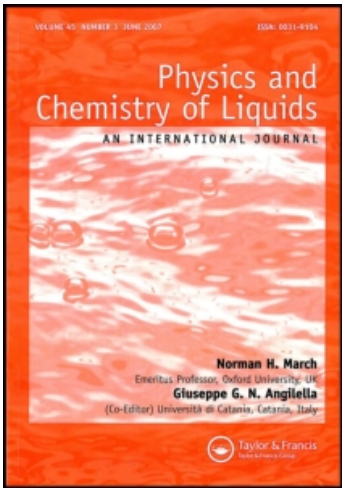

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Excess molar volumes of ternary mixtures containing benzene, cyclohexane, 1-pentanol and anisole at 298.15 K

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The expansive trend of the cosolvents anisole and 1-pentanol for benzene + cyclohexane binary azeotropic mixture by extractive distillation is analyzed by a volumetric study of the ternary mixtures benzene + 1-pentanol + anisole, cyclohexane + 1-pentanol + anisole and benzene + cyclohexane + anisole at 298.15 K and atmospheric pressure. The results obtained of application of the Peng–Robinson equation of state for estimating excess volumetric values shows the versatility of this model for thermodynamic prediction in complex systems.

Keywords: Excess molar volumes; Equation of state; Benzene; Cyclohexane; 1-Pentanol; Anisole

1. Introduction

This article continues our study of various homogeneous and heterogeneous azeotropic mixtures [1–3]. The aim of this research is the measurement of physical properties and study of vapor–liquid and liquid–liquid equilibrium of multicomponent mixtures, as well as the application of several predictive models to obtain theoretical predictions. The objective of the application of these techniques is identification of separation agents for binary azeotropic or binary mixtures with close boiling points in modified rectification processes. This article reports the measured densities as well as excess molar volumes of the ternary mixtures benzene + 1-pentanol + anisole, cyclohexane + 1-pentanol + anisole and benzene + cyclohexane + anisole at $T = 298.15$ K and atmospheric pressure. Experimental data of the corresponding binary mixtures have been published previously [1,3]. The experimental data were fitted by means of Cibulka [4] equation. The Peng–Robinson equation of state was applied with two different mixing rules to correlate binary excess volumes, and then to predict the excess magnitudes in ternary mixtures. Reliable representations of the experimental data were obtained.

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Table 1. Comparison of measured pure component properties data with literature values at $T = 298.15$ K.

	ρ (g cm^{-3})		n_D	
Component	Exptl.	Lit.	Exptl.	Lit.
Benzene	0.8736	0.87370[a]	1.49692	1.49792[a]
Cyclohexane	0.7737	0.77389[a]	1.42320	1.42354[a]
1-Pentanol	0.8110	0.8112[a]	1.40782	1.4079[a]
Anisole	0.9892	0.98932[b]	1.51545	1.51430[b]

[a] [5]. [b] [6].

2. Experimental

The chemicals used for the preparation of the mixtures were Lichrosolv Quality and supplied by Merck. Before use, they were degassed by ultrasound technique, dried over molecular sieves type 4 Å (Aldrich cat. no. 20860-4), and kept in inert argon (N-55, less than 3 ppmv in water) atmosphere. The purity of the chemicals was checked using gas chromatography, obtaining purities better than 99.9, 99.9, 99.0, and 99.7 mass % for benzene, cyclohexane, 1-pentanol, and anisole, respectively. The maximun water contents of the pure liquids (Metrohm 737 Coulometer) were 3.0×10^{-2}, 4.9×10^{-3}, 2.3×10^{-1}, and 6.5×10^{-2} mass % for benzene, cyclohexane, 1-pentanol, and anisole, respectively. The purity of pure compounds was also checked measuring their density and refractive index, and they agree with those founded in the open literature, as shown in the table 1. The mixtures were prepared by weight using a Mettler AE-240 balance, with an accuracy of $\pm 10^{-4}$. The density of the mixtures was measured by means of an Anton Paar DSA-48 densimeter, with an accuracy of $\pm 10^{-4}$ g cm^{-3}. The mole fractions were determined with an accuracy of $\pm 5 \times 10^{-5}$.

