Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 3, 735–745

VOLUMETRIC AND REFRACTIVE PROPERTIES OF BINARY MIXTURES CONTAINING 1,3-DIOXOLANE AND ISOMERIC CHLOROBUTANES

B. Giner, I. Gascón, H. Artigas, A. Villares and C. Lafuente[*]

Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza, Campus Plaza San Francisco
50009 Zaragoza, Spain

The relation between refractive index deviations and excess volumes for binary mixtures formed by a cyclic ether and a haloalkane has been tested using several methods: refractive index mixing rules and equations of state. Refractive index deviations, excess volumes and molar refractions have been calculated from experimental data of refractive indices and densities at two temperatures 298.15 and 313.15 K. Results obtained have been discussed in terms of intermolecular interactions. Refractive indices were compared with those predicted by several mixing rules. Excess volumes have also been correlated using several cubic equations of state and finally a relation between parameter *b* from equations of state and molar refraction has been provided.

Keywords: *chlorobutane, density, 1,3-dioxolane, equation of state, refractive index*

Introduction

It is well known that refractive index can be determined from a small amount of sample with high precision in an easier way than other physical properties, so the relation between refractive index and some thermophysical properties has been studied for a long time, in such a way that there are also many correlations between refractive index and several properties like density, critical constants, dielectric permittivity, equation of state parameters, etc. [1–5]. One of the relations that have been more studied is the relation between refractive index and excess volume so it is common that these two properties are reported together.

In this paper and following previous studies of liquid mixtures involving cyclic ethers and chloroalkanes [6–13], we show here refractive indices and densities measured at two temperatures 298.15 and 313.15 K of binary mixtures formed by 1,3-dioxolane and each one of the isomeric chlorobutanes From experimental data, we have calculate refractive index deviations, excess volumes and molar refractions. All the results have been discussed in terms of the type and nature of components and the specific interactions between them. In a previous work we reported densities of mixtures formed by 1,3-dioxolane and isomeric chlorobutanes at 298.15 K [7] although there was not any discussion or interpretation of the values obtained. So, we include density measurements at 298.15 K in order to complete the present paper.

Apart from these experimental work, we have used several common mixing rules: Lorentz–Lorenz [14, 15], Gladstone–Dale [16], Laplace [17] and Eykman [18] to predict refractive indices of the mixtures from their experimental densities and refractive indices and densities of the pure components. Furthermore we have used several cubic equations of state: Soave–Redlich–Kwong [19, 20] and Peng–Robinson–Stryjek–Vera [21, 22] to correlate the excess volume. Parameter *b* provided from these equations of state have been related with molar refraction through a linear equation. Using this equation, that is, knowing the *b* parameter which is obtained from excess volumes, the molar refraction can be obtained and then the refractive index can be predicted.

Experimental

Chemicals used on experimental measurements were provided by Aldrich (1-chlorobutane and 2-methyl-2-chloropropane have a purity of 99%, 1,3-dioxolane and 2-chlorobutane with a purity better than 99.9 and 99%, respectively) and 2-methyl-1-chloropropane was purchased from Fluka (purity better than 99%). Additional purification has not been made. A comparison between experimental and literature data of densities and refractive indices of pure compounds [23, 24] is reported in Table 1.

Excess volumes have been determined from densities measured with an Anton-Paar DMA-58 vibrating tube densimeter automatically thermostated at ±0.01 K. The precision of the density measurements was $\pm 0.5\cdot 10^{-5}$ g cm^{-3} and the corresponding accuracy $\pm 1\cdot 10^{-5}$.

---

[*] Author for correspondence: celadi@posta.unizar.es

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Experimental and literature data of densities, ρ, and refractive indices, n_D, of pure components at 298.15 K

Compound	ρ/g·cm^{-3}		n_D	
	Exptl.	Lit.	Exptl.	Lit.
1,3-dioxolane	1.05862	1.05866[a]	1.397971	
1-chlorobutane	0.88069	0.88095[a]	1.399499	1.4001[b]
2-chlorobutane	0.86740	0.8671[a]	1.394043	1.3941[b]
2-methyl-1-chloropropane	0.87113	0.8717[a]	1.395284	1.3951[b]
2-methyl-2-chloropropane	0.83645	0.8361[a]	1.382242	1.3828[b]

[a][23]; [b][24]

Refractive indices corresponding to 589.3 nm sodium D wavelength were measured using a high precision automatic refractometer Abemat-HP DR. Kernchen. The temperature of the sample is controlled within ±2·10^{-3} K by a built-in Peltier device while another Peltier thermostat is used to kept constant the temperature of the internal refractometer components. The reproducibility of the measurement is ±1·10^{-6} and the corresponding accuracy is ±2·10^{-5}. Details of the equipment and measure procedure have been described elsewhere [25].

The composition of each mixture was determined by using a mass balance Mettler H20T. The maximum estimated error in the mole fractions is ±1·10^{-4}.

Results and discussion

From experimental results of refractive indices and densities we have calculated refractive index deviations defined on a volume fraction basis [26, 27], Δn_D, and excess volumes, V^E, as follows:

$$\Delta n_D = n_D - \phi_1 n_{D,1} - \phi_2 n_{D,2} \qquad (1)$$

$$V^E = x_1\left(\frac{M_1}{\rho} - \frac{M_1}{\rho_1}\right) + x_2\left(\frac{M_2}{\rho} - \frac{M_2}{\rho_2}\right) \qquad (2)$$

where n_D is the refractive index of the mixture, ϕ_i and n_{Di} are the volume fraction referred to the unmixed state and the refractive index of component *i*, respectively, ρ is the density of the mixture, x_i, M_i and ρ_i are respectively the mole fraction, the molar mass and the density of component *i*.

