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# DENSITY, EXCESS MOLAR VOLUME AND APPARENT MOLAR VOLUME OF BINARY LIQUID MIXTURES

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**ABSTRACT**

Density (ρ), Excess Molar volume and Apparent Molar volume are reported for binary mixtures of Ethanol, Propan-2-ol and 2-Methyl Propan-2-ol with Propan-2-amine over entire range of mole fractions at 298.15 and 308.15 K and atmospheric pressure. Excess molar volume ($V^E$) and apparent molar volume ($V_\phi$) have been calculated. These values were fitted with Redlich-Kister type polynomial equation.

**Keywords**: Density, Excess Molar and Apparent Molar volume, Redlich-Kister parameters.



## INTRODUCTION

Thermodynamics is a fundamental subject of great importance in physical chemistry and Chemical Engineering. Thermodynamic property is one which serves to describe a system. Fundamental variables of thermodynamic properties includes volume, pressure, temperature, energy (Enthalpy, Entropy, free energy etc.) and of course, the amount of substance. The nature and type of interactions in binary organic liquid mixtures have been studied in terms of mixing parameters such as excess molar volume[1,2]. This parameter can be calculated from direct measurement of density (ρ). Such data are useful in process engineering, design applications and other related areas. The properties of a system may be divided into two types, namely extensive and intensive. An extensive property of a system is any property whose magnitude depends on the amount of substance present. The properties of liquid mixtures basically depend on its local structure, expressed in terms of packing density, free volume or radial distribution function[3-6]. However, this local structure depends on forces between molecules and their forms and volume of molecules. It changes with compositions. This change in composition changes thermodynamic properties of mixtures. The investigations regarding the molecular association in organic binary mixtures having alkanol group as one of the components is of particular interest, since alkanol group is highly polar and can associate with groups having some degree of polar attractions[7-8]. Amine is protic, strongly associated due to highly polar - $NH_2$ group, is the molecule having large dipole moment.

In view of the importance mentioned, an attempt has been made to elucidate the molecular interactions in the mixtures of Ethanol, Propan-2-ol and 2 Methyl propan-2-ol with Propan-2-amine at 298.15 and 308.15K. The excess functions are used to explain intermolecular interactions in these binary mixtures.

## EXPERIMENTAL

### Preparation of liquid mixtures

All the chemicals used in the present research work are HPLC grade of minimum assay of 99.5% obtained from Qualigen fine chem., Sisco Research Lab. Pvt. Ltd., which are used as such without further purification. The purities of the above chemicals were checked by density determination at 298.15 and 308.15K; the uncertainty is less than ± $1x10^{-4}$ $gcm^{-3}$. Binary liquid mixtures of various compositions covering the entire mole fraction were made using a single pan balance having sensitivity 0.01 mg (Model: Shimadzu AUW 220 D). The mixtures were prepared by mixing known mass of pure liquids in

air tight, narrow mouth ground stopper bottles taking due precautions to minimize evaporation. The more volatile component was filled directly into bottle and the bottle was closed and weighed. The other component was injected into the bottle through the stopper by means of syringe. This method allowed negligible vapour loss and contamination.

**Density measurement**

For the present research work, densities of pure components and their compositions were measured on a vibrating tube densitymeter (Anton Paar Model DMA - 5000) which was reproducible to 1 x $10^{-5}$ $gcm^{-3}$. This unit offered high temperature accuracy (±0.001K) in a wide temperature range. Calibration of the densitymeter was done with triple distilled water showing density 0.998258 $gcm^{-3}$ at $20^0$C, which was close to literature value[2]. The densitymeter was calibrated at every measurement of each mole fraction of composition.

**Theoretical background and equations**

**Partial and Apparent molar Volumes**

When two components are mixed with each other, the total weight of the mixture is equal to the sum of masses of the individual compound. But it is not true in case of volume. When two miscible liquids are mixed with each other, volume of mixtures may not equal that of the sum of the volumes of the individual components. For example – when one mole of water is added to a large quantity of ethanol, the change in the volume of the solution prima-facie should be equal to the molar volume of water *i.e.* 18 $cm^3$. However, actually this change is 14 $cm^3$, Thus the volume occupied by 1 mole of water is 14 $cm^3$.This volume is called partial molar volume in ethanol. Since, partial molar volume is not a constant, it depends on concentration of mixtures, It is expressed by following equation –

$$V = x_1 V_1 + x_2 V_2 \quad (1)$$

Where, $V_1$ and $V_2$ are the partial molar volumes of components (1) and (2) of the solution. And, $x_1$ and $x_2$ are the moles of components (1) and (2) of the solution.

