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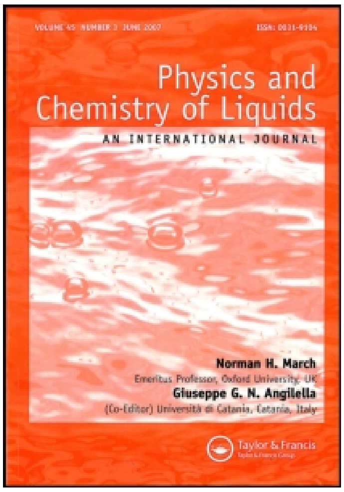

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Prediction of Heat of Mixing from Internal Pressure Data

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PREDICTION OF HEAT OF MIXING FROM INTERNAL PRESSURE DATA

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Excess enthalpies (H_m^E) and excess heat capacities (C_p^E) of three binary liquid mixtures comprising dimethylformamide, acetonitrile and benzene have been evaluated from internal pressure data obtained from three different approaches. The results obtained have been compared with the experimental H_m^E and C_p^E values determined by Miyanaga *et al.* [1]. H_m^E values evaluated through density, viscosity and ultrasonic velocity data [2] show anomalous behaviour. A critical review has been given.

Keywords: Binary liquid mixtures; Internal pressure; Excess enthalpy; Excess heat capacity at constant pressure

INTRODUCTION

In recent years, importance of studies of excess internal pressure and enthalpy in understanding the molecular processes and interactions have been carried out by several workers [3–7]. Recently [8, 9] it has been reported that excess enthalpies H_m^E of ternary liquids mixtures can be established from viscosity data using internal pressure relations [2]. It has been claimed that excess enthalpy value deduced from internal pressure obtained with the help of viscosity and ultrasonic velocity are accurate, and may be treated as experimental H_m^E values. Further, these values were obtained from Flory's statistical theory to

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check the validity of Flory's theory [8]. The validity of Flory's theory has been critically examined and tested by several workers over the past few years [10]. Whereas, no mention of these investigators was made in those papers [8, 9]. Experimentally, H_m^E, is obtained using calorimetric technique. The values obtained *via* internal pressure data should not be claimed as experimental values.

The aim of the present investigation is to evaluate the excess molar enthalpies (H_m^E) and excess molar heat capacities at constant pressure (C_P^E) in binary liquid mixtures of acetonitrile (AN), dimethylformamide (DMF) and benzene at 298.15 K using internal pressure values. Further, internal pressure values have been obtained employing three different approaches. The results obtained are interesting and have been compared with the experimental H_m^E values determined by Miyanaga *et al.* [1]. Furthermore, these values have been compared with the values obtained through viscosity, ultrasonic velocity and internal pressure relationship [2]. The values obtained by viscosity are found to be quite anomalous. Suitable explanations have been given.

EXPERIMENTAL METHOD

Benzene and DMF (BDH AR grade) were fractionally distilled, whereas AN we used without further purification. The viscosity of aforementioned liquids were measured at the temperature of 298.15 K by employing a Ubbelhode viscometer with the temperature of the water bath controlled within ±0.01°C. The accuracy in viscosity measurements was found to be ±0.016%.

THEORETICAL

Thermodynamically, the isothermal internal energy divided by the molar volume coefficient of real fluids measure the internal pressure (P_{in}), *i.e.*,

$$P_{in} = (\partial U/\partial V)_T \tag{1}$$

From thermodynamic equation of state and making use of reciprocity theorem,

$$P_{in} = \frac{\alpha \cdot T}{\beta_T} - P \qquad (2)$$

where α is the coefficient of thermal expansion, T the absolute temperature, β_T the isothermal compressibility and P is external pressure. At zero pressure, above equation reduces to

$$P_{in} = (\alpha \cdot T/\beta_T) \qquad (3)$$

An alternative method for evaluation of internal pressure was suggested by Suryanarayana [2] from the knowledge of ultrasonic velocity, density and viscosity. Suryanarayana emphasized that for a liquid, its state is defined by its internal pressure, P_{in}, free volume, V_f, and temperature T and gave the following relation,

$$P_{in} = bRT(k\eta/u)^{1/2} \cdot (\rho^{2/3}/M^{7/6}) \qquad (4)$$

Where b is the packing factor, k a dimensionless constant having a value of 4.28×10^9 and independent of temperature and nature of the liquid, R, T ρ and u have their usual meaning.