Molar refraction, R_m, has been calculated by means of the Lorentz–Lorenz relation:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m \qquad (3)$$

where V_m is the molar volume of the mixture.

In Table 2 appear experimental values of n_D and ρ as well as calculated values of, Δn_D, V_E and R_m for the studied mixtures. The values of refractive index deviations and excess volumes are graphically represented in Figs 1 to 4.

Refractive index deviations and excess volumes at each temperature were correlated with a Redlich–Kister polynomial equation:

$$Y = y_1(1 - y_1)\sum_i A_i (2y_1 - 1)^i \qquad (4)$$

$Y = \Delta n_D$ or V^E, A_i are adjustable parameters and y_1 is the volume fraction for Δn_D or mole fraction for V^E. The values of the parameters A_i together with the standard deviations $\sigma(Y)$ are given in Table 3.

According Nakata and Sakurai [1] the sign of Δn_D is opposite to that of V^E if the behaviour of refractive index is not too non-linear between $n_{D,1}$ and $n_{D,2}$. In our mixtures this rule is truly fulfilled in all the cases.

Refractive index deviation values for the mixture containing 1-chlorobutane at both temperatures are negative in all the range of composition. The refractive behaviour for the mixtures containing 2-chlorobutane and 2-methyl-1-chloropropane is similar, although Δn_D values for 2-chlorobutane are bigger than for 2-methyl-1-chloropropane and they are positive in all the range of composition at 298.15 K but slightly negative at low mole fractions of 1,3-dioxolane at 313.15 K, while for 2-methyl1-chloropropane Δn_D values display a sigmoidal curve at both temperatures, negative at low mole fractions of 1,3-dioxolane and positive at high mole fractions of the ether. Δn_D values for the mixture which contain 2-methyl-2-chloropropane are positive in the whole composition range and they are the largest ones at both temperatures.

As we have mentioned above the volumetric behaviour is opposite to refractive one. The largest V_E values at 298.15 and 313.15 K correspond now to the mixture containing 1-chlorobutane which are positive in all the range of composition. Mixtures containing 2-chlorobutane and 2-methyl-1-chloropropane show similar V^E curves which are sigmoidal in shape, experimental V^E values are positive at low and medium mole fractions of 1,3-dioxolane but become negative at high mole fractions of ether, although V^E at 298.15 K for 1,3-dioxolane+2-chlorobutane are practically negative for all the compositions. Finally, for

Table 2 Refractive indices, n_D, densities, ρ, refractive index deviations, $\Delta_{\phi nD}$, excess volumes, V^E, and molar refractions, R_m, for the studied mixtures

x_1	ϕ_1	n_D	ρ/g cm^{-3}	Δn_D	V^E/cm^3 mol^{-1}	R_m/cm^3 mol^{-1}
1,3-dioxolane(1)+1-chlorobutane(2) at 298.15 K						
0.0000	0.0000	1.399499	0.88069	0.00000	0.000	25.453
0.0523	0.0354	1.399278	0.88658	–0.000167	0.048	25.008
0.1009	0.0695	1.399125	0.89233	–0.000268	0.084	24.594
0.1599	0.1124	1.398945	0.89964	–0.000382	0.116	24.092
0.2558	0.1862	1.398720	0.91240	–0.000495	0.150	23.273
0.3924	0.3007	1.398459	0.93249	–0.000581	0.166	22.104
0.4876	0.3879	1.398324	0.94794	–0.000582	0.164	21.289
0.5908	0.4901	1.398216	0.96614	–0.000534	0.152	20.406
0.6848	0.5912	1.398144	0.98424	–0.000452	0.135	19.601
0.7751	0.6964	1.398071	1.00317	–0.000364	0.112	18.827
0.8411	0.7790	1.398043	1.01810	–0.000266	0.088	18.260
0.9217	0.8868	1.397989	1.03775	–0.000155	0.051	17.565
0.9643	0.9473	1.397975	1.04888	–0.000076	0.025	17.197
1.0000	1.0000	1.397971	1.05862	0.00000	0.000	16.888
1,3-dioxolane(1)+2-chlorobutane(2) at 298.15 K						
0.0000	0.0000	1.394043	0.86740	0.000000	0.000	25.531
0.0180	0.0119	1.394103	0.86966	0.000013	0.002	25.376
0.1593	0.1105	1.394572	0.88862	0.000095	–0.010	24.157
0.2781	0.2017	1.395050	0.90625	0.000215	–0.030	23.131
0.3908	0.2961	1.395550	0.92447	0.000344	–0.044	22.159
0.4477	0.3470	1.395810	0.93427	0.000404	–0.049	21.669
0.5959	0.4915	1.396501	0.96207	0.000527	–0.060	20.391
0.6381	0.5362	1.396694	0.97067	0.000545	–0.063	20.025
0.7786	0.6975	1.397310	1.00168	0.000527	–0.070	18.807
0.8491	0.7867	1.397568	1.01873	0.000435	–0.066	18.194
0.9323	0.9004	1.397832	1.04019	0.000252	–0.044	17.472
0.9807	0.9709	1.397936	1.05329	0.000079	–0.016	17.054
1.0000	1.0000	1.397971	1.05862	0.000000	0.000	16.888
1,3-dioxolane(1)+2-methyl-1-chloropropane(2) at 298.15 K						
0.0000	0.0000	1.395284	0.87113	0.00000	0.000	25.492
0.0633	0.0426	1.395335	0.87887	–0.000063	0.029	24.951
0.1416	0.0980	1.395453	0.88909	–0.000094	0.047	24.280
0.2787	0.2028	1.395750	0.90867	–0.000079	0.051	23.103
0.3828	0.2900	1.396043	0.92506	–0.000020	0.044	22.208
0.5071	0.4039	1.396452	0.94656	0.000083	0.027	21.140
0.6012	0.4982	1.396775	0.96443	0.000152	0.009	20.329
0.6902	0.5946	1.397084	0.98275	0.000202	–0.011	19.560
0.7747	0.6936	1.397377	1.00156	0.000229	–0.029	18.829
0.8538	0.7937	1.397613	1.02047	0.000196	–0.039	18.144
0.9211	0.8848	1.397800	1.03752	0.000138	–0.034	17.565
0.9878	0.9816	1.397950	1.05529	0.000029	–0.008	16.992
1.0000	1.0000	1.397971	1.05862	0.00000	0.000	16.888

