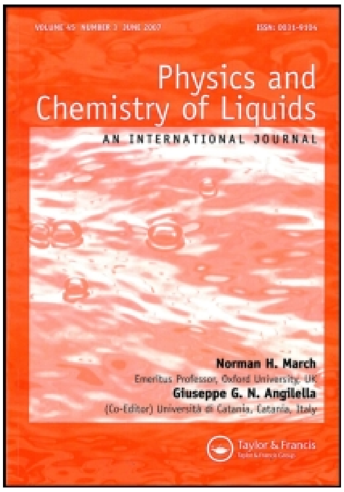

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DERIVED PROPERTIES OF BINARY MIXTURES CONTAINING (ACETONE OR METHANOL) + HYDROXIL COMPOUNDS

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This work reports values of the density, refractive index and speed of sound of the binary mixtures acetone or methanol with (2-methyl, 1-propanol, 3-methyl, 1-butanol, 1,2-ethanediol, 1,2-propanediol and 1,3-propanediol) at 298.15 K and atmosphere, as a function of the mole fraction. From the experimental values, the corresponding excess and derived magnitudes were computed (excess molar volumes, changes of refractive index on mixing and changes of isentropic compressibility on mixing), variable-degree polynomials being fitted to the results. Only expansive trend was observed for those mixtures enclosing branched alcohols. The influence of the hydroxil group in the nonideal behaviour of these mixtures were analyzed in terms of the partial molar excess volumes.

Keywords: Acetone; Methanol; Branched alcohol; Alkanediol

1. INTRODUCTION

Thermochemical magnitudes and phase equilibra of liquid mixtures that have hydroxil groups, highly polarizable electron pairs or ketone groups, depend to a large extent on the molecular hydrogen bonding and polar interactions, as well as, hidrance effects. The length of

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*Corresponding author. Fax: +34 986 812382, e-mail: jtojo@uvigo.es chain and branched structures modify the attractive/repulsive interactions into the mixture, there being high non-ideality and sometimes phase splitting in those with high difference in polar and molecular volume characteristics. Polar substances such as methanol or short alcohols produce strong interactions due to its relatively low molecular volume, large polarity and autoassociative trend, large deviations from ideality being observed in the whole thermophysical properties field. This effect is also shown when other hydroxil compounds envolved such as branched alcohols or poliols, which is of interest into the development of extractive and modified distillation processes. Usually, high deviations and weak accuracy is observed for predictive thermodynamic models, thus experimental data being necessary to extend and improve them. As a continuation of our research on thermodynamic properties of mixtures related to azeotropic separation processes (Iglesias *et al.*, 1996; Canosa *et al.*, 1998; Iglesias *et al.*, 1999), we present in this paper the experimental measurement of densities, refractive indices and speeds of sound of the binary mixtures acetone or methanol + (2-methyl, 1-propanol, 3-methyl, 1-butanol, 1,2-ethanediol, 1,2-propanediol and 1,3-propanediol) at 298.15 K and atmospheric pressure. Only expansive trend was observed for those mixtures enclosing branched alcohols. The influence of the hydroxil group in the nonideal behaviour of these mixtures were analyzed in terms of values and trends of the corresponding partial molar excess volumes for these mixtures.

2. EXPERIMENTAL

Acetone, 3-methyl, 1-butanol and 1,2-propanediol are supplied by Merck (Lichrosolv quality), 2-methyl, 1-propanol by Fluka, 1,2-ethanediol by Panreac and 1,3-propanediol for Riedel de Haën. Their mole-fraction purities tested by means of gas – liquid cromatography were better than 0.998 for acetone, better than 0.995 for 1,2-ethanediol and 1,2-propanediol and better than 0.990 for 3-methyl, 1-butanol and 1,3-propanediol. Usual procedure for chemicals were applied using molecular sieves (3 Å or 4 Å) in order to dehydrate and ultrasonic treatment for degassing solvents. Their maximum water

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

	$\rho/(g \cdot cm^{-3})$		n_D		*Maximum water content mass%*
Component	*Exptl.*	*Lit.*	*Exptl.*	*Lit.*	
Acetone	0.7844	0.78440[a]	1.35580	1.35596[a]	$1.6 \cdot 10^{-1}$
Methanol	0.7866	0.78664[b]	1.32645	1.32652[b]	$2.2 \cdot 10^{-2}$
2-Methyl, 1-propanol	0.7977	0.7978[b]	1.39353	1.3939[b]	$5.5 \cdot 10^{-3}$
3-Methyl, 1-butanol	0.8060	0.8070[b]	1.40531	1.4052[b]	$1.3 \cdot 10^{-2}$
1,2-Ethanediol	1.1097	1.1100[b]	1.43017	1.4306[b]	$1.4 \cdot 10^{-1}$
1,2-Propanediol	1.0325	1.0328[b]	1.43127	1.4314[b]	$5.0 \cdot 10^{-2}$
1,3-Propanediol	1.0498	1.050[a]	1.43853	1.4386[b]	$1.9 \cdot 10^{-2}$

[a] Riddick, J. A. *et al.*
[b] *TRC Thermodynamic Tables* (Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994).

content (Metrohm 737 KF coulometer) are shown in Table I. Manipulation procedure of chemicals and applied techniques in our laboratory are commented in a previous paper (Iglesias *et al.*, 1996). The densities and speeds of sound of mixtures and pure liquids were measured with an Anton Paar DSA-48 densimeter and sound analyzer with a precision of $\pm 5 \cdot 10^{-5}$ $g \cdot cm^{-3}$ and $\pm 10^{-1}$ $m \cdot s^{-1}$ respectively. Refractive indices were measured by an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of $\pm 10^{-5}$. Thermostation of refractometer was realized by a controller bath PolyScience model 9510, with a temperature stability of $\pm 10^{-2}$ K. Samples preparation was made by weight using a Mettler AE-240 balance with a precision of $\pm 10^{-4}$ g, covering the whole composition range of the binary mixtures. Before each serie of measurements, the instrument were calibrated in accordance with the use instructions, no systematic errors being detected in the measurements. The accuracy for mole fractions in samples was estimated better than $\pm 5 \cdot 10^{-5}$.

