Density, Speed of Sound, and Refractive Index of the Binary Systems Cyclohexane (1) or Methylcyclohexane (1) or Cyclo-octane (1) with Benzene (2), Toluene (2), and Ethylbenzene (2) at Two Temperatures

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Densities, speeds of sound, and refractive indices of binary systems containing cycloalkanes (cyclohexane and methylcyclohexane) with aromatic compounds (benzene, toluene, and ethylbenzene) at $T =$ (283.15 and 298.15) K and cyclo-octane with aromatic compounds at $T = 298.15$ K under atmospheric pressure were determined over the whole composition range. From the experimental results, the derived and excess properties (excess molar volumes, isentropic compression, excess molar isentropic compressibility, and refractive index deviations) at $T =$ (283.15 and 298.15) K were calculated and satisfactorily fitted to the Redlich−Kister equation.

Introduction

Information about the physical properties of pure liquids and liquid mixtures containing aromatic and aliphatic compounds and their dependence with composition and temperature is very important basic data for their use in the extraction and separation processes. Aromatic hydrocarbons are very important to the petrochemical industry. Extraction of aromatics from refinery products such as naphtha, kerosene, and fuel jets by liquid−liquid extraction (LLE) has a potential of commercial importance in the oil refining industry.

The binary systems containing alkanes with aromatic compounds are available in the literature[1−16] at $T = 298.15$ K, but review of the literature shows that there are no measurements at lower temperatures. The literature studies usually focus on density and excess molar volume. In this paper, as an extension of our work concerning the study of the behavior of cycloalkanes and alkanes with aromatic compounds,[16,17] the density, speed of sound, and refractive index at $T =$ (283.15 and 298.15) K were measured under atmospheric pressure for the binary systems containing cycloalkanes (1) (cyclohexane and methylcyclohexane) with aromatic compounds (2) (benzene, toluene, and ethylbenzene) and cyclo-octane (1) with benzene (2), toluene (2), and ethylbenzene (2) only at $T = 298.15$ K, since the melting point of cyclo-octane is 287.74[18] K. The experimental results were used to calculate excess molar volumes, isentropic compressibility, excess molar isentropic compressibility, and refractive deviations.

Experimental Section

Chemicals. Cyclohexane and methylcyclohexane were supplied by Fluka with purity higher than 99.9 % and 99.0 %, respectively. Benzene was supplied by Merck with purity higher than 99.8 %, and cyclo-octane, toluene, and ethylbenzene were supplied by Sigma-Aldrich with purity higher than 99.0 %, 99.8 %, and 99.8 %, respectively. They were degassed ultrasonically and dried over molecular sieves of type 4 Å, supplied by Aldrich, and kept in an inert argon atmosphere. Table 1 shows a comparison between experimental and literature (density, heat capacity, isobaric expansibility) data[19−22] of pure components at $T = 298.15$ K; a good agreement can be observed between both data.

Apparatus and Procedure. Samples were prepared by syringing known masses of the pure liquids into stoppered bottles. For mass measurements, a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g was used. Good mixing was ensured by magnetic stirring. All samples were prepared immediately prior to measurements to avoid variations in composition due to the evaporation of solvent.

Densities and speeds of sound were measured using an Anton Paar DSA-48 digital vibrating-tube densimeter. The uncertainty in experimental measurements has been found to be lower than $\pm 10^{-4}$ g·cm^{-3} for the density and ± 1 m·s^{-1} for the speed of sound. The apparatus was calibrated by air and water, according to the manual instruction. The calibration was checked with pure liquids shown in Table 1.

To measure refractive indices of pure components and their mixtures, an automatic refractometer (Abbemat-HP, Dr. Kernchen) with an uncertainty in the experimental measurements of $\pm 4 \cdot 10^{-5}$ was used.

Results and Discussion

The experimental data of density, speed of sound, refractive index, isentropic compressibility, excess molar volume, excess molar isentropic compressibility, and refractive index deviations for the binary systems (cyclohexane (1) or methylcyclohexane (1) + benzene (2), + toluene (2), or + ethyl-benzene (2)) at $T =$ (283.15 and 298.15) K and cyclo-octane (1) with benzene (2), toluene (2), and ethylbenzene (2) at $T = 298.15$ K, under atmospheric pressure are reported in Tables 2 and 3. The excess molar volumes and refractive index deviation were calculated by the following equation:

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10.1021/je900468u CCC: $40.75
Published on Web 10/15/2009

$$V^{E} = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

$$\Delta n_D = n_D - \sum_{i}^{N} x_i n_{D,i} \quad (2)$$

where ρ and ρ_i are the density of the mixture and the density of the pure components, respectively; x_i represents the mole fraction of the component i, and n_D and $n_{D,i}$ are the refractive index of the mixture and the pure component, respectively.

The speed of sound, u, is related to the isentropic compressibility, κ_s, by Laplace equation:

$$\kappa_s = -V_m^{-1}(\partial V_m/\partial p)_S = \rho^{-1}u^{-2} = V_m/(M_m u^2) \quad (3)$$

where, V_m is the molar volume and M_m is the molar mass of the mixture.

To achieve agreement with the other thermodynamic quantities, it is appropriate to shift from the volume-intensive κ_s to the mole-intensive quantity $K_{S,m}$[23,24]

$$K_{S,m} = -(\partial V_m/\partial p)_S = V_m \kappa_s = V_m^2/(M_m u^2) \quad (4)$$

where $K_{S,m}$ is the molar isentropic compressibility.

Experimental values for the speed of sound are reported in Tables 2 and 3, together with derived values of the isentropic