Table 2 Continued

x_1	ϕ_1	n_D	ρ/g cm^{-3}	Δn_D	V^E/cm^3 mol^{-1}	R_m/cm^3 mol^{-1}
1,3-dioxolane(1)+2-methyl-2-chloropropane(2) at 298.15 K						
0.0000	0.0000	1.382242	0.83645	0.00000	0.000	25.770
0.0666	0.0432	1.383325	0.84756	0.000404	–0.192	25.157
0.1356	0.0903	1.384505	0.85912	0.000843	–0.320	24.539
0.20534	0.1404	1.385715	0.88556	0.001264	–0.403	23.922
0.2863	0.2023	1.387155	0.88556	0.001731	–0.466	23.211
0.4059	0.3016	1.389260	0.90852	0.002274	–0.524	22.158
0.1356	0.0903	1.384505	0.85912	0.000843	–0.320	24.539
0.5111	0.3980	1.391059	0.93057	0.002557	–0.551	21.224
0.5996	0.4864	1.392525	0.95055	0.002633	–0.548	20.437
0.68921	0.5837	1.393938	0.97214	0.002515	–0.510	19.639
0.7839	0.6963	1.395340	0.99646	0.002145	–0.419	18.799
0.8590	0.7939	1.396358	1.01693	0.001629	–0.305	18.134
0.9287	0.8917	1.397205	1.03692	0.000938	–0.167	17.519
0.9681	0.9505	1.397646	1.04876	0.000453	–0.077	17.170
1.0000	1.0000	1.397971	1.05862	0.000000	0.000	16.888
1,3-dioxolane(1)+1-chlorobutane(2) at 313.15 K						
0.0000	0.0000	1.391332	0.86382	0.00000	0.000	25.480
0.0411	0.0277	1.391170	0.86837	–0.000141	0.039	25.129
0.1407	0.0982	1.390875	0.88010	–0.000383	0.117	24.280
0.2605	0.1898	1.390614	0.89560	–0.000575	0.178	23.259
0.3986	0.3058	1.390440	0.91561	–0.000661	0.209	22.080
0.4863	0.3863	1.390376	0.92967	–0.000665	0.208	21.329
0.5887	0.4876	1.390375	0.94756	–0.000589	0.191	20.452
0.7122	0.6219	1.390410	0.97154	–0.000453	0.149	19.392
0.7628	0.6813	1.390419	0.98220	–0.000399	0.127	18.956
0.8409	0.7785	1.390470	0.99973	–0.000275	0.088	18.282
0.9247	0.8909	1.390528	1.02008	–0.000132	0.042	17.559
0.9829	0.9745	1.390570	1.03525	–0.000027	0.010	17.057
1.0000	1.0000	1.390578	1.03988	0.00000	0.000	16.909
1,3-dioxolane(1)+2-chlorobutane(2) at 313.15 K						
0.0000	0.0000	1.385735	0.85013	0.00000	0.000	25.562
0.0340	0.0225	1.385810	0.85425	–0.000034	0.020	25.270
0.1659	0.1151	1.386260	0.87163	–0.000033	0.041	24.134
0.2828	0.2051	1.386807	0.88879	0.000079	0.028	23.125
0.3977	0.3017	1.387413	0.90727	0.000217	0.010	22.134
0.4819	0.3783	1.387875	0.92192	0.000308	–0.001	21.407
0.6046	0.5001	1.388610	0.94519	0.000453	–0.016	20.348
0.6969	0.6007	1.389139	0.96443	0.000495	–0.028	19.547
0.7757	0.6934	1.389577	0.98216	0.000484	–0.037	18.863
0.8806	0.8283	1.390130	1.00783	0.000383	–0.039	17.949
0.9461	0.9198	1.390410	1.02503	0.000220	–0.026	17.379
0.9629	0.9444	1.390454	1.02961	0.000145	–0.020	17.231
1.0000	1.0000	1.390578	1.03988	0.00000	0.000	16.909

