Excess Enthalpies of Dibromoalkane + Benzene Binary Mixtures at 298.15 K

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An isobaric and quasi-isothermic calorimeter has been used to determine excess molar enthalpies, H^E, at 298.15 K and atmospheric pressure for seven binary mixtures containing a dibromoalkane (dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, and 1,8-dibromooctane) with benzene. H^E of dibromomethane + benzene is positive, decreases with the chain length of the dibromoalkane, and becomes negative for 1,4-dibromobutane and higher dibromoalkanes + benzene.

Introduction

Following our systematic study of the thermodynamic properties of binary liquid mixtures containing haloalkanes (*1–6*), we present here the experimental molar excess enthalpies H^E at 298.15 K of dibromomethane + benzene and six binary α,ω-dibromoalkane + benzene mixtures. As far as we know, the only previous measurements on these mixtures are those of Singh et al. (*7*) for dibromomethane + benzene, and of Neckel and Volk (*8*), Kalra et al. (*9, 10*), Pérez et al. (*11*), Mahl et al. (*12*), Birdi et al. (*13*), and Spah et al. (*14*) for dibromoethane + benzene. Our results agree satisfactorily with theirs (better than 8 J mol^{-1} at the maximum) except with those by Pérez et al. which are higher than ours (about 40 J mol^{-1} at the maximum at 298.15 K).

Experimental Section

All the α,ω-dibromoalkanes were the same as those used previously (*6*) as well as their physical properties. Dibromomethane was from Fluka AG Buchs (better than 99 mol %), and benzene was from Fluka AG Buchs (better than 99.8 mol %).

Excess molar enthalpies were determined by using an isobaric and quasi-isothermic calorimeter similar to that described in ref 15. Electrical energy was measured to better than 0.5%, and the temperature in the water bath was

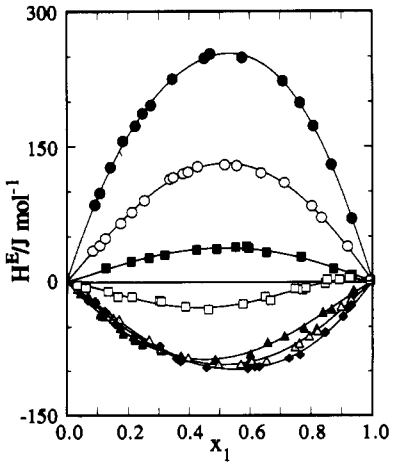

Figure 1. Excess molar enthalpies H^E (298.15 K) of benzene + dibromomethane (○), 1,2-dibromoethane (●), 1,3-dibromopropane (■), 1,4-dibromobutane (□), 1,5-dibromopentane (▲), 1,6-dibromohexane (♦), and 1,8-dibromooctane (△) as a function of the mole fraction x_1 of the α,ω-dibromoalkane.

Table I. Excess Molar Enthalpies H^E at 298.15 K as a Function of the Mole Fraction x_1 of the Dibromoalkane