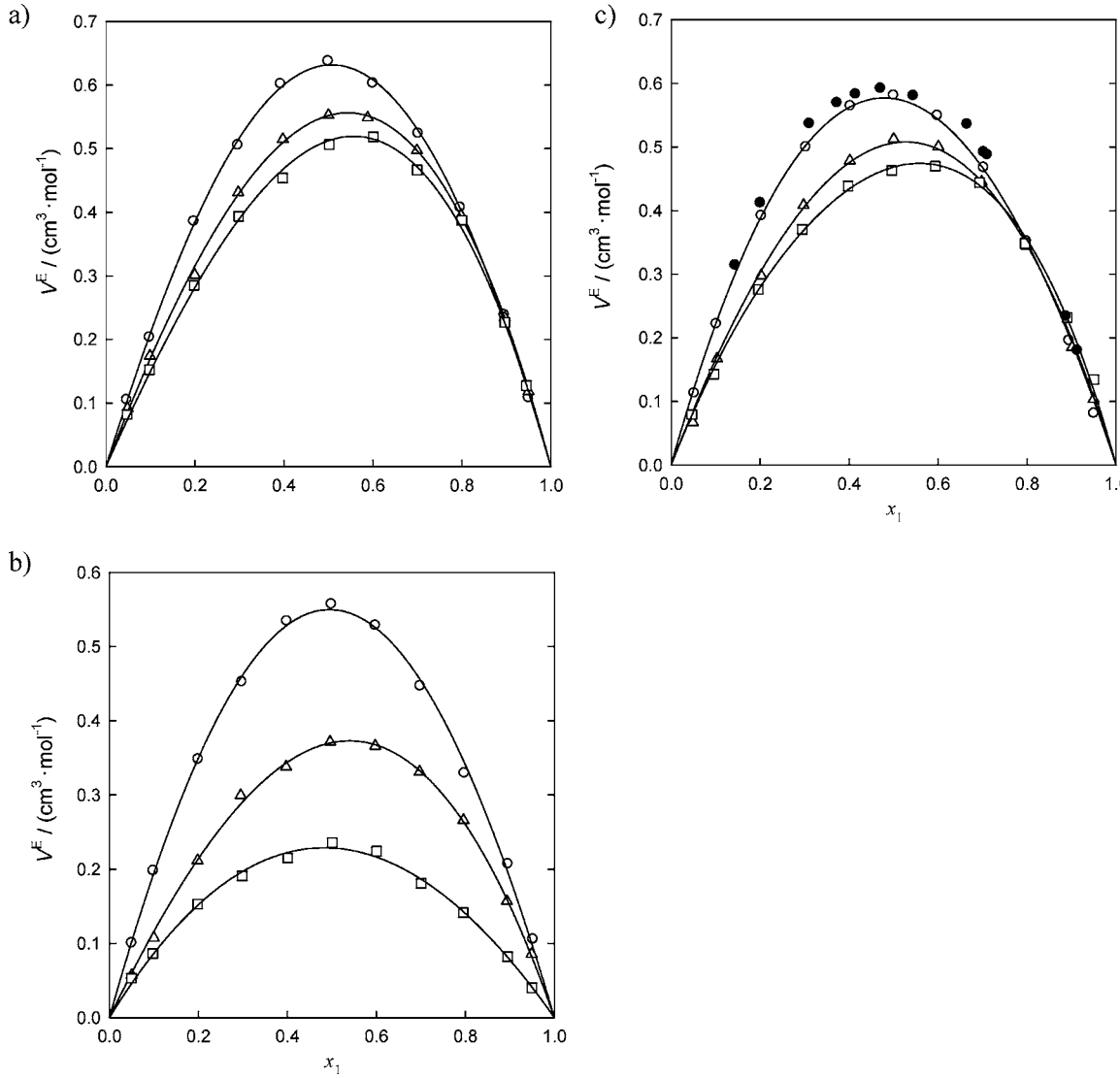

Figure 1. Excess molar volumes, V^E, plotted against the mole fraction for the binary mixture: aromatic compounds (1) + cycloalkane (2) for: (a) cyclohexane at $T = 283.15$ K, (b) methylcyclohexane at $T = 283.15$ K, (c) cyclo-octane at $T = 298.15$ K. Experimental data: ○, benzene; Δ, toluene; □, ethylbenzene. Literature data: ●, cyclo-octane + benzene from Póveda Vilches et al.[10] at $T = 298.15$ K. Solid line: Redlich−Kister fitting.

Table 1. Comparison of Experimental Pure Component Density Data with Literature Values at $T = 298.15$ K and Literature Data of Heat Capacity, $C^*_{p,i}$, and Isobaric Expansibility, $\alpha^*_{p,i}$ at $T = 298.15$ K

	ρ/(g·cm^{-3})		n_D		$C^*_{p,i}$	$\alpha^*_{p,i}$
component	exp.	lit.	exp.	lit.	lit.	lit.
cyclohexane	0.7739	0.77389[19]	1.42360	1.42354[19]	162.07[20]	0.00116[20]
methylcyclohexane	0.7651	0.76506[19]	1.42062	1.42058[19]	192.63[20]	0.00014[20]
cyclo-octane	0.8315	0.83151[21]	1.45598	1.45624[22]	250.11[20]	0.00089[20]
benzene	0.8736	0.87360[19]	1.49774	1.49792[19]	137.86[20]	0.00114[20]
toluene	0.8622	0.86219[19]	1.49399	1.49413[19]	157.48[20]	0.00108[20]
ethylbenzene	0.8625	0.86253[19]	1.49304	1.49320[19]	183.58[20]	0.00100[20]

Table 2. Densities, ρ, Speeds of Sound, u, Refractive Indices, n_D, Isentropic Compressibility, $K_{S,m}$, Excess Molar Volumes, V_m^E, Deviations in the Refractive Index, Δn_D, and Excess Molar Isentropic Compressibility, $K_{S,m}^E$, of the Binary Mixtures Cycloalkanes (1) + Aromatic Compounds (2) at $T = 283.15$ K

