Excess molar volumes and isentropic compressibilities of binary liquid mixtures containing n-alkanes at 298.15 K

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Abstract. Excess molar volumes (V^E) and deviation in isentropic compressibilities ($\Delta\beta_s$) have been investigated from the density ρ and speed of sound u measurements of six binary liquid mixtures containing n-alkanes over the entire range of composition at 298.15 K. Excess molar volume exhibits inversion in sign in one binary mixture, i.e., n-heptane + n-hexane. Remaining five binary mixtures, n-heptane + toluene, cyclohexane + n-heptane, cyclohexane + n-hexane, toluene + n-hexane and n-decane + n-hexane show negative excess molar volumes over the whole composition range. However, the large negative values of excess molar volume becomes dominant in toluene + n-hexane mixture. Deviation in isentropic compressibility is negative over the whole range of composition in the case of all the six binary mixtures. Existence of specific intermolecular interactions in the mixtures has been analyzed in terms of excess molar volume and deviation in isentropic compressibility.

Keywords. Excess molar volume; binary liquid mixtures; isentropic compressibility; intermolecular interactions.

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1. Introduction

The prime object of the ultrasonic velocity and density measurements in binary liquid systems is to estimate the value of isentropic compressibility (β_s), which cannot be done by any other method. Isentropic compressibility (β_s) has been widely used to study the molecular interactions through its excess value. It can also be used to deduce other useful thermodynamic properties, e.g., excess molar volume (V^E), isothermal compressibility (β_T), heat capacity ratio (γ), internal pressure (P_i), cohesive energy density (CED) etc. The knowledge of excess molar volumes and isentropic compressibilities of binary liquid mixtures are essential for fluid flow, mass flow and heat transfer processes in chemical industries. The variation of excess molar volumes with temperature and composition for mixture may be complex due to the existence of specific interactions in the mixtures.

The interesting uses of the n-alkanes and alkanol in many petrochemical refining processes have greatly stimulated the need for an extensive information on the thermodynamic

and transport properties of n-alkanes and their mixtures. Several workers [1–4] have previously studied excess properties of binary liquid mixtures containing chloroalkanes.

In our [5–8] systematic investigation of the thermodynamic, acoustic and transport properties of binary liquid mixtures, we have reported viscosities, speeds of sound, isentropic compressibilities and non-linearity parameters for different binary mixtures. As an extension of our studies and in order to understand specific intermolecular interactions between the binary mixtures of n-alkanes and hydrocarbon liquids, here we have reported experimental excess molar volumes (V^E) and deviation in isentropic compressibilities ($\Delta\beta_s$) for six binary liquid mixtures over the entire range of composition at 298.15 K. This study shed some more light on the formation of mixed species and their influence on the excess properties of the mixtures.

2. Experimental

All the organic liquids used were of analar grade and obtained from BDH Chemicals Ltd, England. These chemicals were further purified. Densities were determined with the help of standard bicapillary pyknometer technique used by other workers [9]. This pyknometer is self-filling in type and offers accuracy up to 1 to 4 parts in 10^4. The pyknometer was immersed in the thermostatic bath maintained at 298.15 K. In the present work, sound velocity measurements were made by a crystal-controlled ultrasonic interferometer supplied by M/s Mittal Enterprises at 2 MHz frequency with an accuracy of 0.3%. The excess molar volumes were computed from measured density data and isentropic compressibilities were computed from measured sound velocity and density data. Experimentally determined sound velocity and density data have been compared with literature values [10].

3. Theoretical

The excess molar volumes (V^E) were calculated from the molar masses M_i and densities of pure liquids and the mixtures as follows:

$$V^E = X_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \tag{1}$$

where X_i, M_i and ρ_i are the mole fraction, molar mass and density of the ith component in the mixtures.

Isentropic compressibilities of the mixtures have been computed with the help of ultrasonic velocity and density data using the relation

$$\beta_s = \left(\frac{1}{u^2 \rho} \right) \tag{2}$$

where β_s, u and ρ represent the isentropic compressibility, sound velocity and density respectively.