3. RESULTS AND DISCUSSION

The experimental results of density, ρ, refractive index, n_D, speed of sound, u, and isentropic compressibility, κ_S ($\kappa_S = \rho^{-1} u^{-2}$) at 298.15 K, for all binary mixtures are reported in Table II. The values

TABLE II Densities, excess molar volumes, refractive indices, changes of refractive index on mixing, speeds of sound, isentropic compressibility, and changes of isentropic compressibility for the binary mixtures at 298.15 K

x_1	ρ $g \cdot cm^{-3}$	V^E $cm^3 mol^{-1}$	n_D	δn_D	u $m \cdot s^{-1}$	κ_S TPa^{-1}	$\delta\kappa_S$ TPa^{-1}
acetone (1) + 2-methyl-1-propanol (2)							
0.0434	0.7971	0.016	1.39227	0.00038	1186.4	891.2	−0.1
0.0969	0.7963	0.040	1.39061	0.00074	1184.7	894.8	0.4
0.2048	0.7948	0.071	1.38702	0.00122	1180.7	902.6	2.1
0.3080	0.7933	0.101	1.38348	0.00157	1176.6	910.6	4.2
0.4033	0.7920	0.112	1.38022	0.00191	1173.2	917.3	5.4
0.5004	0.7907	0.116	1.37671	0.00206	1170.2	923.5	6.1
0.6097	0.7892	0.116	1.37263	0.00210	1167.8	929.1	5.5
0.7030	0.7881	0.092	1.36888	0.00187	1166.2	933.0	4.1
0.8021	0.7869	0.064	1.36465	0.00138	1164.7	936.8	2.2
0.9032	0.7858	0.017	1.36046	0.00101	1163.6	939.8	−0.5
0.9531	0.7852	−0.002	1.35804	0.00047	1162.3	942.7	−0.5
acetone (1) + 3-methyl-1-butanol (2)							
0.0385	0.8053	0.017	1.40388	0.00048	1231.1	819.3	−0.6
0.0975	0.8043	0.030	1.40192	0.00144	1226.7	826.2	−1.4
0.2040	0.8023	0.064	1.39763	0.00242	1218.2	839.9	−1.6
0.3037	0.8004	0.083	1.39393	0.00366	1209.9	853.5	−1.2
0.3953	0.7986	0.092	1.38997	0.00423	1202.5	865.9	−0.7
0.4956	0.7966	0.089	1.38541	0.00464	1194.7	879.5	−0.2
0.5972	0.7945	0.076	1.38040	0.00466	1187.2	893.1	−0.0
0.7026	0.7921	0.065	1.37495	0.00443	1179.9	906.8	−0.1
0.7990	0.7898	0.046	1.36929	0.00354	1173.8	918.9	−0.6
0.9084	0.7871	0.010	1.36243	0.00209	1167.0	932.9	−1.0
0.9467	0.7861	−0.004	1.35961	0.00117	1164.6	937.9	−1.0
acetone (1) + 1,2-ethanediol (2)							
0.0396	1.0958	−0.152	1.42784	0.00062	1629.2	343.8	−9.3
0.0804	1.0816	−0.299	1.42509	0.00090	1601.6	360.4	−17.9
0.1664	1.0521	−0.582	1.41911	0.00132	1544.3	398.6	−32.8
0.2527	1.0220	−0.763	1.41294	0.00156	1486.6	442.8	−41.9
0.3446	0.9904	−0.891	1.40626	0.00172	1428.6	494.7	−46.6
0.4390	0.9588	−0.974	1.39930	0.00178	1373.9	552.5	−47.1
0.5370	0.9261	−0.950	1.39197	0.00174	1323.2	616.8	−43.4
0.6425	0.8928	−0.918	1.38384	0.00145	1279.3	684.4	−40.8
0.7544	0.8584	−0.794	1.37520	0.00113	1239.1	758.7	−35.6
0.8719	0.8225	−0.489	1.36596	0.00063	1203.4	839.5	−27.3
0.9337	0.8039	−0.266	1.36113	0.00040	1185.0	885.8	−19.1
acetone (1) + 1,2-propanediol (2)							
0.0509	1.0211	−0.093	1.42810	0.00067	1487.4	442.7	−8.9
0.1044	1.0091	−0.191	1.42458	0.00119	1464.3	462.2	−17.2
0.2053	0.9861	−0.353	1.41814	0.00236	1421.1	502.1	−29.8
0.3095	0.9615	−0.463	1.41076	0.00285	1377.8	547.9	−38.3
0.4095	0.9368	−0.487	1.40362	0.00326	1336.8	597.3	−41.0
0.5112	0.9117	−0.512	1.39599	0.00330	1299.8	649.2	−42.0
0.6029	0.8884	−0.479	1.38902	0.00325	1268.7	699.3	−39.7
0.7032	0.8629	−0.437	1.38119	0.00299	1238.6	755.4	−35.9

TABLE II (Continued)

