Volumetric Behaviour of Binary Liquid Mixtures at a Temperature of 303.15 K

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Excess molar volumes (V_m^E) of binary liquid mixtures: $xC_6H_5CH_3$ + $(1\text{-}x_1)CH_3CN$ or + $(1\text{-}x_1)C_6H_5NO_2$, or + $(1\text{-}x_1)C_2H_5NO_2$ have been determined as a function of mole fraction of $C_6H_5CH_3$ (x) at a temperature of 303.15 K over a entire range of composition. The densities of the binary liquid mixtures were determined by pycnometrically. The V_m^E values of the mixtures have been found to be negative over the whole composition in order of $C_6H_5CH_3 + C_6H_5NO_2$, < $C_6H_5CH_3 + CH_3CN$, and < $C_6H_5CH_3 + C_2H_5NO_2$. The negative magnitude of V_m^E suggests the presence of intermolecular interaction in the three binary liquid mixtures.

Keywords : Excess molar volumes, Toluene, Nitrobenzene, Nitroethane, Acetonitrile.

Introduction

For the past two decades, a considerable progress has been made in theoretical understanding of liquid-liquid binary mixture. Besides the theoretical importance, the knowledge of physicochemical properties of multi-components mixtures is indispensable for many chemical process industries. Examples are the petroleum, petrochemical etc. are commonly used in industries where physicochemical processes are involved to handle the mixtures of hydrocarbons, alcohols, aldehydes, ketones etc. Importantly, for accurate designing equipment it is necessary to know the interaction between the components of mixtures. Physicochemical analysis method can be used for getting sound information for a specific interaction between the components and the structure of the binary liquid mixtures. The thermodynamic studies of binary solutions have attracted much attention of scientists and experimental data on a number of systems are available from review and publications.[1-12]

In the framework of a research work, which aims to study the thermodynamic properties of binary liquid mixtures with different components. We also reported some works of binary mixtures.[13-19] This paper will describe the excess molar volumes of $xC_6H_5CH_3$ + $(1\text{-}x_1)CH_3CN$, or $(1\text{-}x_1)$-$C_6H_5NO_2$, or $(1\text{-}x_1)C_2H_5NO_2$ in obtaining the interaction information of all the binary liquid mixtures. The components considered in the paper are $C_6H_5CH_3$, CH_3CN, $C_6H_5NO_2$, and $C_2H_5NO_2$ at the temperature 303.15 K. This is a continuation of our previous investigation.

Experimental Section

Materials and Procedure. The toluene (purity 99.5%, Merck), acetonitrile (purity 99%, Fluka), nitrobenzene (purity 99.5%, Merck), and nitroethane (purity 99.5%, Metheson,) were used. The densities of the pure components and binary mixtures were measured by pycnometrically and were reported elsewhere.[15,17] Special attention was given to avoid the evaporation of solutions after preparation. The purity of chemicals was checked by comparing with their densities with literature values,[20,21] and obtained values gave a good agreement with reported values.[22] The comparative results are shown in Table 1. The values of density of the chemicals at the working temperature are, however not available in the literature, we obtained those values at working temperature by plotting the reported values, and considering the density as a linear function of temperature.

The V_m^E of different binary mixtures were calculated from the measured values of the densities (ρ) of all the liquid binary mixtures using equation (1):

$$V_m^E/\text{cm}^3\text{mol}^{-1} = (x_1M_1 + x_2M_2)/\rho_m - x_1M_1/\rho_1 - x_2M_2/\rho_2 \tag{1}$$

Where M_1 and M_2 represent the molar masses of components 1 and 2, respectively. The x_1 and x_2 are the mole fractions of 1 and 2 components having densities ρ_1 and ρ_2, respectively. The ρ_m is experimentally observed density of the binary liquid mixtures. All measurements were carried out in a thermostatically controlled and well-stirred water bath with a temperature accuracy of ± 0.01 °C, read on Beckmann thermometer.

