T_i = temperature at inner boundary
T_o = temperature at outer boundary
ϕ_A = ratio of area of complete sphere to that of sphere minus area intersected by stem

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Heat of Mixing of *n*-Amyl Alcohol and Benzene

DANIEL ALJURE CHALELA[1], HARRY H. STEINHAUSER, AND JOEL O. HOUGEN[2]
Rensselaer Polytechnic Institute, Troy, N.Y.

The objective of this work was to determine experimentally the heat of mixing of *n*-amyl alcohol in benzene over a range of compositions. Such information is useful in predicting thermodynamic properties of this binary mixture, particularly in connection with deviations from ideal behavior of vapor-liquid equilibrium relationships.

Because *n*-amyl alcohol in pure form tends to associate through hydrogen bonding to give linear polymers, its heat of mixing with an inert solvent, such as benzene, is endothermic. This corresponds to the rupture of hydrogen bonds during dilution.

Table I. Heat of Mixing of *n*-Amyl Alcohol in Benzene

Mole Fraction Benzene	ΔH^a of Mixing at 20° C., Cal./Gram Mole
0.158	91
0.260	126
0.325	183
0.331	177
0.473	214
0.483	219
0.485	213
0.497	212
0.650	223
0.758	208
0.837	177

$^a\Delta H$ = enthalpy of mixture − enthalpy of pure components.

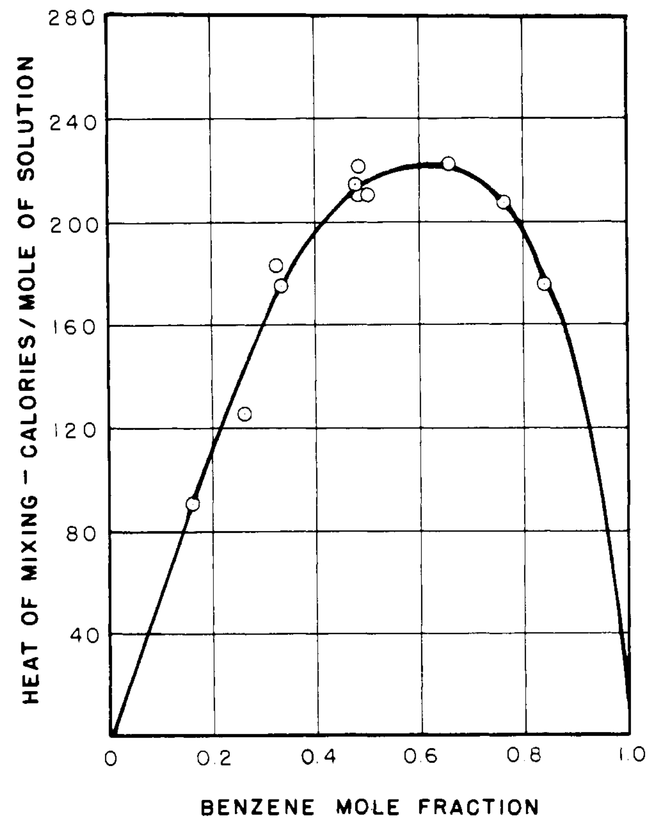

Figure 1. Heat of mixing of *n*-amyl alcohol in benzene

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[1] Present address, National University, Bogota, Colombia, S.A.
[2] Present address, Research and Engineering Division, Monsanto Chemical Co., St. Louis, Mo.

In conducting microcalorimetric determinations it is of utmost importance to obtain the pertinent measurements in such a way that systematic and accidental errors are eliminated or reduced to a minimum. Sources of error may fall in one of three groups: inadequate measurement of temperature, uncontrolled heat transfer, and undesirable side reactions occurring in the system being studied. The use of comparative calorimetric techniques makes it possible to avoid or minimize the effects of these secondary phenomena.

EXPERIMENTAL METHOD

The calorimeter was almost identical to that used by Zellhoefer and Copley (*5*) and by McLeod and Wilson (*2*). The method has been used by Audrieth and Steinmann (*1*) and by Spence (*3*) for measuring exothermic heats of solution.

The method of successive comparative measurements was adapted in this work to endothermic heats of solution. The temperature change from 20°C. which occurred upon mixing of the two components was first measured. Then the measurements were repeated following the introduction of a known quantity of electrical energy. The energy introduced in the latter case was such as to produce a temperature increase approximately equal to the temperature decrease which occurred following the mixing reaction. Thus, when appropriate adjustments are made for heat leaks, for stirring, and for inequality of the temperature changes during mixing and heating, the electrical energy input is equal to the heat of mixing.

Thiophene-free benzene and *n*-amyl alcohol were distilled in a Podbielniak column using a 100 to 1 reflux ratio. The refractive index at 25°C. of benzene differed by no more than 0.00005 from 1.49800 during the distillation (*4*). The value for amyl alcohol was 1.40815.

A Beckmann thermometer was used for the temperature measurements.

RESULTS

The experimental results are summarized in Table I and Figure 1. The data are seen to be reproducible within ± 5%. The results obtained are typical of such systems and show, in this case, a maximum molal heat of mixing of about 225 calories at 60 mole % of benzene.

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