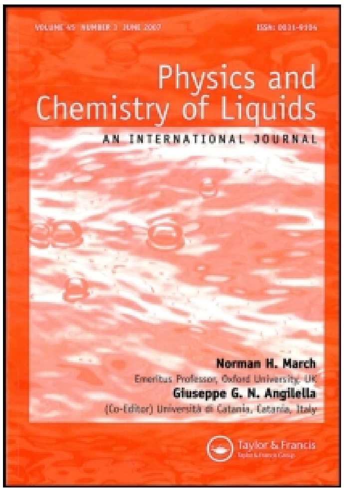

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MIXING PROPERTIES OF THE BINARY MIXTURES OF ACETONE, METHANOL, ETHANOL, AND 2-BUTANONE AT 298.15 K

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Speeds of sound, densities and refractive indices of the binary mixtures containing acetone, methanol, ethanol, or 2-butanone have been measured at 298.15 K and atmospheric pressure, in the whole composition diagram, the derived excess values being determined. Parameters of analytical expressions which represent the composition dependences of excess and variation of properties are reported. Values of physical properties were compared with the results obtained by different prediction methods. The excess volumes were estimated using different applications of the Heller equation, which are depending on the refractive indices of the mixtures. A good agreement between the experimental and theoretical values both in magnitude and sign were obtained by these methods.

Keywords: Densities; refractive indices; isentropic compressibilities

1. INTRODUCTION

Continuing our research on thermodynamic properties of alcohol + ketone multicomponent mixtures [1, 2] related to the azeotropic separation processes, we have determined experimental values of speed of sound, density and refractive indices for the binary mixtures present in the quaternary mixture acetone + methanol + ethanol + 2-butanone at the temperature 298.15 K and atmospheric pressure. Derived excess

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values were computed and then correlated by means of a Redlich-Kister [3] type equation, the parameters of these functions being gathered. Values of physical properties and the derived magnitudes were computed by means of prediction methods and binary contribution models. The application of two equations, which are derived from Heller equation, to predict excess molar volumes from refractive indices showed a good agreement for Lorenz-Lorentz mixing rule over the whole ranges of composition in these mixtures. The values of partial molar excess volumes as well as the corresponding limiting quantities, were determined and commented upon.

2. EXPERIMENTAL SECTION

The substances employed were supplied by Merck (Lichrosolv quality). Their mole fraction purities were better than 0.995 for 2-butanone and better than 0.998 for the other chemicals used, by means of gas-liquid chromatographic test, in accordance with vendor specifications. Values of measured properties, when available, were in accordance with which published in open literature (Tab. I). Usual procedure for chemicals were applied using molecular sieve (3Å) in order to dehydrate and ultrasonic treatment for degassing solvents. General procedure of chemicals manipulation and technique applied in our laboratory are commented in a previous paper [2]. The speeds of sound and densities of the pure substances and binary mixtures were measured with a digital vibrating tube analyser Anton Paar DSA-48

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

	$u/(m\cdot s^{-1})$		$\rho(g.cm^{-3})$		n_D	
Component	*exptl.*	*lit.*	*exptl.*	*lit.*[a]	*exptl.*	*lit.*[a]
Acetone	1161.0	1160.6[b]	0.7844	0.78547	1.35580	1.35596
Methanol	1102.1	1102[c]	0.7866	0.78664	1.32645	1.32652
Ethanol	1142.6	1142.4[b]	0.7850	0.78509	1.35922	1.35941
2-Butanone	1192.2		0.8001	0.7997	1.37616	1.3764
	1170.4[d]	1169[e]				

[a] TRC Thermodynamic Tables (1994). [b] Papaloannou *et al.* (1991). [c] Arce *et al.* (1996). [d] This work; measured at 303.15 K. [e] Rajasekar and Naidu (1996).

with a precision of ±0.00005 $g\cdot cm^{-3}$ and ±0.1 $m\cdot s^{-1}$ and the refractive indices by the automatic refractometer ABBEMAT-HP Dr Kernchen with a precision of ±0.00001. Thermostation of samples were 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 series of measurements, the instruments were calibrated in accordance with the use instructions, no systematic errors being detected in the measurements. The accuracy in the calculation of changes of speed of sound, excess molar volumes and changes of refractive indices on mixing was estimated as better than 2 $m\cdot s^{-1}$, $5.6.10^{-3}$ $cm^3\cdot mol^{-1}$, and 10^{-4}, respectively.

3. RESULTS AND DATA CORRELATION

Speeds of sound, isentropic compressibilities (determined by means of Laplace equation, $\kappa_S = \rho^{-1}u^{-2}$), densities, and refractive indices are given in Table II. The derived magnitudes, changes of isentropic compressibilities on mixing, excess molar volumes, and changes of refractive indices on mixing were determined using eqs. 1, 2 and 3, respectively.

$$\delta\kappa_S = \kappa_S - \sum_{i=1}^{N} x_i \kappa_{Si} \qquad (1)$$

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

$$\delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \qquad (3)$$

In these equations, κ_S is the isentropic compressibility, ρ is the density and n_D is the refractive index in the mixture, and M_i the molecular weight of the component i. The κ_{Si}, ρ_i and n_{Di} magnitudes are the properties of the pure components, N is the number of components in the mixture and δ means the variation of a magnitude. The values of the

