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Excess Volumes of Binary Liquid Mixtures of m-xylene with Nitrotoluenes

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ABSTRACT

Density data were measured for the binary mixtures of m-xylene with o-nitrotoluene and m-nitrotoluene at 298.15 K, 303.15 K, 308.15 K, and 313.15 K. These data have been utilized to compute excess volumes (V^E) for the binary liquid mixtures. The excess volume data have been fitted to the Redlich-Kister polynomial equation to derive the binary coefficients and to estimate the standard deviation. The nature of intermolecular interactions has been analyzed using the excess volume data.

Key words: *M-xylene, O-nitrotoluene, M-nitrotoluene, Density, Excess volume.*

1. INTRODUCTION

The data on excess thermodynamic properties will provide ample and useful information on the intermolecular and structural interactions that are prevailing between the components of the mixtures with different shapes, sizes, and chemical nature [1-3]. A survey of literature has shown that there is no systematic study on the excess volume data of m-xylene with nitrotoluenes. Hence, we report here V^E data of m-xylene with nitrotoluenes to analyze the intermolecular interactions prevailing between component molecules.

2. EXPERIMENTAL

All the chemicals used in this investigation were of analytical grade and purchased from Sigma-Aldrich and were used without further purification. All the binary liquid mixtures were prepared in glass bottles with airtight stoppers. Adequate precautions were taken to minimize evaporation losses. Weights of solutions were measured using digital electronic balance (Acculab, ALC-210-4, India). The uncertainty in mole fraction of solution was found to be less than $\pm 2\times10^{-4}$.

The density measurements were performed with a Rudolph research analytical digital densimeter-2911 model, equipped with a built-in solid-state thermostat and a resident program. After mixing the sample, the bubble-free homogeneous sample was transferred into the U-tube of the densimeter through a syringe. The uncertainty in density measurements was estimated to be $\pm 5\times10^{-5}$ gcm^{-3}.

3. RESULTS AND DISCUSSION

The V^E data of all the binary mixtures were computed from measured densities using the following equation:

$$V^E=[x_1M_1+x_2M_2]/\rho-[x_1M_1/\rho_1+x_2M_2/\rho_2] \quad (1)$$

In the above equation, M_1, M_2, ρ_1, ρ_2, and ρ represent molecular weight and density data of Components 1 and 2 and mixture, respectively.

An examination of V^E data in Tables 1 and 2 shows that the values of V^E are negative for mixtures of m-xylene with nitrotoluenes over the entire composition range at 298.15 K, 303.15 K, 308.15 K, and 313.15 K.

In general, the excess volume data of liquid mixtures may be explained in terms of various factors [4-6]:

1. Chemical or specific interaction, which includes charge-transfer complexes, formation of hydrogen bonding, dipole-dipole interaction, and other complex forming between dissimilar molecules
2. Loss of dipolar association and differences in size and shape
3. Physical interaction consisting dispersion forces or weak dipole-dipole interactions.

The first effect leads to contraction in volume making negative V^E value in liquid mixtures, whereas the remaining effects lead to expansion in volume resulting in positive V^E values. The actual volumes of V^E depend on the resultant of these opposing contributions [7-9]. The experimental results in Figures 1 and 2 suggest

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Table 1: Mole fraction of m-xylene (x_1), densities (ρ), excess volumes (V^E), and predicted excess molar volumes from Redlich-Kister equation at T=298.15-313.15 K for the binary mixture of m-xylene (1) with o-nitrotoluene (2).