x_1	ρ $g \cdot cm^{-3}$	V^E $cm^3 mol^{-1}$	n_D	δn_D	u $m \cdot s^{-1}$	κ_S TPa^{-1}	$\delta\kappa_S$ TPa^{-1}
0.7974	0.8385	−0.355	1.37340	0.00231	1213.7	809.7	−30.7
0.8967	0.8122	−0.208	1.36491	0.00131	1189.7	869.9	−22.1
0.9466	0.7988	−0.112	1.36053	0.00070	1177.1	903.6	−14.5
acetone (1) + 1,3-propanediol (2)							
0.0514	1.0383	−0.169	1.43510	0.00082	1603.1	374.8	−16.3
0.1008	1.0274	−0.344	1.43212	0.00193	1580.5	389.7	−30.3
0.2028	1.0041	−0.656	1.42577	0.00402	1530.2	425.3	−54.3
0.3062	0.9790	−0.870	1.41877	0.00557	1477.4	467.9	−72.1
0.4100	0.9524	−0.981	1.41073	0.00612	1422.0	519.2	−81.6
0.5060	0.9270	−1.020	1.40281	0.00614	1372.3	572.8	−84.1
0.5994	0.9016	−0.996	1.39484	0.00589	1326.3	630.6	−81.0
0.7051	0.8720	−0.886	1.38531	0.00511	1279.2	700.8	−72.6
0.8050	0.8433	−0.702	1.37598	0.00405	1239.2	772.2	−59.6
0.9052	0.8138	−0.429	1.36590	0.00226	1201.5	851.1	−39.3
0.9541	0.7986	−0.210	1.36078	0.00118	1181.7	896.6	−22.4
methanol (1) + 2-methyl-1-propanol (2)							
0.0455	0.7974	0.008	1.39220	0.00172	1185.8	891.9	−4.1
0.1087	0.7969	0.026	1.39020	0.00396	1182.8	896.9	−9.1
0.2041	0.7961	0.049	1.38665	0.00681	1177.5	905.9	−15.1
0.3000	0.7952	0.072	1.38264	0.00923	1171.6	916.2	−19.9
0.4074	0.7942	0.084	1.37755	0.01135	1164.1	929.2	−23.9
0.5071	0.7931	0.096	1.37216	0.01265	1156.1	943.4	−25.5
0.6030	0.7920	0.098	1.36611	0.01303	1147.4	959.0	−24.9
0.7055	0.7907	0.093	1.35842	0.01222	1137.3	977.8	−22.4
0.8018	0.7894	0.078	1.35005	0.01031	1126.6	998.1	−17.2
0.8999	0.7881	0.044	1.33958	0.00642	1115.0	1020.7	−10.1
0.9491	0.7874	0.023	1.33346	0.00360	1109.6	1031.6	−7.0
methanol (1) + 3-methyl-1-butanol (2)							
0.0681	0.8054	0.011	1.40311	0.00317	1229.7	821.1	−9.5
0.0999	0.8051	0.017	1.40208	0.00465	1227.7	824.1	−13.9
0.2067	0.8040	0.034	1.39821	0.00920	1219.8	835.9	−26.8
0.3035	0.8028	0.054	1.39396	0.01258	1211.6	848.6	−36.6
0.4021	0.8014	0.073	1.38906	0.01546	1201.8	863.9	−44.1
0.4962	0.7999	0.084	1.38335	0.01717	1191.0	881.3	−48.5
0.6050	0.7978	0.098	1.37604	0.01844	1176.2	906.1	−49.0
0.7051	0.7956	0.097	1.36730	0.01759	1160.7	933.0	−45.3
0.8034	0.7930	0.088	1.35700	0.01505	1143.2	964.9	−36.2
0.8984	0.7901	0.061	1.34428	0.00982	1124.1	1001.6	−21.4
0.9504	0.7884	0.033	1.33568	0.00532	1113.1	1023.8	−11.3
methanol (1) + 1,2-ethanediol (2)							
0.0571	1.0980	0.098	1.42675	0.00250	1632.1	341.9	−27.8
0.1097	1.0869	0.190	1.42331	0.00452	1609.8	355.0	−52.4
0.2467	1.0559	0.416	1.41360	0.00902	1549.1	394.6	−111.2
0.3154	1.0385	0.491	1.40804	0.01058	1515.6	419.2	−135.9
0.3965	1.0166	0.563	1.40126	0.01221	1474.6	452.4	−161.0
0.5035	0.9852	0.625	1.39139	0.01344	1417.2	505.3	−184.8

TABLE II (Continued)

x_1	ρ $g \cdot cm^{-3}$	V^E $cm^3 mol^{-1}$	n_D	δn_D	u $m \cdot s^{-1}$	κ_S TPa^{-1}	$\delta\kappa_S$ TPa^{-1}
0.6073	0.9520	0.660	1.38077	0.01359	1359.7	568.1	−196.5
0.7056	0.9170	0.627	1.36923	0.01224	1301.2	644.0	−191.2
0.8070	0.8766	0.505	1.35637	0.00990	1236.8	745.8	−162.3
0.8988	0.8363	0.325	1.34320	0.00625	1175.6	865.1	−108.8
0.9542	0.8098	0.165	1.33426	0.00306	1136.1	956.7	−57.0
		methanol (1) + 1,2-propanediol (2)					
0.0518	1.0262	−0.064	1.42868	0.00284	1497.7	434.4	−22.8
0.0901	1.0215	−0.122	1.42660	0.00477	1488.6	441.8	−39.3
0.2086	1.0053	−0.270	1.41959	0.01019	1458.9	467.4	−87.3
0.3105	0.9894	−0.379	1.41267	0.01395	1429.8	494.4	−123.7
0.3979	0.9741	−0.459	1.40619	0.01663	1402.4	521.9	−150.4
0.4957	0.9547	−0.527	1.39787	0.01856	1367.9	559.8	−173.4
0.5858	0.9342	−0.558	1.38903	0.01916	1332.6	602.8	−186.4
0.6923	0.9058	−0.539	1.37718	0.01848	1285.0	668.6	−186.8
0.8031	0.8705	−0.452	1.36210	0.01501	1228.3	761.4	−162.8
0.9007	0.8328	−0.280	1.34627	0.00941	1169.9	877.4	−107.5
0.9553	0.8087	−0.152	1.33588	0.00474	1134.3	961.0	−57.8
		methanol (1) + 1,3-propanediol (2)					
0.0688	1.0404	−0.074	1.43425	0.00343	1603.9	373.6	−34.6
0.0970	1.0366	−0.119	1.43265	0.00499	1595.0	379.2	−48.3
0.1792	1.0246	−0.232	1.42771	0.00926	1567.1	397.4	−86.5
0.2857	1.0073	−0.365	1.42008	0.01357	1528.1	425.2	−131.7
0.4059	0.9846	−0.473	1.41081	0.01777	1477.1	465.5	−173.8
0.4960	0.9652	−0.537	1.40222	0.01928	1435.4	502.8	−198.2
0.5990	0.9398	−0.575	1.39116	0.01977	1382.4	556.8	−214.8
0.7094	0.9077	−0.558	1.37763	0.01861	1317.8	634.4	−212.9
0.7976	0.8772	−0.469	1.36484	0.01571	1259.5	718.7	−189.2
0.8925	0.8392	−0.323	1.34873	0.01023	1190.8	840.4	−132.5
0.9453	0.8148	−0.189	1.33840	0.00582	1148.7	930.0	−79.1

of changes of refractive indices on mixing, excess molar volumes, and changes of isentropic compressibilities on mixing have been computed using the following equations

$$\delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \tag{1}$$

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

$$\delta\kappa_S = \kappa_S - \sum_{i=1}^{N} x_i \kappa_{Si} \tag{3}$$

In these equations, n_D, ρ, and κ_S are the refractive index, density and isentropic compressibility of the mixture, respectively. The properties of pure components are represented by n_{Di}, ρ_i, κ_{Si}, and N is the number of components in the mixture. Excess and derived properties were correlated using the Redlich–Kister expression (Redlich and Kister, 1948) (Eq. (4)) by the unweighted least square method.

