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Thermochimica Acta 328 (1999) 265–275

thermochimica acta

Volumetric properties prediction by cubic EOS for non-ideal mixtures: application to the ternary system acetone+methanol+*n*-hexane

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Accepted 17 November 1998

Abstract

In this work the applicability of simple mixing rules combined with Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state was tested in the prediction of excess molar volume for high polar and partially miscible multicomponent mixtures. To this aim the temperature trend of excess molar volumes of the ternary mixture acetone+methanol+*n*-hexane was measured in the range 278.15–298.15 K and atmospheric pressure. The corresponding interaction parameters were computed. Good accuracy was obtained in general terms when predicting ternary values of the magnitude. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Excess molar volume; Temperature dependence; Equation of state; Mixing rule

1. Introduction

As a continuation of our previous works in thermodynamics of homogeneous and heterogeneous azeotropic liquid mixtures [1,2], this paper comprises physical properties, and further use of data sets to test different theoretical predictive methods. The purpose is to get topology information to identify alternative separation agents for binary azeotropic or binary close boiling mixtures. Among the theoretical methods available, the equations of state (EOS) can be regarded as an attractive prediction instrument, due to its low pure compound data requirements, simplicity of calculus, and wide range of applicability for any practical purpose.

In this paper the application of cubic equations of state over a temperature range to the prediction of volumetric properties is undertaken in order to estimate excess molar volumes in highly non-ideal multicomponent mixtures. The huge number of possible combinations in the formation of multicomponent mixtures and the great cost required to obtain experimental data, make it rather usual that no information can be found for a specific mixture at certain conditions. It arises to be essential to the research and development of predictive mechanisms allowing to obtain reliable estimation of thermodynamic properties of mixtures. A countless number of equations of state are available in open literature, and most of them are suitable to obtain accurate results if combined with simple rules, in the prediction of multicomponent system excess molar volumes, provided that molecular parameters and enclosed binary mixtures data are available.

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PII: S0040-6031(98)00652-2

The excess molar volume is a suitable magnitude for calculating interaction parameters, because experimental data are widely available, due to the great attention it has been receiving, as shown by the number of papers reported in the last few years. Furthermore, excess molar volume data can be accurately determined faster and easier than other thermophysical properties, as for example thermal magnitudes.

This work has been divided into two main sections: the first one is devoted to the acquisition of experimental data, where the excess molar volumes of the ternary mixture acetone+methanol+*n*-hexane were computed from measured density data, at three different temperatures (278.15, 288.15 and 298.15 K), with the corresponding correlation and graphical work. The second part is related to the use of equations of state for excess volumes correlation and prediction. The first stage was the calculation of the binary interaction parameters corresponding to three simple mixing rules that were combined with the equations of state of Peng–Robinson [3] and Soave–Redlich–Kwong [4]. These parameters were then used to estimate the ternary excess molar volume data, and the comparison with experimental values yielded low deviations, taking into account the nature of the mixture, which includes an immiscibility region that had to be evaluated. The obtained results enable us to discuss the temperature dependence of the magnitude, as well as the applicability of the tested equations to achieve good predictions when applied to volumetric properties estimation.

2. Experimental

All chemicals used in the preparation of samples were Merck Lichrosolv quality. The pure components were stored in inert argon atmosphere (N-55, weaker than 3 ppm in water), degassed with ultrasound technique, and stored over molecular sieve types 4a or 3a, $\frac{1}{16}$ in. (Aldrich cat. no. 20,860-4 or 20,858-2, respectively) to remove trace amounts of water. The densities measured experimentally for each component are compared with literature values in Table 1. Precautions were taken, such as cooling chemicals to reduce vapor pressure before the samples were prepared, and vapor space was limited to a minimum into the vessels to avoid preferential evaporation which would lead to composition errors. GLC tests of the solvents showed higher purities than those found in technical specifications supplied by Merck. Their mole fraction purities were better than 0.998 in all cases. A PolyScience controller bath model 9510, ensuring a temperature stability of $\pm 10^{-2}$ K was used to thermostatize the samples. The samples were prepared by mass using a Mettler AE-240 balance with a precision of $\pm 10^{-4}$ g, which made the maximum error in mole fraction determination to be 10^{-4}. The densities of the mixtures, and pure chemicals were measured with an Anton Paar DSA-48 densimeter, with a precision of $\pm 5\times 10^{-5}$ g cm^{-3}. Calibration of the employed device was performed periodically, using a double fluid reference (Millipore quality water, and ambient air). Accuracy in the calculation of excess molar volumes was evaluated to be better than 10^{-3} cm^3 mol^{-1}. The immiscibility region was estimated by means of tie lines correlation, the corresponding liquid–liquid equilibrium study being enclosed in an earlier work [7]. Further details about the experimental methods employed can be found in a previous work [8].

Table 1
Comparison of measured pure chemicals densities with literature values at 298.15 K

Component	ρ (g cm^{-3})	
	Experimental	Literature
Acetone	0.7844	0.78429[a] 0.78547[b]
Methanol	0.7866	0.78664[b]
n-Hexane	0.6551	0.65484[b]

[a] From Ref. [5].
[b] From Ref. [6].

