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ENTHALPY OF MIXING OF BROMOBENZENE WITH *n*-ALKANES, WITH CYCLOHEXANE, AND WITH BENZENE

EMMERICH WILHELM*, A. INGLESE**, J.-P. E. GROLIER† AND H. V. KEHIAIAN††
Centre de Recherches de Microcalorimétrie et de Thermochimie du C.N.R.S., Section de Thermodynamique des Alliages et des Mélanges Moléculaires, 26 Rue du 141e R.I.A., F-13003 Marseille (France)

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ABSTRACT

A dynamic flow microcalorimeter of the Picker design was used to measure enthalpies of mixing at 298.15 K and atmospheric pressure of the six binary systems bromobenzene + *n*-hexane, + *n*-heptane, + *n*-nonane, + *n*-tetradecane, + cyclohexane, and + benzene. Within the homologous series of *n*-alkane systems, the interaction parameter, h_{12}, calculated from rigid-lattice group contribution theory, decreases weakly with increasing chain length of the alkane. This behavior is quite analogous to that observed with chloro-derivatives of benzene + *n*-alkane.

INTRODUCTION

Recently, we reported on systematic experimental determinations of the molar excess enthalpy H^E of binary liquid mixtures of chlorobenzenes with members of the homologous series of *n*-alkanes[1–3]. The importance of such investigations within the frame of the so-called "TOM Project"[4], in particular in view of the determination of group interchange energies, has been demonstrated for some time[4, 5]. However, there are relatively few comprehensive studies on the influence of *n*-alkane chain length upon H^E (and other excess quantities) for mixtures with polar substances as second component, and, prior to our work, none has dealt with polar benzene derivatives. Our interest in the systems cited above resulted also from earlier work by Wilhelm et al.[6] on 1,2,4-trichlorobenzene + *n*-hexane, which system revealed an unusually large negative molar excess volume in conjunction with a substantial

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[*] On leave from: Institut für Physikalische Chemie, Universität Wien, Währingerstrasse 42, A-1090 Wien, Austria.

[**] Post-doctoral fellow from Istituto di Chimica Fisica, Università di Bari, Via Amendola 175, Bari, Italy.

[†] Present address: Laboratoire de Thermodynamique et Cinétique Chimique, Université de Clermont, 63170 Aubière, France.

[††] To whom correspondence should be addressed.

negative molar excess heat capacity. The salient point of our previous investigations[2, 3] was the observed decrease of the molar excess enthalpy in the trichlorobenzene series, when the chain length of the *n*-alkane is increased (in the range $6 \leqslant n \leqslant 14$, where *n* denotes the number of C-atoms). Within both dichlorobenzene series, H^E decreases slightly and increases only for the monochlorbenzene systems, although, even here, the increase is clearly well below that observed for benzene + *n*-alkanes. It has been pointed out already[2, 3] that this behavior is contrary to the influence of chain length upon H^E predicted by rigid-lattice type group contribution theories in which free volume contributions and any "cooperative" effects in *n*-alkanes are neglected. Generally, in the simplest, zeroth approximation version, the interactional excess enthalpy term of a binary mixture is given by[4]

$$H^E_{\text{int}} = q_1 q_2 \frac{x_1 x_2}{q_1 x_1 + q_2 x_2} h_{12} \tag{1}$$

where q_1 and q_2 denote suitably reduced surfaces of the molecular species 1 and 2, x is the mole fraction, and h_{12} is the interaction parameter (corresponding to the parameter $v^* s^{-1} X_{12}$ in the Flory theory[7]). This latter quantity is directly related to the parameters characteristic of the interaction between the various different group surfaces.

$$h_{12} = -\frac{1}{2}\sum_s \sum_t (\alpha_{1s} - \alpha_{2s})(\alpha_{1t} - \alpha_{2t})\, h_{st} \tag{2}$$

Here, h_{st} are molar interchange enthalpies, and α_{is} and α_{it} represent the "surface fractions" of type s and type t surfaces ($s \neq t$) on molecule $i = 1$ or 2. Provided the *n*-alkanes (component 2) are regarded as homogeneous species, the parameter h_{12} is a constant, irrespective of whether component 1 is a homogeneous or heterogeneous molecule.