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

			acetone(1) + methanol(2)				
x	$\rho/(g cm^{-3})$	n_D	$u/(m s^{-1})$	$\kappa_S/(TPa^{-1})$	$V_m^E/(cm^3 mol^{-1})$	δn_D	$\delta\kappa_S$
0.0210	0.7872	1.32805	1106.6	1037.3	−0.036	0.00098	−7.1
0.0804	0.7888	1.33164	1116.8	1016.4	−0.138	0.00283	−22.1
0.1257	0.7893	1.33407	1122.8	1004.9	−0.180	0.00393	−29.1
0.1840	0.7900	1.33668	1129.7	991.8	−0.240	0.00483	−36.3
0.2496	0.7903	1.33976	1135.9	980.7	−0.281	0.00598	−40.7
0.3187	0.7905	1.34235	1141.9	970.2	−0.319	0.00655	−44.3
0.3964	0.7903	1.34485	1146.9	962.0	−0.334	0.00677	−44.7
0.4787	0.7900	1.34714	1151.7	954.3	−0.343	0.00664	−44.0
0.5724	0.7894	1.34956	1155.8	948.2	−0.330	0.00631	−40.7
0.6762	0.7885	1.35161	1159.4	943.4	−0.292	0.00531	−35.1
0.8034	0.7871	1.35360	1162.7	939.7	−0.209	0.00357	−25.8
0.8626	0.7864	1.35447	1163.0	940.1	−0.161	0.00270	−19.6
0.9451	0.7853	1.35543	1162.7	941.9	−0.077	0.00124	−9.5
			acetone (1) + ethanol (2)				
x	$\rho/(g cm^{-3})$	n_D	$u/(m s^{-1})$	$\kappa_S/(TPa^{-1})$	$V_m^E/(cm^3 mol^{-1})$	δn_D	$\delta\kappa_S$
0.0335	0.7854	1.35917	1145.0	971.1	−0.032	0.00006	−3.6
0.1085	0.7857	1.35912	1148.0	965.8	−0.060	0.00027	−6.7
0.1763	0.7858	1.35897	1149.8	962.5	−0.072	0.00035	−7.9
0.2463	0.7858	1.35885	1151.2	960.2	−0.078	0.00047	−8.1
0.3289	0.7857	1.35859	1152.5	958.2	−0.075	0.00049	−7.6
0.4088	0.7856	1.35835	1153.7	956.3	−0.073	0.00053	−7.1
0.4879	0.7855	1.35806	1154.8	954.6	−0.070	0.00051	−6.5
0.5495	0.7854	1.35782	1155.7	953.2	−0.065	0.00048	−6.1
0.5753	0.7853	1.35775	1156.3	952.4	−0.058	0.00050	−6.1
0.6692	0.7851	1.35734	1157.8	950.1	−0.047	0.00041	−5.6

0.7480	0.7849	1.35700	1159.3	947.9	−0.033	0.00034	−5.5
0.8387	0.7846	1.35654	1160.7	946.0	−0.011	0.00019	−4.7
0.8501	0.7846	1.35656	1160.8	945.8	−0.012	0.00025	−4.5
0.9394	0.7844	1.35615	1161.3	945.3	0.003	0.00014	−2.4
0.9453	0.7844	1.35610	1161.3	945.3	0.002	0.00011	−2.2

acetone (1) + 2-butanone (2)

x	$\rho/(g\,cm^{-3})$	n_D	$u/(m\,s^{-1})$	$\kappa_S/(TPa^{-1})$	$V_m^E/(cm^3\,mol^{-1})$	δn_D	$\delta\kappa_S$
0.0533	0.7994	1.37513	1190.5	882.6	−0.001	0.00005	−0.3
0.1671	0.7978	1.37321	1186.6	890.2	−0.009	0.00045	−0.3
0.2527	0.7965	1.37161	1183.8	895.9	−0.020	0.00059	−0.3
0.2927	0.7958	1.37082	1182.5	898.6	−0.034	0.00062	−0.2
0.3445	0.7950	1.36980	1180.7	902.1	−0.039	0.00065	−0.2
0.3968	0.7942	1.36877	1179.2	905.5	−0.041	0.00069	−0.3
0.4488	0.7934	1.36776	1177.7	908.8	−0.043	0.00074	−0.4
0.5002	0.7926	1.36673	1176.1	912.2	−0.043	0.00075	−0.5
0.5535	0.7918	1.36564	1174.4	915.7	−0.039	0.00075	−0.5
0.6309	0.7906	1.36406	1172.0	920.8	−0.033	0.00074	−0.5
0.6827	0.7898	1.36299	1170.5	924.2	−0.027	0.00073	−0.6
0.7482	0.7887	1.36167	1168.6	928.5	−0.026	0.00074	−0.6
0.8169	0.7876	1.36012	1166.5	933.1	−0.016	0.00059	−0.6
0.8956	0.7862	1.35829	1164.2	938.4	−0.015	0.00036	−0.5
0.9620	0.7850	1.35667	1162.4	942.9	−0.011	0.00010	−0.5

TABLE II (Continued)

methanol (1) + ethanol (2)							
x	$\rho/(g cm^{-3})$	n_D	$u/(ms^{-1})$	$\kappa_S/(TPa^{-1})$	$V_m^E/(cm^3 mol^{-1})$	δn_D	$\delta\kappa_S$
0.0704	0.7853	1.35747	1141.0	978.1	−0.016	0.00056	−2.6
0.1854	0.7854	1.35461	1137.6	983.9	−0.013	0.00147	−4.9
0.2907	0.7855	1.35194	1133.8	990.3	−0.010	0.00225	−6.0
0.3813	0.7856	1.34942	1130.6	995.8	−0.008	0.00269	−6.9
0.4688	0.7857	1.34678	1127.3	1001.5	−0.006	0.00292	−7.4
0.5524	0.7858	1.34404	1123.8	1007.6	−0.004	0.00292	−7.3
0.6349	0.7859	1.34120	1120.3	1013.8	−0.002	0.00279	−6.9
0.7081	0.7860	1.33855	1116.9	1019.9	0.000	0.00253	−6.0
0.7081	0.7861	1.33577	1113.7	1025.5	0.002	0.00211	−5.5
0.8459	0.7862	1.33320	1110.3	1031.8	0.004	0.00170	−3.9
0.9078	0.7863	1.33056	1107.1	1037.7	0.005	0.00109	−2.4
0.9691	0.7864	1.32795	1103.9	1043.5	0.007	0.00049	−0.9
0.9700	0.7864	1.32790	1103.8	1043.8	0.007	0.00047	−0.7

