Heats of Mixing: Alcohol- Aromatic Binary Systems at 25°, 35°, and 45°C.

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A new isothermal calorimeter with no vapor space is described. It allows the accurate and rapid determination of heats of mixing of endothermic liquid systems. Data are presented for eighteen binary systems composed of a lower alcohol and a simple benzene derivative at 25°, 35°, and 45°C. Precise equations for representing these data are also presented.

Heat-of-mixing data for binary liquid systems are useful both for design calculations and for providing an insight into the nature of solutions. Unfortunately the amount of reliable data available for nonideal systems is very limited, and the effect of temperature has rarely been investigated. The object of this work was the development of a simple calorimeter for the rapid and precise measurement of endothermic heats of mixing, and the data reported here are the result of a systematic study of the heats of mixing of binary systems composed of a lower alcohol and a simple benzene derivative at 25°, 35°, and 45°C. As used in this paper the term "heat of mixing" refers to the change in enthalpy per mole of solution formed when the pure components are mixed at constant temperature and pressure.

The calorimeter was designed to operate isothermally and to allow the heats of mixing at a given temperature to be determined for the entire composition range of a system in two experimental runs. A thermistor was used as the temperature-sensing device, and isothermal conditions were easily maintained to within ± 0.005°C. The set temperature was readily reproduced to within ± 0.0002°C. The calorimeter contained no vapor space, and thus the source of error due to vaporization-condensation effects was eliminated. Data were taken for the eighteen binary systems composed of methanol, ethanol, *n*-propanol, *i*-propanol, *n*-butanol, and *n*-amyl alcohol, each with benzene, toluene, and ethyl benzene. Each of these systems was run at 25°, 35°, and 45°C. In addition data were taken for the benzene-cyclohexane system at 25° and 35°C. for the purpose of comparison of results with those of other investigators.

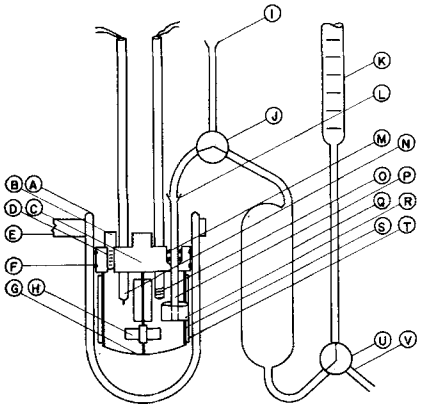

Fig. 1. Calorimeter.

APPARATUS AND PROCEDURE

The apparatus is shown in Figure 1, and the identifying letters refer to its several parts. The calorimeter body was an unsilvered, 150-ml. flask, A, which was fitted with a plug, C, held in a fixed position. The flask was clamped to a rack, E, which could be moved to raise or lower the flask while the plug was held stationary. The plug was fitted with two "O" rings, F, to provide a tight seal with the flask. The plug contained four openings: one for the leads to the heater, O; one for the feed tube, P; one for the leads to the thermistor, N; and one for an air vent, D, which could be closed with a small plug B. The wire heater had a resistance of about 31 ohms. Its leads were sealed in the end of a piece of glass tubing, which led out of the calorimeter. The thermistor was a glass-covered probe with a resistance of about 2,000 ohms at 25°C. It too was sealed in the end of a piece of glass tubing which carried the leads out of the calorimeter. The feed tube was a length of capillary tubing which supported an open-topped cup, R, inside the calorimeter and led to a taper joint, L, outside. All three tubes were sealed in the plug with "O" rings, M.

The plug also supported a stirrer activated by the bar magnet, H. The supporting rod for the stirrer fitted into a small hole in the bottom of the plug, and the lower end was supported in a small indentation in a copper strip, G, which was hung from the plug on two small rods, S. These rods also held two small baffles, T, which were included to provide for thorough mixing in the flask. A rotating magnet below the apparatus actuated the stirrer.

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The liquid to be added to the calorimeter during operation was contained in the bulb, Q, of about 80-ml. capacity. The lower end of the bulb was connected through a three-way stopcock, U, to a calibrated burette, K, graduated in 0.10-ml. divisions and to an arm, V, to which a bottle of mercury could be attached. The upper end of the bulb was connected through another three-way stopcock, J, to a loading port, I, and to the taper joint, L, on the end of the feed tube leading to the flask. This section of the apparatus was held stationary along with the plug.

