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Research Article

EXCESS MOLAR ENTHALPY OF BINARY LIQUID MIXTURES CONTAINING PROPYL ACETATE + 1-ALKANOLS

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ABSTRACT

Excess molar enthalpy has been calculated from the experimental value of densities and viscosities of binary mixtures of propyl acetate with alkan-1-ols 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 density and viscosity of liquid mixtures plays an important role in finding their heat content, mass transport, fluid flow and molecular structure etc. The thermodynamic and transport properties generally yield a valuable information regarding the molecular interactions in pure liquid as well as in liquid mixtures. The Jouyban - Acree model used for correlating the density and viscosity of liquid mixtures at various temperatures. Excess properties considered, and yielded acceptable results.

Keywords: *Propyl Acetate, Alkan-1-ol, Thermodynamic Properties, Excess Molar Enthalpy*

INTRODUCTION

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 varying intermolecular interactions may be generated. In the present study interactions of propyl acetate with methanol, ethanol, propan-1-ol, butan-1-ol and pentan-1-ol at different temperatures have been reported. The transport and thermodynamic studies on the binary mixtures containing nitrobenzene, aniline, chloroform and benzonitrile have been reported previously by Aminabhavi *et al.,* (1990), Gill *et al.,* (1993), Hasan *et al.,* (2006) and Nikam *et al.,* (1998, 2000, 2003).

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

MATERIALS AND METHODS

Methanol (E.merck, purity 99.5%), ethanol (S.D. fine chemicals, purity 99%), propan-1-ol (S.D. fine chemicals, purity 99%), butan-1-ol (S.D. fine chemicals, purity 99%), pentan-1-ol (S.D. fine chemicals, purity 99%) 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, 308.15and 313.15 K. Binary mixtures were prepared by mixing known mass of each liquid in an airtight stoppered glass bottle (Gill *et al.*, 1993), the masses were recorded on Adairdutt balance to an accuracy of ± 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^3 double arm pycnometer as describe earlier (Hasan *et al.*, 2006; Jouyban *et al.*, 2005; Marsh, 1987; Nikam *et al.*, 1998). The pycnometer was calibrated by using conductivity water with 0.99705 g/cm^3 as its density (Nikam *et al.*, 2000) at 298.15 K. The pycnometer fitted with air bubble free experimental liquid was kept in transparent walled water bath 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^3. The dynamic viscosities were measured using Ubbelohde suspended level viscometer (Gill *et al.*, 1993; Hasan *et al.*, 2006; Jouyban *et al.*, 2005; Marsh, 1987), calibrated with conductivity water. An electronic digital stopwatch with readability of ± 0.01 sec. was used for the flow time measurement, at least three repetitious of each data reproducible to ±0.05 sec. were obtained and the results 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, respectively were found to be negligible. The uncertainties in dynamic viscosities are of the order ± 0.003 m Pa s.

RESULTS AND DISCUSSION

The values of excess molar enthalpy ΔH# for all binary mixtures are listed in table 1. The enthalpy of activation depends on geometrical effects as well as intermolecular interaction (Oswal and Dave, 1994; Oswal and Patel, 1998; Reddick and Bunger, 1986; Treszezanowicz and Benson, 1981; Wankhede *et al.*, 2005). Insertion of alkanols molecule between ester molecule increases the distance separating the permanent dipoles associated with carboxylate group there by reducing the dipole-dipole attraction.

On other hand insertion of ester molecule between alkanol molecule reduces the area of contact between the alkanol chain there by reducing the vander waal attraction forces.

These two effects combine to give rise to a process that is overall endothermic. With expansion effect eighter of two effects may predominate depending upon the molecular size.

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 $\Delta S^{\#}$ values should be expected (Hasan *et al.,* 2006; Oswal and Patel, 1998; Reddick and Bunger, 1986; Treszezanowicz and Benson, 1981; Wankhede *et al.*, 2005).

