

Excess Enthalpies of Dibromomethane with Acetone, 1,4-Dioxane, Pyridine, Diethyl Ether, Ethyl Methyl Ketone, and Tetrahydrofuran at 303.15 K

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Excess enthalpies H^E at 303.15 K have been determined for binary liquid mixtures of dibromomethane with acetone, 1,4-dioxane, pyridine, diethyl ether, ethyl methyl ketone, and tetrahydrofuran. Values of H^E have been fitted by the method of least-squares to the equation: $H^E = x_1x_2 \sum_{i=0}^m A_i(x_1 - x_2)^i$ where x_1 refers to the mole fraction of dibromomethane and A_i are constants characteristic of the system. The excess enthalpies for all systems are exothermic in nature. The excess enthalpies decrease in the following order: tetrahydrofuran > 1,4-dioxane > diethyl ether > pyridine > acetone > ethyl methyl ketone.

Introduction

The study of dibromomethane, 1,4-dioxane, diethyl ether, pyridine, acetone, ethyl methyl ketone, and tetrahydrofuran is of interest not only because the compounds are of industrial importance but also because their interactions are pronounced, making them better solvents and also useful in day-to-day life. For example, acetone is used as a solvent for acetylene, cellulose acetate, and varnishes. Major use of acetone entails its condensation with phenol to give bisphenol A, which is a component of many polymers such as polycarbonates, polyurethanes, and epoxy resins. Diethyl ether is an industrial solvent for oils, resins, cellulose plastics, and gums, and so forth and is also used as refrigerant and for liquid–liquid extraction. It is a starting fluid for diesel and gasoline engines because of its high volatility and low autoignition temperatures. Ethyl methyl ketone dissolves many substances and is used as a solvent in processes involving gums, resins, cellulose acetate, and nitrocellulose coatings and in vinyl films. For this reason it finds use in the manufacturing of plastics and textiles and in the production of paraffin wax. 1,4-Dioxane is primarily used in solvent applications and as a foaming agent. It may be contained in cosmetics and personal care products such as deodorants, shampoos, toothpastes, and mouthwashes. Tetrahydrofuran is a raw material for the manufacturing of adipic acid and nylon. It is an industrial solvent for polyvinyl chloride (PVC) and in varnishes. It is an aprotic solvent and can dissolve a wide range of nonpolar and polar chemical compounds. It can be used to dissolve rubber using gel permeation technology. It dissolves PVC as well and is the main ingredient in PVC adhesives. It liquefies old PVC cement, and is often used industrially to degrease metal parts. Pyridine is miscible with water and has good solvent action on most of the organic acid and many of the inorganic compounds. It is also used as a denaturant for ethyl alcohol and as a raw material in the preparation of sulphapyridine, a sulphadiazine drug. It is a polar but aprotic solvent. Deuterated pyridine, called pyridine- d_5 , is a common solvent for ^1H NMR spectroscopy. It is also used as a denaturant for antifreeze mixtures, ethyl alcohol, and fungicides and as a dyeing aid for textiles. Dibromomethane is naturally produced by marine algae and liberated in the ocean

and is used as a fumigant for soils, grains, and fruits, as a solvent, and as an intermediate in the chemical industry.

Binary systems of dibromomethane (CH_2Br_2) with n-donor compounds are of considerable interest because of the occurrence of specific interactions in the liquid state. This is caused by the presence of two Br atoms and two H atoms in CH_2Br_2 , which can thus act as σ -acceptors and be involved in the formation of hydrogen bonds with acetone, 1,4-dioxane, pyridine, ethyl methyl ketone, diethyl ether, and tetrahydrofuran. The latter compounds will act as n-donors. These systems were selected to find out the effect of the substitution of the large alkyl group in acetone (ethyl methyl ketone) and the effect of the aliphatic ether and cyclic ethers and also to establish the effect of one oxygen (tetrahydrofuran) or two oxygens (dioxane) in the cyclic ethers. A literature survey revealed that extensive studies on such systems have not been carried out to date. In the present study we report the excess molar enthalpies of dibromomethane with the above-mentioned compounds at 303.15 K, and the results obtained have also been interpreted.