3. Data correlation

The physical, and derived properties corresponding to the binary mixtures were gathered in earlier papers [1,2,9], respectively. Excess molar volumes for the binary mixtures at the considered temperatures, shown in Table 2, were computed by applying the equation

$$V^{\mathrm{E}} = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}), \tag{1}$$

Table 2
Densities (ρ) and excess molar volumes (V^E) for the ternary mixture acetone+methanol+*n*-hexane at 278.15, 288.15 and 298.15 K

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
T=278.15 K			
0.0560	0.8929	0.7852	0.079
0.0689	0.0906	0.6807	0.329
0.0733	0.8219	0.7682	0.174
0.1014	0.1315	0.6852	0.435
0.1056	0.7884	0.7691	0.146
0.1167	0.7002	0.7503	0.250
0.1215	0.2108	0.6919	0.466
0.1216	0.2967	0.6983	0.448
0.1415	0.4064	0.7111	0.393
0.1517	0.5954	0.7382	0.297
0.1618	0.4920	0.7244	0.352
0.2004	0.1215	0.6933	0.576
0.2031	0.4931	0.7316	0.351
0.2046	0.6924	0.7734	0.055
0.2054	0.3018	0.7087	0.486
0.2093	0.3941	0.7193	0.424
0.2122	0.5863	0.7498	0.237
0.2148	0.2043	0.7010	0.551
0.2960	0.4019	0.7348	0.358
0.2978	0.5975	0.7752	0.025
0.2996	0.5008	0.7526	0.238
0.3026	0.2963	0.7215	0.478
0.3064	0.1197	0.7040	0.651
0.3094	0.1935	0.7112	0.577
0.3967	0.4014	0.7548	0.228
0.3970	0.4958	0.7765	0.014
0.3993	0.2967	0.7371	0.416
0.4045	0.1005	0.7135	0.709
0.4122	0.1855	0.7241	0.569
0.4923	0.2085	0.7398	0.477
0.4970	0.2864	0.7539	0.306
0.5002	0.1065	0.7269	0.670
0.5068	0.3858	0.7780	0.032
0.5821	0.1193	0.7413	0.583
0.5986	0.1943	0.7572	0.361
0.6072	0.2850	0.7789	0.073
0.6432	0.1959	0.7672	0.246
0.6909	0.1020	0.7583	0.447
0.7410	0.2076	0.7942	−0.039
0.7981	0.1025	0.7817	0.201
T=288.15 K			
0.0558	0.8934	0.7759	0.091
0.0654	0.0844	0.6709	0.487
0.0705	0.7333	0.7359	0.365
0.0969	0.6465	0.7256	0.412
0.0986	0.6965	0.7352	0.360
0.1039	0.2176	0.6813	0.593
0.1042	0.4224	0.6979	0.528
0.1061	0.7854	0.7587	0.188
0.1098	0.3137	0.6888	0.584
0.1146	0.1246	0.6766	0.609
0.1150	0.4912	0.7069	0.492
0.1191	0.2614	0.6858	0.602
0.1207	0.5520	0.7156	0.459
0.1971	0.3043	0.6983	0.602
0.2027	0.1086	0.6832	0.729
0.2046	0.6929	0.7637	0.083
0.2063	0.4968	0.7230	0.426
0.2111	0.5876	0.7399	0.301
0.2147	0.3875	0.7096	0.532
0.2151	0.2046	0.6915	0.685
0.2890	0.2073	0.7002	0.701
0.2899	0.6013	0.7639	0.067
0.2967	0.5037	0.7427	0.282
0.2982	0.1185	0.6933	0.793
0.2992	0.4038	0.7257	0.441
0.3090	0.2836	0.7110	0.607
0.3872	0.4166	0.7455	0.282
0.3884	0.1187	0.7036	0.799
0.3933	0.2996	0.7265	0.499
0.3987	0.4939	0.7662	0.051
0.4000	0.1994	0.7140	0.672
0.4888	0.2146	0.7300	0.551
0.4930	0.3950	0.7663	0.074
0.4968	0.2952	0.7453	0.345
0.5017	0.1057	0.7170	0.773
0.5779	0.1244	0.7313	0.642
0.5929	0.2955	0.7673	0.115
0.5947	0.1998	0.7471	0.413
0.6820	0.1136	0.7483	0.486
0.6870	0.2054	0.7688	0.162
0.7905	0.1086	0.7706	0.231
T=298.15 K			
0.0531	0.7053	0.7169	0.424
0.0537	0.5977	0.7007	0.475
0.0547	0.4057	0.6806	0.532
0.0878	0.1408	0.6659	0.551
0.0943	0.4145	0.6861	0.554
0.0974	0.5081	0.6964	0.514
0.0995	0.7909	0.7489	0.165
0.1003	0.2186	0.6715	0.587
0.1003	0.6065	0.7102	0.441
0.1018	0.3132	0.6783	0.584
0.1019	0.7014	0.7275	0.336
0.1918	0.1201	0.6733	0.720
0.1922	0.3147	0.6888	0.622
0.1966	0.6089	0.7310	0.293
0.1973	0.7005	0.7538	0.074
0.2006	0.6999	0.7544	0.085
0.2007	0.2086	0.6805	0.693
0.2008	0.5035	0.7131	0.437
0.2012	0.3971	0.6988	0.553

Table 2 (*Continued*)

