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# Studies of Interactions between Binary Mixtures of N-(1-Methylethyl)-2-Propanamine with Acetic Acid Methyl Ester At 323.15 K

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## Abstract

Densities, ( ... ) of N-(1-Methylethyl)-2-propanamine with acetic acid methyl ester at 323.15K and atmospheric pressure along with pure liquids have been measured over entire composition range. By using the experimental results, excess molar volumes ( $V_m^E$ ), partial molar volume ( $\bar{V}$ ), excess partial molar volume ( $\bar{V}^E$ ) and apparent molar volume were calculated for a better understanding of the intermolecular interactions between these binary components. These excess properties were fitted with composition using the Redlich–Kister polynomial equation.

**Keywords:** excess molar volume, N-(1-Methylethyl)-2-propanamine, acetic acid methyl ester, excess functions.

## 1. Introduction

Approximately two dozen of aliphatic amines produced commercially in the United States. The aliphatic amines are important industrial chemicals. Their most important use is as intermediates for the manufacture of insecticides and herbicides, rubber, accelerators, ion exchange resins, surfactants, dyes and medicines etc.[1] banana and other fruit is a clear colorless liquid with an ammonia-like odor. Flash point of N-(1-Methylethyl)-2-propanamine is 30°F. It is less dense than water. Its vapors are heavier than air. Toxic oxides of nitrogen produced during combustion. It is also used to make other chemicals. Excess thermodynamic functions and deviations of non-thermodynamic properties of binary liquid mixtures are fundamental for understanding of the intermolecular interactions between molecules in these types of mixtures. The thermodynamic functions have also been used as a qualitative and quantitative guide to predict the extent of bonding in this kind of mixtures [2, 3]. Mixtures which contain associating components such as acetates and/or amines are highly non-ideal systems. Due to the formation of hydrogen bonds between these two species and disruptive of hydrogen bonding between like species, large negative heats as well as volumetric effects are observed upon mixing. Because the interaction between molecules of pure aliphatic amines and that of the aliphatic acetate are smaller than that of interaction between aliphatic amine and aliphatic acetates. The Prigogine–Flory–Patterson (PFP) Theory of Binary Mixtures has been successfully applied in order to calculate molecular interaction parameters from binary excess molar volumes data. Methyl acetate is found in apple, grapes, banana and other fruits. Methyl acetate is synthesized from acetic acid and methanol in the presence of strong acids such as sulfuric acid in an esterification reaction. In the presence of strong bases such as sodium hydroxide or strong acids such as hydrochloric acid or sulfuric acid it is hydrolyzed back into methanol and acetic acid, especially at elevated temperature. Methyl acetate, also known as acetic acid methyl ester or methyl ethanoate, is a clear, flammable liquid with a characteristic, not unpleasant smell like certain glues or nail polish removers. Methyl acetate is a non-polar (lipophilic) to weak polar (hydrophilic) aprotic solvent [4-6].

## 2. Experimental

### 2.1 Materials

Chemicals used in the present study are N-(1-Methylethyl)-2-propanamine methyl acetate were purchased from Merck India, HPLC and S.D. fine chemicals respectively. In cases of all chemicals with purity greater

than 99.5% by mass were used for the experimental investigations. All the chemicals used in the present study were purified by standard procedures [7, 8]. Prior to making the experimental measurements, all liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were distilled and partially degassed under vacuum.

## 2.2 Apparatus and Procedure

The binary mixture was prepared by weighing appropriate amounts of N-(1-Methylethyl)-2-propanamine and acetates on CAUW 220 D electronic balance, with a precision of  $\pm 0.05$  mg, by syringing each constituent into sealed fine mouthed stoppered bottles to minimize evaporation losses. The pure components were individually degassed shortly before sample preparation. The accuracy of mole fraction was  $\pm 1 \times 10^{-4}$ . Density of the mixture and pure components was measured by using a digital vibrating tube density and speed of sound analyzer (Anton Paar DMA 5000), having two integrated Pt 100 thermometers with a proportional temperature controller that kept the sample at the required temperature. The apparatus was calibrated at the working temperatures with dry air, double distilled toluene, cyclohexane and water. The temperature in the cell was regulated to  $\pm 1 \times 10^{-2}$  K with a built-in solid state thermostat by the Peltier method. Uncertainty in density measurement is  $\pm 2 \times 10^{-3}$  kg m<sup>-3</sup> and for the speed of sound is  $\pm 0.1$  m×s<sup>-1</sup>. An acoustic signal indicated when the measurement was completed. The densities, ... for the pure liquid components 323.15 K with values reported in the literatures [9-13].