x_1	ρ (g. cm^{-3})	m-xylene (1)+*o*-nitrotoluene (2)	
		Excess Volume (V^E)	
		Experimental	Redlich-Kister
T=298.15 K			
0.09693	1.12893	−0.031	−0.029
0.19452	1.10120	−0.046	−0.049
0.29278	1.07335	−0.060	−0.062
0.39173	1.04540	−0.071	−0.069
0.49135	1.01733	−0.074	−0.071
0.59167	0.98912	−0.070	−0.069
0.69268	0.96081	−0.061	−0.062
0.79441	0.93241	−0.047	−0.049
0.89684	0.90391	−0.030	−0.029
T=303.15 K			
0.09693	1.12891	−0.0281	−0.0274
0.19452	1.10118	−0.0447	−0.0463
0.29278	1.07332	−0.0575	−0.0585
0.39173	1.04536	−0.0657	−0.0652
0.49135	1.01730	−0.0700	−0.0673
0.59167	0.98909	−0.0658	−0.0650
0.69268	0.96079	−0.0574	−0.0583
0.79441	0.93239	−0.0448	−0.0462
0.89684	0.90389	−0.0280	−0.0275
T=308 K			
0.09693	1.12008	−0.025	−0.025
0.19452	1.09218	−0.041	−0.043
0.29278	1.06419	−0.054	−0.054
0.39173	1.03612	−0.062	−0.061
0.49135	1.00795	−0.065	−0.063
0.59167	0.97968	−0.061	−0.060
0.69268	0.95133	−0.053	−0.054
0.79441	0.92290	−0.042	−0.043
0.89684	0.89441	−0.026	−0.026
T=313.15 K			
0.09693	1.12007	−0.0247	−0.0242
0.19452	1.09216	−0.0396	−0.0409
0.29278	1.06417	−0.0509	−0.0517
0.39173	1.03609	−0.0584	−0.0577
0.49135	1.00793	−0.0620	−0.0595
0.59167	0.97966	−0.0583	−0.0575
0.69268	0.95131	−0.0508	−0.0516
0.79441	0.92289	−0.0397	−0.0409
0.89684	0.89440	−0.0248	−0.0243

Table 2: Mole fraction of m-xylene (x_1), densities (ρ), excess volumes (V^E), and predicted excess molar volumes from Redlich-Kister equation at T=298.15-313.15 K for the binary mixture of m-xylene (1) with m-nitrotoluene (2).

x_1	ρ (g. cm^{-3})	m-xylene (1)+*o*-nitrotoluene (2)	
		Excess volume (VE)	
		Experimental	Redlich-Kister
T=298.15 K			
0.09651	1.13457	−0.0321	−0.0312
0.19377	1.10651	−0.0513	−0.0528
0.29179	1.07832	−0.0657	−0.0667
0.39057	1.05001	−0.0751	−0.0744
0.49014	1.02157	−0.0800	−0.0768
0.59050	0.99296	−0.0752	−0.0742
0.69165	0.96424	−0.0656	−0.0665
0.79362	0.93541	−0.0512	−0.0527
0.89639	0.90646	−0.0320	−0.0313
T=303.15 K			
0.09651	1.12906	−0.031	−0.030
0.19377	1.10143	−0.048	−0.050
0.29179	1.07365	−0.061	−0.063
0.39057	1.04574	−0.072	−0.071
0.49014	1.01769	−0.076	−0.073
0.59050	0.98946	−0.071	−0.071
0.69165	0.96111	−0.062	−0.063
0.79362	0.93263	−0.049	−0.050
0.89639	0.90403	−0.030	−0.030
T=308 K			
0.09651	1.12293	−0.028	−0.028
0.19377	1.09514	−0.046	−0.048
0.29179	1.06723	−0.061	−0.061
0.39057	1.03919	−0.068	−0.068
0.49014	1.01103	−0.073	−0.070
0.59050	0.98272	−0.069	−0.068
0.69165	0.95430	−0.060	−0.061
0.79362	0.92577	−0.047	−0.048
0.89639	0.89713	−0.029	−0.029
T=313.15 K			
0.09651	1.12021	−0.027	−0.027
0.19377	1.09242	−0.043	−0.046
0.29179	1.06451	−0.058	−0.058
0.39057	1.03647	−0.066	−0.064
0.49014	1.00833	−0.069	−0.066
0.59050	0.98004	−0.065	−0.064
0.69165	0.95164	−0.057	−0.057
0.79362	0.92314	−0.044	−0.046
0.89639	0.89454	−0.028	−0.027

that the former effect is dominant in this investigation for binary mixtures of m-xylene with nitrotoluenes.