The values of $\Delta H^{\#}$ are positive for the binary mixtures of propyl acetate with methanol, ethanol, propan-1-ol, butan-1-ol and pentan-1-ol for entire composition range, suggesting the presence of specific interaction between constituent molecules (Nikam *et al.*, 2000). A close perusal of the tables show that with decreasing alcohol concentrations $\Delta H^{\#}$ gradually decreases for the binary mixtures of propyl acetate with ethanol and propan-1-ol as is expected due to the breaking of H-bonds and the values of $\Delta S^{\#}$ changes from negative to more negative. The $\Delta S^{\#}$ values become more negative as the alcohol concentration decreases (Oswal and Dave, 1994; Reddick and Bunger, 1986).

Table 1: Excess Molar Enthalpy of Propyl Acetate with 1-Alkanols

X1	Methanol	Ethanol	Propanol	Butanol	Pentanol
0	5.6	9.8	12.09	12.74	16.99
0.1022	5.69	9.35	11.56	13.26	16.85
0.2	5.74	9.16	11.35	13.11	16.71
0.2991	5.81	9.13	10.71	13.1	15.88
0.3996	5.88	9.07	10.34	12.46	14.72
0.5003	5.93	8.5	9.82	11.14	13.32
0.5987	5.98	7.67	9.4	9.24	11.2
0.6998	6.03	6.93	8.84	8.28	9.01
0.7983	6.11	6.67	7.84	7.79	8.2
0.8991	6.19	6.51	7.24	7.15	7.52
1	6.21	6.21	6.21	6.21	6.21

Recently Jouyaban *et al.,* (2005) 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 Ai along with the standard deviations [σ] are given in table 2.

Table 2: Parameters and Average Percentage Deviation of the System

Parameter of Jouyban-Acree Model and Average Percentage Deviation for Density

Propyl Acetate	**A0**	**A1**	**A2**	**APD**
+ Methanol.	23.847	-8.94	3.338	0.0662
PA + Ethanol.	6.313	-0.088	0.365	0.0068
PA + Propan-1-ol.	2.599	0.532	0.628	0.0095
PA + Butan-1-ol.	-0.08	0.729	-1.648	0.0085
PA + Pentan-1-ol.	-2.145	0.303	0.178	0.0062

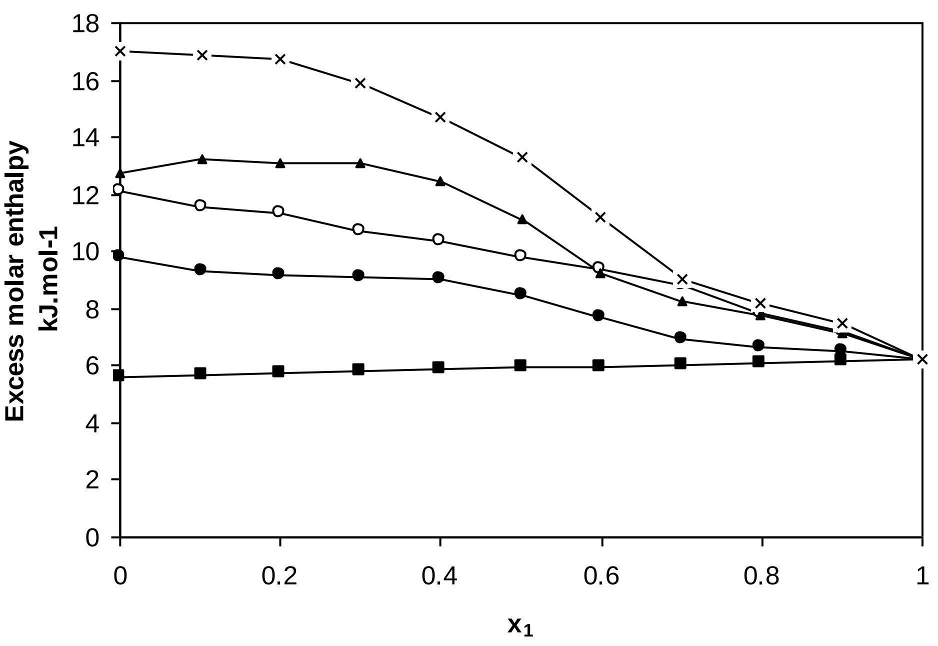

Figure.1. Excess molar enthalpy for propyl acetate (x1) + alkanols (1-x1)

Methanol (■),Ethanol (●),Propanol (o)Butanol (Δ),Pentanol (×),

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