Deviation in isentropic compressibility can be calculated by using the following relation:

$$\Delta\beta_s = \beta_{s(exp)} - \beta_{s(idl)} \tag{3}$$

where

$$\beta_{s(\exp)} = \left(\frac{1}{u_{(\exp)}^2 p_{(\exp)}} \right)$$

and

$$\beta_{s(\mathrm{idl})} = \sum \phi_i (\beta_{si}^0 + T V_i^0 (\alpha)^2 / C_{pi}^0) - T \left(\sum X_i V_i^0 \left(\sum \Phi_i \alpha_i^0 \right)^2 / \sum X_i C_{pi}^0 \right) \qquad (4)$$

where $\beta_{si}^0, V_i^0, \phi_i$ and C_{pi}^0 are the isentropic compressibility, molar volume, volume fraction and heat capacity respectively of the ith component.

4. Results and discussion

The six binary liquid mixtures taken for the present investigation are as follows:
(1) n-heptane + toluene, (2) n-heptane + n-hexane, (3) toluene + n-hexane, (4) cyclo-hexane + n-heptane, (5) cyclohexane + n-hexane and (6) n-decane + n-hexane.

Experimental values of densities, sound velocities and isentropic compressibilities of pure components are recorded in table 1. Experimentally determined values of density (ρ) and sound velocity (u) for various binary liquid mixtures at 298.15 K and also excess molar volume computed from eq. (1) and isentropic compressibilities along with deviation in isentropic compressibilities computed from eqs (2) and (3), are given in tables 2–7. The result of excess molar volume and deviation in isentropic compressibility plotted against the mole fraction of component one of various binary liquid mixtures also graphically represented in figures 1 and 2.

The results of tables 2–7 show that excess molar volume, V^E, exhibits inversion in sign in one binary liquid mixture, i.e., n-heptane + n-hexane. Remaining five binary mixtures show negative excess molar volumes over the whole composition range. However, the large negative values of excess molar volume become dominant in toluene + n-hexane mixture, due to the existence of strong intermolecular interaction between the two liquid components. The curve in figure 1 shows that the replacement of n-heptane with toluene as component one leads to a more negative values of V^E. However, the positive values of V^E changes into negative values with increasing mole fraction of component one in the case of the n-heptane + n-hexane binary mixture.

Table 1. Experimental values of sound velocity, density and isentropic compressibility of pure liquid components.

Component liquids	Density (kg m^{-3})	Ultrasonic velocity (m s^{-1})	Isentropic compressibility (T pa^{-1})
Toluene	862.6	1304.3	681.5
Cyclohexane	773.6	1252.0	824.7
n-Hexane	654.8	1075.8	1319.6
n-Heptane	679.0	1131.0	1151.3
n-Decane	726.0	1225.0	917.9

Table 2. Density (ρ), speed of sound (u), isentropic compressibility (β_s) and deviation in isentropic compressibility $(\Delta\beta_s)$ of binary liquid mixture (1) n-heptane + toluene.

X_1	ρ (g/cc)	u (m/s)	V^E (m^3 mol^{-1})	β_s(exp) (T pa^{-1})	$\Delta\beta_s$ (T pa^{-1})
0.2979	0.8693	1247.0	−0.0102	739.8	−133.7
0.3162	0.8667	1243.0	−0.0105	746.8	−137.4
0.3325	0.8637	1240.5	−0.0106	752.4	−141.1
0.3519	0.8601	1237.2	−0.0107	759.6	−144.8
0.3707	0.8564	1233.7	−0.0109	767.2	−147.4
0.3902	0.8532	1230.0	−0.0111	774.7	−150.7
0.4029	0.8500	1228.0	−0.0110	780.2	−151.8
0.4282	0.8468	1224.0	−0.0114	788.2	−157.5
0.4484	0.8433	1220.0	−0.0116	796.7	−159.6
0.4684	0.8394	1216.0	−0.0117	805.7	−160.9
0.4874	0.8363	1213.8	−0.0118	811.6	−164.7
0.5023	0.8225	1211.0	−0.0103	829.0	−150.7
0.5227	0.8188	1206.5	−0.0105	839.0	−151.1
0.5442	0.8153	1203.7	−0.0106	846.6	−154.0
0.5646	0.8122	1199.0	−0.0108	856.4	−154.0

Table 3. Density (ρ), speed of sound (u), isentropic compressibility (β_s) and deviation in isentropic compressibility $(\Delta\beta_s)$ of binary liquid mixture (2) n-heptane + n-hexane.