$$h_{12} = -\frac{1}{2}\sum_s \sum_t \alpha_{1s}\alpha_{1t} h_{st} + \sum_{s \neq a} \alpha_{1s} h_{as} \tag{3}$$

where a indicates the aliphatic surface. Since $(\partial H^E_{\text{int}}/\partial q_2)_{q_1, x} > 0$, independent of x, it follows that an increase of n, and hence an increase of q_2, should result in a concomitant increase of H^E_{int} (and also of H^E, if we assume that $H^E \approx H^E_{\text{int}}$).

Consideration of orientational effects, conditioned by energy differences and molecular heterogeneity, in terms of the quasi-chemical approximation[4, 5], does not change the sign of $(\partial H^E_{\text{int}}/\partial q_2)_{q_1, x}$, it merely shifts the maximum of the H^E_{int} vs. x_1 curves toward the *n*-alkane side ($x_1 = 0$).

Orientational effects governed by the packing geometry of the pure liquid *n*-alkanes contribute with a positive excess enthalpy term[8]. Hence, h_{12} in eqn. (1) should rather increase with q_2, contrary to our observations.

Conformational changes in the *n*-alkanes upon mixing with the second component may be correlated with the observed effect[2]. However, in order to draw reliable conclusions, the discussion should be based on the h_{12} parameters calculated after elimination of, as far as possible, the free volume (or equation-of-state) contributions[5].

Evidently, at the present stage, much more systematic experimental studies on binary *n*-alkane systems are needed to eventually assist in the discussion of this behavior. In particular, the role of the second component with respect to shape, polarity, and equation-of-state parameters is of interest. To this end, we report in this paper the calorimetrically determined excess enthalpies within the homologous series bromobenzene + *n*-alkane ($n = 6, 7, 9$ and 14), the former compound having about the same structure and dipole moment as chlorobenzene (1.55 D vs. 1.54 D). For the sake of comparison, we include measurements on bromobenzene + cyclohexane and bromobenzene + benzene.

EXPERIMENTAL

All calorimetric measurements were performed with a dynamic flow microcalorimeter of the Picker design used in the discontinuous mode[9-12]. Since measurements were performed at certain preselected, calibrated positions of the pumps, the respective volume fractions, ϕ_1, are identical for all systems. The volume fractions (and hence the mole fractions) are considered to be accurate to within 0.001.

The calorimeter was thermostated to ±0.001 K as checked by a calibrated Hewlett-Packard quartz thermometer (model 2801A) with a possible maximum absolute inaccuracy of the temperature reading of ±0.005 K. All liquids were partially degassed before being used.

As usual, electrical calibration was carried out by Joule effect via a Zener diode serving as heater. The primary experimental result is the volumetric excess enthalpy of mixing $\mathscr{H}^E$, which quantity is easily converted to the more conventional molar excess enthalpy H^E with the aid of the relations

$$\frac{1}{x_1} = 1 - \frac{V_1}{V_2} + \frac{V_1}{V_2\phi_1} \tag{4}$$

$$H^E = \frac{V_1V_2\mathscr{H}^E}{\phi_1V_2 + \phi_2V_1} \tag{5}$$

Here, V_1 and V_2 denote the molar volumes of the pure liquid constituents.

All liquids were of Fluka puriss grade (GLC purity > 99.5%; for *n*-nonane and *n*-tetradecane > 99%). They were carefully dried with molecular sieve (Union Carbide Type 4A, 8 × 12 mesh, beads, from Fluka) and used without further purification. Densities were determined with a precision densimeter (model 01D of Sodev Inc., Sherbrooke, Canada), and were in good agreement with reliable literature data.

