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# CHANGES OF REFRACTIVE INDICES FOR THE TERNARY MIXTURE ACETONE + METHANOL + *n*-HEXANE AT 288.15 AND 298.15 K

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The refractive indices of the ternary mixture acetone + methanol + *n*-hexane have been measured at 288.15 and 298.15 K and atmosphere in the whole composition diagram. Parameters of polynomial equations which represent the composition dependence of physical and derived property are gathered. The use of a multicomponent extension of Heller equation in order to predict excess molar volumes from refractive indices on mixing are tested against literature data, a comparative accuracy with currently available models being obtained.

*Keywords:* Refractive index; acetone; methanol; *n*-hexane

## 1. INTRODUCTION

Phase equilibria and thermochemical magnitudes of liquid mixtures that have hydroxyl groups and highly polarizable electron pairs, depend to a large extent on the molecular hydrogen bonding interactions. Moreover, the length of chain and the 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

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characteristics. Polar substances such as methanol or short alcohols produce strong interactions due to its relatively low molecular volume, large polarity and its autoassociative trend, large deviations from ideality being observed in the whole thermophysical properties field. This effect is also shown when inert diluents are involved such as *n*-alkanes, the capability of predictive models being hugely reduced due their different behaviour. In the last few years some authors have pointed out the availability of a set of magnitudes which are of accurate measurement and non-complex relation to fundamental thermophysical properties in design and development of industrial processes. This relation was commented upon about refractive indices related to excess molar volumes in a previous paper [1]. As a continuation of our research on thermodynamic properties of azeotropic separation processes, we present in this paper the experimental measurement of the refractive indices of the ternary mixture acetone + methanol + *n*-hexane at 288.15 and 298.15 K and atmospheric pressure. Changes of refractive indices on mixing were derived and correlated, as well as the physical property, by means of appropriate polynomials, the parameters of these functions being gathered. Values of both of them were computed by estimative methods and binary contribution models. The application of two equations, which are derived from Heller equation [2] to predict excess molar volumes from refractive indices showed a good agreement over ranges of composition and temperature in these multicomponent mixtures.

## 2. EXPERIMENTAL

The substances employed were supplied by Merck (Lichrosolv quality). Their mole-fraction purities were better than 0.995 for *n*-hexane 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 as is shown in Table I. Usual procedure for chemicals were applied using molecular sieves (3Å or 4Å) in order to dehydrate and ultrasonic treatment for

TABLE I Comparison of experimental data with literature for pure liquids

Component	$n_D(298.15\text{ K})$	
	<i>exptl.</i>	<i>lit</i> <sup>a</sup>
Acetone	1.35580	1.35596
Methanol	1.32645	1.32652
<i>n</i> -Hexane	1.37234	1.37226

<sup>a</sup> Ref. [3].

degassing solvents. Manipulation procedure of chemicals and applied techniques in our laboratory are commented in a previous paper [4]. The refractive indices were measured by an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of  $\pm 0.00001$ . Thermostation of refractometer was realized by a controller bath PolyScience model 9510, with a temperature stability  $\pm 10^{-2}$  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 ternary mixtures. Before each series of measurements, the instrument were calibrated in accordance with the use instructions, no systematic errors being detected in the measurements. The accuracy for both, changes of refractive indices on mixing and mole fractions, were estimated better than  $10^{-4}$ .

### 3. DATA CORRELATION

The refractive indices and changes of refractive indices on mixing are given in Table II, the Eq. (1) being applied to compute the corresponding derived magnitude:

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

In these equation,  $n_D$  is the refractive index in the mixture,  $n_{Di}$  is the property of pure components,  $x_i$  the molar fraction of component  $i$  in the mixture,  $N$  is the number of components and  $\delta$  means the variation of a magnitude. A Redlich-Kister type equation [5] was used to correlate the changes of refractive indices on mixing of the

TABLE II Refractive indices and changes of refractive indices on mixing of acetone + methanol + *n*-hexane

