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Volumetric properties of binary mixtures of cyclohexane with 2-ethoxyethanol at 303.15, 308.15, 313.15 and 318.15 K

M Durgabhavani^{a,*}, Ch Kavitha^a, K Narendra^b, M Srilakshmi^a & A Ratnakar^a

^aDepartment of Chemistry, V. R. Siddhartha Engineering College, Vijayawada 520 007, Andhra Pradesh, India

^bDepartment of Physics, V. R. Siddhartha Engineering College, Vijayawada 520 007, Andhra Pradesh, India

Email: mopidevi1986@gmail.com

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The excess molar volumes (V_m^E) for binary liquid mixtures of cyclohexane+2-ethoxyethanol have been calculated from the experimental values of density and ultrasonic velocity at temperatures 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure over the entire composition range. The results have been used to estimate the partial molar volumes $\bar{V}_{m,i}$ of the components. The excess values have been fitted to Redlich-Kister polynomial equation. The changes of V_m^E and $\bar{V}_{m,i}^E$ with composition and temperature have been discussed with reference to the nature of interactions between the component molecules.

Keywords: Binary liquid mixtures, Cyclohexane, 2-ethoxyethanol, Molar volume, Partial molar volume

Investigation of molecular interaction in liquid mixtures using ultrasonic studies has proved to be a very useful method due to its simplicity and accuracy. These studies show that extensive research work on study of interactions exists in the case of organic molecules in mixtures. In the present study we were interested in investigating the possible interactions occurring between the two molecules namely cyclohexane and 2-ethoxyethanol. There are no literature reports showing the study of molecular interactions between the selected molecules using ultrasonic measurements

Cyclohexane is a colourless liquid with a distinctive detergent-like odour, reminiscent of cleaning products. It is a non-polar organic solvent used in various fields. The main use of cyclohexane in industries is as a good solvent. 2-Ethoxyethanol (2-EE) belonging to the group of cellosolves and amphiphilic compounds has both alcoholic –OH and partially etheric –O– in its structure, and is noted for its both donating and accepting ability, making it a potential candidate to form inter- and intra-molecular hydrogen bond. 2-Alkoxyalkanols can be placed between protic and aprotic solvents. It is due to the fact that the physical and chemical properties of 2-alkoxyalkanols are due to their self association. 2-Ethoxyethanol in both pure form and aqueous solutions is used as a solvent of electrolytes, to some extent as an aprotic

solvent and is often defined as a ‘quasi-protic’ solvent.

2-Alkoxyethanols have been reported to be used in paints, coating, inks, cleaners, polishes, brake fluids and jet fuels and in the manufacturing of printed circuit boards laminates and to find wide application as a solvent, chemical intermediate and solvent coupler of mixtures and water-based formulations¹⁻⁵.

Molecular interactions can affect physico-chemical behaviour as well as hydrogen bonds and their strength. Study of thermoacoustical parameters is of much use in understanding these changes⁶⁻⁸. The present article explores the results of work on thermodynamic properties of liquid mixtures containing cyclohexane and 2-ethoxyethanol at $T = 303.15, 308.15, 313.15$ and 318.15 K. By using experimentally determined values, partial molar volumes $V_{m,i}$ of the components are calculated. The excess values are fitted to Redlich-Kister polynomial equation. The changes of V_m^E and $\bar{V}_{m,i}^E$ with composition and temperature have been discussed with reference to the nature of interactions between the component molecules.

Materials and Methods

Cyclohexane and 2-Ethoxyethanol (Sigma-Aldrich, USA, mass fraction purity 0.99) used in this study were AR grade and were purified by standard procedures⁹. The sample provenance and purity are listed in Table 1.

The mixtures were stored in air tight stoppered volumetric flasks. The flasks were allowed to attain thermal equilibrium. The ultrasonic velocities were measured by using a single-crystal variable-path multi frequency ultrasonic interferometer (Mittal Enterprises, India, model F-81) operating at 2 MHz. The measurements of speeds of sound were reproducible within $\pm 0.67 \text{ ms}^{-1}$. The temperature of the liquids during measurements was maintained to an accuracy of $\pm 0.02 \text{ K}$. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of $\pm 0.5\%$. Weights were measured with an electronic balance (Shimadzu AUY220, Japan) capable of measuring up to 0.1 mg. An average of 3 to 4 measurements was taken for each sample.

Theory

The excess molar volume data were obtained from the densities of the pure liquids and their mixtures using the following equation:

$$V_m^E = V_m - V_m^{id} = \frac{x_1 M_1 + (1 - x_2) M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{(1 - x_2) M_2}{\rho_2} \right) \quad \dots (1)$$

Where x_1 and x_2 are the mole fractions, M_1 and M_2 are molar masses, and ρ_1 and ρ_2 are the densities of the pure liquid components 1 and 2, respectively.

