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Excess Molar Enthalpies of Dibromomethane with Benzene, Methanol, Dimethylsulfoxide, and Pyrrolidin-2-one at 303.15 K

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Excess molar enthalpies at 303.15 K have been determined for dibromomethane (DBM) with benzene, methanol, dimethylsulfoxide, and pyrrolidin-2-one. The excess molar enthalpies for DBM + benzene and + methanol are endothermic whereas exothermic for the system DBM + dimethylsulfoxide and + pyrrolidin-2-one. These results indicate the existence of specific interactions of DBM with all these compounds.

Introduction

In the investigation of intermolecular interactions between molecules having different functional groups and of the effect of structure on them, we have studied the effect of different proton acceptor and donor groups on the strength of hydrogen bonding.[1−5]

The investigation of thermodynamic properties have been extensively used to understand the molecular interactions between the components of the mixture, to develop new theoretical models, and also for engineering applications in the process industry.

In the present work, we studied the interactions between dibromomethane with benzene, hydro (methanol), S═O, and −NH−CO− groups. The study of benzene, methanol, dimethylsulfoxide, and pyrrolidin-2-one is of interest, not only because the compounds are of industrial importance, but also because their interactions are more pronounced, actually making them better solvents. For example, methanol is used as a solvent in paints, varnishes, and chiefly for making formaldehyde, which in turn is used as a preservative for biological specimens and for making synthetic resins. It is also used for denaturing ethyl alcohol, that is, to make it unfit for drinking purposes, called as methylated spirit. Today benzene is used as an intermediate to make other chemicals. Its most widely produced derivatives include styrene, which is used to make polymers and plastics, and phenol for resins and adhesives. Dimethylsulfoxide is used as topical analgesic, as an anti-inflammatory, and an antioxidant. Because dimethylsulfoxide increases the rate of absorption of some compounds through organic tissues including skin, it can be used as a drug delivery system. It is frequently compounded with antifungal medications, enabling them to penetrate not just skin but also toe and fingernails. It dissolves a variety of organic substances including carbohydrate, polymers, peptides, as well as many inorganic salts and gases. Dibromomethane is naturally produced by marine algae and liberated to the oceans. It is used as a fumigant for soils, grains, and fruits. It is also used as a solvent and as an intermediate in the chemical industry.

These systems were selected in order to find out the effect of π-electrons of a ring (benzene), and also to establish effect of hydroxyl oxygen (methanol), oxygen of S═O and oxygen of −NH−CO− groups of cyclic amides (lactams).

The compound γ-butyrolactum ($n = 5$), pyrrolidin-2-one, has generated special interest because the amide group is a structural part of peptides, polypeptides, and proteins and the nitrogen and carbon of a peptide bond are linked by a ring composed of methylene groups. We report here excess molar enthalpies of dibromomethane (CH_2Br_2) (DBM) with benzene, methanol, dimethylsulfoxide, and pyrrolidin-2-one at 303.15 K. No literature values could be found for comparison at 303.15 K. As far as we know, the only previous measurements on these mixtures are those of Singh et al.[6] for DBM + methanol at 298.15 K and 308.15 K, Singh et al.[7] and Blanco et al.[8] at 298.15 K for DBM + benzene, and of Jambdon et al.[9] and Joly et al.[10] at 308.15 K and 298.15 K for DBM + dimethylsulfoxide. Binary systems of CH_2Br_2 with all these compounds are of considerable interest due to the occurrence of specific interactions between these components. This is caused by the presence of two Br and two H atoms in CH_2Br_2, which can thus act as a σ-acceptor toward, and be involved in the hydrogen bond formation with methanol, dimethylsulfoxide, and pyrrolidin-2-one. Latter will act as n-donors. Benzene in their interaction with DBM will act as π-donor. The results obtained have also been interpreted in this paper.

Experimental Section

Benzene (B.D.H.) and methanol (A.R.) were purified in a manner similar to that described earlier.[1,11] Dibromomethane (Fluka) was further purified by fractional distillation and the constant middle fraction was used for the experiment. Dimethyl sulfoxide (B.D.H.) and pyrrolidin-2-one (Fluka) were purified as described earlier.[2,11] The chemicals were specified to have a minimum purity of 99.7 mol %. All the compounds were dried over freshly activated molecular sieve before use.

