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Excess Molar Volumes of Binary Liquid Mixtures of Cyclohexanone + Dichloromethane, + Trichloromethane, + 1,1,1-Trichloroethane and 1,2 Dichloroethane at 308.15 K

Abstract

Excess molar volumes, Vm ^{E}, at T 308.15 K have been measured for binary liquid mixtures of cyclohexanone ($C_6H_{10}O$) + dichloromethane (CH_2Cl_2), + trichloromethane ($CHCl_3$), + 1,1,1trichloroethane (CCl_3CH_3), and + l,2-dichloroethane (CH_2ClCH_2Cl). The values of Vm ^{E} have been fitted in appropriate equations using a least-squares method. V_m ^{E} has been found to be negative throughout the entire range of composition for mixtures of $C_6H_{10}O$ + CH_2Cl_2, + $CHCl_3$, and + CCl_3CH_3. For $C_6H_{10}O$ + CH_2ClCH_2Cl, V_m ^{E} has been found to be positive at lower mole fractions of $C_6H_{10}O$, and negative at higher mole fractions. These results indicate presence of specific interactions between these components.

Keywords: Excess molar volumes; Cyclohexanone; Trichloromethane.

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1. INTRODUCTION

Binary mixtures of cyclohexanone ($C_6H_{10}O$) with dichloromethane (CH_2Cl_2)), trichloromethane ($CHCl_3$), 1,1,1-trichloroethane (CCl_3CH_3), and 1,2 dichloroethane (CH_2ClCH_2Cl) are of particular interest from the viewpoint of electron donor-acceptor interaction leading to the formation of intermolecular adducts between the components in the liquid state. A binary mixture is formed by the replacements of like contacts by unlike contacts in the mixture. The specific interaction of $C_6H_{10}O$ with the above chloro-compounds can be visualized as being due to the presence of lone-pair electrons on the oxygen atom of $C_6H_{10}O$, which can make this species act as an n-donor toward these chloro-compounds. On the other hand, CH_2Cl_2, $CHCl_3$, CCl_3CH_3, and CH_2ClCH_2Cl, can be involved in the formation of H-bond with, and act as σ-acceptors toward, $C_6H_{10}O$. These experimental data are very useful to the development of new thermodynamic property predictive methods and for verifying the existing theories of liquids. Literature survey revealed that measurements on [1-5] excess molar volumes, V_m^E, speeds of sound, u, relative permittivities, ε_r, and refractive indexes, n_D, for mixtures of acetone (CH_3COCH_3) or methylethyl ketone (CH3COC2H5) with CH_2Cl_2, CH_2ClCH_2Cl, $CHClCCl_2$, and CCl_2CCl_2 are available. Extensive studies concerning interactions between the components of mixtures of chloroalkanes with ketones of more complexity have not been made. Therefore, the study of excess thermodynamic properties, such as excess molar volume, is quite important to understand molecular interactions in mixtures and to develop and test theories of solutions and mathematical models. Hence, in this work, we have measured V_m ^{E} of $C_6H_{10}O$ + CH_2Cl_2, + CHCl3, + CCl_3CH_3, and + CH_2ClCH_2Cl and the results of these measurements are reported and interpreted here.

2. EXPERIMENTAL SECTION

Materials., dichloromethane and 1,2-dichloroethane, both of stated minimum purity of 99.8% (GLC), were all obtained from Sisco Research Laboratories, Ltd., Mumbai, India. CH_2Cl_2, CH_2ClCH_2Cl, were used without further purification. Cyclohexanone (AR quality, minimum purity of 99.5%, HPLC quality) was placed over anhydrous sodium sulfate to remove traces of water and then fractionally distilled. Trichloromethane (AR quality, Qualigens Fine Chemicals Ltd., Mumbai, India) was shaken repeatedly with distilled water to remove ethanol present as stabilizer, dried over anhydrous calcium chloride, distilled fractionally, and stored in dark colored bottles. 1,1,1-Trichloroethane (Spectrochem product, AR quality) stated minimum purity of 99.0% (GLC) was washed with 10% potassium carbonate solution, dried over calcium chloride, and then distilled fractionally. An Anton- Paar vibrating – tube densimeter (Model DMA 60/ 602) was used for the measurement of densities It was equipped with calibrated thermometers with a precision of 0.01 K, connected with a Heterofrig constant-temperature bath circulator, with a precision of 0.01 K. For the densimeter calibration, nitrogen and double-distilled water 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 comparing experimental values with the best available literature values (Table 1).

3. METHOD

Excess molar volumes, V_m^E, were measured with an imprecision of the order of (0.002 cm^3,mol^{-1}, using a two-limbed Pyrex glass dilatometer that was similar to that used in earlier measurements [6]. Known amounts of the two liquid components were confined separately over mercury in the absence of air spaces in the two limbs of the dilatometer, which (mounted on a stand) was immersed in water of a thermostat (controlled to 0.01 K). The mixing of the components was achieved by rocking the cell back and forth through a definite angle, and the mercury levels in the capillary of the dilatometer were noted with a cathetometer that had an accuracy of 0.001 cm. The working of the dilatometer was tested by measuring V_m^E for the system of Benzene+ Cyclohexane at 298.15 K as described elsewhere [7]. The measured value of excess molar volume for this system agrees well with the literature values.