methanol (1) + 2-butanone (2)							
x	$\rho/(g cm^{-3})$	n_D	$u/(ms^{-1})$	$\kappa_S/(TPa^{-1})$	$V_m^E/(cm^3 mol^{-1})$	δn_D	$\delta\kappa_S$
0.1005	0.7999	1.37404	1191.6	880.5	−0.048	0.00288	−15.7
0.1561	0.7999	1.37282	1190.1	882.7	−0.087	0.00442	−22.8
0.2818	0.7998	1.36972	1185.9	889.0	−0.165	0.00757	−37.5
0.3364	0.7997	1.36815	1183.2	893.2	−0.195	0.00871	−42.4
0.4138	0.7994	1.36548	1178.9	900.1	−0.224	0.00989	−48.5
0.5358	0.7985	1.36071	1170.5	914.1	−0.241	0.01118	−54.9
0.6454	0.7972	1.35551	1160.8	931.0	−0.233	0.01143	−56.3
0.7322	0.7957	1.35016	1151.2	948.3	−0.208	0.01040	−53.5
0.8054	0.7940	1.34518	1141.3	967.0	−0.171	0.00906	−47.1
0.8697	0.7922	1.33992	1131.7	985.6	−0.133	0.00699	−39.2
0.9294	0.7900	1.33427	1119.3	1010.4	−0.082	0.00431	−24.4
0.9776	0.7877	1.32902	1107.9	1034.3	−0.024	0.00146	−8.6

ethanol (1) + 2-butanone (2)							
x	ρ/(g cm^{-3})	n_D	u/(m s^{-1})	κ_S/(TPa^{-1})	V^E_m/(cm^{3}mol^{-1})	δn_D	$\delta\kappa_S$
0.9703	0.7862	1.36017	1147.4	966.2	−0.040	0.00045	−6.7
0.8586	0.7891	1.36318	1158.4	944.4	−0.084	0.00156	−17.6
0.8050	0.7902	1.36445	1162.1	937.1	−0.091	0.00192	−19.8
0.6939	0.7922	1.36674	1168.9	923.9	−0.095	0.00233	−22.3
0.6739	0.7925	1.36710	1169.9	922.0	−0.092	0.00236	−22.3
0.5744	0.7940	1.36876	1175.4	911.6	−0.087	0.00233	−23.1
0.4715	0.7954	1.37038	1179.2	904.1	−0.080	0.00221	−20.7
0.4106	0.7961	1.37128	1181.8	899.4	−0.069	0.00207	−19.6
0.3851	0.7964	1.37164	1183.1	897.0	−0.066	0.00200	−19.4
0.2714	0.7977	1.37319	1186.8	890.1	−0.056	0.00163	−15.5
0.1006	0.7993	1.37501	1191.3	881.5	−0.024	0.00055	−7.6

excess properties are gathered in Table II, too. A Redlich-Kister type equation was used to correlate the changes of isentropic compressibilities on mixing, excess molar volumes and changes of refractive indices on mixing of the binary mixtures, by the method of least squares with all points weighting equally. This equation can be expressed as:

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

where δQ is $\delta\kappa_S/(\mathrm{TPa}^{-1})$, $V_m^E/(\mathrm{cm^3 mol^{-1}})$ or δn_D. The degree of this equation (m parameter) was optimized by applying the F-test [8]. Figures 1a, 1b and 1c show the experimental points of the derived excess and variation of properties plotted against molar fraction as well as the curves fitted. The parameters B_p in equation 4, and corresponding standard deviations (eq. 5) are gathered in Table III. In this expression the value of the property and the number of experimental data are represented by z and n, respectively.

$$\sigma = \sqrt{\frac{\sum_{i}^{n} (z_{\mathrm{exp}} - z_{\mathrm{pred}})^2}{n}} \tag{5}$$

4. DISCUSSION

4.1. Partial Excess Molar Volumes

Partial molar quantities are important in the study of the dependence of a 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 of pressure, temperature and mole numbers of the components, the differential of E should be expressed as:

