

Thermodynamic and Transport Properties of Binary Liquid Mixtures of Propyl Acetate with Normal Alkanols at Different Temperature

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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 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), deviation in viscosity ($\Delta\eta$) 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 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 excess molar volumes are fitted to 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, Alkan-1-ol, Thermodynamic properties, Excess molar volume.

INTRODUCTION

Thermodynamic and transport properties of binary liquid mixtures containing protic, aprotic and associated liquids have already been studied¹⁻⁸. 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 and propan-1-ol at different temperatures have been reported. The transport and thermodynamic studies on the binary mixtures containing aniline and benzonitrile have been reported previously by Ali *et al.*¹, Nikam *et al.*³⁻⁷ and Gill *et al.*⁸.

The variations of the excess molar volumes and thermodynamic properties of liquid mixtures of propyl acetate and alkan-1-ols, with 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.

EXPERIMENTAL

Methanol (E. Merck, purity 99.5 %), ethanol (SD fine chemicals, purity 99 %), propan-1-ol (SD fine chemicals, purity 99 %) and propyl acetate (SD 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 bottle², 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 cm³ double arm pycnometer as describe earlier⁴⁻⁷. The pycnometer was calibrated by using conductivity water with 0.99705 g/cm³ as its density⁹ 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/cm³. The dynamic viscosities were measured using Ubbelohde suspended level viscometer³⁻⁷, calibrated with conductivity water. An electronic digital stopwatch with readability of ± 0.01 s was used for the flow time measurement, at least three repetitions of each data reproducible to ± 0.05 s were obtained and the result were averaged. Since all flow time were greater than 200 s and capillary radius (0.5 mm) was far less than its length (50-60 mm). The kinetic energy and corrections, respectivity were found to be negligible. The uncertainties in dynamic viscosities are of the order ± 0.003 mPas.

RESULTS AND DISCUSSION

Experimental values of densities (ρ) have been used to calculate excess molar volumes¹⁰⁻¹³. (V^E) using following equation.

$$V^E \text{ cm}^3 \text{ mol}^{-1} = (x_1M_1 + x_2M_2)/\rho_{\text{mix}} - (x_1M_1/r_1) - (x_2M_2/\rho_2) \quad (1)$$

where ρ_{mix} is the density of mixture and x_1 , M_1 , ρ_1 and x_2 , M_2 , r_2 are the mole fraction, molecular weight and density of pure components 1 and 2, respectively.

The free energy of activation of viscous flow ΔG^\ddagger is calculated as

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

The value of ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger for all binary mixtures are listed in Tables 1-3. The enthalpy of activation depends on geometrical effects as well as intermolecular interaction¹⁴. It could be taken as a measure of the cooperation degree between the

TABLE-1
THERMODYNAMIC ACTIVATION PARAMETER FOR THE
PROPYL ACETATE (1) + METHANOL (2) SYSTEM

X_1	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)			
			298.15 K	303.15 K	308.15 K	313.15 K
0.0000	5.60	-14.40	9.90	9.97	10.04	10.11
0.1022	5.69	-15.70	10.37	10.44	10.52	10.60
0.2000	5.74	-16.80	10.75	10.84	10.92	11.01
0.2991	5.81	-17.70	11.09	11.18	11.27	11.36
0.3996	5.88	-18.40	11.36	11.46	11.55	11.64
0.5003	5.93	-19.20	11.65	11.75	11.84	11.94
0.5987	5.98	-19.80	11.88	11.98	12.08	12.18
0.6998	6.03	-20.40	12.11	12.21	12.31	12.42
0.7983	6.11	-20.80	12.31	12.41	12.52	12.62
0.8991	6.19	-21.20	12.51	12.61	12.72	12.83
1.0000	6.21	-21.70	12.68	12.79	12.90	13.01

TABLE-2
THERMODYNAMIC ACTIVATION PARAMETER FOR THE
PROPYL ACETATE (1) + ETHANOL (2) SYSTEM

X_1	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)			
			298.15 K	303.15 K	308.15 K	313.15 K
0.0000	9.80	-8.90	12.45	12.50	12.54	12.59
0.1022	9.35	-10.40	12.45	12.50	12.55	12.61
0.1999	9.16	-11.00	12.44	12.49	12.55	12.60
0.3000	9.13	-11.00	12.41	12.46	12.52	12.57
0.4002	9.07	-11.20	12.41	12.47	12.52	12.58
0.5003	8.50	-13.00	12.38	12.44	12.51	12.57
0.5995	7.67	-15.80	12.38	12.46	12.54	12.62
0.6996	6.93	-18.40	12.41	12.50	12.60	12.69
0.7991	6.67	-19.60	12.51	12.61	12.71	12.81
0.8987	6.51	-20.50	12.62	12.72	12.82	12.93
1.0000	6.21	-21.70	12.68	12.79	12.90	13.01

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 ΔS^\ddagger values is expected^{15,15-20}.

TABLE-3
THERMODYNAMIC ACTIVATION PARAMETER FOR THE
PROPYL ACETATE (1) + PROPAN-1-OL (2) SYSTEM

X_1	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)			
			298.15 K	303.15 K	308.15 K	313.15 K
0.0000	12.09	-8.00	14.48	14.52	14.56	14.60
0.1022	11.56	-8.80	14.19	14.23	14.27	14.32
0.1998	11.35	-8.50	13.88	13.93	13.97	14.01
0.2995	10.71	-9.70	13.61	13.66	13.70	13.75
0.3993	10.34	-10.20	13.38	13.43	13.48	13.53
0.5002	9.82	-11.20	13.16	13.22	13.27	13.33
0.5989	9.40	-12.10	13.01	13.07	13.13	13.19
0.7006	8.84	-13.50	12.87	12.93	13.00	13.07
0.7995	7.84	-16.60	12.79	12.87	12.95	13.04
0.8998	7.24	-18.50	12.76	12.85	12.94	13.04
1.0000	6.21	-21.70	12.68	12.79	12.90	13.01

The values of ΔH^\ddagger are positive for the binary mixtures of propyl acetate with methanol, ethanol and propan-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 ΔH^\ddagger 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 ΔS^\ddagger changes from negative to more negative. The ΔS^\ddagger values become more negative as the alcohol concentration decreases^{13,15}.

The negative value of ΔS^\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 ΔG^\ddagger are positive for all the binary systems studied at all temperature and the values of ΔG^\ddagger depend on sign and magnitude of corresponding ΔH^\ddagger and ΔS^\ddagger ^{5,16-20}. The values of ΔG^\ddagger increases as temperature increases²⁰.

Recently Jouyaban and Acree²¹ 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 [σ] are given in Table-4.

TABLE-4
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	-8.940	3.338	0.0662
+ Ethanol	6.313	-0.088	0.365	0.0068
+Propan-1-ol	2.599	0.532	0.628	0.0095

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