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Thermophysical Properties of Binary Mixtures of Cyclopentanone and Isomeric Forms of *n*-Butyl Alcohol at 303.15 K

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The density and speed of sound of binary mixtures of cyclopentanone and isomeric forms of *n*-butyl alcohols (butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylpropan-2-ol) were measured over the entire composition range at 303.15 K. From the experimental data, the various thermophysical properties such as excess molar volume (V^E) and deviation in isentropic compressibility ($\Delta\kappa_s$) were calculated and then fitted to Redlich-Kister polynomial equation. The results are discussed in terms of non-specific interactions present in the above mentioned binary mixtures.

Keywords: Speed of sound, Cyclopentanone, Thermodynamic properties, Excess molar volume, Isentropic compressibility.

INTRODUCTION

The extensive research has been carried out in our laboratories to study the molecular interactions in liquid mixtures for the last many years [1-5]. The molecular interactions greatly affect the arrangement, orientation and conformations of the molecules in solutions. Cyclopentanone is an important industrial chemical, which acts as a versatile synthetic intermediate in organic synthesis [6]. It is widely used as a fragrant in soaps, cosmetics and perfumes. Thus mixing cyclopentanone with alcohols will generate interesting properties due to various specific and non-specific interactions. Alcohols are considered to be the most well known solvents to study the hydrophobic effects due to varying chain lengths. In the present study an effort is made to study the effect of varying chain lengths of *n*-butyl alcohol [Bu-OH] on thermophysical properties of its binary mixtures with cyclopentanone. The data on some of the physical properties associated with the liquids and liquid mixtures like density, viscosity, refractive index, surface tension and speed of sound find extensive application in solution theory and molecular dynamics [7-13]. The evaluated data of excess thermodynamic functions of liquid mixtures give an insight of molecular interactions, which can be used to test thermodynamic models [14].

The thermophysical properties of binary mixtures of cyclopentanone and all four isomers of Bu-OH *i.e.* butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylpropan-2-ol are very interesting as the cyclopentanone contains >C=O group and alcohols contain –OH group for molecular interactions.

To our best of knowledge the results of thermo-physical properties of cyclopentanone + Bu-OH are not available in literature. In present work the properties such as density and speed of sound have been measured at 303.15 K. The experimental values of the density and speed of sound have been used to calculate the excess molar volume V^E and deviation in isentropic compressibility ΔK_s. The results thus obtained are discussed in terms of various specific and non-specific interactions. The V^E and ΔK_s are then fitted to Redlich-Kister polynomial equation [15] to estimate the coefficients and standard errors.

EXPERIMENTAL

Cyclopentanone, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylpropan-2-ol (purity > 99 %) were taken from Sigma Aldrich. The chemicals were used after drying them under vacuum over beads in a vacuum desiccators. An electronic single pan five digit analytical balance (Mettler; Model AE-240) with a precision of ± 0.00001 g was used for weighing. Known masses of pure liquids were taken in an airtight stopper bottles, which were thoroughly homogenized. Each solution prepared, in this way, was divided into two parts for measuring density and ultrasonic velocity. The extra precaution was taken during measurements, to prevent losses due to evaporation. The possible error in the mole fraction is calculated to be less than $\pm 1 \times 10^{-4}$. The density of solutions was measured using density meter (model: DMA 4500 M, Anton Paar, Austria) with an uncertainty of ± 0.00005 g cm^{-3}. Before each series of

measurements, it was calibrated using doubly distilled water and dry air at atmospheric pressure. The temperature was automatically kept constant within ± 0.03 K with the help of in-built peltier system. The speed of sound in the solution was measured using a single-crystal variable-path multi frequency ultrasonic interferometer (model: M-82S, Mittal Enterprises, India) having stainless steel sample cell operating at a fixed frequency of 2 MHz. The uncertainty in speed of sound measurement was found within ± 0.5 m s^{-1}. The temperature of the sample solution was maintained with an accuracy of ± 0.02 K using an electronic-controlled thermostatic water bath (model: TIC-4000N, Thermotech, India).

RESULTS AND DISCUSSION

The experimental determined values for density (ρ) and speed of sound (u) for various binary constituents at 303.15 K are reported in Table-1.

The experimental data was used for evaluating various thermodynamic parameters, namely, excess molar volume (V^E), isentropic compressibility (κ_s) and deviation in isentropic compressibility ($\Delta\kappa_s$) of binary mixtures. The results are reported in Table-2.