4. RESULTS AND DISCUSSIONS

The values of V_m^E of the present mixtures of $C_6H_{10}O$ at T 308.15 K are reported in Table 2. The values of V_m^E for various mixtures of $C_6H_{10}O$ have been plotted against x_1 in Figure 1. The values of V_m^E for the present mixtures have been fitted by the method of least-squares to the equation

$$V^E/(J.mol^{-1}) = x_1 x_2 \sum_{i=0}^{m} A_i(x_1-x_2)^i \qquad (1)$$

where x_1 is the mole fraction of $C_6H_{10}O$. The parameters A_i and standard deviations, σ, are listed in Table 3.

The standard deviations, σ, are calculated using equation

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

where V^E is the experimental excess molar volume and V^E_{calc} calculated excess molar volume using equation (1), m is number of experimental data & n is number of constants characteristic of a system. Graphical presentation of experimental values of data is presented in figure1.

It is clear that the interaction factor is dominant for the mixtures with negative V_m^E values while the steric factor prevails for mixtures with positive V_m^E values.

Negative V_m^E arise due to increased interactions between the unlike molecules or it would arise from specific interactions between the molecules of the two components. These negative values of V_m^E indicate that, between unlike molecules, strong intermolecular forces (probably of the H-bonded type) appear at mixing. Such behavior could be explained also by the packing effect. Positive V_m^E can be attributed to the decrease in specific interactions.

The data show (see Table 1) that V_m^E is negative throughout the entire range of x_1 for mixtures of $C_6H_{10}O$ + CH_2Cl_2, + $CHCl_3$, + and + CCl_3CH_3 . For $C_6H_{10}O$ + CH_2ClCH_2Cl , V_m^E is positive at lower values of x and negative at its higher values. At x_1 = 0.5, V^Em for the various systems of $C_6H_{10}O$ has the sequence:

CH_2ClCH_2Cl > CH_2Cl_2 > CHCl3 > CCl_3CH_3

The negative values of V^E_m for mixtures of $C_6H_{10}O$ + CH_2Cl_2, + $CHCl_3$, and + CCl_3CH_3 can be visualized as being due to a closer approach of the unlike molecules in solution, thus indicating the existence of specific interaction between O (of cyclohexanone) and H (of CH_2Cl_2, CHCl3, CCl_3CH_3), as it is also known that a complex is formed through hydrogen bonding between acetone and dibromomethane in the liquid state [9]. Cyclohexanone in this case will act as n-donor. The specific interactions of cyclohexanone with all these compounds may also be due to a charge transfer interaction of Cl atoms of chloroalkanes with lone pair electrons on oxygen atom of cyclohexanone. Generally, it seems that the strength of these intermolecular forces is higher for the systems with more chlorine atoms connected to carbon−hydrogen pair atoms. It may be concluded that the interaction factor is dominant for the mixtures with negative V^E_m values while the steric factor prevails for mixtures with positive V^E_m values.