At the beginning of an experiment the flask contained a measured amount of one of the pure components, and the feed section from the cup, R, to the bottom of the glass bulb, Q, contained the second component. Details of the loading procedure

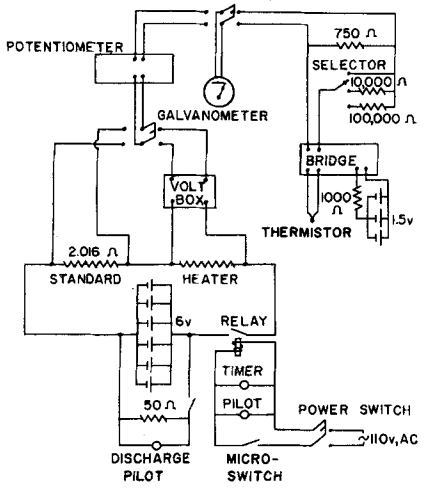

Fig. 2. Heating and measuring circuits.

are given by Mrazek (7). The two components were separated in the calorimeter by mercury held in the cup, R. The burette, K, and the tube leading to the feed bulb were also filled with mercury. This column of mercury exerted pressure on the component in the bulb to drive it into the flask when the flask was lowered. This second component entered the flask by bubbling through the mercury in the cup, R. The calorimeter was completely sealed, and no vapor space was present in the system.

Since all of the systems investigated were endothermic, the heat of mixing was measured by supplying electrically a quantity of heat to the calorimeter equal to the heat absorbed on mixing. The heating and measuring circuits are shown in Figure 2.

The heater was connected in series with a standard resistance of 2.016 ohms and with six 6-v. storage cells connected in parallel. An auxiliary discharge circuit was connected to the storage cells to allow the batteries to discharge for about 30 min. before data were taken so that a more nearly constant voltage could be maintained during the actual run.

The heater–standard resistance–potentiometer circuit was used to measure the energy input. The heater was connected to a volt box to reduce the measured voltage drop across the heater by a factor of 10. The volt box and standard resistance were each connected through a double-pole, double-throw knife switch to a potentiometer. The time of current flow was recorded on a timer synchronized with the heating circuit.

The thermistor was used in a simple bridge circuit as a temperature-sensing device. A galvanometer was connected either to the bridge or to the potentiometer through a double-pole, double-throw knife switch. A resistance of 750 ohms was added in parallel with the galvanometer in the bridge circuit to provide proper damping. To prevent damage to the galvanometer by excessive voltage during the initial balancing of the bridge, a sensitivity selector was included between the galvanometer and the bridge. This selector switch allowed resistances of 10,000 or 100,000 ohms to be put in series with the galvanometer to decrease the sensitivity by factors of approximately 10 and 100, respectively. A deflection of 2.5 mm./0.001°C. was attained when the full sensitivity of the bridge was used. Also a resistance of 1,000 ohms was connected in series with the three 1.5-v. dry cells in parallel which were used with the bridge. This reduced the voltage across the bridge to a value below 1 v., the highest voltage which could be applied and produce no appreciable self-heating of the thermistor.

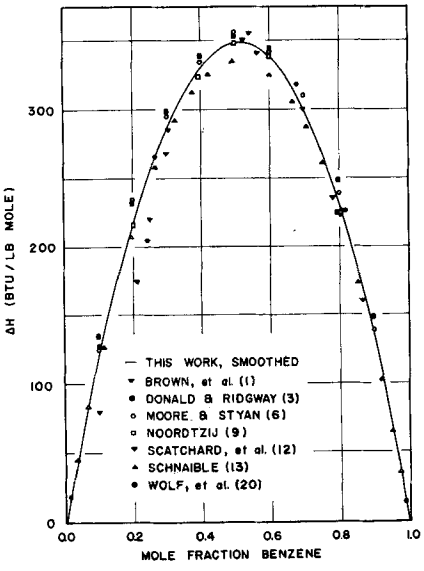

Fig. 3. Heats of mixing: benzene-cyclohexane at 25°C.

While data were being taken, the calorimetric unit was immersed in a constant-temperature bath in which the temperature was controlled to within ±0.005°C. Temperatures were set to within ±0.01°C. with a thermometer which had been calibrated against a thermometer standardized by the U.S. National Bureau of Standards.

A run was started by switching the heater on. Then the flask was lowered so that the second liquid was introduced into the flask at a rate such that the contents of the flask were kept at the set temperature within ± 0.005°C. The temperature drift was indicated by the deflection of the galvanometer. This procedure was interrupted at intervals for readings of the burette (to indicate the volume of the second component added to the flask) and for readings of the time of heating. For each such data point the set temperature was reproduced to within ± 0.0002°C. by appropriate heating or addition of liquid. The power to the heater was determined from measurements of the potentials across both the heater and the standard resistance. The latter allowed determination of the current flowing in the heater. Account was taken of the fact that the heater was in parallel with the volt box. The heat of mixing for the solution in the flask was calculated from the measured quantities for each data point. A run was terminated

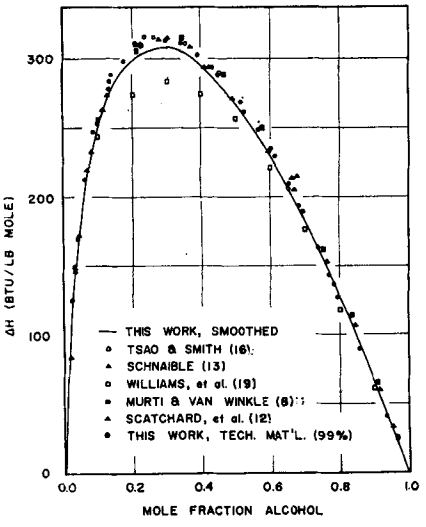

Fig. 4. Heats of mixing: methanol-benzene at 25°C.

when the component in the flask had been diluted to a little less than 50% by volume. A second run was then made with the initial location of the components reversed.