S. No.	Sample	CAS No.	Make	Initial Mass Fraction Purity	Purification Method	Final Mass Fraction Purity	Analysis Method
1.	N-(1-Methylethyl)-2-propanamine	121-44-8	Merck, India	0.995	Distillation	0.995	None
2.	Methyl Acetate	79-20-9	Merck, India	0.995	Distillation	0.995	None

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**Table 1: Sample Information Table**

**Table2.** Experimental and literature values of densities,  $\rho^*$ , isobaric expansivity,  $\Gamma_P^*$ , isobaric molar heat capacity,  $C_{P,m}^*$  of pure liquid components at 323.15 K and atmospheric pressure:

Components	Density	Isobaric expansivity	Isobaric molar heat capacity
	$\rho^* \times 10^{-3}$ (kg·m <sup>-3</sup> ) Experimental Literature	$\Gamma_P^*$ (kK <sup>-1</sup> )	$C_{P,m}^*$ (J K <sup>-1</sup> mol <sup>-1</sup> )
298.15K			
N-(1-Methylethyl)-2-propanamine	0.687237	1.411	280
Methyl Acetate	0.890875	1.562	149.6

**Table3.** Densities,  $\rho$ , excess molar volumes,  $V_m^E$ , Partial molar volume,  $V_1$ , excess partial molar isentropic volume and Apparent volume for the binary mixtures at different temperatures:

$x_1$	$\rho \times 10^{-3}$ (kg m <sup>-3</sup> )	$V_m^E \times 10$ (m <sup>3</sup> mol <sup>-1</sup> )	$V_1 \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	$V_1^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	$V_{\phi 1} \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )
TEA + MA					
T =323.15 K					
0.0000	0.890875	0.0000	125.788	-21.453	0.000
0.0499	0.880510	-0.68317	127.943	-19.299	133.841
0.1041	0.869010	-1.33216	130.263	-16.978	134.250
0.2044	0.848778	-2.44924	134.308	-12.934	135.278
0.3020	0.829008	-3.27361	137.726	-9.516	136.496
0.4039	0.807463	-3.73456	140.644	-6.598	137.885
0.5009	0.788156	-4.03583	142.802	-4.440	139.253
0.6005	0.767614	-3.92469	144.460	-2.782	140.670
0.7008	0.747844	-3.60665	145.666	-1.575	142.120
0.7938	0.729311	-2.94432	146.457	-0.785	143.523
1.000	0.687237	0.0000	147.242	0.000	147.242

**Table4** Coefficients of  $A_i$ , of Equation and standard deviations for the binary mixtures at 323.15K

Excess property	Temperature	$A_0$	$A_1$	$A_2$	$A_3$	†
N-(1-Methylethyl)-2-propanamine + Methyl Acetate						
$V_m^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	323.15K	-16.0046	-1.8263	-1.5496	-2.0728	0.0277

**Table 5.** PFP interaction parameter,  $t_{12}$  and calculated values of the three contributions from the PFP theory with experimental excess molar volumes at equimolar composition:

Binary mixtures	$t_{12} \times 10^6$ (J m <sup>-3</sup> )	$V_m^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )		Calculated contributions		
		Exptl.	PFP	$V_m^E$ (int.)	$V_m^E$ (fv)	$V_m^E$ (P*)
Methyl Acetate	-3024.18	-0.618245	-0.61832	-0.618315	0.000556947	0.002493

**Table 6.** Molar volume and molar volume at infinite

COMPONENTS	$V_0$	$V^\infty$
<b>323.15K</b>		
N-(1-Methylethyl)-2-propanamine	147.242	125.788
Methyl acetate	83.1542	61.7009