RESULTS

Experimental molar excess enthalpy data were fitted by polynomials of the type

TABLE 1

EXPERIMENTAL MOLAR EXCESS ENTHALPIES H^E OF BROMOBENZENE(1) + n-ALKANE(2) MIXTURES AT 298.15 K AND ATMOSPHERIC PRESSURE

ϕ_1	$C_6H_5Br(1)$ + *n-hexane(2)*		$C_6H_5Br(1)$ + *n-heptane(2)*		$C_6H_5Br(1)$ + *n-nonane(2)*		$C_6H_5Br(1)$ + *n-tetradecane(2)*	
	x_1	$H^E/J\ mole^{-1}$	x_1	$H^E/J\ mole^{-1}$	x_1	$H^E/J\ mole^{-1}$	x_1	$H^E/J\ mole^{-1}$
0.0418	0.0516	150.2	0.0575	174.4	0.0692	192.5	0.0975	230.1
0.0800	0.0979	273.0	0.1084	304.0				
0.1338	0.1616	428.7	0.1776	469.4	0.2083	517.1	0.2767	621.9
0.1648	0.1975	510.9	0.2162	552.4				
0.2529	0.2969	659.6	0.3212	700.2	0.3657	739.4	0.4560	809.8
0.3386	0.3897	741.8	0.4171	775.8	0.4658	800.1	0.5591	831.4
0.4266	0.4813	767.5	0.5098	793.8	0.5589	800.5	0.6482	803.2
0.5128	0.5677	752.9	0.5953	769.9	0.6419	763.0	0.7228	748.1
0.5972	0.6491	704.9	0.6745	717.7	0.7163	703.1	0.7860	681.5
0.6885	0.7338	612.3	0.7555	621.8	0.7901	598.9	0.8455	578.5
0.7794	0.8151	482.5	0.8316	490.1	0.8575	465.2	0.8974	451.8
0.8328	0.8614	386.9	0.8744	396.9				
0.9233	0.9376	194.4	0.9439	207.9	0.9535	187.2	0.9676	188.6

TABLE 2

EXPERIMENTAL MOLAR EXCESS ENTHALPY H^E OF BROMOBENZENE(1) + CYCLOHEXANE(2), AND BROMOBENZENE(1) + BENZENE(2) AT 298.15 K AND ATMOSPHERIC PRESSURE

ϕ_1	$C_6H_5Br(1)$ + *cyclohexane(2)*		$C_6H_5Br(1)$ + *benzene(2)*	
	x_1	$H^E/J\ mole^{-1}$	x_1	$H^E/J\ mole^{-1}$
0.0418	0.0430	142.2		
0.1338	0.1374	403.4	0.1158	21.79
0.2529	0.2587	613.0	0.2229	30.47
0.3386	0.3454	695.3		
0.4266	0.4340	733.2	0.3867	37.87
0.5128	0.5204	735.4	0.4714	39.09
0.5972	0.6045	705.5	0.5568	38.61
0.6885	0.6950	630.0	0.6519	36.35
0.7794	0.7846	507.3	0.7496	32.43
0.9233	0.9254	220.3	0.9167	17.62

TABLE 3

VALUES OF THE COEFFICIENTS A_i OF EQN. (6) DETERMINED BY LEAST SQUARES ANALYSIS, AND CORRESPONDING STANDARD DEVIATIONS σ, EQN. (7) (298.15 K)

System	A_0	A_1	A_2	A_3	$\sigma/J\ mole^{-1}$
Bromobenzene(1) + *n*-hexane(2)	3088.1	−121.5	234.2	345.8	4.5
+ *n*-heptane(2)	3182.1	−4.5	426.8	509.7	3.2
+ *n*-nonane(2)	3221.8	205.3	448.8	599.0	2.0
+ *n*-tetradecane(2)	3296.2	366.8	720.5	1701.8	5.8
+ cyclohexane(2)	2959.9	−204.0	538.0		3.2
+ benzene(2)	154.57	−1.60	84.39		0.68

$$H^E/\mathrm{J\,mol^{-1}} = x_1 x_2 \sum_{i=0}^{m-1} A_i(x_1 - x_2)^i \tag{6}$$

The coefficients A_i and the standard deviation

$$\sigma = \left[\sum_{i=1}^{N} (H_i^E - H_{\mathrm{calc},i}^E)^2/(N - m)\right]^{1/2} \tag{7}$$

were determined by least squares analysis (the total number of points is denoted by N).