$x_1$	$x_2$	$n_D$	$\delta n_D$
$T = 288.15 \text{ K}$			
0.7905	0.1086	1.36149	0.0015
0.6820	0.1136	1.36303	0.0015
0.6870	0.2054	1.36042	0.0033
0.5779	0.1244	1.36444	0.0017
0.5947	0.1998	1.36226	0.0034
0.5929	0.2955	1.35926	0.0049
0.5017	0.1057	1.36638	0.0014
0.4888	0.2146	1.36381	0.0038
0.4968	0.2952	1.36106	0.0051
0.4930	0.3950	1.35743	0.0061
0.3884	0.1187	1.36792	0.0017
0.4000	0.1994	1.36543	0.0032
0.3933	0.2996	1.36303	0.0055
0.3872	0.4166	1.35882	0.0068
0.3987	0.4939	1.35522	0.0071
0.2982	0.1185	1.36965	0.0019
0.2890	0.2073	1.36759	0.0039
0.3090	0.2836	1.36496	0.0052
0.2992	0.4038	1.36110	0.0070
0.2967	0.5037	1.35701	0.0076
0.2899	0.6013	1.35233	0.0075
0.2027	0.1086	1.37161	0.0017
0.2151	0.2046	1.36915	0.0041
0.1971	0.3043	1.36668	0.0061
0.2147	0.3875	1.36375	0.0074
0.2063	0.4968	1.35983	0.0086
0.2111	0.5876	1.35521	0.0084
0.2046	0.6929	1.34951	0.0076
0.1146	0.1246	1.37302	0.0024
0.1039	0.2176	1.37111	0.0048
0.1191	0.2614	1.36978	0.0058
0.0986	0.6965	1.35260	0.0091
0.1061	0.7854	1.34622	0.0071
0.0558	0.8934	1.33916	0.0043
0.0705	0.7333	1.35101	0.0088
0.0654	0.0844	1.37458	0.0012
0.1042	0.4224	1.36487	0.0083
0.1150	0.4912	1.36216	0.0091
0.1207	0.5520	1.35953	0.0095
0.1098	0.3137	1.36822	0.0066
0.0969	0.6465	1.35550	0.0095
$T = 298.15 \text{ K}$			
0.7885	0.1120	1.35588	0.0017
0.6875	0.1181	1.35689	0.0013
0.6782	0.2225	1.35460	0.0037
0.5764	0.1252	1.35880	0.0017
0.5939	0.2076	1.35631	0.0033
0.6119	0.2845	1.35381	0.0046

TABLE II (Continued)

$x_1$	$x_2$	$n_D$	$\delta n_D$
0.5031	0.1044	1.36045	0.0012
0.4866	0.2195	1.35788	0.0037
0.5025	0.2964	1.35536	0.0049
0.4937	0.4045	1.35157	0.0060
0.3837	0.1319	1.36202	0.0021
0.3955	0.2074	1.35976	0.0035
0.3901	0.3095	1.35700	0.0053
0.3857	0.4213	1.35314	0.0065
0.3975	0.5039	1.34952	0.0069
0.2942	0.1180	1.36399	0.0019
0.2953	0.1995	1.36203	0.0037
0.3076	0.3203	1.35853	0.0060
0.2903	0.4185	1.35553	0.0072
0.2910	0.5137	1.35153	0.0076
0.2913	0.6107	1.34673	0.0072
0.1918	0.1201	1.36597	0.0023
0.2007	0.2086	1.36363	0.0042
0.1922	0.3147	1.36098	0.0063
0.2012	0.3971	1.35820	0.0074
0.2008	0.5035	1.35405	0.0081
0.1966	0.6089	1.34940	0.0083
0.2006	0.6999	1.34392	0.0070
0.0878	0.1408	1.36755	0.0031
0.1003	0.2186	1.36542	0.0048
0.1018	0.3132	1.36304	0.0068
0.0943	0.4145	1.35992	0.0082
0.0974	0.5081	1.35662	0.0092
0.1003	0.6065	1.35210	0.0093
0.1019	0.7014	1.34685	0.0084
0.0531	0.7053	1.34831	0.0092
0.0537	0.5977	1.35355	0.0095
0.0547	0.4057	1.36113	0.0083
0.1973	0.7005	1.34430	0.0074
0.0995	0.7909	1.34115	0.0068

corresponding binary mixtures, which are presented in early papers [1, 6, 7]. The parameters of these binary mixtures are those corresponding to the Redlich-Kister equation which is expressed as:

$$\delta Q = x_i x_j \sum_{p=0}^m B_p (x_i - x_j)^p \quad (2)$$

where  $m$  is the limit of the expansion (Bevington test [8]) and  $B_p$  are the fitting parameters. The ternary correlation was realized by means a