## Results and Discussion

The experimental values of density were used to calculate the excess molar volume  $V_m^E$  of the mixtures using equation:

$$V_m^E = \sum_{i=1}^2 x_i M_i (\dots^{-1} - \dots_i^{-1}) \quad (1)$$

Where  $\dots$  is the density of the mixture and  $x_i$ ,  $M_i$ , and  $\dots_i$  are the mole fraction, molar mass and density of pure component  $i$ , respectively. We have also calculated the excess partial molar volumes,  $\bar{V}_1^E = (\bar{V}_1 - \bar{V}_1^o)$  and from  $V_m^E$ . The excess molar volumes,  $\bar{V}_1^E$  and  $\bar{V}_2^E$ , were evaluated using following equations:

$$\bar{V}_1 = \bar{V}_m^E + \bar{V}_1^o + (1 - x_1)(\partial \bar{V}_m^E / \partial x_1)_{p,T} \quad (2)$$

$$\bar{V}_2 = \bar{V}_m^E + \bar{V}_2^o - x_1(\partial \bar{V}_m^E / \partial x_1)_{p,T} \quad (3)$$

Differentiation of equation (2) with respect to  $x_1$  and combination of the results of equation (2) and (3) leads to the following equation for the partial molar volumes of TEA ( $\bar{V}_1$ ) and esters ( $\bar{V}_2$ )

$$\bar{V}_1 = V^o_1 + (1 - x_1)^2 \sum_{j=0}^{j=n} A_j (1 - 2x_1)^j + 2x_1 (1 - x_1)^2 \sum_{j=0}^{j=n} A_j(j) (1 - 2x_1)^{j-1} \quad (4)$$

$$\bar{V}_2 = V^o_2 + x_1^2 \sum_{j=0}^{j=n} A_j (1 - 2x_1)^j + 2x_1^2 (1 - x_1) \sum_{j=0}^{j=n} A_j(j) (1 - 2x_1)^{j-1} \quad (5)$$

The calculated results for partial molar volume and excess partial molar volumes are plotted in Figures 5 to 7. Much of our present interest is focused on the partial molar volume at infinite dilution. The partial properties

at infinite dilution are of interest since, at the limit of infinite dilution, the solute- solute interactions disappear. The values of partial molar volume at infinite dilution provide information about solute solvent interaction, independent of the composition effect. Therefore, we get from equation (4), by setting  $x_2 = 1$  and  $x_1 = 0$

$$\bar{V}_1^\infty = V_1^o + \sum_{j=0}^{j=n} A_j \quad (6)$$

$$\bar{V}_2^\infty = V_2^o + \sum_{j=0}^{j=n} A_j (-1)^j \quad (7)$$

Equation (6) and (7) represent the partial molar volume of TEA  $\bar{V}_1^\infty$  and esters  $\bar{V}_2^\infty$  at infinite dilution, respectively. These properties are listed in Table 3. Also, we have considered the approach, which may be more convenient and accurate, by calculating the partial molar at infinite dilution through apparent volumes of esters in amine  $V_{w1}$  and the apparent molar volume of amine in esters  $V_{w2}$  can be expressed as

$$V_{w1} = (V_m - x_2 V_2^o) / x_1 \quad (9)$$

$$V_{w2} = (V_m - x_1 V_1^o) / x_2 \quad (10)$$

Combination of equation (2), (10) and (11) leads to

$$V_{w1} = V_1^o + (V_m^E / x_1) \quad (11)$$

$$V_{w2} = V_2^o + (V_m^E / x_2) \quad (12)$$

Simple graphic or analytical extrapolation of  $V_{w1}$  to  $x_1 = 0$  ( $x_2 = 1$ ) leads to desired value of  $\bar{V}_1^\infty$  and a simple extrapolation of  $V_{w2}$  to  $x_2 = 0$  ( $x_1 = 1$ ) leads to the desired value of  $\bar{V}_2^\infty$ . The values of  $\dots, V_i^\infty, V_i^E$  and  $V_{wi}^E$  for the binary mixtures at 293.15 to 313.15 K are listed in Tables 3. The partial molar volume at infinite dilution is reported in Table 4. The values of  $V_m^E, V_i^\infty, V_i^E$  and  $V_{wi}^E$  were fitted to a Redlich-Kister equation [14]:

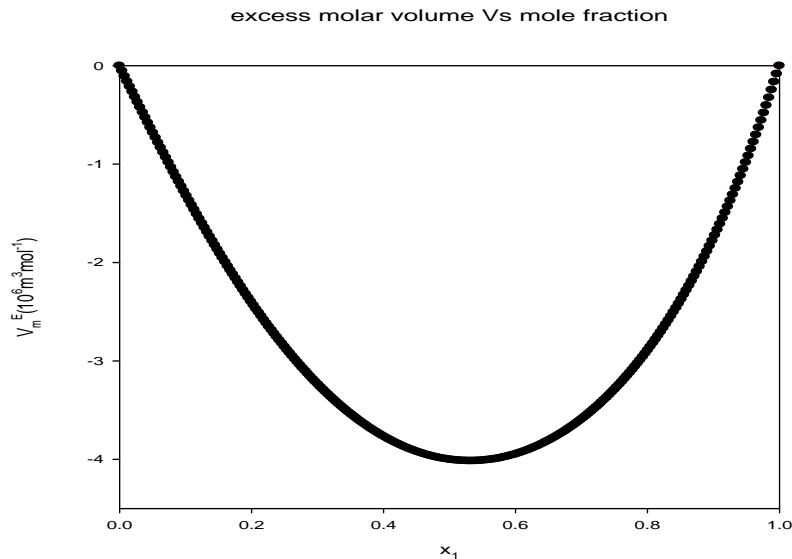
$$Y(x) = x_1 x_2 \sum_{i=1}^p A_i (x_1 - x_2)^i \quad (13)$$

Where  $p$  is the number of estimated parameters  $A_i$ . The standard deviation was calculated using the equation:

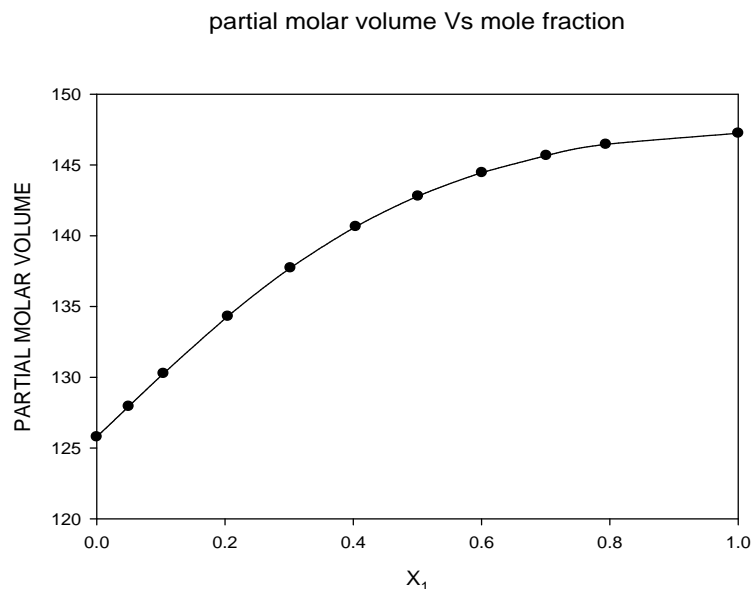
$$\dagger = \left[ \sum_{i=1}^n \{Y(x)_{\text{exptl}} - Y(x)_{\text{cal}}\}^2 / (n - p) \right]^{1/2} \quad (14)$$

Where  $Y(x)_{\text{exptl}}$  and  $Y(x)_{\text{cal}}$  are the values of the experimental and calculated properties ( $V_m^E, V_i^\infty, V_i^E$  and  $V_{wi}^E$ ) respectively, and  $n$  is the number of experimental data points. The calculated values of the coefficients,  $A_i$  along with the standard deviations ( $\dagger$ ) are given in Table 5. The values of  $V_m^E$  is plotted as a function of  $x_1$  in Figures 1 which shows that mixtures of N-(1-Methylethyl)-2-propanamine with methyl acetate exhibit negative  $V_m^E$  values for the whole range of composition and at all of the studied temperatures. The negative

