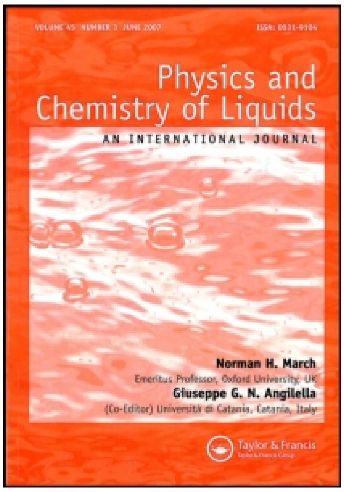

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H. Iloukhani[a]; N. Zoorasna[a]; R. Soleimani[a]
[a] Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hamadan, Iran

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Excess molar volumes and speeds of sound of tetrahydrofuran with chloroethanes or chloroethenes at 298.15 K

H. ILOUKHANI*, N. ZOORASNA and R. SOLEIMANI

Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hamadan, Iran

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Excess molar volumes, V_m^E and speeds of sound, u of the binary liquid mixtures of tetrahydrofuran (THF) with chloroethanes or chlororethenes at 298.15 K have been measured over the entire range of (THF) compositions. The chloroethanes are 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane and the chloroethenes are trichloroethylene and tetrachloroethylene. Partial molar volumes $\overline{V}_i$, were also calculated and their values have been extrapolated to zero concentration to obtain the limiting values at infinite dilution, $\overline{V}_i^\circ$. The V_m^E values are negative in mixtures of THF + tetrachloroethylene, + trichloroethylene, + 1,1, 1-trichloroethane, and + 1,1,2,2-tetrachloroethane over the entire composition range of THF. The V_m^E values are positive for THF with 1,2-dichloroethane. An inversion of the sign of V_m^E was observed at $x \approx 0.75$ of THF for the mixtures of THF with 1,2-dichloroethane. Further, isentropic compressibilities, k_s of the mixtures were computed by combining speeds of sound and density data. Deviation in isentropic compressibility, Δk_s were evaluated using volume fraction ϕ weighing of the individual component properties to estimate ideal mixture behaviour. The Δk_s values are negative over the whole of volume fraction for all the mixtures except for 1,2-dichloroethane. The Δk_s values were positive over the entire volume fraction of THF with 1,2-dichloroethane. For all systems, V_m^E and Δk_s values were satisfactorily correlated by the Redlich–Kister polynomial. The results are explained in terms of dissociation of the self-associated chloroethanes or chloroethene molecules and the formation of aggregates between unlike molecules.

Keywords: Excess molar volumes; Speeds of sound; Isentropic compressibility; Redlich–Kister; Tetrahydrofuran (THF)

1. Introduction

Following our study on the measurement of thermodynamic and acoustic properties of non-electrolyte solutions in which specific interactions between unlike molecules can occur [1–5], we present, here, excess molar volumes V_m^E at 298.15 K and also partial molar volumes $\overline{V}_i$ of THF with the chloroethanes (1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethene) or chloroethenes (trichloroethylene and tetrachloroethylene). For these completely miscible mixtures, it is interesting to use

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*Corresponding author. Email: iloukhani@basu.ac.ir

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volumetric data for calculations of the effects of pressure on thermodynamic properties and also to extend our understanding of molecular interactions in mixtures. By extrapolation of partial molar volumes to infinite dilution, limiting partial molar volumes, $\overline{V}_i^\circ$ are also obtained. These values are interesting from a theoretical point of view since at infinite dilution the only interactions present are solute–solvent interactions. Speeds of sound, u, isentropic compressibility, k_s and deviation in isentropic compressibilities, Δk_s are also obtained.

2. Experimental

Characterization data for the chemicals used in this study are listed in table 1. Materials used were purified by distillation using a 1m fractionation column. The purified components were stored in brown glass bottles and fractionally distilled immediately before use. The purity of each component was ascertained by the constancy of the boiling point, and also from the density. Densities were measured at 298.15 K using an Anton Paar DMA 4500 oscillating U-tube densitometer with an accuracy of 5 parts in 10^{-5}. Table 1 also give the density measurements that agree with values obtained from the literature [6]. The speeds of sound, u in pure liquids and the binary mixtures were measured with a single crystal multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi). In the present work, a steel cell fitted with a quartz crystal of 1 MHz frequency was employed. In these measurements the temperature was maintained constant by circulating water around a liquid cell from a thermostat controlled at 298.15 K. The densities of pure components and mixtures were measured with an Anton Paar DMA 4500 having an accuracy of 5 parts in 10^5.

