

## Thermodynamic Properties and Excess Molar Volume of Binary Liquid Mixtures of Propyl Acetate with Butan-1-Ol at Different Temperature

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**Abstract:** The study of thermodynamic properties such as enthalpy of activation, entropy of activation and free energy of activation, excess parameters such as excess molar volume ( $V^E$ ) of binary liquid mixtures is useful in understanding the nature of intermolecular interactions between two liquids. The thermodynamic parameters and excess molar volumes have been calculated from the experimental value of densities and viscosities of binary mixtures of propyl acetate with butan-1-ol at (298.15, 303.15, 308.15 and 313.15) K. All the mixtures exhibited endothermic enthalpies which decreased with increasing concentration of propyl acetate. The excess molar volumes are fitted to Redlich-Kister equation and Jouyban - Acree model for correlating the density and viscosity of liquid mixtures at various temperatures. Excess properties considered, and yielded acceptable results.

**Key words -** Propyl acetate, Butan-1-ol, Thermodynamic properties, Excess molar volume,

### I. INTRODUCTION

Thermodynamic and transport properties of binary liquid mixtures have been studied previously<sup>1-8</sup>. The calculated excess quantities from such data have been interpreted in terms of differences in size of the molecules and strength of the specific and nonspecific interactions taking place between the components of the mixtures. When propyl acetate is mixed with different alkan-1-ols, mixing properties with various intermolecular interactions may be generated. In the present study interactions of propyl acetate with butan-1-ol at different temperatures have been reported. The variations of the excess molar volumes and

thermodynamic properties of liquid mixtures of propyl acetate and butan-1-ols, with concentration have been interpreted on the basis of molecular interactions. The studies carried out more precise understanding of intermolecular interactions of and the relationship between the thermodynamic properties of mixing.

### II. EXPERIMENTAL

Butanol (E.merck, purity 99.5%) and propyl acetate (S.D. fine chemicals, purity 99%) were used after single distillation. The purity of the solvent after purification, was ascertained by comparing their densities and viscosities with corresponding literature value at 298.15, 303.15, 308.15 and 313.15 K. Binary mixtures were prepared by mixing known mass of each liquid in an airtight stoppered glass bottle,<sup>2</sup> the masses were recorded on Adairdutt balance to an accuracy of  $\pm 0.0001$  g. Care was taken to avoid contamination during mixing.

The density of pure liquids and binary mixtures were measured by using 15 cm<sup>3</sup> double arm pycnometer as describe earlier<sup>4-7</sup>. The pycnometer was calibrated by using conductivity water with 0.99705 g/cm<sup>3</sup> as its density<sup>9</sup> at 298.15 K. The pycnometer fitted with air bubble free experimental liquid was kept in transparent walled waterbath for 10–15 min. to attain thermal equilibrium, the position of liquid levels in the two arms were recorded. The estimated uncertainty in density measurement of solvent and binary mixtures was 0.00005 g/cm<sup>3</sup>. The dynamic viscosities were measured using Ubbelohde suspended level viscometer<sup>3-7</sup>, calibrated with conductivity water. An electronic digital stopwatch with readability of  $\pm 0.01$  sec. was used for the flow time measurement, at least three repetitious of each data reproducible to  $\pm 0.05$

sec. were obtained and the result were averaged. Since all flow time were greater than 200 sec. and capillary radius ( 0.5 mm ) was far less than its length ( 50 to 60 mm). The kinetic energy and corrections, respectivity were found to be negligible. The uncertainties in dynamic viscosities are of the order  $\pm 0.003$  m Pa s.

### III. RESULT AND DISCUSSION

Experimental values of densities ( $\rho$ ) of binary mixtures of propyl acetate with butan-1-ol, at ( 298.15, 303.15, 308.15 and 313.15 ) K. have been used to calculate excess molar volumes ( $V^E$ ) using following equation and are listed in table-1.

$$V^E \text{ cm}^3 \cdot \text{mole}^{-1} = (x_1 M_1 + x_2 M_2) / \rho_{\text{mix}} - (x_1 M_1 / \rho_1) - (x_2 M_2 / \rho_2) \dots\dots\dots (1)$$

Where  $\rho_{\text{mix}}$  is the density of mixture and  $x_1, M_1, \rho_1$  and  $x_2, M_2, \rho_2$  are the mole fraction, molecular weight and density of pure components 1 and 2 respectively.

