International Journal of Thermophysics, Vol. 27, No. 3, May 2006 (© 2006)
DOI: 10.1007/s10765-006-0063-0

Speeds of Sound and Isentropic Compressibilities for Binary Mixtures of a Cyclic Diether with a Cyclic Compound at Three Temperatures

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Received April 21, 2005

Speeds of sound of the binary mixtures of 1,3-dioxolane (or 1,4-dioxane) + cyclopentane (or cyclohexane, or benzene) have been measured at 283.15, 298.15, and 313.15 K. The excess isentropic compressibilities were calculated from experimental data and fitted with a Redlich-Kister polynomial function. Results were analyzed taking into account molecular interactions and structural effects in the mixtures and were compared with literature data. Isentropic compressibilities have been estimated at 298.15 K using the Prigogine-Flory-Patterson theory

KEY WORDS: benzene; cyclohexane; cyclopentane; 1,4-dioxane; 1,3-dioxolane; isentropic compressibility; Prigogine-Flory-Patterson theory; speed of sound.

1. INTRODUCTION

Our research group has reported in recent years thermodynamic properties of binary mixtures containing cyclic diethers and other compounds, such as haloalkanes [1], alcohols [2–4], or hydrocarbons [5,6]. Continuing our systematic studies, we report here speeds of sound, isentropic compressibilities, and excess isentropic compressibilities of binary mixtures of 1,3-dioxolane (or 1,4-dioxane) + cyclopentane (or cyclohexane or benzene) at the temperatures of 283.15, 298.15, and 313.15 K.

Considerable interest has been shown in the investigation of excess thermodynamic functions of cyclic ethers in polar and nonpolar solvents.

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Speeds of sound and excess isentropic compressibilities have been previously reported for 1,3-dioxolane + cyclohexane (or benzene) [7] and 1,4-dioxane + benzene binary mixtures at 298.15 K [8]. Speeds of sound, isentropic compressibilities, and excess isentropic compressibilities were obtained for the 1,4-dioxane + cyclohexane (or benzene) systems at 303.15 K [9]. Our study of these systems together allows a better understanding of the properties of the mixtures containing cyclic ethers and their interactions with other cyclic compounds. Furthermore, estimation of isentropic compressibilities using the Prigogine-Flory-Patterson theory has been provided and comparisons between the reported and estimated isentropic compressibilities have been performed.

2. EXPERIMENTAL

The liquids used were 1,3-dioxolane (better than 99.0 mol%), 1,4-dioxane (better than 99.9 mol%), cyclopentane (better than 99.0 mol%), cyclohexane (better than 99.9 mol%), and benzene (better than 99.9 mol%) obtained from Aldrich. The purity of the liquids was checked by gas chromatography and by measuring their densities. Table I shows experimental values of density for the pure compounds at 283.15, 298.15, and 313.15 K compared with literature data at 298.15 K. No further purification was considered necessary.

Densities, ρ, of the pure compounds and speeds of sound, u, of the pure compounds and their mixtures 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 and density measurements is $\pm 0.1\ \mathrm{m \cdot s^{-1}}$ and $\pm 3 \times 10^{-5}$ $\mathrm{g \cdot cm^{-3}}$, respectively. The uncertainty of the speed-of-sound measurements is $\pm\ 1\ \mathrm{m \cdot s^{-1}}$ while the uncertainty for the density is $\pm 10^{-5}\ \mathrm{g \cdot cm^{-3}}$ Calibration of the apparatus was carried out with air and deionized double-distilled water. Experimental values of the speed of sound of the pure compounds at three temperatures, along with literature values at 298.15 K, are also reported in Table I.

The mixtures were prepared by mass using a Mettler H20T balance. The uncertainty of mole fraction is estimated to be less than 1×10^{-4}.

3. RESULTS AND DISCUSSION

The experimental speeds of sound, u, of the binary mixtures at 283.15, 298.15, and 313.15 K are reported in Table II. The isentropic compressibilities have been calculated from Newton-Laplace's equation:

Table I. Physical Properties of Pure Compounds and Comparisons with Literature Density and Sound-Speed Data at 298.15 K