The performance of the calorimeter was checked by determining the excess enthalpy of test systems. Our results for carbon tetrachloride + benzene and benzene + cyclohexane are in accord with the results of Stokes et al.[13] to within 1% or 1 J/mole, whichever is greater.

Tables 1 and 2 contain the molar excess enthalpies H^E at 298.15 K and atmospheric pressure for the six binary systems investigated. Values of the coefficients A_i are collected in Table 3, together with the standard deviation in each case.

The equimolar H^E for bromobenzene + cyclohexane and bromobenzene + benzene, determined respectively by Amaya[14] at 298.15 K (735 J mole^{-1}) and Canning and Cheesman[15] at 297.48 K (29 Jmole^{-1}), are close to our results (740 and 39 Jmole^{-1}).

DISCUSSION

As indicated in the introduction, the most interesting aspect of our experimental results is the dependence of the excess enthalpy on the chain length, n, of the alkane component*. This is perhaps most conveniently demonstrated by plotting the quantity h_{12}, eqn. (1), against n. According to simple group contribution theory as discussed above, such a plot should yield a horizontal line. Figure 1 shows that in the range investigated, both halobenzene series exhibit a negative deviation with increasing n. For the sake of comparison, the benzene series is included in Fig. 1. For the numerical calculations, we adopted the following relative group increments for molecular surface areas, calculated[5] by Bondi's method[16]: 0.73103(CH_3); 0.46552(CH_2); 1.83793(C_6H_5); 0.62414(Cl); 0.73448(Br).

Tancrède et al.[17, 18] presented H^E data for binary mixtures of the type n-hexadecane + structural isomer of nonane or hexane, and for a few mixtures n-octane + nonane isomer. In some cases, which involved highly branched nonanes, an exo-

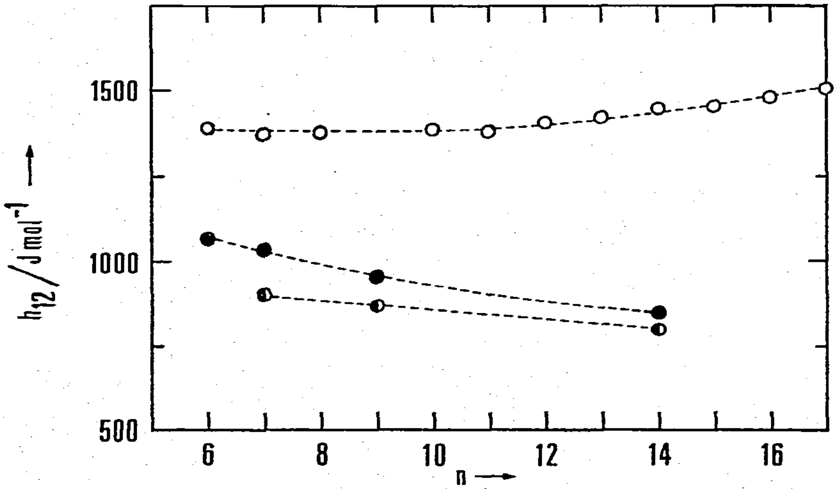

Fig. 1. Plot of the interaction parameter $h_{12} = H^E(q_1 x_1 + q_2 x_2)/x_1 x_2 q_1 q_2$ (evaluated from H_{max}^E) against chain length, n, of the alkane for the series benzene + n-alkane (○), chlorobenzene + n-alkane (◐), and bromobenzene + n-alkane (●). T = 298.15 K.

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[*] For the range $6 \leq n \leq 14$, the increase of the maximal molar excess enthalpy, H_{max}^E, with respect to concentration[2, 3] is given by H_{max}^E/J mole^{-1} = 746.2 + 6.0 n.

thermic enthalpic contribution was observed and, in conjunction with corresponding results on excess volumes and excess entropies, tentatively discussed in terms of a "condensation" of the normal alkane onto the sterically hindered nonane. However, the enthalpy of mixing actually increases when going from 3,3-dimethylpentane + *n*-octane to 3,3-dimethylpentane + *n*-hexadecane, which behavior is quite different from the one observed with the systems investigated by us.

