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Viscosity and density data of the system water + *n*-pentyl acetate + methanol Calculations with a modified Redlich–Kwong–Soave equation of state

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Abstract

The viscosities and the densities of the ternary mixtures water + *n*-pentyl acetate + methanol and those of the constituent binaries have been measured at 303.15 K and atmospheric pressure in the homogeneous region. The respective viscosity deviations and excess molar volumes were fitted to a Redlich–Kister (RK) type equation.

A modified Redlich–Kwong–Soave equation of state due to Fuller was used with the Eyring kinematic viscosity model to correlate viscosities of binary data. The equation of state constants were calculated using the van der Waals one-fluid mixing rules with the cross-parameters, a_{ij}, obtained with the classical and a two-parameter Redlich–Kister combining rules. The new model correlates the viscosity of the binaries with an average absolute deviation <2%. Using the binary interaction parameters obtained from the regression of viscosity data the ternary viscosity and the binary and ternary density were also successfully predicted with an average absolute deviation of the same order of magnitude.
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1. Introduction

Thermodynamic and transport properties are essential in process design and operation. Density and viscosity of multicomponent mixtures are required in many chemical engineering calculations involving fluid flow, heat and mass transfer. However, one cannot hope to have direct measurements for the multitude of complex systems of practical interest which justifies the theoretical and practical importance of

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prediction methods. Ternary mixtures are by far the easiest multicomponent systems to treat experimentally, and clearly represent the most appropriate ground for prediction models.

While equations of state had been widely applied for calculating thermodynamic properties, viscosity estimation is essentially based into two major approaches: the corresponding-states principle and the Eyring's theory [1]. The corresponding-states principle has been applied to correlate viscosity data by several authors. Some notable models have been developed by Ely and Hanley [2], Teja and Rice [3], and Lee and Wei [4]. The method of Ely and Hanley is a one-reference-fluid corresponding states viscosity model which uses methane as the reference fluid. However, its applicability is limited to nonpolar mixtures. The two-reference-fluid model due to Teja and Rice [3] is valid to nonpolar mixtures although Papaloannou et al. [5] pointed out that is also applicable to aqueous binary mixtures. The model developed by Lee and Wei [4] is a three-reference-fluid model using oxygen, *n*-octane and water as reference components and its applicability includes multicomponent aqueous and nonaqueous mixtures.

Based in the Eyring's absolute rate theory some researchers [6,7] have predicted the excess activation free energy of flow using a group-contribution method (UNIFAC-VISCO). Cao et al. [8] have developed a "viscosity-thermodynamic" model (UNIMOD) to correlate both the viscosity and VLE data by the UNIQUAC model with the same interaction energy parameters.

Those previous models appear to have certain limitations for a variety of pure liquids and liquid mixtures, especially for aqueous solutions.

Using the relationship between fugacity coefficient and excess Gibbs free energy of mixture, the equations of state had been applied to calculate the excess thermodynamic and transport properties of mixtures. For viscosity estimations, Lee et al. [9] have presented a new viscosity model that estimates the excess activation free energy of flow, $G^{\neq E}$, in Eyring's theory with the aid of the Patel–Teja equation of state [10]. For nonaqueous systems an adjustable binary parameter, k_{ij}, was considered in the classical combining rule for the cross parameter, a_{ij}, to match the experimental viscosity data of binary systems, assuming that the excess molar free energy, G^{E}, is equal to $G^{\neq E}$. For aqueous systems a similar procedure was adopted using a two-parameter Redlich–Kister (RK) type combining rule for a_{ij}. The optimized values of k_{ij} were then used directly to predict density and ternary viscosity data. Recently, Lee and Lee [11] have used two-parameter van der Waals type equations of state with the Eyring kinematic viscosity model to study the influence of the selected mixing rule on the viscosity estimations of binary nonaqueous mixtures.

In the present work we have used a modified Redlich–Kwong–Soave equation of state (MRKS) due to Fuller [12]. This EOS was applied to the liquid density prediction of pure substances [12] and as far as we know it has not been used before in the calculation of PVT and transport properties of mixtures. The necessary data for the calculations with MRKS EOS are the critical properties, the parachor and the Pitzer's acentric factor of the pure substances which can be estimated in the lack of experimental information. This is one important characteristic when compared with other EOS (namely the Patel–Teja), which applications to polar substances require detailed experimental PVT data to implement a trial and error procedure.

2. Experimental

2.1. Materials

Tridistilled water was used. Methanol was supplied by Riedel de Haën with a purity >99.8 mass%, (HPLC grade). *n*-Pentyl acetate was supplied by Merck with a purity >99%. Table 1 lists the measured

Table 1
Viscosities, η, and densities, ρ, of the pure components at 303.15 K

Component	η (mPa s)		ρ (g cm^{-3})	
	Experimental	Literature	Experimental	Literature
Water	–	0.797 [13]	–	0.99570 [17]
Methanol	0.504	0.516 [14]	0.78191	0.78199 [14]
n-Pentyl acetate	0.819	0.615 [15]	0.86470	0.8630 [18]
	–	1.064 [16]	–	0.86644 [19]

viscosities and densities of the three components together with the values found in the literature. Mixtures were prepared by mass using a Mettler AT 200 balance with a precision of $\pm 10^{-5}$ g.