$$\delta Q = x_i \cdot x_j \cdot \sum_{p=0}^{m} B_p \cdot (x_i - x_j)^p \tag{4}$$

In this equation x_i and x_j are the mole fraction of the components, m is the degree of the polynomial and B_p are the fitting parameters. The degree of this polynomial, m, was optimized applying the F-test (Bevington, 1969). These parameters are compiled in Table III as well as the root mean square deviations calculated according to the expression:

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

where z_{exp} is the experimental value, z_{cal} is the calculated value and n_{DAT} is the number of experimental data points. In Figures 1–6, the derived values as well as correlation lines are shown, only expansive trend being observed for those mixtures enclosing branched alcohols. In order to analyze the influence of functional type and number in the solvent of acetone or methanol component, the partial excess molar volumes were derived from these results. In general, the partial molar quantities are important in the study of the dependence of an extensive property on the phase composition at constant pressure and temperature, because show its trend with molar fraction variation. They should be applied to any extensive property of a single-phase system such as volume, Gibbs energy or any other. If we let E represent any extensive property of a single phase which is a function

TABLE III Parameters B_p of equation fitted (2) to the excess and derived properties and standard deviations σ

	B_0	B_1	B_2	B_3	B_4	B_5	σ
acetone (1) + 2-methyl-1-propanol (2)							
δn_D	$8.3665\cdot10^{-3}$	$1.9413\cdot10^{-3}$	$-2.5401\cdot10^{-3}$	$-9.8066\cdot10^{-4}$	$6.4308\cdot10^{-3}$		$1\cdot10^{-4}$
$V^E/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	$4.7042\cdot10^{-1}$	$4.8251\cdot10^{-2}$	$1.0191\cdot10^{-2}$	$-3.1168\cdot10^{-1}$	$-4.0289\cdot10^{-1}$		$3\cdot10^{-3}$
$\delta\kappa_S/(\mathrm{TPa}^{-1})$	$2.4762\cdot10^{1}$	$3.6919\cdot10^{0}$	$-3.5518\cdot10^{1}$	$-1.2444\cdot10^{1}$			$2\cdot10^{-1}$
acetone (1) + 3-methyl-1-butanol (2)							
δn_D	$1.8811\cdot10^{-2}$	$5.3520\cdot10^{-3}$					$1\cdot10^{-4}$
$V^E/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	$3.4790\cdot10^{-1}$	$-1.9932\cdot10^{-1}$	$1.1778\cdot10^{-1}$	$6.8545\cdot10^{-1}$	$-4.2403\cdot10^{-1}$	$-9.4730\cdot10^{-1}$	$2\cdot10^{-3}$
$\delta\kappa_S/(\mathrm{TPa}^{-1})$	$-9.1338\cdot10^{-1}$	$6.6900\cdot10^{0}$	$-1.2337\cdot10^{1}$	$2.3942\cdot10^{0}$	$-1.1102\cdot10^{1}$	$-1.4663\cdot10^{1}$	$1\cdot10^{-1}$
acetone (1) + 1,2-ethanediol (2)							
δn_D	$7.0782\cdot10^{-3}$	$-1.5246\cdot10^{-3}$	$-1.7480\cdot10^{-3}$	$-3.1618\cdot10^{-3}$	$7.1097\cdot10^{-3}$		$1\cdot10^{-4}$
$V^E/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	$-3.8622\cdot10^{0}$	$-1.1309\cdot10^{-1}$	$-1.5778\cdot10^{0}$	$-9.1038\cdot10^{-2}$	$1.5225\cdot10^{0}$		$1\cdot10^{-2}$
$\delta\kappa_S/(\mathrm{TPa}^{-1})$	$-1.8019\cdot10^{2}$	$6.1783\cdot10^{1}$	$-1.1526\cdot10^{2}$	$-1.2345\cdot10^{2}$			$5\cdot10^{-1}$
acetone (1) + 1, 2-propanediol (2)							
δn_D	$1.3263\cdot10^{-2}$	$6.2037\cdot10^{-4}$	$5.0726\cdot10^{-3}$	$-4.0296\cdot10^{-4}$	$-6.4805\cdot10^{-3}$		$1\cdot10^{-4}$
$V^E/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	$-2.0106\cdot10^{0}$	$1.2669\cdot10^{-1}$	$-8.2617\cdot10^{-1}$	$-3.9218\cdot10^{-1}$	$9.6334\cdot10^{-1}$		$6\cdot10^{-1}$
$\delta\kappa_S/(\mathrm{TPa}^{-1})$	$-1.6771\cdot10^{2}$	$1.5326\cdot10^{1}$	$-3.3437\cdot10^{1}$	$-3.0364\cdot10^{1}$	$-6.0760\cdot10^{1}$	$-7.7090\cdot10^{1}$	$3\cdot10^{-1}$
acetone (1) + 1, 3-propanediol (2)							
δn_D	$2.4703\cdot10^{-2}$	$-3.2950\cdot10^{-3}$	$5.9687\cdot10^{-3}$	$1.0579\cdot10^{-2}$	$-1.1748\cdot10^{-2}$		$1\cdot10^{-4}$
$V^E/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	$-4.0956\cdot10^{0}$	$-6.5530\cdot10^{-2}$	$-3.8163\cdot10^{-1}$	$-9.1352\cdot10^{-1}$			$9\cdot10^{-3}$
$\delta\kappa_S/(\mathrm{TPa}^{-1})$	$-3.3672\cdot10^{2}$	$9.3473\cdot10^{0}$	$-2.1927\cdot10^{1}$	$-1.2751\cdot10^{2}$	$-1.0155\cdot10^{2}$		$2\cdot10^{-1}$
methanol (1) + 2-methyl-1-propanol (2)							
δn_D	$5.0135\cdot10^{-2}$	$1.8801\cdot10^{-2}$	$8.6875\cdot10^{-3}$				$1\cdot10^{-4}$
$V^E/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	$3.7679\cdot10^{-1}$	$1.4082\cdot10^{-1}$	$1.4098\cdot10^{-1}$	$8.7542\cdot10^{-3}$	$-2.3675\cdot10^{-1}$		$1\cdot10^{-3}$
$\delta\kappa_S/(\mathrm{TPa}^{-1})$	$-1.0161\cdot10^{2}$	$-1.4575\cdot10^{1}$					$5\cdot10^{-1}$