Excess molar volume (V^E): The excess molar volume has been computed by using the following relation:

$$V^E = \frac{(M_1x_1 + M_2x_2)}{\rho_m} - \left(\frac{M_1x_1}{\rho_1} + \frac{M_2x_2}{\rho_2}\right)$$

where ρ_m is the density of mixture while M_1, x_1, ρ_1 and M_2, x_2, ρ_2 are the molecular weight, mole fraction and density of pure components 1 (cyclopentanone) and 2 (Bu-OH), respectively. The V^E values of binary mixtures of cyclopentanone + Bu-OH isomer are reported in Table-2. The V^E values may be interpreted in terms of physical, chemical and structural contributions. The physical interactions are non-specific and involve mainly the dispersion forces giving rise to positive V^E values. The chemical or specific interactions such as formation of the hydrogen bond, charge transfer interactions, dipole-dipole interactions give rise to negative V^E values. The structural contributions arising due to the geometrical fitting of one component into the other leads to negative V^E values. It has

TABLE-1
COMPARISON OF DENSITY (ρ) AND SPEED OF SOUND (u) OF PURE LIQUIDS WITH LITERATURE VALUE AT 303.15 K

Component	ρ (g cm^{-3})		u (m s^{-1})	
	Experimental	Literature	Experimental	Literature
Butan-1-ol	0.80205	0.80201 [Ref. 16]	1235.1	1235.6 [Ref. 16]
Butan-2-ol	0.79851	0.79855 [Ref. 16]	1151.4	1152.2 [Ref. 16]
2-Methylpropan-1-ol	0.79418	0.79417 [Ref. 16]	1074.1	1075.2 [Ref. 16]
2-Methylpropan-2-ol	0.77632	0.77629 [Ref. 16]	1060.2	1061.3 [Ref. 16]
Cyclopentanone	0.93939	0.93942 [Ref. 17]	1376.2	1378.0 [Ref. 17]

TABLE-2
EXPERIMENTAL VALUES OF DENSITY (ρ), SPEED OF SOUND (u) AND CALCULATED VALUES OF EXCESS MOLAR VOLUME (V^E), Isentropic Compressibility (κ_s), DEVIATION IN ISENTROPIC COMPRESSIBILITY ($\Delta\kappa_s$) AT VARIOUS MOLE FRACTIONS (x_1) FOR THE DIFFERENT BINARY MIXTURES AT 303.15 K

x_1	ρ (g cm^{-3})	u (m s^{-1})	V^E (cm^3 mol^{-1})	κ_s (T Pa^{-1})	$\Delta\kappa_s$ (T Pa^{-1})	x_1	ρ (g cm^{-3})	u (m s^{-1})	V^E (cm^3 mol^{-1})	κ_s (T Pa^{-1})	$\Delta\kappa_s$ (T Pa^{-1})
Cyclopentanone + Butan-1-ol						Cyclopentanone + 2-Methylpropan-1-ol					
0.0000	0.80205	1235.1	0	817.32	0.00	0.0000	0.79418	1074.1	0	1091.42	0.00
0.0985	0.81443	1248.008	0.087	788.34	-3.84	0.1013	0.80666	1103.593	0.195	1017.87	-19.93
0.2023	0.82736	1261.175	0.198	759.90	-5.78	0.1972	0.819328	1130.994	0.288	954.16	-32.87
0.3079	0.84111	1274.525	0.251	731.89	-6.83	0.2966	0.832774	1159.283	0.358	893.50	-40.92
0.3982	0.85296	1285.906	0.294	709.01	-6.67	0.3972	0.846875	1188.514	0.385	835.93	-45.23
0.4974	0.86640	1299.563	0.302	683.41	-6.94	0.5105	0.86305	1222.402	0.398	775.42	-45.77
0.6048	0.88118	1314.877	0.298	656.39	-6.55	0.5972	0.875728	1248.754	0.387	732.28	-43.01
0.6958	0.89402	1328.297	0.27	633.96	-5.76	0.7023	0.891542	1281.125	0.341	683.40	-36.26
0.7991	0.90896	1344.373	0.212	608.72	-4.63	0.8024	0.90668	1312.825	0.304	639.93	-26.74
0.8937	0.92288	1359.511	0.145	586.26	-2.95	0.9079	0.9234	1346.597	0.205	597.22	-13.60
1.0000	0.93939	1376.2	0	562.07	0.00	1.0000	0.93939	1376.2	0	562.07	0.00
Cyclopentanone + Butan-2-ol						Cyclopentanone + 2-Methylpropan-2-ol					
0.0000	0.79851	1151.4	0	944.64	0.00	0.0000	0.77632	1060.2	0	0	0.00
0.0912	0.809449	1170.882	0.171	901.12	-8.63	0.1013	0.790038	1090.901	0.225	0.225	-23.24
0.1930	0.822529	1192.116	0.268	855.48	-15.32	0.1972	0.803803	1119.625	0.358	0.358	-38.41
0.3125	0.838368	1217.09	0.338	805.23	-19.86	0.2966	0.818595	1149.326	0.451	0.451	-48.02
0.4104	0.851708	1237.888	0.365	766.21	-21.43	0.3972	0.834296	1179.925	0.481	0.481	-53.12
0.4910	0.863012	1255.897	0.36	734.64	-22.16	0.5105	0.852399	1215.398	0.494	0.494	-53.72
0.5984	0.878277	1280.29	0.343	694.63	-21.08	0.5972	0.866632	1242.935	0.482	0.482	-50.37
0.6944	0.89229	1302.521	0.301	660.58	-18.40	0.7023	0.884552	1276.807	0.421	0.421	-42.43
0.7993	0.90796	1327.603	0.232	624.88	-13.97	0.8024	0.901849	1309.938	0.365	0.365	-31.25
0.9007	0.923287	1352.187	0.161	592.36	-7.69	0.9079	0.92101	1345.176	0.241	0.241	-15.81
1.0000	0.93939	1376.2	0	562.07	0.00	1.0000	0.93939	1376.2	0	0	0.00

