

# Heats of Mixing for Some Benzene Solutions

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Heats of mixing ( $\Delta H^M$ ) have been measured at 25° C. for six binary systems involving benzene with each of methyl iodide, ethyl iodide, methylene dichloride, ethylene dichloride, diethyl ether, and methylal.  $\Delta H^M$  is negative (exothermic mixing) for the benzene + methylene dichloride system. It changes sign for the benzene + diethyl ether system, being positive for solutions rich in benzene. For all other systems it is positive. The measurements for the benzene + ethylene dichloride system confirm those of Korvezee, Ruiter, and Stuyts.

ALTHOUGH capable of subtle behavior (13), benzene is a relatively inert substance in solution with other non-electrolytes. It usually mixes endothermally with other liquids, and only a relatively small number of binary systems involving benzene are known in which the heat of mixing or excess enthalpy is negative (exothermic mixing); in most of these the other component is a halogenated compound. Furthermore, only one system has been found reported for which the heat of mixing changes sign (with composition) at a particular temperature.

To investigate these aspects of the behavior of benzene solutions further, heats of mixing have been measured at 25° C. over the whole range of composition for benzene with each of methyl iodide, ethyl iodide, methylene dichloride, ethylene dichloride (1,2-dichloroethane), diethyl ether, and methylal. The measurements for the ethylene dichloride system do not provide new data, but were made because there exist two sets of data at 25° C. which differ significantly for solutions rich in the dichloride.

## EXPERIMENTAL

Various reagent grades of the materials were purified by methods described by Weissberger *et al.*, (16). The final step in purification was fractional distillation using a packed, refluxed column; the products were each removed over a temperature range of 0.1° C. or less, except ethyl iodide, in which case it was 0.12° C. The densities at 25° C. were as follows: benzene, 0.8734; methyl iodide, 2.2643; ethyl iodide, 1.9226; methylene dichloride, 1.3168; ethylene dichloride, 1.2460; diethyl ether, 0.7082; and methylal, 0.8542. Although there is considerable disparity in accepted values of physical properties of most of these compounds, the densities lie within or close to accepted ranges (14), except for the density of ethyl iodide, which is probably low.

The apparatus and procedure used to measure the heat of mixing ( $\Delta H^M$ ) have been described (8, 10). In this method, the two substances are initially separated by a thin metal disk in two compartments of a brass calorimeter, immersed in ethylene glycol inside a Dewar flask, which in turn is placed in a thermostat. Mixing is brought about by causing the Dewar flask and contents to undergo an inverting, reciprocating motion, whereby a metal pellet initially in the lower compartment pierces the thin disk. The heat effect is transmitted through the glycol to a thermistor, which is made one arm of a Wheatstone bridge. The heat effect is actually observed as the displacement of a galvanometer mirror-image on a horizontal scale. The extent of the heat effect is determined subsequently by comparison with a known input of energy to a calibrating heater inside the Dewar flask. Measurements of the heat of mixing for the six binary systems were made over the whole range of composition at 25° C.

## RESULTS and DISCUSSION

The measured values of the heat of mixing at 25° C. are given in Table I, in which  $x_1$  is the mole fraction of benzene and  $\Delta H^M$  is the heat of mixing in calories per mole, and are plotted as the experimental points in Figure 1. (The benzene + ethylene dichloride system is omitted from the figure, since the results merely confirm the work of Ruiter *et al.*, as described below.)

In each case the results were fitted to the Scatchard-Guggenheim equation:

$$\Delta H^M = x_1 x_2 [h_0 + h_1(x_1 - x_2) + h_2(x_1 - x_2)^2] \quad (1)$$

Table I. Heats of Mixing ( $\Delta H^M$ ) at 25° C. in Cal. per Mole

$x_1$  = mole fraction of benzene

C <sub>6</sub> H <sub>6</sub> + CH <sub>3</sub> I		C <sub>6</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>5</sub> I		C <sub>6</sub> H <sub>6</sub> + (CH <sub>3</sub> O) <sub>2</sub> CH <sub>2</sub>	
$x_1$	$\Delta H^M$	$x_1$	$\Delta H^M$	$x_1$	$\Delta H^M$
0.110	26.8	0.076	7.0	0.280	10.0
0.214	37.4	0.077	7.1	0.281	9.1
0.344	47.2	0.140	12.9	0.432	10.6
0.372	47.9	0.148	13.3	0.453	11.4
0.442	48.4	0.270	19.9	0.532	10.7
0.630	45.6	0.513	26.2	0.540	10.3
0.793	32.2	0.545	26.5	0.564	10.4
0.888	17.9	0.553	27.5	0.723	7.9
		0.697	24.2		
		0.829	19.0		
		0.840	17.8		
		0.916	9.3		
		0.916	9.9		
C <sub>6</sub> H <sub>6</sub> + CH <sub>2</sub> Cl <sub>2</sub>		C <sub>6</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>		C <sub>6</sub> H <sub>6</sub> + (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	
$x_1$	$\Delta H^M$	$x_1$	$\Delta H^M$	$x_1$	$\Delta H^M$
0.054	-2.1	0.065	7.9	0.093	-4.3
0.062	-2.2	0.067	8.6	0.094	-3.7
0.109	-3.6	0.139	13.3	0.173	-4.8
0.115	-3.4	0.142	13.0	0.175	-6.0
0.221	-9.2	0.256	17.6	0.302	-5.8
0.225	-8.4	0.262	17.3	0.314	-5.7
0.347	-15.3	0.264	17.6	0.461	-2.9
0.351	-16.1	0.402	16.5	0.468	-2.5
0.454	-19.3	0.407	15.9	0.474	-3.5
0.455	-19.1	0.425	16.6	0.574	-0.3
0.488	-19.4	0.437	15.8	0.577	0.0
0.648	-19.6	0.509	15.5	0.747	5.4
0.801	-14.1	0.683	10.4	0.751	3.9
0.889	-8.4	0.687	9.4	0.865	3.9
		0.690	9.8	0.865	5.4
				0.931	2.6
				0.933	3.4

