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Excess isentropic compressibilities of halohydrocarbon + butanol mixture at 298.15 K

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Abstract

Isentropic compressibilities, κ_s, and excess isentropic compressibilities, κ_s^E, of various halohydrocarbons, namely, chlorocyclohexane, chlorobenzene, bromocyclohexane and bromobenzene in isomeric butanols were calculated from density and speed of sound measurements at 298.15 K. Excess isentropic compressibilities were fitted to the Redlich–Kister equation. Mixtures containing an aromatic halohydrocarbons show a decrease in the κ_s^E values with respect to those containing the corresponding halocycloalkane. The same effect can be observed when the chlorine atom is substituted by bromine.

Keywords: Isentropic compressibilities; Halohydrocarbons; Isomeric butanols

1. Introduction

This paper is a continuation of our work on the determination of isentropic compressibilities of binary mixtures of haloalkanes with isomeric butanols [1]. We present here density and speed of sound measurements of chlorocyclohexane, chlorobenzene, bromocyclohexane and bromobenzene + isomeric butanols at 298.15 K and their calculated isentropic compressibility functions. A knowledge of these properties helps in understanding molecular interactions in the liquid mixtures. Our interest lies in studying how both the change from cyclic alkane to the corresponding aromatic hydrocarbon and the substitution of the chlorine atoms by a bromine affect the compressibility behaviour of these mixtures.

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2. Experimental

2.1. Materials

The liquids used were 1-butanol (better than 99.8 mol%), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol%), and 2-butanol and chlorocyclohexane (better than 99 mol%), obtained from Aldrich, together with chlorobenzene and bromobenzene (better than 99.5 mol%), and bromocyclohexane (better than 99 mol%) provided by Fluka. The purity of the chemicals was checked by GLC and was considered sufficient. The isomeric butanols were carefully dried with Merck molecular sieves (type 0.3 nm).

2.2. Measurements

The density, ρ, and speed of sound, u, of pure liquids and mixtures were measured with an Anton Paar DSA-48 density and sound analyser. Calibration of the apparatus was carried out with deionized doubly-distilled water and dry air. The uncertainty of the density measurements was $\pm 1 \times 10^{-4}$ g cm^{-3} and of the speed of sound measurements, ± 0.1 m s^{-1}. Experimental and literature [2] values of ρ and experimental values of u for pure liquids are listed in Table 1.

3. Results and discussion

Densities and speeds of sound of the mixtures are given in Table 2. Assuming that ultrasonic absorption is negligible, isentropic compressibilities can be obtained from the densities and speeds of sound using the relation

$$\kappa_s = (\rho u^2)^{-1} \tag{1}$$

Table 1
Physical properties of pure compounds at $T = 298.15$ K

Component	ρ/g cm^{-3}		u ms^{-1}	κ_s T Pa^{-1}	α k K^{-1}	$C_{p,m}$ J mol^{-1} K^{-1}
	Exp$_{tl}$	Lit.				
Chlorocyclohexane	0.9934	–	1301.0	594.7	0.975	178.6[b]
Chlorobenzene	1.1011	1.1009[a]	1267.8	565.0	0.981	150.1[c]
Bromocyclohexane	1.3262	–	1183.0	538.8	0.913	182.1[d]
Bromobenzene	1.4885	1.48820[a]	1153.3	505.1	0.900	154.3[c]
1-Butanol	0.8060	0.80575[a]	1239.6	807.4	0.928	177.2[c]
2-Butanol	0.8024	0.80241[a]	1212.0	848.4	1.059	196.9[c]
2-Methyl-1-propanol	0.7978	0.7978[a]	1188.0	888.1	0.978	181.5[c]
2-Methyl-2-Propanol	0.7810	0.7812	1121.5	1018.0	1.387	218.6[c]

[a] Ref. [2]. [b] Ref: [4]. [c] Ref. [5]. [d] Ref. [6].