MATERIALS

The materials used in the present work and their specifications are as follows:

Benzene
thiophene free; boiling range 79.9° to 80.2°C.

Toluene
boiling range 110.3° to 110.7°C.

Ethylbenzene
density at 20°C., 0.867 g./ml.

Methanol
99.85 wt. % pure; boiling range 64.6° to 65.0°C.

Ethanol
200 proof, U.S.P., dehydrated

i-Propanol
boiling range 82.0° to 82.3°C.; Sp. gr. at 25°C., 0.782

n-Propanol
boiling range, 97.0° to 97.4°C., Sp. gr. at 25°C., 0.8026

n-Butanol
boiling range, 116.6° to 117.8°C.;

butyric acid, 0.002 wt. %, aldehydes, 0.03 wt. %

n-Amyl alcohol

refractive index (after purification), 1.40811 at 25°C. compared with a value of 1.4081 given in the literature (*10*)

Cyclohexane

boiling range, 80.5° to 80.7°C.

With the exception of the *n*-amyl alcohol *no purification* was done. The amyl alcohol was purified by distillation in a 100-plate Podbielniak column. Chromatographic analysis of the materials used indicated only trace amounts of impurities. Densities for these pure components were taken from Timmermans (*15*) and Rossini (*10*).

EXPERIMENTAL RESULTS

Accuracy of Data

The main source of error in isothermal calorimetry, vaporization–condensation effects, has been eliminated in this work. Careful consideration of other sources of error allowed calculation of the maximum error in the derived quantities, based on the propagation of the maximum errors assumed in the measured quantities. On this basis values of the mole fraction of a component are believed accurate within ± 0.001 and the heats of mixing within $\pm 2\%$. These are thought to represent maximum errors, and in fact they probably are overestimates. Substance is given to this contention by the fact that the data proved to be reproducible to within better than $\pm 1\%$.

Data are available in the literature for several of the systems studied in this work. The heats of mixing determined in this investigation are compared with the data of previous investigators for benzene–cyclohexane at 25°C. and for methanol–benzene at 25°C. in Figures 3 and 4, respectively. Data of the other investigators given for 20°C. were corrected to 25°C. on the basis of the change in the heats of mixing with temperature found in the present work. Thus all the data shown in Figures 3 and 4 are for a temperature of 25°C. It is interesting to note that data taken in this work with technical grade materials (99 mole %) for the methanol–benzene system at 25°C. agree very well with the data of a number of investigators shown in Figure 4. Variation in the purity of materials is of course a possible source of discrepancy between sets of data. Also the presence of a vapor space in the calorimeters used by several of the investigators (*8, 13, 16*) whose data are shown in Figures 3 and 4 may make these sets of data less reliable because of vaporization–condensation effects. This is particularly true of the methanol–benzene system for which the vapor–liquid equilibrium exhibits a marked maximum-pressure azeotrope.

The agreement between the data of other investigators and those of the present investigation ranged from excellent to poor. The agreement with the work of Scatchard, et al. (*12*), which was done with a nonisothermal calorimeter having no vapor space, is good for both benzene–cyclohexane and methanol–benzene. The agreement with the most recent work of Brown and Fock (*2*), who used the same type of calorimeter as Scatchard, for *n*-propanol–benzene and *n*-butanol–benzene at 45°C. is excellent.

Heat-of-Mixing-Data

The treatment of thermodynamic data for binary systems has already been discussed by the authors (*17*). The heat-of-mixing data for the eight-een alcohol–aromatic binary systems were smoothed by means of plots of $\Delta H/x_1x_2$ vs. x_1 and $x_1x_2/\Delta H$ vs. x_1. The data for the *n*-butanol–benzene system, a typical set, are shown in Figures 5 and 6. Of the two plots the one showing $x_1x_2/\Delta H$ vs. x_1 is the more nearly linear, and for this reason it was especially useful for smoothing data, particularly in the dilute-alcohol region where the heat of mixing changes very rapidly with concentration. For the same reason this function is much more easily represented analytically, as is discussed in the following section. On the other hand the function $\Delta H/x_1x_2$ is more convenient to use, and for this reason the smoothed data given in Table 1 are for this function.

