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Temperature dependent study of thermophysical properties of binary mixtures of 1,4-butanediol + picolines

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The experimental values of densities (ρ) and speeds of sound (u) of (1,4-butanediol + α-, orβ- picoline) binary mixtures have been used to calculate the internal pressure (π_i), free volume (V_f), enthalpy (H), entropy (T_s), excess internal pressure (π_i^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) at temperatures 303.15, 308.15, 313.15 and 318.15K over the entire composition range. The results have been discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules. It has been observed that the strength of intermolecular interaction between 1,4-butanediol and picoline molecules is in order α-picoline>β-picoline.

Keywords: Thermodynamic properties, Internal pressure, Excess Gibbs energy of activation, Molecular interactions, 1,4-butanediol, Picoline

1 Introduction

The speed of sound (u) is a property that can be experimentally determined with great precision over a broad range of temperature and pressure. Since u can be related to the first pressure partial derivative of density, accurate sound-speed data can be used to enhance the development of equation of state. Furthermore, it is a very useful source of information for computing values of other thermodynamic properties which are difficult to obtain at extreme experimental conditions, such as calorimetric data at high pressures.

We have previously reported the excess molar volumes, excess isentropic compressibility's, excess partial molar volume, excess partial molar compressibility's in binary mixtures of 1,4-butanediol with picolines[1]. This work forms part of an investigation into the thermodynamic properties of 1,4-butanediol and its mixtures.

Our literature survey shows that no measurements on above parameters have been reported for the mixtures investigated in this work. For examining the nature of inter- and intra-molecular interactions, characterizing the thermodynamic and physicochemical aspects of binary liquid mixtures such as molecular association and dissociation, the study of propagation of ultrasonic waves in liquids and liquid mixtures is of great importance[2-5]. These studies find several applications in industries. Such studies as variations in concentration and temperature are useful in giving insight into structure and various bonding of associated molecular complexes and other related molecular processes[6-8].

1,4-butanediol is a clear viscous liquid, which is miscible with water and most of the polar organic solvents. The presence of two hydroxyl groups in vicinal positions (at the positions 1 and 4) of this diol makes it suitable as a useful chemical intermediate in the manufacture of many chemical products[9,10].

Picoline refers to three different methylpyridine isomers, all three are colourless liquids at room temperature and pressure and are miscible with water and most organic solvents. The picolines are cyclic compounds with molecules having nitrogen atom in the aromatic ring. The nitrogen atom has one lone pair of electrons and it is capable of forming the hydrogen bond with a proton-donating molecule. α-picoline is used as an adhesive for textile tire cord and also a precursor to the agrochemical, nitrapyrin, which prevents loss of ammonia from fertilizers. β-picoline is a useful precursor to agrochemicals, such as chlorpyrifos and used to make antidotes for

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poisoning by organo phosphate acetyl cholinesterase inhibitors [11,12].

From the experimental values of density and speed of sound the internal pressure (π_i), free volume (V_f), enthalpy (H), entropy (Ts), excess internal pressure (π_i^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) at temperatures 303.15, 308.15, 313.15 and 318.15 K over the entire composition range have been evaluated. The results are fitted to the Redlich-Kister polynomial equation.

2 Experimental

1,4-butanediol and picolines (Sigma-Aldrich, mass fraction purity 0.99) used in this study were purified by using the standard methods[13,14]. Before use, the chemicals were stored over 0.4 nm molecular sieves for 72 h to remove the water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. The weighing was done with an electronic balance with a precision of ± 0.1mg.

The densities of the pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ≈10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The densities of pure water at the required temperature were taken from the literature[15]. The reproducibility of the density measurements was within $\pm 2 \times 10^{-5}$ g.cm^{-3}. The temperature of the test liquids during the measurements was maintained to an accuracy of ±0.02 K in an electronically controlled thermostatic water bath (Julabo). The speeds of sound in pure liquids and their binary mixtures were measured using a single-crystal variable-path multi frequency ultrasonic interferometer (Mittal Enterprises, India, modelF-81) operating at 2 MHz. The speeds of sound data were reproducible within ±0.2 m s^{-1}.