Table 2 Continued

x_1	ϕ_1	n_D	ρ/g cm^{-3}	Δn_D	V^E/cm^3 mol^{-1}	R_m/cm^3 mol^{-1}
1,3-dioxolane(1)+2-methyl-1-chloropropane(2) at 313.15 K						
0.0000	0.0000	1.386856	0.85351	0.000000	0.000	25.526
0.0434	0.0290	1.386905	0.85880	–0.000059	0.013	25.151
0.1352	0.0931	1.387091	0.87059	–0.000112	0.032	24.362
0.2801	0.2035	1.387501	0.89102	–0.000113	0.046	23.117
0.3890	0.2948	1.387912	0.90801	–0.000041	0.045	22.183
0.5596	0.4549	1.388633	0.93799	0.000084	0.029	20.715
0.4824	0.3797	1.388298	0.92389	0.000029	0.038	21.380
0.6975	0.6023	1.389296	0.96566	0.000198	0.008	19.527
0.7751	0.6936	1.389660	0.98281	0.000222	–0.002	18.856
0.8540	0.7935	1.390027	1.00152	0.000217	–0.009	18.174
0.9320	0.9001	1.390334	1.02138	0.000128	–0.009	17.498
0.9918	0.9876	1.390549	1.03760	0.000017	–0.002	16.980
1.0000	1.0000	1.390578	1.03988	0.000000	0.000	16.909
1,3-dioxolane (1) + 2-methyl-2-chloropropane (2) at 313.15 K						
0.0000	0.0000	1.373143	0.81831	0.00000	0.000	25.781
0.0989	0.0647	1.374846	0.83394	0.000575	–0.169	24.899
0.1456	0.0969	1.375700	0.84168	0.000867	–0.242	24.485
0.2684	0.1876	1.378048	0.86324	0.001634	–0.396	23.401
0.3979	0.2939	1.380493	0.88798	0.002227	–0.495	22.254
0.5078	0.3938	1.382585	0.91079	0.002575	–0.526	21.283
0.6093	0.4954	1.384364	0.93354	0.002583	–0.512	20.380
0.7028	0.5982	1.386000	0.95614	0.002427	–0.462	19.549
0.7815	0.6925	1.387327	0.97650	0.002109	–0.390	18.848
0.8635	0.7994	1.388669	0.99909	0.001589	–0.282	18.120
0.9313	0.8952	1.389603	1.01886	0.000853	–0.160	17.515
0.9666	0.9479	1.390059	1.02952	0.000389	–0.083	17.202
1.0000	1.0000	1.390578	1.03988	0.00000	0.000	16.910

the mixture containing 2-methyl-2-chloropropane V^E is clearly negative at both temperatures.

We can remark that the effect of the temperature is not very significant, being values of Δn_D a little smaller if the temperature increases and V^E values became larger when temperature increases.

The values of the thermodynamic properties of solutions are the results of several energetic and structural effects. For the systems and properties studied here, the energetic effects, that is the molecular interactions between the components of the mixture, are quite counterbalanced; the disruption of dipole–dipole interactions in 1,3-dioxolane and in chlorobutanes is compensated by specific interactions between the oxygen and chloride atoms. So, structural effects, interstitial accommodation and consequently changes in free volume, must play a main role in the explanation of refractive and volumetric behaviour. The linear isomer, 1-chlorobutane, is the chlorobutane that in the pure state has the minimum reduced molar free volume, i.e. the unoccupied part of the molar volume [28], as show his values of molar refraction and isothermal compressibility [13] and therefore the possibility of interstitial accommodation of 1,3-dioxolane molecules is reduced, while the 2-methyl-2-chloropropane has the maximum reduced molar free volume and the 1,3-dioxolane can be easily accommodated leading to positive Δn_D values and V^E negative values. Refractive index deviations and excess volumes for 2-chlorobutane and 2-methyl-1-chloropropane show intermediate values between 1-chlorobutane and 2-methyl-2-chloropropane, according to the pure state properties of these isomers.

Refractive index mixing rules

The refractive index of a liquid mixture can be predicted from his density together with the refractive in-

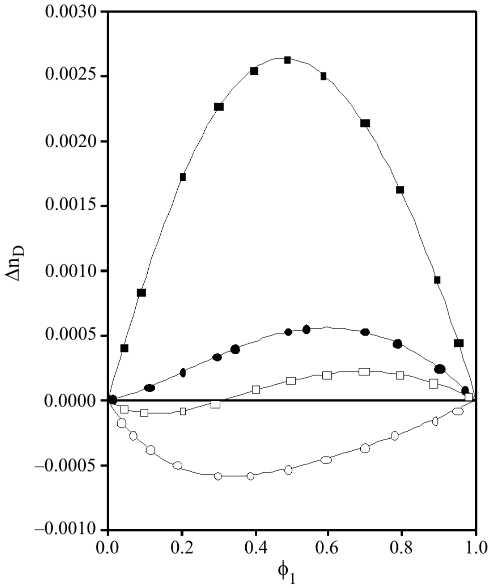

Fig. 1 Refractive index deviations for 1,3-dioxolane(1)+isomeric chlorobutane(2) at 298.15 K as a function of volume fraction, ϕ_1: ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane; —– Redlich–Kister equation

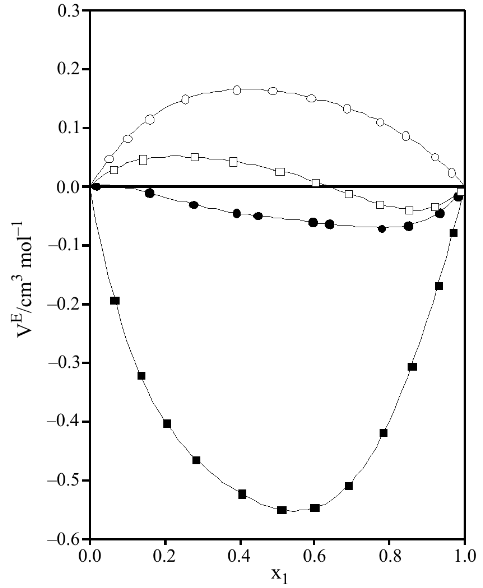

Fig. 3 Excess volumes for 1,3-dioxolane(1)+isomeric chlorobutane(2) at 298.15 K as a function of mole fraction, x_1: ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane, —– Redlich–Kister equation