Excess isentropic compressibilities were evaluated, according to Benson and Kiyohara [3], as follows

$$\kappa_s^{\mathrm{E}} = \kappa_s - \kappa_s^{\mathrm{id}} \tag{2}$$

$$\kappa_s^{\mathrm{id}} = \sum_i \phi_i\{\kappa_{s,i} + TV_i(\alpha_i)^2/C_{p,i}\} - T(\sum_i x_iV_i)(\sum_i \phi_i\alpha_i)^2/(\sum_i x_iC_{p,i}) \tag{3}$$

where ϕ_i is the volume fraction of component i in the mixture referred to the unmixed state, x_i is the corresponding mole fraction, T is the temperature, and $\kappa_{s,i}$, V_i, α_i and $C_{p,i}$ are respectively the isentropic compressibility, molar volume, isobaric thermal expansivity, and molar heat capacity of component i. Experimental isentropic compressibilities and isobaric thermal expansivities along with literature molar heat capacities [4–6] are collected in Table 1 for pure compounds.

The estimated quantities κ_s and κ_s^{E} are given in Table 2, and κ_s^{E} values are plotted in Figs. 1–4.

Table 2.
Experimental densities, ρ, and speeds of sound, u, calculated isentropic compressibilities, κ_s, and excess isentropic compressibilities, κ_s^{E}, at $T = 298.15$ K

x_1	ρ g cm^{-3}	u m s^{-1}	κ_s T Pa^{-1}	κ_s^{E} T Pa^{-1}	x_1	ρ g cm^{-3}	u m s^{-1}	κ_s T Pa^{-1}	κ_s^{E} T Pa^{-1}
			Chlorocyclohexane(1) + 1-butanol(2)						
0.0402	0.8154	1242.2	794.8	−2.3	0.5947	0.9278	1266.2	672.3	0.9
0.0971	0.8287	1245.2	778.3	−4.5	0.6968	0.9450	1271.8	654.2	3.2
0.1985	0.8512	1249.7	752.2	−6.0	0.8012	0.9621	1278.6	635.8	4.8
0.2999	0.8724	1253.8	729.2	−5.5	0.8948	0.9768	1287.3	617.8	4.2
0.4009	0.8921	1258.0	708.3	−3.8	0.9440	0.9845	1292.9	607.7	2.9
0.4962	0.9100	1262.0	690.0	−1.7					
			Chlorocyclohexane(1) + 2-butanol(2)						
0.0399	0.8120	1215.0	834.2	−1.8	0.5968	0.9250	1254.0	687.5	2.7
0.1027	0.8264	1219.4	813.8	−3.2	0.6954	0.9423	1262.7	665.6	4.1
0.2045	0.8487	1226.1	783.8	−3.5	0.7966	0.9593	1272.7	643.6	5.0
0.2975	0.8680	1232.1	758.9	−2.5	0.8910	0.9750	1284.1	622.0	4.2
0.3991	0.8882	1239.0	733.4	−0.9	0.9475	0.9843	1292.3	608.3	2.6
0.4960	0.9067	1246.0	710.4	0.8					
			Chlorocyclohexane(1) + 2-methyl-1-propanol(2)						
0.0349	0.8066	1193.0	871.1	−4.5	0.4982	0.9073	1242.3	714.2	−12.4
0.1017	0.8230	1201.8	841.3	−10.8	0.5959	0.9252	1251.2	690.4	−8.4
0.2014	0.8461	1213.3	802.9	−15.5	0.6987	0.9434	1261.1	666.5	−4.3
0.2961	0.8667	1223.2	771.1	−16.6	0.8045	0.9615	1272.6	642.2	−0.9
0.4027	0.8885	1233.3	740.0	−14.9	0.8965	0.9764	1284.1	621.1	1.2
			Chlorocyclohexane(1) + 2-methyl-2-propanol(2)						
0.1014	0.8056	1136.6	960.9	−4.6	0.5905	0.9151	1222.5	731.2	−14.3
0.1942	0.8279	1151.8	910.5	−9.3	0.6869	0.9340	1239.5	696.9	−10.7
0.3029	0.8532	1170.9	854.9	−13.8	0.7947	0.9547	1259.0	660.8	−6.3
0.3918	0.8731	1186.9	813.0	−15.8	0.8932	0.9730	1277.7	629.5	−2.1
0.4883	0.8939	1204.2	771.5	−15.9	0.9574	0.9849	1291.4	608.8	−0.4