3 Results and Discussion

The internal pressure of a fluid is related to the thermal pressure coefficient $(\partial P/\partial T)_V$ by the following well-known thermodynamic equation of state:

$$\pi_i = \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\alpha_P}{k_T}\right) - P \quad \ldots (1)$$

where α_P is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. For most of the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e., $T(\alpha_P/k_T)$ is very high so that the external pressure (P) becomes negligible in comparison[16], therefore it may be neglected in Eq. (1) in the present calculations. Thus, the internal pressure can be shown to be equal to the following relationship[17,18]:

$$\pi_{i=}\frac{\alpha_P}{k_T}T \quad \ldots (2)$$

The free volume, V_f of the mixtures are calculated from the relation[19,20]:

$$V_f = \frac{RT}{(P+\pi_i)} \quad \ldots (3)$$

since P is very small as compared to π_i, it has been neglected in the Eq. (3) in the present calculations. k_T is calculated using the well-known thermodynamic relationship[21,22]:

$$k_T = k_s + \frac{TV\alpha_P^2}{C_P} \quad \ldots (4)$$

where k_s [= $1/(\rho u^2)$] is isentropic compressibility, V is the molar volume and C_p is the heat capacity of the mixture. The α_p values for the mixtures were evaluated from temperature dependence of density data[1]. The C_p values of pure liquids have been taken from the literature[23-25] and the C_p values for the mixtures have been calculated by using the following relationship:

$$C_p = x_1C_{p,1} + x_2C_{p,2} \quad \ldots (5)$$

The values of various parameters, C_p, α_p, k_s and k_T of pure liquids used in the calculations are taken from our earlier paper[1]. The π_i^E and V_f^E of binary mixtures have been calculated using the relationship:

$$Y^E = Y - (x_1Y_1 + x_2Y_2) \quad \ldots (6)$$

where Y is π_i or V_f and subscripts 1 and 2 refer to pure 1,4-butanediol and picolines, respectively. The excess enthalpies (H^E) and excess entropies (T_S^E) are calculated from π_i and V_f by using the following relations based on regular solution theory[19,20,25]:

$$H^E = \pi_i V - [x_1\pi_{i,1}V_1 + x_2\pi_{i,2}V_2] \quad \ldots (7)$$

$$T_S^E = R\,[x_1\ln V_{f,1} + x_2\ln V_{f,2} - \ln V_f] \quad \ldots (8)$$

The excess free energy (G^E) of mixtures is given by the relationship:

$$G^E = H^E - T_s^E \quad \ldots (9)$$

The values of π_i^E, V_f^E, H^E, T_S^E and G^E were fitted to a Redlich-Kister[26] type polynomial equation:

$$Y^E = x_1(1\text{-}x_1)\sum_{i=1}^{n} A_i\,(2x_1 - 1)^{i-1} \quad \ldots (10)$$

where Y^E is π_i^E or V_f^E or H^E or T_S^E or G^E. The values of coefficients, A_i in Eq. (10) were evaluated by using least-square method with all points weighted equally. The standard deviations (σ) of fit have been calculated by using the relation:

$$\sigma\,(Y^E) = [\sum(Y_{obs}{}^E - Y_{cal}{}^E)^2/(m-n)]^{1/2} \quad \ldots (11)$$

where m is the total number of experimental points and n is the number of coefficients.

The values of u, ρ, π_i, H, and V_f for the binary mixtures of 1,4-butanediol + α-picoline/β-picoline as function of mole fraction, x_1 of 1,4-butanediol at various temperatures are listed in Table 1. The values of coefficients, A_i of Eq. (10) for the excess functions and the corresponding standard deviations, σ are listed in Table 2. The variations of π_i^E, V_f^E, H^E, T_S^E and G^E with composition and temperature of the mixtures are presented graphically in Figs 1-5, respectively.