			methanol (1) + 3-methyl-1-butanol (2)				
δn_D	$6.9470 \cdot 10^{-2}$	$3.0187 \cdot 10^{-2}$	$1.5729 \cdot 10^{-2}$	$6.9692 \cdot 10^{-3}$			$1 \cdot 10^{-4}$
$V^E/(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$	$3.4371 \cdot 10^{-1}$	$2.8422 \cdot 10^{-1}$	$1.1366 \cdot 10^{-1}$				$2 \cdot 10^{-3}$
$\delta \kappa_S/(\mathrm{TPa}^{-1})$	$-1.9460 \cdot 10^{2}$	$-5.3581 \cdot 10^{1}$					$2 \cdot 10^{-1}$
			methanol (1) + 1,2-ethanediol (2)				
δn_D	$5.3488 \cdot 10^{-2}$	$1.3140 \cdot 10^{-2}$	$5.5084 \cdot 10^{-3}$				$1 \cdot 10^{-4}$
$V^E/(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$	$-2.5402 \cdot 10^{0}$	$-9.4073 \cdot 10^{-1}$	$-3.9359 \cdot 10^{-1}$				$8 \cdot 10^{-3}$
$\delta \kappa_S/(\mathrm{TPa}^{-1})$	$-7.3717 \cdot 10^{2}$	$-3.4749 \cdot 10^{2}$	$-1.9599 \cdot 10^{2}$	$-1.0265 \cdot 10^{2}$			$5 \cdot 10^{-1}$
			methanol (1) + 1,2-propanediol (2)				
δn_D	$7.4257 \cdot 10^{-2}$	$2.7033 \cdot 10^{-2}$	$1.1315 \cdot 10^{-2}$	$2.9073 \cdot 10^{-3}$			$1 \cdot 10^{-4}$
$V^E/(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$	$-2.1109 \cdot 10^{0}$	$-1.0297 \cdot 10^{0}$	$-3.3085 \cdot 10^{-1}$				$4 \cdot 10^{-3}$
$\delta \kappa_S/(\mathrm{TPa}^{-1})$	$-6.9720 \cdot 10^{2}$	$-3.7143 \cdot 10^{2}$	$-1.8888 \cdot 10^{2}$	$-1.2709 \cdot 10^{2}$	$-6.6853 \cdot 10^{1}$		$4 \cdot 10^{-1}$
			methanol (1) + 1,3-propanediol (2)				
δn_D	$7.7378 \cdot 10^{-2}$	$2.4664 \cdot 10^{-2}$	$7.7136 \cdot 10^{-3}$	$1.0824 \cdot 10^{-2}$			$1 \cdot 10^{-4}$
$V^E/(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$	$-2.1669 \cdot 10^{0}$	$-9.8926 \cdot 10^{-1}$	$-3.2454 \cdot 10^{-1}$	$-4.3635 \cdot 10^{-1}$			$6 \cdot 10^{-3}$
$\delta \kappa_S/(\mathrm{TPa}^{-1})$	$-7.9699 \cdot 10^{2}$	$-4.4411 \cdot 10^{2}$	$-2.2481 \cdot 10^{2}$	$-7.0765 \cdot 10^{1}$	$-8.5794 \cdot 10^{1}$	$-9.6089 \cdot 10^{1}$	$2 \cdot 10^{-1}$

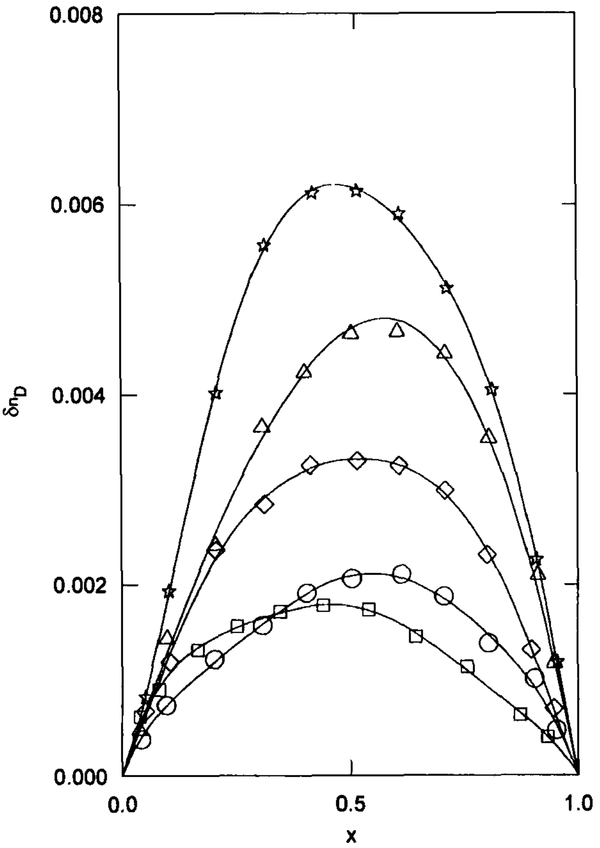

FIGURE 1 Changes of refractive indices on mixing at 298.15 K for the binary mixtures of acetone with (○) 2-methyl-1-propanol, (△) 3-methyl-1-butanol, (□) 1,2-ethanediol, (◇) 1,2-propanediol and (☆) 1,3-propanediol.