These smoothed results are based on approximately 2,500 data points (*7*). The degree of smoothing required is indicated by Figure 5. The values of $\Delta H/x_1x_2$ at the ends of the curves must of course be determined by extrapolation, because the function becomes indeterminate as both ΔH and either x_1 or x_2 approach zero. That this function does approach a finite limit is clear from the experimental curves. However these limiting values are not easily determined at the infinitely dilute alcohol end of the curves because of the very large change in ΔH with composition. In this region the reciprocal function, $x_1x_2/\Delta H$, was found to be more easily extrapolated, as indicated in Figure 6.

It is seen from Figures 5 and 6 that the heat of mixing for the butanol-benzene system increases with temperature. This is true for all of the alcohol–aromatic systems studied. In the temperature range from 25° to 45°C.

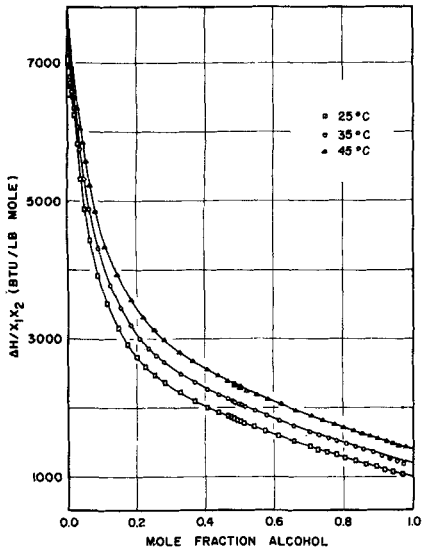

Fig. 5. *n*-Butanol-benzene: $\Delta H/x_1x_2$ vs. x_1.

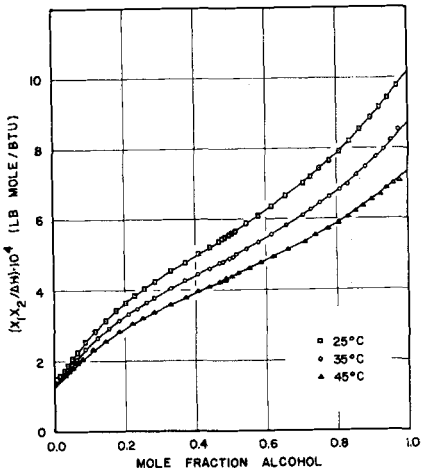

Fig. 6. *n*-Butanol-benzene: $x_1x_2/\Delta H$ vs. x_1.

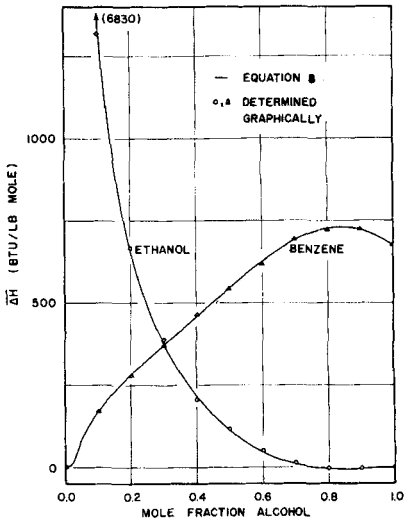

Fig. 7. Partial molal heats of mixing for ethanol-benzene at 25°C.

TABLE 1. SMOOTHED RESULTS, VALUES OF $\Delta H/x_1x_2$, B.T.U./LB. MOLE OF SOLUTION

x_1	Methanol-benzene 25°C.	35°C.	45°C.	Methanol-toluene 25°C.	35°C.	45°C.	Methanol-ethylbenzene 25°C.	35°C.	45°C.	Ethanol-benzene 25°C.	35°C.	45°C.
0.000	6,750	7,140	7,540	7,100	7,400	7,690	7,350	7,700	8,000	6,850	7,250	7,700
0.050	3,870	4,330	4,780	3,970	4,430	4,890	4,030	4,600	5,080	4,310	4,740	5,190
0.100	2,780	3,170	3,570	2,790	3,230	3,650	2,830	3,360	3,800	3,180	3,610	4,030
0.200	1,870	2,170	2,480	1,870	2,200	2,540	1,900	2,310	2,650	2,230	2,580	2,950
0.300	1,470	1,720	1,980	1,440	1,750	2,030	1,515	1,825	2,120	1,780	2,090	2,405
0.400	1,225	1,440	1,670	1,220	1,475	1,730	1,305	1,565	1,820	1,510	1,785	2,065
0.500	1,070	1,260	1,465	1,070	1,310	1,530	1,165	1,405	1,630	1,310	1,565	1,820
0.600	955	1,125	1,320	965	1,185	1,395	1,085	1,305	1,510	1,160	1,390	1,630
0.700	865	1,015	1,205	890	1,100	1,295	1,030	1,230	1,435	1,025	1,240	1,465
0.800	785	920	1,105	835	1,035	1,225	995	1,185	1,380	900	1,100	1,310
0.900	715	840	1,015	800	980	1,170	995	1,175	1,375	785	965	1,165
1.000	650	760	935	770	940	1,120	1,020	1,190	1,390	675	835	1,025