Treszczanowicz et al<sup>10</sup>, suggested that  $V^E$  is the resultant contribution from several opposing effects. These may be divided arbitrarily in to three type, namely chemical, physical and structural. Physical contribution that is nonspecific interactions between the real species present in the mixture, contributes positive term to  $V^E$ . The chemical or specific interaction result in a volume decrease, and these include charge transfer type forces and other complex forming interactions. This effect contributes negative value to  $V^E$ . The structural contributions are mostly negative and arises from several effect, specially from interstitial accommodation and change in free volume. In other words structural contribution arising from geometrical fitting (interstitial accommodation) of one component into another due to the differences in the free volume and molar volume between components lead to a negative contribution to  $V^E$ . The extent of hydrogen bonding and interstitial fittings decrease, therefore positive excess molar volumes are expected.<sup>10,11</sup>

The free energy of activation of viscous flow  $\Delta G^\ddagger$  is calculated as

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \dots\dots\dots (2)$$

The value of  $\Delta H^\ddagger, \Delta S^\ddagger$  and  $\Delta G^\ddagger$  for all binary mixtures are listed in table-2. The enthalpy of activation depends on geometrical effects as well as intermolecular interaction. It could be taken as a measure of the cooperation degree between the species taking part in the flow process. In the low temperature range, as well as for highly structured components, one may expect a considerable degree of order, so that transport phenomena takes place cooperatively; as a consequence a great heat of activation associated to a relatively high value of flow entropy is

observed. When the breaking in the ordered and polymerized fluid structure becomes very quick, by increasing the temperature or by adding a component that breaks a homopolymer H-bond network, the movement of the individual units becomes more disordered and the cooperation degree is reduced, facilitating the viscous flow via the activated state of molecular species. As a consequence, the overall molecular order in the system should be reduced, and positive  $\Delta S^\ddagger$  values should be expected.<sup>5, 11-13</sup>

The values of  $\Delta H^\ddagger$  are positive for the binary mixtures of propyl acetate with butan-1-ol for entire composition range, suggesting the presence of specific interaction between constituent molecules. A close perusal of the tables show that with decreasing alcohol concentrations  $\Delta H^\ddagger$  gradually decreases for the binary mixtures of propyl acetate with butan-1-ol as is expected due to the breaking of H-bonds and the values of  $\Delta S^\ddagger$  changes from negative to more negative. The  $\Delta S^\ddagger$  values become more negative as the alcohol concentration decreases.

The negative value of  $\Delta S^\ddagger$  indicates that the formation of activated complex introduces molecular order probably due to interactions between the two components of a mixtures. The values of  $\Delta G^\ddagger$  are positive for all the binary systems studied at all temperature and the values of  $\Delta G^\ddagger$  depend on sign and magnitude of corresponding  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ <sup>5, 12,13</sup>. The values of  $\Delta G^\ddagger$  increases as the alcohol concentration decreases.

The result of  $V^E$  are fitted to Redlich-Kister equation.<sup>14</sup>

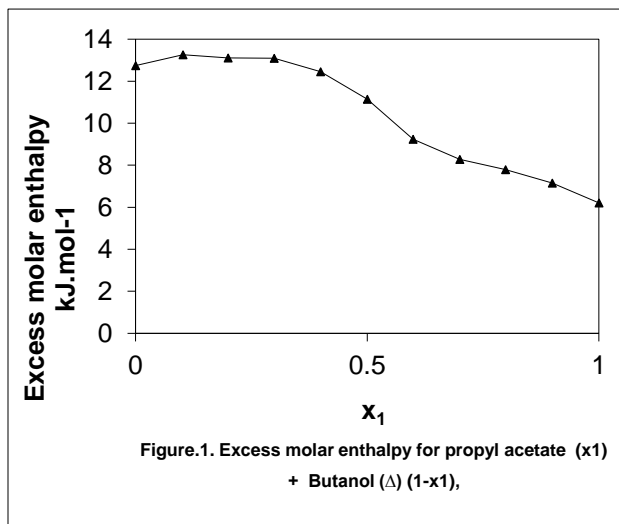
$$Y = x_1 x_2 \sum a_i (x_1 - x_2)^i \dots\dots\dots (3)$$

