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Excess Molar Volumes of Binary Liquid Mixtures of Ketocyclohexane ($C_6H_{10}O$), + CH_2Cl_2, +$CHCl_3$, + CH_2ClCH_2Cl, +$CHClCCl_2$, and + CCl_3CH_3 at 303.15 K

Abstract

Excess molar volumes, V^E, at T = 303.15 K, have been measured for binary liquid mixtures of ketocyclohexane ($C_6H_{10}O$) + dichloromethane (CH_2Cl_2), + trichloromethane ($CHCl_3$), + l,2-dichloroethane (CH_2ClCH_2Cl), + trichloroethene ($CHClCCl_2$), and + 1,1,1- trichloroethane (CCl_3CH_3). The values of V^E have been fitted in appropriate equations using a least-squares method. V^E has been found to be negative throughout the entire range of composition for mixtures of $C_6H_{10}O$ + CH_2Cl_2, + $CHCl_3$, + $CHClCCl_2$, and + CCl_3CH_3. For $C_6H_{10}O$ + CH_2ClCH_2Cl, V^E has been found to be positive at lower mole fractions of $C_6H_{10}O$, and negative at higher mole fractions. The results obtained have been discussed from the viewpoint of existence of specific interactions between the components.

Keywords: Dilatometer, Excess Volume, Specific interaction, Hydrogen bonding, Binary mixtures

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1. INTRODUCTION

Ketocyclohexane (or oxocyclohexane, or ketohexamethylene, or cyclohexyl ketone or cyclohexanone) is a 6-C molecule which is cyclic saturated ring having a keto functional group. It is a colorless, oily liquid with an acetone-like smell. It appears as a colorless to pale yellow liquid with a pleasant odor. It is lighter than H_2O. Its vapors are heavier than air. It may be used as solvent or to make nylon, or as a chemical reaction medium.

Mixtures of Ketocyclohexane ($C_6H_{10}O$) + CH_2Cl_2, + $CHCl_3$, + CH_2ClCH_2Cl, + $CHClCCl_2$, and + CCl_3CH_3, are of meticulous attention from the perspective of donor - acceptor interaction of electrons which leads to the creation of adducts between the components. In this case ketocyclohexane, because of the occurrence of non-bonding pair of electrons on the O atom, goes about as an n-contributor (donor) toward all these chloro-compounds. Dichloromethane, trichloromethane, 1,2-dichloroethane, trichloroethene, and 1,1,1-trichloroethane can be involved in the creation of H-bond type of interaction, and all these chloro compounds perform as σ-acceptors toward, $C_6H_{10}O$. Although Nath et al. [1], Chadha et al. [2] and Pathak et al. [3] have estimated excess volumes, V^E, speeds of sound, u, excess enthalpy, dielectric constants

and refractive indexes, for acetone or cyclopentanone, furan or methylfuran with tetrachloroethane and dibromomethane, wide-ranging studies about interactions between the mixtures of chloroalkanes and chloroalkenes with compounds having keto groups have not been made as revealed by literature survey. Hence, in this work, we have measured excess molar volumes, V^E, of Ketocyclohexane + CH_2Cl_2, + $CHCl_3$,+CH_2ClCH_2Cl, + $CHClCCl_2$, and + CCl_3CH_3, at 303.15K, and the obtained data are reported and deciphered here.

2. EXPERIMENTAL SECTION

Materials: CH_2Cl_2 and CH_2ClCH_2Cl, having marked purity of 99.8% (GLC), obtained from Qualickem, India. Dichloromethane, 1,2-dichoroethane, and trichloroethene were used as obtained. Ketocyclohexane (AR, purity 99.5%, HPLC grade) was placed over anh. Na_2SO_4 to take away small drops of H_2O and fractionally distilled. Trichloromethane (AR quality, Qualigens, India) was shaken time after time with distilled water to take away C_2H_5OH, dehydrated over anh. $CaCl_2$, distilled fractionally, and collected in Ambered reservoirs. CCl_3CH_3 (Spectrochem AR quality, with purity of 99.0% obtained from gas liquid chromatography was rinsed with ten percent K_2CO_3 solution, dehydrated over $CaCl_2$, and distilled. An Anton- Paar vibrating – tube densimeter was used for the measurement of densities. Calibrated thermometers, connected with a constant-temperature bath circulator, were attached with densimeter. For the densimeter calibration, N_2 and extra-distilled H_2O were used. The estimated precision in density measurement is higher than $3x10^{-5}$ $g.cm^{-3}$.