X_1	ρ (g/cc)	u (m/s)	V^E (m^3 mol^{-1})	β_s(exp) (T pa^{-1})	$\Delta\beta_s$ (T pa^{-1})
0.3388	0.6614	1091.1	0.4	966.3	−200.0
0.3598	0.6628	1092.2	0.3	967.2	−289.1
0.3782	0.6606	1093.9	0.8	967.6	−286.1
0.4001	0.6639	1094.4	0.3	970.7	−279.0
0.4193	0.6636	1095.1	0.4	973.7	−273.1
0.4394	0.6646	1096.5	0.3	978.4	−268.6
0.4604	0.6656	1097.0	0.2	977.6	−262.4
0.4782	0.6663	1098.5	0.2	978.6	−258.5
0.4986	0.6672	1199.6	0.1	980.7	−253.0
0.5191	0.6681	1101.8	0.1	981.4	−248.8
0.5395	0.6693	1102.8	−0.2	983.2	−243.6
0.5594	0.6729	1104.0	−0.8	997.5	−225.6
0.5795	0.6716	1104.9	−0.4	1000.4	−219.7
0.6025	0.0007	1105.6	−0.6	1003.4	−212.7
0.6135	0.6736	1106.0	−0.7	1006.5	−207.7

The deviation in isentropic compressibility, $\Delta\beta_s$, is negative over the whole range of composition for all the binary mixtures. The curve in figure 2 indicates that deviation become more negative in n-heptane + n-hexane and n-decane + n-hexane mixtures. The variation in V^E and $\Delta\beta_s$ shows that both the parameters give similar trend in all the liquid mixtures. Values of V^E and $\Delta\beta_s$ in tables 2–7 represent the increasing trend with increasing mole fraction of component 1, which shows the occurrence of strong intermolecular interactions between two liquids.

Excess molar volume can be expressed as a function of mole fraction of the component 1 and 2 in the case of binary systems. It has been expressed that the sign and magnitude

Table 4. Density (ρ), speed of sound (u), isentropic compressibility (β_s) and deviation in isentropic compressibility ($\Delta\beta_s$) of binary liquid mixture (3) toluene + n-hexane.

X_1	ρ (g/cc)	u (m/s)	V^E (m^3 mol^{-1})	β_s(exp) (T pa^{-1})	$\Delta\beta_s$ (T pa^{-1})
0.4074	0.7936	1149.7	−9.9	953.3	−132.3
0.4299	0.7984	1153.3	−9.8	927.7	−129.5
0.4486	0.8018	1159.5	−9.6	927.7	−131.6
0.4704	0.8058	1163.3	−9.5	917.0	−128.2
0.4919	0.8111	1167.0	−9.6	905.3	−125.4
0.5114	0.8157	1172.0	−9.6	892.5	−125.0
0.5290	0.8188	1176.0	−9.3	883.4	−122.3
0.5491	0.8236	1181.0	−9.3	871.6	−120.1
0.5584	0.8278	1183.0	−9.6	863.2	−121.2
0.5880	0.8323	1188.0	−9.3	851.3	−113.0
0.6088	0.8368	1194.0	−9.2	838.2	−111.3
0.6275	0.8400	1199.1	−9.0	828.0	−108.3
0.6453	0.8512	1203.6	−9.9	811.0	−108.7
0.6637	0.8527	1208.6	−9.4	803.4	−103.9
0.6829	0.8537	1213.1	−8.9	796.0	−98.5

Table 5. Density (ρ), speed of sound (u), isentropic compressibility (β_s) and deviation in isentropic compressibility ($\Delta\beta_s$) of binary liquid mixture (4) cyclohexane + n-heptane.

X_1	ρ (g/cc)	u (m/s)	V^E (m^3 mol^{-1})	β_s(exp) (T pa^{-1})	$\Delta\beta_s$ (T pa^{-1})
0.2227	0.7184	1156.0	−4.4	1041.6	−51.9
0.2689	0.7214	1162.1	−4.2	1026.4	−54.2
0.3158	0.7236	1167.8	−3.9	1013.4	−53.9
0.3588	0.7191	1171.8	−2.3	1012.8	−42.6
0.4016	0.7243	1177.2	−2.6	996.3	−46.1
0.4433	0.7307	1182.0	−2.9	979.5	−49.9
0.4861	0.7334	1187.7	−2.8	966.6	−49.3
0.5270	0.7361	1191.9	−2.5	956.3	−46.6
0.5642	0.7384	1196.0	−2.2	946.8	−44.0
0.6019	0.7412	1201.2	−2.1	935.0	−43.1
0.6414	0.7438	1205.8	−1.9	924.7	−39.8
0.6795	0.7463	1210.6	−1.6	914.3	−37.0
0.7164	0.7482	1215.9	−1.2	904.0	−34.2
0.7521	0.7518	1220.0	−1.1	893.7	−31.2
0.7877	0.7547	1224.0	−1.0	884.4	−27.1