3. Results and discussion

3.1. *Data correlation*

The values corresponding to densities are enclosed in table 2. The excess molar volumes were calculated using the following expressions:

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

where, ρ, stands for the density of the mixture, and M_i and ρ_i are the molecular weight and density of the pure component i. The accuracy obtained in the calculations of excess molar volumes was $\pm 8 \times 10^{-3}$ cm^3 mol^{-1}. The excess molar volumes are also presented in table 2. These magnitudes were correlated using the Cibulka equation:

$$\delta Q_{123} = \delta Q_{12} + \delta Q_{13} + \delta Q_{23} + x_1 \cdot x_2 \cdot x_3 \cdot (C_0 + C_1 \cdot x_1 + C_2 \cdot x_2), \tag{2}$$

where δQ_{12}, δQ_{13}, and δQ_{23} represent the binary contribution fitted with the Redlich–Kister [7] expression for every binary mixture. The parameters of binary

Table 2. Densities ρ, and excess molar volumes V^E for the ternary mixtures at $T = 298.15$ K.

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})
			Benzene + 1-pentanol + anisole				
0.0597	0.8904	0.8226	0.071	0.3079	0.0868	0.9415	0.059
0.0602	0.0507	0.9740	0.040	0.3590	0.5928	0.8380	0.238
0.0703	0.7377	0.8487	0.097	0.3877	0.1969	0.9109	0.137
0.1070	0.0898	0.9622	0.049	0.3958	0.4995	0.8511	0.235
0.1082	0.5987	0.8691	0.128	0.3960	0.0975	0.9295	0.076
0.1095	0.7945	0.8334	0.113	0.3978	0.3772	0.8745	0.213
0.1106	0.2937	0.9242	0.129	0.4081	0.2835	0.8915	0.180
0.1114	0.6652	0.8567	0.117	0.4540	0.4887	0.8453	0.270
0.1122	0.3874	0.9070	0.132	0.4805	0.2860	0.8820	0.191
0.1142	0.1932	0.9423	0.098	0.4926	0.1917	0.8992	0.157
0.1148	0.5025	0.8858	0.130	0.5010	0.3796	0.8606	0.249
0.1666	0.7905	0.8267	0.135	0.5153	0.0972	0.9156	0.085
0.1883	0.0893	0.9538	0.062	0.5526	0.3921	0.8511	0.279
0.1955	0.4944	0.8776	0.153	0.5847	0.2814	0.8693	0.226
0.1956	0.7070	0.8382	0.163	0.5885	0.1905	0.8874	0.171
0.1988	0.5941	0.8587	0.162	0.5989	0.0943	0.9060	0.090
0.2043	0.2014	0.9310	0.114	0.6510	0.2965	0.8571	0.272
0.2064	0.3765	0.8981	0.153	0.6892	0.1844	0.8754	0.195
0.2098	0.3103	0.9100	0.146	0.6929	0.0922	0.8945	0.104
0.2381	0.6501	0.8433	0.173	0.7490	0.1393	0.8769	0.174
0.2927	0.3917	0.8849	0.177	0.7532	0.1969	0.8640	0.226
0.2966	0.4759	0.8685	0.188	0.7932	0.0832	0.8832	0.112
0.3004	0.1992	0.9206	0.127	0.8453	0.1008	0.8721	0.154
0.3040	0.2884	0.9032	0.152	0.8948	0.0516	0.8764	0.080
0.3066	0.5914	0.8453	0.208				
			Cyclohexane + 1-pentanol + anisole				
0.0429	0.9013	0.8188	0.078	0.3046	0.3918	0.8498	0.534
0.0445	0.0487	0.9700	0.116	0.3073	0.0939	0.9021	0.532
0.0849	0.7102	0.8431	0.183	0.3228	0.2031	0.8791	0.570
0.0939	0.8026	0.8249	0.149	0.3515	0.2055	0.8722	0.611
0.0942	0.1958	0.9322	0.236	0.4017	0.2095	0.8604	0.653
0.0949	0.1224	0.9453	0.209	0.4045	0.4972	0.8101	0.460
0.0957	0.4970	0.8783	0.243	0.4051	0.0957	0.8799	0.645
0.0970	0.4082	0.8937	0.259	0.4105	0.3348	0.8366	0.606
0.0975	0.3019	0.9125	0.256	0.4170	0.4961	0.8076	0.458
0.0993	0.5861	0.8617	0.238	0.4669	0.1085	0.8640	0.694
0.1682	0.6362	0.8374	0.303	0.4932	0.1969	0.8426	0.704
0.2103	0.3967	0.8701	0.417	0.5028	0.4001	0.8056	0.543
0.2112	0.6894	0.8187	0.294	0.5085	0.2990	0.8216	0.648
0.2123	0.3028	0.8862	0.438	0.5523	0.0582	0.8545	0.708
0.2143	0.0937	0.9231	0.406	0.5872	0.3124	0.8028	0.582
0.2143	0.2057	0.9031	0.423	0.6018	0.2037	0.8182	0.688
0.2169	0.4688	0.8559	0.412	0.6154	0.1005	0.8334	0.717
0.2301	0.5474	0.8392	0.394	0.6904	0.2065	0.7994	0.587
0.2805	0.6156	0.8164	0.366	0.7011	0.1018	0.8152	0.661
0.2981	0.5048	0.8316	0.469	0.7982	0.0972	0.7962	0.516
0.3036	0.3093	0.8646	0.542	0.8858	0.0576	0.7857	0.332
			Benzene + cyclohexane + anisole				
0.0428	0.0368	0.9766	0.063	0.2442	0.2827	0.8975	0.461
0.0495	0.1418	0.9517	0.235	0.2454	0.0996	0.9411	0.159
0.0691	0.8772	0.7887	0.343	0.2603	0.1936	0.9169	0.319
0.0743	0.4388	0.8815	0.607	0.3160	0.0954	0.9344	0.150
0.0812	0.0807	0.9626	0.138	0.3422	0.3693	0.8653	0.557

