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THERMODYNAMIC PROPERTIES OF BINARY MIXTURES FORMED BY CYCLIC ETHERS AND CHLOROALKANES

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Densities, speeds of sound and refractive indices of the binary mixtures 1,3-dioxolane or 1,4-dioxane+1-chloropentane or 1-chlorohexane have been measured at the temperatures of 298.15 and 313.15 K. Excess molar volumes, isentropic compressibilities, isentropic compressibility deviations and refractive index deviations have been obtained from experimental data. Excess molar volumes, isentropic compressibility and refractive index deviations have been fitted to a Redlich–Kister equation. Excess molar volumes, speeds of sound and isentropic compressibilities have been estimated at 298.15 K using the Prigogine–Flory–Patterson theory.

Keywords: *chloroalkane, cyclic ether, density, PFP theory, refractive index, speed of sound*

Introduction

Our research group has been involved in the last years in the determination of thermodynamic properties of binary liquid mixtures containing cyclic diethers and halogenated compounds [1–7]. The main objective of this research is to obtain experimental data of relevant properties of this kind of mixtures. These properties are used to test the applicability of different models and theories, comparing their predictions with experimental data, and also provide useful information for a better understanding of the phenomena taking place in the liquid mixtures, especially about the balance between molecular interactions in the pure compounds and in the mixture.

In this paper we report densities, speeds of sound and refractive indices of the binary mixtures 1,3-dioxolane or 1,4-dioxane+1-chloropentane or 1-chlorohexane at the temperatures of 298.15 and 313.15 K. From experimental data we have obtained excess molar volumes, isentropic compressibilities, isentropic compressibility deviations and refractive index deviations. Excess molar volumes, isentropic compressibility and refractive index deviations have been fitted to a Redlich–Kister equation and their values compared with those previously reported for other binary mixtures of the same cyclic ethers with 1-chlorobutane [1, 4, 6, 7]. We also have used the Prigogine–Flory–Patterson theory to estimate excess molar volumes, speeds of sound and isentropic compressibilities at 298.15 K.

To the best of our knowledge, we have no found any previous reference for the properties reported here for these systems. We only have reported [5] isentropic compressibility correlation coefficients for the binary mixtures 1,3-dioxolane or 1,4-dioxane+ 1-chloropentane at 298.15 K. These coefficients were used to calculate the composition of liquid and vapour phases in the study of isobaric VLE of these systems.

Experimental

The compounds used were: 1,3-dioxolane (>99%), 1,4-dioxane (>99.9%), 1-chloropentane (>99%) and 1-chlorohexane (99>%) obtained from Aldrich. The purity of the chemicals was checked by comparing the measured densities and refractive indices with those reported in the literature. Additional purification has not been made.

Densities, ρ, of the pure compounds and their mixtures were determined with an Anton Paar DMA-58 vibrating tube densimeter automatically thermostated within ±0.01 K. The accuracy of the densimeter after proper calibration with deionized doubly distilled water and dry air is $\pm 10^{-5}$ g cm^{-3} and the precision of the density measurements was $\pm 5 \cdot 10^{-6}$ g cm^{-3}.

Speeds of sound, u, were obtained with an Anton Paar DSA-48 vibrating tube densimeter and sound analyzer. The temperature was automatically kept constant within ±0.01 K. The precision of the speed of sound measurements is ±0.1 m s^{-1}. The accuracy of the speed of sound is ±1 m s^{-1}. Calibration of the ap-

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Table 1 Properties of the pure components

Compound	ρ/g cm^{-3}		u/m s^{-1}		n_D	
	T=298.15 K	T=313.15 K	T=298.15 K	T=313.15 K	T=298.15 K	T=313.15 K
1,3-Dioxolane	1.05862	1.03988	1338.8	1270.8	1.397971	1.390578
1,4-Dioxane	1.02787	1.01069	1344.0	1278.6	1.419948	1.412637
1-Chloropentane	0.87700	0.86152	1164.5	1099.9	1.409818	1.402160
1-Chlorohexane	0.87356	0.85901	1198.4	1136.3	1.417325	1.410068

paratus was carried out with air and deionized double-distilled water.

The corresponding refractive indices at 589.3 nm sodium D wavelength were measured using a high precision automatic refractometer Abbemat-HP DR. Kernchen whose temperature was internally controlled within ±0.01 K. The apparatus was calibrated with deionized double-distilled water. The reproducibility of the measurements is $\pm 1\cdot 10^{-6}$ and the corresponding accuracy is $\pm 2\cdot 10^{-5}$.