of excess function give a good estimate of the strength of the unlike interaction in a binary mixture. The negative magnitude of V^E values of toluene + n-hexane system is greater than the other five binary mixtures. The order of negative magnitude of V^E is; toluene + n-hexane > cyclohexane + n-heptane > n-decane + n-hexane > cyclohexane + n-hexane > n-heptane + toluene > n-heptane + n-hexane. The n-alkane molecules form random coils due to internal rotation about the C–C bond but the presence of toluene molecules may put the n-alkane molecules under constraint and may decrease their coiling up. As a

Table 6. Density (ρ), speed of sound (u), isentropic compressibility (β_s) and deviation in isentropic compressibility $(\Delta\beta_s)$ of binary liquid mixture (5) cyclohexane + n-hexane.

| X_1	ρ (g/cc)	u (m/s)	V^E (m^3 mol^{-1})	β_s(exp) (T pa^{-1})	$\Delta\beta_s$ (T pa^{-1})
0.2189	0.6821	1110.0	−1.0	1189.9	−32.3
0.2541	0.6860	1118.8	−1.0	1164.6	−42.2
0.2981	0.6914	1134.9	−1.1	1122.9	−64.3
0.3150	0.6932	1135.0	−1.0	1119.8	−59.8
0.3647	0.6990	1142.3	−1.0	1096.4	−60.4
0.3897	0.7022	1149.8	−1.1	1077.2	−68.1
0.4258	0.7065	1155.4	−1.1	1060.3	−67.9
0.4777	0.7129	1163.2	−1.2	1036.7	−66.7
0.5029	0.7157	1170.0	−1.2	1020.7	−70.5
0.5675	0.7232	1180.3	−1.1	992.6	−66.8
0.5799	0.7250	1182.7	−1.1	986.1	−67.0
0.6012	0.7275	1188.9	−1.1	972.5	−69.9
0.6695	0.7356	1200.0	−1.0	944.1	−63.2
0.7187	0.7415	1210.6	−1.0	920.2	−74.6
0.7888	0.7499	1221.8	−0.9	893.3	−50.5

Table 7. Density (ρ), speed of sound (u), isentropic compressibility (β_s) and deviation in isentropic compressibility $(\Delta\beta_s)$ of binary liquid mixture (6) n-decane + n-hexane.

X_1	ρ (g/cc)	u (m/s)	V^E (m^3 mol^{-1})	β_s(exp) (T pa^{-1})	$\Delta\beta_s$ (T pa^{-1})
0.0187	0.6663	1075.5	−1.9	1297.5	−14.3
0.0588	0.6697	1080.1	−1.7	1279.9	−28.2
0.1008	0.6730	1087.9	−1.7	1255.5	−47.7
0.1436	0.6774	1094.6	−1.7	1232.1	−26.3
0.1896	0.6777	1100.0	−1.0	1219.5	−70.9
0.2348	0.6850	1108.4	−1.7	1188.3	−93.9
0.2886	0.6883	1118.8	−1.4	1160.7	−112.3
0.3350	0.6917	1127.5	−1.4	1137.2	−125.6
0.3872	0.6943	1135.4	−1.1	1117.3	−134.8
0.4449	0.6887	1142.8	−1.2	1095.9	−143.4
0.5009	0.7012	1152.3	−0.9	1047.1	−152.9
0.5627	0.7071	1161.9	−1.3	1047.6	−164.4
0.6248	0.7099	1173.9	−1.1	1022.2	−175.4
0.6944	0.7114	1184.1	−0.4	1002.6	−179.4
0.7655	0.7144	1195.6	−1.0	979.2	−189.2
0.8421	0.7191	1205.4	−0.3	957.1	−189.7
0.9191	0.7232	1218.6	−0.3	931.1	−197.2

