Excess Molar Volumes of Binary Liquid Systems at 298.15 K

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Abstract. Excess molar volumes, V_m^E, of four binary liquid systems have been experimentally determined at 298.15 K. The systems under the present investigations are: (i) cyclohexane + benzene, (ii) n-hexane + cyclohexane, (iii) n-hexane + benzene and (iv) n-decane + cyclohexane. The values of V_m^E are found to be positive for all the systems over the entire range of compositions. The results have been analysed using equation given by Redlich and Kister. The positive values of V_m^E show that weak intermolecular interactions are present in the liquid mixtures. It also shows the dependence of V_m^E on composition of pure liquid components.

1. Introduction

Studies of excess thermodynamic functions of mixtures of n- alkanes have been important in the development of the corresponding state principles[1,2] in which all alkane segments were considered to have identical interactions. Values of excess molar volume provide a very sensitive test for the molecular solutions theories. The values of V^E depend on several factors, such as size, shape, chemical nature and polarity of the component liquids. The net V^E is considered as a sum of free volume, internal pressure, molecular orientation, weak or specific interaction etc. Extensive work on excess volume of binary liquid mixtures has been carried out and still in progress by various workers[3-12].

The aim of the present paper is to report the excess molar volume, V_m^E, of the four binary systems: (i) n-hexane + cyclohexane, (ii) cyclohexane + benzene, (iii) n-hexane + benzene and (iv) n-decane + cyclohexane at 298.15 K. The dependence of V_m^E on composition is studied and the experimental data are discussed in terms of molecular interactions. Experimental V_m^E values are compared with the theoretical calculation based upon the equations suggested by Redlich and Kister[13].

2. Experimental

Excess molar volume, V_m^E, were determined from the densities of mixture and pure liquid components using bicapillary pyknometer. All the organic chemicals used (AR grade) were further distilled to ensure their purity. Densities of all the four binary systems were measured over the entire range of mole fractions at temperature 298.15 K. the estimated error in the density measurements was found to be ±0.012 percent.

3. Theoretical

Excess molar volume has been given by the expression,

(1)
$$V^E = V_m - V_{id}$$

where V_{id} is the ideal molar volume and V_m is the molar volume of the mixture evaluated with the help of the density data as:

(2)
$$V_m = \frac{\Sigma M_i x_i}{\rho_m}$$

ρ_m being the density of the liquid mixture.

4. Results and Discussion

The values of excess molar volume of binary systems are presented in table 2 and a graphical representation is displayed in Fig. The dependence of V_m^E on mole fractions, x_1, for each liquid system has been shown.
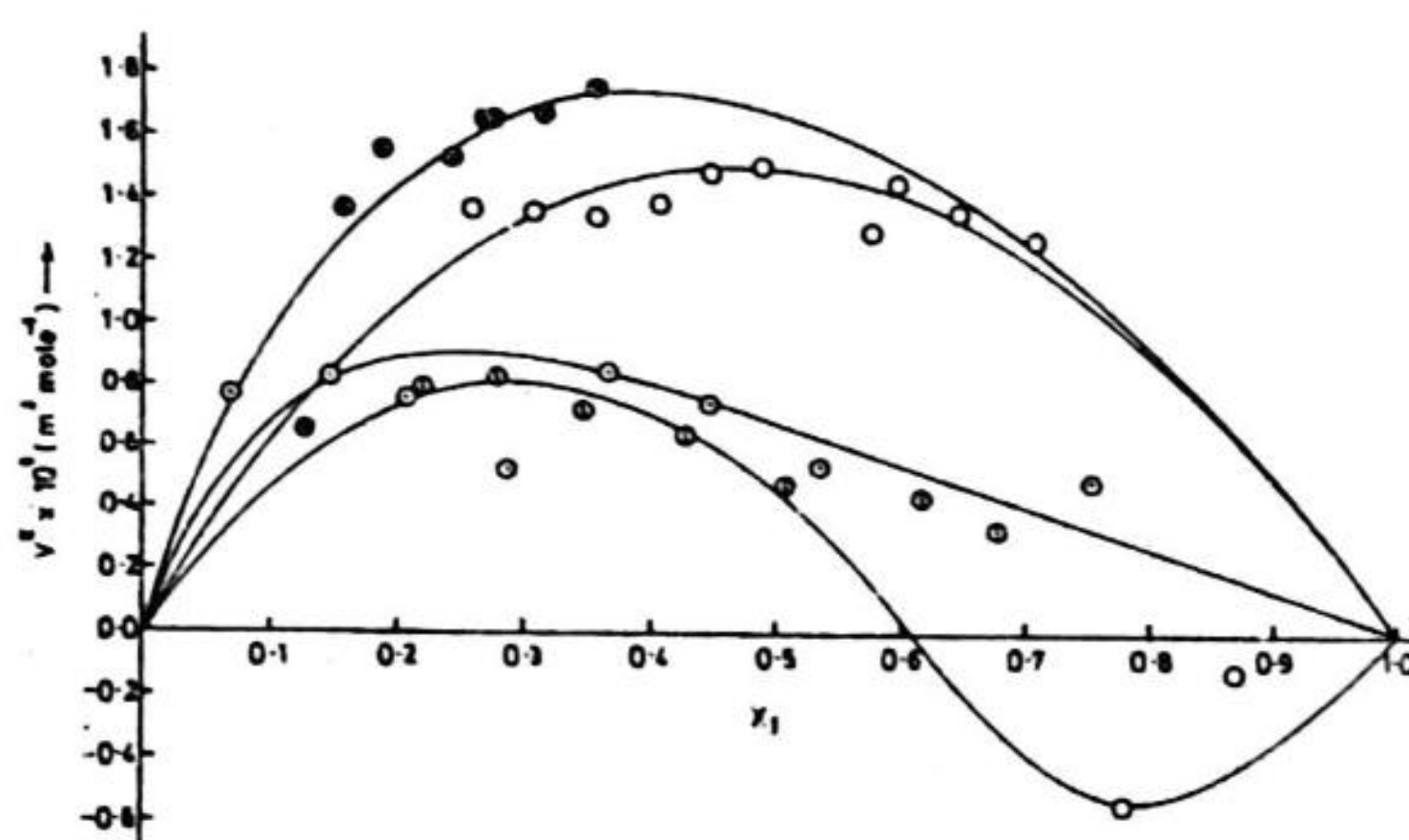