**Excess Molar Volume ($v^E$)**

Ideal binary liquid mixture formation is accompanied with no volume change. But due to molecular interactions between components of binary liquid mixture, there occurs a real liquid mixture either with increase or decrease of volume. This increase or decrease in the volume on mixing the liquids can be taken as a criterion and measure of molecular interaction. This volume change ($V^E$) for the binary mixture is calculated by employing following equation -

$$V^E = ( M_1X_1+M_2X_2 ) / \rho_{1,2} - ( M_1X_1 ) / \rho_1 - ( M_2X_2 ) / \rho_2 \quad (2)$$

Where, $V^E$ – is the excess molar volume of liquid mixture, $x_1$ and $x_2$ are mole fractions, $M_1$ and $M_2$ are molecular weights, $V_1$ and $V_2$ are the molecular volumes of components 1 and 2 of liquid mixtures respectively and $\rho_1$, $\rho_2$ and $\rho_{1,2}$ are the density of components 1, 2 and liquid mixture respectively.

The excess properties $y^E$ are fitted by the method of non linear least squares to a Redlich kister type polynomial.[5]

$$y^E = X_1 X_2 \sum Ai (X_1 - X_2 )^i ) \quad (3)$$

In each case the optimum number of coefficients Ai was determined from an examination of the variation of standard deviation as calculated by :

$$\sigma y^E = [ \sum (y^E_{obs} - y^E_{cal}) / ( n-m ) ]^{1/2} \quad (4)$$

Where n represents the number of experimental points and m represents the number of coefficients in fitting the data.

## RESULTS AND DISCUSSION

Figures 1.1 and 1.2 represent variation of $V^E$ with $x_1$ (Propan-2-amine) at 298.15 and 308.15K yielding a U-shaped nature of the graph is attributed to the equilibria of State effects[1] and steric factors arising from the change of orientation of Propan-2-amine molecules with change in its mole fraction. Similar result is reported earlier by many workers[10-11] for other binary systems. For the solutions of Propan-2-amine with Ethanol, Propan-2-ol and 2-Methyl propan-2-ol the graphs are inverted v-shaped. Treszcznowicz et al.[12] and later Aminabhavi et al.[13] observed that $V^E$ many be discussed in terms of several effects which may be arbitrarily divided into physical, chemical and geometrical contributions. The Physical interaction

involved mainly dispersion forces giving a positive contribution. The chemical or specific interactions result in a volume contraction and these include charge-transfer type forces, forming or breaking of H-bonds and other complex forming interactions such as donor-acceptor, dipole-dipole, dipole-induced dipole. Structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volume and free volume between the components lead to negative contribution to $V^E$. The systems studied exhibits very strong hydrogen bonding between -OH and $–NH_2$ groups, as a consequence of this strong inter- molecular association, all three systems have very large negative $V^E$. As the molecular weight increases (Ethanol to 2-Methyl propan-2-ol), the magnitude of $V^E$ increases, this is due to increase in size and chain length of molecules.

Knowing that $V^E$ is the result of sum of several effects– chemical, structural and physical, these values would represent the breaking of the associated species formed through hydrogen bonds and the subsequent formation of bonds of the same type between -OH and $–NH_2$ groups, processes that will yield a greater packing of molecules and therefore a negative excess volume of the mixtures. The close observations of Figures 1 and 2 indicate that molecular interactions between Propan-2-amine and Propan-2-ol, 2Methyl propan-2-ol molecules are most favored in the region at $x_1$= 0.7 and $x_1$= 0.5 with minima respectively. This may be attributed to variable size and shape of 2-Methylpropan-2-ol and Propan-2-ol molecules causing strong interactions with Propan-2-amine molecules.