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

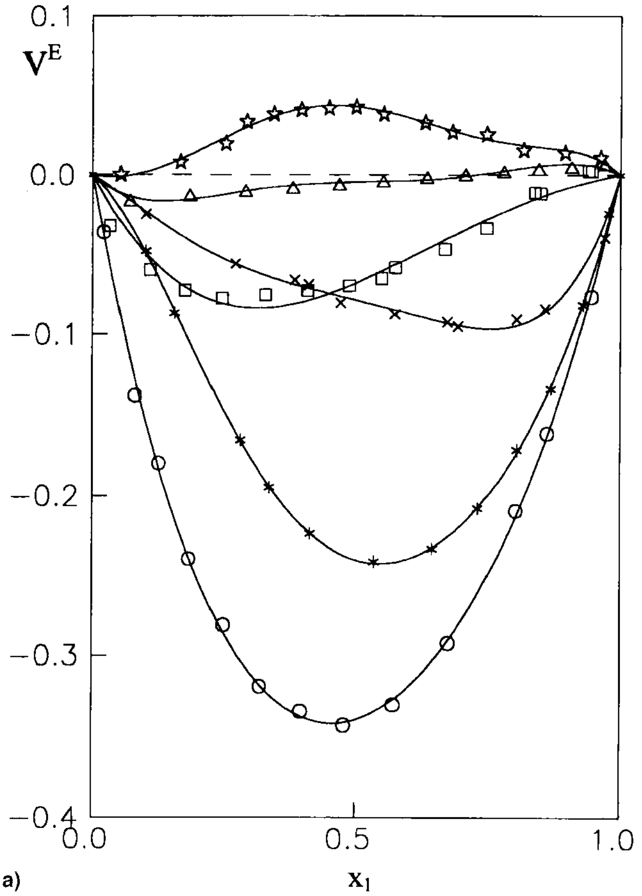

FIGURE 1 Curves of constant (a), changes of isentropic compressibility (TPa^{-1}), (b), excess molar volumes ($cm^3 mol^{-1}$), and (c), changes of refractive index on mixing at 298.15 K for (○)Acetone(1) + Methanol(2); (□) Acetone(1) + Ethanol(2); (∗)Acetone(1) + 2-Butanone(2); (Δ)Methanol(1) + Ethanol(2); (∗)Methanol(1) + 2-Butanone(2); (×) Ehtanol(1) + 2-Butanone(2).

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

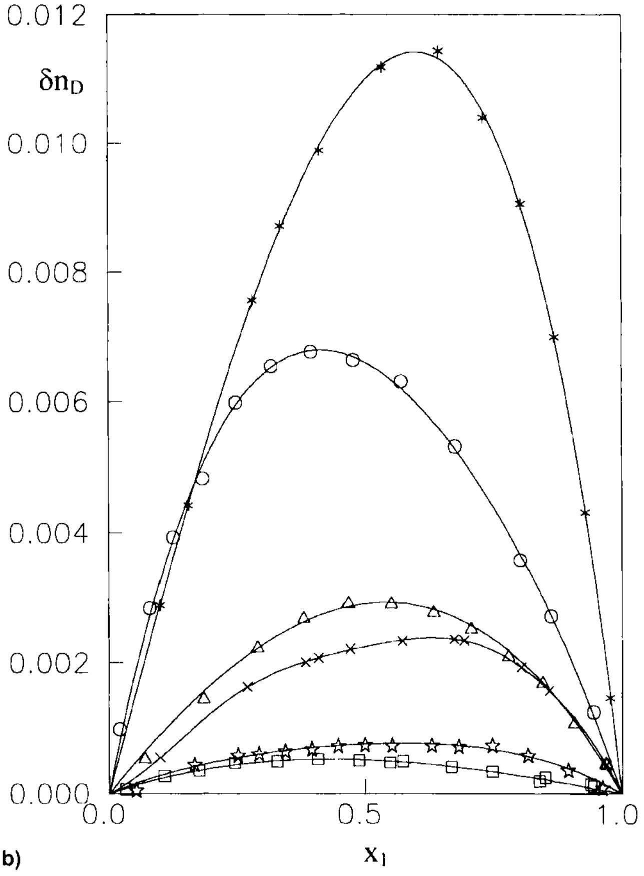

FIGURE 1 (Continued).

mixture can be determined from excess molar volume data by means of the following 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, thus the parameters enclosed in Table III for eq. 4 are applied. The expressions for the partial excess molar volumes, once the differentiation is

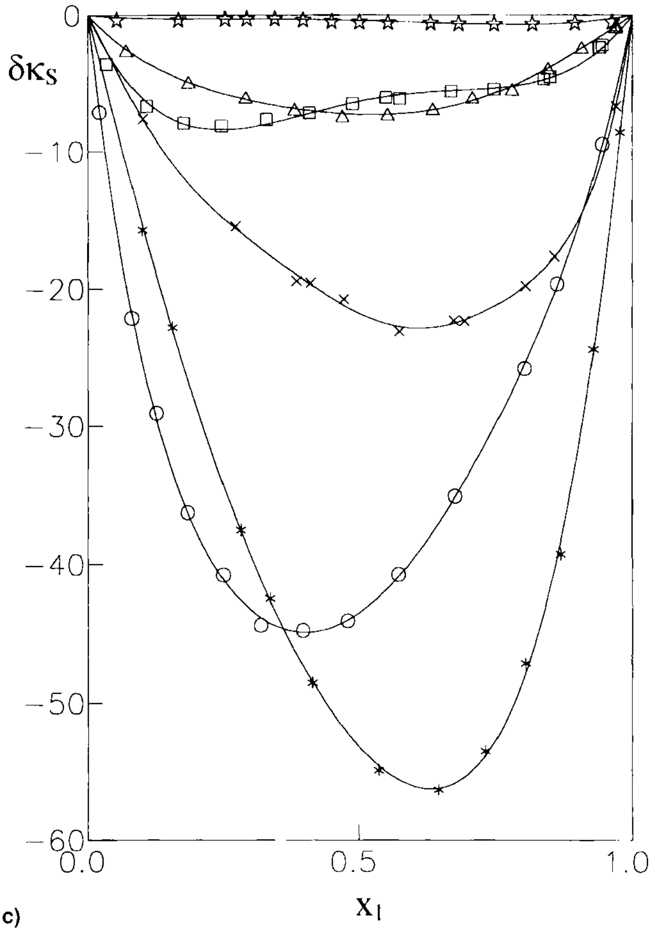

FIGURE 1 (Continued).

performed and some algebra carried out, should be written as:

$$\overline{V}_1^E = (1-x_1)^2\left[\sum_{p=0}^{m}(2x_1-1)^p + x_1\sum_{p=1}^{m}2p\,B_p\,(2x_1-1)^{p-1}\right] \tag{8}$$

$$\overline{V}_2^E = (1-x_2)^2\left[\sum_{p=0}^{m}B_p(1-2x_2)^p + x_2\sum_{p=1}^{m}(-2)p\,B_p\,(1-2x_2)^{p-1}\right] \tag{9}$$