Table 2 (*Continued*)

x_1	ρ g cm^{-3}	u m s^{-1}	κ_s T Pa^{-1}	κ_s^E T Pa^{-1}	x_1	ρ g cm^{-3}	u m s^{-1}	κ_s T Pa^{-1}	κ_s^E T Pa^{-1}
Chlorobenzene(1) + 1-butanol(2)									
0.0312	0.8163	1240.5	796.1	−3.5	0.6080	0.9930	1244.5	650.2	−8.0
0.0937	0.8370	1241.6	775.0	−8.9	0.6977	1.0185	1245.4	633.0	−3.7
0.1999	0.8710	1242.7	743.4	−14.0	0.8041	1.0476	1249.1	611.8	0.4
0.3029	0.9034	1242.6	716.9	−15.2	0.8984	1.0732	1255.2	591.4	2.4
0.4029	0.9333	1242.8	693.7	−14.0	0.9538	1.0882	1261.0	577.9	2.0
0.5022	0.9632	1243.0	672.0	−11.7					
Chlorobenzene(1) + 2-butanol(2)									
0.0353	0.8141	1213.3	834.4	−3.4	0.4989	0.9576	1226.6	694.1	−9.6
0.0946	0.8334	1215.2	812.6	−7.7	0.5982	0.9865	1231.0	668.9	−6.9
0.1994	0.8668	1217.9	777.8	−11.7	0.7036	1.0167	1236.9	642.9	−3.6
0.3029	0.8989	1220.4	746.9	−12.6	0.7985	1.0436	1243.9	619.3	−1.0
0.4008	0.9283	1223.1	720.1	−11.4	0.8992	1.0718	1254.0	593.3	0.7
Chlorobenzene(1) + 2-methyl-1-propanol(2)									
0.0339	0.8094	1191.2	870.7	−5.9	0.4992	0.9566	1219.5	702.9	−19.8
0.0951	0.8300	1196.1	842.1	−13.7	0.6063	0.9885	1225.9	673.2	−15.2
0.1982	0.8637	1203.2	799.8	−21.5	0.6931	1.0138	1231.7	650.2	−10.6
0.2982	0.8953	1208.9	764.3	−23.9	0.7972	1.0433	1240.1	623.3	−4.8
0.4010	0.9273	1214.3	731.4	−23.1	0.8927	1.0703	1250.7	597.3	−1.0
Chlorobenzene(1) + 2-methyl-2-propanol(2)									
0.0559	0.7989	1125.6	988.0	−3.0	0.5943	0.9737	1197.3	716.4	−24.9
0.0904	0.8103	1128.8	968.5	−5.8	0.7002	1.0069	1213.6	674.3	−20.1
0.1953	0.8450	1140.7	909.5	−15.0	0.7894	1.0347	1227.9	641.0	−14.4
0.3016	0.8799	1154.9	852.1	−22.6	0.8870	1.0649	1244.8	606.0	−7.2
0.4003	0.9116	1169.2	802.5	−26.6	0.9500	1.0846	1257.5	583.1	−3.2
0.5010	0.9440	1183.9	755.8	−27.4					
Bromocyclohexane(1) + 1-butanol(2)									
0.0493	0.8394	1231.3	785.8	−4.7	0.5966	1.1500	1178.7	625.9	−5.3
0.0986	0.8720	1223.3	766.3	−7.7	0.6993	1.1984	1175.6	603.8	−2.2
0.2017	0.9369	1209.4	729.7	−11.5	0.7942	1.2405	1174.7	584.2	0.4
0.3044	0.9975	1198.2	698.3	−12.0	0.8877	1.2799	1176.4	564.6	1.8
0.3950	1.0474	1190.4	673.8	−10.7	0.9476	1.3046	1179.2	551.2	1.4
0.5009	1.1029	1183.2	647.7	−8.1					
Bromocyclohexane(1) + 2-butanol(2)									
0.0995	0.8688	1197.7	802.4	−7.1	0.5866	1.1418	1167.6	642.4	−5.3
0.2017	0.9327	1186.6	761.5	−10.3	0.7048	1.1972	1168.2	612.1	−2.3
0.3018	0.9914	1178.4	726.4	−10.6	0.7857	1.2344	1169.5	592.3	−0.3
0.4019	1.0471	1172.7	694.4	−9.6	0.8883	1.2788	1174.0	567.4	1.2
0.5018	1.0995	1169.0	665.5	−7.4	0.9517	1.3054	1178.6	551.5	1.0
Bromocyclohexane(1) + 2-methyl-1-propanol(2)									
0.0477	0.8309	1184.4	857.9	−8.8	0.5917	1.1446	1165.0	643.7	−16.4
0.0980	0.8647	1180.9	829.3	−15.6	0.6975	1.1949	1166.1	615.5	−10.9
0.1983	0.9286	1174.9	780.1	−23.0	0.7869	1.2357	1168.4	592.8	−6.4
0.3027	0.9910	1170.2	736.9	−25.3	0.8860	1.2783	1172.9	568.7	−1.7