Table-1: Densities, Excess molar volumes and Apparent molar volumes of Ethanol (1) + Propan-2-amine (2) at 298.15K and 308.15K.

| $x_1$ | $\rho$ (g/cm$^3$) | | $V^E$ ( cm$^3$mol$^{-1}$) | | $V_\phi$ ( cm$^3$mol$^{-1}$) | |
|---|---|---|---|---|---|---|
| | 298.15K | 308.15K | 298.15K | 308.15K | 298.15K | 308.15K |
| 0.0000 | 0.682342 | 0.670884 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.12480 | 0.702485 | 0.691256 | -1.27479 | -1.32162 | 48.16109 | 48.43656 |
| 0.242906 | 0.719659 | 0.708721 | -2.0308 | -2.10935 | 50.01527 | 50.34268 |
| 0.354844 | 0.733989 | 0.723511 | -2.37466 | -2.48513 | 51.68359 | 52.02303 |
| 0.461084 | 0.745373 | 0.735183 | -2.36546 | -2.47548 | 53.24550 | 53.65765 |
| 0.562049 | 0.755122 | 0.745192 | -2.17614 | -2.27611 | 54.50391 | 54.97682 |
| 0.658125 | 0.764236 | 0.754381 | -1.91889 | -1.9893 | 55.46002 | 56.00381 |
| 0.749657 | 0.772032 | 0.762723 | -1.54654 | -1.62487 | 56.31271 | 56.85900 |
| 0.83696 | 0.778708 | 0.769675 | -1.08979 | -1.1493 | 57.07363 | 57.65330 |
| 0.92032 | 0.784138 | 0.775363 | -0.54943 | -0.58637 | 57.77872 | 58.38934 |
| 1.0000 | 0.789198 | 0.780497 | 0.0000 | 0.0000 | 58.37571 | 59.02649 |

Table-2 : Densities, Excess molar volumes and Apparent molar volumes of propane- 2-ol (1) + Propan-2-amine (2) at 298.15K and 308.15K.

| $x_1$ | $\rho$ (g/cm$^3$) | | $V^E$ ( cm$^3$mol$^{-1}$) | | $V_\phi$ ( cm$^3$mol$^{-1}$) | |
|---|---|---|---|---|---|---|
| | 298.15K | 308.15K | 298.15K | 308.15K | 298.15K | 308.15K |
| 0.0000 | 0.682342 | 0.670884 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.098518 | 0.694576 | 0.683432 | -0.43285 | -0.46134 | 72.56396 | 73.13448 |
| 0.19736 | 0.706694 | 0.695814 | -0.80014 | -0.84519 | 72.90332 | 73.53478 |
| 0.29653 | 0.719095 | 0.708437 | -1.15181 | -1.20481 | 73.07324 | 73.75424 |
| 0.396027 | 0.731915 | 0.721423 | -1.50208 | -1.55376 | 73.16467 | 73.89391 |
| 0.495855 | 0.745163 | 0.735020 | -1.84942 | -1.91784 | 73.22778 | 73.94953 |
| 0.596014 | 0.759407 | 0.750079 | -2.25043 | -2.38287 | 73.18174 | 73.81928 |
| 0.696505 | 0.775748 | 0.766843 | -2.6063 | -2.6898 | 72.92843 | 73.56896 |
| 0.797334 | 0.772758 | 0.76372 | -1.40377 | -1.4718 | 75.19697 | 75.97138 |
| 0.898498 | 0.7806 | 0.771511 | -1.07584 | -1.09304 | 75.76017 | 76.60076 |
| 1.0000 | 0.78095 | 0.772322 | 0.0000 | 0.0000 | 76.95755 | 77.81728 |

In Fig. 3 and 4 show variation of apparent molar volumes for the systems - Ethanol, Propan-2-ol, 2Methyl propan-2-ol (1) + Propan-2-amine (2) Most of the significant changes occurring in organic mixtures are in the Propan-2-amine rich region. Apparent molar property reflect more appropriate characteristic interactions and structural changes induced by addition of small, increasing amounts of second component. A minimum in apparent molar volume ($V_{ø}$) in the organic co- solvent rich region has been observed in alkanol (1) + Propan-2-amine (2) systems. The apparent molar volumes has order of interactions Ethanol > Propan-2-ol > 2Methyl propan-2-ol. This variation of apparent molar volumes follows same order as variation of excess molar volumes.The derived parameters $A^0$, $A^1$, $A^2$, $A^3$, $A^4$ and σ are presented in Table 4.