Nagata type equation [9] as follows:

$$\begin{aligned} \delta Q_{123} = & \delta Q_{12} + \delta Q_{13} + \delta Q_{23} \\ & + x_1 x_2 x_3 RT (B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 \\ & - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2) \end{aligned} \quad (3)$$

where  $\delta Q_{12}$ ,  $\delta Q_{13}$ , and  $\delta Q_{23}$  are the binary contributions by the Redlich-Kister expression for each binary mixture. Figures 1a and 1b show the derived property against molar fraction as well as the curves

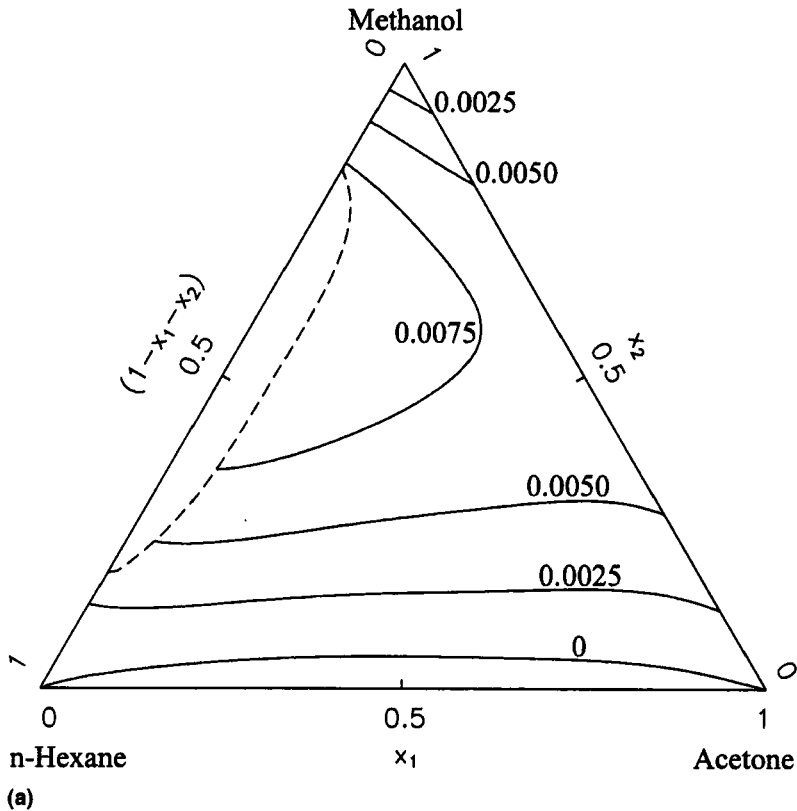


FIGURE 1 Curves of constant changes of refractive indices in accordance with Eq. (3) for acetone + methanol + *n*-hexane at (a) 288.15 and (b) 298.15 K.