Table 2 (*Continued*)

x_1	ρ g cm^{-3}	u m s^{-1}	κ_s T Pa^{-1}	κ_s^E T Pa^{-1}	x_1	ρ g cm^{-3}	u m s^{-1}	κ_s T Pa^{-1}	κ_s^E T Pa^{-1}
0.4015	1.0463	1167.1	701.2	−23.8	0.9454	1.3032	1177.9	553.1	−0.6
0.4948	1.0957	1165.4	672.0	−20.6					
Bromocyclohexane(1) + 2-methyl-2-propanol(2)									
0.0552	0.8179	1118.4	977.5	−6.8	0.5905	1.1326	1139.8	679.6	−26.3
0.0981	0.8465	1117.1	946.6	−12.2	0.6860	1.1808	1147.9	642.7	−21.2
0.1988	0.9105	1117.6	879.3	−22.1	0.7686	1.2204	1155.5	613.7	−15.5
0.2934	0.9687	1120.7	821.9	−28.5	0.8729	1.2686	1166.3	579.5	−7.7
0.3942	1.0273	1126.0	767.8	−31.1	0.9282	1.2934	1172.8	562.1	−3.7
0.4871	1.0784	1132.0	723.6	−30.0					
Bromobenzene(1) + 1-butanol(2)									
0.0442	0.8405	1230.9	785.3	−7.3	0.5969	1.2361	1157.3	604.0	−15.3
0.0951	0.8801	1220.9	762.3	−13.4	0.7053	1.3067	1150.9	577.8	−9.9
0.2044	0.9626	1202.2	718.8	−21.3	0.7926	1.3617	1147.9	557.3	−5.4
0.3034	1.0349	1187.7	685.0	−23.6	0.9015	1.4288	1147.8	531.2	−0.9
0.3965	1.1006	1176.0	657.0	−22.6	0.9502	1.4581	1150.3	518.3	−0.4
0.4928	1.1668	1166.0	630.4	−19.9					
Bromobenzene(1) + 2-butanol(2)									
0.0403	0.8339	1204.6	826.4	−6.5	0.5944	1.2297	1146.5	618.7	−16.6
0.0943	0.8754	1195.2	799.7	−12.8	0.6825	1.2872	1144.1	593.5	−12.6
0.1988	0.9537	1179.8	753.3	−20.4	0.7966	1.3610	1143.7	561.2	−7.3
0.2958	1.0244	1167.9	715.7	−22.9	0.8903	1.4199	1146.2	536.1	−3.2
0.3967	1.0959	1158.2	680.2	−22.7	0.9513	1.4577	1150.2	518.5	−1.6
0.4954	1.1638	1151.2	648.4	−20.4					
Bromobenzene(1) + 2-methyl-1-propanol(2)									
0.0296	0.8213	1184.5	867.8	−7.7	0.5942	1.2290	1141.0	625.0	−25.6
0.1035	0.8787	1175.6	823.5	−20.9	0.6991	1.2984	1139.4	593.3	−18.6
0.1996	0.9515	1165.5	773.7	−30.9	0.8012	1.3639	1140.4	563.8	−11.1
0.3022	1.0263	1156.4	728.6	−34.6	0.8952	1.4231	1144.3	536.6	−4.9
0.3991	1.0965	1149.4	690.3	−34.7	0.9467	1.4551	1147.7	521.7	−1.8
0.4968	1.1636	1144.3	656.3	−31.0					
Bromobenzene(1) + 2-methyl-2-propanol(1)									
0.0487	0.8178	1115.9	982.2	−8.4	0.5956	1.2167	1116.6	659.2	−40.4
0.0977	0.8553	1111.5	946.4	−16.5	0.7126	1.2967	1124.2	610.2	−31.4
0.1948	0.9285	1107.1	878.7	−30.6	0.7993	1.3553	1131.2	576.6	−23.0
0.3038	1.0092	1106.3	809.6	−40.9	0.9023	1.4225	1140.9	540.1	−10.6
0.4001	1.0792	1108.0	754.8	−44.9	0.9380	1.4469	1145.3	526.9	−7.0
0.4974	1.1486	1111.6	704.6	−44.8					