Table-3: Densities, Excess molar volumes and Apparent molar volumes of 2-Methylpropan-2-ol (1) + Propan-2-amine (2) at 298.15K and 308.15K.

| $x_1$ | ρ (g/cm$^3$) | | $V^E$ ( cm$^3$mol$^{-1}$) | | $V_{ø}$ ( cm$^3$mol$^{-1}$) | |
|---|---|---|---|---|---|---|
| | 298.15K | 308.15K | 298.15K | 308.15K | 298.15K | 308.15K |
| 0.0000 | 0.682009 | 0.670548 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.081398 | 0.692861 | 0.681637 | -0.26876 | -0.29929 | 91.658959 | 92.55617 |
| 0.166232 | 0.704065 | 0.693020 | -0.54901 | -0.60113 | 91.65805 | 92.61703 |
| 0.254724 | 0.715692 | 0.704997 | -0.84804 | -0.94224 | 91.631477 | 92.53416 |
| 0.347115 | 0.727717 | 0.717162 | -1.1612 | -1.26918 | 91.615447 | 92.57672 |
| 0.443671 | 0.740416 | 0.729767 | -1.52005 | -1.61244 | 91.534655 | 92.59875 |
| 0.544677 | 0.754452 | 0.744193 | -2.00017 | -2.13827 | 91.288514 | 92.30730 |
| 0.65045 | 0.755212 | 0.744878 | -0.86435 | -0.94452 | 93.631884 | 94.78097 |
| 0.761336 | 0.764203 | 0.754045 | -0.67836 | -0.75723 | 94.069721 | 95.23846 |
| 0.877713 | 0.772516 | 0.762473 | -0.37496 | -0.44037 | 94.533530 | 95.73134 |
| 1.00000 | 0.780550 | 0.770230 | 0.0000 | 0.0000 | 94.96073 | 96.23307 |

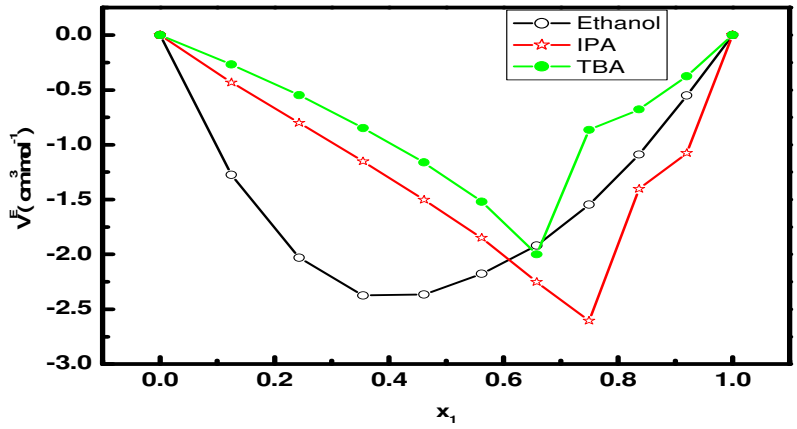


Fig.-1: $V^E$ values v/s $X_1$ for Alkanols (1) + Propan-2-amine (2) solutions at 298.15K.

Table-4: The binary coefficients ($A_i$) and standard errors (σ) calculated from $V^E$ for Alkanol (1) + Propan-2-amine (2) systems.

| Temp.(K) | System | Binary coefficients | | | | | |
|---|---|---|---|---|---|---|---|
| | | $A^0$ | $A^1$ | $A^2$ | $A^3$ | $A^4$ | σ |
| 298.15 | Ethanol + Propan-2-amine | -9.5930 | 2.5311 | -0.3279 | 0.4047 | -0.6224 | 0.07712 |
| | Propan-2-ol + Propan-2-amine | -7.6970 | -4.4051 | -1.4158 | -0.4248 | 1.9601 | 0.35427 |
| | 2 Methylpropan-2-ol + Propan-2-amine | -5.9587 | 0.7737 | 4.2604 | -0.6144 | 0.15307 | 0.35101 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 308.15 | Ethanol + Propan-2-amine | -10.017 | 2.5478 | -0.18708 | 0.6373 | -0.4663 | 0.08178 |
| | Propan-2-ol + Propan-2-amine | -7.9995 | -4.4496 | -1.4920 | -0.4152 | 2.2653 | 0.36819 |
| | 2 Methylpropan-2-ol + Propan-2-amine. | -6.4158 | 0.7003 | 4.2498 | -0.6172 | 0.0594 | 0.36663 |