Mixtures were prepared by mixing known masses of pure components in air-tight, narrow-mouthed ground-glass stoppered bottles. All the mass measurements were preformed on an electronic balance (Mettler AE 163, Switzerland) accurate to 0.01 mg. The possible error in the mole fraction is estimated to be less than $\pm 1 \times 10^{-4}$. The accuracies in the values of speed of sound, u and density, ρ were estimated to be within $\pm 1.0\,\mathrm{m\,s^{-1}}$, and 0.01%, respectively.

3. Results and discussion

The measured excess molar volumes, V_m^E, speeds of sound, u, isentropic compressibility, k_s and deviation in isentropic compressibilities, Δk_s of binary mixtures

Table 1. Source, purity grades, and density ρ of pure components at 298.15 K.

			ρ (g cm^{-3})	
Component	Source	Purity (mass %)	Experiment	Literature[a]
THF	Merck	99.0	0.88207	0.8842[b]
1,2-Dicohloroethane	Merck	99.0	1.24564	1.2458
1,1,1-Trichloroethane	Merck	98.0	1.32712	1.3209[c]
1,1,2,2-Tetrachloroethane	Fluka	98.0	1.57892	1.5786
Trichloroethylene	Merck	99.5	1.45559	1.4514[c]
Tetrachloroethylene	Merck	99.0	1.61421	1.6064[c]

[a] Ref. 6; [b] At 298.15 K; [c] At 303.15 K.

Table 2. Densities ρ ($\mathrm{g\,cm^{-3}}$), excess molar volumes V_m^E ($\mathrm{cm^3\,mol^{-1}}$), and partial molar volumes $\overline{V}_i$ ($\mathrm{cm^3\,mol^{-1}}$) for the mixtures of xTHF + $(1-x)$ chloroethanes or chloroethenes at 298.15 K.

x	ρ	V_m^E	$\overline{V}_1$	$\overline{V}_2$	x	ρ	V_m^E	$\overline{V}_1$	$\overline{V}_2$
xTHF + $(1-x)$ 1,2-dichloroethane									
0.0508	1.22606	0.030	57.42	79.22	0.5818	1.03095	0.048	78.62	70.70
0.1201	1.1998	0.064	64.81	78.56	0.6088	1.02146	0.031	79.29	69.71
0.1819	1.17651	0.092	68.05	77.99	0.6634	1.00177	0.032	80.44	67.70
0.2710	1.14370	0.089	70.49	77.29	0.7068	0.98864	0.011	81.12	66.22
0.3449	1.11644	0.092	72.11	76.57	0.7438	0.97312	0.008	81.53	65.14
0.4220	1.08860	0.738	74.08	75.34	0.8255	0.94406	−0.005	81.93	65.37
0.4329	1.08461	0.076	74.38	75.11	0.9005	0.91744	−0.012	81.89	64.14
0.5017	1.05973	0.063	76.37	73.35	0.9508	0.89949	−0.002	81.79	63.75
0.5023	1.05947	0.067	76.39	73.34					
xTHF + $(1-x)$ 1,1,1-trichloroethane									
0.0516	1.29695	−0.042	80.64	101.49	0.5788	1.09180	−0.370	81.48	100.98
0.1200	1.27355	−0.139	80.44	101.50	0.6608	1.05447	−0.342	81.55	100.86
0.2002	1.24506	−0.241	80.60	101.47	0.7423	1.01579	−0.296	81.63	100.68
0.2790	1.21547	−0.292	80.89	101.38	0.8197	0.97735	−0.222	81.69	100.44
0.3594	1.18424	−0.345	81.14	101.26	0.8993	0.93638	−0.131	81.74	100.17
0.4444	1.14970	−0.372	81.32	101.14	0.9484	0.91025	−0.070	81.75	100.07
0.4993	1.12659	−0.381	81.40	101.07					
xTHF + $(1-x)$ 1,1,2,2-tetrachloroethane									
0.0683	1.54958	−0.095	80.83	105.82	0.5042	1.28444	−0.596	81.94	105.45
0.1020	1.53125	−0.144	81.03	105.81	0.5854	1.22673	−0.600	81.91	105.44
0.1924	1.48051	−0.276	81.46	105.74	0.6491	1.17973	−0.606	81.87	105.46
0.2583	1.44196	−0.365	81.69	105.68	0.7007	1.14036	−0.601	81.84	105.50
0.3054	1.41324	−0.405	81.80	105.63	0.7556	1.09623	−0.517	81.81	105.56
0.3547	1.3826	−0.460	81.88	105.57	0.8040	1.05648	−0.455	81.78	105.62
0.4099	1.34741	−0.520	81.93	105.52	0.8820	0.98948	−0.303	81.76	105.73
0.4810	1.30022	−0.580	81.95	105.47	0.9562	0.92285	−0.127	81.75	105.81
xTHF + $(1-x)$ trichloroethylene									
0.0659	1.42225	−0.065	80.61	90.26	0.5379	1.16605	−0.352	81.44	89.85
0.1044	1.40266	−0.113	80.64	90.25	0.6130	1.12200	−0.331	81.54	89.72
0.1690	1.36895	−0.164	80.74	90.24	0.6506	1.09959	−0.310	81.58	89.64
0.2535	1.32453	−0.251	80.93	90.19	0.7029	1.06823	−0.287	81.64	89.52
0.3038	1.29743	−0.288	81.04	90.14	0.8044	1.00591	−0.203	81.72	89.27
0.3717	1.26034	−0.333	81.17	90.08	0.9032	0.94406	−0.118	81.75	89.11
0.4246	1.23069	−0.330	81.26	90.01	0.9552	0.91075	−0.042	81.75	89.15
0.5057	1.18459	−0.344	81.39	89.90					
xTHF + $(1-x)$ tetrachloroethylene									
0.1010	1.55434	−0.016	81.54	102.73	0.5060	1.28686	−0.103	81.59	102.69
0.1568	1.52026	−0.029	81.52	102.73	0.5800	1.23222	−0.101	81.62	102.66
0.2072	1.48876	−0.043	81.52	102.73	0.6516	1.17764	−0.101	81.65	102.61
0.2554	1.45784	−0.044	81.53	102.73	0.7011	1.13874	−0.097	81.67	102.56
0.3290	1.40977	−0.069	81.54	102.73	0.8086	1.05091	−0.085	81.71	102.42
0.4142	1.35168	−0.079	81.56	102.71	0.8787	0.99101	−0.063	81.74	102.31
0.4747	1.30631	−0.097	81.58	102.70	0.9580	0.92048	−0.022	81.75	102.20
0.5060	1.28686	−0.103	81.59	102.69					