x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	$K_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	V^E / cm^3·mol^{-1}	Δn_D	$K_{S,m}^E$ / m^3·TPa^{-1}·mol^{-1}
				Cyclohexane (1) + Benzene (2)			
0.0000	0.8895	1.50765	1371	0.05255	0.000	0.0000	0.00000
0.0470	0.8827	1.50275	1364	0.05406	0.105	−0.0013	0.00037
0.0984	0.8756	1.49741	1358	0.05571	0.203	−0.0028	0.00078
0.1978	0.8624	1.48772	1346	0.05882	0.386	−0.0049	0.00148
0.2968	0.8504	1.47886	1338	0.06176	0.505	−0.0063	0.00202
0.3929	0.8394	1.47071	1331	0.06447	0.602	−0.0072	0.00241
0.4996	0.8283	1.46247	1326	0.06725	0.637	−0.0074	0.00261
0.6003	0.8188	1.45532	1323	0.06965	0.603	−0.0069	0.00257
0.7022	0.8099	1.44865	1322	0.07187	0.524	−0.0058	0.00233
0.7963	0.8023	1.44324	1322	0.07370	0.407	−0.0041	0.00188
0.8954	0.7949	1.43781	1325	0.07533	0.239	−0.0020	0.00111
0.9501	0.7912	1.43453	1327	0.07608	0.108	−0.0012	0.00054
1.0000	0.7878	1.43193	1329	0.07675	0.000	0.0000	0.00000
				Methylcyclohexane (1) + Benzene (2)			
0.0000	0.8895	1.50765	1371	0.05255	0.000	0.0000	0.00000
0.0504	0.8806	1.50135	1359	0.05523	0.101	−0.0023	0.00034
0.0990	0.8724	1.49548	1350	0.05778	0.198	−0.0043	0.00065
0.1998	0.8569	1.48438	1333	0.06300	0.348	−0.0074	0.00119
0.2978	0.8434	1.47501	1320	0.06790	0.452	−0.0090	0.00157
0.3991	0.8307	1.46578	1308	0.07294	0.534	−0.0102	0.00192
0.4993	0.8195	1.45783	1299	0.07774	0.557	−0.0102	0.00208
0.5980	0.8096	1.45078	1293	0.08225	0.528	−0.0094	0.00202
0.6991	0.8005	1.44435	1288	0.08672	0.447	−0.0078	0.00182
0.7981	0.7924	1.43862	1284	0.09091	0.329	−0.0057	0.00142
0.8961	0.7849	1.43330	1282	0.09491	0.207	−0.0033	0.00089
0.9523	0.7810	1.43058	1282	0.09705	0.105	−0.0015	0.00042
1.0000	0.7779	1.42833	1281	0.09883	0.000	0.0000	0.00000
				Cyclohexane (1) + Toluene (2)			
0.0000	0.8761	1.50278	1371	0.06390	0.000	0.0000	0.00000
0.0484	0.8710	1.49880	1365	0.06488	0.092	−0.0005	0.00035
0.0990	0.8658	1.49476	1360	0.06585	0.174	−0.0010	0.00068
0.1997	0.8558	1.48684	1351	0.06770	0.302	−0.0018	0.00123
0.2973	0.8461	1.47919	1344	0.06946	0.431	−0.0025	0.00174
0.3975	0.8366	1.47167	1337	0.07111	0.515	−0.0029	0.00209
0.4999	0.8273	1.46416	1331	0.07265	0.553	−0.0032	0.00233
0.5881	0.8196	1.45803	1328	0.07382	0.549	−0.0031	0.00236
0.6990	0.8103	1.45054	1325	0.07511	0.497	−0.0027	0.00222
0.7985	0.8024	1.44407	1324	0.07599	0.395	−0.0021	0.00183
0.8961	0.7951	1.43794	1325	0.07654	0.234	−0.0014	0.00113
0.9497	0.7913	1.43489	1327	0.07670	0.119	−0.0006	0.00059
1.0000	0.7878	1.43193	1329	0.07675	0.000	0.0000	0.00000
				Methylcyclohexane (1) + Toluene (2)			
0.0000	0.8761	1.50278	1371	0.06390	0.000	0.0000	0.00000
0.0500	0.8698	1.49797	1363	0.06578	0.057	−0.0011	0.00013
0.0998	0.8637	1.49331	1356	0.06765	0.108	−0.0020	0.00026
0.1980	0.8520	1.48436	1342	0.07137	0.212	−0.0037	0.00055
0.2951	0.8410	1.47614	1330	0.07503	0.299	−0.0047	0.00082
0.3968	0.8303	1.46797	1320	0.07874	0.338	−0.0053	0.00098
0.4959	0.8203	1.46042	1311	0.08232	0.372	−0.0054	0.00110
0.5973	0.8107	1.45319	1302	0.08588	0.366	−0.0051	0.00111
0.6970	0.8018	1.44643	1296	0.08930	0.331	−0.0045	0.00105
0.7954	0.7935	1.44018	1290	0.09253	0.266	−0.0034	0.00084
0.8932	0.7858	1.43420	1285	0.09560	0.157	−0.0021	0.00049
0.9487	0.7816	1.43118	1283	0.09733	0.086	−0.0010	0.00029
1.0000	0.7779	1.42833	1281	0.09883	0.000	0.0000	0.00000
				Cyclohexane (1) + Ethylbenzene (2)			
0.0000	0.8757	1.50129	1382	0.07246	0.000	0.0000	0.00000
0.0476	0.8714	1.49802	1377	0.07296	0.082	0.0000	0.00030
0.0982	0.8669	1.49455	1372	0.07350	0.153	0.0001	0.00062
0.1983	0.8579	1.48762	1364	0.07436	0.285	0.0001	0.00105
0.2982	0.8489	1.48066	1356	0.07516	0.394	0.0000	0.00142
0.3973	0.8401	1.47373	1349	0.07586	0.454	0.0000	0.00170
0.5016	0.8307	1.46641	1342	0.07651	0.506	−0.0001	0.00190
0.6008	0.8218	1.45942	1337	0.07701	0.518	−0.0002	0.00197
0.6995	0.8132	1.45257	1332	0.07732	0.466	−0.0002	0.00186
0.7998	0.8044	1.44558	1329	0.07746	0.388	−0.0002	0.00156
0.8967	0.7963	1.43898	1328	0.07730	0.227	−0.0001	0.00099
0.9451	0.7923	1.43569	1328	0.07712	0.127	0.0000	0.00060
1.0000	0.7878	1.43193	1329	0.07675	0.000	0.0000	0.00000
				Methylcyclohexane (1) + Ethylbenzene (2)			
0.0000	0.8757	1.50129	1382	0.07246	0.000	0.0000	0.00000
0.0494	0.8703	1.49728	1376	0.07378	0.053	−0.0004	0.00002
0.0975	0.8652	1.49353	1369	0.07516	0.086	−0.0007	0.00013

Table 2. Continued

x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	$K_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	V^E / cm^3·mol^{-1}	Δn_D	$K^E_{S,m}$ / m^3·TPa^{-1}·mol^{-1}
0.1983	0.8546	1.48550	1356	0.07793	0.153	−0.0013	0.00024
0.2981	0.8444	1.47786	1345	0.08053	0.191	−0.0017	0.00020
0.4008	0.8341	1.47018	1333	0.08329	0.215	−0.0019	0.00026
0.5005	0.8242	1.46281	1323	0.08596	0.236	−0.0020	0.00030
0.6001	0.8146	1.45566	1313	0.08858	0.224	−0.0018	0.00029
0.7006	0.8052	1.44856	1304	0.09123	0.181	−0.0016	0.00029
0.7952	0.7964	1.44194	1297	0.09363	0.141	−0.0013	0.00020
0.8949	0.7873	1.43542	1289	0.09612	0.082	−0.0006	0.00005
0.9495	0.7824	1.43163	1285	0.09751	0.040	−0.0004	0.00000
1.0000	0.7779	1.42833	1281	0.09883	0.000	0.0000	0.00000

compressibility and its excess, $K^E_{S,m}$. The excess molar isentropic compressibility $K^E_{S,m}$ is calculated by the following equation:

$$K^E_{S,m} = K_{S,m} - K^{id}_{S,m} \tag{5}$$

where $K^{id}_{S,m}$ is defined by the approach developed by Benson and Kiyohara:[25]

$$K^{id}_{S,m} = \sum_i x_i \left[K^*_{S,i} + T\frac{(E^*_{p,i})^2}{C^*_{p,i}} \right] - T\left[\frac{(\sum_i x_i E^*_{p,i})^2}{\sum_i x_i C^*_{p,i}} \right] \tag{6}$$