Recently, Pandey *et al.* [11] have proposed an empirical relationship for computation of internal pressure as

$$P_{in} = 44.2 \cdot T^{4/3} \cdot u^{3/2} \cdot \rho \qquad (5)$$

Uniqueness of the above equation is that the internal pressure of a liquid system can be computed directly from experimental data of density and ultrasonic velocity.

Furthermore, excess enthalpy (H_m^E) and excess heat capacity (C_P^E) have been computed by employing the values of internal pressure obtained from various means. Patterson *et al.* [12] reported the H_m^E and C_P^E values for chloronapthalene + linear or branched alkanes and recently for cyclohexane mixtures with globular alkanes [4] and found that mixing functions $\Delta(\gamma VT)$, deviated from equality $\Delta(\gamma VT) = -\Delta H^E$ as predicted by Flory theory and other theories which assumed van der Waals behaviour. For van der Waals type of liquids, change during mixing process of (γVT) can be obtained by thermodynamic equation of state.

$$
\begin{aligned}
&(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P \\
&\text{if } P \cong 0 \text{ then, } -\Delta(P_{in} \cdot V) = H^E
\end{aligned}
\tag{6}
$$

where V is the molar volume and other symbols have their usual meaning. The excess heat capacity, C_P^E, is given by,

$$\Delta C_V = C_P^E - \Delta(\alpha\gamma VT) \tag{7}$$

where the symbols have their usual meaning. In the Flory theory, $\Delta(\alpha\gamma VT)$ may be used, but ΔC_V is set to zero so that,

$$C_P^E = \Delta(\alpha\gamma VT) \tag{8}$$

As in other theories of smoothed potential types.

In terms of internal pressure, above equation can be expressed as

$$C_P^E = \Delta(\alpha P_{in} V) \tag{9}$$

RESULTS AND DISCUSSION

The estimated values of excess enthalpy, and excess molar heat capacity of three binary systems under investigation, *viz.*, x_1(acetonitrile) AN + x_2 benzene; x_1 benzene + x_2 (dimethylformamide) DMF and x_1 (acetonitrile) AN + x_2 (dimethylformamide) DMF have been reported in Tables I, II and III respectively. These values have been denoted by H_1^E, H_2^E, H_3^E, C_{P1}^E, C_{P2}^E and C_{P3}^E respectively. In addition, viscosities of the aforementioned binary liquid mixtures have been experimentally measured at different compositions of constituent liquids. These values are plotted graphically to find out the viscosity data at required mole fractions of the binary mixtures and reported along with the values of H^E and C_P^E in the respective tables. Experimental values of density and ultrasonic velocity have been taken from literature [3]. Internal pressure has been computed by making use of the Eqs. (3)–(6) and (9) respectively.

TABLE I Experimental value of viscosity and calculated values of excess enthalpy and excess heat capacity at constant pressure for the binary system acetonitrile (x_1) + benzene at 298.15 K

x_1	$\eta \times 10^3$ (Nsm^{-2})	H_1^E (J/mol)	H_2^E (J/mol)	H_3^E (J/mol)	C_{P1}^E ($J/Kmol$)	C_{P2}^E ($J/Kmol$)	C_{P3}^E ($J/Kmol$)
0.0000	0.5961						
0.0325	0.5825	−98.510	237.500	−68.08	0.1293	−0.3297	0.1247
0.0416	0.5745	−188.33	406.100	−860.12	0.1456	−0.5587	0.1486
0.1420	0.5155	−265.64	1417.47	−196.33	0.3347	−1.9400	0.3915
0.2578	0.4835	−267.32	1454.31	−202.35	0.3191	−2.1464	0.4924
0.3588	0.4590	−257.72	1373.16	−182.29	0.3470	−2.1001	0.5953
0.4751	0.4295	−176.54	1313.40	−108.85	0.2523	−2.0943	0.6272
0.5786	0.3940	−95.740	1628.20	−40.270	0.1467	−2.5380	0.5965
0.6908	0.3750	−16.000	1231.50	24.620	0.0450	−2.0137	0.5903
0.7901	0.3690	−99.000	416.590	53.190	−0.2787	−1.1145	0.4581
0.8962	0.3455	15.520	263.560	50.260	0.0674	−0.4405	0.7188
0.7943	0.3235	17.320	365.910	15.860	−0.0207	−0.5665	0.7176
1.0000	0.3150						
0.0341	0.5800	−93.970	297.67	−68.730	0.1098	−0.4208	0.1140
0.0854	0.5740	−202.92	65.620	−145.27	0.2620	−0.1852	0.2772
0.2097	0.4930	−304.00	4570.17	−222.33	0.3996	−2.1986	0.5050
0.3076	0.4790	−278.06	1157.74	−200.81	0.3667	−1.7886	0.5679
0.4192	0.4365	−219.47	1601.00	−148.86	0.3011	−2.4335	0.6070
0.5205	0.4045	−147.64	1803.70	−82.050	0.2071	−2.7479	0.6057
0.6344	0.3880	−56.620	1294.72	−05.190	0.1038	−2.1002	0.5975
0.7377	0.3790	7.500	571.570	38.810	0.0099	−1.1296	0.5964
0.8416	0.3535	44.040	511.350	55.480	−0.1458	−0.9618	0.6230
0.9472	0.3275	27.000	489.900	28.490	−0.0250	−0.7682	0.6998