2.2. Measurements

Viscosities were obtained by an Haake Falling Ball viscosimeter (Hoppler design), calibrated with tridistilled water. An electronic stopwatch, with an uncertainty of ± 0.01 s, was used to measure the falling time of the ball. In all the measurements, the temperature was maintained and controlled at (303.15 ± 0.01 K) using an Ultraterm P Selecta bath.

Densities were measured in an Anton Paar DMA 60 digital vibrating tube densimeter with a DMA 602 measuring cell. Air and tridistilled water were used for the calibration of the densimeter. A Pt resistance thermometer (calibrated against a precision mercury thermometer, graduate in 0.01 °C, certified by NPL) was placed inside the vibrating tube densimeter to find the actual temperature of the measurements. The temperature was maintained at (303.15 ± 0.01 K).

2.3. Uncertainties

Densities were measured with a precision of 10^{-5} g cm^{-3}. Using the propagation law of errors, and taking into consideration the uncertainties in the measured time and in the density, the experimental uncertainty in the viscosity is ± 0.001 mPa s.

3. Results

The excess molar volumes, V^{E}, of a mixture were obtained from the measured density ρ by the usual equation

$$V^{\mathrm{E}} = \rho^{-1}\left(\sum_i x_i M_i\right) - \sum_i x_i M_i \rho_i^{-1}, \tag{1}$$

where x_i, M_i and ρ_i are the mole fraction, the molecular weight and density of the ith component, respectively.

The dynamic viscosity was determined using the equation

$$\eta = K(\rho_{\mathrm{b}} - \rho)t, \tag{2}$$

where t is the falling time of the ball measured with the stopwatch, K a calibration constant, and ρ_b represent the density of the ball.

The viscosity deviations, $\Delta\eta$, were obtained using the expression

$$\Delta\eta = \eta - \sum_i x_i \eta_i, \tag{3}$$

where η is the measured mixture viscosity and η_i represents the pure component viscosity. The viscosity measurements were made for different compositions than those for the density measurements, since they were not performed simultaneously. For that reason, the density value needed to obtain the viscosity from Eq. (2) was calculated with Eq. (1).

Table 2 lists the measured viscosities, η, and the corresponding $\Delta\eta$ values for the ternary system. Table 3 presents the measured densities, ρ, and the corresponding values of V^E for the same system. Results for the constituent binaries water + methanol and ester + methanol are also included.

Table 2
Experimental viscosity, η, and viscosity deviation, $\Delta\eta$, for the system water (1) + n-pentyl acetate (2) + methanol (3) at 303.15 K and atmospheric pressure

x_1	x_2	η (mPa s)	$\Delta\eta$ (mPa s)	x_1	x_2	η (mPa s)	$\Delta\eta$ (mPa s)
0.3155	0.0848	0.968	0.345	0.0121	0.9879	0.796	−0.023
0.3405	0.1729	1.013	0.355	0.0385	0.9615	0.801	−0.017
0.2629	0.2061	0.895	0.249	0.0645	0.9355	0.805	−0.013
0.1511	0.2036	0.764	0.152	0.0655	0.9345	0.805	−0.013
0.0625	0.7221	0.779	0.029	0.0854	0.9146	0.809	−0.008
0.0395	0.2819	0.650	0.046	0.1000	0	0.618	0.085
0.0613	0.0844	0.616	0.067	0.2080	0	0.755	0.190
0.1791	0.0750	0.751	0.171	0.3041	0	0.878	0.285
0.1799	0.3063	0.804	0.151	0.4036	0	1.030	0.408
0.1122	0.4503	0.767	0.088	0.5016	0	1.153	0.502
0.2369	0.0989	0.838	0.233	0.5599	0	1.263	0.595
0.4319	0.0810	1.139	0.483	0.6148	0	1.306	0.622
0.2089	0.3885	0.846	0.158	0.6476	0	1.335	0.641
0.1372	0.4043	0.791	0.119	0.7054	0	1.340	0.629
0.1174	0.3574	0.775	0.125	0.7982	0	1.308	0.570
0.1382	0.6299	0.784	0.041	0.9043	0	1.108	0.339
0.2629	0.2680	1.055	0.390	0	0.0524	0.537	0.016
0.5117	0.0338	1.159	0.494	0	0.1018	0.561	0.025
0.1307	0.6466	0.779	0.033	0	0.1038	0.533	0.025
0.0802	0.7954	0.779	0.001	0	0.1608	0.547	0.038
0.1260	0.5112	0.799	0.097	0	0.1934	0.608	0.043
0.0939	0.2851	0.722	0.101	0	0.3024	0.652	0.053
0.0796	0.1599	0.670	0.092	0	0.4255	0.695	0.057
0.2214	0.1915	0.877	0.248	0	0.5168	0.719	0.052
0.0439	0.5987	0.738	0.033	0	0.5951	0.733	0.042
–	–	–	–	0	0.6976	0.753	0.029
–	–	–	–	0	0.7910	0.775	0.022
–	–	–	–	0	0.8949	0.794	0.008

Table 3
Experimental densities, ρ and excess molar volume, V^E for the system water (1) + n-pentyl acetate (2) + methanol (3) at 303.15 K and atmospheric pressure

