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Excess Molar Enthalpies of Binary Mixtures Containing Mono- and Polybromoalkanes at 298.15 K

Sofía T. Blanco, José Muñoz, Inmaculada Velasco, and Santos Otín*

Departamento de Química Orgánica y Química Física, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain

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An isobaric and quasi-isothermic calorimeter has been used to determine excess molar enthalpies, H_m^E, at 298.15 K and atmospheric pressure for 10 binary mixtures containing dibromomethane, tribromomethane, 1,2-dibromoethane, 1,1,2,2-tetrabromoethane, and 1-bromopropane. H_m^E values for these mixtures are negative except for 1,2-dibromoethane or dibromomethane + 1-bromopropane and 1,1,2,2-tetrabromoethane + tribromomethane.

Introduction

Following our studies on the thermodynamics of binary mixtures containing organic bromine compounds *(1−3)*, we report here the experimental excess molar enthalpies at 298.15 K for the following binary mixtures: tribromomethane + 1,2-dibromoethane, + dibromomethane, or + 1-bromopropane; tetrabromoethane + tribromomethane, + 1,2-dibromoethane, + dibromomethane, or + 1-bromopropane; 1,2-dibromoethane + dibromomethane or + 1-bromopropane; and dibromomethane + 1-bromopropane. As far as we know, the only previous measurements on these mixtures are those of Kiselev et al. *(4)* for tribromomethane + 1,2-dibromoethane. A similar study of H^E of mixtures containing the corresponding mono- and polychloroalkanes was carried out by Muñoz Embid et al. *(5)*.

Experimental Section

The liquids used were dibromomethane, from Fluka AG, Buchs, Switzerland (better than 99 mol %); 1-bromopropane, 1,1,2,2-tetrabromoethane, and 1,2-dibromoethane from Fluka (better than 98 mol %); and tribromomethane from Fluka (better than 97 mol %). Tribromomethane was purified according to a low-pressure distillation method *(6)*.

Table 1. Refractive Index n_D and Density ϱ for the Pure Liquids at 298.15 K and 1 atm

component	n_D (exptl)	n_D (ref 7)	ϱ (exptl)/ (g cm^{-3})	ϱ (ref 7)/ (g cm^{-3})
tribromomethane	1.59476	1.5956	2.8751	2.8758
1,1,2,2-tetrabromoethane	1.63574	1.6323	2.9508	2.9529
1,2-dibromoethane	1.53469	1.5360	2.1687	2.1687
dibromomethane	1.53674	1.5389	2.4778	2.4841
1-bromopropane	1.43692	1.4317	1.3450	1.3452

No further purification was made for the other liquids. Refractive indices and densities of the pure liquids are listed in Table 1 along with other literature values *(7)*.

Excess molar enthalpies were determined by using an isobaric and quasi-isothermic calorimeter similar to that described in ref 8. Electrical energy was measured to better than 0.5%, and the temperature in the water bath was controlled to within 0.002 K. The estimated errors are $\delta x < 0.0002$ and δT (reproducibility) = 0.01 K *(9)*. The calorimeter was checked against hexane + cyclohexane and hexane + tetrachloromethane at 298.15 K, the agreement with the data reported *(10, 11)* being better than 0.5% over the central range of concentration.

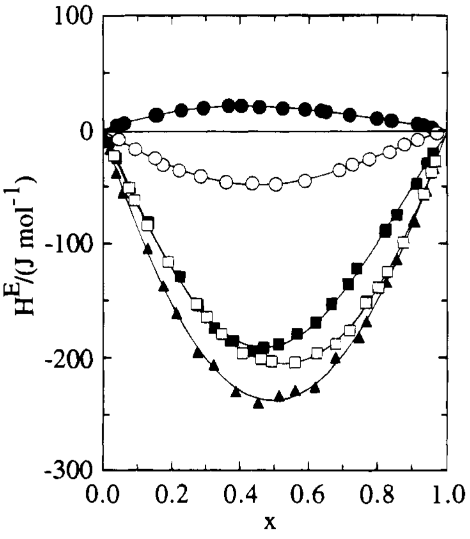

Figure 1. Excess molar enthalpies, H_m^E, for tribromomethane (1) + 1,2-dibromoethane (2) (□), + dibromomethane (2) (○), or + 1-bromopropane (2) (■) and for 1,1,2,2-tetrabromoethane (1) + tribromomethane (2) (●) or + 1,2-dibromoethane (2) (▲) at 298.15 K.