Table 1 — Values of u, ρ, π_i, H, and V_f for the binary mixtures of 1,4-butanediol + α-picoline/β-picoline as function of mole fraction, x_1 of 1,4-butanediol at various temperatures.

x_1	u (m s^{-1})	ρ (kg m^{-3})	π_I (10^8 N m^{-2})	H (kJ mol^{-1})	V_f (10^{-6} m^{3}mol^{-1})
		1,4-Butanediol + α-picoline			
		T = 303.15 K			
0.0000	1360.2	935.2	3.976	39.60	6.339
0.1236	1380.9	945.8	4.006	39.29	6.291
0.2410	1406.0	955.5	4.032	39.00	6.250
0.3524	1431.8	964.3	4.038	38.55	6.241
0.4585	1456.3	972.4	4.016	37.89	6.276
0.5594	1479.6	979.8	3.967	37.02	6.353
0.6557	1502.1	986.7	3.895	35.98	6.471
0.7477	1523.8	993.1	3.801	34.78	6.631
0.8355	1545.3	998.9	3.688	33.46	6.834
0.9195	1567.0	1004.3	3.560	32.03	7.079
1.0000	1590.4	1009.4	3.424	30.57	7.362
		T = 308.15 K			
0.0000	1340.4	930.3	3.948	39.53	6.489
0.1236	1367.3	941.4	4.032	39.72	6.355
0.2410	1394.6	951.4	4.098	39.80	6.251
0.3524	1422.6	960.5	4.150	39.78	6.173
0.4585	1448.1	968.9	4.174	39.53	6.138
0.5594	1472.4	976.5	4.175	39.10	6.136
0.6557	1495.5	983.6	4.156	38.52	6.165
0.7477	1517.5	990.1	4.117	37.79	6.223
0.8355	1539.4	996.1	4.064	36.97	6.305
0.9195	1561.4	1001.6	3.998	36.07	6.408
1.0000	1580.5	1006.8	3.907	34.98	6.557
		T = 313.15 K			
0.0000	1320.3	925.7	3.918	39.41	6.645
0.1236	1352.3	937.1	4.049	40.07	6.431
0.2410	1382.7	947.4	4.159	40.56	6.260
0.3524	1412.1	956.8	4.252	40.92	6.123
0.4585	1439.1	965.3	4.322	41.08	6.025
0.5594	1463.6	973.1	4.367	41.04	5.962

(*Contd*.)

Table 1 — Values of u, ρ, π_i, H, and V_f for the binary mixtures of 1,4-butanediol + α-picoline/β-picoline as function of mole fraction, x_1 of 1,4-butanediol at various temperatures. (*Contd*.)

x_1	u (m s^{-1})	ρ (kg m^{-3})	π_I (10^8 N m^{-2})	H (kJ mol^{-1})	V_f (10^{-6} m^{3}mol^{-1})
		1,4-Butanediol + α-picoline			
		T = 313.15 K			
0.6557	1487.2	980.2	4.397	40.89	5.921
0.7477	1510.0	986.8	4.413	40.64	5.900
0.8355	1532.7	993.0	4.418	40.31	5.893
0.9195	1553.4	998.6	4.403	39.84	5.913
1.0000	1569.2	1003.8	4.356	39.11	5.977
		T = 318.15 K			
0.0000	1300.4	920.9	3.885	39.29	6.808
0.1236	1338.2	932.5	4.066	40.44	6.506
0.2410	1370.3	943.1	4.212	41.27	6.279
0.3524	1400.9	952.6	4.343	41.97	6.090
0.4585	1429.0	961.3	4.454	42.51	5.939
0.5594	1453.7	969.2	4.540	42.83	5.827
0.6557	1477.5	976.5	4.613	43.06	5.734
0.7477	1500.6	983.3	4.676	43.22	5.657
0.8355	1522.8	989.5	4.727	43.29	5.596
0.9195	1543.0	995.1	4.761	43.23	5.556
1.0000	1555.2	1000.4	4.747	42.76	5.572
		1,4-butanediol + β-picoline			
		T = 303.15 K			
0.0000	1404.2	947.4	3.576	35.15	7.049
0.1224	1425.3	956.0	3.605	34.98	6.991
0.2389	1447.2	963.9	3.629	34.79	6.945
0.3498	1468.0	971.2	3.639	34.50	6.926
0.4556	1487.9	977.9	3.637	34.13	6.930
0.5566	1506.7	984.2	3.623	33.67	6.956
0.6531	1524.6	989.9	3.599	33.14	7.003
0.7455	1541.7	995.3	3.565	32.55	7.070
0.8339	1557.9	1000.3	3.522	31.91	7.156
0.9187	1573.4	1005.0	3.472	31.22	7.259
1.0000	1590.4	1009.4	3.424	30.57	7.362
		T = 308.15 K			
0.0000	1385.0	942.7	3.674	36.29	6.974
0.1224	1408.8	951.6	3.744	36.49	6.843
0.2389	1431.9	959.8	3.803	36.62	6.736
0.3498	1453.7	967.4	3.851	36.65	6.654
0.4556	1474.3	974.4	3.885	36.59	6.594
0.5566	1494.1	980.9	3.910	36.46	6.552
0.6531	1513.0	986.8	3.926	36.27	6.525
0.7455	1530.9	992.3	3.932	36.02	6.515
0.8339	1548.2	997.5	3.931	35.72	6.517
0.9187	1564.5	1002.3	3.921	35.36	6.533
1.0000	1580.5	1006.8	3.907	34.98	6.557
		T = 313.15 K			
0.0000	1365.2	938.1	3.760	37.32	6.925
0.1224	1391.5	947.3	3.868	37.88	6.731
0.2389	1415.5	955.8	3.960	38.29	6.574
0.3498	1438.4	963.5	4.042	38.63	6.441
0.4556	1460.1	970.7	4.114	38.89	6.329