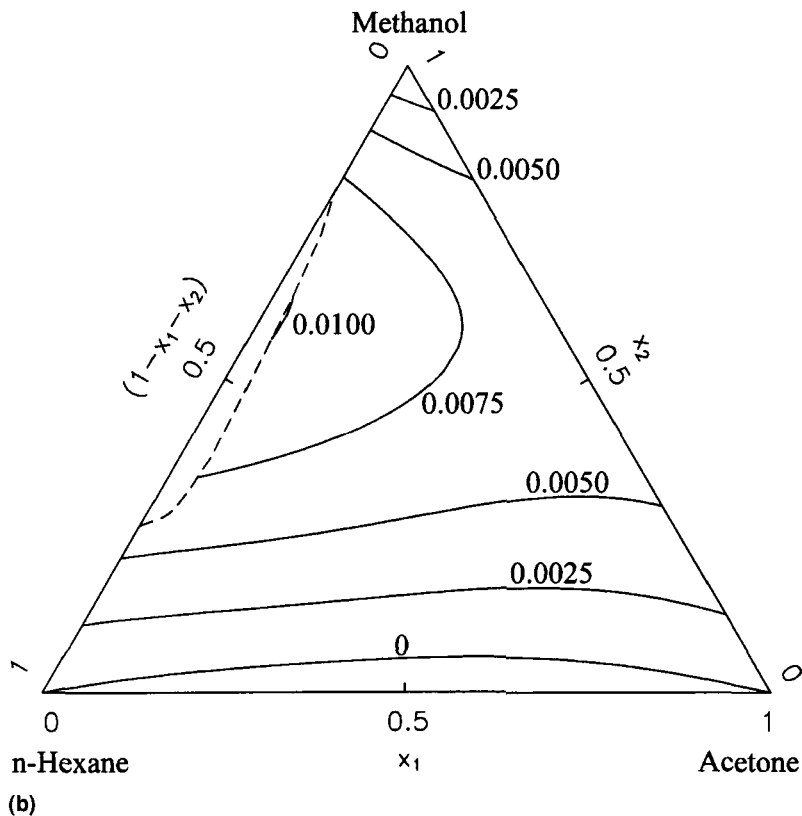


FIGURE 1 (Continued).

fitted. The binodal line enclosed which limiting the homogeneous zone was taken from a previous reference [10]. The correlation was realized taking into account the binary contributions, by the method of least squares with all points weighting equally by means a routine developed in accordance with Marquard algorithm [11]. The binary, and ternary physical property have been fitted to a polynomial of the form:

$$Q = \sum_{i=1}^N A_i x_i + \sum_{i<j}^N B_{ij} x_i x_j + \sum_{k=2}^N \sum_{i \neq j}^N C_{ijk} x_i^k x_j \quad (4)$$



where  $Q$  is  $n_D$ ,  $x_i$  or  $x_j$ , the mole fraction of the component  $i$  or  $j$ , and  $A_i$ ,  $B_{ij}$  and  $C_{ijk}$  are the corresponding fitting parameters. No values of these properties for the investigated ternary system has been published in currently available literature. The parameters of Eqs. (3) and (4) and corresponding root mean square 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.

$$\sigma = \sqrt{\frac{\sum_i^n (Z_{\text{exp}} - Z_{\text{pred}})^2}{n}} \quad (5)$$

## 4. DISCUSSION

### 4.1. Physical Properties Estimation

The prediction of different thermodynamic properties of multi-component mixtures have been the subject of study in the last few years, applying different empirical or semiempirical models. In this paper, the measured experimental refractive indices were compared with those estimated applying several mixing rules [12] (Lorentz-Lorenz (LL), Dale-Gladstone (DG), Arago-Biot (AB), Eykman (Ey), Newton (N), Oster (O), and Eyring-John (EJ)). In Table IV the root mean square deviations of the estimations are gathered. The best refractive indices estimation are those obtained by L-L, D-G, A-B and O equations considering non additivity on mixing.

### 4.2. Binary Contribution Rules for Derived Properties

The ternary excess properties of mixtures may be estimated from binary values applying the Eq. (6):

$$\delta Q_{ijk} = \sum_{i < j} (x_i x_j / x'_i x'_j) \delta Q_{ij}(x'_i, x'_j) \quad (6)$$

For each ternary mixture the molar fractions  $x'$  may be obtained from a triangular diagram by projecting the point representing the

TABLE III Parameters of Eq. (4) and root mean square deviations ( $\sigma$ )