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
0.0504	0.6971	0.86208	−0.080	0.1127	0.0000	0.80241	−0.438
0.0549	0.6388	0.86000	−0.075	0.2034	0.0000	0.81876	−0.675
0.0576	0.7918	0.86543	−0.052	0.2997	0.0000	0.83713	−0.865
0.0578	0.0952	0.81413	−0.193	0.4147	0.0000	0.85989	−0.992
0.0585	0.7403	0.86389	−0.066	0.4895	0.0000	0.87570	−1.028
0.0642	0.4671	0.85254	−0.104	0.0000	0.1011	0.80714	−0.002
0.0643	0.4674	0.85253	−0.103	0.0000	0.1467	0.81543	−0.009
0.0719	0.3579	0.84632	−0.156	0.0000	0.2475	0.82921	−0.012
0.0905	0.2751	0.84164	−0.237	0.0000	0.3025	0.83501	−0.012
0.1007	0.1787	0.83288	−0.318	0.0000	0.3474	0.83911	−0.018
0.1028	0.6956	0.86465	−0.081	0.0000	0.3783	0.84155	−0.015
0.1031	0.5260	0.85786	−0.104	0.0000	0.4998	0.85000	−0.033
0.1493	0.4276	0.85675	−0.214	0.0000	0.5768	0.85401	−0.031
0.1506	0.1688	0.83814	−0.450	0.0000	0.5988	0.85511	−0.037
0.1601	0.3360	0.85222	−0.268	0.0000	0.7809	0.86234	−0.035
0.1638	0.4905	0.86031	−0.150	0.0000	0.8999	0.86578	−0.029
0.1765	0.2490	0.84853	−0.426	0.0000	0.9505	0.86711	−0.012
0.1787	0.5304	0.86286	−0.134	–	–	–	–
0.1813	0.1084	0.83356	−0.492	–	–	–	–
0.1911	0.4543	0.86043	−0.162	–	–	–	–
0.1928	0.0512	0.82654	−0.571	–	–	–	–
0.2016	0.1587	0.84314	−0.533	–	–	–	–
0.2073	0.4078	0.86000	−0.257	–	–	–	–
0.2123	0.3272	0.85554	−0.269	–	–	–	–
0.2166	0.2293	0.85054	−0.447	–	–	–	–
0.2326	0.3698	0.85954	−0.241	–	–	–	–
0.2597	0.3075	0.85864	−0.322	–	–	–	–
0.2636	0.1482	0.84883	−0.569	–	–	–	–
0.2689	0.1024	0.84521	−0.645	–	–	–	–
0.2843	0.0511	0.84143	−0.739	–	–	–	–
0.2999	0.1830	0.85600	−0.555	–	–	–	–
0.3019	0.2433	0.86057	−0.524	–	–	–	–
0.3483	0.1478	0.85973	−0.651	–	–	–	–
0.3726	0.1013	0.86001	−0.751	–	–	–	–
0.3930	0.0519	0.85958	−0.853	–	–	–	–
0.4650	0.0500	0.87213	−0.896	–	–	–	–
0.5062	0.0456	0.88043	−0.951	–	–	–	–

The $\Delta\eta$ and V^E binary data were correlated using a Redlich–Kister type equation for the binary systems:

$$X_{ij} = x_i x_j \sum_{k=0}^{q} A_k (x_i - x_j)^k, \tag{4}$$

where X represents $\Delta\eta$ and V^E.

The ternary data ($\Delta\eta$ and V^E) were also correlated by a Redlich–Kister type equation:

$$X_{123} = X_{12} + X_{23} + X_{13} + x_1x_2x_3[B_0 + B_1(x_1 - x_2) + B_2(x_2 - x_3)], \quad (5)$$

where X_{123} represents the viscosity deviations and the excess molar volumes for the ternary mixture and X_{ij} are the values of the Redlich–Kister polynomial for the same properties, obtained by fitting Eq. (4) to the binary data. For the water + *n*-pentyl acetate binary, only one parameter was considered in $\Delta\eta$ since only five experimental points were used. The approximation $V^E_{12} = 0$ was taken because the components are practically immiscible.

The standard deviation (S.D.), σ, of the fittings is defined as

$$\sigma = \left[\sum_{i=1}^{N} \frac{(X_{exp} - X_{calc})_i^2}{N - q}\right]^{1/2}, \quad (6)$$

where X is V^E or $\Delta\eta$ and N and q represent the numbers the experimental points and parameters, respectively. The optimized coefficients, A_k, for binary $\Delta\eta$ and V^E data, the parameters B_i of Eq. (5) and the S.D., σ, of the corresponding fittings are given in Table 4.

In Fig. 1 we have plotted the experimental $\Delta\eta$ values for the binaries water + methanol and *n*-pentyl acetate + methanol as a function of the compositions of water and *n*-pentyl acetate, respectively. The results obtained for water + methanol binary show a good agreement with those obtained in a previous work [14]. We have not found in the literature any binary viscosity data, at 303.15 K, for the system *n*-pentyl acetate + methanol. As we can see from Fig. 1, the viscosity deviations values of the ester + methanol binary are about 10% of those corresponding to the water + methanol system and the shape of the curves of both systems are highly assymmetrical.

