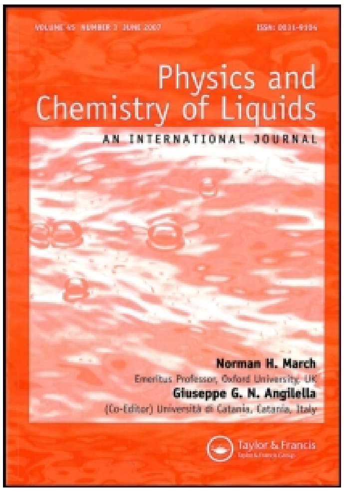

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Excess molar internal pressures and changes in refractive indices of acetone + methanol + (2-methyl-1-propanol or 3-methyl-1-butanol) at 298.15 K

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Excess molar internal pressures and changes in refractive indices of acetone + methanol + (2-methyl-1-propanol or 3-methyl-1-butanol) at 298.15 K

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This study aims at extending the characterisation by refractive index of ternary systems containing potential separation agents for extractive distillation of minimum azeotropes. The systems considered are acetone + methanol + (2-methyl-1-propanol or 3-methyl-1-butanol), which have been studied at 298.15 K and atmospheric pressure for the whole composition diagram. Parameters of polynomial equations, which represent the molar fraction dependence of the refractive index and derived property, are gathered. Based on the variations of the derived values with composition, conclusions about the molecular interactions and their dependence on branched alcohol structure were drawn.

Keywords: Refractive index; Ternary systems; Molecular interactions

1. Introduction

Over the last few years, we have conducted systematic studies on the thermodynamic properties of mixtures related to industrial processes (modified rectification, liquid extraction, etc.) involving azeotropic, and close boiling mixtures [1–3]. With this aim, our research team is carrying out a project focussed on linear or branched aliphatic alkanol agents for modified distillation, which makes it necessary to gain a fuller understanding of the influence of the hydroxyl group position in the molecule and, topological dependence on mixing thermodynamics. To this end, the refractive indices on mixing for the ternary mixtures acetone + methanol + (2-methyl-1-propanol or 3-methyl-1-butanol) have been measured at 298.15 K, and atmospheric condition, covering the whole composition diagrams. Parameters of polynomial equations representing the molar fraction dependence on the derived property are gathered.

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Based on the variations of the derived values with composition, conclusions about the molecular interactions and the dependence on branched alcohol structure in these kind of mixtures were obtained. The application of the Buchler–Hirschfelder–Curtis equation of state [4] leads to the analysis of the excess molar internal pressure of the liquid mixture, and an interpretation of this magnitude is made in terms of the separation capability of these branched solvents.

2. Experimental

The substances used were supplied by Merck (Lichrosolv quality). Their mole-fraction purities were better than 0.995 for the branched alcohols 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 those published in open literature, as shown in table 1. Usual procedure for chemicals was applied using molecular sieves (3 or 4 Å) for dehydration and ultrasonic treatment for degassing solvents. Manipulation procedure for chemicals and applied techniques in our laboratory are commented in a previous paper [5]. The refractive indices were measured by an automatic refractometer ABBEMAT-HP Dr. Kernchen with a precision of ±0.00001. Thermostation of refractometer was conducted by a controller bath PolyScience model 9510, with a temperature stability of $\pm 10^{-2}$ K. Samples were prepared 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 instruments were calibrated in accordance with the instructions for use, with no systematic errors being detected in the measurements. The accuracy for both changes in refractive indices on mixing and mole fractions, were estimated at better than 10^{-4}. The experimental values of pure chemicals, and those from open literature are enclosed in table 1.

3. Data correlation

The refractive indices and changes of refractive indices on mixing are given in table 2, equation (1) being applied to compute the corresponding derived magnitude:

$$\delta n_{\mathrm{D}} = n_{\mathrm{D}} - \sum_{i=1}^{N} x_i n_{\mathrm{D}_i}. \tag{1}$$

Table 1. Comparison of experimental data with literature for pure liquids.

	n_{D} (298.15 K)	
Component	Exptl.	Lit. [6]
Acetone	1.35580	1.35596
Methanol	1.32645	1.32652
2-Methyl-1-propanol	1.39353	1.3939
3-Methyl-1-butanol	1.40528	1.4052

Table 2. Refractive indices and changes of refractive indices on mixing of acetone + methanol + (2-methyl-1-propanol or 3-methyl-1-butanol).