of xTHF + $(1-x)$ chloroethanes or chloroethenes at 298.15 K are listed in table 2. The experimental data of V_m^E at 298.15 K are graphically presented in figure 1. Each set of results for V_m^E was fitted using a Redlich–Kister [7] equation of the type

$$V_\mathrm{m}^\mathrm{E}\ (\mathrm{cm^3\,mol^{-1}}) = x(1-x)\sum_{k=1} A_k(1-2x)^{k-1} \tag{1}$$

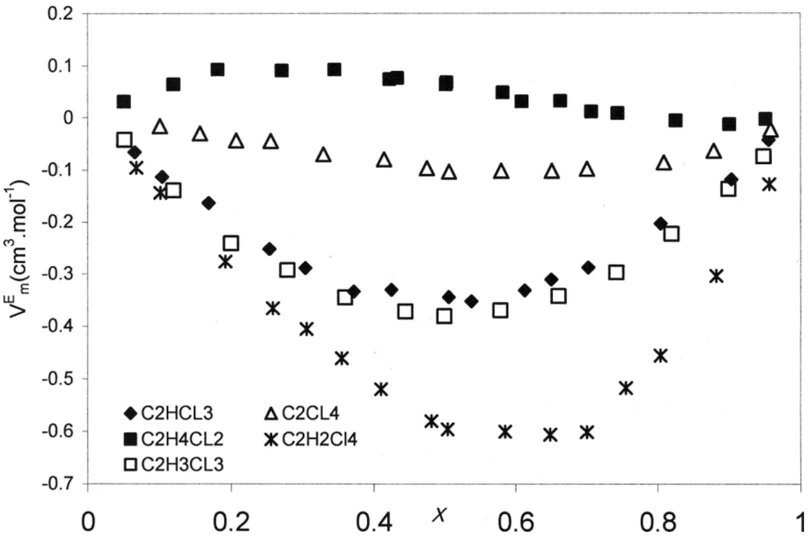

Figure 1. Excess molar volumes of binary mixtures of THF with chloroethanes or chloroethenes at 298.15 K.

where A_k is the coefficient obtained by a linear least squares fitting procedure and x is the mole fraction of THF. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation $\sigma(V^{E}_{m})$ with

$$\sigma(V^{E}_{m}) = \left[\sum_{k=1}^{n} \left(V^{E}_{m,\,\text{expt.}} - V^{E}_{m,\,\text{calcd.}} \right)^{2} \Big/ (n-p) \right]^{1/2} \qquad (2)$$

in which n is the number of results and p is the number of parameters retained in equation (1). The values adopted for the coefficients, A_k and the standard deviation, $\sigma(V^{E}_{m})$ estimated with the use of equations (1) and (2), respectively, are summarized in table 5.

