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TEMPERATURE DEPENDENCE OF THE REFRACTIVE INDEX FOR THE MIXTURES {$CH_3(CH_2)_xOH$, x=1, 2}+ {$(CH_3)_2CH(CH_2)_yOH$, y=0, 1, 2} AND ESTIMATION BY MEANS OF CUBIC EQUATIONS OF STATE

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Abstract

The applicability of cubic equations of state for refractive index estimation for binary alcohol mixtures {$CH_3(CH_2)_xOH$, x=1, 2}+{$(CH_3)_2CH(CH_2)_yOH$, y=0, 1, 2} at different temperatures was evaluated by using a derivation of the Heller equation. A qualitatively accurate response was obtained from the cubic equations and mixing rules applied, and the binary parameter obtained can be used for multicomponent refractive index prediction, or even for other thermodynamic properties.

Keywords: alcohol, binary mixtures, equation of state, estimation, refractive index

Introduction

In the past few years we have conducted systematic studies on the thermodynamic properties of binary and multicomponent mixtures connected with industrial separation processes (azeotropic distillation, liquid–liquid extraction, etc.), involving azeotropic and close boiling mixtures [1, 2]. With this aim, our research team is carrying out a project focussed on alkanol mixtures to study the influence of the position of the hydroxy group in the molecule and the thermal factor on the thermophysical mixing properties. To this end, the refractive indices on mixing for the binary mixtures (ethanol or 1-propanol)+(2-propanol, 2-methyl-1-propanol or 3-methyl-1-butanol) were measured at several temperatures. In what is referred to as the estimation field, cubic equations of state have been adapted, from a derivation of the Heller equation [3], to obtain an expression of refractive indices of mixtures. By means of such a derivation, the Peng-Robinson [4] (PR) and Soave-Redlich-Kwong [5] (SRK) cubic equations of state have been applied to compute binary interaction parameters from experimental data.

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Experimental and data correlation

All the chemicals had been recently obtained from Merck (LiChrosolv quality), and were kept in an argon atmosphere (maximum of 2 ppmv in water) as soon as the bottles were opened. A PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K was used to thermostat the samples. Refractive indices were measured by using an automatic refractometer Abbemat-HP Dr. Kernchen with a precision of $\pm 10^{-5}$. The accuracy in the calculated derived quantities was estimated as better than $5 \cdot 10^{-5}$. Information relating to the purification of the chemicals, the laboratory procedure and the technical characteristics of the device is available in the literature [6]. The experimental results on the refractive index, n_D, and the changes in the refractive index on mixing at the measured temperatures for all the binary mixtures are reported in Table 1. The changes in refractive index on mixing were evaluated for each composition point, using the following equation:

$$\delta n_D = n_D - \sum_{i=1}^{2} x_i n_{D,i} \tag{1}$$

where n_D is the refractive index, and the corresponding quantities with subscript i refer to pure chemicals. Derived values were correlated by means of a temperature-dependent Redlich-Kister expression [7] for every binary mixture.

$$\delta Q_{ij} = x_i x_j \sum_{p=0}^{4} \left(\sum_{q=0}^{4} A_{pq} T^q \right) (x_i - x_j)^p \tag{2}$$

In this equation, δQ_{ij} is the derived property, x is the mole fraction, A_{pq} are the temperature-dependent fitting parameters for these binary mixtures (Table 2) and T is the temperature. The unweighted least-squares method was used to fit the polynomials to the experimental data. The root mean square deviations were computed by using Eq. (3), where z is the value of the property and n_{DAT} is the number of experimental data:

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

The fitted curves and the derived values are shown in Fig. 1a to 1e for all binaries and temperatures. In these Figures, similar trends can be observed for mixtures involving chemicals with similar structures. Positive values occur for all cases and temperatures studied. The lowest deviations were computed for 1-propanol+2-propanol and 1-propanol+2-methyl-1-propanol, and the highest for ethanol+3-methyl-1-butanol at the measurement temperatures.