The pure compound properties at 298.15 and 313.15 K are collected in Table 1. Mixtures were prepared by mass using a Sartorius semi-micro balance with a precision of $\pm 10^{-5}$ g. The possible error in the mole fractions is estimated to be less than 10^{-4}.

Results and discussion

Excess molar volumes, V^E, were calculated from the density of the mixture, ρ, densities, ρ_i, and molar masses, M_i, of the pure compounds, and the corresponding molar fractions, x_i, by means of the equation:

$$V^E = x_1\left(\frac{M_1}{\rho} - \frac{M_1}{\rho_1}\right) + x_2\left(\frac{M_2}{\rho} - \frac{M_2}{\rho_2}\right) \qquad (1)$$

Isentropic compressibilities, κ_S, and isentropic compressibility deviations, $\Delta\kappa_S$, were estimated from densities, ρ, and speeds of sound, u, by using the following equations:

$$\kappa_S = \frac{1}{\rho u^2} \qquad (2)$$

$$\Delta\kappa_S = \kappa_S - \sum_i x_i \kappa_{S,i} \qquad (3)$$

Refractive index deviations, Δn_D, were calculated following the suggestions of Fialkov and Fenerly [8] and Fialkov [9] by means of the equation:

$$\Delta n_D = n_D - \phi_1 n_{D,1} - \phi_2 n_{D,2} \qquad (4)$$

where n_D is the refractive index of the mixture, $n_{D,i}$ is the refractive index of component i and ϕ_i is the volume fraction of component i in the mixture referred to the unmixed state.

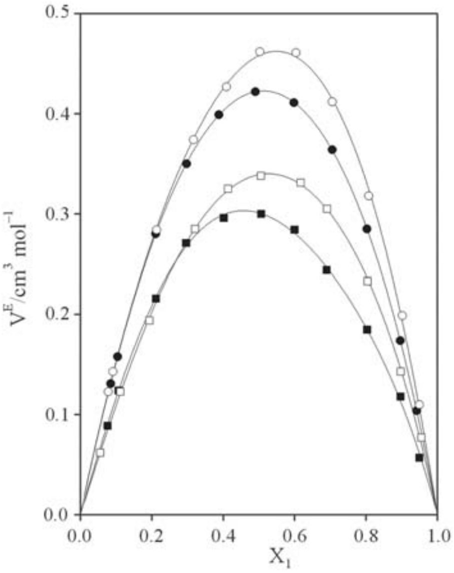

Fig. 1 Excess volumes at 298.15 K for ■ – 1,3-dioxolane +1-chloropentane, ● – 1,3-dioxolane+1-chlorohexane, □ – 1,4-dioxane+ 1-chloropentane, ○ – 1,4-dioxane +1-chlorohexane; — – Redlich–Kister equation

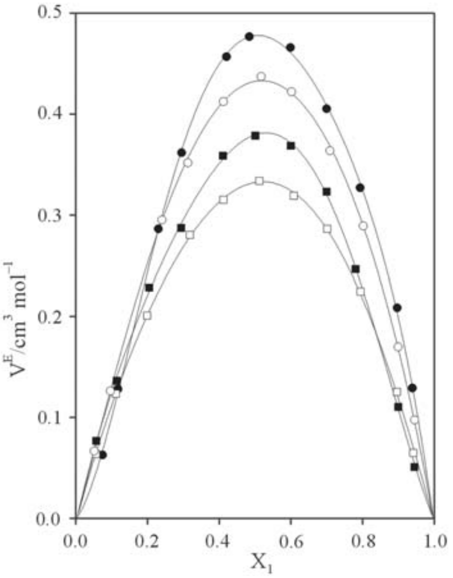

Fig. 2 Excess volumes at 313.15 K for ■ – 1,3-dioxolane +1-chloropentane, ● – 1,3-dioxolane+1-chlorohexane, □ – 1,4-dioxane+ 1-chloropentane, ○ – 1,4-dioxane +1-chlorohexane; — – Redlich–Kister equation

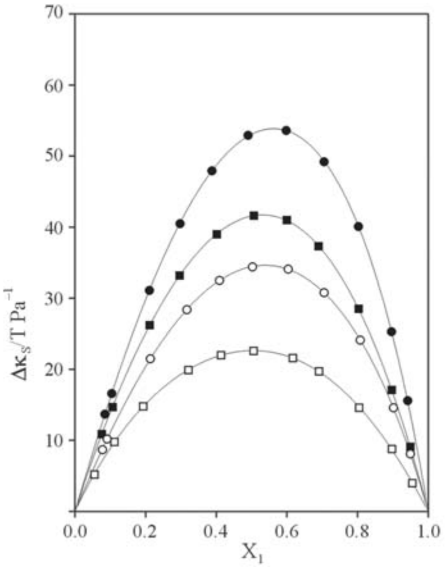

Fig. 3 Isentropic compressibility deviations at 298.15 K for ■ – 1,3-dioxolane +1-chloropentane, ● – 1,3-dioxolane+1-chlorohexane, □ – 1,4-dioxane+ 1-chloropentane, ○ – 1,4-dioxane +1-chlorohexane; — – Redlich–Kister equation

