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Examination of Excess and Apparent Molar Volumes in Binary Liquid Mixtures

Kum Shanti Devi Bais¹ and Dr. Sundar Pal²

Research Scholar, Department of Chemistry¹ Assistant Professor, Department of Chemistry² NIILM University, Kaithal, Haryana, India

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_{Φ}) have been calculated. These values were fitted with Redlich-Kister type polynomial equation.

Keywords: Volumetric behavior, Non-ideal mixtures

I. INTRODUCTION

A basic topic that is crucial to both physical chemistry and chemical engineering is thermodynamics. A system's thermodynamic properties are used to characterize it. The volume, pressure, temperature, energy (entropy, free energy, etc.), and, of course, the quantity of material are the fundamental variables of thermodynamic attributes. Researchers have examined the kind and character of interactions in binary organic liquid mixtures in relation to mixing factors such excess molar volume1,2. Density (ρ) may be directly measured to compute this value. Process engineering, design applications, and other relevant fields may benefit from such data. Systems may be categorized into two sorts of properties: extensive and intense. Any characteristic whose magnitude is dependent on the quantity of material present is considered an extended property of a system. Liquid mixes' characteristics are mostly determined by their local structure, which may be described using terminology like packing density, free volume, or radial distribution function.3-6. Nevertheless, the interactions between molecules, as well as their shapes and volumes, determine this local structure. With compositions, it changes.

The thermodynamic characteristics of mixtures are altered by this compositional shift. Since alkanol group is very polar and may interact with groups having some degree of polar attraction, studies into the molecular association in organic binary mixtures including alkanol group as one of the components are particularly interesting.7-8. Amine is a protic molecule with a significant dipole moment and is strongly associated because of its highly polar NH2 group. Given the significance highlighted, an effort has been made to clarify the molecular interactions between propan-2-amine and ethanol, propan-2-ol, and 2-methyl propan-2-ol at 298.15 and 308.15 K. These binary mixes' intermolecular interactions are explained by the excess functions.

II. 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 $\pm 1 \times 10^{-4}$ 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.

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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 1×10^{-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^oC, which was close to literature value². 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 cm³. However, actually this change is 14 cm³, Thus the volume occupied by 1 mole of water is 14 cm³. 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 –

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

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 - $V^E = (M_1X_1+M_2X_2) / \rho_{1,2} - (M_1X_1) / \rho_1 - (M_2X_2) / \rho_2$ (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 ρ_1 , ρ_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 $y^{E} = X_{1} X_{2} \sum Ai (X_{1} - X_{2})^{i}$ (3)

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

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

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

III. 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 effects¹ 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 workers¹⁰⁻¹¹ 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 projecules.

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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) at298.15K and 308.15K.

x ₁	ρ (g/cm ³)		V^{E} (cm ³ mol ⁻¹)		V_{g} (cm ³ mol	V_{φ} (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	ρ (g/cm ³)		V^{E} (cm ³ mol	V^{E} (cm ³ mol ⁻¹)		V_{φ} (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_{o}) 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.

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

x ₁	ρ (g/cm ³)		V^{E} (cm ³ mol ⁻¹)		V_{φ} (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 X₁ 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-2amine (2) systems.

Temp.(K)	System	Binary coefficients							
		A ⁰	A ¹	A ²	A ³	A ⁴	σ		
	Ethanol + Propan-2-amine	-9.5930	2.5311	-0.3279	0.4047	-0.6224	0.07712		
298.15	Propan-2-ol + Propan-2- amine	-7.6970	-4.4051	-1.4158	-0.4248	1.9601	0.35427		
	2 Methylpropan-2-ol + Propan-	-5.9587	0.7737	4.2604	-0.6144	0.15307	0.35101		
	2-amine								
	Ethanol + Propan-2-amine	-10.017	2.5478	-0.18708	0.6373	-0.4663	0.08178		
308.15	Propan-2-ol + Propan-2 amine	-7.9995	-4.4496	-1.4920	-0.4152	2.2653	0.36819		
	2 Methylpropan-2-ol	+-6.4158	0.7003	4.2498	-0.6172	0,95,94	0.36663		
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Fig.-3: V_{Φ} values v/s X₁ for Alkanols (1) +Propan-2 amine (2) solutions at 298.15K

×₁





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Fig.-4: V₀ values v/s X₁ for Alkanols (1) + Propan-2-amine (2) solutions at 308.15K

IV. 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-E2-amine molecules and hence the values of V become more negative. This shows strong interactions between -OH and -NH₂ groups.

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