(*Contd*.)

Table 1 — Values of u, ρ, π_i, H, and V_f for the binary mixtures of 1,4-butanediol + α-picoline/β-picoline as function of mole fraction, x_1 of 1,4-butanediol at various temperatures. (*Contd*.)

x_1	u (m s^{-1})	ρ (kg m^{-3})	π_I (10^8 N m^{-2})	H (kJ mol^{-1})	V_f (10^{-6} m^{3}mol^{-1})
			1,4-Butanediol + α-picoline		
			T = 313.15 K		
0.5566	1480.7	977.3	4.175	39.07	6.235
0.6531	1500.4	983.4	4.228	39.19	6.158
0.7455	1519.0	989.1	4.272	39.26	6.094
0.8339	1536.8	994.3	4.308	39.26	6.043
0.9187	1553.7	999.2	4.337	39.22	6.003
1.0000	1569.2	1003.8	4.356	39.11	5.977
			T = 318.15 K		
0.0000	1345.3	934.5	3.836	38.23	6.896
0.1224	1373.6	943.9	3.977	39.09	6.651
0.2389	1398.6	952.4	4.099	39.78	6.453
0.3498	1422.2	960.2	4.211	40.38	6.281
0.4556	1444.6	967.4	4.314	40.91	6.132
0.5566	1466.1	974.1	4.408	41.39	6.000
0.6531	1486.4	980.2	4.494	41.80	5.886
0.7455	1505.5	985.8	4.571	42.14	5.787
0.8339	1523.7	991.0	4.640	42.43	5.700
0.9187	1540.8	995.8	4.702	42.67	5.626
1.0000	1555.2	1000.4	4.747	42.76	5.572

Table 2 — Coefficients (A_i) of Eq. (10) for π_i^E, V_f^E, H^E, T_s^E and G^E along with standard deviations (σ) for 1,4-butanediol + α-picoline/β-picoline binary mixtures at different temperatures.