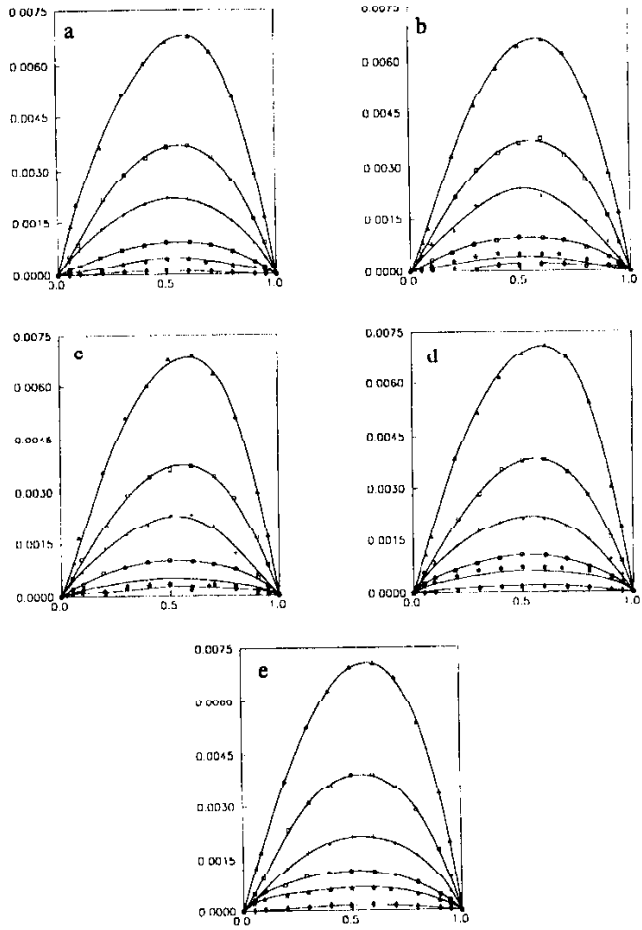

Fig. 1 Changes in refractive index on mixing (δn_D) *vs.* mole fraction of the first component (x_1) in ○ – ethanol+2-propanol; □– ethanol+2-methyl-1-propanol; △ – ethanol+3-methyl-1-butanol; ◇ – 1-propanol+2-propanol; ☆ – 1-propanol+2-methyl-1-propanol and + – 1-propanol+3-methyl-1-butanol at a – 288.15 K; b – 293.15 K; c – 298.15 K; d – 303.15 K and e – 308.15 K

In every case, the maximum deviation was computed for almost equimolar conditions. Although all these compounds are simple aliphatic alcohols and hydrogen-bonds are formed between the molecules, steric hindrance leads to different behaviour in what is referred to as the packing capability in some cases. Lengthening of the aliphatic chain produces a general low packing tendency and then higher derived values. There is a slight dependence on temperature, although increasing values are obtained when the temperature is raised for every mixture.

Table1 Refractive index and changes in refractive index on mixing at different temperatures for the binary mixtures

x	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D
					Ethanol+2-propanol					
0.0000	1.37927	0.00000	1.37694	0.00000	1.37474	0.00000	1.37253	0.00000	1.37026	0.00000
0.0537	1.37856	0.00014	1.37622	0.00012	1.37412	0.00022	1.37195	0.00026	1.36974	0.00031
0.1007	1.37794	0.00027	1.37571	0.00035	1.37351	0.00035	1.37139	0.00043	1.36925	0.00055
0.1930	1.37672	0.00052	1.37448	0.00056	1.37238	0.00057	1.37014	0.00063	1.36797	0.00071
0.2927	1.37534	0.00072	1.37315	0.00079	1.37095	0.00081	1.36879	0.00083	1.36668	0.00097
0.3950	1.37384	0.00085	1.37165	0.00089	1.36949	0.00096	1.36734	0.00098	1.36520	0.00108
0.4964	1.37232	0.00094	1.37015	0.00098	1.36795	0.00101	1.36584	0.00107	1.36370	0.00115
0.6035	1.37062	0.00094	1.36846	0.00096	1.36624	0.00098	1.36414	0.00104	1.36200	0.00112
0.6987	1.36903	0.00086	1.36690	0.00089	1.36465	0.00089	1.36255	0.00094	1.36041	0.00101
0.8008	1.36723	0.00068	1.36510	0.00069	1.36291	0.00075	1.36072	0.00071	1.35859	0.00077
0.9031	1.36530	0.00038	1.36324	0.00043	1.36105	0.00050	1.35884	0.00043	1.35666	0.00043
0.9466	1.36446	0.00023	1.36239	0.00026	1.36015	0.00028	1.35801	0.00028	1.35584	0.00029
1.0000	1.36338	0.00000	1.36129	0.00000	1.35903	0.00000	1.35690	0.00000	1.35472	0.00000
					Ethanol+2-methyl-1-propanol					
0.0000	1.39784	0.00000	1.39573	0.00000	1.39360	0.00000	1.39146	0.00000	1.38931	0.00000
0.0519	1.39660	0.00055	1.39455	0.00061	1.39234	0.00053	1.39024	0.00057	1.38800	0.00049
0.0930	1.39552	0.00088	1.39335	0.00082	1.39143	0.00105	1.38911	0.00086	1.38701	0.00092
0.2090	1.39279	0.00215	1.39064	0.00211	1.38837	0.00200	1.38637	0.00213	1.38441	0.00233
0.3071	1.39014	0.00288	1.38807	0.00292	1.38588	0.00290	1.38368	0.00283	1.38178	0.00309
0.4071	1.38717	0.00336	1.38509	0.00338	1.38293	0.00340	1.38091	0.00352	1.37880	0.00357