$n_D$	$A_1 = 1.361593$		$A_3 = 1.378464$
	$B_{12} = -1.422422 \cdot 10^{-1}$		$B_{23} = 1.564207 \cdot 10^{-1}$
	$C_{122} = 4.928569 \cdot 10^{-2}$		$C_{212} = 2.881941 \cdot 10^{-1}$
	$C_{232} = -2.382975 \cdot 10^{-1}$		$C_{322} = 6.018743 \cdot 10^{-3}$
	$C_{123} = 1.149598 \cdot 10^{-1}$		$C_{213} = -1.097966 \cdot 10^{-1}$
	$C_{233} = 1.461694 \cdot 10^{-1}$		$C_{323} = -1.466358 \cdot 10^{-1}$
	$B_0 = 3.273857 \cdot 10^{-5}$		$B_2 = 1.310106 \cdot 10^{-5}$
	$B_3 = -4.342972 \cdot 10^{-4}$		$B_5 = -1.707036 \cdot 10^{-4}$
	$B_6 = 2.910418 \cdot 10^{-4}$		$B_8 = 2.272407 \cdot 10^{-4}$
	$\delta n_D$		
$n_D$	$T = 288.15 \text{ K}$		
	$A_2 = 1.330628$		
	$B_{13} = 2.455085 \cdot 10^{-2}$		
	$C_{132} = 6.825249 \cdot 10^{-2}$		
	$C_{312} = -1.246374 \cdot 10^{-1}$		
	$C_{133} = -9.942917 \cdot 10^{-2}$		
	$C_{313} = 9.288874 \cdot 10^{-2}$		
	$B_1 = 2.226658 \cdot 10^{-4}$		
	$B_4 = 1.491079 \cdot 10^{-4}$		
	$B_7 = -1.312404 \cdot 10^{-4}$		
$\delta n_D$			$\sigma = 10.1 \cdot 10^{-5}$
$n_D$	$T = 298.15 \text{ K}$		
	$A_2 = 1.326496$		
	$B_{13} = 5.051330 \cdot 10^{-3}$		
	$C_{132} = 9.466105 \cdot 10^{-2}$		
	$C_{312} = -1.159200 \cdot 10^{-1}$		
	$C_{133} = -1.065417 \cdot 10^{-1}$		
	$C_{313} = 1.048722 \cdot 10^{-1}$		
	$B_1 = -2.695444 \cdot 10^{-5}$		
	$B_4 = 1.247072 \cdot 10^{-5}$		
	$B_7 = -7.564755 \cdot 10^{-6}$		
$\delta n_D$			$\sigma = 9 \cdot 10^{-5}$
$n_D$	$T = 298.15 \text{ K}$		
	$A_3 = 1.372391$		
	$B_{23} = 1.818442 \cdot 10^{-1}$		
	$C_{212} = 2.851996 \cdot 10^{-1}$		
	$C_{322} = -2.312166 \cdot 10^{-2}$		
	$C_{213} = -1.026604 \cdot 10^{-1}$		
	$C_{323} = -1.365734 \cdot 10^{-1}$		
	$B_2 = 1.629979 \cdot 10^{-5}$		
	$B_5 = 4.967001 \cdot 10^{-5}$		
	$B_8 = -9.616152 \cdot 10^{-5}$		
$\delta n_D$			$\sigma = 9.7 \cdot 10^{-5}$

TABLE IV Root mean square 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) and Eyring-Jhon (E-J) equations

<i>L-L</i>	<i>D-G</i>	<i>A-B</i>	<i>Eyk</i>	<i>Nw</i>	<i>Os</i>	<i>E-J</i>
<i>T</i> = 288.15 K						
0.00221	0.00230	0.00230	0.00227	0.00239	0.00235	0.00225
0.00019*	0.00023*	0.00541*	0.00014*	0.00057*	0.00034*	0.01305*
<i>T</i> = 298.15 K						
0.00207	0.00215	0.00215	0.00212	0.00224	0.00219	0.00210
0.00034*	0.00020*	0.00568*	0.00023*	0.00045*	0.00026*	0.01343*

\* An asterisk indicates non additivity on mixing.

ternary mixture onto the corresponding binary axis, using different symmetric or asymmetric criteria of binary contribution to the ternary value. According to the aforementioned equation, symmetry is understood to be the contribution of the three binaries to the ternary excess, all three of which contribute equally. Asymmetry is understood to indicate the different individual contribution of one of the binaries, the latter being normally attributed to polar components. In the estimation of changes of refractive indices on mixing, the type b asymmetric equation of Tsao-Smith, Scatchard or Toop (methanol as polar component) show the lowest deviations with respect to experimental results for both temperatures. Comparative accuracy were obtained when symmetric rules as Kohler, Jacob-Fitzner or Colinet were applied. In the Figures 2a and 2b, the isolines corresponding to the ternary contribution of the changes of refractive indices on mixing are shown. It could be observed as the zone corresponding to approximately equimolar ternary compositions presents the highest dependence with interactions of the three components in the mixture. In Table V the root mean square deviations of each method are gathered.