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
0.2903	0.4185	0.7162	0.455
0.2910	0.5137	0.7333	0.283
0.2913	0.6107	0.7568	0.034
0.2942	0.1180	0.6828	0.835
0.2953	0.1995	0.6902	0.740
0.3076	0.3203	0.7052	0.586
0.3837	0.1319	0.6941	0.832
0.3857	0.4213	0.7358	0.287
0.3901	0.3095	0.7170	0.527
0.3955	0.2074	0.7040	0.707
0.3975	0.5039	0.7581	0.030
0.4866	0.2195	0.7198	0.588
0.4937	0.4045	0.7582	0.059
0.5025	0.2964	0.7361	0.359
0.5031	0.1044	0.7066	0.820
0.5764	0.1252	0.7205	0.690
0.5939	0.2076	0.7377	0.421
0.6119	0.2845	0.7586	0.109
0.6782	0.2225	0.7599	0.136
0.6875	0.1181	0.7394	0.490
0.7885	0.1120	0.7599	0.238

were ρ and ρ_i stand for the density of the mixture and the pure chemical i, respectively, x_i the molar fraction, and N is the number of components. The computed excess molar volumes, were fitted to a Redlich–Kister [10] type expression for every binary mixture, according to the equation

$$V_{ij}^{\mathrm{E}} = x_i x_j \sum_{p=0}^{M} A_p (x_i - x_j)^p, \tag{2}$$

where A_p are the fitting parameters obtained by the unweighted least squares method, and M is the degree of the polynomic expansion, optimized by means of the F test due to Bevington [11]. The excess ternary volumes, presented in Table 2, were correlated using the Nagata [12] expression

$$\begin{aligned} V_{123}^{\mathrm{E}} = V_{12}^{\mathrm{E}} + V_{13}^{\mathrm{E}} + V_{23}^{E} + x_1 x_2 x_3 RT(B_0 - B_1 x_1 \\ - B_2 x_2 - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 \\ - B_7 x_2^3 - B_8 x_1^2 x_2), \end{aligned} \tag{3}$$

where V_{ij}^{E} are the binary contributions correlated with Eq. (2). Fig. 1(a)–(c) shows the curves of constant ternary excess molar volume by application of Eq. (3) for the three temperatures considered. As expected, the mixture presents an expansive trend with the increasing temperature. In Table 3, the fitting parameters corresponding to Eqs. (2) and (3) are enclosed. The root mean square deviations presented were computed using Eq. (4), where z is the value of the excess volume, and n_{DAT} is the number of experimental data

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\mathrm{DAT}}} \left(z_{\mathrm{exp}} - z_{\mathrm{pred}} \right)^2}{n_{\mathrm{DAT}}} \right)^{1/2}. \tag{4}$$

In Fig. 2(a)–(c) the ternary contribution to the derived magnitude can be observed in accordance to the last term of Eq. (3).

4. Equations of state

The Peng–Robinson [3] (PR) and Soave–Redlich–Kwong [4] (SRK), two parameters cubic equations of state were applied. A general expression of both equations of state can be

$$P = \frac{RT}{V - b} - \frac{a}{(V + \delta_1 b)(V + \delta_2 b)}, \tag{5}$$

where δ_1=1, δ_2=0 for SRK, and $\delta_1 = 1 + \sqrt{2}, \delta_2 = 1 - \sqrt{2}$ for PR equations The repulsion-covolume factor, b, is kept constant at its critical point values, and can be expressed as follows, for every pure substance and the two equations considered:

$$b_i = K_1 \frac{R \cdot T_{\mathrm{c}i}}{p_{\mathrm{c}i}}, \tag{6}$$

where T_{ci} and P_{ci} are the critical temperature and pressure of the component i in the mixture, and K_1 is a constant, the value of which should be 0.08664 for SRK and 0.0778 for PR. The attraction–cohesion parameter, a, contains a generalized function of temperature

$$a_i = K_2 \frac{R^2 \cdot T_{\mathrm{c}i}^2}{p_{\mathrm{c}i}} \alpha_i, \tag{7}$$

where

$$\alpha_i = \left[1 + m_i \left(1 - T_{ri}^{1/2} \right) \right]^2 \tag{8}$$

and

$$m_i = K_3 + K_4 \omega_i - K_5 \omega_i^2 \tag{9}$$

in these equations, ω_i stands for the accentric factor, and K_i are constant with values K_2=0.42748, K_3=0.480, K_4=1.574 and K_5=0.176 for SRK, and