Property	T(K)		1,3 -Dioxolane	1,4 -Dioxane	Cyclopentane	Cyclohexane	Benzene
ρ(g·cm^{-3})	283.15	Exptl.	1.0771	1.0452	0.7459	0.7880	0.8899
	298.15	Exptl.	1.0588	1.0279	0.7397	0.7737	0.8735
		Lit.	1.05857 [10]	1.02797 [11]	0.74045 [11]	0.77389 [11]	0.87360 [11]
	313.15	Exptl.	1.0402	1.0110	0.7247	0.7596	0.8575
α (kK^{-1})	283.15		1.142	1.059	1.261	1.170	1.175
	298.15		1.164	1.087	1.327	1.212	1.219
	313.15		1.226	1.094	1.393	1.253	1.263
C_p (J·mol^{-1}·K^{-1})	283.15		119.59	142.10 [12]	122.15 [13]	150.41 [13]	133.82 [13]
	298.15		122.21	147.90 [12]	126.90 [13]	156.20 [13]	136.03 [13]
	313.15		125.01	153.70 [12]	132.05 [13]	162.00 [13]	138.84 [13]
u (m·s^{-1})	283.15		1406.3	1409.6	1283.5	1327.8	1368.7
	298.15	Exptl.	1339.9	1343.6	1206.6	1254.4	1298.3
		Lit.	–	1344.85 [8]	1206 [14]	1254.1 [15]	1299.73 [8]
	313.15		1271.6	1278.8	1129.9	1181.1	1229.5

Table II. Speeds of Sound, u, Isentropic Compressibilities, κ_S, and Excess Isentropic Compressibilities, κ_S^E, for the Binary Mixtures at 283.15, 298.15, and 313.15 K

x_1	u ($m \cdot s^{-1}$)	κ_S ($T\,Pa^{-1}$)	κ_S^E ($T\,Pa^{-1}$)
	1,3-dioxolane (1) + cyclopentane (2) at 283.15 K		
0.1010	1277.3	788.9	7.4
0.2019	1275.8	766.1	9.0
0.3024	1278.6	738.4	7.8
0.4023	1285.0	706.9	5.0
0.5028	1295.3	672.1	1.5
0.6000	1307.9	635.7	−2.0
0.6995	1325.7	596.0	−5.1
0.7960	1347.3	555.6	−6.9
0.8999	1375.7	511.4	−5.8
	1,3-dioxolane (1) + cyclopentane (2) at 298.15 K		
0.0998	1201.4	909.5	7.5
0.1993	1200.8	882.2	9.2
0.3005	1204.5	848.6	7.6
0.4041	1212.0	809.8	4.3
0.5024	1222.7	768.9	0.3
0.6002	1236.4	725.1	−3.8
0.7004	1255.5	677.3	−7.2
0.7988	1278.8	627.9	−9.1
0.8992	1307.4	576.4	−7.7
	1,3-dioxolane (1) + cyclopentane (2) at 313.15 K		
0.1028	1125.3	1057.3	10.2
0.2032	1125.9	1023.7	12.4
0.3014	1130.2	983.4	9.9
0.4030	1138.5	936.3	5.2
0.5008	1150.0	886.3	−0.5
0.6008	1165.5	832.1	−5.6
0.6991	1184.8	775.8	−9.6
0.7991	1209.0	715.9	−11.4
0.8987	1237.8	655.4	−9.1
	1,3-dioxolane (1) + cyclohexane (2) at 283.15 K		
0.1044	1322.0	711.2	8.0
0.2011	1317.6	700.4	13.8
0.3005	1315.4	685.5	17.5
0.4009	1316.0	666.3	19.0
0.4998	1319.7	643.7	18.7
0.6020	1327.3	615.8	16.2
0.7002	1339.0	585.1	12.5
0.7989	1355.7	550.1	7.7
0.8989	1377.7	511.1	2.9
	1,3-dioxolane (1) + cyclohexane (2) at 298.15 K		
0.0998	1245.1	817.1	14.3
0.2014	1240.0	805.2	23.0
0.3019	1238.7	786.8	26.9

Table II. (*Continued*)