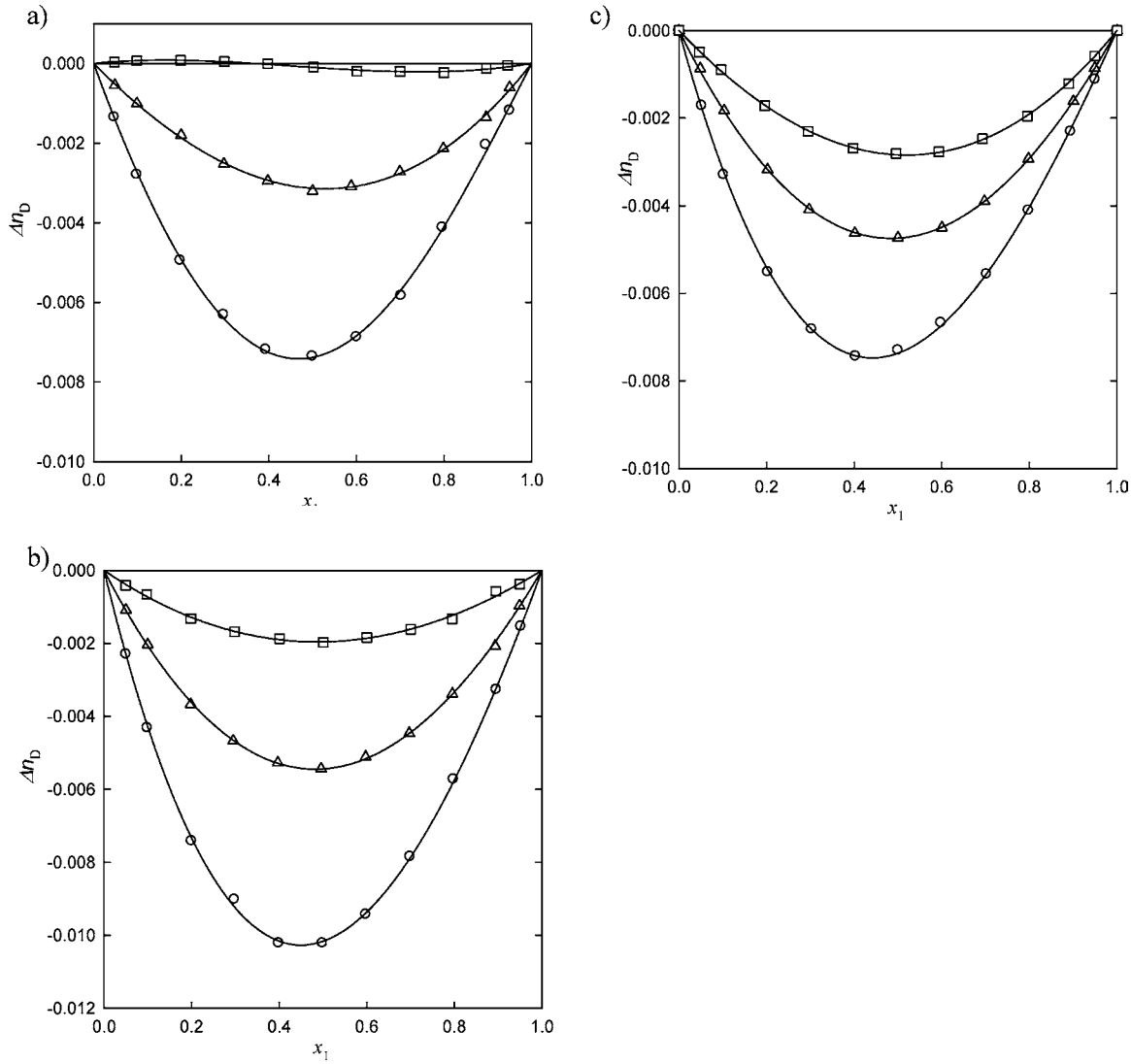

Figure 2. Refractive index deviations, Δn_D, plotted against the mole fraction for the binary mixture: aromatic compounds (1) + cycloalkane (2) for: (a) cyclohexane at $T = 283.15$ K, (b) methylcyclohexane at $T = 283.15$ K, (c) cyclo-octane at $T = 298.15$ K. Experimental data: ○, benzene; Δ, toluene; □, ethylbenzene. Solid line: Redlich−Kister fitting.

Table 3. Densities, ρ, Speeds of Sound, u, Refractive Indices, n_D, Isentropic Compressibility, $K_{S,m}$, Excess Molar Volumes, V_m^E, Deviations in the Refractive Index, Δn_D, and Excess Molar Isentropic Compressibility, $K_{S,m}^E$, of the Binary Mixtures Cycloalkanes (1) + Aromatic Compounds (2) at $T = 298.15$ K