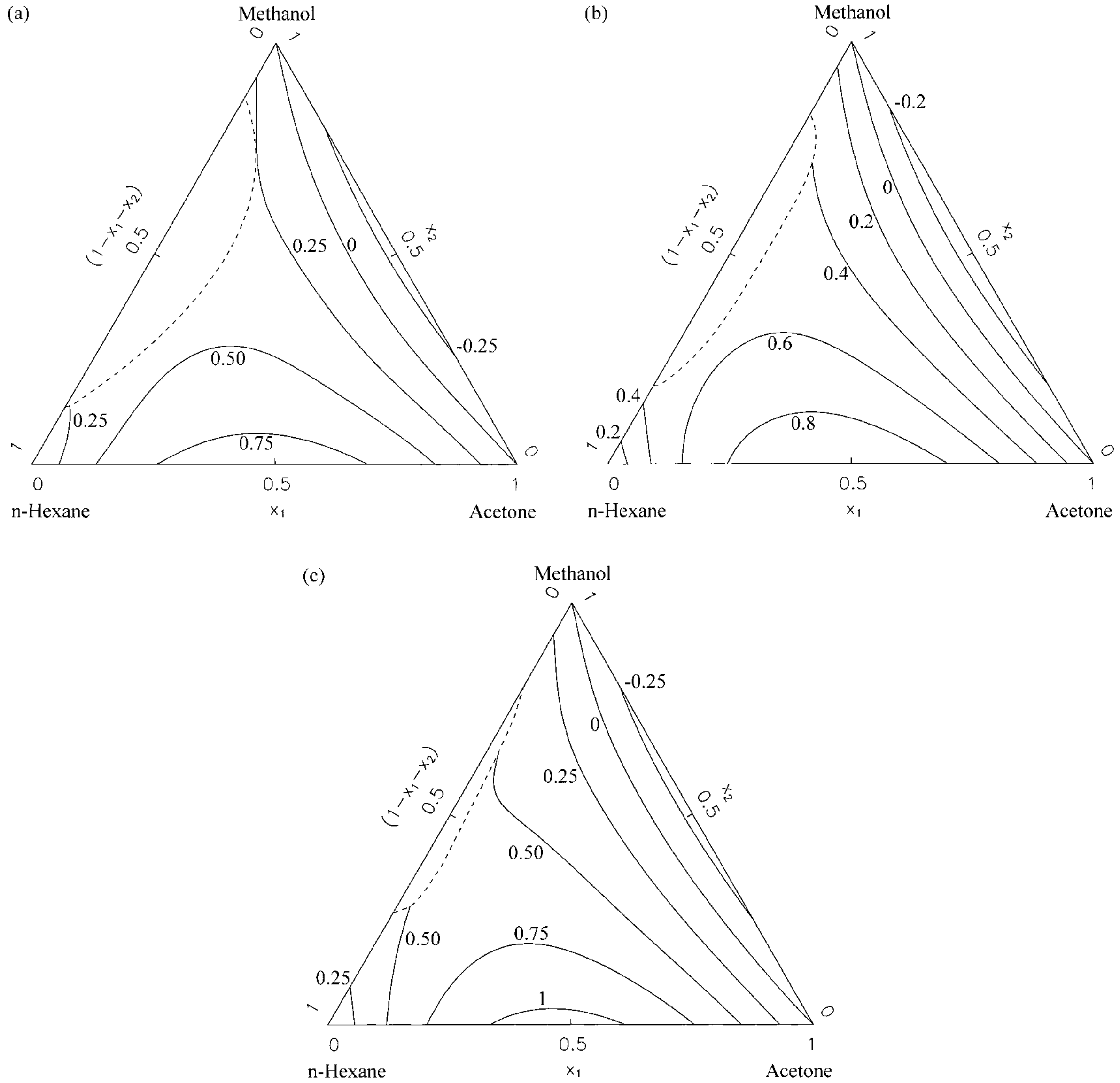

Fig. 1. Constant value lines of ternary excess volume, correlated using Eqs. (2) and (3), at these temperatures: (a) 278.15, (b) 288.15, and (c) 298.15 K.

K_2=0.45724, K_3=0.37464, K_4=1.54226 and K_5= 0.26992 for PR. Both equations require relatively simple solving methods, and have proved to offer good predictions of the mixtures density data, because of their flexibility and the possibility of extension to polar compounds as those involved in this mixture. Mixing rules play a fundamental role in extending an equation state to the mixtures property calculations, and the results obtained will depend, to a higher extent, on the right election made. Consequently, the study of different types of mixing rules, and the applicability to the mixtures, depending on the nature of the compounds, arises to be essential. Three different simple combining rules were incorporated to the above described EOS to calculate the values of *a* and *b* in the mixture. These rules can be expressed in a

Table 3
Parameters A_i and B_i (cm^3 mol^{-1}) of Eqs. (2) and (3), respectively, and root mean square deviations σ

Temperature (K)	Parameters (cm^3 mol^{-1})					σ
Acetone+methanol						
278.15[c]	A_0=−1.355538	A_1=2.001079×10^{-1}	A_2=−2.124065×10^{-1}			0.0045
288.15[c]	A_0=−1.352600	A_1=1.639329×10^{-1}	A_2=−1.461775×10^{-1}			0.0026
298.15[a]	A_0=−1.357790	A_1=1.910419×10^{-1}	A_2=−2.885361×10^{-1}			0.004
Acetone+n-hexane						
278.15[c]	A_0=3.536891	A_1=−2.901295×10^{-1}	A_2=8.273848×10^{-1}	A_3=−4.680908×10^{-1}		0.0043
288.15[c]	A_0=3.857698	A_1=−3.932955×10^{-1}	A_2=8.449447×10^{-1}	A_3=−3.554783×10^{-1}		0.0049
298.15[c]	A_0=4.325232	A_1=−5.255542×10^{-1}				0.028
Methanol+n-hexane						
278.15[c]	A_0=1.895572	A_1=6.340789×10^{-2}	A_2=1.015647	A_3=1.172108		0.003
288.15[c]	A_0=1.933777	A_1=−1.645561×10^{-1}	A_2=2.353347			0.0083
298.15[b]	A_0=2.074061	A_1=3.195044×10^{-1}	A_2=1.773293			0.008
Acetone+methanol+n-hexane						
278.15	B_0=−5.535550×10^{-3}	B_1=−1.610943×10^{-2}	B_2=−5.505584×10^{-3}	B_3=2.140348×10^{-2}	B_4=3.357776×10^{-3}	
	B_5=−6.847413×10^{-3}	B_6=−1.350593×10^{-2}	B_7=−3.179933×10^{-3}	B_8=1.779819×10^{-2}		0.0081
288.15	B_0=−4.215691×10^{-3}	B_1=−1.508654×10^{-2}	B_2=−7.752114×10^{-3}	B_3=1.896572×10^{-2}	B_4=−6.045168×10^{-3}	
	B_5=2.170958×10^{-2}	B_6=−8.912928×10^{-3}	B_7=9.007020×10^{-3}	B_8=−1.820684×10^{-2}		0.0036
298.15	B_0=−2.091104×10^{-3}	B_1=8.642831×10^{-4}	B_2=−4.967025×10^{-3}	B_3=−4.841583×10^{-3}	B_4=4.215917×10^{-3}	
	B_5=−1.019769×10^{-2}	B_6=−9.036976×10^{-4}	B_7=9.561687×10^{-4}	B_8=1.672656×10^{-2}		0.0051