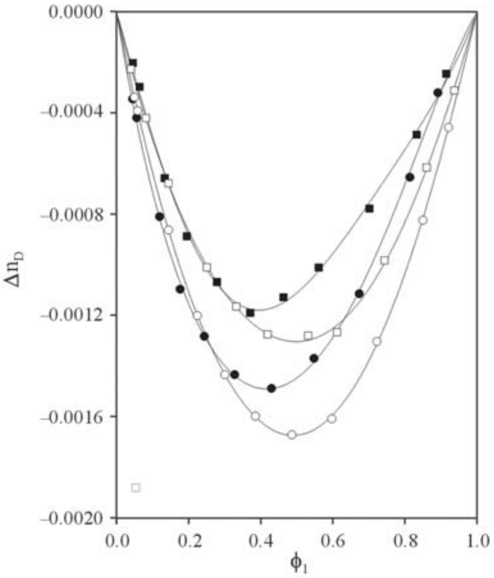

Fig. 5 Refractive index deviations at 298.15 K for ■ – 1,3-dioxolane +1-chloropentane, ● – 1,3-dioxolane+1-chlorohexane, □ – 1,4-dioxane+ 1-chloropentane, ○ – 1,4-dioxane +1-chlorohexane; — – Redlich–Kister equation

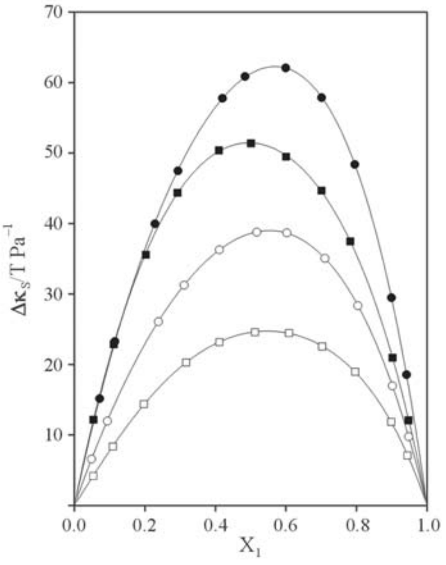

Fig. 4 Isentropic compressibility deviations at 313.15 K for ■ – 1,3-dioxolane +1-chloropentane, ● – 1,3-dioxolane+1-chlorohexane, □ – 1,4-dioxane+ 1-chloropentane, ○ – 1,4-dioxane +1-chlorohexane; — – Redlich–Kister equation

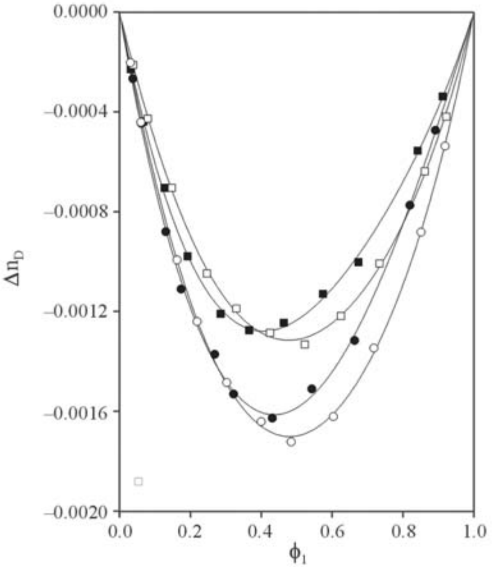

Fig. 6 Refractive index deviations at 313.15 K for ■ – 1,3-dioxolane +1-chloropentane, ● – 1,3-dioxolane+1-chlorohexane, □ – 1,4-dioxane+ 1-chloropentane, ○ – 1,4-dioxane +1-chlorohexane; — – Redlich–Kister equation

In Table 2 appear experimental values of ρ, u, n_D as well as calculated values of κ_S, V^E, $\Delta\kappa_S$, and Δn_D for the studied mixtures at both temperatures. The excess molar volumes, isentropic compressibility and refractive index deviations have been plotted in Figs 1 to 6.