From figure 1 it can be observed that the V^{E}_{m} is negative for the mixtures of THF + tetrachloroethylene, + trichloroethylene, + 1,1,1-trichloroethane, and + 1,1,2, 2-tetrachloroethane, over the entire composition range of THF. V^{E}_{m} is positive for the mixtures of THF with 1,2-dichloroethane and an inversion of the sign of V^{E}_{m} is observed at around $x \approx 0.75$ mole fraction of the THF. The observed values of V^{E}_{m} in all of the systems over the entire range of compositions can be attributed to the interactions between the unlike molecules, dispersion forces, dipole induced dipole interactions, formation of new hydrogen bonds between unlike molecules, and due to size and shape. The negative values of V^{E}_{m} also mean that the mixture is less compressible than the corresponding ideal mixture. Therefore in the systems, a compression in free volume is considered to occur, making the mixtures less compressible than the ideal mixture, which ultimately culminates in the negative values of V^{E}_{m}. On the other hand, positive V^{E}_{m} values showed disruption of the ordered structure of pure components during the formation of the mixture. The V^{E}_{m} *vs.* x curves for all the mixtures are almost symmetrical with a minimum or maximum around $x \approx 0.5$

of THF, except for the mixtures of THF with 1,2-dichloroethane. The values of $V_{\mathrm{m}}^{\mathrm{E}}$ at that concentration follow the order:

1,2-dichloroethane > tetrachloroethylene > trichloroethylene
> 1,1,1-trichloroethane > 1,1,2,2-tetrachloroethane.

The partial molar volumes of components, $\overline{V}_i$ in binary mixtures can be determined from excess molar volumes data as follows:

$$\overline{V}_1 = V^E + V_1^* + (1-x)\left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial x}\right) \tag{3}$$

$$\overline{V}_2 = V^E + V_2^* - x\left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial x}\right) \tag{4}$$

in which V_1^* and V_2^* are molar volumes of pure components, x and $(1-x)$ are the mole fraction of THF and chloroethanes or chloroethenes, respectively.

To obtain values of the partial molar volumes, we start by differentiation of equation (1) with respect to x and substitution of the result in equations (3) and (4) leads to the following equations for the partial molar volumes of THF, $\overline{V}_1$ and chloroethanes or chloroethenes, $\overline{V}_2$

$$\overline{V}_1 = (1-x)^2 \sum_{k=1} A_k (1-2x)^{k-1} - 2x(1-x)^2 \sum_{k=1} A_k (k-1)(1-2x)^{k-2} + V_1^* \tag{5}$$

$$\overline{V}_2 = x^2 \sum_{k=1} A_k (1-2x)^{k-1} + 2x^2(1-x) \sum_{k=1} A_k (k-1)(1-2x)^{k-2} + V_2^*. \tag{6}$$

Partial molar volumes of THF, $\overline{V}_1$ and of chloroethanes or chloroethenes, $\overline{V}_2$ for all the compositions can be calculated by using the Redlich–Kister coefficients (table 5) in equations (5) and (6). Results at 298.15 K are also listed in table 2 and $\overline{V}_1$ and $\overline{V}_2$ *vs.* composition for THF and chloroethanes or chloroethenes in mixtures shown in figures 2 and 3, respectively.

Much of our present interest in the volumetric properties of (THF + chloroethanes or chloroethenes) systems is focused on the partial molar volume of the THF at infinite dilution ($x = 0$) in chloroethanes or chloroethenes and of chloroethanes or chloroethenes in THF at infinite dilution ($x = 1$). Setting $x = 0$ in equation (5) leads to chloroethanes and chloroethenes:

$$\overline{V}_1^{\circ} = \sum_{k=1} A_k + V_1^* \tag{7}$$

Similarly, setting ($x = 1$) in equation (6) leads to

$$\overline{V}_2^{\circ} = \sum_{k=1} A_k (-1)^{k-1} + V_2^* \tag{8}$$

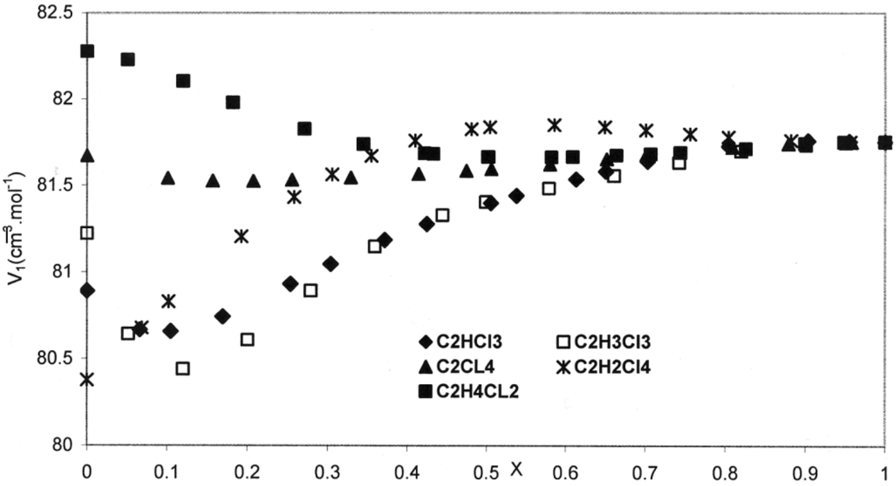

Figure 2. Partial molar volumes of (x) THF in mixtures of ($1-x$) chloroethanes or chloroethenes at 298.15 K.

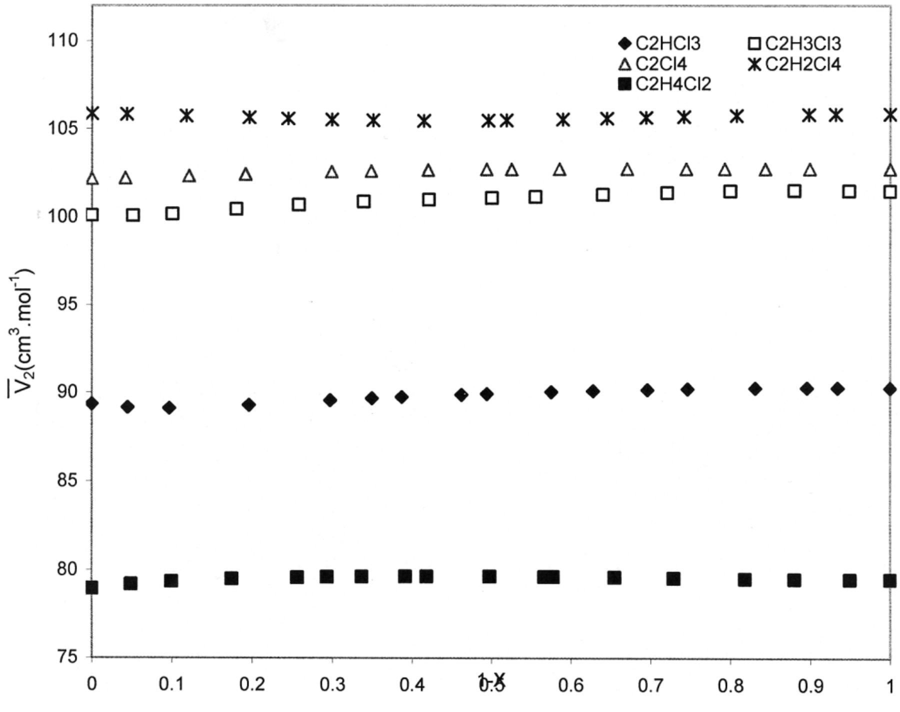

Figure 3. Partial molar volumes of the binary mixtures of ($1-x$) chloroethanes or chloroethenes with THF (x) at 298.15 K.

In equations (7) and (8), $\overline{V}_1^\circ$ and $\overline{V}_2^\circ$ represent the partial molar volumes of THF at infinite dilution in chloroethanes or chloroethenes and the partial molar volume of chloroethanes and chloroethenes at infinite dilution in THF, respectively. All partial molar volumes at infinite dilution, $\overline{V}_1^\circ$ were calculated at different temperatures

Table 3. Partial molar volumes of THF at infinite dilution in chloroethanes or chloroethenes, $\overline{V}_1^\circ$ (cm^3 mol^{-1}) and chloroethanes or chloroethenes at infinite dilution in THF, $\overline{V}_2^\circ$ (cm^3 mol^{-1}) from equations (7) and (8), for xTHF + $(1-x)$ chloroethanes or chloroethenes at 298.15 K.