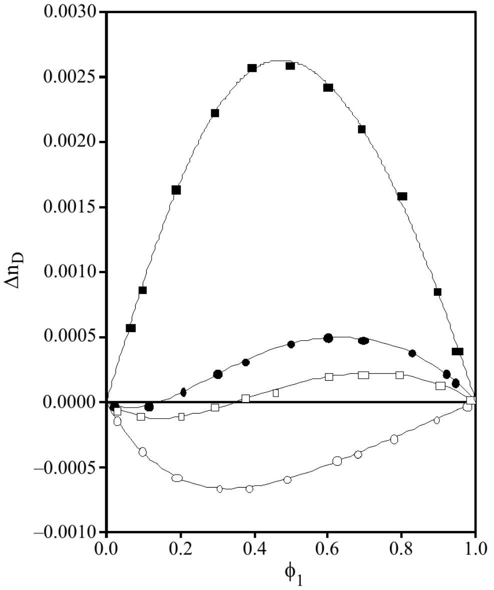

Fig. 2 Refractive index deviations for 1,3-dioxolane(1)+isomeric chlorobutane(2) at 313.15 K as a function of volume fraction, ϕ_1: ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane; —– Redlich–Kister equation

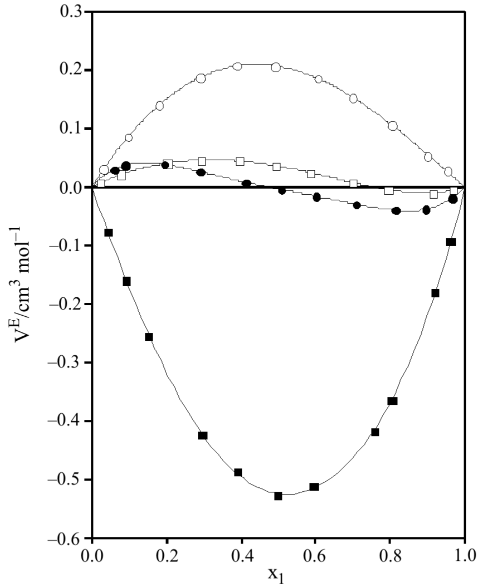

Fig. 4 Excess volumes for 1,3-dioxolane(1)+isomeric chlorobutane(2) at 313.15 K as a function of mole fraction, x_1: ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane; —– Redlich–Kister equation

dices and densities of the pure components by using a mixing rule:

$$\left(\frac{1}{\rho}\right)f(n_D)=\left(\frac{w_1}{\rho_1}\right)f(n_{D1})+\left(\frac{w_2}{\rho_2}\right)f(n_{D,2}) \qquad (5)$$

where w_i is the mass fraction of component i and $f(n_D)$ denotes a function of the refractive index. The mixing rules used in this paper were:

- Lorentz–Lorenz (LL)

$$f(n_D)=\frac{n_D^2-1}{n_D^2+2} \qquad (6)$$

Table 3 Parameters, A_i, and standard deviations, $\sigma(Y)$, for the Redlich-Kister equation

Function	Temperature/K	A_0	A_1	A_2	A_3	σ(Y)
			1,3-dioxolane(1)+1-chlorobutane(2)			
Δn_D	298.15	–0.002090	0.001281	–0.000932	0.000362	0.000011
	313.15	–0.002325	0.001692	–0.000833	0.000272	0.000009
V^E	298.15	0.652	–0.162	0.241	0.023	0.002
	313.15	0.828	–0.217	–0.043	–0.006	0.002
			1,3-dioxolane(1)+2-chlorobutane(2)			
Δn_D	298.15	0.002137	0.001072	–0.000387	0.000053	0.000005
	313.15	0.001793	0.001478	–0.000857	0.000854	0.000010
V^E	298.15	–0.213	–0.14	–0.164	–0.366	0.001
	313.15	–0.012	–0.247	0.034	–0.435	0.001
			1,3-dioxolane(1)+2-methyl-1-chloropropane(2)			
Δn_D	298.15	0.000622	0.001337	–0.000730	0.000305	0.000005
	313.15	0.000524	0.001537	–0.000606	0.000339	0.000009
V^E	298.15	0.114	–0.324	–0.165	–0.329	0.001
	313.15	0.144	–0.226	–0.088	–0.040	0.000
			1,3-dioxolane(1)+2-methyl-2-chloropropane(2)			
Δn_D	298.15	0.010524	–0.000745	–0.000729	0.000952	0.000011
	313.15	0.010493	–0.001282	–0.001213	0.001038	0.000042
V^E	298.15	–2.196	–0.309	–0.809	0.856	0.001
	313.15	–2.102	–0.184	–0.117	–0.250	0.000

- Gladstone–Dale (GD)

$$f(n_D)=n_D-1 \tag{7}$$

- Laplace (LP)

$$f(n_D)=n_D^2-1 \tag{8}$$

- Eykman (EK)

$$f(n_D)=\frac{n_D^2-1}{n_D+0.4} \tag{9}$$

Experimental refractive indices were compared with those predicted by these mixing rules. The root mean square deviations, RMSD, between experimental and predicted n_D values are given in Table 4, the RMSD is defined as:

$$\mathrm{RMSD}=\left(\frac{1}{N}\left(\sum_{i} n_{D,\exp tl}-n_{D,\mathrm{pred}}\right)^2\right)^{1/2} \tag{10}$$

being N the number of experimental data.

As RMSD values indicate, refractive indices are predicted with high accuracy for all the mixtures studied in this work and on the other hand if temperature increases, RMSD values also increase. We should remark that all the mixing rules provide similar predictions.

Table 4 Root mean square deviations, RMSD, for the Lorentz–Lorenz (LL), Gladstone–Dale (GD), Laplace (LP) and Eykman (EK) equations

Temperature/K	LL	GD	LP	EK
		1,3-dioxolane(1)+1-chlorobutane(2)		
298.15	0.0002	0.0001	0.0001	0.0002
313.15	0.0002	0.0002	0.0001	0.0002
		1,3-dioxolane(1)+2-chlorobutane(2)		
298.15	0.0001	0.0001	0.0001	0.0001
313.15	0.0002	0.0002	0.0002	0.0002
		1,3-dioxolane(1)+2-methyl-1-chloropropane(2)		
298.15	0.0001	0.0001	0.0001	0.0001
313.15	0.0001	0.0001	0.0001	0.0001
		1,3-dioxolane(1)+2-methyl-2-chloropropane(2)		
298.15	0.0002	0.0001	0.0003	0.0001
313.15	0.0001	0.0002	0.0003	0.0001

Equations of state

We have chosen two equations of state to correlate excess volumes.