x_1	u ($m \cdot s^{-1}$)	κ_S ($T\,Pa^{-1}$)	κ_S^E ($T\,Pa^{-1}$)
0.4043	1240.5	763.2	28.2
0.4993	1245.3	736.0	26.4
0.6028	1254.2	702.1	22.9
0.6998	1266.9	665.6	17.8
0.8003	1284.9	623.0	11.5
0.8992	1308.9	576.5	4.9
	1,3-dioxolane (1) + cyclohexane (2) at 313.15 K		
0.1213	1172.5	938.1	21.8
0.2006	1167.6	925.9	29.0
0.2996	1166.6	904.6	33.9
0.3996	1168.8	877.3	35.4
0.5009	1174.2	843.3	33.4
0.6000	1183.2	804.8	29.3
0.6979	1196.3	760.7	22.7
0.7987	1215.2	709.6	14.3
0.8991	1240.0	654.1	6.1
	1,3-dioxolane (1) + benzene (2) at 283.15 K		
0.1037	1373.9	584.9	−4.6
0.2005	1377.2	572.3	−7.1
0.2977	1380.5	559.6	−8.9
0.4007	1383.5	546.8	−9.6
0.4995	1386.6	534.4	−9.7
0.5967	1389.7	522.1	−9.3
0.6984	1393.7	509.1	−8.0
0.7942	1397.3	496.7	−6.3
0.8973	1401.7	483.1	−3.6
	1,3-dioxolane (1) + benzene (2) at 298.15 K		
0.1000	1303.1	662.4	−5.2
0.2022	1306.8	646.8	−8.3
0.3002	1310.1	632.3	−10.1
0.4021	1313.6	617.5	−10.9
0.4957	1317.0	603.6	−11.2
0.5968	1320.7	588.3	−10.9
0.6965	1325.1	573.2	−9.6
0.7985	1329.4	557.7	−7.3
0.8973	1334.2	542.5	−4.1
	1,3-dioxolane (1) + benzene (2) at 313.15 K		
0.1006	1233.5	753.0	−4.9
0.2000	1237.2	735.5	−8.4
0.2985	1240.9	718.1	−10.9
0.4136	1245.1	698.3	−12.4
0.4928	1248.1	684.5	−12.7
0.5953	1252.0	667.0	−12.0
0.6979	1256.3	649.2	−10.4
0.7968	1261.2	631.2	−8.4
0.8979	1266.3	613.0	−4.9

Table II. (*Continued*)

x_1	u ($m \cdot s^{-1}$)	κ_S ($T\,Pa^{-1}$)	κ_S^E ($T\,Pa^{-1}$)
	1,4-dioxane (1) + cyclopentane (2) at 283.15 K		
0.0516	1280.7	795.0	3.7
0.0950	1279.4	785.9	5.7
0.1944	1280.5	759.9	6.4
0.2987	1286.0	728.3	4.3
0.3973	1294.2	696.2	1.7
0.4990	1305.8	661.4	−1.1
0.6003	1320.5	625.7	−3.4
0.7063	1339.6	587.2	−5.2
0.8072	1361.0	550.4	−5.5
0.9076	1385.1	514.1	−3.7
0.9528	1397.0	497.9	−2.3
	1,4-dioxane (1) + cyclopentane (2) at 298.15 K		
0.0488	1204.5	917.7	3.6
0.0945	1203.8	905.5	5.4
0.1818	1205.5	878.0	5.7
0.2983	1211.9	836.0	3.1
0.3959	1221.4	797.0	−0.8
0.4962	1234.1	755.1	−4.7
0.6067	1251.5	707.8	−7.8
0.7034	1269.8	665.9	−9.1
0.8110	1293.3	619.4	−8.3
0.9025	1316.4	579.9	−5.7
0.9506	1329.6	559.5	−3.3
	1,4-dioxane (1) + cyclopentane (2) at 313.15 K		
0.0449	1128.5	1068.3	3.4
0.0940	1128.3	1051.9	4.9
0.1950	1131.3	1012.5	4.5
0.2962	1138.6	966.5	0.0
0.3969	1149.5	916.8	−5.7
0.4983	1163.6	864.8	−10.8
0.5994	1180.8	811.6	−14.6
0.6987	1200.2	759.8	−15.5
0.8026	1223.8	705.8	−13.4
0.9066	1250.8	652.5	−7.84
0.9482	1263.0	631.0	−4.9
	1,4-dioxane (1) + cyclohexane (2) at 283.15 K		
0.0502	1323.1	717.1	6.1
0.0999	1319.7	712.9	10.9
0.1953	1315.8	701.1	17.0
0.2899	1315.6	684.9	19.7
0.3996	1318.4	662.4	20.5
0.5017	1324.5	638.1	19.4
0.6007	1333.5	611.7	16.9
0.6990	1346.1	582.8	13.2
0.7956	1362.2	552.2	8.9