### 4.3. Excess Molar Volume Estimation

For many practical purposes it is necessary to show the capability to predict the non-ideality of liquid mixtures which goes expressed by means of excess or changes of physical properties. The methods

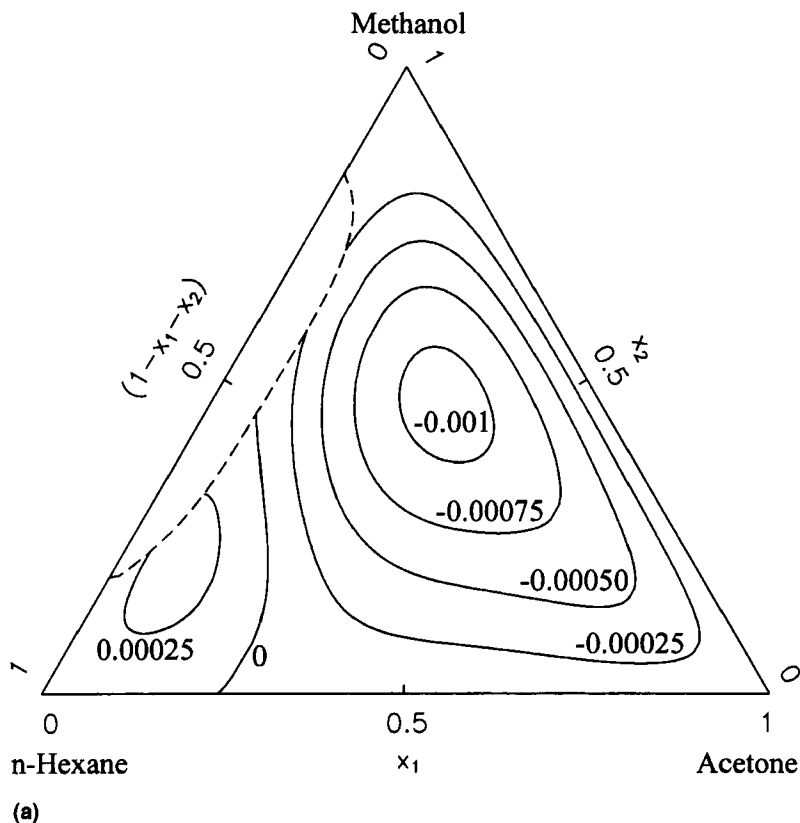


FIGURE 2 Curves of constant ternary contributions of changes of refractive indices using Eq. (3) without binary contributions for acetone+methanol+n-hexane at (a) 288.15 and (b) 298.15 K.

applied to these mixtures compute the excess molar volume from refractive indices on mixing based on the Heller equation and different mixing rules for the refractive indices on mixing. In the last few years, prediction of excess volumes from refractive index mixing rules was suggested for binary mixtures by some authors [1, 13, 14]. In some cases it have been proposed that the mixing rules for refraction 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:

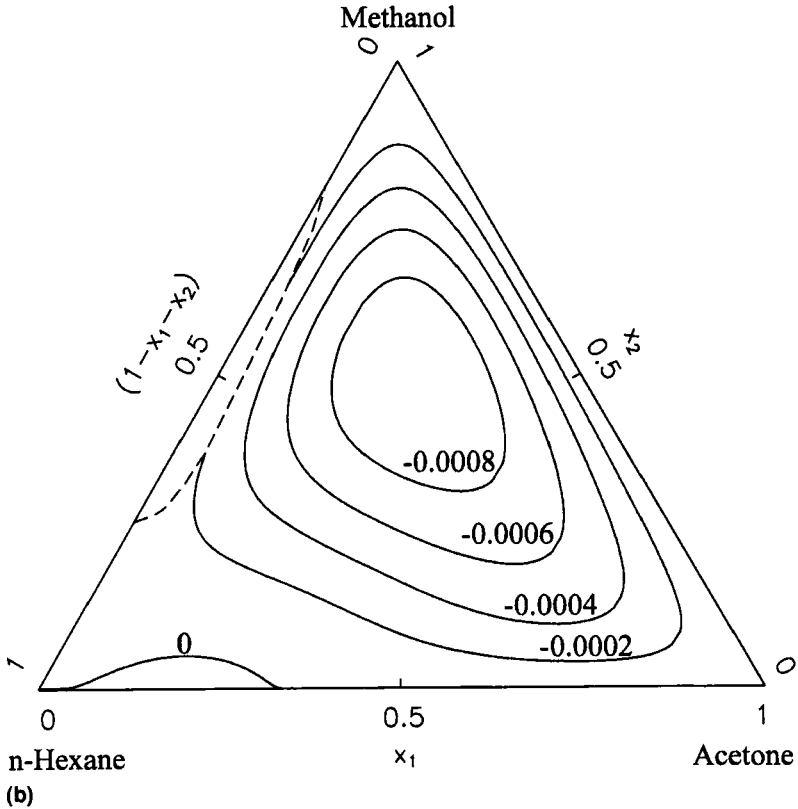


FIGURE 2 (Continued).