Acetone + methanol + 2-methyl-1-propanol			
x_1	x_2	n_D	δn_D
0.0436	0.0470	1.39061	0.0019
0.0473	0.9056	1.33572	0.0047
0.1020	0.1073	1.38686	0.0044
0.0938	0.2015	1.38336	0.0069
0.1015	0.3000	1.37886	0.0093
0.1025	0.4024	1.37376	0.0111
0.0963	0.5006	1.36833	0.0120
0.0966	0.6034	1.36150	0.0121
0.1023	0.7013	1.35324	0.0106
0.0999	0.8008	1.34398	0.0079
0.2028	0.1017	1.38349	0.0044
0.2034	0.1909	1.37980	0.0067
0.1987	0.3045	1.37460	0.0090
0.2063	0.3897	1.36983	0.0102
0.1990	0.5113	1.36342	0.0117
0.2047	0.5989	1.35598	0.0103
0.2038	0.6943	1.34803	0.0088
0.3046	0.0925	1.38014	0.0043
0.3051	0.2020	1.37545	0.0070
0.2982	0.3075	1.37045	0.0088
0.2975	0.4052	1.36483	0.0097
0.3008	0.4999	1.35849	0.0098
0.3016	0.5977	1.35078	0.0087
0.3751	0.1213	1.37615	0.0049
0.3986	0.1964	1.37191	0.0066
0.3972	0.3031	1.36630	0.0081
0.4037	0.3949	1.36047	0.0087
0.4026	0.4952	1.35336	0.0082
0.5038	0.0983	1.37209	0.0042
0.5104	0.1921	1.36725	0.0059
0.5074	0.2986	1.36162	0.0073
0.4701	0.3735	1.35855	0.0078
0.6071	0.0964	1.36789	0.0037
0.5758	0.2365	1.36186	0.0059
0.5960	0.3050	1.35673	0.0061
0.7101	0.0928	1.36381	0.0033
0.7058	0.1995	1.35798	0.0045
0.7963	0.1061	1.35923	0.0029
0.0554	0.0617	1.40130	0.0036
0.0480	0.9090	1.33724	0.0060
0.1150	0.1145	1.39710	0.0065
0.0956	0.2001	1.39442	0.0096
0.0973	0.2910	1.39014	0.0126
0.0949	0.4022	1.38417	0.0153
0.0979	0.4930	1.37831	0.0167
0.0936	0.6004	1.37031	0.0170
0.1020	0.6967	1.36046	0.0151
0.1017	0.8006	1.34788	0.0107
0.2059	0.0955	1.39413	0.0065
0.2002	0.1917	1.39020	0.0099
0.1972	0.3021	1.38471	0.0130
0.2033	0.3981	1.37854	0.0147
0.2042	0.5005	1.37116	0.0154
0.1977	0.5998	1.36271	0.0145
0.1957	0.7055	1.35121	0.0112

(*Continued*)

Table 2. Continued.

Acetone + methanol + 2-methyl-1-propanol			
x_1	x_2	n_D	δn_D
0.3023	0.0851	1.39041	0.0068
0.2959	0.2041	1.38509	0.0105
0.2988	0.4004	1.37275	0.0138
0.2982	0.5019	1.36446	0.0135
0.3080	0.5927	1.35442	0.0111
0.4041	0.1062	1.38471	0.0078
0.3990	0.1958	1.38014	0.0100
0.4054	0.2885	1.37392	0.0114
0.4051	0.3956	1.36595	0.0119
0.4093	0.4920	1.35661	0.0104
0.4987	0.1010	1.38007	0.0074
0.5030	0.1953	1.37413	0.0091
0.5020	0.2956	1.36720	0.0101
0.5141	0.3928	1.35791	0.0090
0.6100	0.0899	1.37452	0.0065
0.6039	0.2021	1.36744	0.0080
0.6090	0.2929	1.35984	0.0078
0.7115	0.0897	1.36862	0.0056
0.7156	0.1882	1.36102	0.0060
0.8141	0.0867	1.36221	0.0040
0.8940	0.0527	1.35919	0.0023