Property	T (K)	A_1	A_2	A_3	A_4	A_5	σ
				1,4-butanediol + α-picoline			
π_i^E (10^8) (Nm^{-2})	303.15	1.1976	0.1983	-0.1573	0.0595	-0.0806	0.0004
	308.15	1.0015	0.1440	-0.1828	0.1134	0.2250	0.0010
	313.15	0.8234	0.0814	-0.0933	0.2416	0.3062	0.0006
	318.15	0.6990	0.0494	-0.0821	0.2675	0.5640	0.0008
V_f^E (10^{-6}) (m^{3}mol^{-1})	303.15	-2.1924	-0.6182	0.0185	-0.1478	0.1501	0.0007
	308.15	-1.5646	-0.2249	0.1863	-0.2108	-0.3510	0.0016
	313.15	-1.2642	0.0128	0.0822	-0.3401	-0.4132	0.0008
	318.15	-1.2007	0.1359	0.0588	-0.2800	-0.7072	0.0012
H^E (kJ mol^{-1})	303.15	-9.9289	-1.3901	1.5985	-0.6613	0.7144	0.0034
	308.15	-8.5350	-0.9525	1.7867	-1.0623	-2.0614	0.0096
	313.15	-7.2922	-0.4132	0.9037	-2.2154	-2.7582	0.0056
	318.15	-6.5221	-0.1450	0.8227	-2.3601	-5.2587	0.0081
T_S^E (10^{-2}) (J mol^{-1})	303.15	-0.8126	-0.1826	0.0568	-0.0463	0.0562	0.0002
	308.15	-0.6334	-0.0909	0.0947	-0.0784	-0.1411	0.0006
	313.15	-0.5204	-0.0228	0.0478	-0.1463	-0.1842	0.0004
	318.15	-0.4729	0.0126	0.0392	-0.1416	-0.3229	0.0005
G^E (kJ mol^{-1})	303.15	-9.1163	-1.2075	1.5445	-0.6152	0.6523	0.0032
	308.15	-7.9015	-0.8619	1.6918	-0.9830	-1.9219	0.0090
	313.15	-6.7719	-0.3904	0.8574	-2.0686	-2.5789	0.0053
	318.15	-6.0491	-0.1584	0.7828	-2.2165	-4.9343	0.0076
				1,4-butanediol + β-picoline			
π_i^E(10^8) (Nm^{-2})	303.15	0.5307	0.0499	-0.0161	-0.0162	-0.1341	0.0003
	308.15	0.4283	0.0377	0.0161	0.0074	-0.0583	0.0003
	313.15	0.3365	0.0404	-0.0008	-0.0093	0.0621	0.0002

(*Contd*.)

Table 2 — Coefficients (A_i) of Eq. (10) for π_i^E, V_f^E, H^E, T_s^E and G^E along with standard deviations (σ) for 1,4-butanediol + α-picoline/β-picoline binary mixtures at different temperatures. (*Contd*.)

Property	T (K)	A_1	A_2	A_3	A_4	A_5	σ
			1,4-butanediol + β-picoline				
	318.15	0.2587	0.0469	0.0215	-0.0013	0.1341	0.0005
V_f^E (10^{-6}) (m^3mol^{-1})	303.15	-1.0656	-0.1416	-0.0180	0.0316	0.2775	0.0007
	308.15	-0.7684	-0.0179	-0.0465	-0.0160	0.1013	0.0005
	313.15	-0.6605	0.0246	-0.0118	0.0216	-0.0954	0.0002
	318.15	-0.6471	0.0375	-0.0386	0.0366	-0.1898	0.0006
H^E(kJ mol^{-1})	303.15	-4.3138	-0.2635	0.1176	0.0887	1.2661	0.0027
	308.15	-3.6322	-0.1793	-0.2060	-0.0882	0.5945	0.0025
	313.15	-3.0401	-0.2129	-0.0203	0.0665	-0.5717	0.0013
	318.15	-2.5477	-0.2979	-0.2240	0.0037	-1.2778	0.0045
T_S^E(10^{-2}) (J mol^{-1})	303.15	-0.3774	-0.0426	0.0019	0.0109	0.0977	0.0002
	308.15	-0.2903	-0.0167	-0.0142	-0.0046	0.0377	0.0002
	313.15	-0.2419	-0.0085	-0.0015	0.0075	-0.0395	0.0001
	318.15	-0.2182	-0.0085	-0.0144	0.0079	-0.0801	0.0003
G^E (kJ mol^{-1})	303.15	-3.9367	-0.2203	0.1179	0.0769	1.1656	0.0025
	308.15	-3.3416	-0.1630	-0.1937	-0.0842	0.5576	0.0023
	313.15	-2.7984	-0.2053	-0.0179	0.0601	-0.5339	0.0011
	318.15	-2.3295	-0.2893	-0.2096	-0.0043	-1.1977	0.0042