Experimental Section

Dibromomethane (Fluka), 1,4-dioxane (SD Chemicals Analar), and ethyl methyl ketone (BDH, AR) were further purified by fractional distillation, and the constant middle fraction was used for the experiments. Acetone was purified as described earlier.¹ Tetrahydrofuran (E. Merck) was used without further purification. All compounds were dried over freshly activated molecular sieves. Diethyl ether (AR) was further distilled and stored over sodium. Purities of chemicals used are > 99.6 %.

Method

The excess molar enthalpies (H^E) were determined by means of a heat flux microcalorimeter (C-80 model from Setaram, France),² whose temperature was controlled within ± 0.003 K. Experimental details are given elsewhere.³ Mixtures were prepared by mass, and the possible uncertainty in mole fractions is estimated to be less than 10^{-4} . The testing procedure of microcalorimeter for the system benzene and methyl benzene is given in an earlier communication.⁴ The mean deviations of the excess enthalpy are estimated to be about 1 % over most of the mole fraction range. Possible uncertainties in the experi-

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mental values of this work are estimated to be 0.5 % at the equimolar composition.

Results and Discussion

The excess molar enthalpies of dibromomethane with acetone, 1,4-dioxane, methyl ethyl ketone, diethyl ether, pyridine, acetone, and tetrahydrofuran at 303.15 K are given in Table 1. The values of H^E have been fitted by the least-squares method to the equation

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

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

$$\sigma = [\sum (H^E - H_{\text{calc}}^E)^2 / m - n]^{1/2} \quad (2)$$

where H^E is the experimental excess enthalpy and H_{calc}^E the calculated excess enthalpy obtained by using eq 1, m is number of experimental data, and n is the number of constants characteristic of the system. A graphical presentation of experimental values of data is presented in Figure 1.

All six systems show exothermic behavior attributable mainly to specific interactions. Exothermicity showed a marked dependence on the functional group having the order (in absolute values) tetrahydrofuran > 1,4-dioxane > diethyl ether > pyridine > acetone > methyl ethyl ketone. Specific interactions are expected to be in hydrogen bond formation between one or two hydrogen atoms of dibromomethane and lone pair electrons on the oxygen or nitrogen atom of other compounds. H^E values for dibromomethane + acetone are more negative than those for dibromomethane + ethyl methyl ketone, which is in accordance with the electron donor capacity of ketones: acetone is a better proton acceptor than methyl ethyl ketone and forms a stronger complex with dibromomethane. The maximum excess enthalpy for dibromomethane + pyridine ($H^E(\text{max}) = -446 \text{ J} \cdot \text{mol}^{-1}$) is a little higher than that of acetone ($H^E(\text{max}) = -381 \text{ J} \cdot \text{mol}^{-1}$). This may be attributed to the fact that dibromomethane forms a complex with pyridine through H-bonding, and there is also the possibility of formation of a charge transfer complex between Br of dibromomethane and π -electrons of pyridine.

Similarly, Davidson et al.¹⁰ have obtained evidence for the formation of charge transfer complexes between pyridine and CCl_4 . Diethyl ether is a better proton acceptor than pyridine and forms a stronger complex ($H^E(\text{max}) = -504 \text{ J} \cdot \text{mol}^{-1}$). The values of H^E for 1,4-dioxane and tetrahydrofuran are negative. Hydrogen bonded complex formation of chloroform with tetrahydrofuran has been reported in the literature.⁵ The values of H^E for the system dibromomethane + 1,4-dioxane can be discussed from the viewpoint of specific interaction between the H atom of dibromomethane and lone pair electrons on both oxygen atoms of dioxane as it is known that a complex is formed between $\text{CHCl}_2\text{CHCl}_2$ and 1,4-dioxane.² The high negative values of H^E for the system dibromomethane + tetrahydrofuran similarly indicate the presence of strong specific interaction due to hydrogen bonding between one H atom of dibromomethane (A) and lone pair electrons on the oxygen atom of tetrahydrofuran. Where H-bond formation is concerned, dioxane (B) can form more numerous H-bond species of complexes (it can form AB, A_2B , and AB_2 types of complexes) than tetrahydrofuran