System	$\overline{V}_1^\circ$	$\overline{V}_2^\circ$
xTHF + $(1-x)$ 1,2-dichloroethane	82.27	78.94
xTHF + $(1-x)$ 1,1,1-trichloroethane	81.22	100.07
xTHF + $(1-x)$ 1,1,2,2-tetrachloroethane	80.38	105.84
xTHF + $(1-x)$ trichloroethylene	80.70	89.31
xTHF + $(1-x)$ tetrachloroethylene	81.67	102.17

by using the Redlich–Kister coefficients (table 5) in equations (7) and (8) and are listed in table 3. We note that all of the $\overline{V}_1^\circ$ and $\overline{V}_2^\circ$ values are smaller than the corresponding molar volumes of the pure THF, $\overline{V}_1^*$ and chloroethanes or chloroethenes, $\overline{V}_2^*$. This observation is consistent with the idea that the molar volumes of pure THF are a result of the sum of the "actual" molecular volumes plus the "empty" volume that arises from the hydrogen-bonded open structure of liquid THF.

The specific compression of solution is defined as the partial derivative of specific volumes, V, with respect to pressure, p under isentropic conditions: $k_s = -(\partial V/\partial p)_\mathrm{s}$. Then, the isentropic compressibility, k_s values can be estimated from the relation

$$k_\mathrm{s} = (\rho u^2)^{-1} \tag{9}$$

where ρ and u are the density and speed of sound of mixture, respectively.

Defining the ideal isentropic solution property, k_s^id, is not as straightforward as for the ideal molar volumes, V^id [8]. However, one may write the defining equation in terms of the volume fraction average [9–11]

$$k_\mathrm{s}^\mathrm{id} = \sum_i (k_{\mathrm{s},i}^*)\phi_i \tag{10}$$

where $k_{\mathrm{s},i}^*$ is the isentropic compressibility of pure component i, and $\phi_i = x_i V_i^\circ / \sum x_j V_j$ is the volume fraction of component i. Then the deviation in isentropic compressibility, Δk_s from the ideal mixing values can be estimated from the following equation,

$$\Delta k_\mathrm{s} = k_\mathrm{s} - \sum_i (k_{\mathrm{s},i}^*)\phi_i. \tag{11}$$

Dependence of k_s and Δk_s on compositions and volume fractions, respectively, is shown in figures 4 and 5. The isentropic compressibility, k_s and deviations in isentropic compressibility, Δk_s values are believed to be reliable to within 1.0 TPa^{-1}. The Δk_s values were correlated with the composition data by means of the Redlich–Kister polynomial [7], which for binary mixtures is

$$\Delta k_\mathrm{s} = \phi(1-\phi) \sum_{k=1} A_k (1-2\phi)^{k-1} \tag{12}$$

Table 4. Volume fraction, ϕ of THF, densities, ρ ($\mathrm{g\,cm^{-3}}$), speed of sound, u ($\mathrm{m\,s^{-1}}$), isentropic compressibility, k_s ($\mathrm{TPa^{-1}}$), and deviation isentropic compressibility Δk_s ($\mathrm{TPa^{-1}}$) for the mixtures of ϕTHF + $(1-\phi)$ chloroethanes and chloroethenes at 298.15 K.