The purity of chemicals was checked by measuring their densities and obtained results were in good conformity with best accessible literature data [4].

3. METHOD

Excess volumes, V^E, were obtained (in the order of reproducibility of ± 0.002 cm^3mol^{-1}), with the help of a two-branched, glass made dilatometer that was a similar which is was utilized in our prior publication [5]. Weighed quantities of the two liquids were locked up individually over Hg in the inadequacy of air spaces in the two extremities of the dilatometer, which (situated on a wooden stand) was submerged in water of a thermostat (reproducibility ± 0.01 K). Both the liquids were mixed by shaking the cell from side to side through a specific angle, and the Hg level in the capillary was noted by means of a cathetometer (accuracy of 0.001 cm). The functioning of the dilatometer was tested by measuring V_m^E for the system of C_6H_6+ cyclohexane at 303.15 K as described elsewhere [1]. The measured value of excess molar volume for this system agrees well with the literature data.

4. RESULTS AND DISCUSSION

The data obtained for V^E of the binary mixtures of Ketocyclohexane at the Temperature 303.15 K are reported in Table 1 and presented graphically against, $x1$, in Figure 1. V^E data for all binary mixtures have been fitted by using following equation

$$V^E/(\text{J.mol}^{-1}) = x1x2\sum_{i=0}^{m} Ai(x1-x2)^i \qquad (1)$$

where $x1$ refers to the mole fraction of Ketocyclohexane. The values of all constants A_i along with standard deviations, σ, are collected in Table 2.

Following equations have been used to calculate standard deviations, σ, for all mixtures

$$\sigma = \left[\frac{\sum(V^E - V^E_{cal})^2}{(m-n)}\right]^{1/2} \qquad (2)$$

Where, V^E is the experimental value of excess molar volume and V^E_{calc} refers to calculated value by means of eq. 1, m represents number of experimental data and n, the number of constants.

It is observed that if V^E values are negative, interaction factor leads whereas the positive V^E values are indicative of steric factor in the binary mixtures.

When values of V^E are negative, it is due to increased interactions between the dissimilar molecules or it would arise from specific interactions between the molecules of the two components. These -ve values of V^E shows that between contrasting molecules, high probability of the H-bonded type interaction

takes place at the time of mixing. It may also be explained due to the packing effect. When the values of V^E are positive, the decrease in specific interactions takes place.

The sign of V^E shows the force of association acting between the molecules of the different parts. A negative value of V^E is due to a nearer approach of dissimilar molecules, cause to cause to decrease in absolute volume and compressibility. Various types of powers acting between the contrasting components are dispersion, hydrogen bonding, dipole–dipole, charge transfer and dipole induced dipole type interactions. Attraction between the molecules is expected due to dispersion forces, and the relative magnitudes of the A–A, B–B, A–B type contacts between the molecules of components A and B of a mixture are essential for determination of excess properties. In the case, if shape and size of components of a mixture do not differ very much, the dispersion forces causes +ve contributions to V^E. However, other remaining interactions must lead to -ve contributions to V^E. All systems are operated by dispersion forces , and if there is more than one type of interaction occur in a system, the sign of V^E depends upon the total effect of the contributions made by all types of interactions.