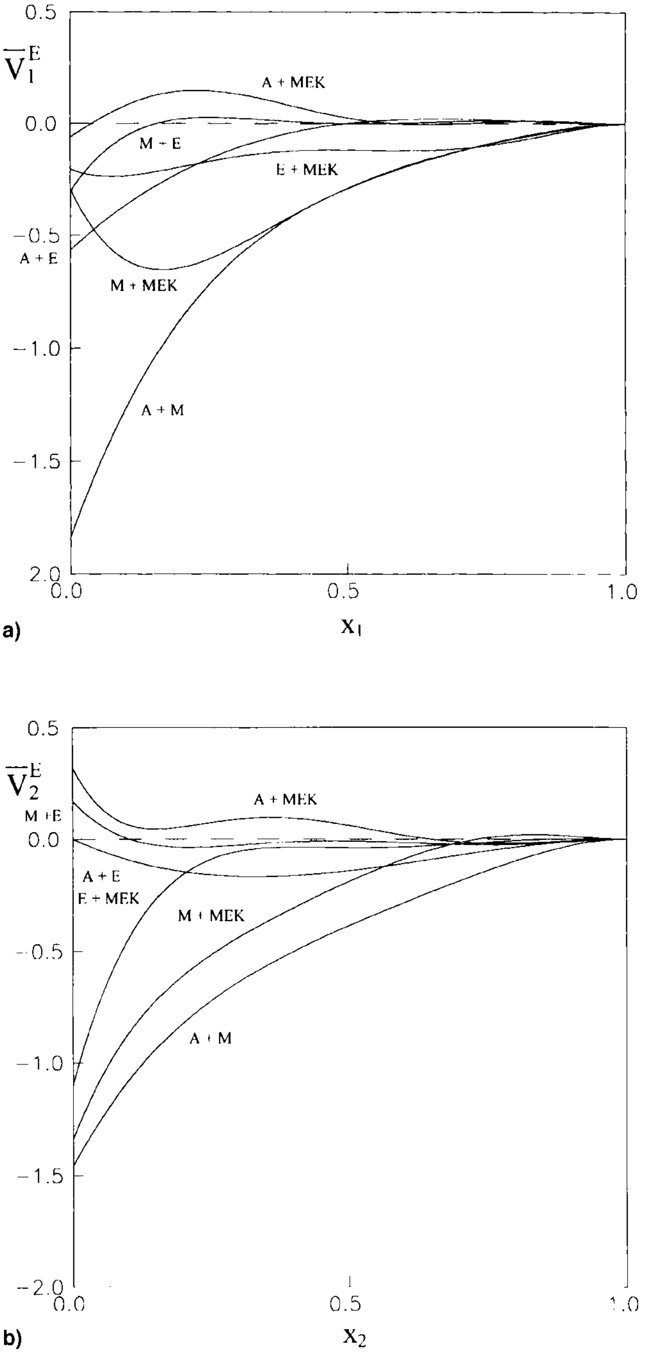

FIGURE 2 Partial excess molar volumes (cm^3 mol^{-1}) of the binary systems, (a)$\bar{V}_1^E$ and (b) $\bar{V}_2^E$ at 298.15 K.

where the symbols keep the meaning explained above. From eq. 8 and 9, 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. Figure 2a, and 2b show the trends of partial excess molar volumes with the corresponding molar fraction for the six binary mixtures. In Table IV, the values of limiting partial excess molar volumes at 298.15 K for the binary mixtures are enclosed. In these figures it can be observed a similar behaviour in the ketone + alcohol mixtures (acetone + methanol or ethanol and methanol or ethanol + 2-butanone) showing a strong decreasing negative trend in the first case, and a similar path for the second one. In both of them is shown a lower effect with higher chain of alcohol. In alcohol + 2-butanone mixtures a minimum is shown at almost the same composition due to the similar molecular interactions in low molar fraction of alcohol.

4.2. Physical Properties Estimation

The prediction of different thermodynamic properties of multicomponent mixtures have been the subject of study in recent years, applying different empirical or semiempirical models. In this paper, the measured experimental properties were compared with those estimated applying several relations. The density of the mixtures were estimated by application of the Hankinson-Brobst-Thompson (HBT), Rackett (R), Spencer and Danner modified Rackett (SDR), Bradford-Thodos (BT), Riedel (RI), Narsimhan (N), and Yen-Woods (YW) equations [2] using expansioned mixing rule [9]. The refractive indices were compared

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

	$V_1^{E,\infty}/(cm^3\,mol^{-1})$	$V_2^{E,\infty}/(cm^3\,mol^{-1})$
Acetone(1) + Methanol(2)	−1.837	−1.455
Acetone(1) + Ethanol(2)	−0.565	0.000
Acetone(1) + 2-Butanone(2)	−0.060	0.321
Methanol(1) + Ethanol(2)	0.302	0.170
Methanol(1) + 2-Butanone(2)	−0.292	−1.336
Ethanol(1) + 2-Butanone(2)	−0.204	−1.904

TABLE III Parameters of equation 4 and standard deviations (σ)