The first is the Peng–Robinson–Stryjek–Vera (PRSV) cubic equation of state that has the following expression:

$$P=\frac{RT}{V_m-b}-\frac{a(T)}{V_m(V_m+b)+b(V_m-b)} \tag{11}$$

where P and T denote pressure and temperature, respectively and R is the gas constant.

For pure component i, the parameter a, copressure parameter, and parameter b, covolume parameter, are given by following equations:

$$a_i(T) = 0.457235\frac{(RT_{ci})^2}{P_{ci}}[1+m_i\,(1-T_{ri}^{1/2})]^2 \quad (12)$$

$$m_i = k_{0i}+k_{1i}(1-T_{ri}^{1/2})(0.7-T_{ri}) \quad (13)$$

$$k_{0i} = 0.378893+1.4897153\omega_i-0.17138\omega_i^2+0.0196554\omega_i^3 \quad (14)$$

$$b_i = 0.077796\frac{RT_{ci}}{P_{ci}} \quad (15)$$

subscripts c and r denote critical and reduced values, respectively, ω_i is the acentric factor of pure compounds and k_{1i} is a pure component adjustable parameter that can be obtained by minimizing differences between the saturation pressures given for the corresponding Antoine's equation and those calculated from the equation of state. Critical properties were obtained from literature or calculated using group contribution methods [23, 29]. In Table 5, pure compounds parameters are collected.

The second equation is the Soave–Redlich–Kwong (SRK) cubic equation of state:

$$P = \frac{RT}{V_m-b} - \frac{a(T)}{V_m(V_m+b)} \quad (16)$$

Parameters a and b for pure components can be evaluated as follows:

$$a_i(T) = 0.42748\frac{(RT_{ci})^2}{P_{ci}}[1+m_i\,(1-T_{ri}^{1/2})]^2 \quad (17)$$

$$m_i = 0.480+1.574\omega_i-0.176\omega_i^2 \quad (18)$$

$$b_i = 0.08664\frac{RT_{ci}}{P_{ci}} \quad (19)$$

For both equations of state PRSV–EoS and SRK–EoS parameters a and b for the mixtures can be obtained from the following mixing rules [30]:

Table 5 Critical temperature, T_c, and pressure, P_c, acentric factor, ω, and adjustable parameter k_1 of the pure compounds

Compound	T_c/K	P_c/bar	ω	k_1
1,3-dioxolane	554.08	58.56	0.2616	0.1038
1-chlorobutane	542.2	36.85	0.2166	0.1843
2-chlorobutane	520.6	36.8	0.2672	0.0003
2-methyl-1-chloropropane	517.3	35.62	0.2895	–0.0088
2-methyl-2-chloropropane	501.2	38.36	0.2273	0.0445

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (a_i a_j)^{1/2}(1-k_{ij}) \quad (20)$$

$$b = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \left(\frac{b_i+b_j}{2}\right)(1-m_{ij}) \quad (21)$$

were k_{ij} and m_{ij} are adjustable parameters. Estimation of these parameters was based on minimization using the Marquardt algorithm [31] of the following objective function:

$$F = (V_{exptl}^E - V_{pred}^E)^2 \quad (22)$$

These parameters are enclosed for each mixture and equation of state in Table 6 together with the corresponding root mean square deviations, RMSD, between correlated and experimental values of excess volume. In Figs 5 and 6 the experimental and correlated V^E values are compared. Results show that both equations correlate satisfactorily the experimental V^E values, the worst correlation is for the mixture 1,3-dioxolane+2-methyl-2-chloropropane at 298.15 K.

The molar refraction, R_m, is considered the hard core volume of one mole of molecules [29], on the other hand parameter b is related to the size of the hard spheres. So, we have related the molar refraction with parameter b and we have found that these magnitudes, at least for the systems studied here, are closely correlated through an equation that we have supposed to be linear:

$$R_m = Ab+B \quad (23)$$

where molar refraction is calculated using experimental refractive index and density data and parameter b is estimated using an equation of state, SRK or PRSV.

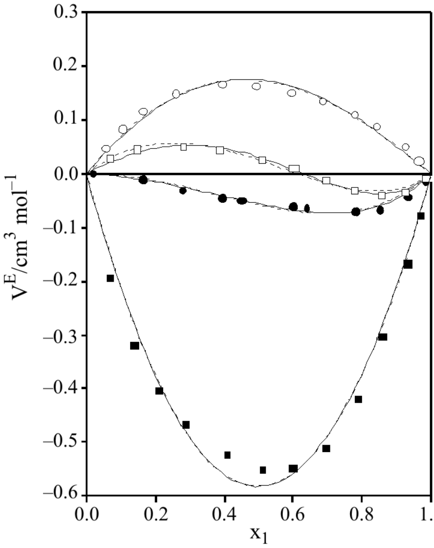

Fig. 5 Experimental and correlated V^E for 1,3-dioxolane(1)+isomeric chlorobutane(2) at 298.15 K: ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane, —— SRK equation, – – – PRSV equation