The algebraic excess volumes data for the mixtures of m-xylene with nitrotoluene fall in the following order:

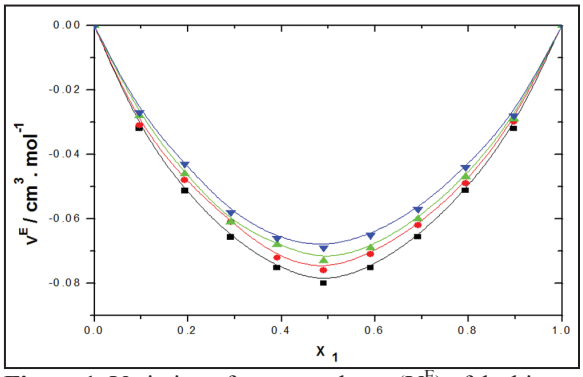

Figure 1: Variation of excess volume (V^E) of the binary liquid mixture of m-xylene (1) with o-nitrotoluene (2) at 298.15 K (▪), 303.15 K (●), 308.15 K (Δ), and 313.15 K (∇).

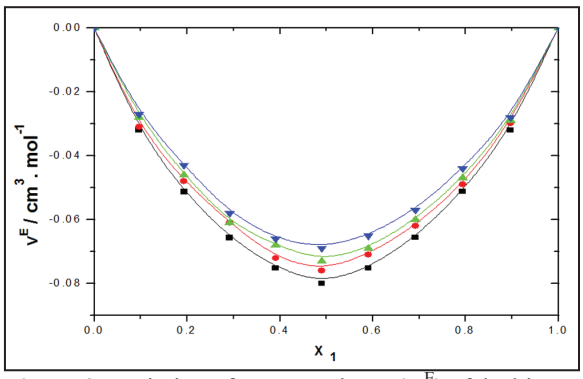

Figure 2: Variation of excess volume (V^E) of the binary liquid mixture of m-xylene (1) with o-nitrotoluene (2) at 298.15 K (▪), 303.15 K (●), 308.15 K (Δ), and 313.15 K (∇).

Table 3: Coefficients of a_i and the corresponding standard deviations $\sigma(V^E)$ of all the binary systems at 298.15-313.15 K of Redlich-Kister equation.

Temperature	cm^3 mol^{-1}			
	a_0	a_1	a_2	$\sigma(V^E)$
m-xylene (1)+*o*-nitrotoluene (2)				
298.15 K	−0.31	0.01	−0.06	0.002
303.15 K	−0.29	0.01	−0.06	0.002
308.15 K	−0.28	0.01	−0.06	0.002
313.15 K	−0.27	0.01	−0.06	0.002
m-xylene (1)+*m*-nitrotoluene (2)				
298.15 K	−0.28	0.01	−0.06	0.002
303.15 K	−0.27	0.01	−0.06	0.002
308.15 K	−0.25	0.01	−0.05	0.001
313.15 K	−0.24	0.01	−0.05	0.001

o-nitrotoluene<m-nitrotoluene

The V^E composition profiles for the mixtures of m-xylene with o-nitrotoluene and m-nitrotoluene are fitted to Redlich-Kister [10] polynomial equation of the following form:

$$V^E=x_1x_2[a_0+a_1(x_1-x_2)+a_2(x_1-x_2)^2] \quad (2)$$

Where, x_1 and x_2 are represented, respectively, the mole fractions of m-xylene and o-nitrotoluene, m-nitrotoluene. The values of the parameters a_0, a_1, and a_2 are the coefficients of the polynomial equation and were obtained by method of least - squares and were given in Table 3 along with standard deviation $\sigma(V^E)$ values at 298.15 K, 303.15 K, 308.15 K, and 313.15 K, respectively. The standard deviations were calculated using the equation.

$$\sigma(V^E)=[\Sigma(V^E_{obs}-V^E_{cal})^2/(n-m)]^{1/2} \quad (3)$$

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

4. CONCLUSION

Excess volume V^E data have been calculated from measured density data of binary liquid mixtures of m-xylene with o-and m-nitrotoluenes. The results were found to be negative in the entire mole fraction range. The results were discussed in terms of molecular interactions between component molecules.

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Bibliographical Sketch

Professor P. Venkateswarlu has more than 30 years of teaching and research experience in the Department of Chemistry, S. V. University, Tirupati. He guided 15 Ph. D. students. He has more than 115 publications in internationally reputed journals which are indexed in Science Citation Index. He is the reviewer for many Elsevier journals.