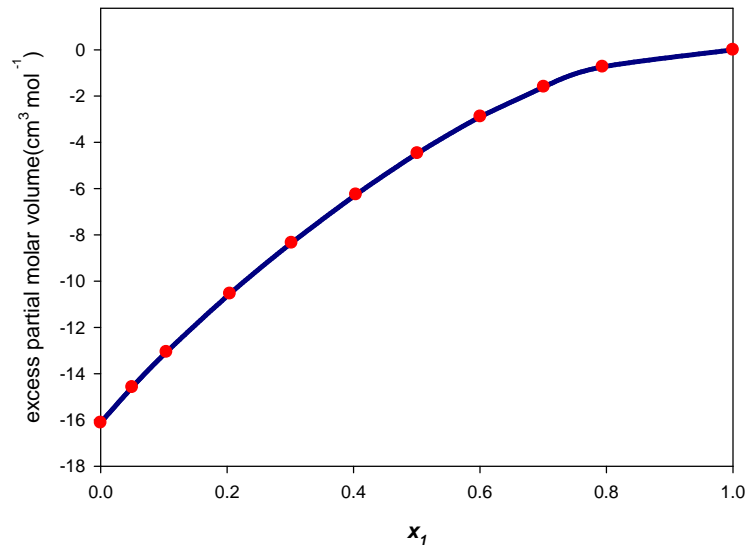
trend in the values of  $V_m^E$  is observed the binary mixtures. The negative  $V_m^E$  values show the presence of strong intermolecular forces of attraction. The present results can be interpreted qualitatively by contraction in volumes and hydrogen bonding between amine and ester in binary liquid mixture. A large deviation is observed in this binary mixture. For the mixtures of N-(1-Methylethyl)-2-propanamine with methyl acetate, the values of  $V_i^\infty$ ,  $V_i^{-E}$  and  $V_{wi}$  are plotted in Figures 5, 6 and 7 respectively.



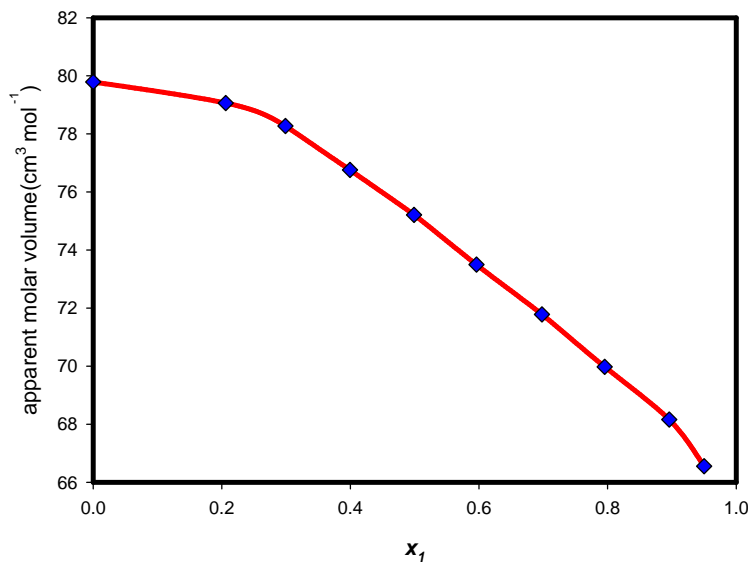
**FIGURE: 1** Excess molar volumes against mole fractions of N-(1-Methylethyl)-2-propanamine and methyl acetate at 323.15K



**FIGURE: 2** Partial molar volume against mole fractions of N-(1-Methylethyl)-2-propanamine and methyl acetate at 323.15K



**FIGURE: 3** Excess Partial molar volume against mole fractions of N-(1-Methylethyl)-2-propanamine and methyl acetate at 323.15K



**FIGURE: 4** Apparant molar volume against mole fractions of N-(1-Methylethyl)-2-propanamine and methyl acetate at 323.15K

**Theoretical Model:** The Prigogine–Flory–Patterson (PFP) theory [18-22] has been commonly employed to estimate and analyze excess thermodynamic functions theoretically. This theory has been described in details by Patterson and co-workers [23-24]. The details of the notations and terms used in equations may be obtained from literature [19-22, 25-26]. The interaction parameter  $t_{12}$  was obtained by employing the Marquardt algorithm [27] in an optimization procedure, using all experimental  $V_m^E$  data at 323.15 K over the complete concentration range. The resulting  $t_{12}$  was used to calculate  $V_m^E$ . The various parameters involved in

equation for the pure components are obtained through Flory theory and are given the interaction term, which is proportional to  $\tau_{12}$ , is negative for all the systems.

## Conclusion

The negative trend in the values of  $V_m^E$  is observed in the binary mixtures. The negative  $V_m^E$  values show the presence of strong intermolecular forces of attraction. The negative value of  $V_1^E$  also indicates that after the mixing process, the molar volume of both components in the mixture is much lower than that of their molar volumes in their pure liquid state which indicates strong molecular interaction. PFP theory is in good agreement with the experimental results.

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