The excess isentropic compressibilities were fitted to the Redlich–Kister equation

$$\kappa_s^E/T\mathrm{Pa}^{-1} = x_1(1-x_1)\sum_i A_i(2x_1-1)^i \qquad (4)$$

where A_i are adjustable parameters determined by least-square optimization. The values of these parameters are given in Table 3 together with the standard deviations.

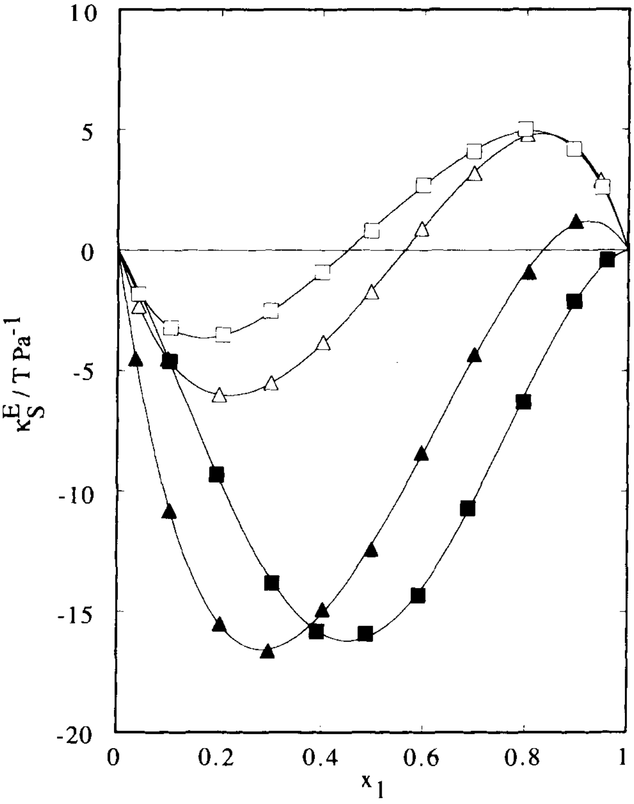

Fig. 1. Excess isentropic compressibilities of chlorocyclohexane(1) + a butanol(2) at $T = 298.15$ K: △, 1-butanol; □, 2-butanol; ▲, 2-methyl-1-propanol; ■, 2-methyl-2-propanol.

Table 3
Values of parameters A_i for Eq.(4) and standard deviations, σ, at $T = 298.15$ K

	A_0	A_1	A_2	A_3	σ
Chlorocyclohexane(1) +					
1-butanol(2)	−6.2	49.8	6.1	16.9	0.0
2-butanol(2)	3.7	36.4	1.7	21.4	0.1
2-methyl-1-propanol(2)	−48.6	69.5	−6.9	18.9	0.2
2-methyl-2-propanol(2)	−63.8	20.5	43.0	−3.5	0.1
Chlorobenzene(1) +					
1-butanol(2)	−47.1	62.8	13.2	30.5	0.2
2-butanol(2)	−38.1	49.4	−3.9	17.7	0.1
2-methyl-1-propanol(2)	−79.9	78.1	−6.1	25.1	0.1
2-methyl-2-propanol(2)	−109.8	19.8	56.5	−30.1	0.2
Bromocyclohexane(1) +					
1-butanol(2)	−32.9	55.8	−2.5	18.1	0.1
2-butanol(2)	−30.1	46.6	−5.0	18.2	0.1

Table 3 (*Continued*)