x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	$K_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	V^E / cm^3·mol^{-1}	Δn_D	$K_{S,m}^E$ / m^3·TPa^{-1}·mol^{-1}
				Cyclohexane (1) + Benzene (2)			
0.0000	0.8736	1.49774	1299	0.06062	0.000	0.0000	0.00000
0.0470	0.8671	1.49298	1293	0.06235	0.090	−0.0013	0.00038
0.0984	0.8599	1.48771	1286	0.06432	0.215	−0.0027	0.00088
0.1978	0.8470	1.47808	1275	0.06799	0.396	−0.0050	0.00169
0.2968	0.8352	1.46965	1266	0.07144	0.522	−0.0061	0.00230
0.3929	0.8245	1.46157	1259	0.07465	0.610	−0.0070	0.00276
0.4996	0.8136	1.45354	1254	0.07797	0.649	−0.0072	0.00302
0.6003	0.8042	1.44654	1251	0.08083	0.625	−0.0067	0.00300
0.7022	0.7955	1.44001	1249	0.08344	0.541	−0.0057	0.00269
0.7963	0.7880	1.43431	1249	0.08565	0.430	−0.0044	0.00220
0.8954	0.7808	1.42891	1250	0.08762	0.251	−0.0024	0.00133
0.9501	0.7772	1.42611	1252	0.08853	0.115	−0.0012	0.00067
1.0000	0.7739	1.42360	1255	0.08929	0.000	0.0000	0.00000
				Cyclo-octane (1) + Benzene (2)			
0.0000	0.8736	1.49774	1299	0.06062	0.000	0.0000	0.00000
0.0522	0.8693	1.49384	1300	0.06256	0.113	−0.0017	0.00071
0.1020	0.8654	1.49019	1301	0.06435	0.222	−0.0033	0.00134
0.2030	0.8585	1.48375	1306	0.06765	0.392	−0.0055	0.00229
0.3029	0.8528	1.47827	1313	0.07057	0.500	−0.0068	0.00288
0.4033	0.8479	1.47346	1322	0.07318	0.564	−0.0074	0.00315
0.5002	0.8439	1.46955	1331	0.07544	0.581	−0.0073	0.00315
0.5985	0.8405	1.46607	1342	0.07748	0.549	−0.0067	0.00290
0.7025	0.8375	1.46284	1354	0.07943	0.467	−0.0056	0.00243
0.7983	0.8352	1.46030	1365	0.08104	0.352	−0.0041	0.00180
0.8946	0.8333	1.45808	1377	0.08249	0.195	−0.0023	0.00101
0.9504	0.8324	1.45694	1384	0.08326	0.081	−0.0011	0.00048
1.0000	0.8315	1.45598	1391	0.08394	0.000	0.0000	0.00000
				Methylcyclohexane (1) + Benzene (2)			
0.0000	0.8736	1.49774	1299	0.06062	0.000	0.0000	0.00000
0.0504	0.8650	1.49162	1289	0.06366	0.097	−0.0022	0.00036
0.0990	0.8571	1.48594	1280	0.06660	0.188	−0.0042	0.00072
0.1998	0.8419	1.47509	1263	0.07264	0.355	−0.0072	0.00141
0.2978	0.8288	1.46597	1250	0.07832	0.457	−0.0088	0.00189
0.3991	0.8165	1.45706	1240	0.08408	0.534	−0.0099	0.00228
0.4993	0.8057	1.44934	1231	0.08956	0.545	−0.0099	0.00244
0.5980	0.7960	1.44247	1225	0.09478	0.525	−0.0091	0.00243
0.6991	0.7872	1.43623	1220	0.09986	0.435	−0.0076	0.00214
0.7981	0.7793	1.43061	1217	0.10460	0.318	−0.0056	0.00163
0.8961	0.7720	1.42549	1216	0.10914	0.195	−0.0031	0.00097
0.9523	0.7682	1.42279	1215	0.11165	0.093	−0.0015	0.00049
1.0000	0.7651	1.42062	1215	0.11369	0.000	0.0000	0.00000
				Cyclohexane (1) + Toluene (2)			
0.0000	0.8622	1.49399	1305	0.07282	0.000	0.0000	0.00000
0.0484	0.8572	1.49021	1300	0.07392	0.081	−0.0004	0.00029
0.0990	0.8520	1.48614	1294	0.07510	0.166	−0.0009	0.00064
0.1997	0.8420	1.47829	1285	0.07737	0.296	−0.0016	0.00125
0.2973	0.8323	1.47073	1276	0.07954	0.429	−0.0023	0.00182
0.3975	0.8228	1.46320	1269	0.08162	0.514	−0.0028	0.00225
0.4999	0.8134	1.45580	1263	0.08357	0.566	−0.0030	0.00251
0.5881	0.8057	1.44964	1258	0.08509	0.563	−0.0030	0.00258
0.6990	0.7964	1.44216	1254	0.08675	0.510	−0.0026	0.00242
0.7985	0.7884	1.43580	1252	0.08803	0.419	−0.0020	0.00206
0.8961	0.7811	1.42971	1252	0.08889	0.252	−0.0012	0.00131
0.9497	0.7774	1.42663	1253	0.08916	0.122	−0.0005	0.00070
1.0000	0.7739	1.42360	1255	0.08929	0.000	0.0000	0.00000
				Cyclo-octane (1) + Toluene (2)			
0.0000	0.8622	1.49399	1305	0.07282	0.000	0.0000	0.00000
0.0488	0.8598	1.49127	1307	0.07377	0.067	−0.0009	0.00040
0.1031	0.8570	1.48824	1309	0.07484	0.167	−0.0018	0.00087
0.2021	0.8525	1.48313	1315	0.07660	0.298	−0.0032	0.00153
0.2973	0.8485	1.47861	1321	0.07812	0.409	−0.0041	0.00199
0.4014	0.8447	1.47411	1329	0.07953	0.479	−0.0046	0.00224
0.5000	0.8415	1.47026	1337	0.08070	0.513	−0.0047	0.00231
0.6005	0.8387	1.46667	1347	0.08170	0.500	−0.0045	0.00220
0.6976	0.8364	1.46358	1356	0.08250	0.445	−0.0039	0.00192
0.7981	0.8344	1.46073	1367	0.08318	0.345	−0.0029	0.00148
0.9007	0.8328	1.45814	1378	0.08365	0.185	−0.0016	0.00081
0.9494	0.8321	1.45705	1384	0.08383	0.103	−0.0009	0.00045
1.0000	0.8315	1.45598	1391	0.08394	0.000	0.0000	0.00000
				Methylcyclohexane (1) + Toluene (2)			
0.0000	0.8622	1.49399	1305	0.07282	0.000	0.0000	0.00000
0.0500	0.8559	1.48937	1297	0.07499	0.067	−0.0010	0.00013
0.0998	0.8499	1.48481	1290	0.07717	0.114	−0.0019	0.00027