Table II. (*Continued*)

x_1	u ($m \cdot s^{-1}$)	κ_S ($T\,Pa^{-1}$)	κ_S^E ($T\,Pa^{-1}$)
0.8994	1383.9	517.1	4.2
0.9446	1394.9	501.3	2.2
	1,4-dioxane (1) + cyclohexane (2) at 298.15 K		
0.0535	1250.0	817.8	7.5
0.1053	1246.9	812.4	13.1
0.1998	1244.4	797.5	19.3
0.3003	1245.0	776.7	22.4
0.4026	1248.6	751.6	23.2
0.5006	1255.2	723.8	21.6
0.5971	1264.5	693.5	18.9
0.7028	1278.6	656.9	14.6
0.8089	1296.9	617.2	9.5
0.9038	1318.4	578.6	4.0
0.9485	1330.2	559.8	1.5
	1,4-dioxane (1) + cyclohexane (2) at 313.15 K		
0.0497	1177.3	939.8	8.3
0.1020	1174.3	933.6	15.3
0.1944	1172.4	916.3	22.6
0.2926	1173.7	891.8	25.7
0.3973	1178.3	860.6	26.0
0.4969	1185.8	826.3	23.7
0.5992	1196.7	787.5	20.0
0.6988	1211.0	745.8	14.7
0.7966	1229.0	701.9	9.0
0.8972	1251.3	654.7	3.8
0.9505	1264.9	629.2	1.8
	1,4-dioxane (1) + benzene (2) at 283.15 K		
0.0521	1370.8	592.7	−1.8
0.0942	1372.6	587.0	−2.9
0.1987	1376.5	573.5	−5.2
0.2956	1380.2	561.4	−6.5
0.3936	1383.8	549.7	−6.9
0.4947	1387.4	538.0	−6.8
0.5964	1391.1	526.6	−6.1
0.6956	1395.1	515.5	−5.1
0.7963	1399.3	504.4	−3.6
0.8949	1404.1	493.4	−1.9
0.9526	1407.1	486.9	−0.9
	1,4-dioxane (1) + benzene (2) at 298.15 K		
0.0516	1300.8	670.5	−2.4
0.0888	1302.4	664.6	−3.8
0.1966	1307.3	647.7	−7.1
0.3160	1312.2	630.1	−9.1
0.4145	1316.3	616.2	−9.7
0.5004	1320.0	604.3	−9.7
0.5975	1324.1	591.2	−9.0

Table II. (*Continued*)

x_1	u ($m \cdot s^{-1}$)	κ_S ($T\,Pa^{-1}$)	κ_S^E ($T\,Pa^{-1}$)
0.6932	1328.4	578.5	−7.7
0.7962	1333.1	565.1	−5.6
0.8938	1338.0	552.5	−3.2
0.9535	1341.1	544.9	−1.4
	1,4-dioxane (1) + benzene (2) at 313.15 K		
0.0568	1232.1	760.5	−3.2
0.0913	1233.6	754.0	−4.8
0.2021	1239.2	733.2	−9.5
0.2963	1243.7	716.4	−12.0
0.3981	1248.6	698.9	−13.4
0.4975	1253.1	682.5	−13.5
0.5981	1257.9	666.5	−12.5
0.6972	1262.7	651.0	−10.5
0.7941	1267.5	636.1	−7.9
0.9034	1273.3	619.5	−4.0
0.9424	1275.5	613.6	−2.5

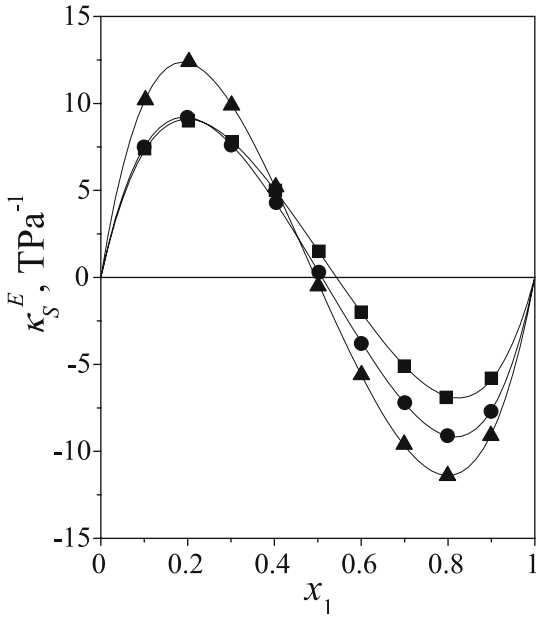

Fig. 1. Excess isentropic compressibilities of the 1,3-dioxolane (1) + cyclopentane (2) binary mixture at: 283.15 K (■); 298.15 K (●); and 313.15 K (▲).