x_1	Ethanol-toluene 25°C.	35°C.	45°C.	Ethanol-ethylbenzene 25°C.	35°C.	45°C.	*i*-Propanol-benzene 25°C.	35°C.	45°C.	*i*-Propanol-toluene 25°C.	35°C.	45°C.
0.000	7,150	7,350	7,520	7,600	7,900	8,200	7,250	7,460	7,570	7,600	7,750	7,870
0.050	4,150	4,760	5,180	4,400	4,910	5,430	4,970	5,450	5,730	4,920	5,380	5,800
0.100	3,030	3,570	4,020	3,170	3,650	4,140	3,910	4,400	4,760	3,770	4,250	4,670
0.200	2,100	2,520	2,900	2,190	2,570	2,990	3,020	3,420	3,750	2,860	3,260	3,630
0.300	1,680	2,020	2,370	1,770	2,080	2,445	2,620	2,960	3,250	2,450	2,805	3,125
0.400	1,420	1,730	2,035	1,505	1,800	2,120	2,375	2,685	2,955	2,215	2,540	2,840
0.500	1,240	1,515	1,795	1,335	1,600	1,890	2,210	2,505	2,760	2,055	2,365	2,650
0.600	1,095	1,355	1,620	1,200	1,455	1,725	2,080	2,360	2,610	1,935	2,230	2,515
0.700	970	1,215	1,470	1,090	1,335	1,595	1,965	2,235	2,485	1,840	2,130	2,415
0.800	855	1,090	1,335	990	1,230	1,485	1,855	2,120	2,380	1,750	2,050	2,330
0.900	750	975	1,215	905	1,135	1,385	1,745	2,015	2,280	1,675	1,980	2,255
1.000	645	860	1,095	825	1,045	1,295	1,645	1,915	2,190	1,610	1,915	2,195

x_1	*i*-Propanol-ethylbenzene 25°C.	35°C.	45°C.	*n*-Propanol-benzene 25°C.	35°C.	45°C.	*n*-Propanol-toluene 25°C.	35°C.	45°C.	*n*-Propanol-ethylbenzene 25°C.	35°C.	45°C.
0.000	7,520	7,690	7,870	7,350	7,350	7,350	7,300	7,410	7,500	7,750	7,820	7,870
0.050	4,930	5,470	5,870	4,680	5,070	5,420	4,580	5,010	5,330	4,680	5,220	5,540
0.100	3,790	4,300	4,770	3,520	3,960	4,360	3,420	3,870	4,270	3,460	4,000	4,370
0.200	2,860	3,290	3,670	2,570	2,960	3,290	2,440	2,820	3,200	2,490	2,920	3,270
0.300	2,460	2,820	3,180	2,130	2,440	2,750	2,005	2,325	2,665	2,040	2,405	2,730
0.400	2,235	2,565	2,885	1,850	2,130	2,410	1,720	2,015	2,335	1,765	2,105	2,405
0.500	2,080	2,400	2,705	1,630	1,900	2,165	1,515	1,795	2,100	1,575	1,895	2,190
0.600	1,980	2,290	2,580	1,455	1,705	1,965	1,350	1,620	1,910	1,425	1,730	2,020
0.700	1,905	2,215	2,495	1,305	1,535	1,785	1,205	1,470	1,745	1,290	1,590	1,870
0.800	1,840	2,160	2,435	1,165	1,380	1,620	1,070	1,330	1,590	1,165	1,455	1,730
0.900	1,790	2,110	2,395	1,030	1,230	1,460	950	1,195	1,450	1,055	1,325	1,595
1.000	1,745	2,070	2,360	905	1,085	1,305	835	1,065	1,310	945	1,190	1,465