TABLE II Experimental values of viscosity and calculated values of excess enthalpy and excess molar heat capacity at constant pressure for the binary system benzene (x_1) + dimethylformamide ($1 - x_1$) at 298.15 K

x_1	$\eta \times 10^3$ (Nsm^{-2})	H_1^E (J/mol)	H_2^E (J/mol)	H_3^E (J/mol)	C_{P1}^E ($J/Kmol$)	C_{P2}^E ($J/Kmol$)	C_{P3}^E ($J/Kmol$)
0.0000	0.8020						
0.0257	0.7990	−292.000	2741.66	−6943.21	0.0262	−1.4421	3.9828
0.1031	0.7830	−1230.93	895.580	−6490.24	0.3662	0.1161	4.1573
0.2083	0.7590	−2159.84	854.660	−5851.36	0.8233	0.6197	4.2412
0.3129	0.7455	−2750.92	822.920	−5189.95	1.2638	0.9550	4.1948
0.4202	0.7250	−3046.01	718.110	−4509.13	1.6154	1.1683	4.0018
0.5167	0.7175	−3041.33	627.320	−3848.01	1.7990	1.2285	3.6840
0.6247	0.6970	−2802.27	536.210	−3097.20	1.8499	1.1373	3.1956
0.7167	0.6710	−2375.80	454.300	−2392.32	1.7032	0.9534	2.6197
0.8262	0.6430	−1663.40	288.620	−1525.85	1.3053	0.6719	1.7771
0.9372	0.6150	−681.490	101.800	−570.150	0.5887	0.2862	0.7088
0.9761	0.6050	−268.030	40.4600	−216.730	0.2353	0.1087	0.2725
1.0000	0.5961						
0.0509	0.7950	−638.900	807.36	−6805.50	0.1518	−0.1378	4.0655
0.1578	0.7650	−1752.07	879.62	−6159.85	0.5949	0.3903	4.2120

TABLE II (Continued)

x_1	$\eta \times 10^3$ (Nsm^{-2})	H_1^E (J/mol)	H_2^E (J/mol)	H_3^E (J/mol)	C_{P1}^E $(J/Kmol)$	C_{P2}^E $(J/Kmol)$	C_{P3}^E $(J/Kmol)$
0.2579	0.7500	−2484.00	841.18	−5542.90	1.0437	0.8006	4.2401
0.3651	0.7390	2981.08	760.45	−4857.38	1.4308	1.0769	4.1051
0.4690	0.7110	−3074.73	671.50	−4174.66	1.7352	1.2244	3.8626
0.5779	0.7000	−2928.21	576.07	−3417.61	1.8439	1.1960	3.4186
0.6758	0.6825	2586.07	488.57	−2703.21	1.7982	1.0613	2.8948
0.7855	0.6530	−1957.25	360.77	−1853.17	1.4915	0.7853	2.1161
0.8944	0.6255	−1101.07	185.94	−954.540	0.9226	0.4405	1.1599
0.9409	0.6140	−647.410	98.680	−538.830	0.5657	0.2709	0.6746