$$\kappa_S = \frac{1}{\rho u^2} \tag{1}$$

The excess isentropic compressibilitiy, κ_S^E, is defined as

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{2}$$

where the isentropic compressibility for the ideal mixture, κ_S^{id}, was obtained according to Benson and Kiyohara [16] and Acree [17]:

$$\kappa_S^{id} = \sum_i \phi_i \left[\kappa_{S,i} + \frac{T V_i \alpha_i^2}{C_{p,i}} \right] - T \left(\sum_i x_i V_i \right) \frac{\left(\sum_i \phi_i \alpha_i \right)^2}{\left(\sum_i x_i C_{p,i} \right)} \tag{3}$$

where ϕ_i is the volume fraction of component i in the mixture, x_i is the corresponding mole fraction, T is the absolute temperature, and $\kappa_{S,i}$, V_i, α_i, and $C_{p,i}$, are the isentropic compressibility, the molar volume, the cubic expansion coefficient, and the molar heat capacity of pure components, respectively. The cubic expansion coefficients were obtained from experimental density measurements performed in our laboratory at several temperatures, and the heat capacity of 1,3-dioxolane was determined with a programmable differential scanning microcalorimeter (Seteram DSC II). All the properties of pure substances are shown in Table I.

The excess isentropic compressibilities of the binary mixtures were fitted with a Redlich-Kister polynomial equation [18]:

$$\kappa_S^E = x_1 x_2 \sum_{j=0}^{n} A_j (x_1 - x_2)^j \tag{4}$$

where A_j's are adjustable parameters and $(n+1)$ is the number of parameters. The values of the coefficients of Eq. (4) for all the binary mixtures along with values of the standard deviation are presented in Table III.

Excess isentropic compressibilities for the mixtures containing 1,3-dioxolane at three temperatures are plotted in Figs 1 to 3, while the excess isentropic compressibilities of the binary systems containing 1,4-dioxane are represented in Figs 4 to 6.

Excess isentropic compressibilities are s-shaped at three temperatures for the 1,3-dioxolane (or 1,4-dioxane) + cyclopentane mixtures, with κ_S^E values positive for small mole fractions of the cyclic diether. In the system containing 1,3-dioxolane, positive κ_S^E values slightly increase with an increase in temperature; however, for the system containing 1,4-dioxane, κ_S^E values are larger at 283.15 K than at 298.15 or 313.15 K (κ_S^E values decrease with an increase in temperature). In this region larger κ_S^E values are obtained for the binary system containing 1,3-dioxolane than for

Table III. Values of Parameters A_j of the Redlich-Kister Equation (Eq. (4)) and Corresponding Standard Deviations, $\sigma(\kappa_S^E)$, for the Binary Systems at 283.15, 298.15, and 313.15 K

T(K)	A_0	A_1	A_2	A_3	σ (T Pa^{-1})
		1,3-dioxolane (1) + cyclopentane (2)			
283.15	6.2	−72.4	2.2	−29.5	0.1
298.15	1.6	−83.1	−3.7	−34.5	0.1
313.15	−1.2	−111.9	11.5	−32.6	0.1
		1,3-dioxolane (1) + cyclohexane (2)			
283.15	74.7	−28.4	−23.3	−8.7	0.1
298.15	106.2	−51.2	2.0	−22.5	0.2
313.15	134.0	−60.8	5.0	−45.5	0.2
		1,3-dioxolane (1) + benzene (2)			
283.15	−38.9	4.3	−7.9	3.1	0.1
298.15	−45.0	0.9	−9.9	11.8	0.1
313.15	−50.3	3.7	−4.9	−6.4	0.1
		1,4-dioxane (1) + cyclopentane (2)			
283.15	−4.9	−52.4	21.8	−24.0	0.1
298.15	−19.1	−68.9	27.4	−14.4	0.1
313.15	−44.0	−90.4	41.2	−5.7	0.1
		1,4-dioxane (1) + cyclohexane (2)			
283.15	77.5	−38.2	9.2	−13.9	0.1
298.15	87.0	−41.1	9.8	−26.4	0.2
313.15	94.6	−63.8	13.7	−22.2	0.2
		1,4-dioxane (1) + benzene (2)			
283.15	−27.2	8.8	−0.6	0.0	< 0.1
298.15	−38.8	7.6	−2.3	1.8	< 0.1
313.15	−54.0	10.3	2.1	−3.8	0.1

1,4-dioxane. The inversion of the sign for both systems is shifted to smaller mole fractions of the cyclic diether when the temperature increases. For the region with negative values of κ_S^E we realize that, in both systems, minimum values decrease (more negative values) as the temperature increases; this effect is more pronounced in the mixture containing 1,4-dioxane.

