Heats of Mixing of Toluene and Ethylbenzene

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Heats of mixing of toluene and ethylbenzene have been measured at 30° C. Values of χ_H have been obtained for correlation with polymer solution thermodynamic data.

THE RESULTS of calorimetric measurements of the excess enthalpy of mixing at 30° C. for toluene and ethylbenzene are reported. Isolated measurements have been made on this system (*1, 5*), but no systematic study has been reported. Ethylbenzene is sometimes regarded as a representative segment of a polystyrene chain (*1*); hence, precise thermodynamic data should be of value in interpreting polymer solution behavior.

EXPERIMENTAL

The calorimeter (*4*) consisted of a cylindrical glass vessel of length 5 cm. and diameter 2.5 cm., closed at both ends. Access to the vessel was via a ground glass socket at right angles to and half-way along the length of the vessel. An internal glass diaphragm divided the upper section of the vessel into two compartments, so that a weighed quantity of two liquids, up to ~2 cc., could be confirmed separately above degassed mercury with no vapor space. The liquids were introduced by means of a syringe. The lower half of the vessel was provided with a glass pocket for an electric heater. An expansion volume, ~3 cc., filled with air at atmospheric pressure, was attached to the calorimeter via a capillary tube fitted with a ground glass cone, in order to accommodate any volume changes occurring on mixing, thus preventing any appreciable change in pressure within the vessel. The mixing vessel was contained in an insulating jacket, which was placed in a thermostated tank controlled to ±0.001° C. The mixing and stirring were achieved by repeated inversion of the jacketed vessel in a manner which avoided the liquid's contacting the greased glass joint. Temperature changes were detected by thermistors cemented to the exterior surface of the mixing cell, which formed one arm of a Wheatstone bridge circuit. After mixing, a stirring calibration was made, followed by electrical calibration.

The main modifications to the published design (*4*) were as follows: The mixing cell was insulated by a closely fitting foamed polystyrene jacket which was then inserted in a Dewar vessel, which in turn was placed in the thermostated tank; d.c. amplification microvolt amplifier Type 9290, Guildline Instruments) of the out-of-balance voltage of the thermistor bridge circuit permitted the use of a pen recorder to display the mixing thermogram; the whole apparatus was used in a room thermostated to ±0.5° C.; the three thermistors used (Type M52, Standard Telephones and Cables Ltd.) were connected in series, giving a total resistance of about 1100Ω at 30° C.; the time of heating was measured with an electric stop-clock to ±0.01 second. These modifications enhanced the precision of the calorimeter to ±0.38 J. mole^{-1}, with heats of mixing of less than 13 J. mole^{-1}. The accuracy of the calorimeter was verified by measuring the heats of mixing of benzene and carbon tetrachloride at 25° C. The results are given in Table I, and are compared with those of Larkin and McGlashan (*4*).

Table I. Heats of Mixing for Benzene and Carbon Tetrachloride at 25° C.

x_B	h^E, J. Mole^{-1}	Δ, J. Mole^{-1}
0.1107	48.95	+0.22
0.3076	101.36	+0.61
0.5117	115.28	−0.22
0.7024	96.40	+0.34
0.8804	48.73	+0.25

The amount of each liquid present in the calorimeter was found by weighing a syringe before and after introduction of contents into the mixing vessel, and the mole fractions are estimated to be accurate to ±0.0002.

Toluene and ethylbenzene were purified by the usual methods (*7*), followed by two fractional distillations through a 30-plate fractionating column, discarding generous head and tail fractions each time. A reflux ratio of 10 to 1 was used. The products were stored over calcium hydride. The fraction of toluene collected had a boiling range 110.6–110.8° C.; d_4^{30} 0.85765; and n_D^{30} 1.4910. The fraction of ethylbenzene collected had a boiling range 136.1–136.3° C.; d_4^{30} 0.85825; and n_D^{30} 1.4904. Literature values are: toluene,

Table II. Heats of Mixing for Toluene and Ethylbenzene at 30° C.

x_A	$-h^E$, J. Mole^{-1}
0.0570	3.42
0.1195	5.30
0.1683	8.55
0.2986	10.78
0.3856	12.66
0.4394	12.50
0.5045	12.55
0.5664	12.73
0.5713	12.32
0.7129	9.73
0.7988	7.90
0.8882	5.24
0.9481	2.80

d_4^{30} 0.85769 (*7*) and n_D^{30} 1.4913 (*6*), ethylbenzene, d_4^{30} 0.85828 (*6*) and n_D^{30} 1.4905 (*6*).

RESULTS

The heats of mixing for toluene and ethylbenzene are shown in Table II.

The data were fitted with equations of the type (*3*)

$$h^E = x_A(1 - x_A) \sum_{n=0}^{n} A_n(1 - 2x_A)^n \qquad (1)$$

The least squares program written for an Elliot 803 computer is able to fit Equation 1 with any choice of n up to $n = 9$. The best choice of n was taken as that for which σ was a minimum, where

$$\sigma = \left\{ \sum_i \delta_i^2 / (a - n) \right\}^{1/2} \qquad (2)$$

Equation 3 is obtained from Equation 1, where $n = 2$ and $\sigma = 0.4371$ J. mole^{-1}.