x_1	*n*-Butanol-benzene 25°C.	35°C.	45°C.	*n*-Butanol-toluene 25°C.	35°C.	45°C.	*n*-Butanol-ethylbenzene 25°C.	35°C.	45°C.	*n*-Amyl alcohol-benzene 25°C.	35°C.	45°C.
0.000	7,750	7,750	7,750	7,570	7,570	7,570	8,060	8,060	8,060	7,750	7,750	7,750
0.050	4,840	5,230	5,560	4,650	5,060	5,440	4,740	5,220	5,630	4,860	5,250	5,550
0.100	3,680	4,080	4,480	3,470	3,920	4,330	3,500	3,980	4,430	3,730	4,120	4,470
0.200	2,760	3,080	3,430	2,520	2,880	3,270	2,530	2,930	3,330	2,790	3,090	3,420
0.300	2,300	2,580	2,900	2,090	2,400	2,720	2,090	2,440	2,790	2,335	2,600	2,870
0.400	2,015	2,275	2,550	1,820	2,100	2,390	1,820	2,150	2,470	2,065	2,295	2,530
0.500	1,800	2,040	2,295	1,620	1,885	2,160	1,635	1,950	2,250	1,845	2,065	2,285
0.600	1,605	1,840	2,085	1,440	1,700	1,970	1,480	1,775	2,070	1,660	1,865	2,080
0.700	1,430	1,660	1,895	1,285	1,535	1,800	1,340	1,620	1,905	1,490	1,690	1,895
0.800	1,275	1,490	1,715	1,135	1,380	1,645	1,215	1,480	1,755	1,335	1,525	1,715
0.900	1,130	1,325	1,540	995	1,230	1,490	1,095	1,340	1,610	1,190	1,365	1,550
1.000	985	1,170	1,370	860	1,080	1,345	975	1,210	1,475	1,050	1,210	1,385

x_1	*n*-Amyl alcohol-toluene 25°C.	35°C.	45°C.	*n*-Amyl alcohol-ethylbenzene 25°C.	35°C.	45°C.	Benzene-cyclohexane* 25°C.	35°C.
0.000	7,300	7,300	7,300	7,570	7,570	7,570	1,350	1,303
0.050	4,510	4,960	5,300	4,580	5,070	5,430	—	—
0.100	3,360	3,830	4,210	3,420	3,900	4,320	1,353	1,306
0.200	2,450	2,820	3,170	2,470	2,870	3,230	1,359	1,312
0.300	2,020	2,325	2,625	2,045	2,390	2,695	1,367	1,320
0.400	1,760	2,035	2,305	1,790	2,075	2,380	1,378	1,331
0.500	1,570	1,825	2,080	1,610	1,875	2,160	1,393	1,343
0.600	1,405	1,650	1,895	1,450	1,710	1,985	1,412	1,359
0.700	1,255	1,485	1,725	1,310	1,560	1,825	1,437	1,378
0.800	1,115	1,340	1,570	1,175	1,420	1,680	1,463	1,400
0.900	980	1,200	1,420	1,050	1,285	1,540	1,491	1,426
1.000	845	1,060	1,275	930	1,155	1,400	1,522	1,452

* x_1 = mole fraction benzene.

the heat of mixing for these systems is very nearly linear with temperature.

Correlation of Data

An analytical representation of heat-of-mixing data is convenient if a large number of calculations based on the data are to be made. An equation which has frequently been used is (*11*)

$$\Delta H/x_1x_2 = \sum_0^n B_n(x_1 - x_2)^n \qquad (1)$$

where n takes the integral values 0, 1, 2, . . .

However Schnaible, Van Ness, and Smith (*14*) found that the alcohol–aromatic systems were very difficult to fit with an equation of this type because of the shape of the curve of $\Delta H/x_1x_2$ vs. x_1. As shown by Figures 5 and 6 the reciprocal function, that is $x_1x_2/\Delta H$, presents a much more nearly linear curve. Therefore the correlation used here is based on an equation of the form

$$(x_1x_2/\Delta H)10^4 = \sum_0^n A_n(x_1 - x_2)^n \qquad (2)$$

where the factor of 10^4 has been included for convenience.

An advantageous method for determining the constants in Equation (2) is through the use of a set of orthogonal polynomials. Gram polynomials were used for this purpose (*4*), and when modified for convenience in application to the function $x_1x_2/\Delta H$ they become identical with the Vettin polynomials used by Jost and Röck (*5*). These polynomials are defined so that a least-squares fit of the resulting equation is obtained for a set of equally-spaced values of the independent variable. For convenience let w be $x_1 - x_2$, where x_1 is the mole fraction of the alcohol, and let $f(w)$ be $(x_1x_2/\Delta H)10^4$. Then Equation (2) takes the polynomial form

$$f(w) = \sum_0^r a_r p_r(w) \qquad (3)$$

where $p_r(w)$ represents the Gram polynomial of order r. With the eleven-point fit used here w takes on values of 0, ± 0.2, ± 0.4, . . ., ± 1.0. The coefficients, a_r, are then given by

$$a_r = (1/\gamma_r) \sum_{w=-1}^{w=+1} f(w)p_r(w) \qquad (4)$$

where

$$1/\gamma_r = \frac{(2r+1)}{11} \prod_{\lambda=0}^{r} \frac{10-(\lambda-1)}{10+(\lambda+1)} \qquad (5)$$

and λ is a dummy variable. It is easily seen from Equation (4) that the values of the coefficients are independent of the point of truncation of the series given by Equation (3). The first six polynomials for an eleven-point fit are given by

$$\begin{aligned} p_0 &= 1 \\ p_1 &= w \\ p_2 &= (5/9)(3w^2 - 6/5) \\ p_3 &= (25/72)(10w^3 - 7.12w) \\ p_4 &= (125/504)(35w^4 + 35w^2 + 4.032) \\ p_5 &= (625/3024)(126w^5 - 159.6w^3 + 38.4384w) \end{aligned} \qquad (6)$$

and the values of the first six polynomials for the eleven points and the values of $1/\gamma_r$ are given in Table 2.