Method. Excess molar enthalpies, H^E, were measured in a heat flux microcalorimeter[5] (C-80 model from Setaram, France), whose temperature was controlled to within ± 0.001 K.[12,13] The uncertainties in pressure measurement was ± 5 %. The solutions were prepared by mass. Possible uncertainties in the mole fractions are ± 0.0001.[13] The precision of the analytical balance used to prepare solutions was 0.0001 g. The reliability of the microcalorimeter was checked by measuring H^E at 303.15 K for cyclohexane + hexane for which values are accurately known from the literature.[14] Possible uncertainties in the

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Table 1. Excess Molar Enthalpies of Dibromomethane (CH_2Br_2) (1) with Benzene (2), Methanol (2), Dimethylsulfoxide (2), and Pyrrolidin-2-one (2) at 303.15 K

x_1	$H^E/(J \cdot mol^{-1})$
Dibromomethane (1) + Methanol (2)	
0.1506	181
0.2779	409
0.3148	472
0.4026	577
0.5040	639
0.6195	709
0.7224	782
0.9210	645
0.9515	466
0.9781	244
Dibromomethane (1) + Benzene (2)	
0.0931	40
0.2530	82
0.3416	101
0.4618	119
0.5464	133
0.6705	130
0.7405	127
0.8394	99
0.9506	41
Dibromomethane (1) + Dimethylsulfoxide (2)	
0.0620	−212
0.1162	358
0.2682	−733
0.3407	−840
0.4342	−949
0.5251	−1011
0.5030	−1005
0.6466	−952
0.7285	−846
0.8234	−638
0.8934	−433
Dibromomethane (1) + Pyrrolidin-2-one (2)	
0.0955	−384
0.1510	−560
0.2158	−742
0.2999	−905
0.4044	−1030
0.5247	−1008
0.6130	−922
0.7203	−726
0.7913	−533
0.8401	−405
0.9084	−212

experimental values of this work are estimated to be about 1% over most of the mole fraction range.

Results and Discussions

Excess molar enthalpies, H^E, for various systems are summarized in Table 1. They were fitted by least-squares to the equation

$$H^E/(J \cdot mol^{-1}) = x_1 x_2 \sum_{i=0}^{m} A_i (x_1 - x_2)^i \qquad (1)$$

where x_1 refers to the mole fraction of DBM. The least-squares parameters along with the standard deviations, σ, are reported in Table 2. The standard deviations, σ, are calculated using equation

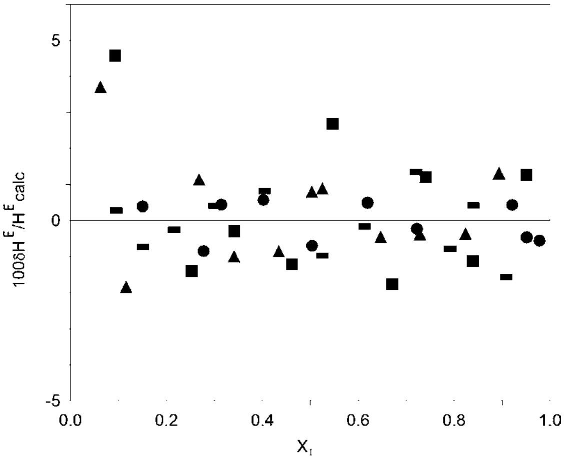

Figure 1. Fractional deviations $\delta H^E = H^E(\text{exptl}) - H^E(\text{calc})$ of the experimental excess molar enthalpy $H^E(\text{exptl})$ of dibromomethane + benzene, ■; + methanol, ●; + dimethylsulfoxide, ▲; and + pyrrolidin-2-one, ■, at 303.15 K from values $H^E(\text{calc})$ obtained with the Redlich−Kister equation.

$$\sigma = [\Sigma(H^E - H^E_{cacl})^2/(m - n)]^{1/2} \qquad (2)$$

where H^E is experimental excess enthalpy and H^E_{calc} calculated excess enthalpy using eq 1, m is number of experimental data and n is number of constants characteristic of a system. A plot between fractional relative deviation, 100 $\delta H^E/H^E_{calc}$ versus x_1, is shown in Figure 1. The value of fractional deviation is approximately ± 1 % over most of the mole fraction range in all systems. The relative deviation of excess enthalpy value reported for DBM + benzene and + methanol differ significantly (from 4 % to 5 %) for dilute region of dibromomethane as shown in Figure 1. This may be due to volatile impurities present in methanol and benzene and also error in pressure measurement. Graphical presentations of experimental values of H^E data are presented in Figure 2.

The excess enthalpy results from the disruption of interactions between like molecules and the introduction of new interactions between unlike molecules. The values of H^E for the system DBM + benzene and + methanol is positive whereas it is negative for DBM + dimethylsulfoxide and + pyrrolidin-2-one. The values of excess molar enthalpies for the benzene and methanol system are also positive over the entire composition range in the literature.[6−8] For DBM + methanol system, maximum occurs at around $x_1 = 0.75$; the same trend was also observed at 298.15 K in the literature.[6]

Methanol is known to be extremely self-associated through hydrogen-bonding in the pure liquid state[15] with the value of H^E shown as a maximum at $x_1 \approx 0.75$; this might be due to breaking of H-bonds in alcohol, as the alcohol rich mixtures are less endothermic. There is also a possibility of existence of specific interactions between Br of DBM and OH of methanol.