ϕ	ρ	u	k_s	Δk_s	ϕ	ρ	u	k_s	Δk_s
ϕTHF + $(1-\phi)$ 1,2-dicohloroethane									
0.0738	1.21768	1193	577	2.43	0.5152	1.05738	1215	641	9.09
0.0934	1.21055	1193	580	3.30	0.6105	1.02291	1223	654	9.74
0.1249	1.19907	1194	585	3.80	0.7115	0.98640	1233	667	9.94
0.2098	1.16819	1197	597	5.31	0.8065	0.95217	1244	679	9.50
0.3315	1.12396	1203	615	6.93	0.9003	0.91841	1258	688	6.76
0.4282	1.08890	1209	628	7.96	0.9531	0.89944	1267	693	4.52
ϕTHF + $(1-\phi)$ 1,1,1-trichloroethane									
0.0423	1.29679	988	790	−2.61	0.5482	1.08154	1129	725	−1.52
0.0820	1.28072	998	784	−4.57	0.6598	1.03242	1164	715	−1.42
0.1824	1.23925	1023	771	−7.13	0.7714	0.98318	1199	708	−1.01
0.2618	1.20573	1045	759	−1.05	0.8795	0.93554	1235	701	−5.7
0.4283	1.13398	1092	740	−1.34	0.9343	0.91148	1254	698	−3.19
0.4506	1.12425	1099	736	−1.42					
ϕTHF + $(1-\phi)$ 1,1,2,2-tetrachloroethane									
0.0429	1.55689	1149	487	−3.58	0.4786	1.25720	1182	569	−13.7
0.1120	1.50997	1153	498	−6.68	0.5273	1.22288	1187	580	−13.0
0.1569	1.47941	1155	507	−7.73	0.6705	1.12105	1206	613	−10.6
0.2172	1.43828	1160	517	−10.6	0.6903	1.10684	1209	618	−10.0
0.3215	1.36659	1168	536	−13.1	0.7602	1.05645	1221	635	−8.11
0.3760	1.32889	1172	548	−13.3	0.8421	0.99715	1237	655	−5.07
0.4405	1.28389	1178	561	−13.6	0.9461	0.92121	1262	682	−1.05
ϕTHF + $(1-\phi)$ trichloroethylene									
0.0550	1.42520	1039	649	−2.55	0.4751	1.18785	1126	663	−7.03
0.1203	1.38892	1051	651	−3.60	0.5938	1.11934	115	669	−6.55
0.1946	1.34742	1066	653	−5.56	0.6824	1.06787	1178	674	−5.32
0.2847	1.29655	1084	656	−6.26	0.7890	1.00571	1208	681	−3.45
0.3854	1.23927	1106	659	−7.41	0.8919	0.94540	1240	687	−1.44
0.4227	1.21796	1114	661	−7.11	0.9500	0.91125	1260	691	−0.70
ϕTHF + $(1-\phi)$ tetrachloroethylene									
0.0811	1.55500	1049	584	−1.25	0.5444	1.21699	1139	622	−6.96
0.1656	1.49342	1063	593	−3.05	0.6498	1.13968	1165	633	−6.29
0.2098	1.46128	1070	593	−3.13	0.7613	1.05774	1196	646	−5.01
0.2546	1.42861	1078	598	−3.79	0.8317	1.00595	1218	661	−4.17
0.3472	1.36114	1096	602	−5.45	0.9381	0.92759	1254	670	−1.25
0.4447	1.28992	1116	612	−6.12					

where ϕ is the volume fraction of THF, A_k is the polynomial coefficient, and k is the number of the polynomial coefficient. The results for k_s and Δk_s are recorded in table 4.

In each case, the optimum number of the polynomial coefficient was ascertained from an examination of the variation of the standard deviation, $\sigma(\Delta k_s)$ with

$$\sigma(\Delta k_s) = \left[\sum \left(\Delta k_{s(\text{expt.})} - \Delta k_{s(\text{calcd.})}\right)^2 \Big/ (n-p)\right]^{1/2} \tag{13}$$

where n and p are the number of results and number of adjustable parameters, A_k, retained in equation (12), respectively. The values adopted for the polynomial coefficient, A_k and the standard deviation, $\sigma(\Delta k_s)$, estimates associated with the use of equations (12) and (13), respectively, are also summarized in table 5.

Table 5. Redlich–Kister equation fitting coefficients, A_i in equations (1) and (12) and standard deviations, σ in equations (2) and (13) for THF + chloroethanes or chloroethenes at 298.15 K.

Property	A_1	A_2	A_3	A_4	A_5	σ
THF + 1,2-dichloroethane						
V_m^E (cm^3 mol^{-1})	0.1649	0.5115	0.0347	0.0063	−0.1928	0.002
Δk_s (TPa^{-1})	−11.71	−7.8410	22.5969	17.8127	−11.3155	4.0
THF + 1,1,1-trichloroethane						
V_m^E (cm^3 mol^{-1})	−1.4955	−0.1107	−0.3296	0.5372	0.8736	0.003
Δk_s (TPa^{-1})	−24.1756	4.3186	6.7235	−7.6765	−7.4190	0.7
THF + 1,1,2,2-tetrachloroethane						
V_m^E (cm^3 mol^{-1})	−0.5827	−0.9231	−0.1275	0.2307	0.0293	0.000
Δk_s (TPa^{-1})	−22.9480	−1.2427	6.3527	−9.7522	−6.6396	0.9
THF + trichloroethylene						
V_m^E (cm^3 mol^{-1})	−1.4108	0.0473	0.0665	−0.0973	0.3524	0.005
Δk_s (TPa^{-1})	−15.9198	−0.7712	6.1094	−5.1679	−8.4584	0.4
THF + tetrachloroethylene						
V_m^E (cm^3 mol^{-1})	−0.3867	0.2523	−0.0600	−0.0149	0.1293	0.000
Δk_s (TPa^{-1})	−15.0690	2.7565	0.0793	−2.4736	2.9860	0.5