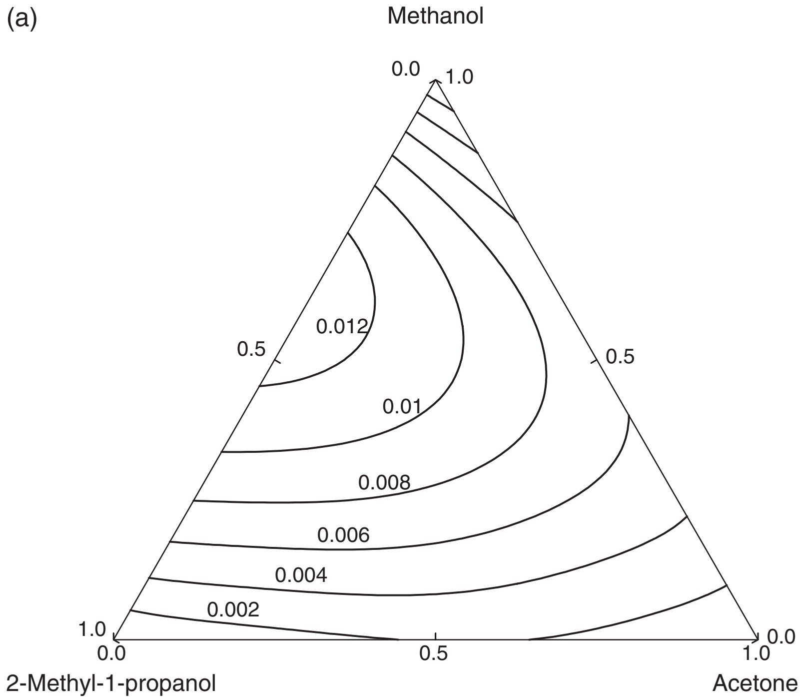
In this equation, n_D is the refractive index in the mixture, n_{D_i} is the property of pure components, x_i the molar fraction of component i in the mixture, N is the number of components and δ means the variation of a magnitude. A Redlich–Kister type equation [7] was used to correlate the changes in refractive indices on mixing of the corresponding binary mixtures, as presented in earlier papers [8,9]. The parameters of these binary mixtures are those corresponding to the Redlich–Kister equation, which is expressed as:

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

where m is the limit of the expansion computed by the F-test [10] and B_p are the fitting parameters. The ternary correlation was made by means of a Nagata type equation [11] as follows:

$$\begin{aligned}\delta Q_{123} = {} & \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + x_1 x_2 x_3 RT \\ & \times \left(B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2\right)\end{aligned} \tag{3}$$

where δQ_{12}, δQ_{13}, and δQ_{23} are the binary contributions by the Redlich–Kister expression for each binary mixture. Figures 1(a) and 1(b) show the derived property against molar fraction as well as the curves fitted. The correlation was made by taking into account the binary contributions, using the least squares method with all points weighing equally, by means of a routine developed in accordance with the Marquardt algorithm [12]. No values of these properties for the ternary system