Excess isentropic compressibilities are positive in the full composition range for binary mixtures of cyclic diether + cyclohexane and, in both systems, κ_S^E values increase with an increase in temperature. Maximum values of κ_S^E in these systems are obtained for a mole fraction of the cyclic diether close to 0.4, and this composition does not change significantly when either the temperature or the cyclic diether is varied.

Excess isentropic compressibilities obtained at 303.15 K by Oswal and Phalak [9] for the 1,4-dioxane + cyclohexane binary mixture are in

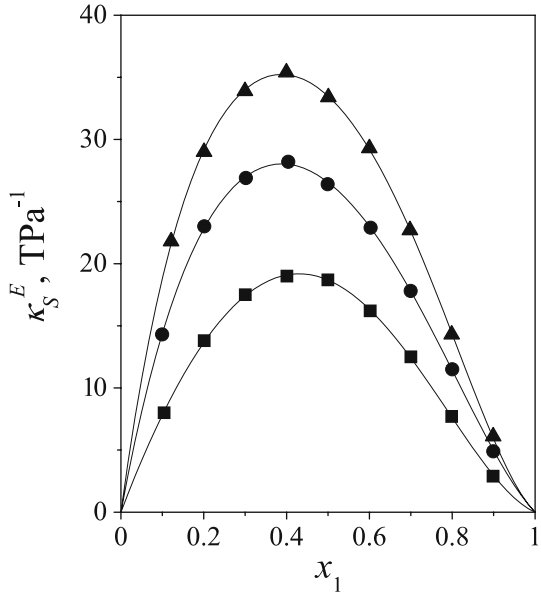

Fig. 2. Excess isentropic compressibilities of the 1,3-dioxolane (1) + cyclohexane (2) binary mixture at: 283.15 K (■); 298.15 K (●); and 313.15 K (▲).

complete agreement with our results, being intermediate between our values at 298.15 and 313.15 K.

Finally, excess isentropic compressibilities for the cyclic diether + benzene binary mixtures are negative over the complete composition range at the three temperatures studied, and κ_S^{E} values decrease (more negative values) with an increase in the temperature. Minimum κ_S^{E} values for these systems are obtained for mixtures close to the equimolecular composition.

κ_S^{E} values reported at 303.15 K by Oswal and Phalak [9] for the 1,4-dioxane + benzene binary mixture are almost identical to our results at 298.15 K, while κ_S^{E} values reported at 298.15 K by Takigawa and Tamura [8] for the same mixture are also in good agreement with our data.

The observed behavior for the excess isentropic compressibilities can be interpreted in terms of molecular interactions and structural effects; our previous investigations of excess molar volumes and viscosity deviations for the 1,3-dioxolane + cyclopentane [5] binary mixture reflect the absence of specific interactions between these compounds, and the same occurs with excess molar volumes for 1,4-dioxane + cyclopentane [6, 19]. Generally negative values of κ_S^{E} indicate specific interactions among the

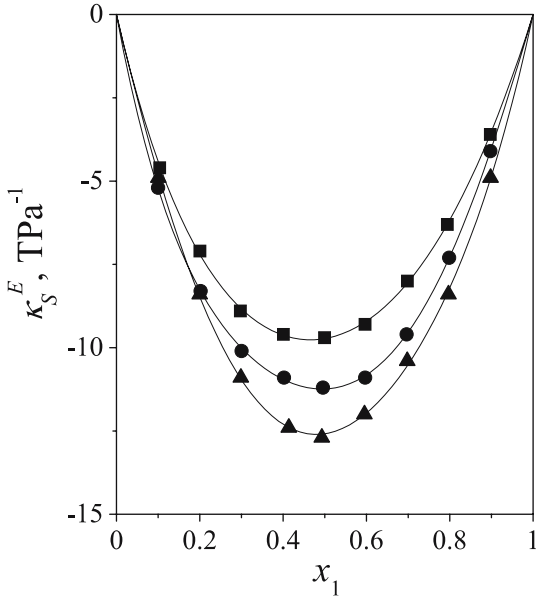

Fig. 3. Excess isentropic compressibilities of the 1,3-dioxolane (1) + benzene (2) binary mixture at: 283.15 K (■); 298.15 K (●); and 313.15 K (▲).

components in the mixture, but in this case it appears that packing effects, due to the similar size and shape of the molecules, are playing an important role in our mixtures and are responsible for the shape of the curves obtained. Usually V^{E} and κ_S^{E} have the same sign, but it is not rare to find systems with different signs in both properties. We have found a similar behavior in other mixtures containing cyclic diethers, which showed positive V^{E} values, and κ_S^{E} varying from positive to negative [20, 21].