Excess molar volumes, isentropic compressibility deviations and refractive index deviations at each temperature have been correlated with a Redlich–Kister polynomial equation

$$Y = y_1 y_2 \sum_{p=0}^{r} A_p (y_1 - y_2)^p \tag{5}$$

where $Y=V^E$, $\Delta\kappa_S$, or Δn_D; A_p are adjustable parameters and y is the mole fraction for excess molar vol-

Table 2 Densities, ρ, speeds of sound, u, isentropic compressibilities, κ_S, refractive indices, n_D, excess volumes, V^E, isentropic compressibility deviations, $\Delta\kappa_S$, and refractive index deviations, Δn_D, for the studied mixtures

x_1	ϕ_1	ρ/g cm^{-3}	u/m s^{-1}	κ_S/T Pa^{-1}	n_D	V^E/cm^3 mol^{-1}	$\Delta\kappa_S$/T Pa^{-1}	Δn_D
1,3-dioxolane (1)+1-chloropentane (2) at 298.15 K								
0.0759	0.0452	0.88453	1168.6	827.9	1.409081	0.089	10.9	–0.000202
0.1064	0.0642	0.88770	1170.5	822.2	1.408760	0.124	14.7	–0.000297
0.2115	0.1338	0.89954	1178.3	800.7	1.407575	0.216	26.2	–0.000658
0.2963	0.1951	0.91012	1186.0	781.1	1.406619	0.271	33.2	–0.000888
0.4015	0.2786	0.92489	1197.6	753.9	1.405448	0.296	39.0	–0.001069
0.5061	0.3710	0.94143	1211.6	723.6	1.404232	0.300	41.6	–0.001191
0.5998	0.4632	0.95812	1226.7	693.6	1.403201	0.284	41.0	–0.001129
0.6893	0.5609	0.97610	1244.2	661.8	1.402161	0.244	37.3	–0.001012
0.8029	0.7011	1.00201	1271.4	617.4	1.400734	0.185	28.5	–0.000778
0.8962	0.8325	1.02660	1299.7	576.7	1.399469	0.118	17.1	–0.000486
0.9489	0.9145	1.04227	1318.1	552.2	1.398739	0.057	9.1	–0.000245
1,3-dioxolane (1)+1-chlorohexane (2) at 298.15 K								
0.0844	0.0446	0.88094	1200.2	788.0	1.416117	0.132	13.7	–0.000345
0.1042	0.0557	0.88277	1200.8	785.6	1.415828	0.162	16.6	–0.000419
0.2110	0.1194	0.89366	1204.6	771.2	1.414204	0.275	31.1	–0.000810
0.2972	0.1765	0.90355	1208.9	757.3	1.412812	0.348	40.5	–0.001097
0.3879	0.2431	0.91528	1214.9	740.2	1.411337	0.398	47.9	–0.001283
0.4897	0.3272	0.93034	1223.8	717.7	1.409557	0.425	52.9	–0.001435
0.5977	0.4295	0.94901	1236.4	689.3	1.407523	0.414	53.6	–0.001489
0.7050	0.5477	0.97104	1253.0	655.9	1.405354	0.36	49.2	–0.001371
0.8024	0.6730	0.99475	1272.8	620.5	1.403185	0.281	40.1	–0.001115
0.8960	0.8136	1.02177	1298.5	580.4	1.400925	0.178	25.3	–0.000654
0.9418	0.8913	1.03700	1314.2	558.3	1.399755	0.107	15.6	–0.000320
1,4-dioxane (1)+1-chloropentane (2) at 298.15 K								
0.0550	0.0394	0.88249	1168.9	829.3	1.409991	0.062	5.2	–0.000226
0.1116	0.0814	0.88835	1173.9	816.9	1.410223	0.123	9.8	–0.000420
0.1934	0.1446	0.89730	1182.4	797.1	1.410605	0.194	14.8	–0.000678
0.3210	0.2500	0.91236	1198.0	763.7	1.411340	0.285	19.9	–0.001011
0.4136	0.3322	0.92430	1210.9	737.9	1.412017	0.325	22.0	–0.001166
0.5058	0.4192	0.93718	1225.4	710.6	1.412789	0.338	22.6	–0.001275
0.6168	0.5316	0.95403	1245.2	676.0	1.413922	0.331	21.6	–0.001281
0.6906	0.6115	0.96622	1260.1	651.8	1.414745	0.305	19.7	–0.001267
0.8043	0.7435	0.98669	1286.6	612.3	1.416367	0.233	14.6	–0.000983
0.8973	0.8604	1.00520	1311.5	578.4	1.417918	0.143	8.8	–0.000616
0.9549	0.9372	1.01750	1329.3	556.2	1.419001	0.077	4.0	–0.000311
1,4-dioxane (1)+1-chlorohexane (2) at 298.15 K								
0.0777	0.0497	0.88042	1202.3	785.8	1.417117	0.123	8.7	–0.000338
0.0909	0.0584	0.88163	1203.0	783.8	1.417087	0.143	10.2	–0.000391
0.2134	0.1441	0.89380	1210.6	763.4	1.416840	0.284	21.5	–0.000863
0.3171	0.2238	0.90530	1218.9	743.5	1.416711	0.374	28.4	–0.001201
0.4092	0.3007	0.91660	1227.7	723.8	1.416679	0.427	32.5	–0.001435
0.5025	0.3854	0.92919	1238.5	701.6	1.416737	0.462	34.4	–0.001599
0.6038	0.4861	0.94449	1252.3	675.1	1.416927	0.461	34.1	–0.001673