[a] From Ref. [1].
[b] From Ref. [2].
[c] From Ref. [9].

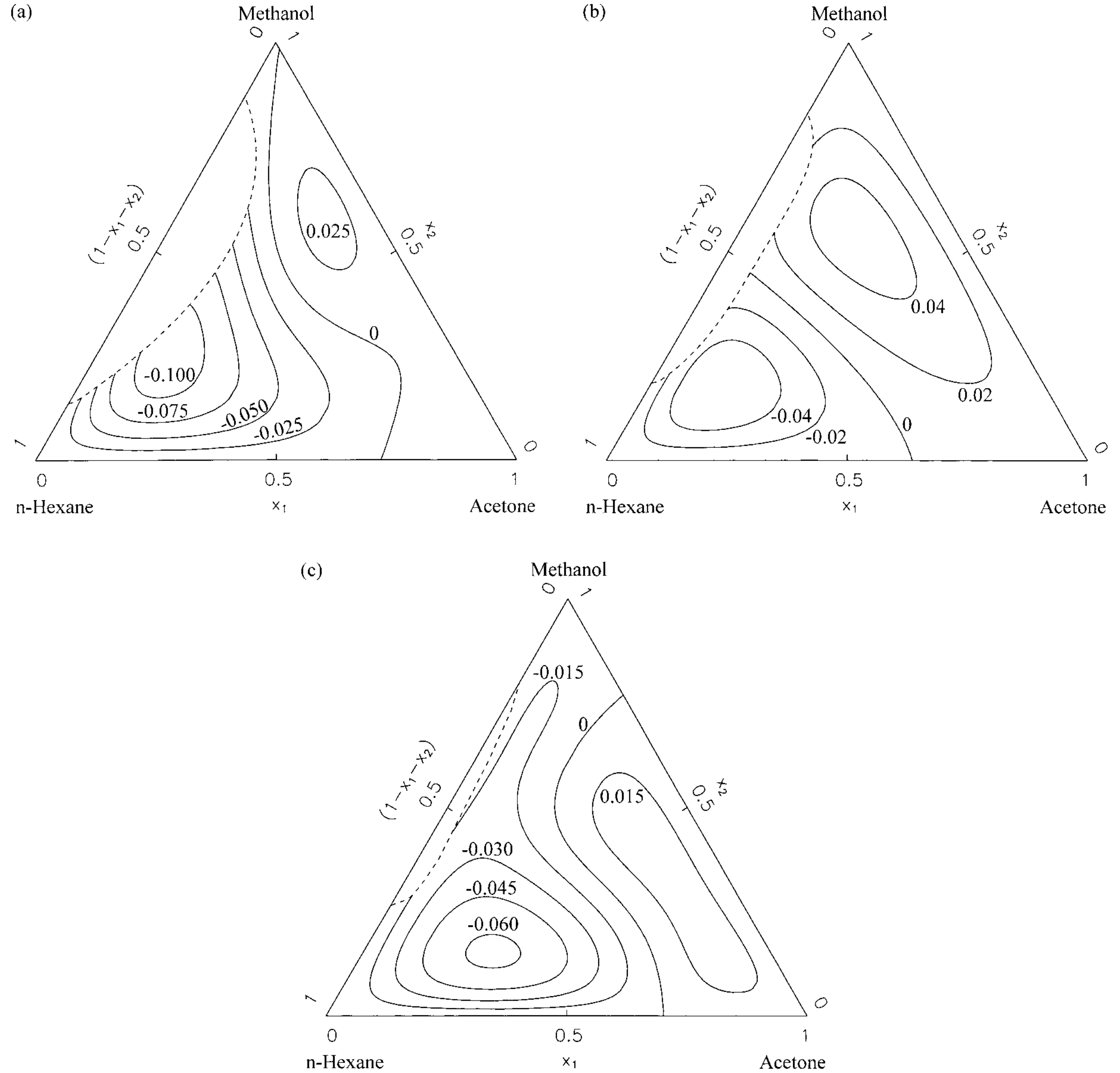

Fig. 2. Constant value lines of ternary contribution to the excess volume, in accordance with Eq. (3), at these temperatures: (a) 278.15, (b) 288.15, and (c) 298.15 K.

general way as follows:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (1 - k_{ij} - 1_{ij}T)(a_i a_j)^{1/2}, \quad (10)$$

$$b = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (1 - m_{ij})(b_i b_j)^{1/2}, \quad (11)$$

where k_{ij}, l_{ij} and m_{ij} are the adjustable binary parameters to be calculated for each binary mixture, with $l_{ij}=m_{ij}=0$ for the first mixing rule (R1), $l_{ij}=0$ for the second one (R2), and k_{ij}, l_{ij} and $m_{ij}\neq 0$ for the last one (R3).