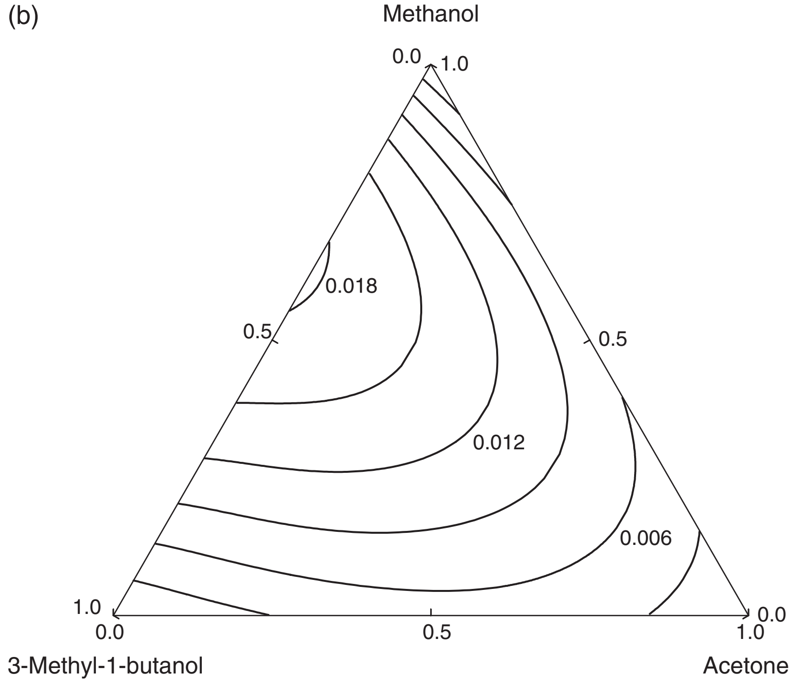


Figure 1. Curves of constant changes of refractive indices in accordance with equation (3) for (a) acetone + methanol + 2-methyl-1-propanol and (b) acetone + methanol + 3-methyl-1-butanol at 298.15 K.

Table 3. Parameters for changes of refractive indices by equation (4) and root mean square deviations (σ).

	Acetone + methanol + 2-methyl-1-propanol		
$B_0 = -1.2779 \times 10^{-5}$	$B_1 = -6.4407 \times 10^{-5}$	$B_2 = -1.6571 \times 10^{-5}$	
$B_3 = 1.3867 \times 10^{-4}$	$B_4 = -5.2621 \times 10^{-5}$	$B_5 = 1.5622 \times 10^{-4}$	
$B_6 = -5.7540 \times 10^{-5}$	$B_7 = 8.6812 \times 10^{-5}$	$B_8 = -2.1628 \times 10^{-4}$	$\sigma = 1.3 \times 10^{-4}$
	Acetone + methanol + 3-methyl-1-butanol		
$B_0 = -8.5184 \times 10^{-6}$	$B_1 = -9.4647 \times 10^{-5}$	$B_2 = 5.6223 \times 10^{-6}$	
$B_3 = 2.4357 \times 10^{-4}$	$B_4 = -7.7128 \times 10^{-5}$	$B_5 = 1.1886 \times 10^{-4}$	
$B_6 = -1.5973 \times 10^{-4}$	$B_7 = 8.4861 \times 10^{-5}$	$B_8 = -2.1488 \times 10^{-4}$	$\sigma = 4.6 \times 10^{-5}$

being studied have been published in currently available literature. The parameters of equations (2) and (3) and the corresponding root mean square deviations (equation (4)) are gathered in table 3. In this expression, the value of the property and the number of experimental data are represented by z and n, respectively.

$$\sigma = \sqrt{\frac{\sum_i^n \left(z_{\mathrm{exp}} - z_{\mathrm{pred}}\right)^2}{n}}. \tag{4}$$

4. Estimation procedures

4.1. *Multicomponent changes of refractive indices*

The prediction of different thermodynamic properties of multicomponent mixtures have been the subject of study in the last few years, applying different empirical or semiempirical models for multicomponent systems.

The ternary derived properties of mixtures may be estimated from binary values applying the equation (5) [5]:

$$\delta Q_{ijk} = \sum_{i<j} \left(\frac{x_i x_j}{x'_i x'_j}\right) \delta Q_{ij}(x'_i, x'_j). \tag{5}$$

For each ternary mixture the molar fractions x' may be obtained from a triangular diagram by projecting the point representing the 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 or c asymmetric equation of Tsao–Smith (methanol as polar component) show the lowest deviations with respect to experimental results for both systems, as well as when symmetric rules as Kohler, Jacob–Fitzner or Colinet were applied. In table 4 the root mean square deviations of each method are gathered for both the mixtures.

Table 4. Root mean square deviations of the experimental data from the prediction results for different empirical equations.

	$\sigma(\delta n_D)$	
	Acetone + methanol + 2-methyl-1-propanol	Acetone + methanol + 3-methyl-1-butanol
Kohler	0.0006	0.0004
Jacob–Fitzner	0.0004	0.0001
Colinet	0.0005	0.0002
Knobeloch	0.0024	0.0027
Tsao–Smith[a]	0.0026	0.0030
Tsao–Smith[b]	0.0003	0.0002
Tsao–Smith[c]	0.0020	0.0020
Scatchard[a]	0.0006	0.0002
Scatchard[b]	0.0003	0.0007
Scatchard[c]	0.0010	0.0010
Toop[a]	0.0007	0.0004
Toop[b]	0.0003	0.0007
Toop[c]	0.0010	0.0010
Mathieson–Tynne[a]	0.0005	0.0001
Mathieson–Tynne[b]	0.0002	0.0004
Mathieson–Tynne[c]	0.0007	0.0005
Hillert[a]	0.0007	0.0003
Hillert[b]	0.0003	0.0007
Hillert[c]	0.0010	0.0010