(*Continued*)

Table 2. Continued.

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})
0.0818	0.8225	0.7982	0.448	0.3521	0.2686	0.8881	0.443
0.0833	0.3445	0.9016	0.530	0.3531	0.4609	0.8424	0.624
0.0845	0.6246	0.8394	0.665	0.3553	0.5524	0.8209	0.653
0.0927	0.5406	0.8566	0.679	0.3681	0.1937	0.9045	0.315
0.1122	0.8339	0.7919	0.418	0.4489	0.3659	0.8524	0.573
0.1187	0.7841	0.8013	0.512	0.4515	0.4549	0.8307	0.642
0.1202	0.6820	0.8227	0.623	0.4523	0.1775	0.8983	0.305
0.1207	0.0920	0.9560	0.150	0.4573	0.2729	0.8740	0.462
0.1314	0.2944	0.9077	0.467	0.4589	0.0878	0.9200	0.139
0.1352	0.5506	0.8494	0.660	0.5476	0.3609	0.8406	0.566
0.1368	0.4658	0.8681	0.628	0.5489	0.1767	0.8864	0.326
0.1378	0.1284	0.9457	0.210	0.5503	0.0839	0.9101	0.134
0.1390	0.3761	0.8881	0.562	0.5535	0.2710	0.8621	0.466
0.1395	0.1013	0.9519	0.163	0.6480	0.2603	0.8521	0.470
0.1411	0.0480	0.9643	0.070	0.6494	0.1762	0.8735	0.342
0.1424	0.1878	0.9313	0.306	0.6578	0.0822	0.8970	0.158
0.1903	0.6186	0.8275	0.655	0.7424	0.1726	0.8620	0.341
0.2437	0.6611	0.8113	0.623	0.7486	0.0829	0.8851	0.162
0.2438	0.4508	0.8585	0.623	0.8341	0.0817	0.8739	0.170
0.2441	0.3687	0.8774	0.559				

Table 3. Parameters C_i of equation (2) and root mean square deviations σ.

	V^E (cm^3 mol^{-1})			
Mixture	C_0	C_1	C_2	σ
Benzene + 1-pentanol + anisole	2.143978	−2.062566	−4.128914	7×10^{-3}
Cyclohexane + 1-pentanol + anisole	3.617352×10^{-2}	5.601711	3.567611×10^{-1}	7×10^{-3}
Benzene + cyclohexane + anisole	-9.058360×10^{-1}	-2.887664×10^{-1}	7.765145×10^{-1}	7×10^{-3}

contributions were gathered in a previous works [1,3]. B_i, $i = 0$, 1, 2, are the ternary fitting parameters, that have been calculated applying the non-linear algorithm due to Marquardt [8], and they are displayed in table 3, as well as the root mean square deviations calculated according to the expression:

$$\sigma = \left(\sum_{i}^{n_{DAT}} \frac{(z_{exp} - z_{cal})^2}{n_{DAT}} \right)^{1/2}, \tag{3}$$

where z_{exp} is the experimental value, z_{cal} is the calculated value and n_{DAT} is the number of experimental data points. Figures 1(a), (b) and (c), show respectively, the computed isolines corresponding to ternary excess molar volumes. The rupture of alcohol hydrogen bonding and dipole–dipole interactions lead to a positive excess molar volumes in the whole composition range. Only a negative trend is observed close to binary mixture benzene + anisole due to the high molecular packing.