	A_0	A_1	A_2	A_3	σ
2-methyl-1-propanol(2)	−82.0	81.2	−22.0	28.0	0.2
2-methyl-2-propanol(2)	−120.1	52.3	28.8	−11.0	0.3
Bromobenzene(1)+					
1-butanol(2)	−78.4	76.7	−9.2	19.3	0.2
2-butanol(2)	−80.5	65.0	−16.4	11.4	0.2
2-methyl-1-propanol(2)	−123.4	92.1	−23.2	29.8	0.2
2-methyl-2-propanol(2)	−179.1	50.0	33.5	−15.9	0.3

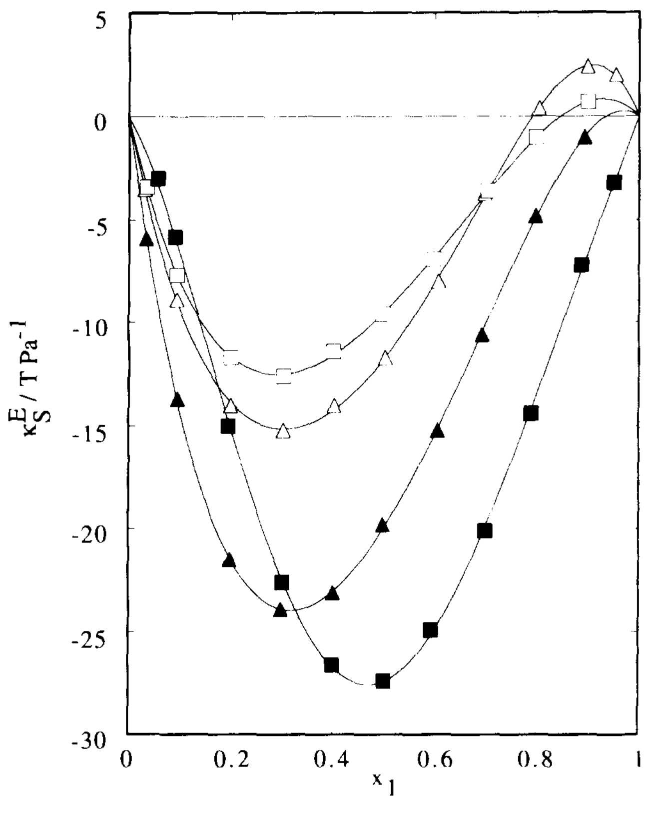

Fig. 2. Excess isentropic compressibilities of chlorobenzene(1)+a butanol(2) at $T = 298.15$ K: △, 1-butanol; □, 2-butanol; ▲, 2-methyl-1-propanol; ■, 2-methyl-2-propanol.

Results show that κ_s^E values exhibit an inversion in sign for the mixtures chlorocyclohexane, chlorobenzene and bromocyclohexane with 1-butanol and 2-butanol, and for chlorocyclohexane with 2-methyl-1-propanol. For the remaining mixtures, the κ_s^E values are negative in the whole composition range although the mixture chlorobenzene with 2-methyl-1-propanol has slightly positive κ_s^E values in the region very rich in