Table 1 Continued

x_1	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D
0.5007	1.38425	0.00366	1.38213	0.00364	1.37989	0.00360	1.37791	0.00375	1.37590	0.00391
0.5983	1.38091	0.00369	1.37889	0.00377	1.37662	0.00370	1.37455	0.00377	1.37253	0.00392
0.7038	1.37696	0.00337	1.37480	0.00331	1.37268	0.00341	1.37057	0.00343	1.36852	0.00355
0.7956	1.37315	0.00273	1.37098	0.00265	1.36890	0.00280	1.36676	0.00280	1.36465	0.00286
0.8985	1.36847	0.00159	1.36638	0.00159	1.36418	0.00164	1.36197	0.00156	1.35999	0.00176
0.9482	1.36609	0.00092	1.36390	0.00083	1.36169	0.00087	1.35958	0.00089	1.35748	0.00097
1.0000	1.36338	0.00000	1.36129	0.00000	1.35903	0.00000	1.35690	0.00000	1.35472	0.00000
					Ethanol + 3-methyl-1-butanol					
0.0000	1.40919	0.00000	1.40725	0.00000	1.40528	0.00000	1.40326	0.00000	1.40110	0.00000
0.0592	1.40788	0.00140	1.40536	0.00083	1.40350	0.00096	1.40160	0.00108	1.39961	0.00126
0.0839	1.40735	0.00200	1.40451	0.00122	1.40306	0.00166	1.40095	0.00158	1.39892	0.00171
0.1951	1.40390	0.00365	1.40158	0.00330	1.39980	0.00354	1.39803	0.00381	1.39580	0.00375
0.2939	1.40063	0.00513	1.39820	0.00469	1.39657	0.00511	1.39455	0.00515	1.39250	0.00526
0.3991	1.39695	0.00604	1.39470	0.00579	1.39282	0.00600	1.39090	0.00614	1.38890	0.00631
0.4974	1.39303	0.00663	1.39078	0.00639	1.38902	0.00674	1.38700	0.00680	1.38499	0.00696
0.6055	1.38823	0.00678	1.38599	0.00657	1.38413	0.00685	1.38228	0.00709	1.38009	0.00707
0.7010	1.38344	0.00636	1.38123	0.00620	1.37919	0.00633	1.37748	0.00672	1.37527	0.00668
0.8044	1.37741	0.00507	1.37519	0.00491	1.37320	0.00512	1.37141	0.00544	1.36916	0.00537
0.9036	1.37071	0.00291	1.36855	0.00283	1.36645	0.00296	1.36440	0.00303	1.36254	0.00335
0.9488	1.36738	0.00165	1.36531	0.00167	1.36309	0.00169	1.36118	0.00191	1.35907	0.00198
1.0000	1.36338	0.00000	1.36129	0.00000	1.35903	0.00000	1.35690	0.00000	1.35472	0.00000