x_1 = mole fraction of cyclopentanone

already been established that in higher alcohols the latter contributions is negligible. Therefore the liquid mixtures of cyclopentanone + Bu-OH give positive V^E values as compared to lower alcohols. The higher alcohols possess less proton-donating ability, thus inhibiting the hetero-association of the liquids and thus gives rise to positive V^E values. A sample plot of excess molar volume of cyclopentanone with Bu-OH isomers *versus* mole fraction is given in Fig. 1.

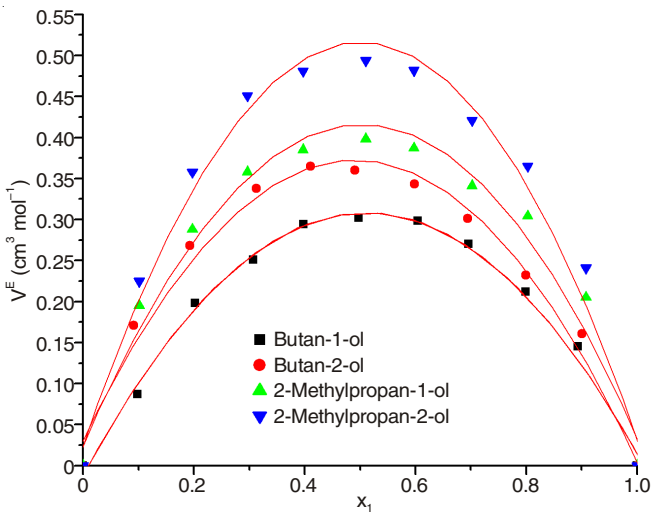

Fig. 1. Plot of excess molar volume of cyclopentanone with Bu-OH isomers *versus* mole fraction

The maxima of the curves in the Fig. 1 shows that the V^E values of cyclopentanone with Bu-OH follow the order:

Butan-1-ol < Butan-2-ol < 2-Methylpropan-1-ol < 2-Methylpropan-2-ol

The positive V^E values may further be explained on the basis of +I effect of -CH_3 group. More the branching in the alcohols, more will be the electron density on –OH group and less will be the tendency to form hydrogen bonding with O-atom of cyclopentanone, rather there will be electron repulsion between electron rich centre on –OH of Bu-OH and >C=O in cyclopentanone, thus giving rise to positive V^E values.

Deviation in isentropic compressibility ($\Delta\kappa_s$): The deviation in isentropic compressibility is evaluated by using following expression :

$$\Delta\kappa_s = \kappa_s^{mix} - (x_1\kappa_{s_1} + x_2\kappa_{s_2})$$

where, κ_s^{mix}, k_{s_1} and k_{s_2} represent isentropic compressibility of mixture, components 1 and 2, respectively. In order to evaluate isentropic compressibility, Newton-Laplace equation, $\kappa_s = (u^2\rho)^{-1}$, was employed. Table-2 and Fig. 2 reflects that the $\Delta\kappa_s$ values are negative in all the binary systems over the entire range of composition. The negative values of $\Delta\kappa_s$ suggest more compact structure and hence less compressibility than ideal systems.