For the system DBM + benzene, the values of H^E are less endothermic. Benzene molecules themselves interact through

Table 2. Least Squares Coefficients of Equation 1 for the Excess Molar Enthalpies, and the Standard Deviations, σ, of Dibromomethane + Methanol, + Benzene, + Dimethylsulfoxide, and + Pyrrolidin-2-one at 303.15 K

system	*A*0	*A*1	*A*2	*A*3	*A*4	$\sigma/(J \cdot mol^{-1})$
dibromomethane (1) + methanol (2)	2565.4	1068.9	1664	5153.3	2223.5	5.1
dibromomethane (1) + benzene (2)	500.4	221.1	200.1			2.6
dibromomethane (1) + dimethylsulfoxide (2)	−3985	−680.4	−50.9	130.2		10.1
dibromomethane (1) + pyrrolidin-2-one (2)	−4122.0	780.8	914.5	525.3		8.1

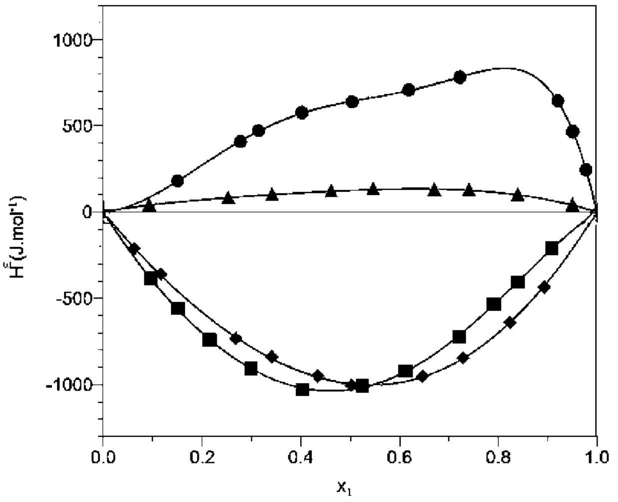

Figure 2. Excess molar enthalpies of binary liquid mixtures of x_1 dibromomethane + x_2 methanol, ●; + x_2 benzene, ▲; + x_2 dimethylsulfoxide, ◆; + x_2 pyrrolidinone-2−one, ■, calculated values from eq 1 (−) at 303.15 K.

π-orbitals of adjacent molecules leading to ordering in the pure liquid state. Thus when DBM and benzene are mixed, both dipole−dipole and $\pi-\pi$ interactions are disrupted. This makes a positive contribution to the values of H^E. There is also formation of charge transfer complex via Br−π electron interaction.The excess enthalpy effect for the system formed by DBM + benzene is rather small in comparison to the DBM + methanol. This is probably the consequence of dissociation of DBM and benzene and association between the unlike molecules. The contribution of dissociation to H^E is in this case dominant over association. Therefore, the total excess enthalpy is weakly endothermic.

The values of H^E are highly negative for DBM + dimethylsulfoxide system. Jambdon et al.[9] and Joly et al.[10] also studied this system at 308.15 K and 298.15 K, respectively, and their values are also negative over the whole composition range. In the pure ketone, there is dipole−dipole as well as the usual dispersive interactions. The effect of adding a polar second component is primarily to disrupt the dipolar interactions. Dimethylsulfoxide and acetone have same structure except C is replaced by S in dimethylsulfoxide. This S atom possess vacant 3d orbital that enhances interactions. Therefore the values of H^E for DBM + acetone is less exothermic than DBM + dimethylsulfoxide.[16] There is also possibility of complexation between O of dimethylsulfoxide and H atom of DBM resulting in the formation of H-bonds which lead to a large negative values of H^E.

In the case of pyrrolidin-2-one, it has high dipole moment and its molecules are self-associated.[11] It possess the basic (>C═O) and acidic (−NH) groups of the −CO−NH−peptide bond leading to the self-association of pyrrolidin-2-one in the pure liquid state.

The lone pair electrons on the oxygen atom are mainly involved in the specific interaction with hydrogen atom of DBM. The values of H^E is the net result of negative and positive contribution due to breaking of bonds or interactions between similar molecules and from the formation of new bonds. The interaction between ketone and bromocompounds are governed essentially by the saturation of ring. When the ring is saturated as in the pyrrolidin-2-one, the interaction become stronger. It is also in the case of ketones with chloroalkanes.[4,17] The H-bond formation between the carbonyl group of ketone and the H-atom of DBM makes negative contribution to the values of H^E. In this system not only the O---H and O−Br interactions but CH_2 group and Br atom contribute to enthalpy of mixing.