Previously reported excess molar enthalpies and volumes for the 1,3-dioxolane (or 1,4-dioxane) + cyclohexane binary systems [5, 6, 22] are large and positive, which indicate that the main effect in these mixtures is the breaking of the dipole-dipole interactions of the pure diether, leading to expanded systems, with a large free volume, which are more compressible than an ideal mixture.

Induced dipole-dipole interactions exist between benzene and dioxane [8]. Therefore, the values of H^{E} are slightly negative and the values of V^{E} are also small and negative for this mixture [23]. It has been reported that 1,4-dioxane associates with benzene even in gaseous mixtures [24]. The small negative values of κ_S^{E} for our systems are a reflection of these interactions.

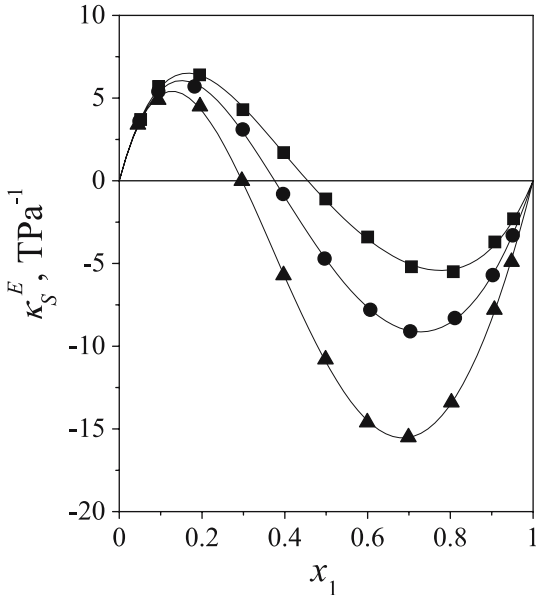

Fig. 4. Excess isentropic compressibilities of the 1,4-dioxane (1) + cyclopentane (2) binary mixture at: 283.15 K (■); 298.15 K (●); and 313.15 K (▲).

4. THEORY

Oswal [25] extended the Prigogine-Flory-Patterson (P-F-P) theory to estimate the isentropic compressibilities and speeds of sound of liquid mixtures. At a given temperature, T, the P-F-P theory can be used to calculate the molar volumes, V, and 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 $(\partial V/\partial T)_T$ can be also calculated by means of the following equations:

$$\left(\partial V \middle/ \partial P\right)_T = \frac{-\tilde{V}^{7/3} + 2\tilde{V}^2 - 2\tilde{V}^{5/3}}{(4/3) - \tilde{V}^{1/3}} \cdot \frac{V^* T^*}{P^* T} \tag{5}$$

$$\left(\partial V \middle/ \partial T\right)_P = \frac{\tilde{V}(\tilde{V}^{1/3} - 1)}{(4/3) - \tilde{V}^{1/3}} \cdot \frac{V^*}{T} \tag{6}$$

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

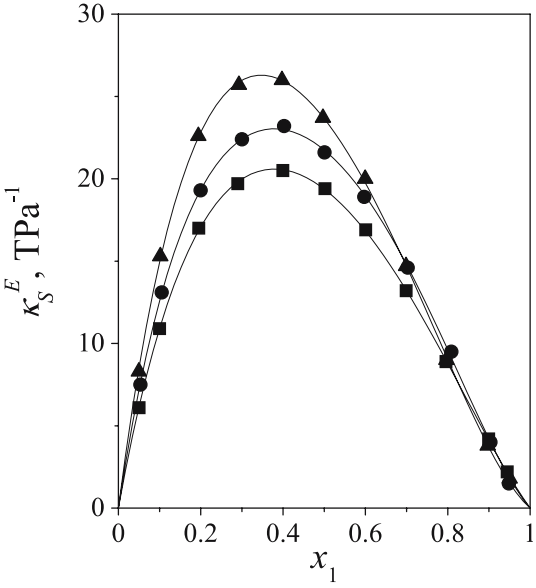

Fig. 5. Excess isentropic compressibilities of the 1,4-dioxane (1) + cyclohexane (2) binary mixture at: 283.15 K (■); 298.15 K (●); and 313.15 K (▲).