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
Dibromomethane + Benzene					
0.0843	34	0.3353	114	0.5566	129
0.1071	40	0.3464	116	0.6366	121
0.1247	48	0.3791	120	0.7136	110
0.1746	65	0.3952	122	0.8036	84
0.2106	77	0.4272	128	0.8345	71
0.2519	90	0.5172	130	0.9192	39
1,2-Dibromoethane + Benzene					
0.0902	85	0.2730	196	0.7642	199
0.1067	98	0.3435	225	0.8083	173
0.1409	127	0.4494	248	0.8666	130
0.1813	156	0.4689	253	0.9330	70
0.2218	173	0.5742	249		
0.2457	187	0.7085			
1,3-Dibromopropane + Benzene					
0.1262	15	0.4900	36	0.7680	27
0.2090	22	0.5528	38	0.8738	14
0.2672	26	0.5890	39	0.9345	7
0.3185	29	0.5964	37		
0.4235	35	0.6545	32		
1,4-Dibromobutane + Benzene					
0.0335	−4	0.3870	−28	0.7831	−7
0.0614	−7	0.4625	−31	0.8466	−2
0.1336	−11	0.5770	−25	0.8525	2
0.1654	−17	0.6501	−17	0.8922	2
0.2111	−17	0.6677	−21	0.9254	4
0.3002	−21	0.7489	−8	0.9932	1
0.3067	−22	0.7733	−9		
1,5-Dibromopentane + Benzene					
0.0444	−13	0.2448	−69	0.7769	−51
0.1074	−36	0.3062	−76	0.8389	−34
0.1140	−38	0.3709	−82	0.8675	−31
0.1723	−51	0.4847	−86	0.9322	−14
0.1817	−57	0.6009	−80	0.9389	−10
0.2152	−60	0.6581	−67		
0.2199	−64	0.7142	−60		
1,6-Dibromohexane + Benzene					
0.0692	−20	0.3554	−85	0.7280	−85
0.0908	−22	0.3702	−89	0.7640	−81
0.0923	−24	0.4573	−96	0.8470	−56
0.1235	−33	0.5928	−97	0.9047	−39
0.1567	−47	0.6169	−95	0.9208	−30
0.3021	−71	0.6311	−95	0.9313	−27
1,8-Dibromooctane + Benzene					
0.0345	−8	0.3948	−84	0.7616	−68
0.0691	−17	0.4964	−92	0.7946	−60
0.1383	−38	0.5702	−92	0.8189	−52
0.1510	−41	0.5983	−88	0.8208	−54
0.1691	−42	0.6057	−88	0.8986	−28
0.2667	−64	0.6543	−88	0.9306	−20
0.3043	−74	0.7476	−72		

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Table II. Parameters A_j of Equation 1 for Dibromomethane and α,ω-Dibromoalkane + Benzene and Standard Deviations $\sigma(H^E)$ at 298.15 K

mixture	A_0	A_1	A_2	A_3	A_4	$\sigma(H^E)$/ (J mol^{-1})
benzene +						
dibromomethane	525	49	−85			1.6
1,2-dibromoethane	1010	110	195	−91	−115	2.3
1,3-dibromopropane	54	64	63			1.5
1,4-dibromobutane	−112	62	123			2.3
1,5-dibromopentane	−341	79	58			2.0
1,6-dibromohexane	−388	−84				2.6
1,8-dibromooctane	−370	−38	83			2.0

controlled to within 0.002 K. The estimated errors are $\delta x \leq 0.0002$ and δT(reproducibility) = 0.01 K (*16*). The calorimeter was checked against hexane + cyclohexane, at 298.15 K, the agreement with the data reported (*17*) being better than 0.5% over the central range of concentration.

Results and Discussion

The H^E values are listed in Table I. The composition dependence of H^E was correlated by the polynomial

$$H^E_{calc}/x_1(1-x_1) = \sum A_j(2x_1-1)^{j-1} \quad (1)$$

where x_1 is the mole fraction of dibromoalkane. The A_j parameters were obtained by least-squares analysis and are collected in Table II, together with the standard deviations $\sigma(H^E)$ calculated as

$$\sigma(H^E) = \{\sum (H^E - H^E_{calc})^2/(N-n)\}^{1/2} \quad (2)$$

where N is the total number of measurements and n is the number of coefficients A_j.

The H^E values for dibromomethane, 1,2-dibromoethane, and 1,3-dibromopropane + benzene are positive and decrease with increasing length of the dibromoalkane. For 1,4-dibromobutane + benzene, H^E changes sign and becomes more and more negative with increasing separation between the two bromine atoms in the dibromoalkane. On the other hand, H^E of these mixtures shows a remarkable exothermic effect relative to dibromoalkane + *n*-hexane or + cyclohexane (*1*, *2*) due to the strong Br/C_6H_6 specific interaction.

Glossary

A_j	coefficients in eq 1
H	molar enthalpy, J mol^{-1}
N	total number of measurements
n	number of coefficients A_j
x	mole fraction

Greek Letters

σ	standard deviation, eq 2

Superscripts

E	excess property

Subscripts

calc	calculated property
i	type of component

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