Table 1 Continued

x_1	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D
					1-Propanol + 2-propanol					
0.0000	1.37927	0.00000	1.37694	0.00000	1.37474	0.00000	1.37253	0.00000	1.37026	0.00000
0.0530	1.37969	0.00000	1.37740	0.00003	1.37537	0.00020	1.37297	0.00000	1.37071	0.00001
0.1017	1.38009	0.00002	1.37780	0.00004	1.37576	0.00019	1.37339	0.00003	1.37115	0.00004
0.2030	1.38092	0.00006	1.37868	0.00009	1.37647	0.00007	1.37426	0.00006	1.37204	0.00008
0.3026	1.38173	0.00008	1.37944	0.00005	1.37747	0.00026	1.37513	0.00012	1.37290	0.00010
0.4038	1.38254	0.00010	1.38041	0.00020	1.37835	0.00031	1.37600	0.00015	1.37379	0.00014
0.4944	1.38327	0.00012	1.38116	0.00021	1.37911	0.00034	1.37675	0.00016	1.37456	0.00015
0.5957	1.38405	0.00010	1.38200	0.00023	1.37977	0.00017	1.37758	0.00016	1.37542	0.00016
0.6999	1.38484	0.00008	1.38284	0.00022	1.38076	0.00031	1.37842	0.00014	1.37627	0.00014
0.7988	1.38558	0.00004	1.38356	0.00014	1.38154	0.00028	1.37920	0.00014	1.37706	0.00010
0.9016	1.38636	0.00001	1.38441	0.00016	1.38223	0.00013	1.37998	0.00005	1.37787	0.00005
0.9504	1.38673	0.00000	1.38482	0.00017	1.38255	0.00005	1.38035	0.00002	1.37826	0.00003
1.0000	1.38712	0.00000	1.38505	0.00000	1.38290	0.00000	1.38074	0.00000	1.37865	0.00000
					1-Propanol + 2-methyl-1-propanol					
0.0000	1.39784	0.00000	1.39573	0.00000	1.39360	0.00000	1.39146	0.00000	1.38931	0.00000
0.0514	1.39735	0.00006	1.39529	0.00011	1.39310	0.00005	1.39110	0.00019	1.38899	0.00023
0.0972	1.39688	0.00008	1.39489	0.00020	1.39267	0.00011	1.39072	0.00030	1.38860	0.00033
0.1998	1.39584	0.00014	1.39391	0.00031	1.39161	0.00015	1.38980	0.00048	1.38762	0.00044
0.2981	1.39497	0.00033	1.39300	0.00045	1.39063	0.00022	1.38889	0.00063	1.38665	0.00052
0.4004	1.39396	0.00041	1.39199	0.00054	1.38963	0.00031	1.38785	0.00068	1.38563	0.00059

Table 1 Continued

x_1	288.15 K		293.15 K		298.15 K		303.15 K		308.15 K	
	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D	n_D	δn_D
0.4983	1.39297	0.00047	1.39093	0.00052	1.38863	0.00036	1.38684	0.00072	1.38461	0.00061
0.5978	1.39191	0.00048	1.38987	0.00052	1.38747	0.00027	1.38576	0.00071	1.38356	0.00062
0.6766	1.39097	0.00038	1.38900	0.00050	1.38665	0.00029	1.38489	0.00068	1.38268	0.00058
0.8010	1.38953	0.00028	1.38753	0.00035	1.38522	0.00019	1.38346	0.00059	1.38123	0.00046
0.9005	1.38839	0.00020	1.38631	0.00020	1.38403	0.00007	1.38219	0.00038	1.37998	0.00027
0.9514	1.38770	0.00006	1.38571	0.00014	1.38346	0.00004	1.38156	0.00030	1.37930	0.00013
1.0000	1.38712	0.00000	1.38505	0.00000	1.38290	0.00000	1.38074	0.00000	1.37865	0.00000
				1-Propanol + 3-methyl-1-butanol						
0.0000	1.40919	0.00000	1.40725	0.00000	1.40528	0.00000	1.40303	0.00000	1.40110	0.00000
0.0519	1.40846	0.00042	1.40660	0.00050	1.40431	0.00019	1.40245	0.00058	1.40022	0.00029
0.0981	1.40774	0.00071	1.40587	0.00080	1.40376	0.00067	1.40161	0.00077	1.39948	0.00058
0.2019	1.40605	0.00132	1.40394	0.00117	1.40212	0.00136	1.39985	0.00132	1.39780	0.00123
0.3013	1.40424	0.00170	1.40243	0.00187	1.40027	0.00173	1.39807	0.00175	1.39603	0.00169
0.3998	1.40238	0.00201	1.40052	0.00215	1.39838	0.00205	1.39615	0.00203	1.39405	0.00193
0.5036	1.40027	0.00219	1.39842	0.00235	1.39635	0.00234	1.39394	0.00213	1.39194	0.00214
0.5977	1.39814	0.00214	1.39511	0.00213	1.39424	0.00234	1.39184	0.00213	1.38982	0.00214
0.6987	1.39570	0.00193	1.39365	0.00191	1.39165	0.00201	1.38938	0.00192	1.38733	0.00192
0.8000	1.39305	0.00152	1.39091	0.00142	1.38858	0.00120	1.38670	0.00150	1.38474	0.00160
0.8992	1.39024	0.00090	1.38814	0.00085	1.38578	0.00062	1.38393	0.00094	1.38189	0.00098
0.9506	1.38872	0.00051	1.38653	0.00038	1.38419	0.00018	1.38234	0.00050	1.38028	0.00052
1.0000	1.38712	0.00000	1.38505	0.00000	1.38290	0.00000	1.38074	0.00000	1.37865	0.00000