Fig. Molar excess volumes of binary mixtures cyclohexane + benzene O, n-hexane + cyclohexane ●, n-hexane + benzene ◑ and n-decane + cyclohexane ◐.

Redlich and Kister proposed the following equation for binary excess volume data:

$$V^E = x_1 x_2 (a_0 + a_1 (x_1 - x_2) + a_2 (x_1 - x_2)^2 + a_3 (x_1 - x_2)^3)$$

Table 1. Parameters of equation (1) of the excess molar volume of Binary System

SYSTEM	A0	A1	A2	A3
n-hexane+cyclohexane	2.0636	1.2212	4.6976	-8.4964
cyclohexane + benzene	6.1128	1.9327	-17.4425	32.7666
n-hexane + benzene	2.4511	-1.3183	-0.9216	-15.3139

Table 2. Experimental and calculated excess molar volumes V_m^E and V_m^E (cal) respectively at 298.15 K. $\delta V_m^E = \{ V_m^E (\text{cal}) - V_m^E (\text{exp})\}$

	x1	V_m^E (cm³ mol⁻¹)	V_m^E (cal) (cm³ mol⁻¹)	δV_m^E (cm³ mol⁻¹)
n-hexane (x1) + cyclohexane (x2)	0.7634	0.4953	0.5000	0.00
	0.6702	0.7417	0.5942	-0.15
	0.5903	0.2100	0.5774	0.37
	0.5365	0.5402	0.5407	0.00
	0.4469	0.7366	0.4936	-0.24
	0.3691	0.8593	0.5209	-0.34
	0.2942	0.5275	0.6124	0.08
	0.2120	0.7637	0.7588	0.00
	0.1504	0.8163	0.8191	0.00
	0.0684	0.7669	0.6356	-0.13
cyclohexane (x1) + benzene (x2)	0.7128	1.2900	1.2901	0.00
	0.6481	1.3738	1.3698	0.00
	0.5965	1.4569	1.4613	0.00
	0.5798	1.3149	1.4886	0.17
	0.4887	1.5143	1.5142	0.00
	0.4513	1.4901	1.4186	-0.07
	0.4089	1.3870	1.2045	-0.18
	0.3586	1.3555	1.0889	-0.27
	0.3095	1.3599	1.2206	-0.14
	0.2609	1.3732	1.2538	-0.12
n-hexane (x1) + benzene (x2)	0.1599	0.8357	1.0398	0.20
	0.2174	0.8027	0.9641	0.16
	0.2978	0.4828	0.8385	0.00
	0.3458	0.7350	0.7238	0.00
	0.4331	0.6497	0.6501	0.00
	0.5070	0.4868	0.6080	0.12
	0.6162	0.4528	0.4499	0.00
	0.6899	0.3477	0.2093	-0.14
	0.7811	-0.5480	-0.2227	0.32
	0.8733	-0.1192	-0.5997	-0.48

Where x_1 and x_2 denote mole fractions of components 1 and 2 and a_0, a_1, a_2, and a_3 are the constants. These constants for the systems (i), (ii) and (iii) are given in table 1. Table 2 shows the experimental and calculated excess molar volumes of the three binary systems. However the experimental values V_m^E for the system n-decane + cyclohexane has been given in figure. Table 2 also shows the deviations δV_m^E, which we take as a measure of precision.

V_m^E data at temperature 298.15 K are positive for all the four binary mixtures over the complete mole fraction range. However, in the case of n-hexane + benzene, V_m^E have

small negative values only at high n-hexane mole fractions.

It has been established that the sign and magnitude of V_m^E give a good estimate of the strength of the unlike interactions in binary liquid mixture. Large positive excess volumes are taken as an indication of weak intermolecular interactions whereas large negative values of V_m^E are usually found when these interactions are strong and intermolecular complexes are believed to form. The theoretical values of V_m^E are in good agreement with the experimental values. The order of magnitude of interaction is n-hexane + benzene > n-hexane + cyclohexane > cyclohexane + benzene n-decane + cyclohexane. It means n-hexane + benzene shows greatest degree of interactions. The n-alkane molecules form random coils due to internal relation about the C-C bond but the presence of benzene molecule may put the n-alkane molecules under constraint and may decrease their coiling up. As a result, their entropy is decreased and thus molecules tends to have their random configuration. Due to the presence of long chain length, n-hexane molecules provide more favourable accomodation to benzene molecule in comparison to cyclohexane molecule resulting in greater degree of interaction.

Cyclohexane molecules possess globular structure. Its presence may increase the coiling up in the n-alkane molecules. Thus, entropy of the n-alkane molecules may decrease. In other words, the presence of cyclohexane may decrease the intermolecular interaction in long chain alkanes. This is the reason why the n- decane molecules inspite of having the longer chain length show lesser interaction in a binary mixture.

Acknowledgement

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