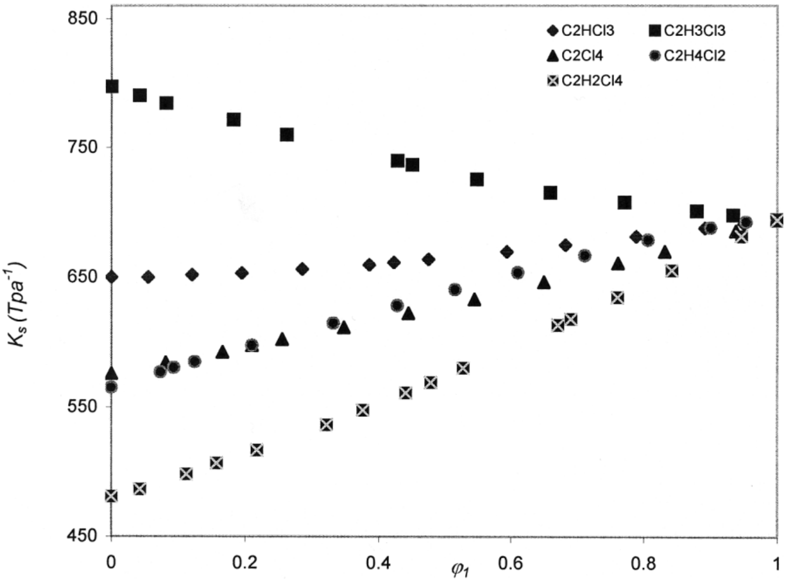

Figure 4. Dependence of isentropic compressibility with volume fraction of the mixtures of (x)THF with chloroethanes or chloroethenes at 298.15 K.

The deviations in isentropic compressibility, Δk_s are negative over the whole range of composition for all the binary mixtures formed by THF with the chloroethanes or chloroethenes, except the Δk_s values that are positive for the mixtures of THF with 1,2-dichloroethane.

Figure 4 shows that for the mixtures of THF with 1,1,1-trichloroethane on increasing the mole fraction of x the k_s values decrease, whereas for the remaining systems the k_s values increase with the mole fraction of THF.

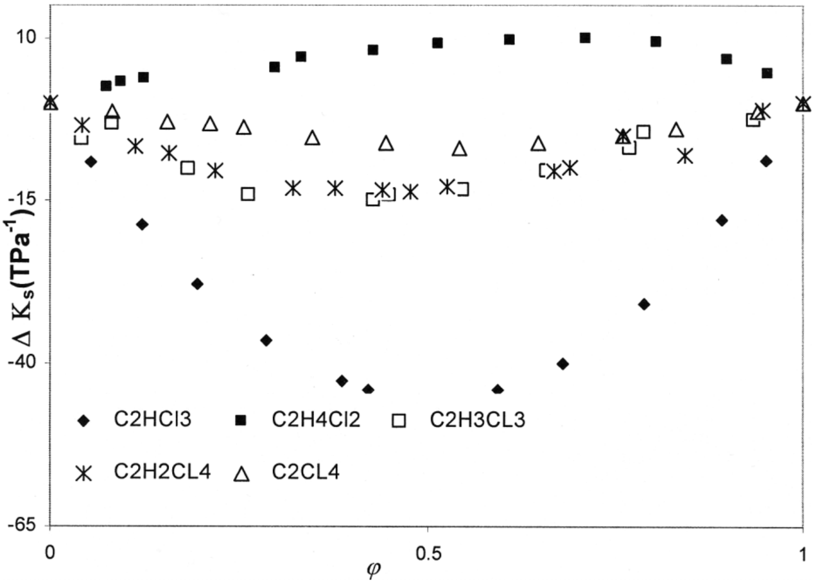

Figure 5. Variation of deviation in isentropic compressibility with volume fraction of the mixture of (x) THF + (1 − x) chloroethanes or chloroethenes at 298.15 K.

The positive values of Δk_s for THF + 1,2-dichloroethane mean that the mixture is more compressible than the corresponding ideal mixture. Therefore, in this system, an expansion in free volume is considered to occur making the mixtures more compressible than the ideal mixture, which ultimately culminates into the positive values of Δk_s. For the mixtures of THF with remaining systems the negative Δk_s values indicate the opposite of the above explanation. Figure 5 shows a maximum or minimum of Δk_s values at different $\phi \approx 0.5$ for all the mixtures. The numerical values of deviation in isentropic compressibility for binary mixtures decrease in the order:

$$\text{1,2-dichloroethane} > \text{tetrachloroethylene} \approx \text{trichloroethylene}$$
$$> \text{1,1,2,2-tetrachloroethane} > \text{1,1,1-trichloroethane}.$$

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