Table 2 Fitting parameters of Eq. (2) and σ

Ethanol + 2-propanol					
A_{01}=−1.442338	A_{02}= 1.496585·10^{-2}	A_{03}=−5.170838·10^{-5}	A_{04}= 5.964595·10^{-8}	A_{11}= 1.322219·10^{+1}	
A_{12}=−1.321329·10^{-1}	A_{13}= 4.400147·10^{-4}	A_{14}=−4.883687·10^{-7}	A_{21}=−4.497197·10^{+1}	A_{22}= 4.517648·10^{-1}	σ=1.75·10^{-5}
A_{23}=−1.512017·10^{-3}	A_{24}= 1.686074·10^{-6}	A_{31}=−2.630049·10^{+1}	A_{32}= 2.612074·10^{-1}	A_{33}=−8.639980·10^{-4}	
A_{34}= 9.517911·10^{-7}	A_{41}= 5.950681·10^{+1}	A_{42}=−5.995373·10^{-1}	A_{43}= 2.012203·10^{-3}	A_{44}=−2.249711·10^{-6}	
Ethanol - 2-methyl-1-propanol					
A_{01}=−5.124808	A_{02}= 5.275176·10^{-2}	A_{03}=−1.804953·10^{-4}	A_{04}= 2.058754·10^{-7}	A_{11}= 3.034996·10^{+1}	
A_{12}=−3.079688·10^{-1}	A_{13}= 1.041419·10^{-3}	A_{14}=−1.173455·10^{-6}	A_{21}=−1.546587·10^{+1}	A_{22}= 1.594114·10^{-1}	σ=4.56·10^{-5}
A_{23}=−5.472510·10^{-4}	A_{24}= 6.257528·10^{-7}	A_{31}=−4.714557·10^{+1}	A_{32}= 4.808775·10^{-1}	A_{33}=−1.634336·10^{-3}	
A_{34}= 1.850845·10^{-6}	A_{41}= 2.325139·10^{+1}	A_{42}=−2.392709·10^{-1}	A_{43}= 8.214990·10^{-4}	A_{44}=−9.387516·10^{-7}	
Ethanol + 3-methyl-1-butarol					
A_{01}= 3.596567·10^{+1}	A_{02}=−3.598004·10^{-1}	A_{13}= 1.200013·10^{-3}	A_{04}=−1.333330·10^{-6}	A_{11}= 4.873326·10^{+1}	
A_{12}=−4.905935·10^{-1}	A_{13}= 1.646021·10^{-3}	A_{14}=−1.840324·10^{-6}	A_{21}= 1.920495·10^{+2}	A_{22}=−1.941052	σ=6.52·10^{-5}
A_{23}= 6.537137·10^{-3}	A_{24}=−7.335915·10^{-6}	A_{31}=−2.292670·10^{+2}	A_{32}= 2.300676	A_{33}=−7.693961·10^{-3}	
A_{34}= 8.574866·10^{-6}	A_{41}=−1.064079·10^{+2}	A_{42}= 1.095657	A_{43}=−3.784494·10^{-3}	A_{44}= 4.337270·10^{-6}	