Table 2 Continued

x_1	ϕ_1	ρ/g cm^{-3}	u/m s^{-1}	κ_S/T Pa^{-1}	n_D	V^E/cm^3 mol^{-1}	$\Delta\kappa_S$/T Pa^{-1}	Δn_D
0.7049	0.5972	0.96180	1268.9	645.7	1.417281	0.412	30.8	–0.001610
0.8073	0.7223	0.98176	1289.6	612.5	1.417916	0.318	24.1	–0.001304
0.9012	0.8499	1.00251	1312.9	578.7	1.418730	0.199	14.6	–0.000824
0.9493	0.9208	1.01438	1327.0	559.8	1.419283	0.110	8.1	–0.000457
1,3-dioxolane (1)+1-chloropentane (2) at 313.15 K								
0.0538	0.0317	0.86662	1100.9	952.1	1.401565	0.077	12.2	–0.000228
0.1117	0.0675	0.87255	1103.2	941.7	1.400940	0.137	22.9	–0.000438
0.2024	0.1275	0.88246	1109.0	921.4	1.399980	0.230	35.6	–0.000703
0.2921	0.1920	0.89338	1116.8	897.5	1.398958	0.289	44.4	–0.000978
0.4097	0.2855	0.90923	1130.4	860.7	1.397645	0.361	50.4	–0.001208
0.5005	0.3658	0.92316	1143.3	828.7	1.396649	0.381	51.4	–0.001274
0.6003	0.4637	0.94045	1159.8	790.5	1.395545	0.371	49.5	–0.001244
0.7007	0.5741	0.96033	1179.0	749.1	1.394383	0.325	44.7	–0.001128
0.7826	0.6745	0.97890	1197.7	712.1	1.393347	0.248	37.5	–0.001001
0.9021	0.8414	1.01013	1232.1	652.1	1.391861	0.111	21.0	–0.000554
0.9476	0.9124	1.02355	1248.7	626.6	1.391256	0.051	12.1	–0.000337
1,3-dioxolane (1)+1-chlorohexane (2) at 313.15 K								
0.0715	0.0376	0.86541	1136.3	894.9	1.409069	0.063	15.2	–0.000266
0.1148	0.0617	0.86933	1137.0	889.8	1.408420	0.129	23.3	–0.000445
0.2283	0.1305	0.88058	1141.4	871.7	1.406646	0.288	40.0	–0.000879
0.2934	0.1740	0.88779	1144.9	859.3	1.405568	0.364	47.5	–0.001109
0.4200	0.2687	0.90387	1154.0	830.8	1.403461	0.460	57.8	–0.001370
0.4836	0.3221	0.91317	1159.5	814.5	1.402261	0.480	60.9	–0.001529
0.5990	0.4311	0.93255	1172.3	780.3	1.400040	0.471	62.1	–0.001626
0.7006	0.5428	0.95295	1186.8	745.0	1.397980	0.408	57.9	–0.001509
0.7951	0.6631	0.97520	1204.7	706.6	1.395829	0.329	48.4	–0.001315
0.8993	0.8192	1.00448	1232.1	655.8	1.393329	0.210	29.5	–0.000773
0.9419	0.8916	1.01851	1246.5	631.9	1.392219	0.130	18.6	–0.000472
1,4-dioxane (1)+1-chloropentane (2) at 313.15 K								
0.0536	0.0384	0.86679	1105.1	944.7	1.402351	0.064	4.2	–0.000210
0.1094	0.0797	0.87250	1110.7	929.1	1.402569	0.124	8.4	–0.000426
0.1969	0.1473	0.88196	1119.9	904.1	1.403000	0.202	14.4	–0.000703
0.3171	0.2465	0.89604	1134.3	867.4	1.403697	0.282	20.3	–0.001046
0.4108	0.3294	0.90801	1147.0	837.1	1.404423	0.317	23.2	–0.001187
0.5118	0.4248	0.92194	1162.4	802.8	1.405327	0.336	24.6	–0.001284
0.6084	0.5226	0.93651	1178.8	768.4	1.406304	0.321	24.5	–0.001331
0.7027	0.6248	0.95193	1197.1	733.1	1.407489	0.288	22.6	–0.001217
0.7960	0.7333	0.96859	1217.5	696.5	1.408837	0.226	19.0	–0.001006
0.8983	0.8616	0.98867	1244.5	653.1	1.410550	0.126	11.9	–0.000637
0.9441	0.9225	0.99840	1258.8	632.1	1.411407	0.065	7.1	–0.000418
1,4-dioxane (1)+1-chlorohexane (2) at 313.15 K								
0.0482	0.0305	0.86322	1138.4	893.9	1.409945	0.067	6.6	–0.000201
0.0934	0.0601	0.86732	1140.8	885.9	1.409782	0.127	12.0	–0.000440
0.2382	0.1626	0.88162	1150.4	857.1	1.409494	0.297	26.1	–0.000992
0.3110	0.2189	0.88967	1156.3	840.7	1.409391	0.354	31.3	–0.001239