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

$$\left(\partial V/\partial P\right)_S = \left(\partial V/\partial P\right)_T + TC_P^{-1}\left(\partial V/\partial T\right)_P^2 \tag{7}$$

and finally the isentropic compressibility is related to the speed of sound, u, by the Newton-Laplace equation, Eq. (1).

Flory parameters [26, 27] of the pure compounds along with their physical properties are given in Table IV. Isothermal compressibilities, κ_T, were calculated from thermal expansion coefficients, experimental isentropic compressibilities, and molar heat capacities. The number of contact sites per segment of a molecule, s, has been estimated using Bondi's method [28].

In this work the interaction parameter for each mixture was obtained by fitting the P-F-P theory to the corresponding experimental equimolar H^{E} values [29–31]. Once the interaction parameter is obtained, the isentropic compressibility and the speed of sound can be estimated.

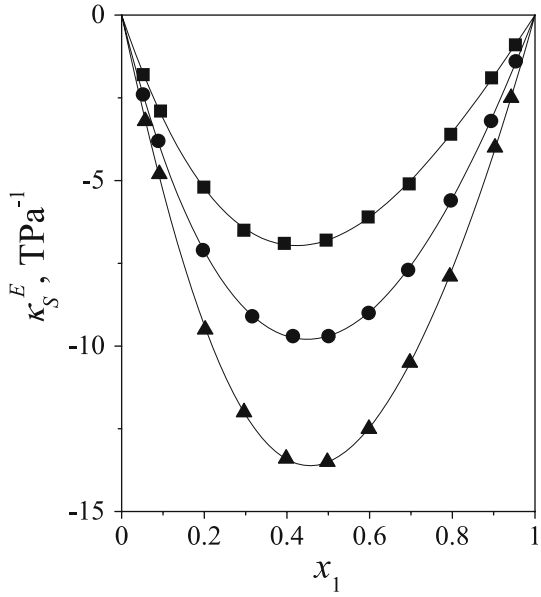

Fig. 6. Excess isentropic compressibilities of the 1,4-dioxane (1) + benzene (2) binary mixture at: 283.15 K (■); 298.15 K (●); and 313.15 K (▲).

Table IV. Physical Properties and Flory Parameters of the Pure Compounds at 298.15 K

Compound	κ_T (T Pa^{-1})	$\tilde{V}$	$P*$ (J · cm^{-3})	s (Å^{-1})
1,3-Dioxolane	757.3	1.28	751.3	1.23
1,4-Dioxane	743.1	1.27	697.9	1.25
Cyclopentane	1320.8	1.31	514.8	1.24
Cyclohexane	1126.5	1.29	533.8	1.25
Benzene	970.4	1.29	624.2	1.14

Table V gives the estimated and experimental equimolar u and κ_S values along with the interaction parameter. Estimated values for speeds of sound and isentropic compressibilities are almost identical to experimental results for benzene mixtures. However, for cyclopentane and cyclohexane mixtures, we obtain nearly 2% deviations between experimental and calculated values. Deviations in isentropic compressibilities for these systems are close to 4%.

Table V. Interaction Parameters, χ_{12}, and Calculated and Experimental Equimolar Speeds of Sound and Isentropic Compressibilities of the Binary Systems at 298.15 K.

System	χ_{12} ($J \cdot cm^{-3}$)	u_{cal} ($m \cdot s^{-1}$)	u_{exp} ($m \cdot s^{-1}$)	κ_S (TPa^{-1})	$\kappa_{S\,exp}$ ($T\,Pa^{-1}$)
1,3-dioxolane +					
cyclopentane	95.7	1250.8	1222.2	738.7	769.7
cyclohexane	91.4	1271.6	1245.2	706.7	736.0
benzene	4.1	1317.2	1317.1	603.7	602.8
1,4-dioxane +					
cyclopentane	80.6	1261.3	1234.6	723.2	753.5
cyclohexane	81.1	1279.0	1255.2	697.0	724.0
benzene	−1.7	1321.8	1320.0	602.5	604.3

ACKNOWLEDGMENT

Authors gratefully acknowledge financial support from DGA.

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