The experimental V^E data are plotted in Fig. 2. As we can see for the system water + methanol there is an excellent agreement between our values and those of the literature. For the system *n*-pentyl acetate + methanol the experimental values are significantly lower than those of the water + methanol binary. We believe that this is the reason for the observed scattering of the data since the former system has values closer to V^E uncertainty (10^{-3} cm^3 mol^{-1}). Figs. 3 and 4 shows the perspective views and the isolines of $\Delta\eta$ and V^E for the ternary system. The viscosity deviation values, $\Delta\eta$, are all positive with a maximum on the binary water + methanol ($x_1 = 0.6893$, $\Delta\eta = 0.665$ mPa s). The values of the excess

Table 4
Coefficients of Eqs. (4) and (5) fitted to the viscosity deviations $\Delta\eta$ (mPa s), and to the excess molar volumes V^E (cm^3 mol^{-1}) for the binary and ternary systems

System	Property							
	$\Delta\eta$				V^E			
	A_0	A_1	A_2	σ (mPa s)	A_0	A_1	A_2	σ (cm^3 mol^{-1})
Water + methanol	2.094	2.044	0.601	0.014	−4.053	0.024	0.316	0.001
n-Pentyl acetate + methanol	0.208	−0.130	−0.039	0.002	−0.113	−0.148	−0.078	0.003
Water + *n*-pentyl acetate	−0.320	–	–	0.030				
Water + *n*-pentyl acetate + methanol[a]	2.487	7.662	3.174	0.031	3.903	5.328	6.233	0.028

[a] Here the coefficients are B_0, B_1, B_2 for viscosity deviations and to the excess molar volumes for the ternary system.

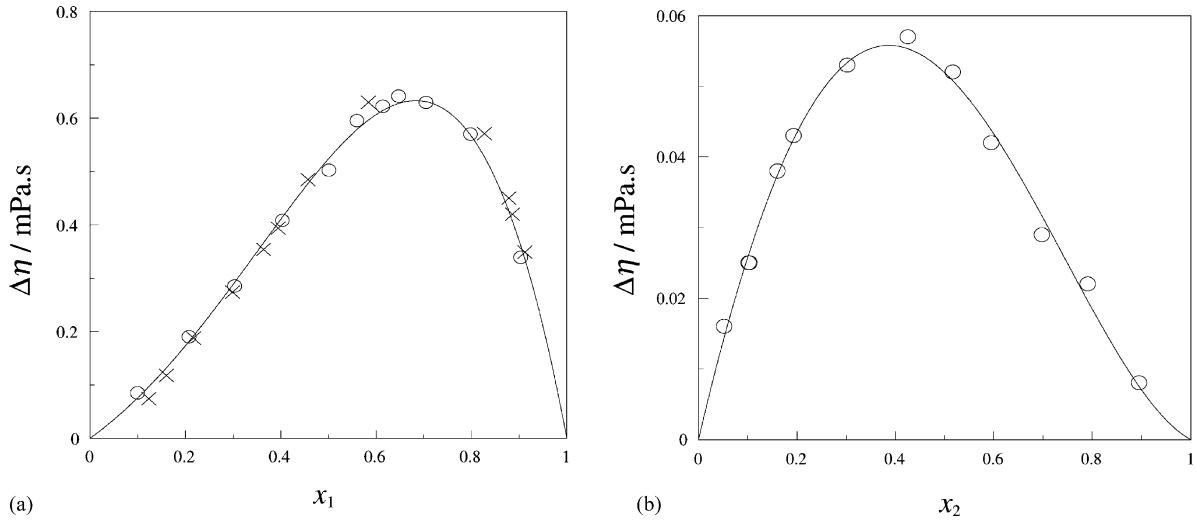

Fig. 1. Viscosity departures, $\Delta\eta$, of the binary systems at 303.15 K and atmospheric pressure as a function of the mole fraction: (a) water (1) + methanol (3); (b) *n*-pentyl acetate (2) + methanol (3). Experimental data: (○) this work; (×) [14]. The curves were calculated with the Redlich–Kister equation.