Results

Table 2 represents the experimental results for V_m^E obtained from liquid mixtures: $xC_6H_5CH_3$ + $(1\text{-}x_1)CH_3CN$, or $(1\text{-}x_1)C_6H_5NO_2$, or $(1\text{-}x_1)C_2H_5NO_2$ systems at a temperature of 303.15 K. The observed results of V_m^E were fitted by least square method to four parameter RedlichKister[23] equation (2) as follow;

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Table 1. Comparison between experimental and literature values of densities (g cm^{-3}) at a temperature of 20 °C

$C_6H_5CH_3$		CH_3CN		$C_6H_5NO_2$		$C_2H_5NO_2$	
Experimental	Literature	Experimental	Literature	Experimental	Literature	Experimental	Literature
0.8669	0.8669	0.7855	0.7857	1.2036	1.2037	1.0440	1.0444

Table 2. Excess molar volumes (V_m^E), and each point of deviations {$xC_6H_5CH_3$ + (1-x$_1$) CH_3CN, + (1-x$_1$) $C_6H_5NO_2$, and + (1-x$_1$) $C_2H_5NO_2$}

$C_6H_5CH_3 + CH_3CN$ mixture			$C_6H_5CH_3 + C_6H_5NO_2$ mixture			$C_6H_5CH_3 + C_2H_5NO_2$ mixture		
Mole fraction (x)	V_m^E cm^3/mol	Deviation cm^3/mol	Mole fraction (x)	V_m^E cm^3/mol	Deviation cm^3/mol	Mole fraction (x)	V_m^E cm^3/mol	Deviation cm^3/mol
0.0999	-0.1260	-0.0020	0.1099	-0.2556	0.0033	0.1000	-0.0584	0.0010
0.1999	-0.2461	-0.0018	0.2012	-0.4865	-0.0028	0.2004	-0.0971	-0.0010
0.3006	-0.3363	0.0057	0.3014	-0.6568	-0.0008	0.2994	-0.1361	-0.0003
0.4016	-0.4013	0.0018	0.4015	-0.7199	0.0005	0.3976	-0.1720	0.0033
0.5004	-0.4286	-0.0080	0.4987	-0.6888	-0.0012	0.4989	-0.2092	-0.0010
0.5979	-0.3968	-0.0010	0.5981	-0.5808	0.0062	0.5995	-0.2254	-0.0033
0.6964	-0.3259	0.0062	0.7005	-0.4559	-0.0042	0.6984	-0.2082	-0.0006
0.7985	-0.2331	0.0007	0.8043	-0.3156	-0.0037	0.7974	-0.1541	0.0064
0.8967	-0.1247	-0.0038	0.8980	-0.1792	0.0049	0.8986	-0.0893	-0.0050

Table 3. The values of the parameters A_j (A_0, A_1, A_2, and A_3) and the standard deviation (S) for all the three binary mixtures of the Redlich-Kister equation at a temperature of 303.15 K

$xC_6H_5CH_3$	A_o, cm^3/mol	A_1, cm^3/mol	A_2, cm^3/mol	A_3, cm^3/mol	S, ±
(1-x) CH_3CN	-1.6825	0.0823	0.5359	-0.0507	0.00568
(1-x) $C_6H_5NO_2$	-2.7464	1.4824	0.6958	-1.7530	0.00047
(1-x) $C_2H_5NO_2$	-0.8340	0.4977	0.1047	-0.4717	0.00425

$$V_m^E/\mathrm{cm}^3\,\mathrm{mol}^{-1} = x_1(1-x_1)\sum_{J=0}^{3}(Aj\,(2x_1-1)^j \qquad (2)$$

The values of the parameter Aj, obtained by a least square method with all points, are summarized in the Table 2 along with each point of deviations. The parameters Aj and standard deviation are given in the Table 3. For all the mixtures, S(V_m^E) < 0.005 cm^3 mol^{-1} showing a good accuracy attainable with the pycnometer used in this research.