Table 1. Excess Molar Enthalpies of Dibromomethane (CH_2Br_2) (1) with Tetrahydrofuran (2), 1,4-Dioxane (2), Diethyl Ether (2), Pyridine (2), Acetone (2), and Ethyl Methyl Ketone (2) at 303.15 K

x_1	H^E
	$\text{J} \cdot \text{mol}^{-1}$
Dibromomethane (1) + Tetrahydrofuran (2)	
0.1215	-559
0.2079	-806
0.2480	-900
0.3173	-1010
0.4033	-1078
0.4942	-1084
0.6375	-974
0.7710	-709
0.8053	-632
0.8739	-434
Dibromomethane (1) + 1,4-Dioxane (2)	
0.0953	-199
0.1526	-311
0.1857	-371
0.3446	-578
0.4358	-628
0.5614	-595
0.6401	-539
0.7512	-384
0.8440	-221
Dibromomethane (1) + Diethyl Ether (2)	
0.1013	-191
0.2043	-353
0.3685	-500
0.4218	-514
0.5570	-477
0.6434	-402
0.6508	-400
0.7096	-322
0.8429	-160
Dibromomethane (1) + Pyridine (2)	
0.0846	-123
0.2331	-314
0.3712	-415
0.4825	-442
0.5788	-436
0.5817	-428
0.6577	-390
0.7271	-326
0.8121	-231
0.8416	-200
0.8823	-149
Dibromomethane (1) + Acetone (2)	
0.0983	-174
0.1828	-268
0.2785	-348
0.3454	-372
0.4410	-386
0.5516	-367
0.6290	-345
0.7501	-281
0.8090	-236
0.9013	-140
Dibromomethane (1) + Ethyl Methyl Ketone (2)	
0.1298	-197
0.2278	-300
0.3652	-361
0.4662	-364
0.5622	-332
0.6035	-312
0.7248	-226
0.8265	-131
0.9132	-63

can owing to the presence of two oxygens. So, from the standpoint of H-bond formation, the 1,4-dioxane system should be more exothermic than the tetrahydrofuran one, but the reverse is observed. Wilhelm et al.^{6,7} studied the heats

Table 2. Least Squares Coefficients of Equation 1 for the Excess Enthalpies of Dibromomethane (1) with Tetrahydrofuran (2), 1,4-Dioxane (2), Diethyl Ether (2), Pyridine (2), Acetone (2), and Ethyl Methyl Ketone (2) at 303.15 K

system	A_0	A_1	A_2	A_3	σ J·mol ⁻¹
dibromomethane (1) + tetrahydrofuran (2)	-4343.65	631.77	-394.29	398.40	6.0
dibromomethane (1) + 1,4-dioxane (2)	-2511.28	483.44	933.41		6.9
dibromomethane (1) + diethyl ether (2)	-2017.82	698.377	745.04		4.3
dibromomethane (1) + pyridine (2)	-1792.78	123.92	444.105		5.2
dibromomethane (1) + acetone (2)	-1523.52	247	-379.62		4.3
dibromomethane (1) + methyl ethyl ketone (2)	-1427.52	595.69	218.74		3.9

of mixing of carboxylic acids with tetrahydrofuran and 1,4-dioxane and found the same interaction trend. This clearly indicates that interactions other than H-bonding play a significant role in the excess enthalpies of these systems.