Table 2 Continued

1-Propanol + 2-propanol					
A_{01}=−1.280617·10^{+1}	A_{02}= 1.273600·10^{-1}	A_{03}=−4.219859·10^{-4}	A_{04}= 4.658463·10^{-7}	A_{11}=−1.588861·10^{+1}	
A_{12}= 1.588204·10^{-1}	A_{13}=−5.289874·10^{-4}	A_{14}= 5.871008·10^{-7}	A_{21}= 6.779665·10^{+1}	A_{22}=−6.800652·10^{-1}	σ=4.09·10^{-5}
A_{23}= 2.272959·10^{-3}	A_{24}=−2.531264·10^{-6}	A_{31}=−1.628331·10^{+1}	A_{32}= 1.648928·10^{-1}	A_{33}=−5.563562·10^{-4}	
A_{34}= 6.254496·10^{-7}	A_{41}=−1.539870·10^{+2}	A_{42}= 1.642762	A_{43}=−5.483306·10^{-3}	A_{44}= 6.098427·10^{-6}	
1-Propanol + 2-methyl-1-propanol					
A_{01}= 1.509590·10^{+1}	A_{02}=−1.511636·10^{-1}	A_{03}= 5.043353·10^{-4}	A_{04}=−5.605493·10^{-7}	A_{11}=−9.274905·10^{-2}	
A_{12}= 2.020261·10^{-3}	A_{13}=−1.043571·10^{-5}	A_{14}= 1.577800·10^{-8}	A_{21}=−1.122770·10^{+1}	A_{22}= 1.117291·10^{-1}	σ=8.52·10^{-5}
A_{23}=−3.708839·10^{-4}	A_{24}= 4.106778·10^{-7}	A_{31}= 6.408732·10^{+1}	A_{32}=−6.474835·10^{-1}	A_{33}= 2.180018·10^{-3}	
A_{34}=−2.446053·10^{-6}	A_{41}= 5.011053·10^{+1}	A_{42}=−5.025940·10^{-1}	A_{43}= 1.679798·10^{-3}	A_{44}=−1.870840·10^{-6}	
1-Propanol + 3-methyl-1-butanol					
A_{01}=−1.846600·10^{+1}	A_{02}= 1.842404·10^{-1}	A_{03}=−6.121205·10^{-4}	A_{04}= 6.775461·10^{-7}	A_{11}= 1.566331·10^{-1}	
A_{12}=−1.579803·10^{-1}	A_{13}= 5.309650·10^{-4}	A_{14}=−5.946162·10^{-7}	A_{21}= 1.097470·10^{+2}	A_{22}=−1.096385	σ=6.70·10^{-5}
A_{23}= 3.649083·10^{-3}	A_{24}=−4.046316·10^{-6}	A_{31}=−4.295514·10^{+1}	A_{32}= 4.434048·10^{-1}	A_{33}=−1.524567·10^{-3}	
A_{34}= 1.746004·10^{-6}	A_{41}=−2.221722·10^{+1}	A_{42}= 2.232800·10^{-1}	A_{43}=−7.471172·10^{-4}	A_{44}= 8.323966·10^{-7}	

Estimation by means of equations of state

For many practical purposes, it is necessary to predict the non-ideality of binary or multicomponent liquid mixtures from physical parameters or from the properties of the pure components in adequate models. In the past few years, interest has increased in work based on equations of state for the prediction of excess molar volume, partial excess molar volume, partial molar volume, phase equilibria or excess molar enthalpies and other properties. This is due to the simplicity of the model, the relative accuracy, the low information requirements and the wide versatility in operation conditions. In order to apply these models to estimate thermodynamic properties of mixtures, the implementation of mixing rules is necessary. In this case, the equations were selected and applied with combining rules of one or two parameters in the a and b factors. We have divided this study into three parts: the first is a brief explanation of the rules and the development of the expressions, the second part presents the correlation procedure of binary values to obtain physical parameters, and the third part is the evaluation of the results obtained.

Theoretical procedure

The methods applied to these mixtures relate to the refractive indices on mixing based on different applications of the Heller equation [3] and a mixing rule. It has been demonstrated [1] that the mixing rules for refractive indices are functions of the volume fractions of the mixture, since it is possible to generalize them as a function of the densities of the mixture and of the pure components:

$$\frac{f(n_D)}{\rho} = \sum_{i=1}^{N} \frac{w_i f(n_{Di})}{\rho_i} \tag{4}$$

In this equation, w_i is the mass fraction, and f is a mathematical function of the refractive index of the mixture (n_D), and the refractive index of each component (n_{Di}). By means of a previously explained substitution [1], it is possible to obtain an expression for the refractive index:

$$\sum_{i=1}^{N}\left[\left(\frac{n_{Di}^2-1}{n_{Di}^2+2}-\frac{n_D^2-1}{n_D^2+2}\right)\left(x_i M_i\left(\frac{n_D^2-1}{n_D^2+2}\right)\rho_i^{-1}\right)^{-1}\right] =$$

$$= \sum_{i=1}^{N} x_i\left(-\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n}\left(\frac{\partial P}{\partial V_m}\right)_{T,n}^{-1} - V_i\right) \tag{5}$$

where f has been substituted by the Lorentz-Lorenz mixing rule [1] and the partial quantities and the molar volume, appearing in the second term, were computed from

the corresponding equation of state, the former being dependent on the applied mixing rule, and the latter on the selected equation of state.

A general expression for both equations of state can be written as follows:

$$P = \frac{RT}{V-b} - \frac{a}{(V+\delta_1 b)(V+\delta_2 b)} \tag{6}$$

where $\delta_1=1$, $\delta_2=0$ for the SRK equation, and $\delta_1=1+\sqrt{2}$, $\delta_2=1-\sqrt{2}$ for the PR equation.