			Acetone (1) + *Methanol* (2)			
$V_m^E/(\mathrm{cm^3\,mol^{-1}})$	$B_0 = -1.357790$	$B_1 = 0.191042$	$B_2 = -0.288536$			$\sigma = 0.0040$
δn_D	$B_0 = 0.026448$	$B_1 = -0.008261$	$B_2 = 0.004711$			$\sigma = 0.00010$
$\delta\kappa_S(\mathrm{TPa^{-1}})$	$B_0 = -173.8324$	$B_1 = 54.3332$	$B_2 = -46.9366$	$B_3 = 21.2880$	$B_4 = 58.2168$	$\sigma = 0.30$
			Acetone (1) + *Ethanol* (2)			
$V_m^E/(\mathrm{cm^3\,mol^{-1}})$	$B_0 = -0.282304$	$B_1 = 0.282743$				$\sigma = 0.0064$
δn_D	$B_0 = 0.002082$	$B_1 = -0.000587$				$\sigma = 0.00003$
$\delta\kappa_S(\mathrm{TPa^{-1}})$	$B_0 = -25.3361$	$B_1 = 16.2587$	$B_2 = -45.4126$			$\sigma = 0.33$
			Acetone (1) + 2-*Butanone* (2)			
$V_m^E/(\mathrm{cm^3\,mol^{-1}})$	$B_0 = 0.172425$	$B_1 = -0.071377$	$B_2 = -0.0258813$	$B_3 = 0.261466$	$B_4 = 0.216897$	$\sigma = 0.0023$
δn_D	$B_0 = 0.003046$	$B_1 = 0.000658$	$B_2 = 0.000904$			$\sigma = 0.00004$
$\delta\kappa_S(\mathrm{TPa^{-1}})$	$B_0 = -1.5418$	$B_1 = -2.0528$	$B_2 = -4.2122$			$\sigma = 0.08$
			Methanol (1) + *Ethanol* (2)			
$V_m^E/(\mathrm{cm^3\,mol^{-1}})$	$B_0 = -0.018020$	$B_1 = 0.016031$	$B_2 = -0.048224$	$B_3 = 0.220003$		$\sigma = 0.0020$
δn_D	$B_0 = 0.011593$	$B_1 = 0.001992$				$\sigma = 0.00006$
$\delta\kappa_S(\mathrm{TPa^{-1}})$	$B_0 = -29.1120$	$B_1 = -2.3326$	$B_2 = -5.9121$	$B_3 = 10.7257$		$\sigma = 0.13$
			Methanol (1) + 2-*Butanone* (2)			
$V_m^E/(\mathrm{cm^3\,mol^{-1}})$	$B_0 = -0.961902$	$B_1 = -0.202248$	$B_2 = 0.147869$	$B_3 = -0.319477$		$\sigma = 0.0020$
δn_D	$B_0 = 0.043868$	$B_1 = 0.017096$	$B_2 = 0.006133$	$B_3 = 0.004164$		$\sigma = 0.00006$
$\delta\kappa_S(\mathrm{TPa^{-1}})$	$B_0 = -212.6240$	$B_1 = -86.9803$	$B_2 = -77.6537$	$B_3 = -45.0477$		$\sigma = 0.45$
			Ethanol (1) + 2-*Butanone* (2)			
$V_m^E/(\mathrm{cm^3\,mol^{-1}})$	$B_0 = -0.314690$	$B_1 = -0.161470$	$B_2 = -0.334278$	$B_3 = -0.283608$		$\sigma = 0.0044$
δn_D	$B_0 = 0.008959$	$B_1 = 0.003238$	$B_2 = 0.006448$	$B_3 = 0.000559$	$B_4 = -0.013251$	
	$B_5 = 0.002569$	$B_6 = 0.008298$				$\sigma = 0.00001$
$\delta\kappa_S(\mathrm{TPa^{-1}})$	$B_0 = -87.0361$	$B_1 = -37.6137$	$B_2 = -20.8626$	$B_3 = 40.5662$	$B_4 = -62.6653$	
	$B_5 = -100.6020$					$\sigma = 0.30$

with the predicted results by Lorentz-Lorenz (LL), Dale-Gladstone (DG), Arago-Biot (AB), Eykman (Eyk), Newton (N), Oster (O), Wiener (W), Heller (H) and Eyring-Jhon (EJ) mixing rules [2]. The prediction of speed of sound was made by means of Nomoto [10], Van Dael [11], Jacobson (Free Length Theory) [12], and Schaffs-Nutsch-Kuhnkies (Collision Factor Theory) [13 – 15] methods. In Tables V, VI and VII the mean square deviations of the estimations are gathered. It can be observed as in density estimation the Yen-Woods method carries to smaller deviations for all the mixtures although Bradford-Thodos equation let to obtain comparative results in the binary systems. The best refractive indices estimation in the binary mixtures are those obtained by Lorenz-Lorentz equation considering non additivity on mixing. The application of the Collision Factor Theory (CFT) presents lower deviation values in predicting the speed of sound in almost all systems.

4.3. Excess Properties Estimation

For many practical purposes it is necessary to show the capability to predict the non-ideality of binary or multicomponent liquid mixtures from other mixture properties or by means of pure components properties. The methods applied to these mixtures evalue the excess molar volume from refractive indices on mixing based on different applications of the Heller equation [16] and different mixing rules for

TABLE V Standard deviations of the experimental results from those estimated for densities (Hankinson-Brobst-Thompson (HBT), Rackett (R), Spencer and Danner Modified Rackett (SDR), Bradford-Thodos (BT), Riedel (Ri), Narsimham (N), and Yen-Woods(YW))

HBT	*R*	*SDR*	*BT*	*Ri*	*N*	*YW*
			Acetone(1) + *Methanol*(2)			
0.01597	0.05328	0.01495	0.01256	0.01412	0.01782	0.00244
			Acetone(1) + *Ethanol*(2)			
0.01552	0.03228	0.01003	0.00912	0.03408	0.01646	0.01171
			Acetone(1) + 2-*Butanone*(2)			
0.01504	0.02552	0.03204	0.00379	0.01548	0.02989	0.00272
			Methanol(1) + *Ethanol*(2)			
0.02170	0.05818	0.02823	0.01996	0.04762	0.01509	0.01365
			Methanol(1) + 2-*Butanone*(2)			
0.03351	0.05261	0.02421	0.01002	0.01364	0.02115	0.00133
			Ethanol(1) + 2-*Butanone*(2)			
0.03002	0.02492	0.02451	0.00605	0.03715	0.01559	0.00836