result their entropy is decreased and hence molecules acquire their random configurations. Due to the presence of long chain length, n-hexane molecule provides more favourable accommodation to toluene molecules (Sys.3) in comparison to the cyclohexane molecules (Sys.5) consequently resulting in a greater degree of interaction. Cyclohexane molecules possess globular structure and its presence may increase the coiling up in the n-alkane molecules. Thus entropy of n-alkane molecules may increase. In other words, the presence of cyclohexane may decrease the intermolecular interactions in long chain alkanes.
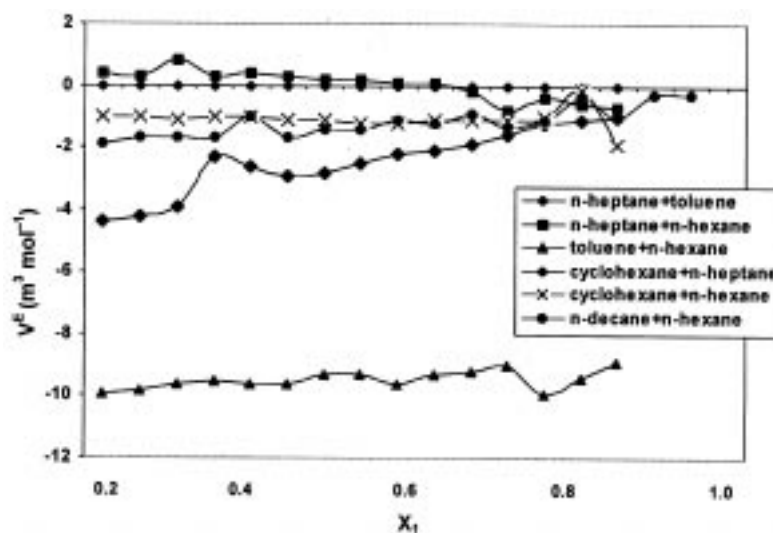
Figure 1. Excess molar volume (V^E) plotted against the mole fraction (X_1) for the component one of the six binary liquid mixtures.
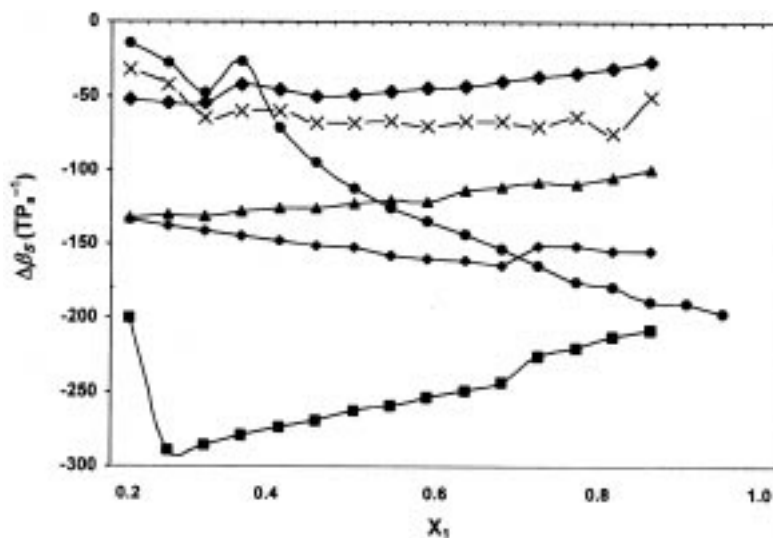
Figure 2. Deviation in isentropic compressibility $(\Delta\beta_s)$ is plotted against the mole fraction (X_1) for the component one of six binary liquid mixtures.

Excess molar volume is a first order thermodynamic quantity and it is sensitive to changes of structure (i.e. order) or randomness during the mixing process. Thus order destruction and order creation processes in solution can also be described through experimental determination of excess molar volume and deviation in isentropic compressibility.

It has been obtained that positive V^E and $\Delta\beta_s$ should be associated with the formation of structure or order in the solution [11]. The negative values of V^E and $\Delta\beta_s$ should be taken as a consequence of order destruction in the solution upon mixing [12]. In addition to the above discussed order destruction and order creation, it has been observed that in one binary mixture containing n-heptane as the first component is characterized by two concentration regions with positive curvature and one with negative curvature. St. Victor and Patterson [13] proposed that this dependence may be due to two contributions: (1) a positive one associated with deviation of local from bulk composition, i.e., non-randomness in the solution, which appears in the middle of the concentration range, and (2) a negative one resulting when order is destroyed during mixing.

The thermodynamic behavior of the binary liquid mixture, i.e., n-heptane + n-hexane fulfills the above conditions for V^E and liquid–liquid phase separation [13,14] like some other binary systems and so present the specific graphical behavior, which is shown in figure 1. In order to elucidate its origin, the molecular size can also be used as additional parameter in a series of n-alkane compounds, which depends on the chain length and their association with other groups.

Acknowledgement

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