Three different combining rules for binary parameters were incorporated in these models, which exhibit different correlation dependences. The general equations for the applied mixing rules are

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j (1 - k_{ij} - l_{ij}x_i)(a_i a_j)^{0.5} \tag{7}$$

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j (1 - m_{ij})\left(\frac{b_i + b_j}{2}\right) \tag{8}$$

The first mixing rule (R1) is obtained when $l_{ij}=m_{ij}=0$, the second (R2) when $l_{ij}=0$, and the third (R3) when k_{ij}, l_{ij}, $m\neq 0$, these parameters being constant values over the whole range of composition for every mixture.

Table 3 presents the values of the parameters for each binary mixture via the SRK and PR equations by application of R1 (σ from experimental values between brackets). It can be observed that similar deviations are obtained for binary correlations with the two equations, and this mixing rule yields the lowest deviations.

Data reduction

In order to compute the binary interaction parameters for each mixing rule, a common correlation procedure was applied so as to minimize an objective function (Eq. (9)), which means the relative accuracy of predicted and experimental values, and leads to zero.

$$OF = \frac{\sum_{i=1}^{n}{}' (z_{exp} - z_{pred})^2}{z_{exp}} \tag{9}$$

A Marquardt [8] routine was applied to calculate the interaction parameters in combination with a Newton-Raphson method. The fitting parameters obtained are listed in Table 3 (σ between brackets) for the R1 mixing rule.

Table 3 Calculated values for the coefficients k_{ij} of the R1 mixing rule (σ between brackets)

System	Soave-Redlich-Kwong				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Ethanol + 2-propanol	$4.288 \cdot 10^{-3}$ ($2.4 \cdot 10^{-5}$)	$-3.136 \cdot 10^{-3}$ ($3.1 \cdot 10^{-5}$)	$-8.253 \cdot 10^{-3}$ ($4.5 \cdot 10^{-5}$)	$-1.221 \cdot 10^{-2}$ ($3.6 \cdot 10^{-5}$)	$-2.435 \cdot 10^{-2}$ ($9.5 \cdot 10^{-5}$)
Ethanol + 2-methyl-1-propanol	$-5.737 \cdot 10^{-3}$ ($5.7 \cdot 10^{-5}$)	$-5.682 \cdot 10^{-3}$ ($8.7 \cdot 10^{-5}$)	$-6.658 \cdot 10^{-3}$ ($6.2 \cdot 10^{-5}$)	$-1.313 \cdot 10^{-2}$ ($8.2 \cdot 10^{-5}$)	$-3.088 \cdot 10^{-2}$ ($8.3 \cdot 10^{-5}$)
Ethanol + 3-methyl-1-butanol	$-4.026 \cdot 10^{-2}$ ($1.5 \cdot 10^{-4}$)	$3.972 \cdot 10^{-4}$ ($1.6 \cdot 10^{-4}$)	$-3.246 \cdot 10^{-2}$ ($9.2 \cdot 10^{-5}$)	$-5.484 \cdot 10^{-2}$ ($1.2 \cdot 10^{-4}$)	$-6.525 \cdot 10^{-2}$ ($6.8 \cdot 10^{-5}$)
1-Propanol + 2-propanol	$-1.588 \cdot 10^{-2}$ ($1.5 \cdot 10^{-5}$)	$-2.746 \cdot 10^{-2}$ ($6.6 \cdot 10^{-5}$)	$-3.889 \cdot 10^{-2}$ ($8.3 \cdot 10^{-5}$)	$-2.186 \cdot 10^{-2}$ ($1.9 \cdot 10^{-5}$)	$-2.138 \cdot 10^{-2}$ ($1.5 \cdot 10^{-5}$)
1-Propanol + 2-methyl-1-propanol	$9.402 \cdot 10^{-3}$ ($4.8 \cdot 10^{-5}$)	$-4.464 \cdot 10^{-3}$ ($1.8 \cdot 10^{-5}$)	$2.128 \cdot 10^{-3}$ ($3.3 \cdot 10^{-5}$)	$-2.637 \cdot 10^{-2}$ ($6.4 \cdot 10^{-5}$)	$-1.489 \cdot 10^{-2}$ ($5.3 \cdot 10^{-5}$)
1-Propanol + 3-methyl-1-butanol	$-3.363 \cdot 10^{-2}$ ($3.3 \cdot 10^{-5}$)	$-3.762 \cdot 10^{-2}$ ($1.2 \cdot 10^{-4}$)	$-3.268 \cdot 10^{-2}$ ($2.0 \cdot 10^{-4}$)	$-1.516 \cdot 10^{-2}$ ($3.4 \cdot 10^{-5}$)	$-2.634 \cdot 10^{-2}$ ($5.2 \cdot 10^{-5}$)