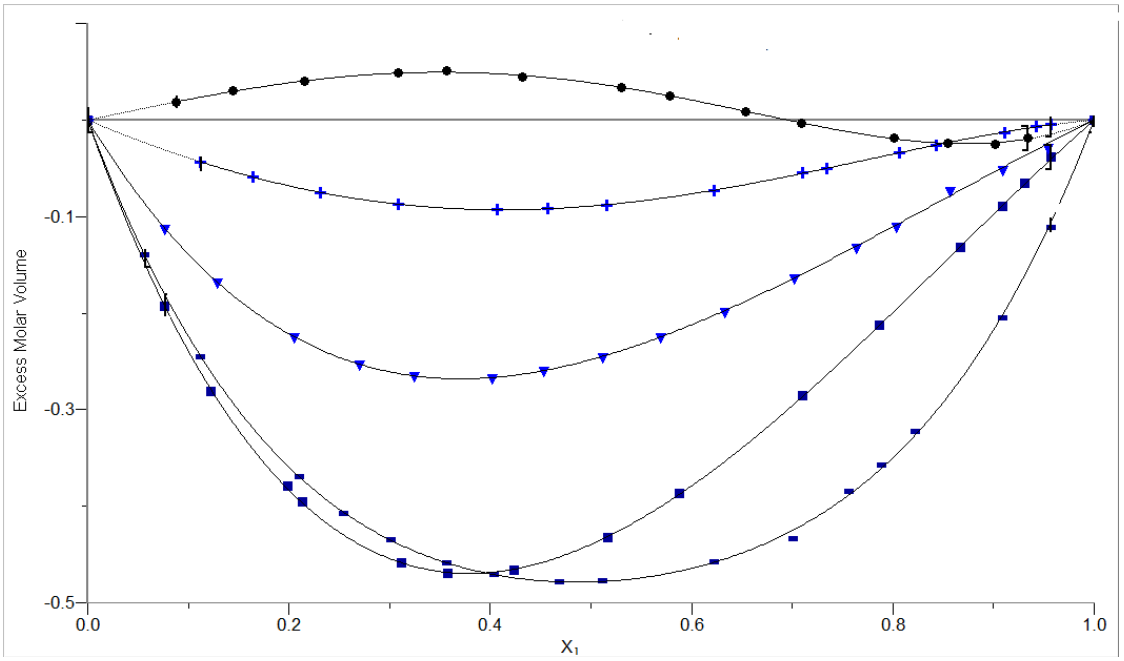

Figure 1: Plot of V^E versus $x1$ for the various mixtures at T =303.15 K: +, $x_1C_6H_{10}O$ + (1 -x_1) CH_2Cl_2; ■ , $x_1C_6H_{10}O$ + (1 - x_1)- $CHCl_3$; ●, $x_1C_6H_{10}O$ + (1 - x_1) CH_2ClCH_2Cl; ▼, $x_1C_6H_{10}O$ + (1 - x_1)- $CHClCCl_2$; ▬, $x_1C_6H_{10}O$ + (1 - x_1)CCl_3CH_3.

Table 1: Experimental Values of the Excess Molar Volumes, V^E, for $C_6H_{10}O + CH_2Cl_2$, + $CHCl_3$, + CH_2ClCH_2Cl, + $CHClCCl_2$, and + CCl_3CH_3, at 303.15 K

$x1C_6H_{10}O + (1 - x1)CH_2Cl_2$		$x1C_6H_{10}O + (1 - x1)CHCl_3$		$x1C_6H_{10}O + (1 - x1)CH_2ClCH_2Cl$	
$x1$	V^E (Cm³.mol⁻¹)	$x1$	V^E (Cm³.mol⁻¹)	$x1$	V^E (Cm³.mol⁻¹)
0.1123	-0.044	0.0765	-0.193	0.0877	0.018
0.1643	-0.059	0.1223	-0.281	0.1444	0.030
0.2311	-0.075	0.1987	-0.379	0.2155	0.040
0.3087	-0.087	0.2137	-0.396	0.3087	0.049
0.4066	-0.093	0.3114	-0.459	0.3566	0.051
0.4576	-0.092	0.3578	-0.47	0.4321	0.044
0.5154	-0.088	0.4233	-0.466	0.5299	0.034
0.6222	-0.073	0.5167	-0.432	0.5782	0.025
0.7098	-0.055	0.5876	-0.387	0.6534	0.009
0.7345	-0.050	0.7098	-0.286	0.7095	-0.003
0.8065	-0.034	0.7865	-0.213	0.8014	-0.019
0.8433	-0.026	0.8675	-0.132	0.8543	-0.024
0.9111	-0.013	0.9088	-0.09	0.9014	-0.025
0.9422	-0.007	0.9311	-0.066	0.9342	-0.019
0.9567	-0.005	0.9567	-0.038		