where the constants  $h_0$ ,  $h_1$ , and  $h_2$  were determined by the method of least squares. The values of the constants and the standard deviation of the fit,  $\sigma$ , are given in Table II for the six systems. The curves in Figure 1 were plotted from these equations.

Of the six systems studied, two are of interest in the sense of having negative heats of mixing.

The exothermic behavior of benzene with methylene dichloride is midway between the behavior of benzene with chloroform (exothermic) and with carbon tetrachloride (endothermic) (5). This is the same sequence as for these three substances with methyl iodide (8), although in this case the methylene dichloride behavior is endothermic. The exothermic mixing of benzene with methylene dichloride is probably due to a weak type of hydrogen bonding between the benzene (a  $\pi$ -electron donor) and the hydrogen atoms of the dichloride. This has been interpreted as the main interaction between chloroform and benzene (13), and could be applied similarly to account for the exothermic mixing of benzene with pentachloroethane (17). The negative heats of mixing of benzene with thionyl chloride and with sulfuryl chloride also have been attributed to a type of association (7).

The behavior of benzene with ether is similar to its behavior with methyl ethyl ketone at 20° C. (4). The heat of mixing changes sign at a benzene mole fraction of about 0.6 in each case, and is positive for solutions rich in benzene. The heat effects are not large (less than 10 calories per

mole), but in the case of ether, the heat of mixing is not zero, as reported by Schmidt (12). The positive heat of mixing is probably due to a predominance of the interaction between the  $\pi$ -electrons of benzene and the dipole of the polar molecule, as in the case of the benzene + acetone system (1). The negative heat of mixing is not interpreted so readily, and may be due primarily either to a dipole-induced dipole interaction, or to a charge-transfer interaction (13). The fact that it occurs for solutions rich in ether indicates that a benzene molecule can make more than one contact of this type. Methylal with two less-exposed oxygen atoms does not show the effect of a change in sign. The effect is sensitive to the nature of the attached groups in the polar molecule and/or temperature, since it is not shown by the benzene + acetone system at 45° C. (1).

The positive heat of mixing of benzene with ethyl iodide contrasts with the negative effect with ethyl bromide (9). However, a similar increase in heat of mixing with decrease in electronegativity of the substituent in a monohalogen-substituted hydrocarbon is shown by the comparison of the benzene + chlorobenzene system (slightly exothermic) and the benzene + bromobenzene system (endothermic) (2, 15).

The measurements for the benzene + ethylene dichloride system agree with the results of Korvezee, Ruiter, and Stuyts (6, 11), which are appreciably different from those of Cheesman and Whitaker (3) for mole fractions of benzene less than 0.4. Recalculation of the authors' data with the equation of Korvezee, Ruiter, and Stuyts results in a standard deviation of 0.6, which is only slightly higher than the value given in Table II.

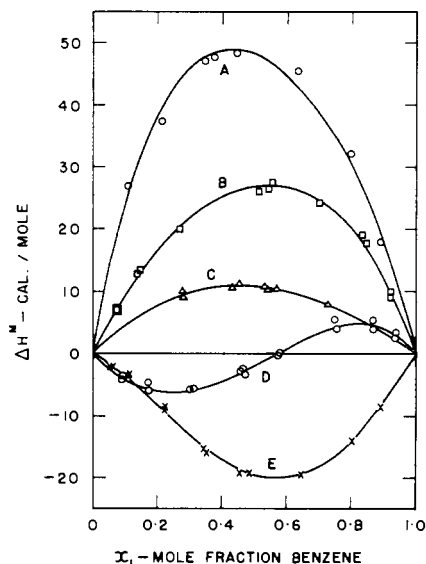


Figure 1. Heats of mixing ( $\Delta H^M$ ) for benzene solutions

- A.  $C_6H_6 + CH_3I$       B.  $C_6H_6 + C_2H_5I$   
 C.  $C_6H_6 + (CH_3O)_2CH_2$       D.  $C_6H_6 + (C_2H_5)_2O$   
 E.  $C_6H_6 + CH_2Cl_2$

Table II. Constants of Equation 1 at 25° C.

System	$h_0$	$h_1$	$h_2$	$\sigma$ , Cal./Mole
$C_6H_6 + CH_3I$	193.0	-44.5	54.4	1.9
$C_6H_6 + C_2H_5I$	108.2	16.9	11.7	0.8
$C_6H_6 + CH_2Cl_2$	-78.5	-29.7	24.3	0.6
$C_6H_6 + C_2H_5Cl_2$	58.2	-47.0	41.8	0.5
$C_6H_6 + (C_2H_5)_2O$	-8.1	55.5	11.5	0.6
$C_6H_6 + (CH_3O)_2CH_2$	43.3	-9.0	...	0.3

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