Table 2 Continued

x_1	ϕ_1	ρ/g cm^{-3}	u/m s^{-1}	κ_S/T Pa^{-1}	n_D	V^E/cm^3 mol^{-1}	$\Delta\kappa_S$/T Pa^{-1}	Δn_D
0.4112	0.3024	0.90172	1165.8	816.0	1.409362	0.415	36.3	–0.001483
0.5172	0.3994	0.91602	1177.7	787.1	1.409454	0.440	38.8	–0.001640
0.6022	0.4845	0.92885	1188.8	761.8	1.409592	0.425	38.7	–0.001721
0.7100	0.6032	0.94712	1205.7	726.3	1.409999	0.366	35.1	–0.001619
0.8035	0.7174	0.96495	1223.8	691.9	1.410566	0.291	28.4	–0.001345
0.9018	0.8508	0.98623	1247.7	651.3	1.411373	0.171	17.0	–0.000881
0.9479	0.9187	0.99727	1261.1	630.5	1.411892	0.098	9.8	–0.000536

umes and isentropic compressibility deviations or the volume fraction for refractive index deviations. The values of adjustable parameters together with standard deviations $\sigma(Y)$ are given in Table 3.

Excess molar volumes and isentropic compressibility deviations are positive for all the binary mixtures at both temperatures, while refractive index deviations are negative for all the systems at two temperatures. It has been reported before [10] that, for a system, values of V^E and Δn_D have an opposite sign when Δn_D are calculated in a volume fraction basis. Therefore, usually V^E and $\Delta\kappa_S$ have the same sign, as it is observed for the binary mixtures studied here.

For a given cyclic ether (1,3-dioxolane or 1,4-dioxane) at both temperatures, excess molar volumes are bigger for his mixture with 1-chlorohexane than those for the system containing 1-chloropentane, and those are bigger than V^E reported for the systems cyclic ether+1-chlorobutane [1, 6]. The effect of temperature on V^E is not very significant, although it is opposite for the two ethers: V^E values slightly increase when temperature rises in systems containing 1,3-dioxolane, while V^E values become a little smaller in the mixtures of 1,4-dioxane. This opposite shift gives that V^E values at 298.15 K are slightly bigger for the mixtures containing 1,4-dioxane instead of 1,3-dioxolane, while at 313.15 K, V^E values are a little bigger for the mixtures containing 1,3-dioxolane. Nevertheless V^E values are very similar for both ethers at both temperatures, when mole fractions of the ether are less than 0.4.

Isentropic compressibility deviations are also bigger for the binary mixtures cyclic ether+1-chlorohexane than for the systems with 1-chloropentane, and those are again bigger than $\Delta\kappa_S$ values obtained for the binary mixtures of the same cyclic ethers with 1-chlorobutane [4]. Therefore $\Delta\kappa_S$ are bigger for the systems containing 1,3-dioxolane than for the mixtures of the chlorinated compounds with 1,4-dioxane. $\Delta\kappa_S$ values slightly increase in all the systems when temperature increases.