TABLE VI Standard deviations of the experimental refractive indices from the prediction results for the Lorentz-Lorenz (L-L), Dale-Gladstone (D-G), Arago-Biot (A-B), Eykman (Eyk), Newton (Nw), Oster (Os), Eyring-Jhon (E-J), Wiener (Wi), and Heller (He) equations

L-L	*D-G*	*A-B*	*Eyk*	*Nw*	*Os*	*E-J*	*Wi*	*He*
Acetone(1) + *Methanol*(2)								
0.00183	0.00178	0.00178	0.00180	0.00172	0.00175	0.00181	0.00146	0.00182
0.00015*	0.00024*	0.00434*	0.00019*	0.00038*	0.00027*	0.01046*		
Acetone(1) + *Ethanol*(2)								
0.00052	0.00052	0.00052	0.00052	0.00051	0.00051	0.00052	0.00051	0.00052
0.00023*	0.00026*	0.00067*	0.00024*	0.00028*	0.00026*	0.00179*		
Acetone(1) + 2-*Butanone*(2)								
0.00014	0.00017	0.00017	0.00016	0.00020	0.00018	0.00016	0.00039	0.00014
0.00005*	0.00006*	0.00033*	0.00005*	0.00009*	0.00007*	0.00084*		
Methanol(1) + *Ethanol*(2)								
0.00007	0.00009	0.00009	0.00007	0.00014	0.00011	0.00007	0.00063	0.00007
0.00010*	0.00012*	0.00025*	0.00011*	0.00017*	0.00014*	0.00043*		
Methanol(1) + 2-*Butanone*(2)								
0.00131	0.00117	0.00117	0.00122	0.00101	0.00109	0.00125	0.00093	0.00134
0.00023*	0.00020*	0.00259*	0.00019*	0.00017*	0.00016*	0.00629*		
Ethanol(1) + 2-*Butanone*(2)								
0.00050	0.00048	0.00048	0.00049	0.00046	0.00047	0.00049	0.00038	0.00049
0.00008*	0.00010*	0.00099*	0.00009*	0.00013*	0.00011*	0.00244*		

*An asterisk indicates non additivity on mixing.

TABLE VII Standard deviations of the experimental speed of sound from the prediction results for the Nomoto, Van Dael, Jacobson (FLT) and Schaaffs-Nutsch-kuhnkies (CFT) methods

Nomoto	*Van Dael*	*Jacobson (FLT)*	*Schaaffs-Nutsch-kuhnkies (CFT)*
Acetone(1) + *Methanol*(2)			
9.98	56.02	27.18	1.91
Acetone(1) + *Ethanol*(2)			
2.35	9.30	66.66	0.67
Acetone(1) + 2-*Butanone*(2)			
1.52	6.46	28.14	0.13
Methanol(1) + *Ethanol*(2)			
0.23	18.29	143.25	0.32
Methanol(1) + 2-*Butanone*(2)			
7.49	95.69	129.76	3.45
Ethanol(1) + 2-*Butanone*(2)			
4.92	33.43	76.58	1.99

TABLE VIII Standard deviations of the experimental excess molar volumes from those estimated by equation 13 and equation 16 applying different mixing rules for refractive index on mixing

	eq. 13 (L-L)	*eq. 13 (D-G)*	*eq. 13 (Eyk)*	*eq. 13 (Os)*
Acetone(1) + Methanol(2)	0.0199	0.0369	0.0270	0.0422
Acetone(1) + Ethanol(2)	0.0376	0.0456	0.0414	0.0488
Acetone(1) + 2-Butanone(2)	0.0093	0.0122	0.0101	0.0155
Methanol(1) + Ethanol(2)	0.0121	0.0162	0.0140	0.0196
Methanol(1) + 2-Butanone(2)	0.0330	0.0324	0.0302	0.0283
Ethanol (1) + 2-Butanone(2)	0.0134	0.0183	0.0154	0.0198
	eq.16 (L-L)	*eq.16 (D-G)*	*eq. 16 (Eyk)*	*eq. 16 (Os)*
Acetone(1) + Methanol(2)	0.0155	0.0312	0.0208	0.0401
Acetone (1) + Ethanol(2)	0.0379	0.0461	0.0418	0.0493
Acetone (1) + 2-Butanone(2)	0.0105	0.0132	0.0117	0.0144
Methanol(1) + Ethanol (2)	0.0149	0.0159	0.0154	0.0163
Methanol(1) + 2-Butanone(2)	0.0184	0.0349	0.0260	0.0418
Ethanol(1) + 2-Butanone(2)	0.0135	0.0208	0.0169	0.0239

the refractive indices in the mixtures. In the last few years, prediction of excess volumes from refractive index mixing rules and relation of excess volumes with density of pure components was suggested for binary mixtures by some authors[17]. They have proposed that the mixing rules for refractive indices are functions of the volume fractions of the mixture, since it is possible to generalize them in a function of the density of the mixture and of the pure components:

$$\frac{f(n_D)}{\rho} = \sum_{i=1}^{N} \frac{w_i f(n_{Di})}{\rho_i} \qquad (10)$$

In this equation, w_i is the weight fraction, and f is a mathematical function of the refractive indices of the mixture (n_D), and the refractive indices of each component (n_{Di}), by substitution in eq. 2, the excess volume of the mixture, by some algebra and reorganizing the expression, can be expressed as:

$$V_m^E = \frac{\left(\sum_{i=1}^{N} x_i M_i\right)\left(\sum_{i=1}^{N} \frac{w_i f(n_{D_i})}{\rho_i}\right)}{f(n_D)} - \sum_{i=1}^{N} \frac{x_i M_i}{\rho_i} \qquad (11)$$