[a] Acetone is the asymmetric component in the equation.
[b] Methanol is the asymmetric component in the equation.
[c] 2-Methyl-1-propanol, or 3-methyl-1-butanol is the asymmetric component in the equation.

4.2. *Multicomponent excess molar volumes*

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 by other physical magnitude. The methods 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. A deeper explanation on this procedure can be encountered in an earlier work [8].

The relation of this magnitude to the function of refractive indices would be expressed as:

$$V_{\mathrm{m}}^{\mathrm{E}} = \sum_{i=1}^{N}\left[\left(f(n_{\mathrm{D_i}}) - f(n_{\mathrm{D}})\right)\frac{x_i M_i}{f(n_{\mathrm{D}})\rho_i}\right]. \tag{6}$$

In this way, Nakata and Sakurai [13] have proposed a expression to relate excess volumes by means of expansions in powers to first order with different mixing rules [5]:

$$V_{\mathrm{m}}^{\mathrm{E}} = -\left(\frac{f'(n_{\mathrm{D_1}})}{f(n_{\mathrm{D_1}})}\right)\sum_{i=1}^{N}\left[\frac{x_i M_i}{\rho_i}\right]\left(n_{\mathrm{D}} - \sum_{i=1}^{N} n_{\mathrm{D}_i}\phi_i\right) \tag{7}$$

where f' means the first derivation of the mathematical relation f and ϕ_i the volumetric fraction attending to the non-additivity of mixing. In this work, experimental and

Table 5. Root mean square deviations of the experimental excess molar volumes from those estimated by equations (6) and (7) applying different mixing rules for refractive index on mixing for the ternary systems.

		(L–L)	(D–G)	(Eyk)	(Os)
Acetone + methanol + 2-methyl-1-propanol	equation (6)	0.070	0.049	0.055	0.038
	equation (7)	0.044	0.050	0.047	0.053
Acetone + methanol + 3-methyl-1-butanol	equation (6)	0.069	0.035	0.044	0.029
	equation (7)	0.029	0.038	0.033	0.042

estimated values of excess molar volumes using equations (6) and (7) are compared applying the Lorentz–Lorenz, Dale–Gladstone, Eykman and Oster refractive index mixing rules [5]. A good concordance are shown between theoretical and experimental values, which keep a diference better than ±5%, approximately, the lowest deviations being obtained for the Oster rule using equation (6) and the Lorentz–Lorenz rule for the equation (7) (table 5). These equations show a good capability in the estimation of excess molar volumes, and can 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.

5. Results and conclusions

The internal pressure of a liquid mixture is a physical magnitude closely related to the isochoric influence of temperature on the molecular cohesive trend. Such magnitude shows the non-ideal deviations due to intermolecular forces in liquid state, thus the usual derivation of any derived property should be computed as a measurement of the intensity of these interactions. The excess molar internal pressure of the liquid mixture (P^{E}) was obtained by the following equation:

$$P^{\mathrm{E}} = P - \sum_{i=1}^{N} x_i P_i \tag{8}$$

where P and P_i are the internal pressure of the mixture and the pure component i. These values can be obtained from the Buchler–Hirschfelder–Curtis equation of state, by applying the following relations:

$$P_i = \frac{2^{1/6} RT}{2^{1/6} V - dN^{1/3} V^{2/3}} \tag{9}$$

where N is the Avogadro number, V the molar volume, and d is the molecular diameter of the mixture or the pure components, which is related to the molecular polarizability (α) as:

$$\alpha = \left(\frac{d}{2}\right)^3. \tag{10}$$

By substitution of the dependence of this magnitude on the density and refractive index:

$$d = 2 \cdot \left(\frac{n_{\mathrm{D}}^2 - 1}{n_{\mathrm{D}}^2 + 2} V \frac{3}{4 \prod N} \right)^{1/3}. \tag{11}$$

Thus we can express the mean molecular diameter in a pure component or any mixture as a function of the refractivity.