The coefficients, A_n, in Equation (2) are easily related to the polynomial coefficients, a_r, in Equation (3) by comparison of the two equations and by noting the constants in the polynomials given in Equation (6). The resulting coefficients in Equation (2) when carried to the fifth order are given by

$$\begin{aligned} A_0 &= a_0 - (2/3)a_2 + a_4 \\ A_1 &= a_1 - (89/36)a_3 + (3003/378)a_5 \\ A_2 &= (5/3)a_2 - (625/72)a_4 \\ A_3 &= (125/36)a_3 - (2375/72)a_5 \\ A_4 &= (625/72)a_4 \\ A_5 &= (625/24)a_5 \end{aligned} \qquad (7)$$

The coefficients for Equation (2) when carried to fourth order are obtained by setting $a_5 = 0$ in Equation (7), for third order by setting both a_5 and a_4 equal to zero, etc.

The coefficients for Equation (2) were determined in this manner for the systems investigated (7). All computations were carried out on an IBM-650 computer. The values for 25°C. are given in Table 3.* The smoothed values of $(x_1x_2/\Delta H)10^4$ used to evaluate the coefficients were read from graphs such as Figure 6 with an accuracy of ± 0.01. The fifth-order equations with the coefficients given reproduce the smooth curves within the limits of uncertainty of the smoothed values themselves.

The fifth-order equations may be used with the equations derived by the authors (*17*) for the partial molal heats of mixing to give the following relations:

$$\overline{\Delta H}_1 = \overline{H}_1 - H_1 = \frac{(1-w)^2[(A_0 - A_1) - 2A_2w - (A_2 + 3A_3)w^2 - (2A_3 + 4A_4)w^3 - (3A_4 + 5A_5)w^4 - 4A_5w^5]10^4}{4(A_0 + A_1w + A_2w^2 + A_3w^3 + A_4w^4 + A_5w^5)^2}$$

$$\overline{\Delta H}_2 = \overline{H}_2 - H_2 = \frac{(1+w)^2[(A_0 + A_1) + 2A_2w + (3A_3 - A_2)w^2 + (4A_4 - 2A_3)w^3 + (5A_5 - 3A_4)w^4 - 4A_5w^5]10^4}{4(A_0 + A_1w + A_2w^2 + A_3w^3 + A_4w^4 + A_5w^5)^2} \qquad (8)$$

The partial molal heats of mixing calculated from Equation (8) are shown in Figure 7 for the ethanol–benzene system at 25°C. Values determined graphically by the methods of the authors (*17*) are also shown. One advantage of the analytical procedure is that it can easily be programed for computer calculation. The only requirement is that the data be very precisely represented by the equation used. The equations given here are entirely adequate for this purpose.

TABLE 2. VALUES OF THE POLYNOMIALS AND OF $1/\gamma_r$

w	$p_0(w)$	$p_1(w)$	$p_2(w)$	$p_3(w)$	$p_4(w)$	$p_5(w)$
−1.0	+1	−1	+1	−1	+1	−1
−0.8	+1	−4/5	+2/5	+1/5	−1	+2
−0.6	+1	−3/5	−1/15	+11/15	−1	+1/3
−0.4	+1	−2/5	−2/5	+23/30	−1/6	−4/3
−0.2	+1	−1/5	−3/5	+7/15	+2/3	−4/3
0	+1	0	−2/3	0	+1	0
+0.2	+1	+1/5	−3/5	−7/15	+2/3	+4/3
+0.4	+1	+2/5	−2/5	−23/30	−1/6	+4/3
+0.6	+1	+3/5	−1/15	−11/15	−1	−1/3
+0.8	+1	+4/5	+2/5	−1/5	−1	−2
+1.0	+1	+1	+1	+1	+1	+1
$1/\gamma_r$	+1/11	+5/22	+75/286	+30/143	+18/143	+3/52

* Similar tables for 35° and 45°C. are available upon request from the Chemical Engineering Department of Rensselaer Polytechnic Institute, Troy, New York.

TABLE 3. COEFFICIENTS FOR EQUATION (2): 25°C.