For a binary mixture, at constant P and T, the excess molar volume is equal to the change in the volume of mixing

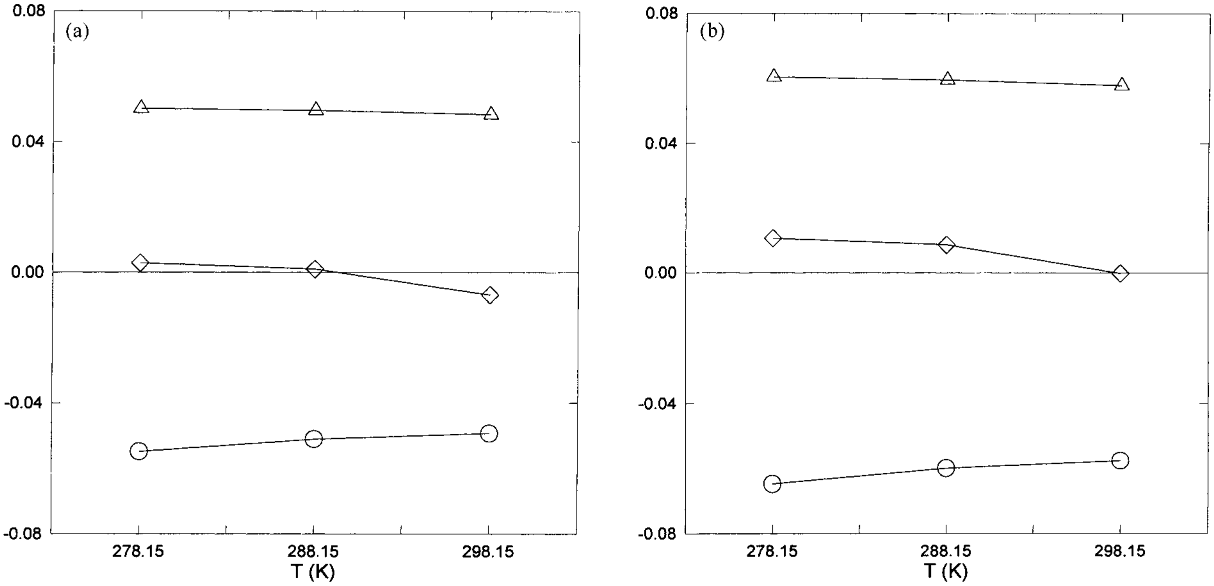

Fig. 3. Values of the k_{ij} parameters for the mixing rule R1, plotted against T/K, for the binary mixtures: (○) acetone+methanol; (△) acetone+n-hexane; (◇) methanol+n-hexane. (a) SRK equation; (b) PR equation.

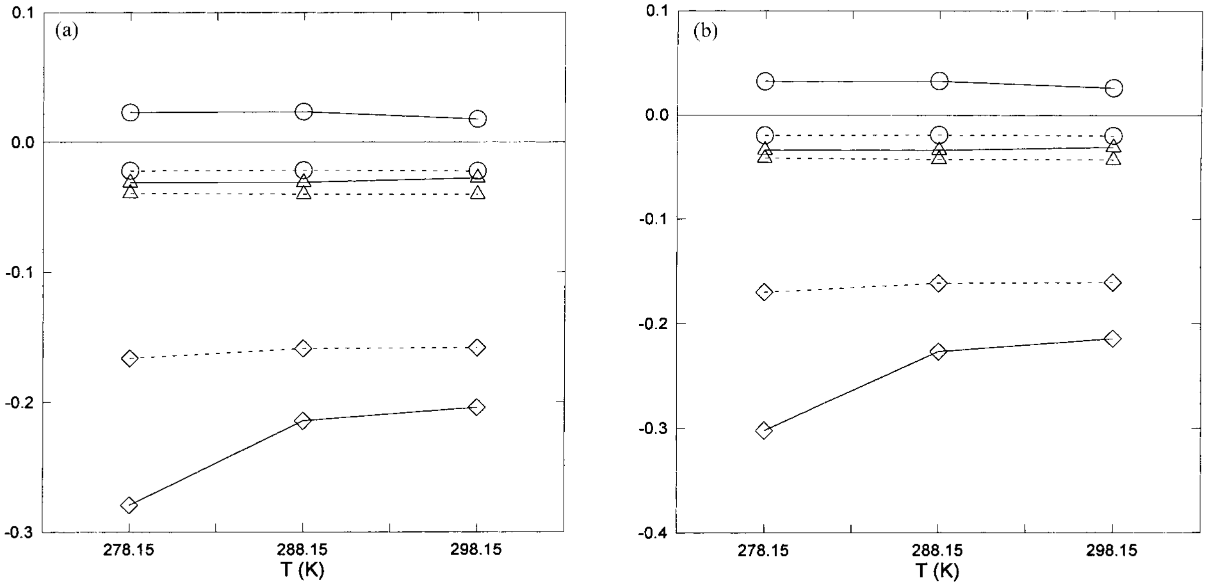

Fig. 4. Values of the (———) k_{ij}, and (- - -) m_{ij} parameters for the mixing rule R2, plotted against temperature, for the binary mixtures: (○) acetone+methanol; (△) acetone+n-hexane; (◇) methanol+n-hexane. (a) SRK equation; (b) PR equation.