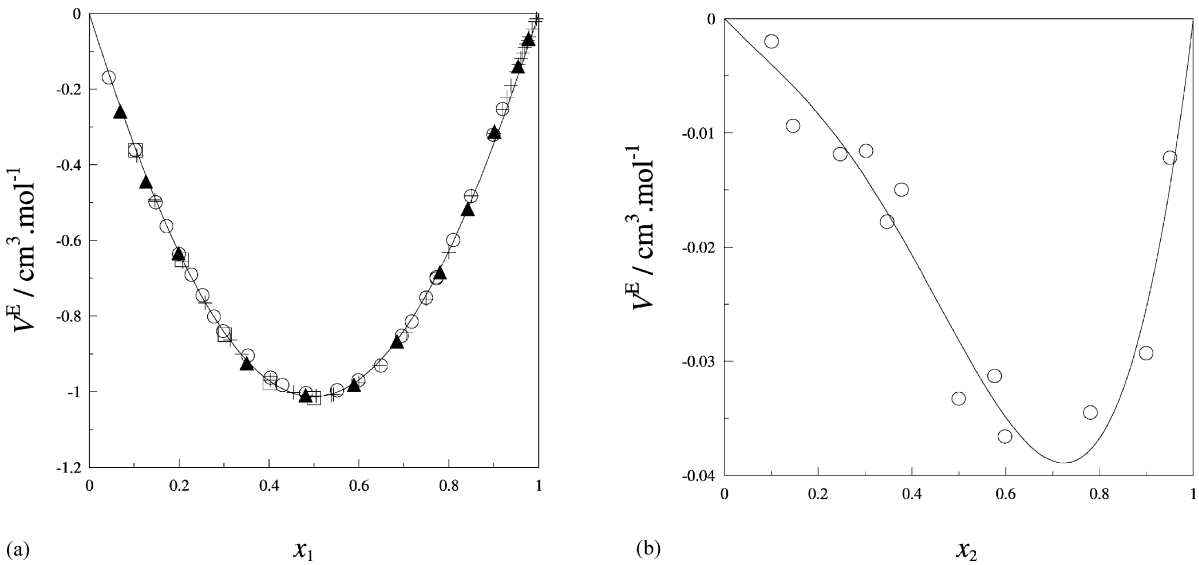

Fig. 2. Excess molar volume, V^E, of the binary systems at 303.15 K and atmospheric pressure as a function of the mole fraction: (a) water (1) + methanol (3); (b) *n*-pentyl acetate (2) + methanol (3). Experimental data: (□) this work; (○) Visak et al. [14]; (+) Benson and Kiyohara [20]; (▲) Dizechi and Marschall [17]. The curves were calculated with the Redlich–Kister equation.

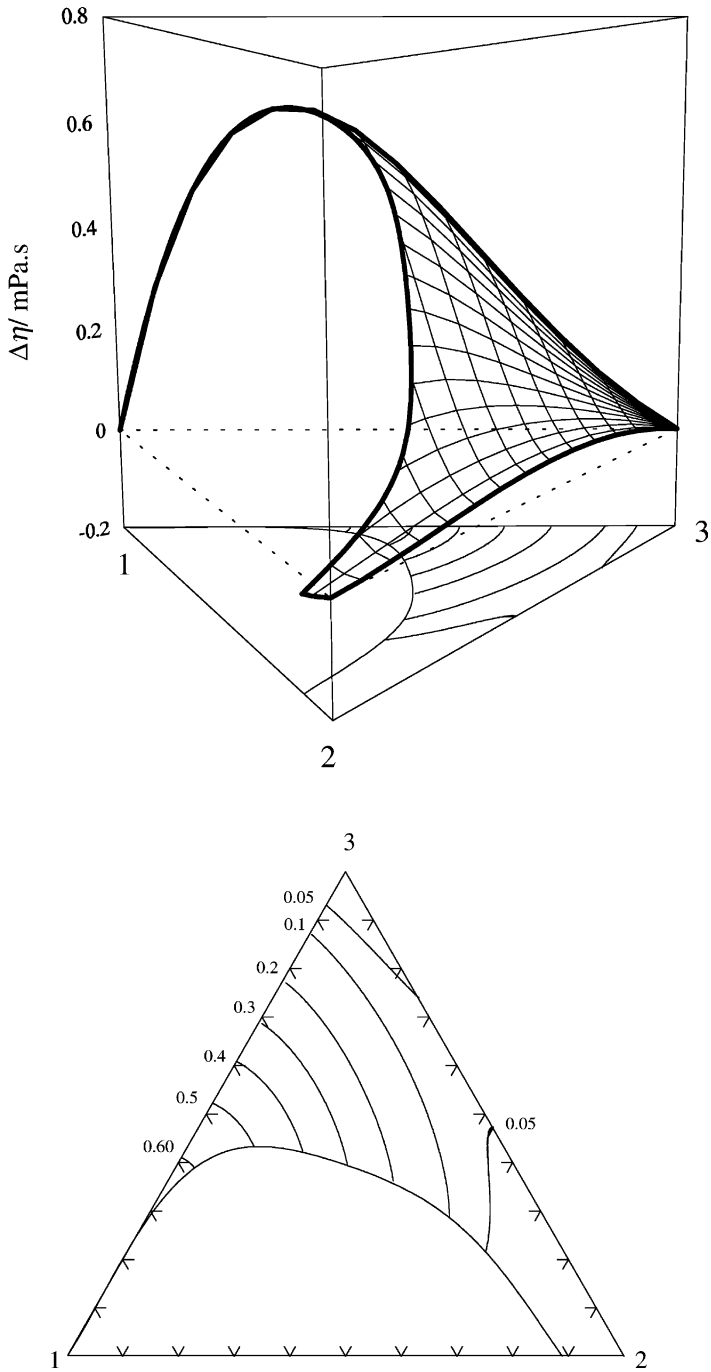

Fig. 3. Perspective view and isolines of $\Delta\eta$ (mPa s) for water (1) + *n*-pentyl acetate (2) + methanol (3) at 303.15 K and atmospheric pressure.