System	A_0	A_1	A_2	A_3	A_4	A_5
Methanol-benzene	9.3177	5.7592	—0.6940	1.0863	—0.1694	0.1302
Methanol-toluene	9.3327	5.2853	—1.6820	0.5686	—0.4625	—0.0751
Methanol-ethylbenzene	8.5699	3.8888	—2.4824	0.2349	—0.5063	0.1002
Ethanol-benzene	7.6091	4.9691	0.5918	1.6027	—0.0747	0.0902
Ethanol-toluene	8.0924	5.0814	0.3073	1.8636	0.0164	0.0751
Ethanol-ethylbenzene	7.4774	4.2228	—0.3490	1.1170	—0.4043	0.0601
i-Propanol-benzene	4.5260	1.4891	—0.3718	0.5154	—0.3861	0.3806
i-Propanol-toluene	4.8700	1.6889	—0.5069	0.4160	—0.5937	0.3455
i-Propanol-ethylbenzene	4.7950	1.3916	—0.7447	0.5484	—0.5263	0.2554
n-Propanol-benzene	6.1107	3.5144	0.5287	1.1753	—0.4480	0.1402
n-Propanol-toluene	6.6024	3.9871	0.3822	1.0085	—0.3187	0.3005
n-Propanol-ethylbenzene	6.3479	3.3455	—0.0893	1.0298	—0.2823	0.3105
n-Butanol-benzene	5.5785	3.1327	0.6576	0.9819	—0.5099	0.3205
n-Butanol-toluene	6.2064	3.5982	0.5473	1.0923	—0.2804	0.4608
n-Butanol-ethylbenzene	6.1011	3.1046	0.2215	1.2057	—0.5864	0.1853
n-Amyl alcohol-benzene	5.4347	2.9059	0.4778	0.7636	—0.5026	0.4507
n-Amyl alcohol-toluene	6.3923	3.5909	0.4627	1.2139	—0.2622	0.4207
n-Amyl alcohol-ethylbenzene	6.2397	3.3322	0.1973	0.9772	—0.3879	0.4207

DISCUSSION

Certain qualitative considerations of the behavior of the alcohol–aromatic systems studied in this work are of interest. It is well known that the pure alcohols are associated by means of hydrogen bonding. If the benzene derivatives are associated at all, the effect is of a much lower order of magnitude. When the associated alcohol is diluted, it dissociates; that is hydrogen bonds are broken. Since energy must be absorbed to produce this dissociation, systems in which no counterbalancing effect occurs are expected to be highly endothermic. This is the case with the systems considered here. The opposite behavior has been noted for highly exothermic systems which tend toward complex formation on mixing (*21*).

If ΔC_p is defined as the heat capacity change of mixing, it can easily be shown that

$$(\partial \Delta H/\partial T)_{p,x} = \Delta C_p$$

Thus the direction of the change in the heat of mixing with temperature may be predicted if the sign of ΔC_p is known. If the alcohol complexes, whether dimer, trimer, or higher order, are considered as molecules, then the dissociation resulting from mixing increases the number of molecules in the solution. Since the total number of atoms remains the same, the total number of degrees of freedom is unchanged. However the number of translational and rotational degrees of freedom is increased at the expense of the vibrational degrees of freedom. If the latter are largely unexcited at the temperatures considered, the mixing process results in an increase in the number of active degrees of freedom, in an increase in heat capacity, and in positive values of ΔC_p. One would then expect the heats of mixing for alcohol–aromatic systems to increase with temperature, and this is the behavior observed. The same result was found by von Elbe (*18*) for alcohol–paraffinic hydrocarbon systems. Since the amount of association of alcohols decreases and the degree of excitation of vibrational degrees of freedom increases with increasing temperature, one would not expect the heats of mixing to increase with temperature indefinitely.

Any quantitative theory of solutions which is to hold for associated components must account not only for long-range molecular forces, such as dispersion forces, but also for strong short-range forces, such as hydrogen bonding. A theory which is this versatile will be difficult to formulate until much more is known about the structure of liquids. Certainly, accurate heat-of-mixing data for nonideal systems provide valuable information on which to base such theories. The results reported in this work are believed to be a significant contribution to the body of reliable data available both for practical calculations and for the testing of theories.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for its three-year support through Fellowships of the doctoral program on which this paper is based.

NOTATION

a, A, B = constants
ΔC_p = heat capacity change of mixing
H_1, H_2 = molal enthalpies of pure components 1 and 2
$\overline{H_1}, \overline{H_2}$ = parital molal enthalpies of components 1 and 2 in solution
ΔH = heat of mixing per mole of solution, B.t.u./lb. mole
$\overline{\Delta H_1}, \overline{\Delta H_2}$ = partial molal heats of mixing, B.t.u./lb. mole
n = a power or subscript taking values 0, 1, 2, 3, etc.
p = pressure
$p_r(w)$ = gram polynomial of order r
T = temperature
w = $x_1 - x_2$
x_1, x_2 = mole fractions of components 1 and 2 in solution
γ_r = defined by Equation (5)
λ = a dummy variable

(Component 1 refers to the alcohol and component 2 to the benzene derivative.)

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Manuscript received June 27, 1960; revision received September 9, 1960; paper accepted September 9, 1960.