of pressure, temperature and mole numbers of the components, the differential of E should be expressed as:

$$\delta E = \left(\frac{\partial E}{\partial T}\right)_{P,n} dT + \left(\frac{\partial E}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{N} \left(\frac{\partial E}{\partial n_i}\right)_{T,P,n} dn_i \qquad (6)$$

where the quantity $(\partial E/\partial n_i)_{T,P,n}$ is defined as the partial molar quantity of the ith component in the phase, the value N refers to all

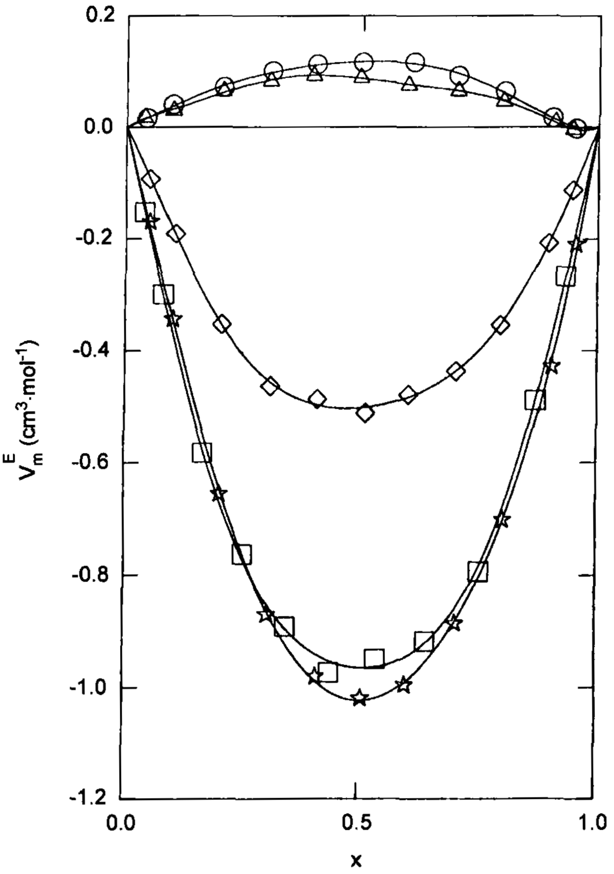

FIGURE 2 Excess molar volumes at 298.15 K for the binary mixtures of acetone with (○) 2-methyl-1-propanol, (△) 3-methyl-1-butanol, (□) 1,2-ethanediol, (◇) 1,2-propanediol and (☆) 1,3-propanediol.

the other components present, showing the finite change in the property on the addition of 1 mol of the component i in an infinite quantity of solution at constant temperature and pressure. In what is referred to an excess property, the partial excess molar volume of a component in a binary mixture can be determined from excess molar volume data by means of the following

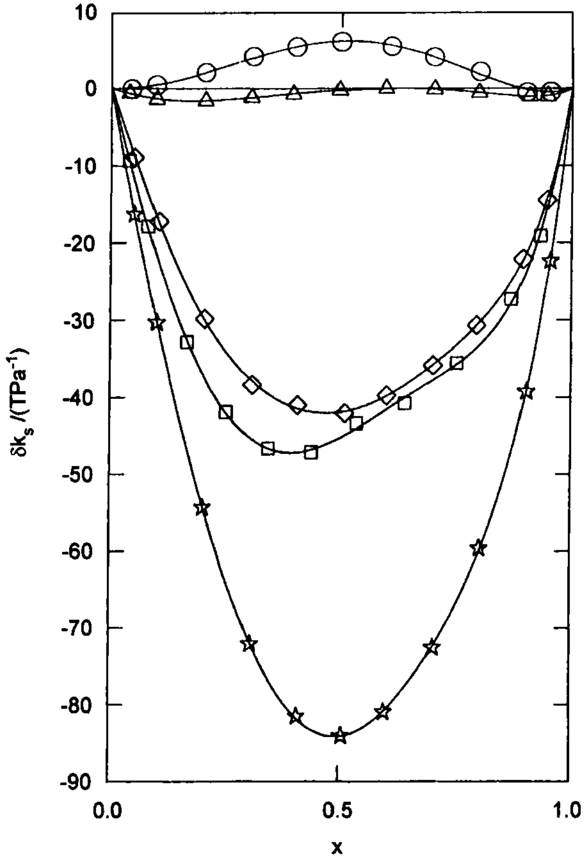

FIGURE 3 Changes of isentropic compressibilities at 298.15 K for the binary mixtures of acetone with (○) 2-methyl-1-propanol, (△) 3-methyl-1-butanol, (□) 1,2-ethanediol (◇) 1,2-propanediol and (☆) 1,3-propanediol.

expression:

$$\overline{V}_i^E = V^E + (1 - x_i)\left(\frac{dV^E}{dx_i}\right) \tag{7}$$

where the differential term is calculated taking into account we have applied the Redlich–Kister expression to correlate the excess values,

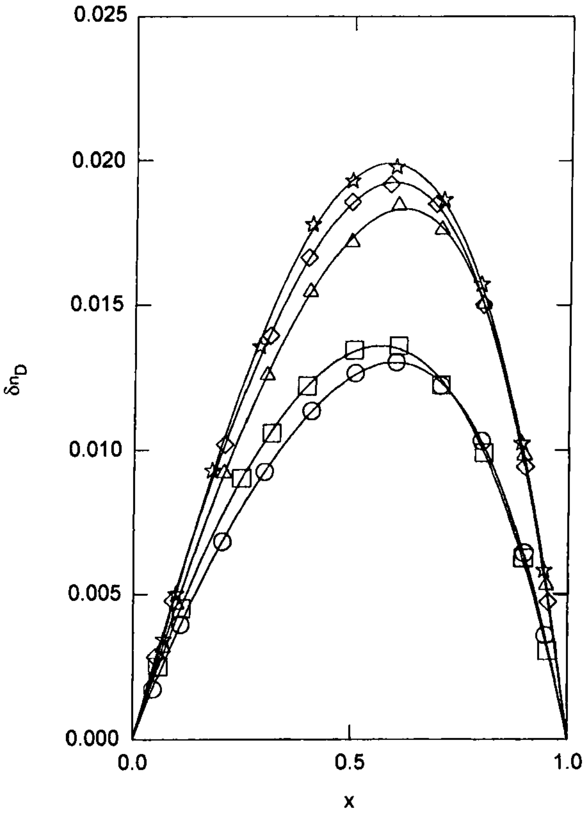

FIGURE 4 Changes of refractive indices on mixing at 298.15 K for the binary mixtures of methanol with (○) 2-methyl-1-propanol, (△) 3-methyl-1-butanol, (□) 1,2-ethanediol, (◇) 1,2-propanediol and (☆) 1,3-propanediol.