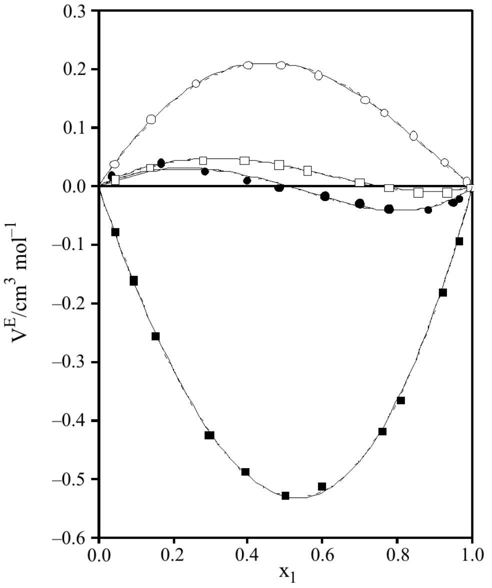

Fig. 6 Experimental and correlated V^E for 1,3-dioxolane(1)+isomeric chlorobutane(2) at 313.15 K: ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane; —– SRK equation, – – – PRSV equation

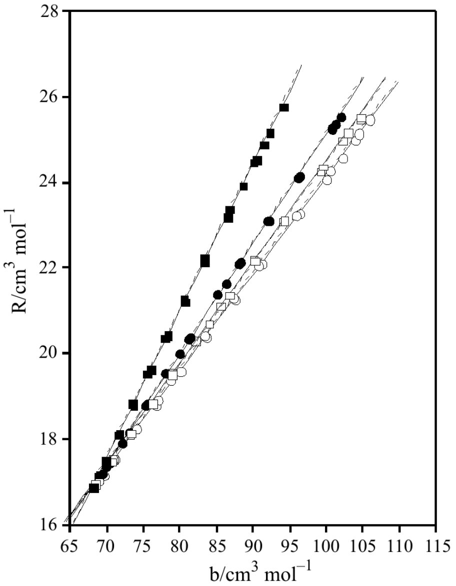

Fig. 7 Molar refraction, R_m, *vs*. parameter b of SRK equation for 1,3-dioxolane(1)+isomeric chlorobutane(2): ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane; —– 298.15 and – – – 313.15 K

In Eq. (23), the parameters A and B can be obtained form the following expressions:

$$A=\frac{R_{\mathrm{m},1}-R_{\mathrm{m},2}}{b_1-b_2} \tag{24}$$

$$B=\frac{R_{m,2}b_1-R_{m,1}b_2}{b_1-b_2} \tag{25}$$

being $R_{\mathrm{m,i}}$ and b_i the molar refraction and parameter b of each of the pure compounds respectively.

In Table 7 parameters A and B are reported together with the root mean square deviation, RMSD.

In Figs 7 and 8 the relation between experimental R_m and estimated parameter b is shown for each mole fraction, in these figures the graphical representation of Eq. (23) also appear.

This relation between R_m and b, can be employed to predict refractive indices from volumetric behaviour. Once the parameter b is obtained from excess volumes the molar refraction can be obtained and finally from this R_m value the refractive index can be estimated.

Table 6 Adjustable parameters, k_{12} and m_{12}, and root mean square deviations, *RMSD*, for V^E correlation using SRK or PRSV equations of state

Temperature/K	SRK			PRSV		
	k_{12}	m_{12}	RMSD	k_{12}	m_{12}	RMSD
			1,3-dioxolane(1)+1-chlorobutane(2)			
298.15	0.006	0.001	0.003	–0.001	0.002	0.003
313.15	0.033	0.007	0.001	0.028	0.012	0.000
			1,3-dioxolane(1)+2-chlorobutane(2)			
298.15	0.038	0.009	0.002	0.012	0.006	0.001
313.15	0.048	0.011	0.002	0.025	0.011	0.000
			1,3-dioxolane(1)+2-methyl-1-chloropropane(2)			
298.15	0.070	0.022	0.001	0.012	0.006	0.002
313.15	0.014	0.006	0.000	0.025	0.011	0.000
			1,3-dioxolane(1)+2-methyl-2-chloropropane(2)			
298.15	0.001	0.009	0.009	–0.006	0.000	0.009
313.15	0.025	0.010	0.002	0.0091	0.005	0.002

Table 7 Parameters, *A* and *B*, and root mean square deviations, RMSD, for Eq. (23)

Temperature/K	SRK			PRSV		
	A	*B*	RMSD	*A*	*B*	RMSD
			1,3-dioxolane(1)+1-chlorobutane(2)			
298.15	0.226	1.469	0.016	0.251	1.467	0.020
313.15	0.227	1.481	0.050	0.256	1.084	0.146
			1,3-dioxolane(1)+2-chlorobutane(2)			
298.15	0.256	–0.551	0.065	0.285	–0.552	0.041
313.15	0.256	–0.549	0.083	0.284	–0.551	0.081
			1,3-dioxolane(1)+2-methyl-1-chloropropane(2)			
298.15	0.236	0.825	0.096	0.270	0.335	0.068
313.15	0.236	0.823	0.041	0.270	0.353	0.039
			1,3-dioxolane(1)+2-methyl-2-chloropropane(2)			
298.15	0.342	–6.429	0.044	0.380	–6.446	0.007
313.15	0.342	–6.382	0.084	0.380	–6.399	0.037

Table 8 Prediction of refractive indices by means of Eq. (23) and SRK or PRSV equations of state

System	SRK		PRSV	
	298.15 K	313.15 K	298.15 K	313.15 K
1,3-dioxolane(1)+				
1-chlorobutane(2)	0.0003	0.0011	0.0004	0.0032
2-chlorobutane(2)	0.0014	0.0017	0.0009	0.0017
2-methyl-1-chloropropane(2)	0.0021	0.0009	0.0015	0.0008
2-methyl-2-chloropropane(2)	0.0008	0.0017	0.0002	0.0008