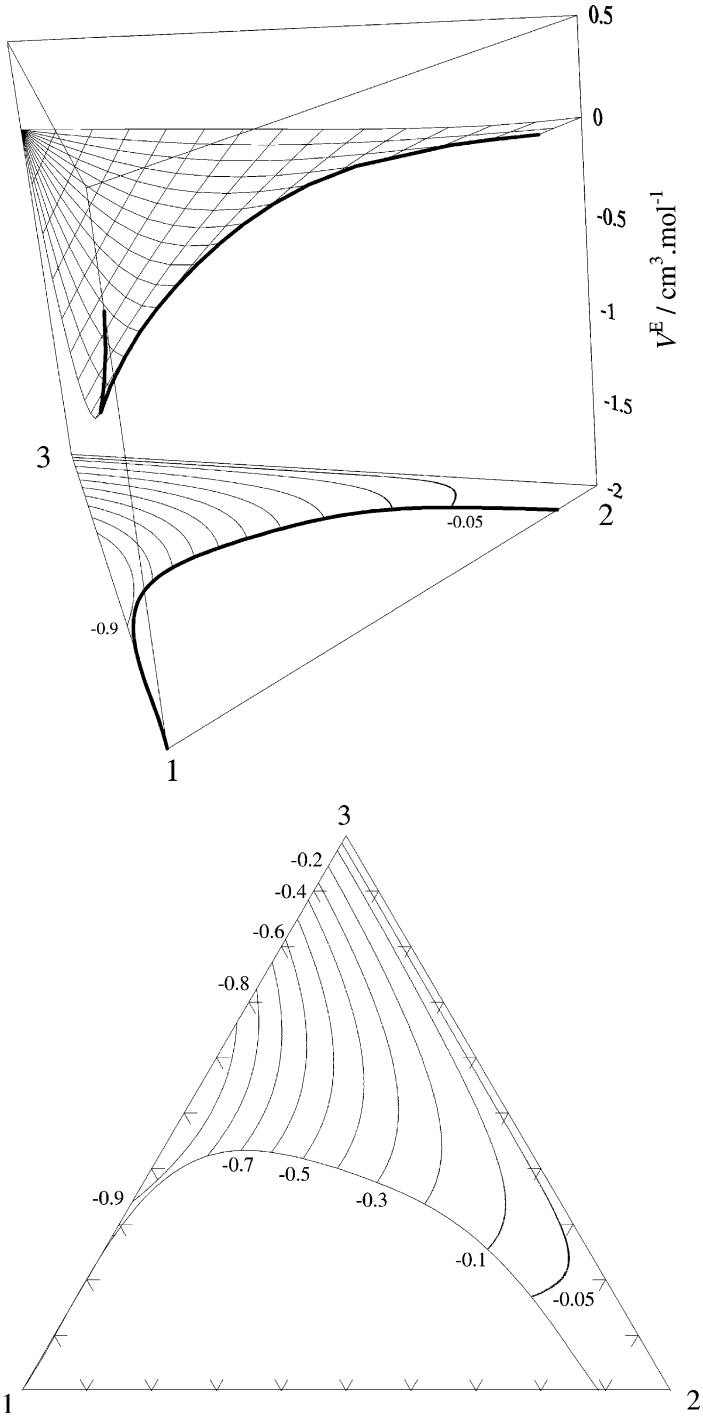

Fig. 4. Perspective view and isolines of V^E (cm^3 mol^{-1}) for water (1) + *n*-pentyl acetate (2) + methanol (3) at 303.15 K and atmospheric pressure.

molar volumes for the binaries and ternary systems are all negative. The minimum V^{E} value is located on the binary water + methanol ($x_1 = 0.498$, $V^{E} = -1.013\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$).

4. Calculations with a modified Redlich–Kwong–Soave equation of state (MRKS)

4.1. Theory

Based on the work of Lee et al. [9] we have incorporated a modified Redlich–Kwong–Soave equation of state due to Fuller [12] with the Eyring's theory, to predict viscosities and densities for the systems under study. The MRKS equation has the functional form,

$$P = \frac{RT}{V-b} - \frac{a}{V(V+cb)}, \tag{7}$$

which is similar to the Soave equation, having an additional parameter, c. The parameters a, b and c are temperature dependent and can be obtained in terms of a single parameter, β. The expressions for the parameters a, b and c are given in Appendix A.

The input data needed to obtain the equation parameters are the critical properties taken from literature [21–23] for water, *n*-pentyl acetate and methanol, respectively.

Accordingly to the Eyring viscosity model [1], the viscosity can be calculated by the expression

$$(\eta V)_{\mathrm{mix}} = (\eta V)_{\mathrm{id}} \exp\left(\frac{G^{\neq \mathrm{E}}}{RT}\right), \tag{8}$$

with

$$(\eta V)_{\mathrm{id}} = \exp\left[\sum_i x_i \ln(\eta_i^* V_i^*)\right]. \tag{9}$$

$(\eta V)_{\mathrm{mix}}$ and $(\eta V)_{\mathrm{id}}$ are the kinematic viscosity of the real mixture and of an ideal mixture at the same P and T. $G^{\neq \mathrm{E}}$ is the excess Gibbs energy of viscous flow required to move the fluid particles from a stable state to an activated state. It is given by the Eyring viscosity model:

$$G^{\neq \mathrm{E}} = RT\left[\ln(\eta V)_{\mathrm{mix}} - \sum_i x_i \ln(\eta_i^* V_i^*)\right], \tag{10}$$

where R is the gas constant, T the absolute temperature, V and V_i^* are the molar volumes of the mixture and pure component i, respectively. There is a certain similarity between $G^{\neq \mathrm{E}}$ and G^{E} which makes possible the assumption, $G^{\neq \mathrm{E}} = G^{\mathrm{E}}$. Therefore, $G^{\neq \mathrm{E}}$ can be calculated alternatively by the well-known expression for G^{E},

$$G^{\mathrm{E}} = RT\sum_i x_i(\ln\phi_i - \ln\phi_i^*), \tag{11}$$

where ϕ_i and ϕ_i^* are the fugacity coefficients of component i in the mixture and of the pure component, respectively. In order to calculate ϕ_i from the MRKS equation we need to specify the mixing rules. We have used the one-fluid van der Waals mixing rules (VDW-1) for the equation parameters. For a_{ij} we

have used the classical combining rule:

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}), \tag{12}$$

and a Redlich–Kister type combining rule [24],

$$a_{ij} = (a_i a_j)^{0.5}[1 - k_{ij} - k_{ji}(x_i - x_j)]. \tag{13}$$

The expressions for the fugacity coefficients (ϕ_i and ϕ_i^*) corresponding to the MRKS equation are given in Appendix A.

