister equation. We, in this paper, have taken into account this fact, and we have expanded the others equations. In Table 9 are shown the binary and ternary correlation parameters and the root-mean-square deviations corresponding to each equation. We can consider that the best correlation method for the ternary systems corresponds to McAllister's equation and the worst is Hind's model.

A comparison between measured viscosity values of ternary mixtures and predictive ones is shown in Table 10; it is observed that the UNIFAC−VISCO model obtains better results for the studied ternary systems. We must take into account, when we observe these results, the fact that the UNIFAC−VISCO and GC−UNIMOD models are predictive ones and they do not require the determination of adjustable parameters that would reduce this deviation.

In Table 11 the relative error percents for the binary and ternary mixtures obtained by applying the predictive model

Table 9. Root Mean Square Deviations σ of Correlative Results of Viscosity for Binary and Ternary Systems at 298.15 K

	Nissan-Grunberg	Katti-Chaudhri	Hind	Frenkel	McAllister
Methyl Acetate (1) + 1-Butanol (3)					
A_{ijk}	−1.7399	−1.7093	−0.2552	0.4181	40.4861
σ	0.024	0.024	0.187	0.024	0.006
Methanol (2) + 1-Butanol (3)					
A_{ijk}	0.4055	0.7190	1.0964	1.4742	70.9866
σ	0.021	0.029	0.019	0.021	0.006
Methyl Acetate (1) + 1-Pentanol (3)					
A_{ijk}	−1.6779	−1.6112	−0.5231	0.4988	48.1623
σ	0.024	0.024	0.238	0.024	0.012
Methanol (2) + 1-Pentanol (3)					
A_{ijk}	0.5521	0.9946	1.1813	1.8348	95.6107
σ	0.030	0.050	0.037	0.034	0.008
Methyl Acetate (1) + Methanol (2) + 1-Butanol (3)					
A_{ijk}	−0.7988	−4.7757	−0.1220	0.6706	37.0338
σ	0.012	0.033	0.076	0.012	0.006
Methyl Acetate (1) + Methanol (2) + 1-Pentanol (3)					
A_{ijk}	0.3865	0.4955	0.5844	1.2128	54.9596
σ	0.015	0.0190	0.083	0.015	0.009

Table 10. Root Mean Square Deviations σ of Prediction Results of Viscosity for Ternary Systems at 298.15 K

model	σ
Methyl Acetate (1) + Methanol (2) + 1-Butanol (3)	
UNIFAC−VISCO	0.060
GC−UNIMOD	0.254
Methyl Acetate (1) + Methanol (2) + 1-Pentanol (3)	
UNIFAC−VISCO	0.041
GC−UNIMOD	0.289

Table 11. Relative Error Percent (*RE*(%)) of Prediction Results of Speed of Sound for Binary and Ternary Systems at 298.15 K

system	RE(%)
methyl acetate + 1-butanol	1.29
methyl acetate + 1-pentanol	1.51
methanol + 1-butanol	0.80
methanol + 1-pentanol	1.30
methyl acetate + methanol + 1-butanol	0.68
methyl acetate + methanol + 1-pentanol	0.85

of Schaaffs (1963) are gathered. The best results for binary and ternary mixtures are obtained for the systems methyl acetate + 1-butanol and the ternary methyl acetate + methanol + 1-butanol, respectively.

Acknowledgment

The authors wish to thank the CACTI (Department of Technological and Scientific Support to the Research of Vigo University) for its technical assistance in the experimental development of this paper.

Registry Numbers Supplied by the Author: Methyl acetate, 79-20-9; methanol, 67-56-1; 1-butanol, 71-36-3; 1-pentanol, 71-41-0.

Literature Cited

Bevington, P. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

Canosa, J.; Rodríguez, A.; Tojo, J. Dynamic Viscosity and Speed of Sound of the Ternary Mixture Methyl Acetate + Methanol + Ethanol at 298.15 K. *J. Chem. Eng. Data.* **1998a**, *43*, 961−966.

Canosa, J.; Rodríguez, A.; Tojo, J. Dynamic Viscosities of (Methyl Acetate or Methanol) with (Ethanol, 1-Propanol, 2-Propanol, 1-Butanol and 2-Butanol) at 298.15 K. *J. Chem. Eng. Data.* **1998b**, *43*, 417−421.

Cao, W.; Knudsen. K.; Fredeslund, A.; Rasmussen, P. Simultaneous Correlation of Viscosity and Vapor−Liquid Equilibrium Data. *Ind. Eng. Chem. Res.* **1993**, *32*, 2088−2092.

Cibulka, I. Estimation of Excess Volume and Density of Ternary Liquid Mixtures of Nonelectrolytes from Binary Data. *Collect. Czech. Commun.* **1982**, *47*, 1414−1419.

Das, A.; Frenkel, M.; Gadalla, N. M.; Marsh, K.; Wilhoit, R. C. *TRC Thermodynamic Tables*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994.

Gaston-Bonhomme, Y.; Petrino, P.; Chevalier, J. L. UNIFAC−VISCO Group Contribution method for predicting kinematic viscosity: extension and temperature dependence. *J. Chem. Eng. Sci.* **1994**, *49*, 1799−1806.

Iglesias, M.; Orge, B.; Canosa, J. M.; Rodríguez, A.; Domínguez, M.; Piñeiro, M. M.; Tojo, J. Thermodynamic behaviour of mixtures containing methyl acetate, methanol, and 1-butanol at 298.15 K: application of the ERAS model. *Fluid Phase Equilib.* **1998**, *147*, 285−300.

Kalidas, R.; Laddha, G. S. Viscosity of Ternary Liquid Mixtures. *J. Chem. Eng. Data.* **1964**, *1*, 142−145.

Linek, J. Excess Volumes of Binary Liquid Mixtures Containing Ethers, Alcohols, Esters or Alkanes. *ELDATA: Int. Electron. J. Phys. Chem. Data* **1995**, *1*, 43−52

Lorenzi, L.; Fermeglia, M.; Torriano, G. Densities and Viscosities of 1,1,1-Trichloroethane with 13 Different Solvents at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1172−1177.

Nagata, I.; Tamura, K. Vapor−Liquid Equilibria for Methanol + Acetone + Acetonitrile + Benzene at 328.15 K. *J. Chem. Eng. Data.* **1996**, *41*, 1135−1137.

Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolytic Solutions. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Riddick, J. A.; Bunger, W. B. *Organic Solvents Techniques of Chemistry*, 4th ed.; Wiley: New York, 1986; Vol. II.

Rodríguez, A.; Canosa, J.; Orge, B.; Iglesias, M.; Tojo, J. Mixing Properties and Derived Magnitudes of the System Methyl Acetate + Methanol + 1-Pentanol at the temperature 298.15 K. *J. Chem. Thermodyn.* **1998a**, *30*, 215−227.

Rodríguez, A.; Canosa, J.; Tojo, J. Dynamic viscosities of the ternary liquid mixture involving CH_3COOCH_3, CH_3OH and $CH_3CH_2CH_2OH$ at $T = 298.15$ K. *J. Chem. Thermodyn.* **1998b**, *30*, 1307−1318.

Rodríguez, A.; Canosa, J.; Tojo, J. Speeds of sound of the ternary liquid mixtures methyl acetate + methanol with 1-propanol, or 2-propanol, or 2-butanol, or 2-methyl-2-butanol at $T = 298.15$ K. *J. Chem. Thermodyn.* **1999**, submitted for publication.

Schaaffs, W. *Molekularakustic*; Springer-Verlag: Berlin, 1963.

Received for review November 8, 1999. Accepted January 31, 2000.

JE9903000