Table 4

Parameters calculated corresponding to the described mixing rules, Eqs. (10) and (11), and between parenthesis, the standard deviations s (cm^3 mol^{-1}) from the experimental values of excess volume

	278.15 K			288.15 K			298.15 K		
	R1	R2	R3	R1	R2	R3	R1	R2	R3
Peng–Robinson EOS									
Acetone+methanol	-6.482×10^{-2} (0.02)	3.216×10^{-2} -1.951×10^{-2} (0.007)	1.989 -7.037×10^{-3} -1.951×10^{-2} (0.007)	-6.000×10^{-2} (0.02)	3.254×10^{-2} -1.907×10^{-2} (0.005) (0.005)	2.015 -6.881×10^{-3} -1.907×10^{-2}	-5.764×10^{-2} (0.02) (0.009)	2.610×10^{-2} $-1.969\times10^{-2}-$ (0.009)	2.107 6.982×10^{-3} -1.969×10^{-2}
Acetone+n-hexane	6.032×10^{-2} (0.04)	-3.369×10^{-2} -4.158×10^{-2} (0.04)	1.849 -6.769×10^{-3} -4.158×10^{-2} (0.04)	5.944×10^{-2} (0.05)	-3.381×10^{-2} -4.266×10^{-2} (0.05) (0.05)	1.897 -6.703×10^{-3} -4.266×10^{-2}	5.774×10^{-2} (0.05) (0.05)	-3.075×10^{-2} -4.302×10^{-2} (0.04)	1.9434 -6.621×10^{-3} -4.301×10^{-2}
Methanol+n-hexane	1.063×10^{-2} (0.1)	-3.023×10^{-1} -1.703×10^{-1} (0.01)	3.542×10^{-1} -2.360×10^{-3} -1.703×10^{-1} (0.01)	8.632×10^{-3} (0.09)	-2.271×10^{-1} -1.617×10^{-1} (0.02)	2.086×10^{-1} -1.512×10^{-3} -1.617×10^{-1} (0.02)	-2.248×10^{-4} (0.09)	-2.144×10^{-1} -1.609×10^{-1} (0.03)	6.742×10^{-2} -9.453×10^{-4} -1.609×10^{-1} (0.03)
Acetone+methanol +n-hexane	(0.1)	(0.07)	(0.07)	(0.09)	(0.07)	(0.07)	(0.09)	(0.08)	(0.08)
Soave–Redlich–Kwong EOS									
Acetone+methanol	-5.496×10^{-2} (0.02)	2.265×10^{-2} -2.234×10^{-2} (0.007)	1.971 -7.007×10^{-3} -2.234×10^{-2} (0.007)	-5.115×10^{-2} (0.02)	2.322×10^{-2} -2.197×10^{-2} (0.006)	2.004 -6.875×10^{-3} -2.197×10^{-2} (0.006)	-4.938×10^{-2} (0.02)	1.754×10^{-2} -2.258×10^{-2} (0.009)	2.089 -6.950×10^{-3} -2.258×10^{-2} (0.009)
Acetone+n-hexane	5.013×10^{-2} (0.04)	-3.135×10^{-2} -3.948×10^{-2} (0.04)	1.842 -6.737×10^{-3} -3.948×10^{-2} (0.04)	4.957×10^{-2} (0.05)	-3.125×10^{-2} -4.038×10^{-2} (0.05)	1.891 -6.671×10^{-3} -4.037×10^{-2} (0.05)	4.828×10^{-2} (0.05)	-2.788×10^{-2} -4.053×10^{-2} (0.04)	1.9535 -6.645×10^{-3} -4.053×10^{-2} (0.04)
Methanol+n-hexane	2.817×10^{-3} (0.1)	-2.795×10^{-1} -1.663×10^{-1} (0.01)	0.4001 -2.443×10^{-3} -1.663×10^{-1} (0.01)	9.418×10^{-4} (0.09)	-2.146×10^{-1} -1.587×10^{-1} (0.02)	0.2463 -1.599×10^{-3} -1.587×10^{-1} (0.02)	-6.833×10^{-3} (0.09)	-2.042×10^{-1} -1.581×10^{-1} (0.03)	8.794×10^{-2} -9.799×10^{-4} -1.581×10^{-1} (0.03)
Acetone+methanol +n-hexane	(0.1)	(0.07)	(0.07)	(0.09)	(0.07)	(0.07)	(0.09)	(0.08)	(0.08)

$$V^{\mathrm{E}} = \Delta V = V_{\mathrm{m}} - \sum_{i=1}^{n} x_i V_i = \sum_{i=1}^{n} x_i(\bar{V}_i - V_i), \tag{12}$$

where $\bar{V}_i$ is the partial molar volume defined by

$$\bar{V}_i = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n}\left(\frac{\partial P}{\partial V_{\mathrm{m}}}\right)^{-1}_{T,n} \tag{13}$$