The variations of V_m^E with mole fraction were fitted to the Redlich-Kister polynomial equation:

$$Y^E = x_1 (1 - x_1) \sum_{i=1}^n A_i (2x_1 - 1)^{i-1} \quad \dots (2)$$

The values of A_i are the coefficients of the polynomial equation and the corresponding standard deviations, $\sigma(Y^E)$ obtained by the method of least squares with equal weights assigned to each point are calculated. The standard deviation $\sigma(Y^E)$ is defined as follows:

$$\sigma(Y^E) = \left(\sum \frac{(Y_{obs}^E - Y_{cal}^E)^2}{m - n} \right)^{1/2} \quad \dots (3)$$

Where n is the total number of experimental points and m is the number of coefficients.

In addition to other volumetric properties, partial molar volumes ($\bar{V}_{m,1}^0$ and $\bar{V}_{m,2}^0$) and excess partial molar volumes ($\bar{V}_{m,1}^E$ and $\bar{V}_{m,2}^E$), of DEC, 2-alkoxyethanols over the entire concentration range in investigated system were determined using Eqns (4) and (5):

$$\bar{V}_{m,1} = V_{m,1}^* + x_2^2 \sum_{i=0}^n A_i (1 - 2x_1)^i - 2x_1 x_2^2 \sum_{i=1}^n A_i (1 - 2x_1)^{i-1} \quad \dots (4)$$

$$\bar{V}_{m,2} = V_{m,2}^* - x_1^2 \sum_{i=0}^n A_i (1 - 2x_1)^i + 2x_1^2 x_2 \sum_{i=1}^n A_i (1 - 2x_1)^{i-1} \quad \dots (5)$$

And the excess partial molar properties, at infinite dilution were calculated by following relations:

$$\bar{V}_{m,1}^E = \bar{V}_{m,1} - \bar{V}_{m,1}^* \quad \dots (6)$$

$$\bar{V}_{m,2}^E = \bar{V}_{m,2} - V_{m,2}^* \quad \dots (7)$$

Results and Discussion

The experimental values of ultrasonic velocities and densities for pure liquids are compared with those reported in literature¹⁰⁻¹³ and are compiled in Table 2, and it was found that they are in good agreement. The values of densities, ultrasonic velocities and excess

Table 2 — Comparison of densities, ρ , speeds of sound, u of pure liquids with their literature values at T = 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure 0.1 Mpa

Table 1 — Compounds considered for the study, with their sources, purification method, and purity					
Chemical name	CAS number	Source	Purification method	Mass fraction purity	Analysis method
Cyclohexane	110-82-7	Sigma Aldrich	Vacuum distillation	≥ 0.99	GC*
2-EE	110-80-5	Sigma Aldrich	Vacuum distillation	≥ 0.99	GC*

*GC = Gas Chromatography

Compounds	T(K)	$\rho/\text{kg m}^{-3}$		u/ms^{-1}	
		(Expt.)	(Lit.)	(Expt.)	(Lit.)
Cyclohexane	303.15	768.9	769.20 ¹⁷ 769.04 ¹⁸	1231.3	
	308.15	764.2		1205.8	
	313.15	759.4	759.4 ¹⁶	1180.7	1180.5 ¹⁷
	318.15	754.6		1163.4	
2-EE	303.15	921.0	921.19 ¹⁴	1285.5	1285.42 ¹⁵
	308.15	916.5	916.52 ¹¹	1267.5	1267.38 ¹⁵
	313.15	912.0	912.24 ¹⁵	1251.6	1250.01 ¹⁵
	318.15	907.3	907.31 ¹¹	1230.3	1232.39 ¹⁵

molar volumes for the binary liquid mixtures at different temperatures are given in Table 3. The results have been used to estimate the partial molar volumes V_{mi} of the components. The excess values are fitted to Redlich-Kister polynomial equation¹⁹ and the data were given in Table 4. The changes of V_m^E and V_{mi} with composition and temperature have been discussed with reference to the nature of interactions between the component molecules.

The partial molar volumes of a solute at infinite dilution reflect the effect of ion-solvent interactions while the magnitude of the slope is related to the ion-ion