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Literature Cited

(1) Nath, J.; Tripathi, A. D. Binary systems of 1,1,2,2-tetrachloroethane with benzene, toluene *p*-xylene acetone and cyclohexane. Excess Volumes, Ultrasonic Velocities, and Adiabatic Compressibilities at 298.15 and 308.15 K. *J. Chem. Eng. Data* **1983**, *28*, 263–266.
(2) Pathak, G.; Tripathi, A. D.; Pradhan, S. D. The Excess Enthalpies of Mixing of 1,1,2,2,-Tetrachloroethane with Acetone n-Dibutylether, Acetonitrile and Dimethylsulfoxide. *Thermochim. Acta* **1992**, *197*, 329–323.
(3) Chadha, R.; Tripathi, A. D. The Excess Molar Enthalpies of Mixing of 1,1,2,2-Tetrachloroethane with Methylfuran, Tetrahydrofuran, 1, 4-Dioxane, and Cyclopentanone at 308.15 and 318.15 K. *J. Chem. Eng. Data* **1995**, *40*, 645–646.
(4) Pathak, G.; Tripathi, A. D.; Phalgune, U. D.; Pradhan, S. D. Enthalpies of Mixing of Tetrachloroethane with Furan, Methylfuran, Tetrahydrofuran, Cyclopentanone and 1,4,-Dioxane. *Thermochim. acta* **1995**, *258*, 109–115.
(5) Tripathi, A. D. Excess Molar Enthalpies of 1,1,2,2-Tetrachloroethane with Acetone, Dibutyl Ether, Acetonitrile, and Dimethyl-Sulfoxide at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1262–1263.
(6) Singh, P. P.; Sharma, V. K.; Sharma, S. P. Topological studies of the molecular species that characterize lower alkanol + methylene bromide mixtures: molar excess volumes and molar excess enthalpies. *Thermochim. Acta* **1986**, *106*, 293–307.
(7) Blanco, S.; Artal, M.; Fernandez, J.; Munoz Embid, J.; Otin, S. Excess Enthalpies of Dibromoalkane + benzene binary mixtures at 298.15 K. *J. Chem. Eng. Data* **1993**, *38*, 587–588.
(8) Singh, P. P.; Nigam, R. K.; Sharma, V. K. Molar excess volumes and molar excess enthalpies of methylene bromide + aromatic hydrocarbon mixtures. *Fluid Phase Equilib.* **1984**, *18*, 313–31.
(9) Jambdon, C.; Phillippe, R. Correlation of excess thermodynamic properties of binary mixtures application to dimethylsulfoxide + halomethane and hexamethyl phosphotriamide + water. *J. Chem. Thermodyn.* **1975**, *7*, 479–84.
(10) Joly, R. D.; Phillippe, R. Enthalpies of mixing at 25 C of binary dmso + halogenated methane systems. *J. Chim. Phys. Phys.−Chim. Biol.* **1972**, *69*, 783–6.
(11) Mehta, S. K.; Chauhan, R. K.; Tripathi, A. D. Excess molar enthalpies of mixtures of pyrrolidin-2-one with lower alkanols at the temperature 303.15 K. *J. Chem. Thermodyn.* **1997**, *29*, 353–358.
(12) Taylor, B. N.; Kuyatt, C. E.; *Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement results*, NIST Technical Note 1297; NIST: Washington DC, 1994.
(13) Polo, C.; Otin, S.; Guitierrez Losa, C.; Gracia, M. Excess enthalpies and excess volumes of monochloroalkane (C3-C5) mixtures with cyclohexane, benzene, or carbon tetrachloride. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1976**, *2*, 139.
(14) McLure, I. A.; Rodriguez, A. T. Excess functions for (n-alkanenitrile + n-alkane) liquid mixtures 2. Excess enthalpies at 298.15 K for propanenitrile and n-butanenitrile with some C5 to C14 n-alkanes. *J. Chem. Thermodyn.* **1982**, *14*, 439–445.
(15) Pikkarainen, L. Viscosities of Binary Solvent Mixtures of N, N-Diethylmethanesulfonamide with Aliphatic Alcohols. *J. Chem. Eng. Data* **1988**, *33*, 299–301.
(16) Tripathi, A. D. Excess Enthalpies of Dibromomethane with acetone 1, 4-dioxane, pyridine, diethyl ether, ethyl methyl ketone and tetrahydrofuran. *J. Chem. Eng. Data* [Online early access]. DOI: 10.1021/je900547w.
(17) Nath, J.; Tripathi, A. D. Binary systems of 1, 1, 2, 2-tetrachloroethane with benzene, toluene, *p*-xylene, acetone and cyclohexane. Part 2.- Dielectric properties at 308.15 K. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1517–1524.

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