$$\frac{f(n_D)}{\rho} = \sum_{i=1}^N \frac{w_i f(n_{Di})}{\rho_i} \quad (7)$$

In this equation,  $w_i$  is the weight fraction, and  $f$  is a mathematical function of the refractive indices of the mixture, and the refractive mixture of each component. Expressed in another way, taking into account the usual expression of excess molar volumes, the relation of this magnitude to the function of refractive indices would be:

$$V_m^E = \sum_{i=1}^N \left[ (f(n_{Di}) - f(n_D)) \frac{x_i M_i}{f(n_D) \rho_i} \right] \quad (8)$$

TABLE V Root mean square deviations of the experimental data from the prediction results for different empirical equations

	$\sigma(\delta n_D)$ at 288.15 K	$\sigma(\delta n_D)$ at 298.15 K
Kohler	0.00069	0.00070
Jacob-Fitzner	0.00057	0.00058
Colinet	0.00055	0.00061
Knobeloch	0.00183	0.00190
Lakhanpal	0.00343	0.00317
Tsao-Smith <sup>a</sup>	0.00225	0.00234
Tsao-Smith <sup>b</sup>	0.00057	0.00030
Tsao-Smith <sup>c</sup>	0.00208	0.00199
Scatchard <sup>a</sup>	0.00069	0.00081
Scatchard <sup>b</sup>	0.00041	0.00020
Scatchard <sup>c</sup>	0.00106	0.00096
Toop <sup>a</sup>	0.00079	0.00086
Toop <sup>b</sup>	0.00043	0.00020
Toop <sup>c</sup>	0.00107	0.00100
Mathieson-Tynne <sup>a</sup>	0.00414	0.00456
Mathieson-Tynne <sup>b</sup>	0.00813	0.00806
Mathieson-Tynne <sup>c</sup>	0.00470	0.00514
Hillert <sup>a</sup>	0.00491	0.00548
Hillert <sup>b</sup>	0.00091	0.00067
Hillert <sup>c</sup>	0.00383	0.00381

<sup>a</sup> Acetone is the asymmetric component in the equation.

<sup>b</sup> Methanol is the asymmetric component in the equation.

<sup>c</sup> *n*-Hexane is the asymmetric component in the equation.

TABLE VI Root mean square deviations of the experimental excess molar volumes from those estimated by Eq. (8) and Eq. (9) applying different mixing rules for refractive index on mixing for the system acetone + methanol + *n*-hexane

		(L-L)	(D-G)	(EyK)	(Os)
$T = 288.15 \text{ K}$	Eq. (8)	0.040	0.050	0.029	0.079
	Eq. (9)	0.028	0.054	0.033	0.074
$T = 298.15 \text{ K}$	Eq. (8)	0.078	0.042	0.052	0.053
	Eq. (9)	0.060	0.038	0.044	0.044

In this way, Nakata and Sakurai have proposed a expression to relate excess volumes by means of expansions in powers to first order with different mixing rules:

$$V_m^E = - \left( \frac{f'(n_{D_1})}{f(n_{D_1})} \right) \sum_{i=1}^N \left[ \frac{x_i M_i}{\rho_i} \right] \left( n_D - \sum_{i=1}^N n_{D_i} \phi_i \right) \quad (9)$$

where:

$$\phi_i = \frac{\left[ \frac{x_i M_i}{\rho_i} \right]}{\sum_{i=1}^N \left[ \frac{x_i M_i}{\rho_i} \right]} \quad (10)$$

where  $f'$  means the first derivation of the mathematical relation  $f$ . In this work, experimental [15] and estimated values of excess molar volumes using Eqs. (8) and (9) are compared applying the Lorentz-Lorentz, Dale-Gladstone, Eykman and Oster (Eqs. (11, 12, 13 and 14), respectively) refractive index mixing rules:

$$f(n_D) = \frac{(n_D^2 - 1)}{(n_D^2 + 2)} \quad (11)$$

$$f(n_D) = n_D - 1 \quad (12)$$

$$f(n_D) = \frac{(n_D^2 - 1)}{(n_D + 0.4)} \quad (13)$$

$$f(n_D) = \frac{[(n_D^2 - 1)(2n_D^2 + 1)]}{n_D^2} \quad (14)$$

In Figures 3a and 3b, the lines corresponding to the experimental data correlation [15], and the estimated values by means of Eykman rule at 288.15 K and Dale-Gladstone rule at 298.15 K in Eq. (8) are presented. A good concordance are shown between theoretical and experimental values, which keep a difference better than  $\pm 5\%$ , approximately, only slight higher deviations being obtained for acetone rich compositions at both temperatures. These equations show a good capability in the estimation of excess molar volumes, although the first derivation computes better results for the gathered system. As it could be observed in this figures, these equations could be used with similar accuracy in estimation of excess volume in multicomponent mixtures, too, although high complex, associative components or partially miscible mixtures are involved.

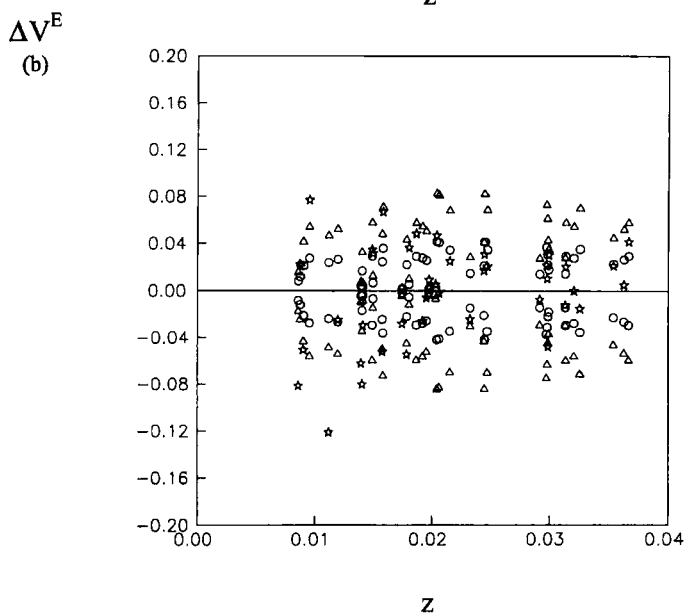
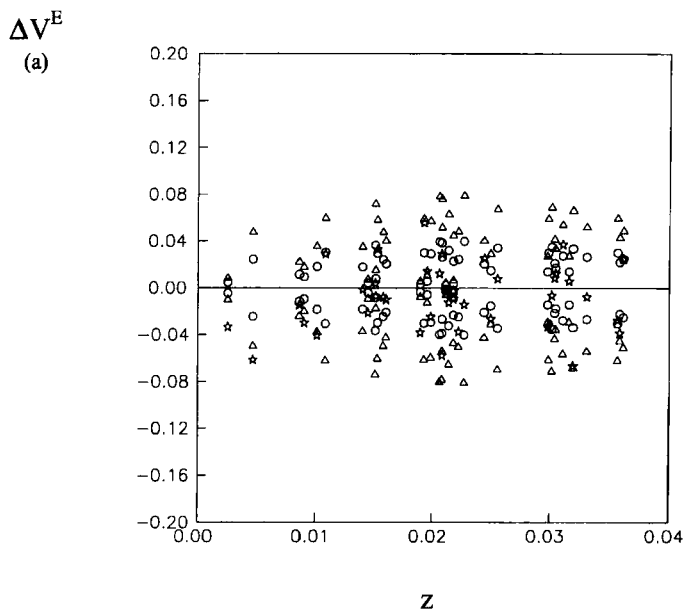


FIGURE 3 Deviations ( $\Delta V^E(\text{cm}^3 \text{mol}^{-1})$ , 5%,  $\circ$  and 10%,  $\Delta$ ) from computed changes of refractive indices by application of Eq. (8) and literature data ( $\star$ , reference 15) for acetone + methanol + *n*-hexane at (a) 288.15 K (Eykmán rule) and (b) 298.15 K (Dale-Gladstone rule). The computed values from experimental data in mixture are shown through the solid line of zero value. Parameter  $z$  is the adimensional product of molar fractions of mixture.



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