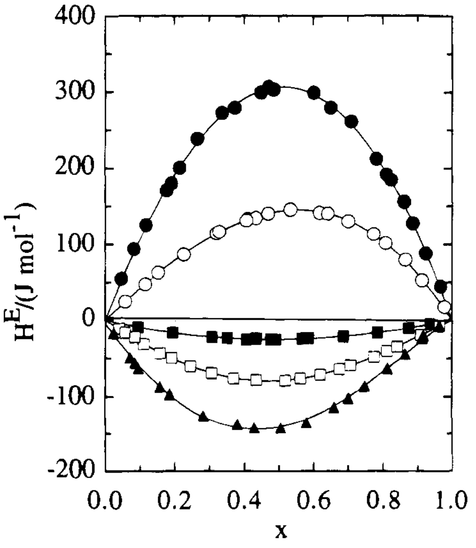

Figure 2. Excess molar enthalpies, H_m^E, for 1,1,2,2-tetrabromoethane (1) + dibromomethane (2) (□) or+ 1-bromopropane (2) (▲), for 1,2-dibromoethane (1) + dibromomethane (2) (■) or + 1-bromopropane (2) (●), and for dibromomethane (1) + 1-bromopropane (2) (○) at 298.15 K.

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Table 2. Excess Molar Enthalpies H_m^E at 298.15 K as a Function of the Mole Fraction x

x	H^E/(J mol^{-1})	x	H^E/(J mol^{-1})	x	H^E/(J mol^{-1})	x	H^E/(J mol^{-1})
xCHBr$_3$ + $(1 - x)$C$_2$H$_4$Br$_2$							
0.0320	−23	0.3018	−164	0.6236	−196	0.8285	−125
0.0746	−51	0.3462	−179	0.6786	−188	0.8745	−99
0.0905	−62	0.4074	−196	0.7192	−176	0.9334	−57
0.1284	−84	0.4610	−201	0.7663	−152	0.9554	−38
0.1895	−116	0.4916	−203	0.7691	−151	0.9672	−28
0.2719	−153	0.5597	−204	0.8017	−139		
xCHBr$_3$ + $(1 - x)$CH$_2$Br$_2$							
0.0454	−8	0.2849	−41	0.6888	−36	0.9158	−9
0.0936	−17	0.3594	−46	0.7274	−31	0.9711	−3
0.1514	−25	0.4357	−47	0.7770	−26		
0.1737	−31	0.5029	−48	0.8354	−20		
0.2216	−36	0.5884	−45	0.8772	−13		
xCHBr$_3$ + $(1 - x)$C$_3$H$_7$Br							
0.0171	−11	0.2780	−154	0.5644	−179	0.8566	−75
0.0402	−25	0.3247	−174	0.6197	−169	0.9131	−48
0.0784	−51	0.3708	−185	0.6660	−153	0.9435	−30
0.1291	−81	0.3803	−185	0.7145	−136	0.9598	−21
0.1320	−82	0.4375	−194	0.7401	−122		
0.2239	−129	0.4690	−191	0.8216	−90		
0.2733	−153	0.5112	−188	0.8245	−88		
xC$_2$H$_2$Br$_4$ + $(1 - x)$CHBr$_3$							
0.0391	4	0.2936	19	0.5888	18	0.8383	8
0.0611	6	0.3670	21	0.6359	17	0.8416	8
0.1512	13	0.4040	21	0.6501	16	0.9149	5
0.1579	13	0.4565	20	0.7194	13	0.9317	4
0.2281	17	0.5232	19	0.7985	10	0.9558	2
xC$_2$H$_2$Br$_4$ + $(1 - x)$C$_2$H$_4$Br$_2$							
0.0208	−17	0.2761	−195	0.6178	−225	0.9033	−80
0.0379	−38	0.3235	−206	0.6782	−200	0.9082	−81
0.0569	−55	0.3880	−229	0.7469	−182	0.9415	−54
0.1287	−104	0.4522	−239	0.7679	−168	0.9619	−34
0.1749	−137	0.5129	−233	0.8256	−134		
0.2129	−161	0.5594	−228	0.8564	−114		
xC$_2$H$_2$Br$_4$ + $(1 - x)$CH$_2$Br$_2$							
0.0394	−11	0.2464	−60	0.6215	−71	0.9095	−19
0.0571	−16	0.3073	−69	0.6776	−64	0.9631	−8
0.0854	−22	0.3701	−76	0.7089	−59		
0.1104	−31	0.4363	−78	0.7752	−48		
0.1585	−43	0.5198	−79	0.8131	−40		
0.1928	−49	0.5630	−76	0.8419	−34		
xC$_2$H$_2$Br$_4$ + $(1 - x)$C$_3$H$_7$Br							
0.0238	−17	0.1872	−97	0.5054	−142	0.8147	−63
0.0714	−49	0.2834	−125	0.5792	−135	0.8645	−44
0.0855	−56	0.3797	−137	0.6615	−114	0.9136	−23
0.0961	−63	0.3804	−137	0.7016	−102	0.9169	−20
0.1581	−87	0.4258	−142	0.7480	−86	0.9624	−7
xC$_2$H$_4$Br$_2$ + $(1 - x)$CH$_2$Br$_2$							
0.0951	−9	0.4072	−25	0.5676	−24	0.8746	−10
0.1952	−16	0.4352	−24	0.5860	−23	0.9362	−5
0.3082	−22	0.4770	−25	0.6878	−21		
0.3513	−23	0.4919	−25	0.7853	−16		
xC$_2$H$_4$Br$_2$ + $(1 - x)$C$_3$H$_7$Br							
0.0466	55	0.2661	239	0.6010	300	0.8615	156
0.0829	94	0.3368	273	0.6507	280	0.8662	128
0.1186	126	0.3734	280	0.7101	262	0.9235	88
0.1781	171	0.4483	300	0.7819	213	0.9672	45
0.1914	180	0.4707	307	0.8120	192		
0.2155	201	0.4849	304	0.8241	185		
xCH$_2$Br$_2$ + $(1 - x)$C$_3$H$_7$Br							
0.0577	25	0.3288	117	0.5341	146	0.8088	102
0.1160	48	0.4071	132	0.6182	142	0.8650	80
0.1530	63	0.4103	134	0.6423	141	0.9131	53
0.2274	87	0.4338	135	0.7015	131	0.9776	18
0.3209	115	0.4694	141	0.7742	114		