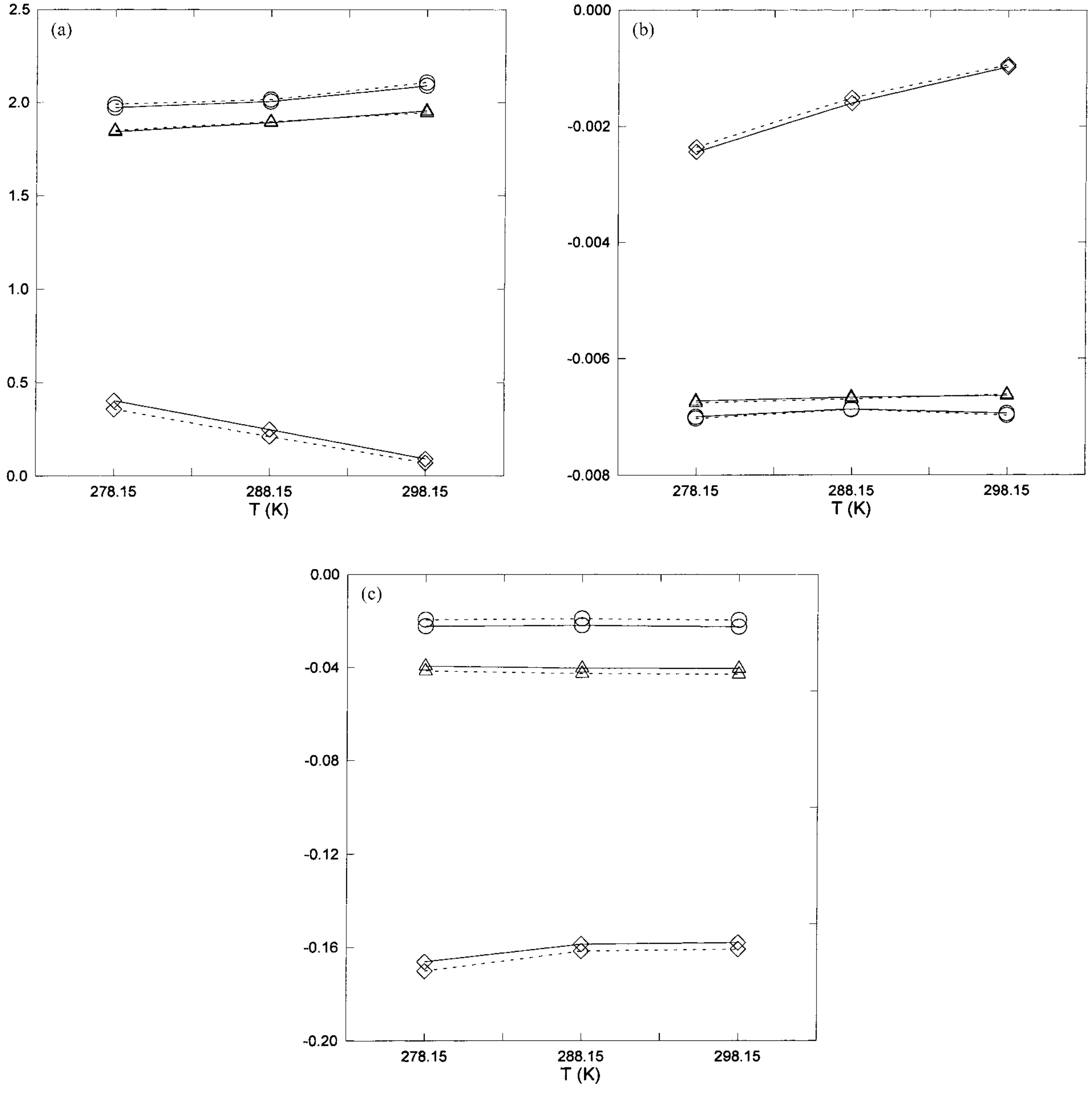

Fig. 5. Values of the parameters: (a) k_{ij}; (b) l_{ij}; and (c) m_{ij} for the mixing rule R3, plotted against temperature, for the binary mixtures: (○) acetone+methanol; (△) acetone+*n*-hexane; (◇) methanol+*n*-hexane. (———) SRK equation; (- - -) PR equation.

the quantities $(\partial P/\partial n_i)_{T,V,n}$, $(\partial P/\partial V_m)_{T,n}$, and the molar volume are computed from the corresponding equation of state, and the partial derivatives are dependent on the applied mixing rule. A Marquardt [13] non-linear algorithm was used to calculate the parameters for Eqs. (10) and (11). Binary experimental excess volume values were used to fit these parameters, and the obtained deviations are listed. After obtaining the binary parameters, the excess molar volumes of a higher order multicomponent mixture can be easily estimated, as it was done in this case to estimate the ternary values, that were compared to the set of experimental data.

In Table 4 the binary coefficients for Eqs. (10) and (11) are listed, together with the standard deviations, s, from the experimental data, as well as the deviations of the predicted ternary values from the experimental ones, at the different temperatures considered. From the results it can be seen that both equations of state offer good agreement with the binary excess volume data when parameters for the mixing rules are calculated. The accuracy in representation of measured data varies when changing the mixing rule, while both equations of state perform equally when using the same mixing rule. The best choice, in this case, is the mixing rule R2, as it offers the lowest deviations using only two parameters for each binary mixture. As it could be expected, the poorest results, if compared with the experimental value of the magnitude, are obtained for the methanol+n-hexane binary mixture, because of the presence of the immiscibility region. The trend of the parameters with the temperature appears to be regular, as shown in Figs. 3–5, except in the case of the immiscible binary. As a result, excess molar volumes could be estimated for the binary mixtures at any intermediate interpolated temperature, ensuring a deviation of the same order than those provided in Table 4. Deviations yielded for the estimated ternary magnitude also show dependence with the mixing rule, and can be considered satisfactory, supporting the validity of the tested equations as predictive method for volumetric properties, having in mind the high non-ideality of the ternary mixture studied, where both associative and phase splitting phenomenon occurs.

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