As we have mentioned above the volumetric behaviour is opposite to refractive one. Consequently, Δn_D values are more negative (bigger in absolute value) for mixtures containing 1-chlorohexane instead of 1-chloropentane, and those are more negative than Δn_D in the binary mixtures containing 1-chlorobutane [6, 7] at both temperatures. For a given halogenated compound, Δn_D values are slightly more negative for the binary system containing 1,4-dioxane instead of 1,3-dioxolane at 298.15 K, while they are very similar for both cyclic ethers at 313.15 K.

Values of thermodynamic properties of solutions are the results of several energetic and structural contributions. Energetic contributions depended on the balance between the breaking of interactions existing in the pure compounds and new specific interactions between the components of the mixture. Among structural effects, we can signal differences in size and shape, and interstitial accommodation, which are related with changes in free volume.

Positive excess molar volumes and isentropic compressibility deviations indicate that, in these systems, the breaking of self-interactions predominates over donor-acceptor interactions between oxygen and chlorine atoms. It is remarkable that V^E values are very similar for both ethers, while more differences are observed in $\Delta\kappa_S$ values. Relatively large and positive isentropic compressibilities deviations indicate a significant disruption of the molecular order existing in the pure compounds. This effect is more marked in mixtures containing 1,3-dioxolane, which can be considered as a polar fluid in contrast with 1,4-dioxane which is a non polar fluid [11].

Δn_D values can be interpreted as a sign-reversed measure of the deviation of reduced free volume, and hence of changes in intermolecular interactions [10]. Consequently negative values of Δn_D indicate an increase of the unoccupied part of the molar volume in the mixture, compared with an ideal solution. From experimental results we can realize that this increase is mostly related with the size of the chlorinated component. The bigger is the chlorinated compound, the deeper is the disruption of the structure of the cyclic ethers. It also makes more difficult interstitial accom-

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

Function	T/K	A_0	A_1	A_2	A_3	$\sigma(Y)$
1,3-dioxolane (1)+1-chloropentane (2)						
V^E	298.15	1.204	–0.203	0.089	0.252	0.003
	313.15	1.527	0.235	–0.304	–0.555	0.004
$\Delta\kappa_S$	298.15	166.2	20.2	5.6	–2.9	0.1
	313.15	205.8	–3.2	45.0	9.8	0.1
Δn_D	298.15	–0.004451	0.002399	–0.000029	–0.001787	0.000026
	313.15	–0.004935	0.001792	–0.000833	–0.000380	0.000020
1,3-dioxolane (1)+1-chlorohexane (2)						
V^E	298.15	1.690	0.079	0.140	0.047	0.004
	313.15	1.923	0.077	–0.336	0.957	0.005
$\Delta\kappa_S$	298.15	212.2	49.9	20.1	14.9	0.1
	313.15	245.1	57.4	49.6	5.4	0.1
Δn_D	298.15	–0.005794	0.002055	0.000142	0.001116	0.000019
	313.15	–0.006341	0.001686	–0.000021	0.000172	0.000026
1,4-dioxane (1)+1-chloropentane (2)						
V^E	298.15	1.356	0.137	0.061	0.146	0.003
	313.15	1.327	0.123	–0.031	–0.114	0.004
$\Delta\kappa_S$	298.15	90.5	1.4	9.5	–6.8	0.1
	313.15	98.3	15.6	15.3	18.1	0.1
Δn_D	298.15	–0.005219	0.000028	–0.000248	0.000424	0.000015
	313.15	–0.005246	0.000428	–0.000562	–0.000486	0.000018
1,4-dioxane (1)+1-chlorohexane (2)						
V^E	298.15	1.832	0.341	0.164	–0.068	0.004
	313.15	1.741	0.132	–0.055	0.193	0.003
$\Delta\kappa_S$	298.15	137.7	19.9	8.9	8.0	0.1
	313.15	154.5	29.6	19.4	1.9	0.0
Δn_D	298.15	–0.006701	0.000266	0.000005	0.000301	0.000007
	313.15	–0.006790	0.000487	–0.000666	–0.000389	0.000018

modation and leads to more expanded mixtures: i.e. V^E, $\Delta\kappa_S$ and $|\Delta n_D|$ values follow the sequence 1-chlorohexane>1-chloropentane>1-chlorobutane.