thus the parameters enclosed in Table III for Eq. (4) are applied. The expression for the partial excess molar volume, once the differentiation is performed and some algebra carried out, should be written as:

$$\overline{V}_i^E = (1 - x_i)^2 \left[\sum_{p=0}^{m} B_p (2x_1 - 1)^p + x_i \sum_{p=1}^{m} (-2)^{i-1} p B_p (2x_1 - 1)^{p-1} \right] \tag{8}$$

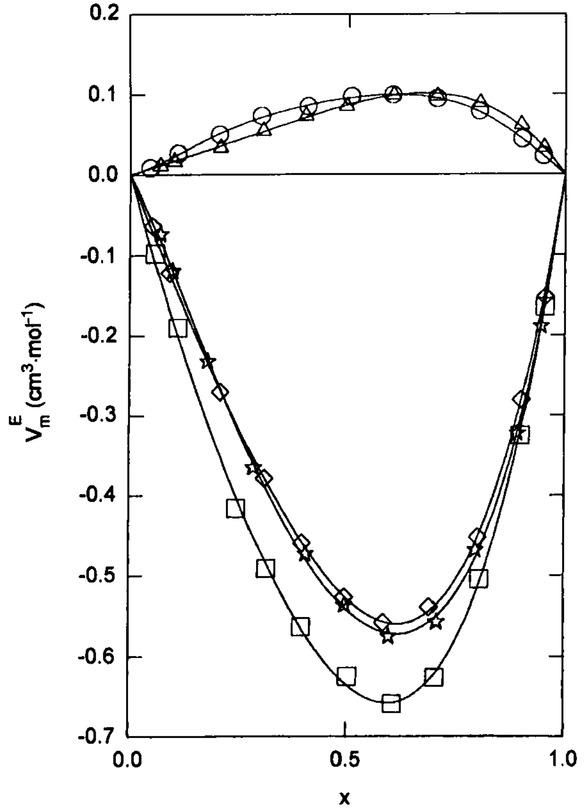

FIGURE 5 Excess molar volumes at 298.15 K for the binary mixtures of methanol with (○) 2-methyl-1-propanol, (△) 3-methyl-1-butanol, (□) 1,2-ethanediol, (◇) 1,2-propanediol and (☆) 1,3-propanediol.

where the symbols keep the meaning explained above. From Eq. (8), the corresponding limiting partial excess molar volumes should be determined by considering x_i nule in every expression, such limiting values being depending only on these correlation parameters. In Table IV, the values of limiting partial excess molar volumes at 298.15 K for the binary mixtures are enclosed. Figures 7 and 8 show the trends of partial excess molar volumes with the corresponding molar fraction for the binary mixtures. It could be observed the disruption rule of acetone or methanol into hydrogen bonds interactions among diol molecules over a slight concentration of each solvent. At the other hand, the branched alcohols reduce the expansive

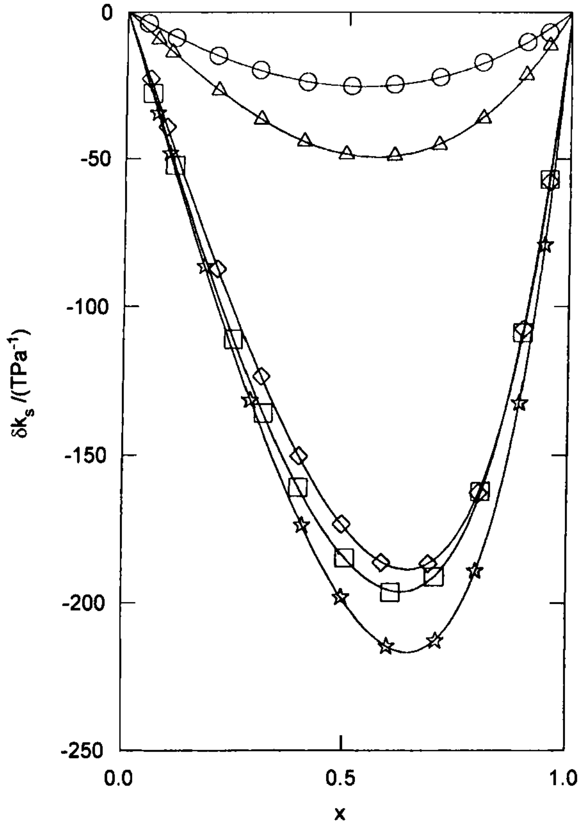

FIGURE 6 Changes of isentropic compressibilities at 298.15 K for the binary mixtures of methanol with (○) 2-methyl-1-propanol, (△) 3-methyl-1-butanol, (□) 1,2-ethanediol (◇) 1,2-propanediol and (☆) 1,3-propanediol.

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

	$\overline{V}_1^{E,\infty}/(cm^3mol^{-1})$	$\overline{V}_1^{E,\infty}/(cm^3mol^{-1})$
Acetone (1) + 1,2-Ethanodiol (2)	−3.71	−4.12
Acetone (1) + 1,2-Propanediol (2)	−1.61	−2.14
Acetone (1) + 1,3-Propanediol (2)	−3.50	−5.46
Acetone (1) + 2-Methyl, 1-Propanol (2)	0.34	−0.19
Acetone (1) + 3-Methyl, 1-Butanol (2)	0.50	−0.42
Methanol (1) + 1,2-Ethanodiol (2)	−1.99	−3.87
Methanol (1) + 1,2-Propanediol (2)	−1.41	−3.47
Methanol (1) + 1,3-Propanediol (2)	−1.07	−3.92
Methanol (1) + 2-Methyl, 1-Propanol (2)	0.13	0.43
Methanol (1) + 3-Methyl, 1-Butanol (2)	0.17	0.74