A preliminary estimate of equation-of-state contributions to the H^E of bromobenzene + *n*-alkane series, in terms of the theory of Flory[7], suggests that these contributions, although significant, do not account for the observed effect. However, as already stated, much more systematic experimental studies on H^E, excess volume, and excess heat capacity of binary systems containing a *n*-alkane are needed, and indeed are in progress.

The enthalpy of mixing (equimolar, at 298.15 K) of bromobenzene + cyclohexane (740 J mole^{-1}) and bromobenzene + *n*-hexane (772 J mole^{-1}) are of the same order of magnitude. These values, lower than H^E of benzene + cyclohexane (800 J mole^{-1}) or benzene + *n*-hexane (811 J mole^{-1}), indicate that the molecular interactions between bromobenzene molecules, specifically the π–π and the n–π interactions[19], are considerably weakened by the direct attachment of the Br atom to the aromatic ring, similar to chlorobenzene[1]. The compensation of π–π and n–π interactions in the bromobenzene + benzene mixture explains the small H^E value (39 J mole^{-1}) in this system[19]. We note that the excess enthalpy for the corresponding system chlorobenzene + benzene is even negative (-6 J mole^{-1}).

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REFERENCES

1 J.-P. E. Grolier, K. Sosnkowska-Kehiaian and H. V. Kehiaian, *J. Chim. Phys.*, 70 (1973) 367.
2 E. Wilhelm, *Ber. Bunsenges. Phys. Chem.*, 81 (1977) 1150.
3 E. Wilhelm, A. Inglese, J.-P. E. Grolier and H. V. Kehiaian, *Ber. Bunsenges. Phys. Chem.*, 82 (1978) 384.
4 H. V. Kehiaian, *Ber. Bunsenges. Phys. Chem.*, 81 (1977) 908.
5 H. V. Kehiaian, J.-P. E. Grolier and G. C. Benson, *J. Chim. Phys.*, 75 (1978) 1031.
6 E. Wilhelm, F. Rott and F. Kohler, *Proc. 1st Int. Conf. Calorimetry and Thermodynamics, Warsaw, 1969*, p. 767.
7 P. J. Flory, *J. Am. Chem. Soc.*, 87 (1965) 1833.
8 D. Patterson, *Pure Appl. Chem.*, 47 (1976) 305.
9 J.-P. E. Grolier, G. C. Benson and P. Picker, *J. Chem. Thermodyn.*, 7 (1975) 89.
10 J.-P. E. Grolier, *Thermochim. Acta*, 16 (1976) 27.
11 J.-P. E. Grolier and A. Inglese, *Can. J. Chem.*, 54 (1976) 1952.
12 A. Inglese and J.-P. E. Grolier, *Thermochim. Acta*, 18 (1977) 257.
13 R. H. Stokes, K. N. Marsh and R. P. Tomlins, *J. Chem. Thermodyn.*, 1 (1969) 211; K. N. Marsh, *Int. Data Ser. Select. Data Mixt. Ser. A*, (1973) 2 and 3.
14 K. Amaya, *Bull. Chem. Soc. Jpn.*, 34 (1961) 1278.

15 J. Canning and G. S. Cheesman, *J. Chem. Soc.*, (1955) 1230.
16 A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York, London, Sydney, 1968.
17 P. Tancrède, P. Bothorel, P. de St. Romain and D. Patterson, *J. Chem. Soc. Faraday Trans. 2*, 73 (1977) 15.
18 P. Tancrède, D. Patterson and P. Bothorel, *J. Chem. Soc. Faraday Trans. 2*, 73 (1977) 29.
19 H. V. Kehiaian, in H. A. Skinner (Ed.), *Thermochemistry and Thermodynamics*, MTP International Review of Science, Vol. 10, Butterworths, London, 1972, p. 121.