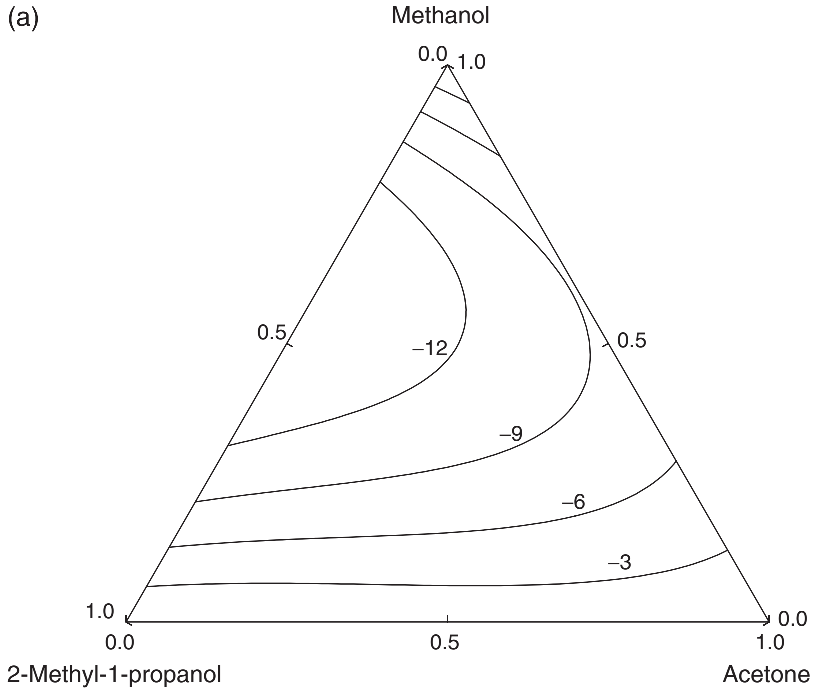
It is well known that when hydroxylic polar and non-polar compounds are being mixed, considerable variations in hydrogen bond interactions and steric hindrance take place. The breakage of alcohol associations produces an expansive trend in the mixture, which gives positive values for excess molar volumes or negative deviations in the non-ideality of refractive index, and a negative trend in excess molar internal pressure. The new specific interactions that appear (dispersive interactions, tautomerism, new hydrogen bond interactions among dislike molecules, etc.) should be suitably measured by combining volumetric or calorimetric techniques. In this work, to complete the previous experimental measurements of volumetric and sonic data, new measurements were made of refractive index for the ternary mixtures acetone + methanol + (2-methyl-1-propanol or 3-methyl-1-butanol).

These kind of mixtures show a moderate non-ideal behaviour, which is severely conditioned by the associative behaviour due to H-bond interaction of the hydroxyl groups among alcohol molecules, and the weak proton acceptor trend of ketone groups from hydroxyl protons, and the difference in molecular volume between the branched alcohols, and the components of the azeotropic mixtures that leads to important steric hindrance. This fact is noted by an expansive trend in mixtures, except for cases of total dilution of the separation agent (both branched alcohols), where a partial contractive effect is reflected by association of ketone groups, and active hydroxyl groups of methanol.

In earlier works, we reported the volumetric behaviour of different aliphatic alcohols with this binary azeotropic mixture, where the functional dependence could be expressed attending to these factors; first, a short aliphatic end in the separation agent leads to a general contractive trend at any molar fraction. The self-association and crossed H-bonds are strong enough to package the mixture, while at high concentrations of entrainer, a mixing expansion is obtained if the residue is C_3 or greater. In other studies, a stronger expansion is noted when branched agents are used (2-propanol or 2-butanol). This trend was changed if 2-methyl-2-butanol was applied, due to an intense attraction with methanol due to the bond potency of the hydroxyl of this compound, and the virtually zero steric hindrance of methanol.

The solvents applied (2-methyl-1-propanol, and 3-methyl-1-butanol) tally with the trend observed for linear aliphatic heavy alcohols, where no interactions occur between alcohols, this trend being of interest in order to separate acetone and methanol by means of an adequate vapor–liquid equilibria topology [14,15].