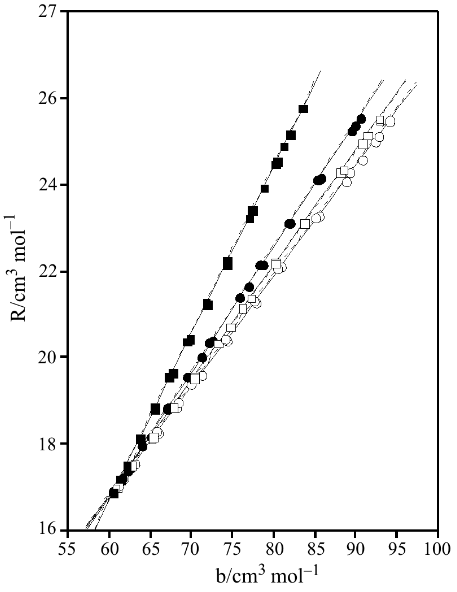

Fig. 8 Molar refraction, R_m, *vs*. parameter *b* of PRSV equation for 1,3-dioxolane(1)+isomeric chlorobutane(2): ○ – 1-chlorobutane, ● – 2-chlorobutane, □ – 2-methyl-1-chloropropane, ■ – 2-methyl-2-chloropropane; —– 298.15 and – – – 313.15 K

In Table 8 the results for the predictions of n_D in terms of root mean square deviations between experimental and predicted data are given.

Acknowledgements

We are grateful for financial assistance from Ministerio de Educación y Cultura (BQU 2003-01765) and Universidad de Zaragoza. B. Giner thanks the predoctoral grant from Ministerio de Educación y Cultura.

References

1 M. Nakata and M. Sakurai, J. Chem. Faraday Trans., 83 (1987) 2449.
2 A. Urbanczyk and W. A. Van Hook, J. Chem. Thermodyn., 28 (1996) 975.
3 M. E. Baur, D. A, Horsma, C. M. Knobler and P. Pérez, J. Chem. Phys., 73 (1969) 641.
4 M. Riazi and Y. Roomi, Ind. Eng. Chem. Res., 40 (2001) 1975.
5 A. H. Buep and M. Barón, J. Phys. Chem., 92 (1988) 840.
6 I. Gascón, S. Martín, B. Giner, M. Haro and C. Lafuente, Can. J. Chem., 81 (2003) 357.

7 I. Gascón, V. Rodríguez, P. Cea, C. Lafuente and M. C. López, J. Therm. Anal. Cal., 76 (2004) 429.
8 I. Gascón, M. C. López, C. Lafuente, F. M. Royo and P. Cea, Thermochim. Acta, 423 (2004) 49.
9 M. Haro, I. Gascón, P. Cea, C. Lafuente and F. M. Royo, J. Therm. Anal. Cal., 79 (2004) 51.
10 B. Giner, H. Artigas, A. Carrión, C. Lafuente and F. M. Royo, J. Mol. Liquids, 108 (2003) 303.
11 B. Giner, M. E. Aldea, S. Martín, I. Gascón and C. Lafuente, J. Chem. Eng. Data, 48 (2003) 1296.
12 B. Giner, A. Reyes, M. Haro, S. Martín and F. M. Royo, Phys. Chem. Liq., 42 (2004) 173.
13 B. Giner, A. Villares, I. Gascón, P. Cea and C. Lafuente, Int. J. Thermophys., 25 (2004) 1735.
14 H. A Lorentz, Wield. Ann. Phys., 9 (1880) 641.
15 L. Lorenz, Wield. Ann. Phys., 11 (1880) 70.
16 D. Dale and F. Gladstone, Phylos. Trans. R. Soc. London, 153 (1864) 317.
17 P. S. Laplace, Traite de Mechanique Celeste IV, X (1821) 32.
18 P. Eykman, Recherches Refractométriques, Haarlem 1919.
19 O. Redlich and J. N. S. Kwong, Chem. Rev., 44 (1949) 233.
20 G. Soave, Chem. Eng. Sci., 27 (1972) 1197.
21 D. Y. Peng and D. B. Robinson, Ind. Eng. Chem. Fund., 15 (1976) 59.
22 R. Stryjek and J. H. Vera, Can. J. Chem. Eng., 64 (1986) 820.
23 J. A. Riddick, W. B Bunger and T. K. Sakano, Organic Solvents. Physical Properties and Methods of Purification (Techniques of Chemistry), 3rd Ed., Wiley, New York 1986.
24 TRC Thermodynamic Tables-Non-Hydrocarbons, Selected Values of Properties of Chemical Compounds. Thermodynamic Research Center, Texas A&M University, College Station TX, 1994.
25 B. Giner, A. Villares, M.C. López, F. M. Royo and C. Lafuente, Phys. Chem. Liq., (2004) accepted.
26 Y. Y. Fialkov and G. N. Fenerly, Russ. J. Inorg. Chem., 9 (1964) 1205.
27 Y. Y. Fialkov, Russ. J. Phys. Chem., 41 (1967) 389.
28 P. Brocos, A. Piñeiro, R. Bravo and A. Amigo, Phys. Chem. Chem. Phys., 5 (2003) 550.
29 B. E. Poling, J. M. Prausnitz and J. P. O'Connell, The properties of Gases and Liquids, 5th Ed., McGraw-Hill, New York 2001.
30 J. F. Arnaud, P. Ungerer, E. Behar, B. Moracchini and J. Sánchez, Fluid Phase Equilib., 124 (1996) 177.
31 D. W. Marquardt, J. Soc. Ind. Appl. Math., 11 (1963) 431.

Received: June 9, 2005
Accepted: November 21, 2005

DOI: 10.1007/s10973-005-6943-x