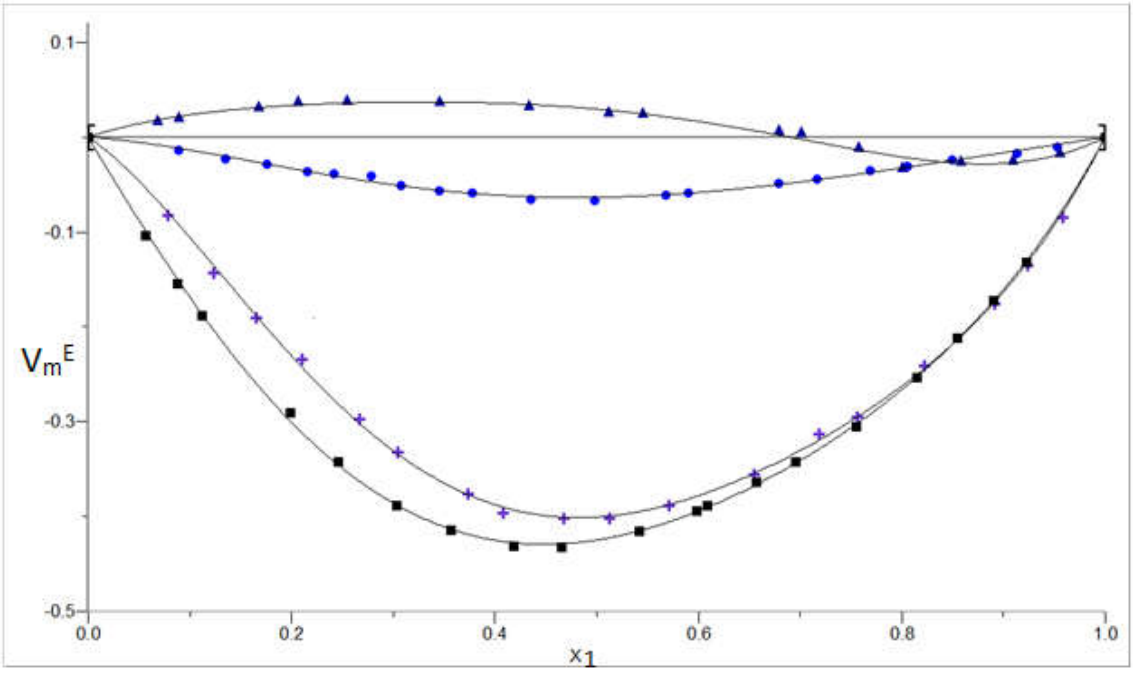

Figure 1: Excess molar volumes of binary liquid mixtures of x_1 of Cyclohexanone ($C_6CH_{10}O$(1) + dichloromethane (⟶) (2), , + trichloromethane (⟶+)(2) ,+1,1,1-trichloroethane (⟶■) , (2) and + 1, 2-dichloroethane (⟶▲) (2) at 308.15 K. The smoothed curves are based on the parameters A1, A2, A3, and A4 given in Table 3.

Table 1: Densities of the Pure Components at 298.15 K

Compound	Density g. cm^{-3} Experimental	Literature Values [8]
Cyclohexanone	0.94614	0.947
Dichloromethane	1.32689	1.327
Chloroform	1.47322	1.47316
1,1,1-Trichloroethane	1.32824	1.32827
1,2-Dichloroethane	1.24559	1.24548

Table 2: Excess Molar Volumes of Cyclohexanone ($C_6H_{10}O$) (1) + CH_2Cl_2 (2), or + $CHCl_3$ (2), or + CCl_3CH_3 (2) or + CH_2ClCH_2Cl at 308.15 K

$X_1C_6H_{10}O + (1 - X_1)CH_2Cl_2$	
X_1	V_m^E ($Cm^3.mol^{-1}$)
0.0884	-0.014
0.1345	-0.023
0.1756	-0.029
0.2156	-0.036
0.2421	-0.039
0.2784	-0.041
0.3078	-0.051
0.3448	-0.057
0.3777	-0.059
0.4356	-0.066
0.4976	-0.067
0.5678	-0.061
0.5897	-0.059
0.6784	-0.049
0.7167	-0.044
0.7688	-0.035
0.8057	-0.031
0.8498	-0.024
0.9134	-0.017
0.9533	-0.011

$X_1C_6H_{10}O + (1 - X_1)CHCl_3$	
X_1	V_m^E ($Cm^3.mol^{-1}$)
0.0789	-0.082
0.1234	-0.143
0.1654	-0.191
0.2098	-0.234
0.2663	-0.297
0.3048	-0.332
0.3732	-0.376

0.4079	-0.397
0.4673	-0.402
0.5122	-0.402
0.5711	-0.389
0.6543	-0.356
0.7188	-0.313
0.7566	-0.295
0.8222	-0.241
0.8907	-0.176
0.9233	-0.135
0.9581	-0.085

$X_1C_6H_{10}O + (1 - X_1)\ CCl_3.CH_3$	
X_1	V_m^E ($Cm^3.mol^{-1}$)
0.0567	-0.104
0.0876	-0.154
0.1121	-0.188
0.1987	-0.291
0.2456	-0.343
0.3034	-0.389
0.3567	-0.415
0.4189	-0.431
0.4654	-0.432
0.5423	-0.416
0.5987	-0.394
0.6091	-0.389
0.6573	-0.364
0.6954	-0.342
0.7555	-0.305
0.8144	-0.254
0.8543	-0.212
0.8906	-0.173
0.9223	-0.132

$X_1C_6H_{10}O + (1 - X_1)\ CH_2\ Cl.CH_2Cl$	
X_1	V_m^E ($Cm^3.mol^{-1}$)
0.0678	0.016
0.0892	0.0193
0.1678	0.031
0.2065	0.037
0.2543	0.038
0.3456	0.037
0.4333	0.032
0.5111	0.025

0.5445	0.024
0.6789	0.006
0.7012	0.004
0.7571	-0.012
0.8001	-0.033
0.8581	-0.026
0.9093	-0.025
0.9554	-0.017

Table 3: Least Squares Coefficients of Eq 1 for the Excess Molar Volumes, and the standard deviations, σ, of Cyclohexanone ($C_6H_{10}O$) (1)+ Dichloromethane (CH_2Cl_2) (2), or + Trichloromethane ($CHCl_3$) (2),or +1,1,1-Trichloroethane (CCl_3CH_3)(2) or + 1,2-Dichloroethane (CH_2ClCH_2Cl) at 308.15 K

System	A0	A1	A2	A3	σ/ (J mol^1)
$C_6H_{10}O$ (1) + CH_2Cl_2 (2)	0.254	0.03102	0.1348	-0.7754	0.002
$C_6H_{10}O$ (1) + $CHCl_3$ (2)	-1.603	0.1335	0.1686	-0.8293	0.004
$C_6H_{10}O$ (1) + CCl_3CH_3(2)	-1.7	0.3365	-0.2014	-0.4327	0.003
$C_6H_{10}O$ (1)+CH_2ClCH_2Cl(2)	0.1179	-0.1918	-0.2204	-0.2550	0.004

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