Table 3. Continued

x_1	ρ / g·cm^{-3}	n_D	u / m·s^{-1}	$K_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	V^E / cm^3·mol^{-1}	Δn_D	$K^E_{S,m}$ / m^3·TPa^{-1}·mol^{-1}
0.1980	0.8382	1.47597	1276	0.08156	0.237	−0.0035	0.00064
0.2951	0.8274	1.46780	1264	0.08582	0.317	−0.0045	0.00093
0.3968	0.8168	1.45982	1253	0.09020	0.359	−0.0051	0.00116
0.4959	0.8069	1.45225	1244	0.09435	0.396	−0.0054	0.00127
0.5973	0.7974	1.44519	1236	0.09856	0.392	−0.0050	0.00133
0.6970	0.7886	1.43850	1229	0.10254	0.357	−0.0044	0.00124
0.7954	0.7804	1.43233	1223	0.10636	0.290	−0.0033	0.00103
0.8932	0.7727	1.42635	1219	0.10999	0.194	−0.0021	0.00067
0.9487	0.7686	1.42344	1216	0.11196	0.113	−0.0009	0.00037
1.0000	0.7651	1.42062	1215	0.11369	0.000	0.0000	0.00000
				Cyclohexane (1) + Ethylbenzene (2)			
0.0000	0.8625	1.49304	1319	0.08210	0.004	0.0000	0.00000
0.0476	0.8582	1.48992	1314	0.08266	0.083	0.0002	0.00022
0.0982	0.8537	1.48645	1309	0.08326	0.150	0.0002	0.00046
0.1983	0.8447	1.47947	1300	0.08447	0.275	0.0002	0.00095
0.2982	0.8356	1.47245	1291	0.08562	0.390	0.0001	0.00138
0.3973	0.8267	1.46552	1283	0.08664	0.456	0.0001	0.00168
0.5016	0.8172	1.45815	1275	0.08762	0.513	−0.0001	0.00192
0.6008	0.8083	1.45116	1268	0.08842	0.516	−0.0002	0.00201
0.6995	0.7995	1.44433	1263	0.08905	0.481	−0.0001	0.00192
0.7998	0.7907	1.43731	1258	0.08949	0.390	−0.0002	0.00164
0.8967	0.7824	1.43062	1255	0.08962	0.243	−0.0002	0.00108
0.9451	0.7784	1.42735	1254	0.08956	0.136	−0.0001	0.00066
1.0000	0.7739	1.42360	1255	0.08929	0.000	0.0000	0.00000
				Cyclo-octane (1) + Ethylbenzene (2)			
0.0000	0.8625	1.49304	1319	0.08210	0.004	0.0000	0.00000
0.0465	0.8604	1.49082	1321	0.08246	0.080	−0.0005	0.00028
0.0962	0.8583	1.48858	1322	0.08286	0.143	−0.0009	0.00058
0.1961	0.8541	1.48405	1327	0.08358	0.276	−0.0017	0.00112
0.2944	0.8503	1.47983	1332	0.08412	0.371	−0.0023	0.00148
0.3975	0.8466	1.47562	1339	0.08453	0.439	−0.0027	0.00170
0.4959	0.8434	1.47185	1346	0.08477	0.463	−0.0028	0.00176
0.5935	0.8404	1.46828	1353	0.08491	0.469	−0.0028	0.00171
0.6929	0.8376	1.46489	1361	0.08491	0.444	−0.0025	0.00154
0.7954	0.8352	1.46160	1370	0.08476	0.349	−0.0020	0.00119
0.8899	0.8332	1.45885	1379	0.08447	0.232	−0.0012	0.00073
0.9497	0.8321	1.45726	1385	0.08423	0.134	−0.0006	0.00038
1.0000	0.8315	1.45598	1391	0.08394	0.000	0.0000	0.00000
				Methylcyclohexane (1) + Ethylbenzene (2)			
0.0000	0.8625	1.49304	1319	0.08209	0.000	0.0000	0.00000
0.0494	0.8572	1.48923	1312	0.08365	0.047	−0.0002	0.00000
0.0975	0.8521	1.48542	1305	0.08520	0.083	−0.0006	0.00002
0.1983	0.8415	1.47754	1292	0.08844	0.155	−0.0011	0.00008
0.2981	0.8312	1.46988	1280	0.09169	0.214	−0.0016	0.00018
0.4008	0.8209	1.46219	1268	0.09499	0.245	−0.0018	0.00024
0.5005	0.8110	1.45484	1258	0.09823	0.272	−0.0020	0.00032
0.6001	0.8014	1.44771	1247	0.10154	0.266	−0.0019	0.00048
0.7006	0.7919	1.44068	1236	0.10495	0.245	−0.0016	0.00073
0.7952	0.7831	1.43414	1230	0.10758	0.212	−0.0013	0.00036
0.8949	0.7742	1.42751	1222	0.11060	0.126	−0.0007	0.00023
0.9495	0.7693	1.42390	1218	0.11230	0.087	−0.0004	0.00021
1.0000	0.7651	1.42062	1215	0.11369	0.000	0.0000	0.00000

where $K^*_{S,i}$ is the product of the molar volume V^*_i and the isentropic compressibility $\kappa^*_{S,i}$ of the pure component i. The molar isobaric expansion of pure component i, $E^*_{p,i}$, is the product of the molar volume and the isobaric expansibility $\alpha^*_{p,i}(\alpha^*_{p,i} = -(1)/(\rho)((\partial\rho)/(\partial T))_P)$ and $C^*_{p,i}$ is the molar isobaric heat capacity of the pure component i. The values of $\alpha^*_{p,i}$ and $C^*_{p,i}$ are obtained from the literature,[20] and these values are shown in Table 1 at $T = 298.15$ K.

The excess and deviation properties at studied temperatures were fitted to a Redlich−Kister[26] type equation:

$$\Delta Q_{12} = x_1 x_2 \sum_{p=0}^{M} B_p (x_1 - x_2)^p \qquad (7)$$

where ΔQ_{12} is the excess property, x_1 and x_2 are the mole fraction of component 1 and 2, respectively, B_P is the fitting parameter, and M is the degree of the polynomic expansion, which was optimized using the F-test.[27] The fitting parameters are given in Table 4 and 5 together with the root-mean-square deviations, σ, given by:

$$\sigma = \{ \sum_{i}^{n_{dat}} (z_{exp} - z_{calc})^2/(n_{dat} - n_{par}) \}^{1/2} \qquad (8)$$

where z_{exp}, z_{calc}, n_{dat}, and n_{par} are the values of the experimental and calculated property, the number of experimental data, and the number of parameters of the fitting equation, respectively.

Figures 1, 2, and 3 show the fitted curves of the excess molar volumes, the refractive index deviation, and the excess molar isentropic compressibility, respectively, of the studied binary systems containing cycloalkanes (1) with aromatic compounds (2) at $T = (283.15$ and $298.15)$ K.