In all above-mentioned systems, interactions among O–H, O–Br, and CH₂–Br contribute to the excess enthalpies. Williamson and co-workers^{8,9} investigated the ether + CCl₄ and ether + CH₂Cl₂ systems and quantified the relative strengths of O–H and O–Cl systems. To this extent, the assumption made by McGlashan and Rastogi¹¹ that the mixture could be treated as “ideal associated” seems to be valid. These authors have interpreted the free energies and heats of mixing of the system CHCl₃ + dioxane in terms of an ideal mixture of CHCl₃ (A), dioxane (B), and two hydrogen bonded complexes, AB and A₂B.

Conclusions

In conclusion, it is pointed out that the present investigation reveals the existence of electron donor–acceptor interactions, leading to the formation of complexes through hydrogen bonding between the components in the liquid state. Dibromomethane (A) has two equivalent proton donors and can thus form AB type of complexes with acetone or dibutyl ether (B) as described elsewhere for the system of tetrachloroethane + acetone¹² or + ether.² For the system of dibromomethane + pyridine, the AB type of complex formation is reported (cross reference of ref 12). The possibility of the formation of charge transfer complexes via Br– π -electron interaction or of weak hydrogen bond formation via a hydrogen atom and π -electron interaction and of a bond between the hydrogen atom of dibromomethane and the lone pair of electrons on the nitrogen

atom of pyridine is believed to be present as suggested for the system of tetrachloroethane with benzene or toluene in our earlier communication.¹²

Aliphatic ethers are weaker proton acceptors than cyclic ethers. For cyclic ether systems, the interaction of the hydrogen and the Br atom is so dominant that the presence of a functional group, that is, oxygen, does not make any significant difference to the excess enthalpy, though dioxane has two oxygen atoms and only one oxygen atom is present in tetrahydrofuran. In these systems not only the O–H and O–Br interactions but also the interaction between CH₂ groups and Br atoms contribute to excess enthalpy. The high negative values of excess enthalpy for the system of dibromomethane + tetrahydrofuran (in comparison to dioxane) indicate the presence of strong specific interactions. AB- and A₂-type complex formations are believed to be present between dibromomethane (A) and tetrahydrofuran; the same type of complex formations are reported between tetrachloroethane and tetrahydrofuran or dioxane as revealed by NMR study.² The saturation of the ring in cyclic ethers makes it more reactive.

Values of excess enthalpy for dibromomethane + acetone are more negative than dibromomethane + ethyl methyl ketone because as the size of the alkyl group increases, the reactivity of the ketone decreases.

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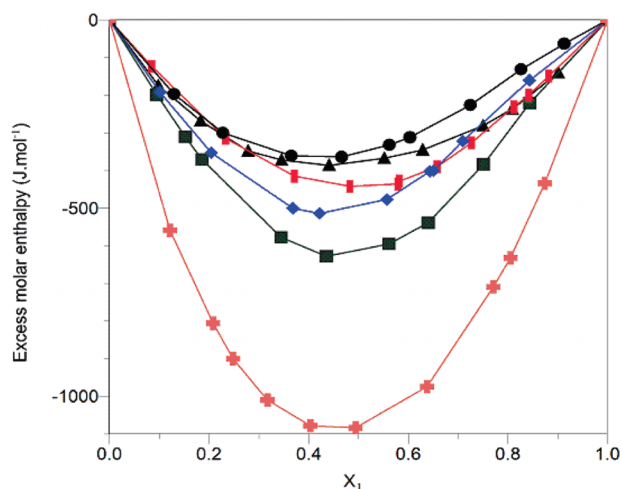


Figure 1. Excess molar enthalpies of binary liquid mixtures of x_1 dibromomethane + the following: black triangle, x_2 acetone; green solid square, x_2 1,4-dioxane; red solid square, x_2 pyridine; blue diamond, x_2 diethyl ether; black solid circle, x_2 ethyl methyl ketone; and pink cross, x_2 tetrahydrofuran; at 303.15 K.

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