The assymmetric combining rule Eq. (13) seems to represent adequately the properties of strongly hydrogen-bonded systems, such as the aqueous mixtures with alcohols [9]. We have found that the calculated G^{E} values from the MRKS equation with optimized values of k_{ij} and k_{ji} parameters quantitatively match the experimental $G^{\neq\mathrm{E}}$ values. The parameters of Eqs. (12) and (13) were adjusted for each binary in order to fit the viscosity data, minimizing the average absolute deviation, AAD (%),

$$\mathrm{AAD}\ (\%) = \frac{1}{N}\sum_{k=1}^{N}\frac{|\eta_{\mathrm{calc}} - \eta_{\mathrm{exp}}|_k}{\eta_{\mathrm{exp},k}} \times 100, \tag{14}$$

where the supercripts ‘calc’ and ‘exp’ refer to calculated and experimental values of the viscosity.

4.2. Results and discussion

Table 5 presents the results obtained for the calculated viscosity and density with the MRKS equation of state. The interaction parameters k_{ij} (and k_{ji}) have been fitted using the experimental data of the binary systems. This case is indicated by the symbol (opt). Since viscosity data are not extensively available, the interaction parameters were also obtained using a single experimental viscosity point near the equimolecular mixture (for k_{ij}) or two experimental points at molar fractions of about 0.4 and 0.7 (for k_{ij} and k_{ji}). We have used in this case the symbol (est). For comparison purposes, we present the model with $k_{ij} = 0$.

For the water + methanol system the RK combining rule gives better viscosity results. This composition dependent rule describes adequately the asymmetrical behavior of this binary since it has two adjustable parameters, making it more flexible. For the ester containing binaries the choice of the combining rule is not so relevant.

The viscosities of the ternary system were predicted using the binary interaction parameters found for the binary systems. The lowest AAD (%) value of 4.2% was obtained with the classical combining rule. The prediction with k_{ij} estimated with one single point for each binary gives also satisfactory results. The composition dependent combining rule gives poor predictions. This is due to the more complex expression of the fugacity coefficients which involve complex derivatives. This feature originates the high differences between G^{E} and $G^{\neq\mathrm{E}}$ obtained for the ternary system using the dependent composition combining rule.

For the binary systems the predicted density with the MRKS EOS using the fitted parameters from binary viscosity is almost independent of the combining rule used. The best prediction of density for the ternary system correspond to the classical combining rule.

Table 5
Calculated viscosities and densities with the MRKS EOS for the binary and ternary systems using the combining rules defined by Eqs. (12) and (13)

System	Property	Combining rule Eq. (12)						Combining rule Eq. (13)					
		$k_{ij} = 0$	AAD (%)	Opt		Est		Opt			Est		
				k_{ij}	ADD (%)	k_{ij}	ADD (%)	k_{ij}	k_{ji}	ADD (%)	k_{ij}	k_{ji}	ADD (%)
Water + *n*-pentyl acetate	η	–	22.7	−0.4606	1.0	−0.4989	1.9	−0.5420	0.5794	0.5	−0.5550	0.9005	0.6
	ρ	–	1.3	–	1.0	–	1.0	–	–	1.0			1.0
Water + methanol	η	–	12.9	0.0403	3.5	0.0306	4.1	0.0036	0.0661	0.6	0.0070	0.0612	0.8
	ρ	–	2.0	–	2.2	–	2.2	–	–	2.3			2.2
n-Pentyl acetate + methanol	η	–	40.2	−0.1170	1.3	−0.1135	1.6	−0.1183	−0.1160	1.3	−0.0986	−0.1309	2.0
	ρ	–	2.7	–	1.9	–	2.0	–	–	1.9			2.0
Water + *n*-pentyl acetate + methanol	η	–	67.9	–	4.2	–	6.3	–	–	24.9			39.3
	ρ	–	4.1	–	2.8	–	2.7	–	–	3.4	–	–	3.6

AAD (%) represents the average absolute deviation of the referred properties.

5. Conclusions

The viscosities and densities of the system water + n-pentyl acetate + methanol have been determined experimentally at 303.15 K and atmospheric pressure.

The binary $\Delta\eta$ and V^E data as well as the ternary one were correlated using only three parameters in the Redlich–Kister polynomials.

The MRKS equation of state correlates well the viscosity of the binaries and the prediction for the ternary system water + n-pentyl acetate + methanol was made with good accuracy using only three adjustable binary interaction parameters, k_{ij}. The prediction is also acceptable when the binary viscosity data is scarce. We stress that the k_{ij} parameter for the practically immiscible water + n-pentyl acetate system was obtained from a very limited range of viscosity data. Both binary and ternary density data were successfully predicted using the fitted parameters obtained from the binary viscosity.