Figure 1a,b shows the excess molar volume for cyclohexane (1) and methylcyclohexane (1) with benzene (2), toluene (2), and ethylbenzene (2), respectively, at $T = 283.15$ K, and Figure 1c shows this excess for the cyclo-octane (1) with aromatic

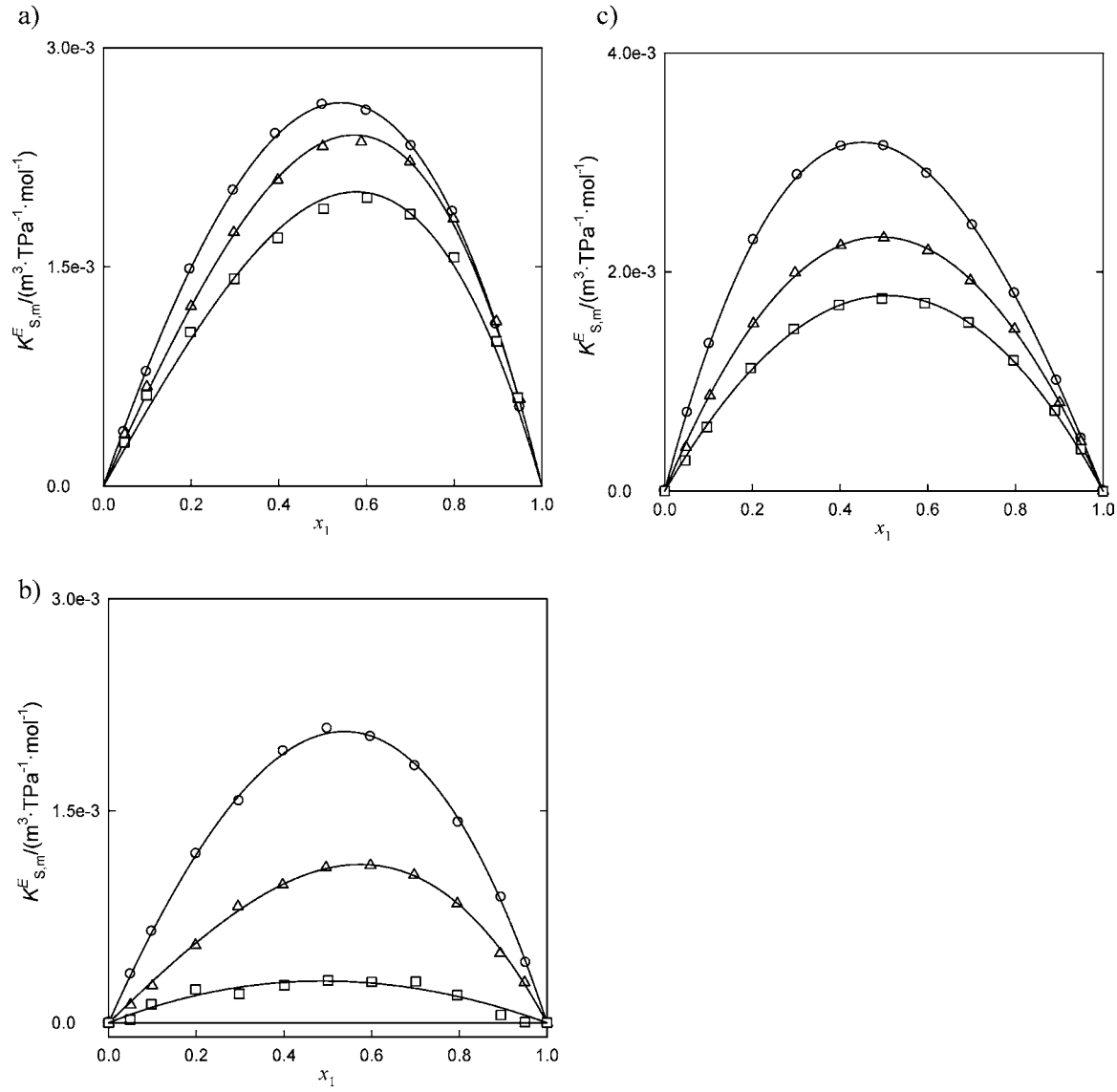

Figure 3. Excess molar isentropic compressibility, $K^E_{S,m}$, plotted against the mole fraction for the binary mixture: aromatic compounds (1) + cycloalkane (2) for: (a) cyclohexane at $T = 283.15$ K, (b) methylcyclohexane at $T = 283.15$ K, (c) cyclo-octane at $T = 298.15$ K. Experimental data: ○, benzene; Δ, toluene; □, ethylbenzene. Solid line: Redlich−Kister fitting.

compounds (2) at $T = 298.15$ K. All studied binary systems present a similar behavior for this physical property. As can be observed in this figure, excess molar volumes are positive over the entire composition range for all of the investigated mixtures with a maximum about $x_1 = 0.5$, except for cyclohexane (1) and cyclo-octane (1) with ethylbenzene (2) which presents the maximum about $x_1 = 0.6$. For all of the studied systems, when the aliphatic chain and the methyl radical of the cycloalkane increase, the excess molar volume decreases, and when the aliphatic chain and the methyl radical of the aromatic compounds increase, this excess property decreases. For comparison purposes the experimental data from Póveda et al.[10] at $T = 298.15$ K are also presented in Figure 1c; it is possible to observe a good agreement between both experimental data.

Figure 2 shows the refractive index deviations for the studied systems over the entire composition range. Figure 2a,b shows this deviation for cyclohexane and methylcyclohexane with benzene, toluene, and ethylbenzene, respectively, at $T = 283.15$ K, and Figure 2c shows the refractive index deviation for the cyclo-octane with aromatic compounds at $T = 298.15$ K. All studied systems present a similar behavior for this physical property with small values of refractive index deviation. For this derived property, all systems present a minimum at approximately $x_1 = 0.5$ except for the binary system cyclohexane (1) + ethylbenzene (2), which presents a maximum and a minimum, showing a small deviation of ideal behavior. As in the excess molar volume case, the studied systems show that when the aliphatic chain and the methyl radical of the cycloalkane increase, the value of the refractive index deviation decrease; nevertheless, when the aliphatic chain and the methyl radical of the aromatic compounds increase, the refractive index increases.