Table 3 Continued

System	Peng-Robinson				
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
Ethanol + 2-propanol	$-3.698\cdot10^{-3}$ ($2.4\cdot10^{-5}$)	$-5.552\cdot10^{-3}$ ($3.1\cdot10^{-5}$)	$-6.806\cdot10^{-3}$ ($4.5\cdot10^{-5}$)	$-7.756\cdot10^{-3}$ ($3.6\cdot10^{-5}$)	$-1.061\cdot10^{-2}$ ($6.9\cdot10^{-5}$)
Ethanol + 2-methyl-1-propanol	$-1.061\cdot10^{-2}$ ($5.7\cdot10^{-5}$)	$-2.271\cdot10^{-2}$ ($8.6\cdot10^{-5}$)	$-2.304\cdot10^{-2}$ ($6.0\cdot10^{-5}$)	$-2.476\cdot10^{-2}$ ($7.9\cdot10^{-5}$)	$-2.939\cdot10^{-2}$ ($8.5\cdot10^{-5}$)
Ethanol + 3-methyl-1-butanol	$-3.082\cdot10^{-2}$ ($1.7\cdot10^{-4}$)	$-3.940\cdot10^{-2}$ ($1.6\cdot10^{-4}$)	$-4.869\cdot10^{-2}$ ($1.0\cdot10^{-4}$)	$-5.512\cdot10^{-2}$ ($1.1\cdot10^{-4}$)	$-5.781\cdot10^{-2}$ ($5.9\cdot10^{-5}$)
1-Propanol + 2-propanol	$-5.894\cdot10^{-4}$ ($1.5\cdot10^{-5}$)	$-3.354\cdot10^{-3}$ ($7.3\cdot10^{-5}$)	$-6.134\cdot10^{-3}$ ($8.1\cdot10^{-5}$)	$-1.857\cdot10^{-3}$ ($2.2\cdot10^{-5}$)	$-1.668\cdot10^{-2}$ ($1.7\cdot10^{-5}$)
1-Propanol + 2-methyl-1-propanol	$-2.175\cdot10^{-3}$ ($5.0\cdot10^{-5}$)	$-6.060\cdot10^{-3}$ ($1.8\cdot10^{-5}$)	$1.101\cdot10^{-3}$ ($3.3\cdot10^{-5}$)	$-1.201\cdot10^{-2}$ ($6.4\cdot10^{-5}$)	$-8.865\cdot10^{-3}$ ($5.4\cdot10^{-5}$)
1-Propanol + 3-methyl-1-butanol	$-2.566\cdot10^{-2}$ ($4.3\cdot10^{-5}$)	$-2.665\cdot10^{-2}$ ($1.2\cdot10^{-4}$)	$-2.513\cdot10^{-2}$ ($2.0\cdot10^{-4}$)	$-2.020\cdot10^{-2}$ ($3.1\cdot10^{-5}$)	$-2.340\cdot10^{-2}$ ($4.5\cdot10^{-5}$)

Comparative study and results

In what is referred to as the capability to correlate experimental data, a good response is obtained for all the binary mixtures, the deviations being close to the accuracy of the measurements. The poorest results were obtained for the mixtures containing 3-methyl-1-butanol. No dependence on temperature was observed for the deviations obtained. Slightly better results were given by the PR equation at high temperatures, but the two equations exhibited similar behaviour. The computed parameters can be used for multicomponent refractive index prediction.

References

1 M. Iglesias, B. Orge, M. Domínguez and J. Tojo, Phys. Chem. Liq., 37 (1998) 9.
2 M. Iglesias, G. Marino, B. Orge, M. M. Piñeiro and J. Tojo, Phys. Chem. Liq., (in press).
3 W. Heller, J. Phys. Chem., 69 (1972) 1123.
4 D. Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fundam., 15 (1976) 59.
5 G. Soave, Chem. Eng. Sci., (1972) 1197.
6 M. Iglesias, B. Orge and J. Tojo, J. Chem. Thermodyn., 27 (1995) 1161.
7 O. Redlich and A. T. Kister, Ind. Eng. Chem., 40 (1948) 345.
8 D. W. Marquardt, J. Soc. Indust. Appl. Math., 11 (1963) 431.