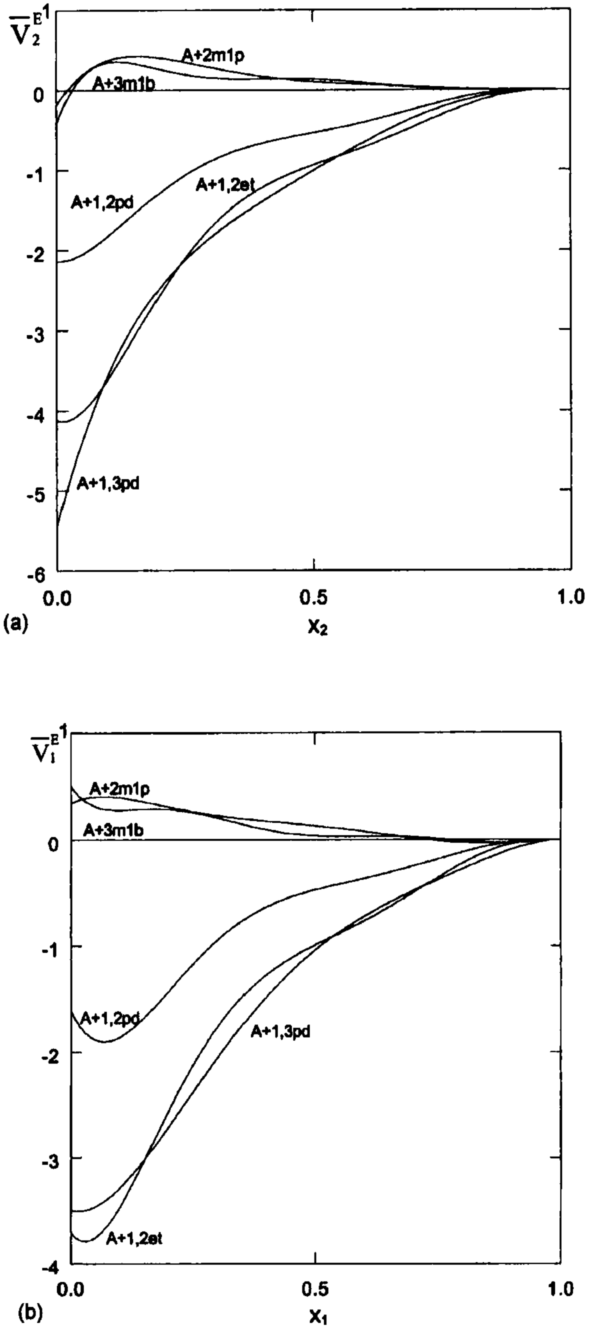

FIGURE 7 Partial excess molar volumes of acetone with 2-methyl-1-propanol, 3-methyl-1-butanol, 1,2-ethanediol, 1,2-propanediol and 1,3-propanediol mixtures at 298.15 K for (a) $\overline{V}_2^E$ and (b) $\overline{V}_1^E$.

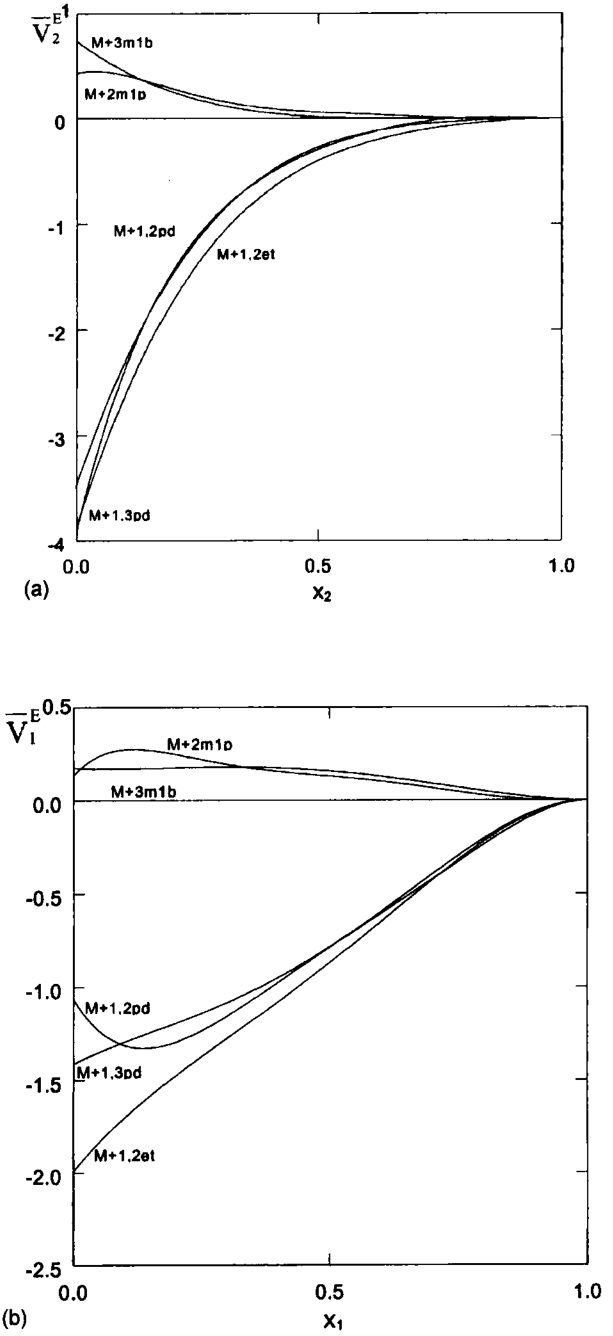

FIGURE 8 Partial excess molar volumes of methanol with 2-methyl-1-propanol, 3-methyl-1-butanol, 1,2-ethanediol, 1,2-propanediol and 1,3-propanediol mixtures at 298.15 K for (a) $\overline{V}_2^E$ and (b) $\overline{V}_1^E$.

trend into these mixtures when molar fraction of acetone or methanol is increased. This effect leads to contractive behaviour in those mixtures where diols are enclosed and expansive for branched alcohols. A curious influence is shown in 1,3-propanediol and 1,2-ethanediol mixtures when methanol is the solvent since a reduction in contractive trend can be observed. Almost comparative results are obtained in excess molar volumes for the three diol mixtures when interaction between alkane residues of acetone and 1,2-propanediol is not possible.

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