The excess molar isentropic compressibilities are plotted in Figure 3 over the entire composition range at $T =$ (283.15 and 298.15) K. Figure 3a,b shows the excess molar isentropic compressibilities for cyclohexane and methylcyclohexane with benzene, toluene, and ethylbenzene at $T = 283.15$ K, and Figure 3c shows this excess for cyclo-octane with aromatic compounds at $T = 298.15$ K. All studied systems present behavior very close to ideality with positive deviations over the entire composition range; the maximum is between $x_1 = 0.5$ and $x_1 = 0.6$. As in the excess molar volume case for all studied systems, when the aliphatic chain and the methyl radical of the aromatic compounds increase, the excess molar isentropic compressibility

Table 4. Fitting Parameters and Root Mean Square Deviations (σ) for Binary Mixtures at $T = 283.15$ K

	B_0	B_1	B_2	σ
Cyclohexane (1) + Benzene (2)				
V^E/cm^3·mol^{-1}	2.5264	0.0795	−0.2028	0.007
Δn_D	−0.0295	0.0043	0.0037	$1\cdot10^{-4}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0104	0.0018		$2\cdot10^{-5}$
Methylcyclohexane (1) + Benzene (2)				
V^E/cm^3·mol^{-1}	2.1996	−0.0501	−0.1149	0.011
Δn_D	−0.0407	0.0083	−0.0006	$1\cdot10^{-4}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0082	0.0013		$3\cdot10^{-5}$
Cyclohexane (1) + Toluene (2)				
V^E/cm^3·mol^{-1}	2.2081	0.3921		0.007
Δn_D	0.0094	0.0029		$6\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0094	0.0029		$4\cdot10^{-5}$
Methylcyclohexane (1) + Toluene (2)				
V^E/cm^3·mol^{-1}	1.4822	0.2386		0.006
Δn_D	−0.0218	0.0015		$6\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0044	0.0014		$2\cdot10^{-5}$
Cyclohexane (1) + Ethylbenzene (2)				
V^E/cm^3·mol^{-1}	2.0502	0.4813		0.009
Δn_D	−0.0004	−0.0015		$2\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0078	0.0026		$8\cdot10^{-5}$
Methylcyclohexane (1) + Ethylbenzene (2)				
V^E/cm^3·mol^{-1}	0.9140	−0.0628		0.007
Δn_D	−0.0078	0.0004		$7\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0012	−0.0001		$5\cdot10^{-5}$

Table 5. Fitting Parameters and Root Mean Square Deviations (σ) for Binary Mixtures at $T = 298.15$ K

	B_0	B_1	B_2	σ
Cyclohexane (1) + Benzene (2)				
V^E/cm^3·mol^{-1}	2.5891	0.1332	−0.1417	0.009
Δn_D	−0.0286	0.0031		$1\cdot10^{-4}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0120	0.0025		$3\cdot10^{-5}$
Cyclo-octane (1) + Benzene(2)				
V^E/cm^3·mol^{-1}	2.3039	−0.1968		0.009
Δn_D	−0.0295	0.0072		$6\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0126	−0.0025		$1\cdot10^{-5}$
Methylcyclohexane (1) + Benzene (2)				
V^E/cm^3·mol^{-1}	2.1879	−0.1260	−0.2141	0.009
Δn_D	−0.0396	0.0082		$9\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0097	0.0013		$4\cdot10^{-5}$
Cyclohexane (1) + Toluene (2)				
V^E/cm^3·mol^{-1}	2.2447	0.5367		0.008
Δn_D	−0.0118	−0.0017		$8\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0101	0.0039		$5\cdot10^{-5}$
Cyclo-octane (1) + Toluene (2)				
V^E/cm^3·mol^{-1}	2.0250	0.2221		0.009
Δn_D	−0.0190	0.0012		$3\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0093	−0.0003		$2\cdot10^{-5}$
Methylcyclohexane (1) + Toluene (2)				
V^E/cm^3·mol^{-1}	1.5688	0.3123	0.2149	0.012
Δn_D	−0.0211	0.0009		$1\cdot10^{-4}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0052	0.0020		$3\cdot10^{-5}$
Cyclohexane (1) + Ethylbenzene (2)				
V^E/cm^3·mol^{-1}	2.0624	0.5645		0.009
Δn_D	−0.0001	−0.0021		$6\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0079	0.0036		$6\cdot10^{-5}$
Cyclo-octane (1) + Ethylbenzene (2)				
V^E/cm^3·mol^{-1}	1.8736	0.3866	0.2932	0.010
Δn_D	−0.0114	−0.0009		$3\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0071	0.0003		$2\cdot10^{-5}$
Methylcyclohexane (1) + Ethylbenzene (2)				
V^E/cm^3·mol^{-1}	1.0649	0.2532	0.2075	0.009
Δn_D	−0.0076	−0.0007		$5\cdot10^{-5}$
$K^E_{S,m}$/m^3·TPa^{-1}·mol^{-1}	0.0016	0.0021		$1\cdot10^{-4}$

decreases, and when the aliphatic chain of the cycloalkane increases, this excess decreases too. However, when the methyl radical of the cycloalkane increases, this excess property increases.

Conclusions

Densities, speeds of sound, and the refractive index of nine binary systems, cyclohexane (1) and methylcyclohexane (1) with benzene (2), toluene (2), and ethylbenzene (2) at $T = (283.15$ and 298.15) K and the cyclo-octane (1) with benzene (2), toluene (2), and ethylbenzene (2) at $T = 298.15$ K, under atmospheric pressure over the whole composition range are presented in this article.

The excess properties (excess molar volume, refractive index deviations, and excess molar isentropic compressibilities) have been determined from experimental data for all binary systems, and these data have been fitted to Redlich−Kister equation to test the quality of the experimental values. Very good results were obtained.

Excess molar volumes and the excess molar isentropic compressibilities are positive over the entire composition range for all studied at both studied temperatures. For the refractive index deviations, all systems present negative values at studied temperatures. All studied systems present values of excess molar isentropic compressibilities and the refractive index deviations very close to zero for both studied temperatures.

It is possible to say the following: when the aliphatic chain of the aromatic compound increases, the excess molar volume and the refractive index deviation decrease, but the excess molar isentropic compressibilities increase; when the aliphatic chain of the cycloalkane is higher, the excess molar volume and the refractive index deviations decrease, but the excess molar isentropic compressibilities increase; and when the methyl radical of the cycloalkane increases, all of the studied excess decrease.

With the experimental data obtained in this article and the experimental data obtained in previous work,[16] we can conclude that the temperature has little influence on the studied excess.

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Received for review June 1, 2009. Accepted September 15, 2009. The authors are grateful to the Ministerio de Educación y Ciencia (project CTQ2007-61272, Ramón y Cajal Program RYC-2008-02388 and FPI Fellowship BES-2008-003074).

JE900468U