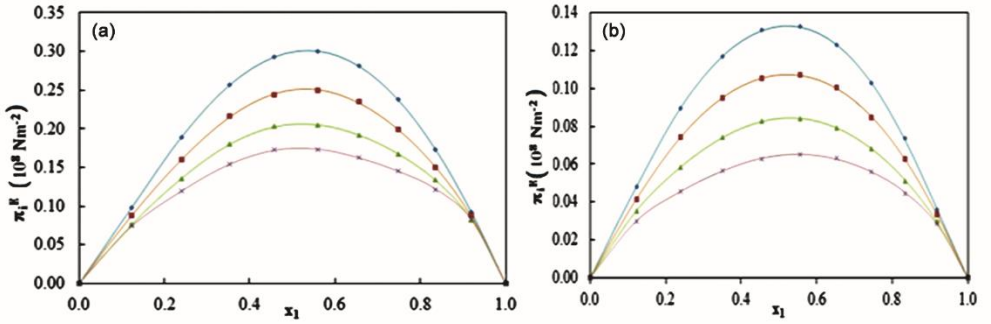

Fig. 1 — Variation of excess internal pressure, π_i^E with mole fraction of 1,4-butanediol for the binary mixture (a) 1,4-butanediol + α-picoline and (b) 1,4-butanediol + β-picoline at temperatures: 303.15 K (♦), 308.15 K (■), 313.15 K (▲) and 318.15 K (x).

The internal pressure (also known as the cohesion pressure or energy-volume coefficient) is an interesting and valuable quantity that describes the macroscopic result of molecular interactions. The internal pressure is the cohesive force which is the resultant of forces of attraction and forces of repulsion between molecules in a liquid, and considerable information can be gained by simply observing and comparing internal pressure-volume curves for pure liquids[27,28].

From Fig. 1(a, b) the π_i^E values are observed to be positive for the two binary mixtures over the entire composition range and at all investigated temperatures. With increase in temperature the decrease in π_i^E values can also be observed. It has been established that the sign and magnitude of excess functions give good estimate of the strength of the unlike interactions in a binary mixture. The introduction of $–CH_3$ group in pyridine ring (as in picolines) would increase the π-electron density of nitrogen atom of picoline and so interaction between 1,4-BD and α- picoline would be stronger than those for 1,4-BD + β-Picolin mixtures. A closer packing of molecules, resulting in a contraction in volume of the mixture, leading to an increase in the internal pressure of the mixture, hence, positive π_i^E values. The magnitude of values are in the order: 1,4-BD + α-picoline>1,4-BD + α-β-picoline, which indicates the order of interactions in these systems.

Free volume is a central concept in considering both equilibrium thermodynamic properties and transport properties in liquids. The V_f^E values are observed (Fig. 2(a, b)) to be negative for the two binary mixtures at all the temperatures studied. The

decrease in V_f^E can also be observed from the same figures with the increase in temperature. The observed negative trend in V_f^E values indicates specific interactions between the molecules of the mixtures. The negative values of excess free volume in binary system assert that the combined effects of the factors are responsible for volume contraction and vice-versa[29]. According to these investigations, the negative values of excess free volume may be attributed to the packing effect and ion-dipole interaction of solvent molecules with the 1,4-BD in these mixtures[30,31].

From Fig. 3(a, b) the H^E values are observed to be negative for the two binary mixtures at all the temperatures studied. It can also be observed from the same figures that with the increase in temperature, the H^E values are decreased. In general, H^E values of mixing depend upon the relative enthalpies of endothermic and exothermic effects that arise on mixing of the components. The factors that cause endothermic effect on mixing are:

(i) Strong specific interactions, usually some type of chemical interactions.
(ii) Favorable geometrical fitting of component molecules due to occupation of void spaces of one component by the other when the molecular sizes of the unlike molecules differ by a large magnitude.
(iii) Ion-dipole interactions of solvent molecules with the 1,4-BD molecules.

The factors that cause exothermic effect on mixing of the components are:

(i) Breakdown of the solvent self-associated molecules from each other.
(ii) Breakdown of the 1,4-BD ion pairs.
(iii) Formation of weaker 1,4-BD-solvent bonds than 1,4-BD-1,4-BD and solvent-solvent bonds.