List of symbols

a_i	parameter a of pure component i
a_{ij}	cross interaction parameter a of MRKS EOS between molecules i and j
a, b, c	parameters in the MRKS EOS
AAD	average absolute deviation
$G^{\neq E}$	activation free energy of flow in Eq. (10)
G^E	excess Gibbs free energy in Eq. (11)
k_{ij}	binary interaction parameters
M	molecular weight
n_i	number of moles of component i
N	number of experimental points
P	pressure
q	number of parameters in Eq. (6)
R	universal gas constant
T	temperature
V, V^*	molar volume
x_i	liquid mole fraction of the ith component

Greek letters

η, η_i^*	viscosity
ϕ_i^*	fugacity coefficient of component i
ϕ_i	fugacity coefficient of component i in the mixture

Subscripts

id	ideal
i, j	components
mix	mixture

Superscripts

calc	calculated value
exp	experimental value

*	pure component
m	molar

Appendix A. Fugacity coefficient expressions derived from the MRKS EOS

The MRKS EOS as the form

$$P = \frac{RT}{V-b} - \frac{a}{V(V+cb)}.$$

The parameters a, b and c are obtained in terms of a single parameter, β, which value at the critical point, β_c, is $\beta_c = b/V_c$. The input data needed to obtain a, b and c are T_c, P_c, Z_c, ω and de parachor $\bar{P}$. $\bar{P}$ can be calculated from the knowledge of the structural formula of the compound by group contributions [25]. In this work $\bar{P}$ is determined from the relation suggested by Macleod [26]

$$\bar{P} = \frac{M\gamma^{1/4}}{\rho^{l} - \rho^{g}}, \tag{A.1}$$

where M, γ, ρ^{l}, ρ^{g} are the molecular weight, the surface tension, and density of the liquid and vapor phases at the given equilibrium temperature T. The parameters a, b and c are derived accordingly to the following steps. First β_c is calculated from

$$Z_c = \frac{(1-\beta_c)(2+c_c\beta_c) - (1+c_c\beta_c)}{(2+c_c\beta_c)(1-\beta_c)^2}, \tag{A.2}$$

where c_c is a function of β_c through the relashionship

$$c = \frac{1}{\beta}\left[\left(\frac{1}{\beta} - \frac{3}{4}\right)^{1/2} - \frac{3}{2}\right], \tag{A.3}$$

with $c = c_c$ and $\beta = \beta_c$. The EOS parameters a and b can be obtained from

$$a(T) = \Omega_a \alpha \frac{(RT_c)^2}{P_c}, \qquad b(T) = \Omega_b \frac{RT_c}{P_c}, \tag{A.4}$$

where Ω_a, Ω_b and α are functions of the temperature as follows:

$$\Omega_b = \beta \frac{(1-\beta)(2+c\beta) - (1+c\beta)}{(2+c\beta)(1-\beta)^2}, \tag{A.5}$$

$$\Omega_a = \Omega_b \frac{(1+c\beta)^2}{\beta(1-\beta)^2(2+c\beta)}, \tag{A.6}$$

$$\alpha = [1 + q(1 - T_r^{1/2})]^2, \tag{A.7}$$

where $q = m(\beta/0.26)^{1/4}$ with $m = 0.480 + 1.574\omega - 0.176\omega^2$ and c is given by Eq. (A.3); ω is the Pitzer acentric factor. The parameter β is obtained from the equation

$$\frac{\beta}{\beta_c} = 1 + \left(\frac{\beta_0}{\beta_c} - 1\right)\left\{\frac{2}{1+\exp[\theta(T_r - 1)]} - 1\right\}, \tag{A.8}$$

where $\beta_0/\beta_c = 7.7880 - 36.8316Z_c + 50.7061Z_c^2$ and $\theta = 10.9356 + 0.0285\bar{P}$.

The fugacity coefficient of a pure substance and of a component i in a mixture are derived for the MRKS EOS using well-known equations. One obtains

$$\ln \phi_i^* = -\ln\left(1 - \frac{b}{V}\right) - \left(\frac{a}{RTcb}\right)\left[\ln\left(1 + \frac{cb}{V}\right) + \frac{cb}{V + cb}\right] + \frac{b}{V - b} - \ln Z, \tag{A.9}$$

for the fugacity coefficient of the pure fluid, and

$$\ln \phi_i = -\ln\left(1 - \frac{b_\mathrm{m}}{V}\right) - \left(\frac{a_\mathrm{m}}{RTc_\mathrm{m}b_\mathrm{m}}\right)\left\{\left[\left(1 + \frac{\bar{a}_i}{a_\mathrm{m}}\right) - \frac{(\overline{cb})_i}{c_\mathrm{m}b_\mathrm{m}}\right]\ln\left(1 + \frac{c_\mathrm{m}b_\mathrm{m}}{V}\right) + \frac{(\overline{cb})_i}{V + c_\mathrm{m}b_\mathrm{m}}\right\} + \frac{\overline{b}_i}{V - b_\mathrm{m}} - \ln Z, \tag{A.10}$$

for the fugacity coefficient of ith component in the mixture.

For the mixture molar parameters a_m, b_m, and c_m we have used the one-fluid van der Waals (VDW-1) mixing rules. Using the (VDW-1) mixing rule for a_m and the classical combining rule we obtain

$$\bar{a}_i = \sum_j x_j a_{ij} - a_\mathrm{m}, \tag{A.11}$$

while using the RK combining rule, we have

$$\bar{a}_i = \sum_j x_j(a_{ij} + a_{ji}) - a_\mathrm{m} + \sum_{j\neq i} x_i x_j (a_i a_j)^{0.5}[(k_{ij} - k_{ji})(1 + x_j - x_i)] + \sum_{j\neq i}\sum_{l>j, l\neq i} x_j x_l (a_j a_l)^{0.5}[(k_{jl} - k_{lj})(x_l - x_j)]. \tag{A.12}$$

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