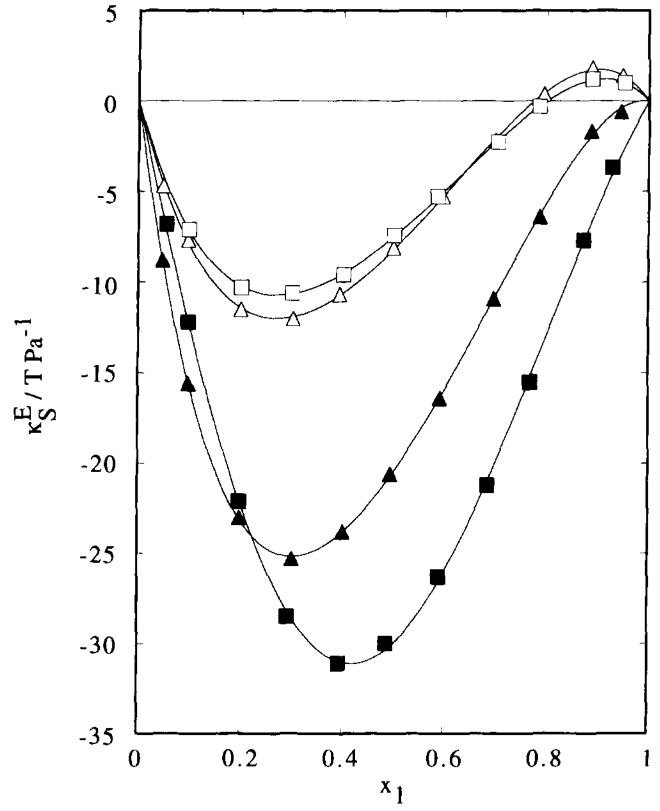

Fig. 3. Excess isentropic compressibilities of bromocyclohexane(1) + a butanol(2) at $T = 298.15$ K: △, 1-butanol; □, 2-butanol; ▲, 2-methyl-1-propanol; ■, 2-methyl-2-propanol.

the chlorinated compound. For a given halohydrocarbon, similar behaviour can be observed in 1-butanol and 2-butanol on the one hand, and 2-methyl-1-propanol and 2-methyl-2-propanol on the other. Mixtures containing the last two isomeric butanols show more negative κ_s^E values. If we now consider an isomeric butanol, it can be pointed out that the mixtures containing the aromatic halohydrocarbon lead to a decrease in the κ_s^E values with respect to those containing the corresponding halocycloalkane and the same effect can be observed when the chlorine atom is substituted by a bromine one.

The behaviour of these mixtures can be explained in terms of molecular interactions. According to Fort and Moore [7], excess adiabatic compressibility decreases and becomes increasingly negative as the strength of the interaction between the components increases, due to a closer approach of unlike molecules leading to reductions in compressibility. Therefore, the breaking of the hydrogen bond association of the butanols in our mixtures, which produces positive κ_s^E values [8], is balanced by the existence of specific interactions, such as the solvation of the OH group by the π-electron cloud of aromatic rings [9] in the mixtures with chlorobenzene and bromobenzene and by the X–OH interaction (X is Cl or Br), to form a weak H-bond

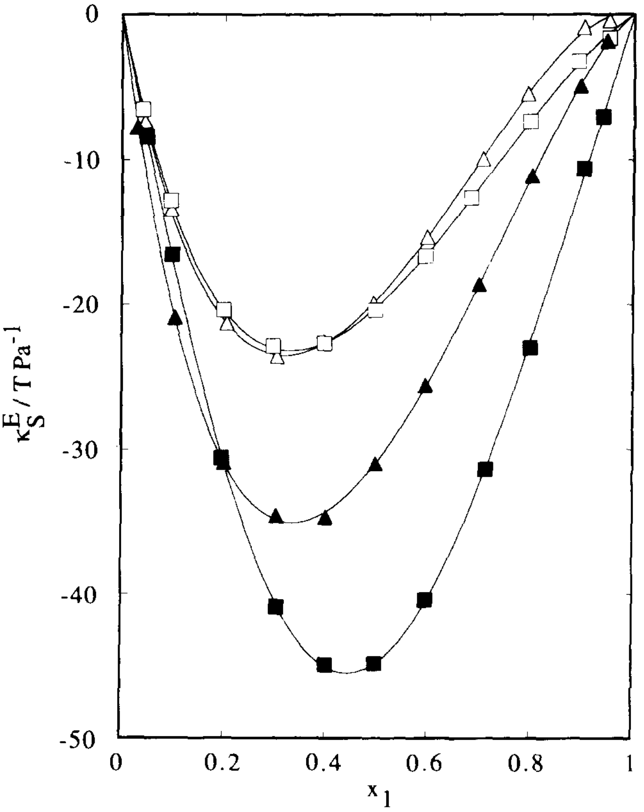

Fig. 4. Excess isentropic compressibilities of bromobenzene(1) + a butanol(2) at $T = 298.15$ K: △, 1-butanol; □, 2-butanol; ▲, 2-methyl-1-propanol; ■, 2-methyl-2-propanol.

[9]. The solvation expanding why the values for the aromatic halohydrocarbon are smaller than those for the corresponding halocycloalkane. The results suggest that the X–OH interaction is somewhat stronger for the bromine atom than for the chlorine.

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