It can be observed that the negative value of H^E indicates exothermic process[32] in the mixing of the 1,4-BD with α-or β-picoline systems. Negative H^E values may be attributed to dipole-dipole or ion-ion

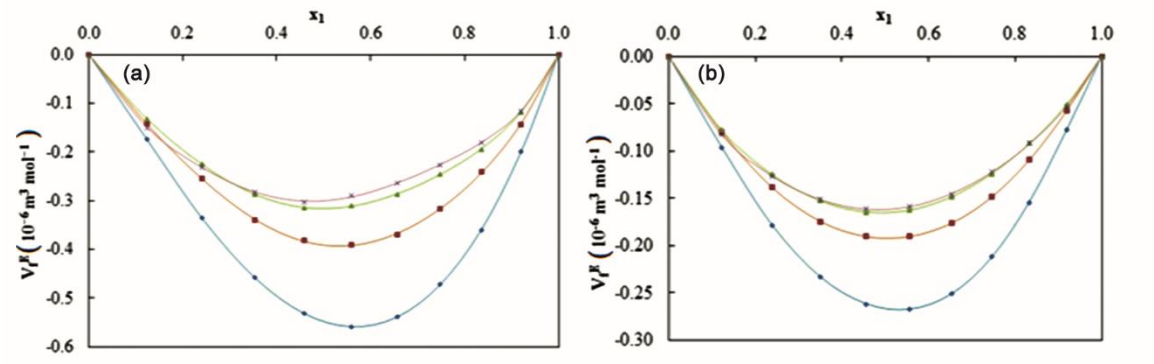

Fig. 2 — Variation of excess free volume, V_f^E with mole fraction of 1,4-butanediol for the binary mixture (a) 1,4-butanediol + α-picoline and (b) 1,4-butanediol + β-picoline at temperatures: 303.15 K (♦), 308.15 K (■), 313.15 K (▲) and 318.15 K (x).

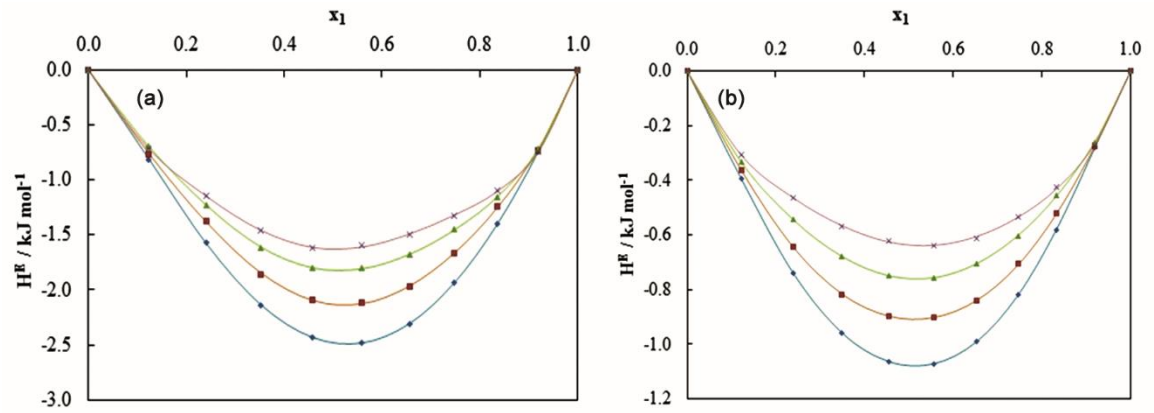

Fig. 3 — Variation of excess enthalpy, H^E with mole fraction of 1,4-butanediol for the binary mixture (a) 1,4-butanediol + α-picoline and (b) 1,4-butanediol + β-picoline at temperatures: 303.15 K (♦), 308.15 K (■), 313.15 K (▲) and 318.15 K (x).