3.2. *Data prediction*

In the last few years, the interest related to theoretical and semiempirical work based on equations of state for prediction of excess molar volumes, partial excess molar

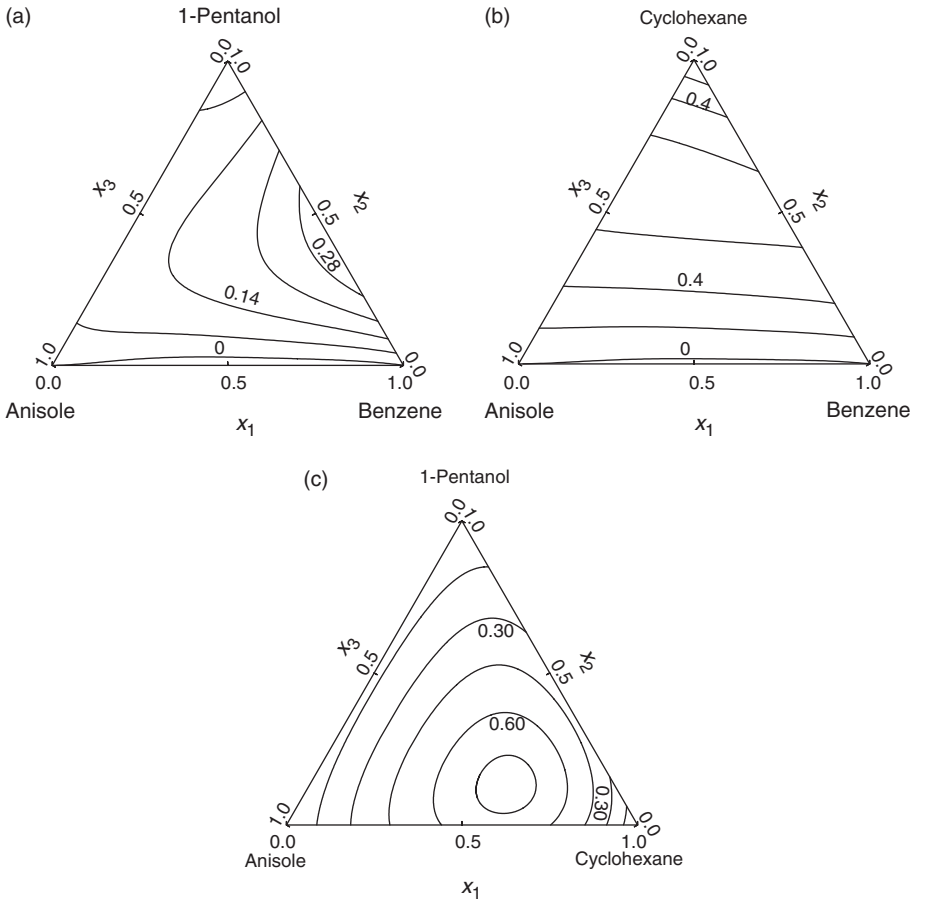

Figure 1. Curves of constant excess molar volumes for (a) benzene + 1-pentanol + anisole, (b) benzene + cyclohexane + anisole (c) cyclohexane + 1-pentanol + anisole at 298.15 K.

and partial molar volumes, saturated molar volumes, vapor–liquid equilibria or excess molar enthalpies has increased. In this case, the Peng–Robinson equation (9) was tested. These two widely used two-parameter cubic equations of state, of the van der Waals type, were applied in combination with simple mixing rules with one or two parameters in the a and b factors. Three different combining rules were incorporated into this equation, showing different correlation dependence to a and b. These mixing rules can be expressed as follows:

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j (1 - k_{ij} - l_{ij}(x_i - x_j))(a_i a_j)^{1/2} \tag{4}$$

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j (1 - m_{ij})\left(\frac{b_i + b_j}{2}\right), \tag{5}$$

Table 4. Computed binary interaction parameters using different mixing rules on the Peng–Robinson equation of state and ternary prediction results, expressed through the root mean square deviations σ.