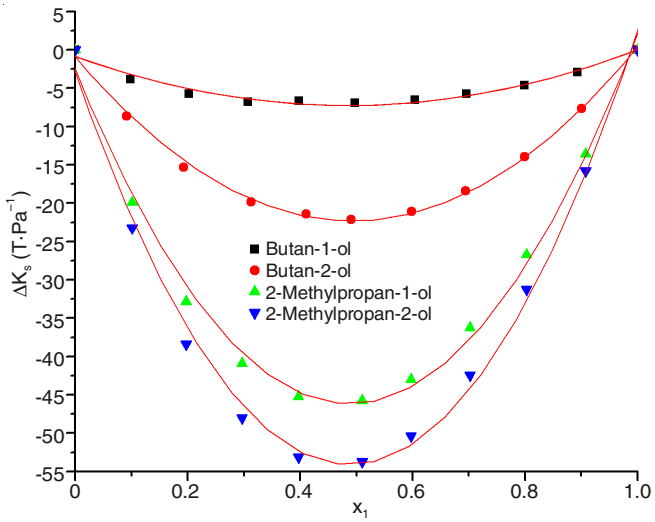

Fig. 2. Plot of deviation in isentropic compressibility of cyclopentanone with Bu-OH isomers *versus* mole fraction

The minima of the curves in the Fig. 2 shows that the V^E values of cyclopentanone with Bu-OH follow the order:

Butan-1-ol < Butan-2-ol < 2-Methylpropan-1-ol < 2-Methylpropan-2-ol

The excess properties, Y^E (V^E, $\Delta\kappa_s$) for the binary mixtures were also fitted to Redlich-Kister polynomial equation [16].

$$Y^E = x_1x_2\sum_{i=0}^{k} A_i(x_1 - x_2)^i$$

where, x_1 and x_2 are mole fraction of components 1 and 2, respectively. The coefficients A_i are obtained using the non linear least square regression method with all points weighed equally and fitting of above to the experimental results and are reported in Table-3.

Using an approximation of variation in the standard deviation, the optimum numbers of coefficients were ascertained. Table-3 represents the estimated values and their standard deviations using following equation, for all the liquid mixtures.

$$\sigma = \left(\frac{(Y^E_{exp} - Y^E_{calcd})^2}{(n-m)}\right)^{1/2}$$

TABLE-3
LEAST SQUARE COEFFICIENTS AND STANDARD DEVIATION OF REDLICH-KISTER EQUATION AT 303.15 K

Binary system	Excess function	A_0	A_1	A_2	A_3	A_4	σ
Cyclopentanone + Butan-1-ol	V^E (cm^3 mol^{-3})	1.2164	0.006	0.192	0.432	-0.176	0.011
	$\Delta\kappa_s$ (T Pa^{-1})	-27.39	4.01	13.00	5.68	-3.40	0.227
Cyclopentanone + Butan-2-ol	V^E (cm^3 mol^{-3})	-1.459	-0.234	0.013	-0.116	1.037	0.007
	$\Delta\kappa_s$ (T Pa^{-1})	-88.07	5.49	-11.34	9.68	1.04	0.216
Cyclopentanone + 2-Methylpropan-1-ol	V^E (cm^3 mol^{-3})	1.593	-0.109	0.308	0.432	1.178	0.008
	$\Delta\kappa_s$ (T Pa^{-1})	-183.37	25.49	-9.74	16.02	-4.71	0.172
Cyclopentanone + 2-Methylpropan-2-ol	V^E (cm^3 mol^{-3})	1.983	-0.209	0.501	0.645	0.847	0.108
	$\Delta\kappa_s$ (T Pa^{-1})	-215.19	30.91	-9.52	16.73	-4.29	0.160

here, n and m represents number of data points and number of coefficients, respectively.

Conclusion

The density and speed of sound for binary mixtures consisting of cyclopentanone and Bu-OH were measured in the liquid phase at ambient pressure at 303.15 K for the whole composition range. The results have been discussed in terms of various excess parameters followed by their correlation by using Redlich-Kister polynomial equation. The A_i coefficients and the standard deviations between the calculated and experimental excess properties are also determined. It has been shown that excess molar volume has positive sign V^E and deviation in isentropic compressibility ΔK_s has negative sign.

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