This trend is clearly shown in figures 1(a) and 1(b), where the isotherms of changes of refractive index show positive values throughout the entire composition range. Three local maxima could be observed in binaries, the highest being that corresponding to methanol and branched alcohol in both cases. This trend could be explained in terms of ternary contributions to the derived magnitude, as a negative



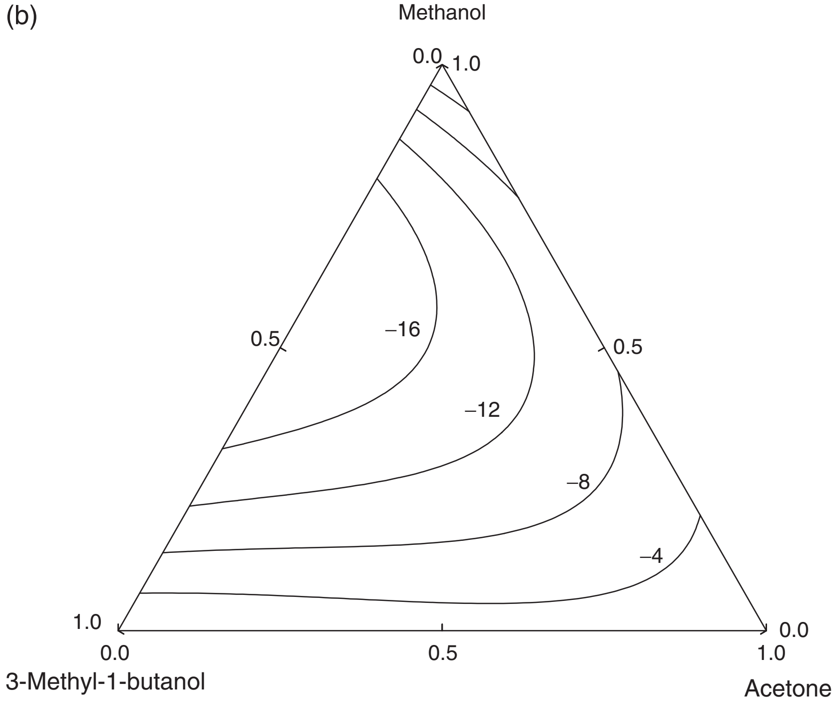


Figure 2. Curves of constant excess molar internal pressure in accordance with equation (5) for (a) acetone + methanol + 2-methyl-1-propanol and (b) acetone + methanol + 3-methyl-1-butanol at 298.15 K.

contribution thoughout the composition range, pointing out the compensation of structural effects for equimolar compositions.

These measurements are closely related to changes in the solvent layer around the entrainer molecules, thus at diluted mixtures of the separation agent, a typical three-dimensional cage-like structure is formed, the solution being predominantly organized by intense hydroxyl donor–carbonil proton aceptor interactions. Under these conditions, linear chains or three-dimensional rings of polar molecules have been proposed to exist [16] attending to steric effects of residual ends, and the rupture of acetone + methanol structure by introduction of the branched aliphatic alcohol molecules.

The solvation layer is progressively dissolved, the strong polar interactions are replaced by weak interactions (dispersion forces), and a weakening of intermolecular interactions is observed. This fact could be noted by the trend in the excess molar internal pressure (figures 2a and 2b), which shows a similar trend as changes in refractive indices (three local minima in binaries). Rising negative excess molar internal pressure suggests that the mixture is loosing cohesion, changing strong bonds by dispersive forces. As expected, the 3-methyl-1-butanol shows the higher negative values. It is worthwhile pointing out that the strong decreasing trend is in accordance with the self-associative trend of acetone and methanol. These types of interactions among heavy branched hydroxyl solvents, acetone, and methanol molecules provide promising expectations. These kind of entrainers show an important capability to disrupt alcohol–ketone interactions, while an adequate vapor–liquid equilibria topology is performed (only one minimum azeotrope in the problem mixture), which highlights the potency of these branched aliphatic alcohols for separation processes and implies simple sequences and low costs for application in extractive or modified distillation procedures.

Our work focuses on the application of aliphatic heavy alcohols and alkanes with splitting induction in mixing, in order to reinforce the observed behaviour for these chemicals, as well as phase equilibria studies on these mixtures.

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