From this equation, considering the relation between the weight fractions and molar fractions, the equation can be transformed so that:

$$V_m^E = \frac{\left(\sum_{i=1}^{N} \frac{M_i x_i f(n_{D_i})}{\rho_i}\right)}{f(n_D)} - \sum_{i=1}^{N} \frac{x_i M_i}{\rho_i} \tag{12}$$

Expressed in another way, the relation of the excess volumes to the function of refractive indices would be:

$$V_m^E = \sum_{i=1}^{N} \left[\left(f(n_{D_i}) - f(n_D) \right) \frac{x_i M_i}{f(n_D)\rho_i} \right] \tag{13}$$

In other way, Nakata and Sakurai [18] have proposed expressions to relate excess volumes by means of expansions in powers to first order, taking into account different mixing rules. By substitution of eqs. 2 and 9,

$$\begin{aligned} f(n_D)|_{n_{D_1}} &= \sum_{n=0}^{\infty} \left[\frac{f^n(n_{D_1})}{n_D!} (n_D - n_{D_1})^n \right] \\ &= f(n_{D_1}) + f'(n_{D_1})(n_D - n_{D_1}) + \cdots \end{aligned} \tag{14}$$

$$\begin{aligned} f(n_{D_2})\Big|_{n_{D_1}} &= \sum_{n=0}^{\infty} \left[\frac{f^n(n_{D_1})}{n_D!} (n_{D_2} - n_{D_1})^n \right] \\ &= f(n_{D_1}) + f'(n_{D_1})(n_{D_2} - n_{D_1}) + \cdots \end{aligned} \tag{15}$$

we obtain:

$$V_m^E = -\left(\frac{f'(n_{D_1})}{f(n_{D_1})} \right) \sum_{i=1}^{N} \left[\frac{x_i M_i}{\rho_i} \right] \left(n_D - \sum_{i=1}^{N} n_{D_i} \phi_i \right) \tag{16}$$

where:

$$\phi_i = \frac{\left[\frac{x_i M_i}{\rho_i} \right]}{\sum_{i=1}^{N} \left[\frac{x_i M_i}{\rho_i} \right]} \tag{17}$$

where f' means the first derivation of the mathematical function f. In this paper, experimental and estimated values of excess molar volumes using eqs. 13 and 16 are compared for the binary mixtures applying the Lorentz-Lorenz, Dale-Gladstone, Eykman and Oster (eqs. 18, 19, 20, and 21, respectively) refractive index mixing rules:

$$f(n_D) = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \tag{18}$$

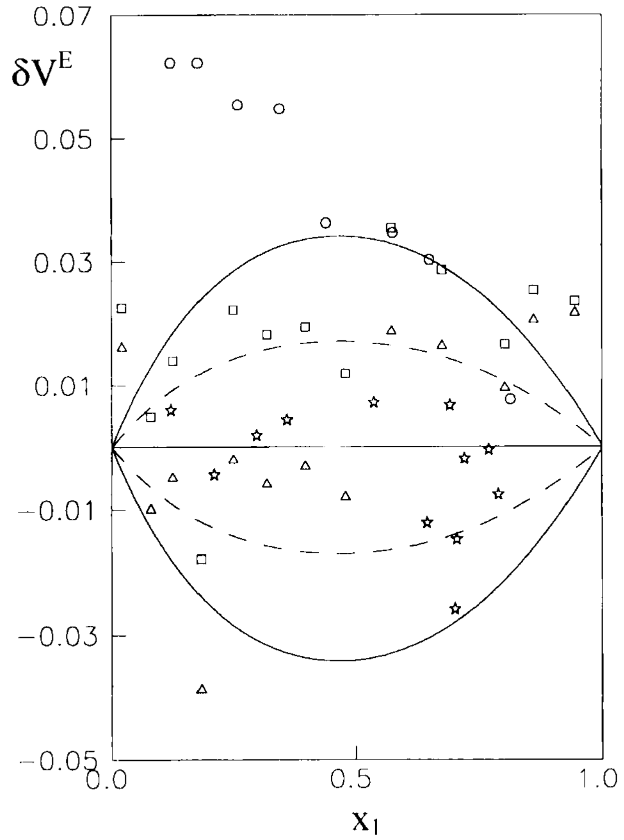

FIGURE 3 Deviations (cm^{3}mol^{-1})(δV^E, 5% dashed line, 10% solid line) from computed excess molar volumes (eq. 4) by application of eq. 13 (□), and 16 (Δ) (Lorenz-Lorentz mixing rule), and literature data (○, Wey and Rowley, 1984; *, Noda *et al.*, 1982) for Acetone (1) + Methanol (2) at 298.15 K. The experimental values of the measured mixture are shown through the solid line of zero value.

$$f(n_D) = n_D - 1 \tag{19}$$

$$f(n_D) = \frac{(n_D^2 - 1)}{(n_D + 0.4)} \tag{20}$$

$$f(n_D) = \frac{[(n_D^2 - 1)(2n_D^2 + 1)]}{n_D^2} \tag{21}$$

In Figure 3, literature data [19, 20], lines corresponding to the experimental data correlation, and the estimated values by means of Lorenz-Lorentz rule in equation 13, and 16 are shown. A good concordance are shown between experimental data and those reported by Noda *et al.*, which keep a difference better than ±5%, approximately. The equations 13 and 16 show a good capability in the estimation of excess molar volumes, although the last one computes a better result for the gathered system. As it could observed in this Figure, these equations could be used with similar accuracy in excess volume estimation, a good sensibility are shown to determine low values of these excess property in high complex or associated mixtures.

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