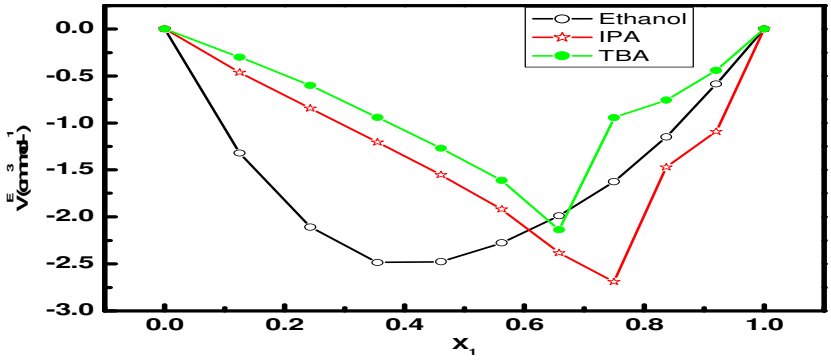


Fig.-2: $V^E$ values v/s $X_1$ for Alkanols (1) + Propan-2-amine (2) solutions at 308.15K

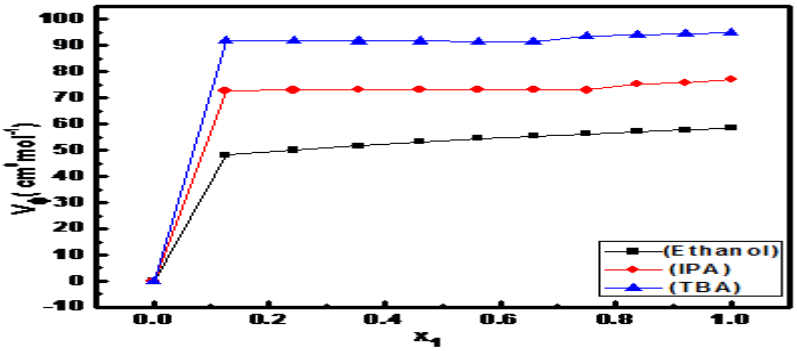


Fig.-3: $V_\Phi$ values v/s $X_1$ for Alkanols (1) +Propan-2 amine (2) solutions at 298.15K

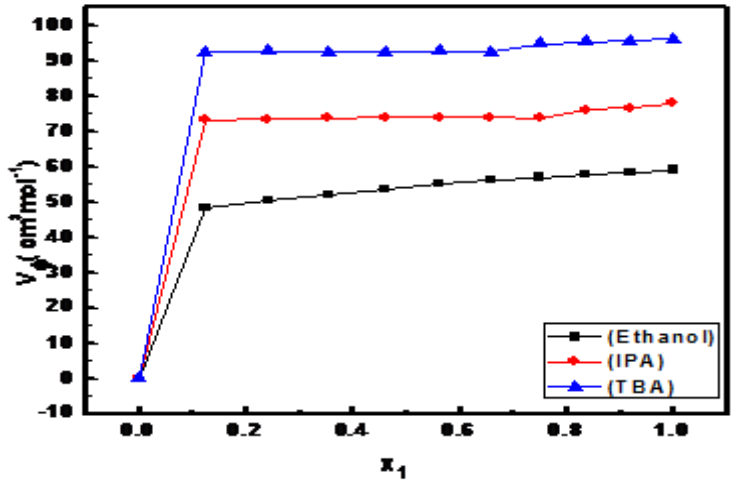


Fig.-4: $V_\Phi$ values v/s $X_1$ for Alkanols (1) + Propan-2-amine (2) solutions at 308.15K

## CONCLUSION

The $V^E$ values increases with increase in chain length of alkanols, while with increase in temperature the $V^E$ values becomes more negative. The molar volumes of alkanol (1) + Propan-2-amine (2) systems at 298.15 and 308.15 differ considerably and hence non associated Propan-2-amine molecules are interstitially accommodated into cluster of alkanols yielding negative $V^E$ values for all temperatures. Also dissociation of self associated alkanol decrees due to breaking of H-bonds predominant over the dispersive forces between alkanol and Propan-2-amine molecules and hence the values of $V^E$ become more negative. This shows strong interactions between -OH and $–NH_2$ groups.

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