$x1C_6H_{10}O + (1 - x1)CHClCCl_2$		$x1C_6H_{10}O + (1 - x1)CCl_3CH_3$	
$x1$	V^E (Cm³.mol⁻¹)	$x1$	V^E (Cm³.mol⁻¹)
0.0766	-0.112	0.0567	-0.140
0.1286	-0.168	0.1123	-0.245
0.2052	-0.225	0.2098	-0.369
0.2699	-0.253	0.2544	-0.407
0.3243	-0.265	0.3012	-0.435
0.4016	-0.267	0.3567	-0.459
0.4534	-0.259	0.4034	-0.471
0.5112	-0.245	0.4689	-0.478
0.5689	-0.225	0.5111	-0.477
0.6332	-0.198	0.6223	-0.457
0.7023	-0.164	0.7012	-0.434
0.7631	-0.132	0.7567	-0.385
0.8032	-0.110	0.7889	-0.357
0.8567	-0.073	0.8223	-0.322
0.9089	-0.051	0.9087	-0.205
0.9543	-0.028	0.9567	-0.111

Table 2: Values of the parameters, Ai, of Eq 1 and the Standard Deviations, σ, for the various mixtures at 303.15K

System σ/ (J mol¹)	A0	A1	A2	A3
$C_6H_{10}O$ (1) +CH_2Cl_2 (2) 0.0003	-0.3566	0.1696	0.08956	0.005
$C_6H_{10}O$ (1)+$CHCl_3$ (2) 0.002	-1.759	0.9295	-0.1722	0.08311
$C_6H_{10}O$ (1)+ CH_2ClCH_2Cl (2) 0.001	0.1537	-0.2874	-0.262	-0.037
$C_6H_{10}O$ (1)+$CHClCCl_2$ (2) 0.002	- 0.9934	0.5673	-0.1269	0.0323
$C_6H_{10}O$ (1)+ CCl3CH3 (2) 0.0033	-1.914	0.06027	-0.8425	-0.02472

Table 1 represents that V^E is negative all over the whole range of mole fraction for mixtures of ketocyclohexane + dichloromethane, + trichloroethene, + trichloromethane, and + 1,1,1- trichloroethane. For $C_6H_{10}O$ +1,2-dichloroethane , V^E is positive at lower mole fraction whereas negative at its higher mole fraction. At $x1$ = 0.5, the values of V^E for the different systems of $C_6H_{10}O$ has the order:

CH_2ClCH_2Cl **>** CH_2Cl_2 **>** $CHClCCl_2$> $CHCl_3$ **>** CCl_3CH_3

The negative sign of V^E for mixtures of ketocyclohexane ($C_6H_{10}O$) + dichloromethane, + trichloromethane, + trichloroethene and + 1,1,1- trichloroethane can be expected due to a nearer approach of the dissimilar molecules , which indicates the presence of specific interaction between O (of ketocyclohexane) and H (of CH_2Cl_2, or $CHClCCl_2$, or CHCl3, or CCl_3CH_3), as an intermolecular adduct is formed due to hydrogen bonding type interactions between acetone and dibromomethane [6]. Ketocyclohexane in this case will act as n-donor. The specific interactions of ketocyclohexane with all these compounds may also be because of charge transfer interaction between Cl atoms of chloroalkanes or chloroalkene with lone pair electrons on O atom of ketocyclohexane.

5. CONCLUSION

The current study reveals presence of electron donor-acceptor interaction between mixtures of Ketocyclohexane ($C_6H_{10}O$) with dichloromethane, trichloromethane, trichloroethene, and 1,1,1-trichloroethane where the values of excess molar volume, V^E is negative throughout the entire range of $x1$.

But in the case of ketocyclohexane with CH_2ClCH_2Cl, sign of excess volume is +ve at lower mole fraction and –ve at its higher mole fraction. The +ve sign of VE is responsible for steric factor between the components whereas negative sign represents that interaction factor is dominating. At $x1$ = 0.5, V^E for the different systems of $C_6H_{10}O$ shows that the values of excess molar volume has more negativity, thus more specific interaction with 1,2-dichloroethane. The occurrence of a specific interaction of ketocyclohexane with all these chlorocompounds can be expected by the creation of hydrogen bonds between the hydrogen atoms present on these chloro compounds and the separate-pair electrons of ketocyclohexane as it is also known that an adduct formation takes place via H-type bonding between CH_3COCH_3 and trichloromethane [7,8]. There is, however, also a possibility of creation of charge-transfer complexes with $C_6H_{10}O$ by means of the contact of C1 atoms in these chloro compounds with the distinct-pair electrons of ketocyclohexane.

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