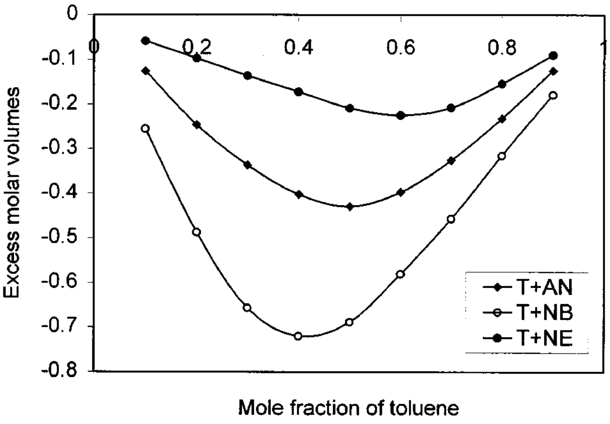


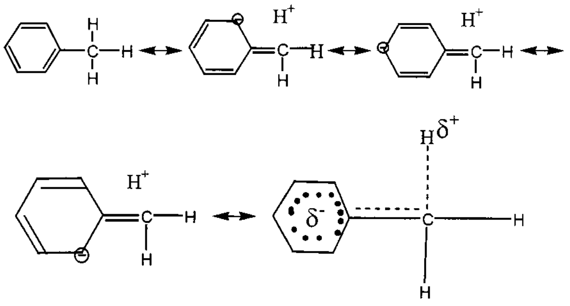
Figure 1. Effect of excess molar volumes (V_m^E) on composition of the mixtures; $x_1C_6H_5CH_3$ and (1-x$_1$)CH_3CN, $x_1C_6H_5CH_3$ and (1-x$_1$)$C_6H_5NO_2$, and $x_1C_6H_5CH_3$ + (1-x$_1$)$C_2H_5NO_2$ at a temperature of 303.15 K. The terms T, AN, NB, and NE inset represent the toluene, acetonitrile, nitrobenzene and nitroethane respectively.

Discussion

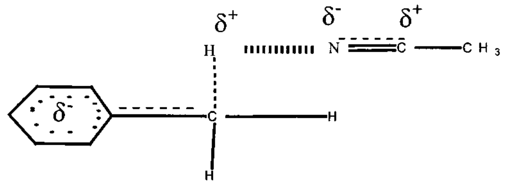
Figure 1 indicates the V_m^E of all three mixtures: $xC_6H_5CH_3$ + (1-x$_1$)CH_3CN, $xC_6H_5CH_3$ + (1-x$_1$)$C_6H_5NO_2$, and $xC_6H_5CH_3$ + (1-x$_1$)$C_2H_5NO_2$ as a function of mole fraction of $C_6H_5CH_3$ (x). The V_m^E for the $C_6H_5CH_3 + CH_3CN$ mixture in Figure 1 decrease with increase of $C_6H_5CH_3$ concentration and pass through a point at about x($C_6H_5CH_3$) = 0.5004 and then increases when the concentration of $C_6H_5CH_3$ component is increased in the mixture. For liquid mixtures; $C_6H_5CH_3$ + $C_6H_5NO_2$ and $C_6H_5CH_3 + C_2H_5NO_2$ systems, the V_m^E decrease with increasing the mole fraction of $C_6H_5CH_3$(x) and pass through a minimum value at about x($C_6H_5CH_3$) = 0.4987 and 0.5995, respectively. And then it increases with mole fraction of $C_6H_5CH_3$. The sequence of the magnitude of excess molar volume against the mole fraction of the $C_6H_5CH_3$ for the liquid mixtures may be due to presence of different ionic interactions or arrangements within the mixtures. The following discussions have been made for this.

According to Fort and Moore,[24] a negative excess volume is an indication of strong heteromolecular interaction in the liquid mixtures and is attributed to charge-transfer, dipole-dipole, dipole-induced-dipole interactions and hydrogen bonding between the unlike components, while a positive sign indicates a weak interaction and is attributed to depersive force (London forces), which are likely to be operative in every cases. The magnitudes of the contributions made by the different types of interactions will vary with the components and composition of the mixtures. In the present investigation, however, all the three mixtures gave negative magnitude of V_m^E, depict the presence of heteromolecular interaction in all the binary liquid mixtures, which support the Fort and Moore observation.

The V_m^E (Figure 1) for $C_6H_5CH_3$ + CH_3CN mixtures can be explained as (i) specific interaction between the unlike molecules, and (ii) geometric effect due to difference in molar volumes. In $C_6H_5CH_3$ + CH_3CN mixture, $C_6H_5CH_3$ is a non-polar aprotic solvent, and the solvents that lies in the aprotic class are not effective in stabilizing the development of charge separation. The molecules of these liquids have small dipole moments and do not have protons capable of forming hydrogen bonding.[25] So in $C_6H_5CH_3$ molecule, there is a possibility of interaction between π and σ systems. In valence bond theory, a special type of resonance called hyper-conjugation is used to describe the interaction.[25] In valence bond language, 'no bond' resonance structures are introduced to indicate this electronic interaction as shown below.