Where Y refers to  $V^E \text{ cm}^3 \cdot \text{mole}^{-1}$  or  $\Delta \eta \text{ m Pa s}$ , and the coefficient  $a_i$  were obtained by fitting equation 3 to experimental result using a least squares regression method. In each case, the optimum number of coefficient is ascertained from the examination of the variation in standard deviation in  $V^E$  and  $\Delta \eta$ . The  $\sigma$  was calculated using

$$\sigma(Y) = [ \sum (Y_{\text{exp}} - Y_{\text{cal}})^2 / (n-m) ]^{1/2} \dots\dots\dots (4)$$

Where n is number of data point and m is the number of coefficient. The calculated value of  $a_i$  along with standard deviation ( $\sigma$ ) are given in table 3.

Recently Jouyaban and Acree<sup>15</sup> proposed a model for correlating the density and viscosity of liquid mixtures at various temperatures. The correlating ability of the Jouyban - Acree model was tested by calculating the average percentage deviation [APD]. The calculated value of the coefficients  $A_i$  along with the standard deviations [ $\sigma$ ] are given in table 3.



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**Table 1. Excess molar volume for binary liquid mixtures.**

system	Propyl acetate (1)+ Butan-1-ol (2)			
Temp	$x_1$	$V^E$	Temp	$V^E$
K		$m^3 \cdot mol^{-1}$	K	$m^3 \cdot mol^{-1}$
298.15	0	0	308.15	0
	0.1022	0.1557		0.1632
	0.2048	0.2145		0.2258
	0.3	0.2499		0.2639
	0.4002	0.2726		0.2933
	0.5002	0.2908		0.3348
	0.6008	0.2588		0.2724
	0.7011	0.2307		0.2425
	0.8008	0.1835		0.1854
	0.8983	0.1202		0.118
1	0.0000	0.0000	0.0000	
303.15	0	0	313.15	0
	0.1022	0.1587		0.1675
	0.2048	0.2194		0.2331
	0.3	0.253		0.2717
	0.4002	0.2879		0.308
	0.5002	0.3119		0.3445
	0.6008	0.2649		0.281
	0.7011	0.236		0.2499
	0.8008	0.1877		0.1909
	0.8983	0.1226		0.121
1	0.0000	0.0000	0.0000	

**Table 2. Thermodynamic Activation Parameter for the binary liquid mixtures system.**

$X_1$	$\Delta H^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$			
			$kJ \cdot mol^{-1}$			
	$kJ \cdot mol^{-1}$	$J \cdot K^{-1}$	298.15 K	303.15 K	308.15 K	313.15 K
0.0000	12.74	-9.90	15.69	15.74	15.79	15.84
0.1022	13.26	-6.80	15.29	15.32	15.35	15.39
0.2048	13.11	-6.00	14.90	14.93	14.96	14.99
0.3000	13.10	-4.70	14.50	14.53	14.55	14.57
0.4002	12.46	-5.60	14.13	14.15	14.18	14.21
0.5002	11.14	-8.80	13.76	13.81	13.85	13.90
0.6008	9.24	-14.00	13.42	13.49	13.56	13.63

0.7011	8.28	-16.50	13.20	13.28	13.36	13.44
0.8008	7.79	-17.50	13.00	13.09	13.18	13.27
0.8983	7.15	-19.30	12.90	13.00	13.09	13.19
1.0000	6.21	-21.70	12.68	12.79	12.90	13.01

**Table 3. Parameters and standard deviation of the system.**

A) Parameters and standard deviation $\sigma(V^E)$ of the system. According to Redlich-Kister.						
Parameter	$T_e$ mp	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
	T/ K	$V^E$ cm <sup>3</sup> / mol	$V^E$ cm <sup>3</sup> / mol	$V^E$ cm <sup>3</sup> / mol	$V^E$ cm <sup>3</sup> / mol	$V^E$ cm <sup>3</sup> / mol
propyl acetate+ butan-1-ol. system	298.15	1.0767	-0.191	0.613	-	0.0124
	303.15	1.1240	-0.196	0.573	-	0.0165
	308.15	1.1757	-0.245	0.483	-	0.0204
	313.15	1.2182	-0.255	0.477	-	0.0203
B) Parameter of Jouyban-Acree Model and Average Percentage Deviation for Density.						
propyl acetate+ butan-1-ol. system	A0	A1	A2	APD		
	-0.08	0.729	-1.648	0.0085		