TABLE III Experimental values of viscosity and calculated values of excess enthalpy and excess heat capacity for the binary system acetonitrile (x_1)+dimethylformamide $(1-x_1)$ at 298.15 K

x_1	$\eta \times 10^3$ (Nsm^{-2})	H_1^E (J/mol)	H_2^E (J/mol)	H_2^E (J/mol)	C_{P1}^E $(J/Kmol)$	C_{P2}^E $(J/Kmol)$	C_{P3}^E $(J/Kmol)$
0.0000	0.8020						
0.0113	0.7940	−168.420	1039.61	−7000.99	0.1140	−0.5279	4.0595
0.1030	0.7470	−825.400	1027.49	−6175.36	0.2820	−0.7797	4.0918
0.2044	0.6850	−1424.45	1056.63	−5315.14	0.5302	−1.0216	4.0811
0.3131	0.6150	−1816.11	993.310	−4398.83	0.7422	−1.1956	3.9177
0.3798	0.6030	−1968.56	989.560	−3874.84	0.8671	−1.3026	3.7712
0.5317	0.5290	−2010.99	1103.64	−2733.63	1.0395	−1.5968	3.2434
0.6348	0.4480	−1843.38	1270.19	−2037.29	1.0676	−1.8434	2.7574
0.7430	0.4080	−1473.65	1463.53	−1348.81	0.9438	−2.1115	2.0943
0.8453	0.3820	−987.340	1812.38	−766.600	0.6999	−2.5392	1.3564
0.9485	0.3460	−362.970	2381.75	−239.690	0.2855	−3.2687	0.2841
0.9723	0.3330	−204.500	2560.59	−131.220	0.1674	−3.5109	0.2697
1.0000	0.3150						
0.0144	0.7920	−219.650	1035.67	−6979.42	0.1498	−0.5094	4.0879
0.0841	0.7610	−733.650	1020.23	−6343.11	0.2894	−0.6849	4.1251
0.1527	0.7120	−1176.81	1022.39	−5746.78	0.4561	−0.8407	4.1382
0.2682	0.6540	−1708.20	1010.91	−4786.12	0.6930	−1.1014	4.0280
0.3696	0.5980	−1976.89	1031.56	−3963.94	0.8877	−1.2943	3.8252
0.4759	0.5520	−2053.51	1081.11	−3148.10	1.0138	−1.5022	3.4810
0.5759	0.4920	−1969.68	1186.92	−2433.04	1.0801	−1.7059	3.0610
0.6876	0.4990	−1671.59	1325.71	−1682.28	1.0107	−1.9381	2.4376
0.7906	0.3820	−1267.72	1598.01	−1071.51	0.8568	−2.2709	1.7710
0.8954	0.3450	−702.240	2046.00	−501.770	0.5308	−2.8215	0.9537

H_m^E and C_P^E for the Binary System x_1 AN + $(1-x_1)$ Benzene

Negative/positive values of H_1^E and H_3^E at low/high concentrations are observed. H_2^E values, on the other hand, exhibit positive values, in which P_{in} has been evaluated by making use of Suryanarayana's relation (Eq. (4)). However, C_{P1}^E and C_{P3}^E of this system change the sign from positive to negative with increase in concentration of AN. Recently [1] Miyanaga *et al.*, have reported positive values of H^E for this system over a different composition range. The excess partial molar enthalpy of AN at infinite dilution is smaller than that of benzene thereby suggesting that the antiparallel dipolar pair of AN molecules is not cleaved even in the dilution mixture. Furthermore, the AN-dimer which cancels dipole moment by antiparallel molecular interactions behaves in the benzene mixture as if it were a non-polar molecule. Futhermore, previously reported values [1] indicate that the dipole moments of the dipolar interactions break down in the mixtures, and on the other hand, a new stable molecular interaction between benzene and a dipolar molecule must be formed resulting in negative effect on H^E and C_P^E changes its sign from negative to positive with increase in AN concentration. However, the positive values of C_P^E in the benzene mixture imply non-random mixing [4] and predict a novel arrangement of benzene and dipolar molecules in the mixture.