Mixture	R1	R2	R3
Benzene + cyclohexane	$k_{ij}=5.93\times10^{-2}$ $\sigma=7\times10^{-3}$	$k_{ij}=5.21\times10^{-2}$ $m_{ij}=-1.33\times10^{-3}$ $\sigma=7\times10^{-3}$	$k_{ij}=-7.84\times10^{-2}$ $l_{ij}=-3.42\times10^{-3}$ $m_{ij}=-2.39\times10^{-2}$ $\sigma=7\times10^{-3}$
Benzene + 1-pentanol	$k_{ij}=5.40\times10^{-2}$ $\sigma=6\times10^{-3}$	$k_{ij}=5.44\times10^{-2}$ $m_{ij}=5.99\times10^{-5}$ $\sigma=7\times10^{-3}$	$k_{ij}=-1.90\times10^{-1}$ $l_{ij}=8.34\times10^{-2}$ $m_{ij}=-3.18\times10^{-2}$ $\sigma=6\times10^{-3}$
Benzene + anisole	$k_{ij}=1.07\times10^{-2}$ $\sigma=7\times10^{-3}$	$k_{ij}=2.07\times10^{-3}$ $m_{ij}=-1.20\times10^{-3}$ $\sigma=3\times10^{-3}$	$k_{ij}=1.20\times10^{-2}$ $l_{ij}=-3.28\times10^{-3}$ $m_{ij}=1.56\times10^{-4}$ $\sigma=3\times10^{-3}$
Cyclohexane + 1-pentanol	$k_{ij}=8.16\times10^{-2}$ $\sigma=2\times10^{-2}$	$k_{ij}=6.93\times10^{-2}$ $m_{ij}=-1.99\times10^{-3}$ $\sigma=1\times10^{-2}$	$k_{ij}=-5.20\times10^{-2}$ $l_{ij}=4.37\times10^{-2}$ $m_{ij}=-1.92\times10^{-2}$ $\sigma=7\times10^{-3}$
Cyclohexane + anisole	$k_{ij}=1.09\times10^{-1}$ $\sigma=3\times10^{-2}$	$k_{ij}=8.47\times10^{-2}$ $m_{ij}=-3.91\times10^{-3}$ $\sigma=9\times10^{-3}$	$k_{ij}=3.89\times10^{-2}$ $l_{ij}=1.70\times10^{-2}$ $m_{ij}=-1.07\times10^{-2}$ $\sigma=5\times10^{-3}$
1-Pentanol + anisole	$k_{ij}=1.59\times10^{-2}$ $\sigma=9\times10^{-3}$	$k_{ij}=-9.27\times10^{-3}$ $m_{ij}=-2.97\times10^{-3}$ $\sigma=9\times10^{-3}$	$k_{ij}=2.26\times10^{-3}$ $l_{ij}=-1.37\times10^{-3}$ $m_{ij}=-2.14\times10^{-3}$ $\sigma=9\times10^{-3}$
Benzene + cyclohexane + anisole	$\sigma=2\times10^{-2}$	$\sigma=1\times10^{-2}$	$\sigma=5\times10^{-2}$
Benzene + 1-pentanol + anisole	$\sigma=2\times10^{-2}$	$\sigma=2\times10^{-2}$	$\sigma=2\times10^{-2}$
Cyclohexane + 1-pentanol + anisole	$\sigma=9\times10^{-2}$	$\sigma=9\times10^{-2}$	$\sigma=5\times10^{-2}$

where k_{ij}, l_{ij} and m_{ij} are the fitting binary parameters to be calculated for each binary mixture, being $l_{ij}=m_{ij}=0$ for the first mixing rule (R1), $l_{ij}=0$ for the second one (R2), and k_{ij}, l_{ij} and $m_{ij}\neq0$ for the last one (R3). In every case $k_{ii}=l_{ii}=m_{ii}=0$, and $k_{ij}=k_{ji}$, $l_{ij}=-l_{ji}$, and $m_{ij}=m_{ji}$. A Marquardt non-linear algorithm was used to calculate the parameters. After obtaining the values for the binary parameters, the excess molar volumes of a multicomponent mixture could be estimated. In table 4 the binary coefficients of the Peng–Robinson equation are listed, together with the root mean square deviations σ from the experimental data, as well as the deviations of the predicted ternary values from the experimental ones. It can be observed that a reliable accuracy is achieved. The equations of state arise to be a powerful instrument when predicting multicomponent excess molar volumes, requiring only binary parameters, and showing a simple calculation procedure.

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