Table 3 — Densities, ρ , speeds of sound, u and excess molar volume, V_m^E as functions of mole fraction, x_1 of cyclohexane for (cyclohexane + 2-ethoxyethanol) mixtures at T = 303.15, 308.15, 313.15 and 318.15 K and at atmospheric pressure 0.1 Mpa

x_1	ρ (kg m ⁻³)	u (m s ⁻¹)	V_m^E (10 ⁶) (m ³ mol ⁻¹)	ρ (kg m ⁻³)	u (m s ⁻¹)	V_m^E (10 ⁶) (m ³ mol ⁻¹)
	303.15 K			308.15 K		
0.0000	768.9	1231.3	0.000	764.2	1205.8	0.000
0.0906	781.1	1235.3	-0.182	776.7	1210.8	-0.229
0.1831	794.1	1239.8	-0.365	789.8	1215.8	-0.425
0.2776	807.8	1244.5	-0.523	803.5	1221.2	-0.582
0.3741	822.4	1249.3	-0.674	818.2	1226.6	-0.744
0.4728	837.9	1254.4	0.804	833.7	1232.3	-0.865
0.5619	851.7	1259.1	-0.814	847.5	1237.5	-0.877
0.6766	869.4	1265.8	-0.712	865.2	1245.3	-0.768
0.7820	885.7	1272.2	-0.522	881.5	1252.5	-0.570
0.8898	903.0	1279.1	-0.297	898.9	1260.2	-0.348
1.0000	921.0	1285.5	0.000	916.5	1267.5	0.000
	313.15 K			318.15 K		
0.0000	759.4	1180.7	0.000	754.6	1163.4	0.000
0.0906	772.1	1186.7	-0.260	767.4	1169.6	-0.280
0.1831	785.2	1192.5	-0.457	780.6	1175.4	-0.493
0.2776	799.0	1198.4	-0.626	794.4	1180.9	-0.663
0.3741	813.7	1204.4	-0.786	809.0	1186.5	-0.810
0.4728	829.2	1210.8	-0.910	824.5	1192.5	-0.934
0.5619	843.2	1216.7	-0.930	838.6	1198.0	-0.965
0.6766	860.8	1225.7	-0.807	856.3	1206.4	-0.849
0.7820	877.2	1234.2	-0.611	872.8	1214.4	-0.659
0.8898	894.5	1243.1	-0.369	890.0	1222.7	-0.398
1.0000	912.0	1251.6	0.000	907.3	1230.3	0.000

Table 5 — The values $\bar{V}_{m,1}^0, \bar{V}_{m,1}^*, \bar{V}_{m,1}^{0E}, \bar{V}_{m,2}^0, \bar{V}_{m,2}^*, \bar{V}_{m,2}^{0E}$ of the components for cyclohexane + 2-EE mixtures at temperatures T = 303.15–318.15 K from Redlich-Kister equation

T/K	$10^6 \bar{V}_{m,1}^0$ m ³ · mol ⁻¹	$10^6 \bar{V}_{m,1}^*$	$10^6 \bar{V}_{m,1}^{0E}$	$10^6 \bar{V}_{m,2}^0$	$10^6 \bar{V}_{m,2}^*$	$10^6 \bar{V}_{m,2}^{0E}$
303.15	91.69	93.20	1.5060	95.19	97.85	2.6626
308.15	91.48	93.63	2.1495	95.11	98.33	3.2175
313.15	91.61	94.09	2.4753	95.29	98.82	3.5215
318.15	91.69	94.56	2.8693	95.30	99.33	4.0313

interactions. The partial molar volume of the ion may be mainly due to following three contributions: i) Intrinsic volume of the power of its crystalline radius. ii) Electrostriction volume of the solvent-generally considered to be proportional to the square of the change of the ion and inversely proportional to its radius and it is the factor that control the volumetric properties of the small cations. iii) Structural contribution- may be change in volume due to structural rearrangement of solvent; it is the factors that determine the influence of temperature and partial molar volume of the large cations. The structural contribution is applicable only for aqueous solutions of large ions.

The V_m^E data for the binary system is graphically represented in Fig. 1. The sign, shape and the magnitude of V_m^E arise from three factors. Firstly, difference in size and shape of unlike molecules, secondly, structural changes originating from correlation of molecular orientation and thirdly, from difference in the intermolecular interaction energy between like and unlike molecules. The values of $\bar{V}_{m,1}^{0,E}$ and $\bar{V}_{m,2}^{0,E}$ are given in Table 5.

In general, the negative $V_{m,1}^{-E}$ and $V_{m,2}^{-E}$ values (Figs. 2 and 3) indicate the presence of significant solute-solvent interactions between unlike molecules, where as the positive $V_{m,1}^{-E}$ and $V_{m,2}^{-E}$ values indicate presence of solute-solute/solvent-solvent (or weak solute-solvent) interactions between like molecules in the mixture. Excess partial molar volumes ($V_{m,1}^{-E}$ and $V_{m,2}^{-E}$) and their limiting values at infinite dilution ($\bar{V}_{m,1}^{-E}$ and $\bar{V}_{m,2}^{-E}$) have been calculated from the experimental density measurements.