Due to this resonance, the negative charge on the methylene group of $C_6H_5CH_3$ molecule is stabilized, so that the hydrogen atom has a positive charge and in $C_6H_5CH_3$ + CH_3CN mixture, there may be an interaction between hydrogen atom of the $C_6H_5CH_3$ molecule and nitrogen atom of the CH_3CN. The interaction can be shown as follow;



$C_6H_5CH_3$ + CH_3CN

The $C_6H_5CH_3$ molecule has an alternate π bond system which overlaps to form a cloud of electrons located centrally above and below the ring, making it highly susceptible to interaction with electrophilic or electron deficient molecules. In $C_6H_5CH_3$ + CH_3CN mixture, there would be dipole-induced-dipole interaction between -CN group of acetonitrile and aromatic ring of toluene. The interaction is greater than the dispersive and dipole-dipole breaking interaction. A weak charge transfer complex may be formed due to the electron donor ability of the methyl group in $C_6H_5CH_3$ and weak electron acceptor ability of the CH_3CN, which is a donor-aceptor type of interaction. This results in negative V_m^E. Interstitial accommodation of small acetonitrile molecules (molar volumes 41.05 at 30 °C) between the toluene molecules (molar volumes 92.14 at 30 °C) may lead to a further decrease of the V_m^E values. Dewan *et al.*[26] reported the excess molar volumes of ethylbenzene + acetonitrile mixture at a temperature of 303.15 K. They reported the negative values of V_m^E but small positive values at very low mole fractions ($x_1 \leq 0.002$) of ethylbenzene were also observed. The general shape of our experimental V_m^E of $C_6H_5CH_3$ + CH_3CN as a function of mole fraction are good agreement with the reported values[27] for bezonitrile + toluene.

The V_m^E of (i) $C_6H_5CH_3$ + $C_6H_5NO_2$ and (ii) $C_6H_5CH_3$ + $C_2H_5NO_2$ systems can be explained in the terms of (i) specific interaction between the polar nitro-compounds and the aromatic ring which behaves as an electron donor and (ii) steric effect, respectively. Introduction of a methyl-group in the benzene ring would increase the liable nature of the electrons of the aromatic ring of toluene.[28] Therefore $C_6H_5CH_3$ would interact strongly with polar $C_2H_5NO_2$ molecules and result in decrease in volume of the mixture. Among the $C_2H_5NO_2$ and $C_6H_5NO_2$ molecules, the polarity of nitrobenzene is expected to be more than the nitro-ethane due to the replacement of electron releasing ethyl-group with a benzene ring and would be greater specific interaction in $C_6H_5CH_3$ + $C_6H_5NO_2$ mixture resulting in a negative V_m^E value of greater magnitude. Relatively low electron cloud in $C_6H_5NO_2$ than that of $C_2H_5NO_2$ would allow more efficient packing in the $C_6H_5CH_3$ + $C_6H_5NO_2$ mixture, leading to a further decrease of V_m^E. Marsh *et al.*[29] has reported V_m^E values for benzene + nitroethane at 298.15 K, which are negative and sigmoid nature. The V^E values reported by Dewan *et al.*[26] at 303.15 K. It was positive for ethylbenzene + nitroethane mixture at $x_1 < 0.45$ and negative for toluene + nitro-ethane system.

Conclusion

The negative magnitude of the V_m^E suggests the presence of a intermolecular interaction in all the three binary liquid mixtures and subsequently presumed that the weak electron donor acceptor interaction for $C_6H_5CH_3$ + CH_3CN and the specific interaction between the polar nitro-group of the $C_6H_5NO_2$ and the $C_2H_5NO_2$ with the liable π electrons of the aromatic ring behaved as an electron donor. The study also shows that the ability of interaction of the nitro-group of $C_6H_5NO_2$ with $C_6H_5CH_3$ is greater than that of the CN group of CH_3CN with $C_6H_5CH_3$ and the NO_2 of $C_2H_5NO_2$ with $C_6H_5CH_3$.

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