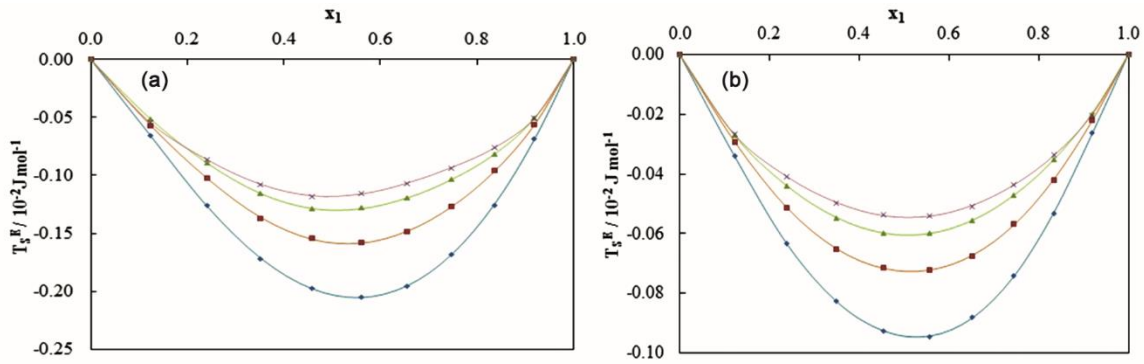

Fig. 4 — Variation of excess entropy, T_s^E with mole fraction of 1,4-butanediol for the binary mixture (a) 1,4-butanediol + α-picoline and (b) 1,4-butanediol + β-picoline at temperatures: 303.15 K (♦), 308.15 K (■), 313.15 K (▲) and 318.15 K (x).

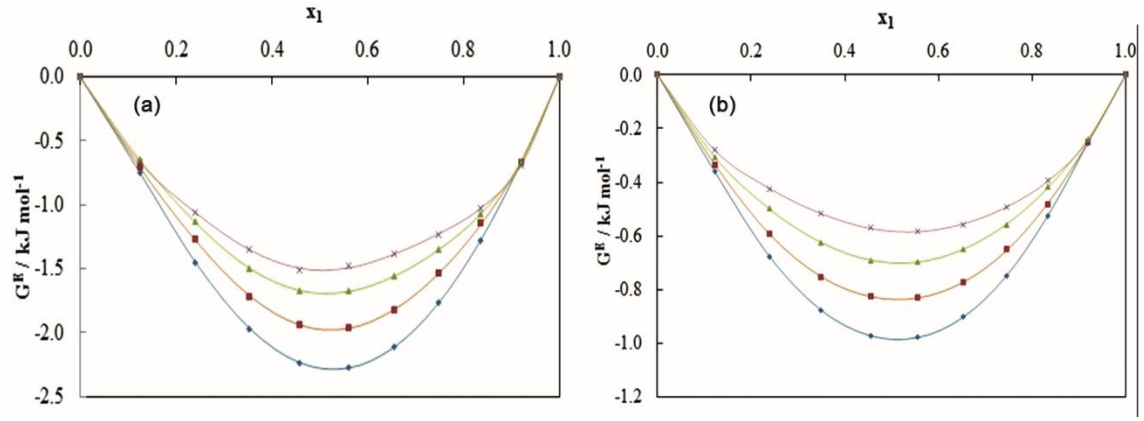

Fig. 5 — Variation of excess free energy, G^E with mole fraction of 1,4-butanediol for the binary mixture (a) 1,4-butanediol + α-picoline and (b) 1,4-butanediol + β-picoline at temperatures: 303.15 K (♦), 308.15 K (■), 313.15 K (▲) and 318.15 K (x).

interactions between the solvent molecules and 1,4-BD and are dominant over the ion-dipole interaction between unlike molecules.

From Fig. 4 (a, b) the T_s^E values are observed to be negative for the two binary mixtures at all the temperatures studied. The negative T_s^E values of the mixtures further support the conclusions drawn from the π_i^E and V_f^E values, that the formation of hydrogen bonding between 1,4-BD ions and picoline molecules leads to closer packing of molecules, resulting in a contraction in volume. This leads to a decrease in the entropy of the mixture resulting in negative T_s^E values.

The G^E values are observed to be negative for the two binary mixtures at all the temperatures studied (Fig. 5 (a, b)). It can also be observed from the same figures that with the increase in temperature, the G^E values are decreased. The negative values of G^E may be attributed to effective geometrical packing effect.

4 Conclusions

In this paper, densities, and speeds of sound of binary mixtures of 1,4-butanediol with α-picoline and β-picoline along with those of pure liquids at temperatures T = 303.15 to 318.15 K at the atmospheric pressure 0.1 MPa, have been reported. Values of the excess internal pressure (π_i^E), excess free volume (V_f^E), excess enthalpy (H^E), excess free energy (G^E) and excess entropy (T_s^E) were obtained from experimentally measured values of densities and speeds of sound. Values of V_f^E, H^E, G^E and T_s^E are negative and become less negative with increase in temperature. The overall negative behaviour of V_f^E, H^E, G^E and T_s^E may be attributed to strong dipole-dipole interaction and easy accommodation of picolines in the voids of 1,4-butanediol molecule.

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