Table 4 — Coefficients A_j of equation (2) along with standard deviations σ of binary mixture properties

Parameter	T/K	a	b	c	σ
V_m^E (10 ⁶ m ³ mol ⁻¹)	303.15	-3.1867	-0.5783	1.1024	0.9987
	308.15	-3.4265	-0.5340	0.7430	0.9984
	313.15	-3.6114	-0.5231	0.6130	0.9983
	318.15	-3.7303	-0.5812	0.2800	0.9991

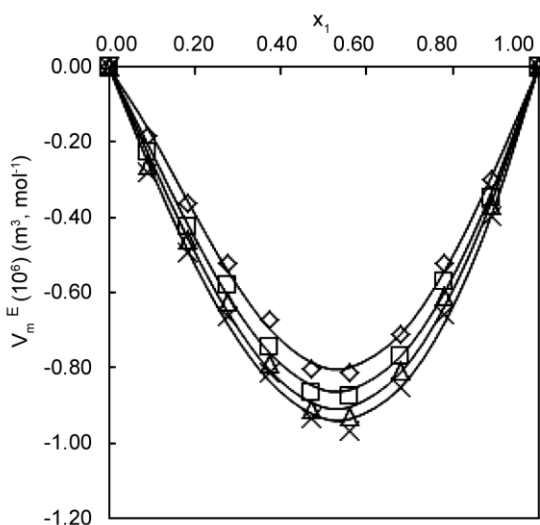


Fig. 1 — Variations of Excess molar volume V_m^E with mole fraction (x_1) in the binary liquid mixtures of cyclohexane with 2-EE; 303.15(\diamond), 308.15(\square), 313.15(\triangle), 318.15(\times). K. Solid lines have been drawn from equation (2) using the coefficients given in Table 4.

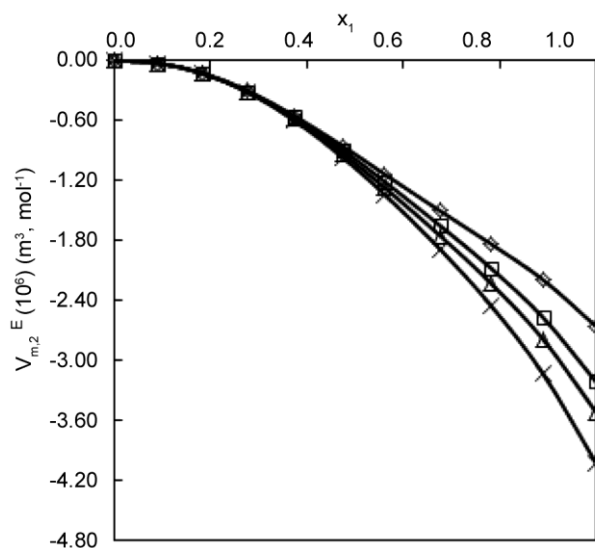


Fig. 2 — Variations of Excess partial molar volume $V_{m,1}^E$ with mole fraction (x_1) in the binary liquid mixtures of cyclohexane with 2-EE at $T = (303.15, 308.15, 313.15, 318.15)$ K.

Conclusions

Data on densities and speeds of sound of binary mixtures of cyclohexane with 2-EE along with those of pure liquids at temperatures $T = (303.15$ to $318.15)$ K at the atmospheric pressure 0.1 MPa, have been reported. Values of the excess molar volume V_m^E were obtained from experimentally measured densities and speeds of sound. Values of V_m^E were negative and becomes more

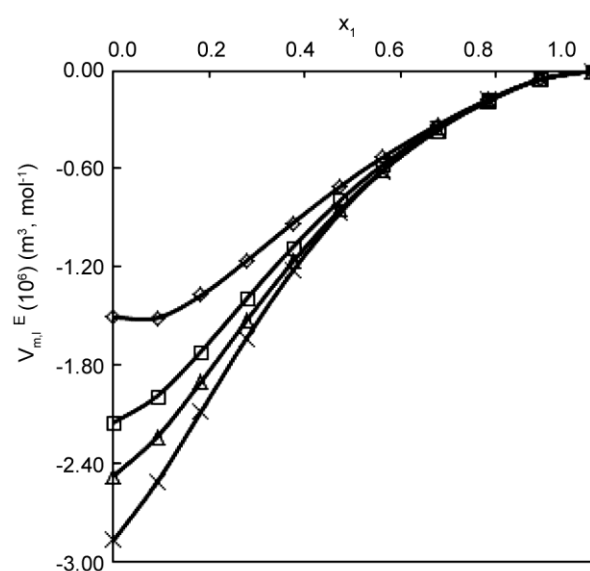


Fig. 3 — Variations of Excess partial molar volume $V_{m,2}^E$ with mole fraction (x_1) in the binary liquid mixtures of cyclohexane with 2-EE at $T = (303.15, 308.15, 313.15, 318.15)$ K.

negative with increase in temperature. The negative behaviour of V_m^E may be attributed to strong dipole-dipole interaction and easy accommodation of 2-EE in the voids of cyclohexane.

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