H_m^E and C_P^E for the Binary System x_1 Benzene + $(1-x_1)$ DMF

Perusal of Table II indicates positive values of H_1^E and H_3^E and negative values over the entire composition range. All the three excess molar heat capacities, *viz.*, C_{P1}^E, C_{P2}^E and C_{P3}^E are found to be positive over the entire composition range. Previously [1] reported values of H^E for the system were anomalous and were found to be $15-30$ KJ mol^{-1} over the entire mole fraction range, thereby suggesting that exothermic interactions which produces a new associated structure between DMF molecules and benzene cancel the endothermic effect due to the breaking of dipolar interactions of DMF molecules by mixing with benzene, as in the AN+benzene system. The smaller endothermic effect in the benzene+DMF system as compared to AN+benzene may be attributed to random orientation of DMF molecules in the pure state on contrary to the antiparallel orientations of AN molecules.

Mixing changes of first and second order and particularly of second order thermodynamic quantities like thermal expansion coefficient α, isothermal compressibility β_T, *etc.*, and heat capacities C_P and C_V constitute indicators of structure in pure components and in their mixtures [4]. Structure or order considered as cohesion, lower the H, S and V. As a result, temperature dependence of these quantities, C_P and α, will contain structure contribution of opposite sign to the above, that is they contain positive contribution form structure. By mixing these two components, structure may undergo a net destruction or creation. Perusal of Table III and the values reported therein thus point towards unlike intermolecular interactions between benzene and DMF which is predominant resulting in negative values of H^E.

H^E_m and C^E_P for the Binary System x_1 AN + $(1-x_1)$ DMF System

In the third and final binary liquid mixture undertaken for the present investigation, values of H^E_1 and H^E_3 are found to be negative over the entire composition range, which is found to be in conjunction with the results obtained previously [1]. Perusal of Table III further reveals that two values of excess molar heat capacities C^E_{P1} and C^E_{P3} are positive over the same concentration range while C^E_{P2} is negative over the entire composition range. Previous studies [1] also report similar results of C^E_P and may be considered as resultant of three contributions. One is negative contribution resulting from further formation of CH_3CN-$HCON(CH_3)_2$ pairs at higher temperature, second a positive contribution resulting from the AN dimer as dilutent being left unbroken at extremely high x_1 and an AN molecule disturbs the random orientation of DMF molecules in pure state at extremely low x_1 and causes DMF to rearrange in some ordered arrangement. Previously reported values of V^E, β^E_S and β^E_T are found to be negative for this system which suggests the formation of molecular interactions between AN and DMF which are also consistent with the results of X-ray diffraction and previously predicted values of H^E. Thus we can make a reasonable consideration that unlike intermolecular interactions between AN and DMF is dominantly formed thereby giving negative values of H^E. Furthermore, dipole moments of DMF and AN are almost equal. According to X-ray analysis [3], the spread out DMF molecules orient randomly in the pure liquid while the simple shaped AN molecules arrange their dipoles in antiparallel pairs in the pure liquid.

Further studies conducted by one of the authors (R.D.) brings us to the conclusion that with increase in mole fraction of first component, deviations from ideality in values of internal pressure are observed and are maximum in the vicinity of equimolar concentrations, and then there is again a shift towards ideality with the shift from equimolar region. In addition, it was also observed that values of excess internal pressure, P_{in}^{E}, are found to be positive in all the three cases.

Literature values [13, 14] for CH_3CN $(x_1)+C_6H_6$ $(1-x_1)$ and C_6H_6 (x_1) + $HCON(CH_3)_2$ $(1-x_1)$ shows that the values of H_m^E, *i.e.*, excess enthalpy for the aformentioned binary mixtures are small, which suggests the dipole moments of the polar components are considerable and the dipole interactions break down in the mixtures, and, on the other hand a new stable molecular interaction between benzene and dipolar molecules must be formed, resulting in negative effect in H_m^E. The values of positive C_P^E in benzene rich mixture suggests a new arrangement of benzene and dipolar molecules in the mixture.

Thus we find that there is a decrease in strength of interaction from acetonitrile to dimethylformamide when they interact with benzene. During his investigation work, Rajendran has evaluated the excess enthalpy by employing Suryanarayana's relation which he has considered as experimental value in the light of these findings he has tried to establish the validity of Flory's statistical theory to calculate excess enthalpy. Flory's theory has been found to be valid on the basis of the work carried out by several investigators, hence checking its validity seems to be highly inappropriate especially in light of Suryanarayana's relation whose validity is yet to be established, as is evident from this present investigation.

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