Prigogine–Flory–Patterson theory

Oswal [12] extended the Prigogine–Flory–Patterson [13, 14] theory to estimate the isentropic compressibilities and speeds of sound of liquid mixtures. At a given temperature, T, the PFP theory can be used to calculate the molar volumes, V, the molar heat capacities, C_P of a liquid mixture if the interaction parameter, χ_{12}, is known. The terms $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ can be also calculated by means of the following equations:

$$(\partial V/\partial P)_T = \frac{-\tilde{V}^{7/3}+2\tilde{V}^{2}-2\tilde{V}^{5/3}}{(4/3)-\tilde{V}^{1/3}}\frac{V^*T^*}{P^*T} \qquad (6)$$

$$(\partial V/\partial T)_P = \frac{\tilde{V}(\tilde{V}^{1/3}-1)}{(4/3)-\tilde{V}^{1/3}}\frac{V^*}{T} \qquad (7)$$

where V^*, P^* and T^* are the characteristic volume, pressure and temperature of the mixture respectively and $\tilde{V}$ is the corresponding reduced volume.

From all these quantities the isentropic compressibility, $\kappa_S=-V^{-1}(\partial V/\partial P)_S$, can be obtained using the following thermodynamic relation:

$$(\partial V/\partial P)_S = (\partial V/\partial P)_T + TC_P^{-1}(\partial V/\partial T)_P^2 \qquad (8)$$

and finally the isentropic compressibility is related to the speed of sound, u, by the Eq. (2).

Table 4 Physical properties and Flory parameters of the pure compounds at 298.15 K

Compound	α/K^{-1}	κ_T/T Pa^{-1}	$\tilde{V}$	P^*	s
1,3-Dioxolane	0.001164	758.1	1.280	750	1.23
1,4-Dioxane	0.001132	738.0	1.274	742	1.25
1-Chloropentane	0.001119	1082.6	1.272	499	1.41
1-Chlorohexane	0.001027	997.9	1.253	482	1.40

Table 5 Comparison between experimental and theoretical V^E, κ_S and u at equimolar composition together with calculated contributions to V^E at equimolar composition at 298.15 K

Function	Exptl	PFP	Interactional	Free volume	Internal pressure
		1,3-dioxolane+1-chloropentane (χ_{12}=18.2 J cm^{-3})			
V^E/cm^3 mol^{-1}	0.301	0.301	0.243	–0.002	0.060
κ_S/T Pa^{-1}	725.5	703.7			
u/m s^{-1}	1210.7	1229.3			
		1,3-dioxolane+1-chlorohexane (χ_{12}=15.6 J cm^{-3})			
V^E/cm^3 mol^{-1}	0.423	0.423	0.213	–0.022	0.231
κ_S/T Pa^{-1}	715.1	694.7			
u/m s^{-1}	1224.8	1242.7			
		1,4-dioxane+1-chloropentane (χ_{12}=21.9 J cm^{-3})			
V^E/cm^3 mol^{-1}	0.339	0.339	0.323	0.000	0.016
κ_S/T Pa^{-1}	712.3	682.0			
u/m s^{-1}	1224.5	1251.4			
		1,4-dioxane+1-chlorohexane (χ_{12}=18.1 J cm^{-3})			
V^E/cm^3 mol^{-1}	0.458	0.458	0.277	–0.015	0.196
κ_S/T Pa^{-1}	702.2	675.3			
u/m s^{-1}	1238.2	1262.6			

Flory parameters [15–18] of the pure compounds along with their physical properties are given in Table 4. Physical properties for the cyclic ethers were taken from a previous work [2], for the chloroalkanes the thermal expansion coefficients, α, were derived from our own density measurements and isothermal compressibilities, κ_T, were calculated from thermal expansion coefficients, experimental isentropic compressibilities, and molar heat capacities [19]. The number of contact sites per segment of a molecule, s, has been estimated using Bondi's method [20].

In this work the interaction parameter for each mixture was obtained by fitting the PFP theory to the corresponding experimental equimolar V^E values. Once the interaction parameter is obtained, the isentropic compressibility and the speed of sound can be estimated. In Table 5 we can see that only one interaction parameter allows a perfect fitting of the experimental V^E values at equimolar composition. In the same table we also have reported the calculated and experimental equimolar u and κ_S values.

Estimated speeds of sound and isentropic compressibilities are in good agreement with experimental values. Predictions are better for 1,3-dioxolane mixtures (nearly 1.5% deviation from experimental data for speed of sound and 2.9% deviation from experimental isentropic compressibilities) than for 1,4-dioxane systems whose deviations in speed of sound are 2.1% from experimental values and nearly 4% for isentropic compressibilities.

It is also interesting to observe the values of the different contributions to V^E values, included in Table 5. The interactional contribution is bigger for the mixtures containing 1,4-dioxane instead of 1,3-dioxolane and for the mixtures containing 1-chloropentane instead of 1-chlorohexane. But these differences are not as relevant as the disparity of the internal pressure effect, which is quite relevant in the binary mixtures of 1-chlorohexane (about 50% of the total value) and small in the mixtures containing 1-chloropentane.

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