Results and Discusion

The experimental values H^E_{exptl} are given in Table 2. They were fitted to the smoothing equation

$$H^E/\text{J mol}^{-1} = x(1 - x)\sum a_i(2x - 1)^i \qquad (1)$$

where x is the mole fraction of the mono- or polybromoalkanes.

Table 3. Parameters a_i of Eq 1 and Standard Deviations $\sigma(H_m^E)$ of Eq 2 of Experimental Molar Excess Enthalpies H_m^E at 298.15 K

mixture	a_0	a$_1$	a_2	a_3	$\sigma(H_m^E$/(J mol^{-1})
tribromomethane +					
1,2-dibromoethane	−818	−91			1
dibromomethane	−191	48	44		1
1-bromopropane	−758	163	193	−150	2
1,1,2,2-tetrabromoethane +					
tribromomethane	80	−30			1
1,2-dibromoethane	−947	19			3
dibromomethane	−317	43	68		1
1-bromopropane	−564	99	93	230	1
1,2-dibromoethane +					
dibromomethane	−99	8			1
1-bromopropane	1228	62			3
dibromomethane +					
1-bromopropane	574	136			1

The values of the coefficients a_i and the standard deviations $\sigma(H^E)$ given by

$$\sigma(H^E) = [\sum(H^E - H^E_{\text{exptl}})^2/(N - n)]^{1/2} \qquad (2)$$

where N is the number of experimental points and n the number of coefficients a_i, were determined by least-squares analysis and are reported in Table 3.

H_m^E values for these mixtures are negative except for 1,2-dibromoethane or dibromomethane + 1-bromopropane and 1,1,2,2-tetrabromoethane + tribromomethane. On the other hand, the calorimetric behavior of these mixtures is similar to that observed in the corresponding mono- and polychloroalkanes systems *(5)* except for trichloromethane and tribromomethane. The explanation of the thermodynamic behavior of these mixtures is very difficult with only H_m^E data, given the variety and complexity of the effects present in the pure components as conformational equilibium in 1,2-dibromoethane, the high degree of orientational order in tribromomethane, self-association, etc.

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