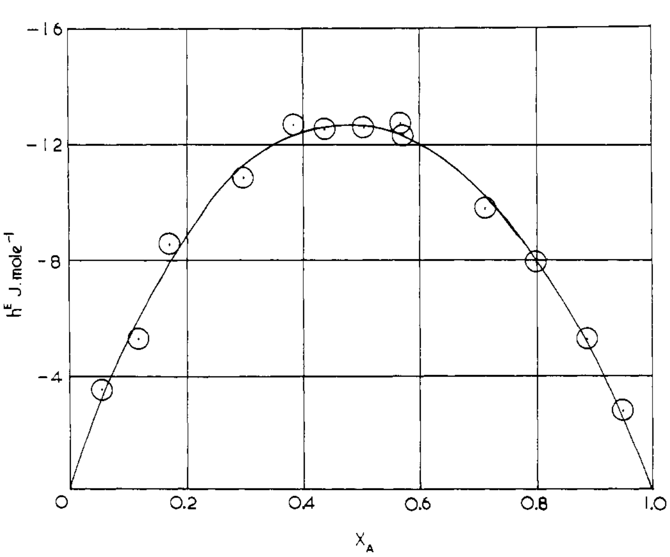

Figure 1. Heats of mixing of toluene and ethylbenzene at 30° C. as a function of mole fraction of ethylbenzene; experimental points circled, Equation 3 shown by solidus

Table III. Values of χ_H over the Entire Composition Range of Toluene and Ethylbenzene at 30° C.

x_A	$-\chi_H$
0.10	0.0203
0.20	0.0207
0.30	0.0193
0.40	0.0190
0.50	0.0188
0.60	0.0188
0.70	0.0190
0.80	0.0193
0.90	0.0198

Table IV. Literature Values for Heats of Mixing of Toluene and Ethylbenzene at 25° C.

x_A	$-h^E$, J. Mole^{-1}	Ref.
0.2244	8.65	(*1*)
0.3027	9.48	(*1*)
0.3027	10.29	(*1*)
0.4647	9.86	(*1*)
0.4647	9.89	(*1*)
0.9340	1.18	(*5*)
0.9400	1.63	(*5*)

$$h^E = x_A(1 - x_A)\{-50.672 - 4.627(1 - 2x_A) - 5.588(1 - 2x_A)^2\} \qquad (3)$$

The experimental points and Equation 3 are plotted as a function of the mole fraction of ethylbenzene in Figure 1.

If the smoothed experimental data as represented by Equation 3 are introduced into the Flory-Huggins expression (*2*) for the heat of mixing of polymer and solvent

$$h^E = RT\chi_H(1 - x_A)\phi \qquad (4)$$

which assumes volume additivity for the mixture, values of χ_H may be obtained as a function of x_A. Table III contains some values of x_A and the corresponding χ_H. Equation 4 interprets the h^E results adequately, in that χ_H is approximately constant. Few systems demonstrate such good agreement. The slight differences in χ_H may be attributable to volume changes on mixing. Preliminary experiments in this laboratory on volume changes of mixing indicate that these are small, $\sim \pm 0.01$ cc. mole^{-1}, but the experimental error is of the same order of magnitude. Such small volume changes indicate that the change in internal energy is essentially the same as the change in enthalpy on mixing; therefore, some very weak dipole interactions must occur. χ_H is of a similar sign and magnitude to that found for the mixing of polystyrene and toluene.

Table IV contains the literature values for the heats of mixing of toluene and ethylbenzene at 25° C. All the values quoted have been obtained with calorimeters which had vapor spaces above the liquids.

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NOMENCLATURE

d_4^{30} = density at 30° C. with reference to water at 4° C.
n_D^{30} = refractive index at 30° C., using sodium D-line
x_A = mole fraction of ethylbenzene in toluene and ethylbenzene mixtures
x_B = mole fraction of carbon tetrachloride in benzene and carbon tetrachloride mixtures
Δ = difference between present h^E results and values obtained by use of the equation of Larkin and McGlashan (*4*) for the benzene and carbon tetrachloride system, J. mole^{-1}
n = integer
A_n = constant
h^E = excess enthalpy of mixing, J. mole^{-1}
a = number of experimental points
δ_i = difference between experimental h^E and the h^E predicted for ith point
χ_H = Flory-Huggins enthalpy interaction parameter
ϕ = volume fraction of ethylbenzene

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Molar Volume of Supercooled Naphthalene at 25° C.

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The molar volume of naphthalene in near-ideal solutions in ethylbenzene from 0 to 0.2 mole fraction is 123.98 ml. per mole at 25.000° ± 0.005° C.

NAPHTHALENE is frequently involved in chemical studies. At the standard temperature of 25° C., naphthalene is about 55° C. below its normal melting point. Precise interpretation of volume-dependent phenomena in liquid mixtures containing naphthalene requires a dependable value for the molar volume of that compound in the dissolved state—i.e., the supercooled liquid state.

Extrapolation of the density of liquid naphthalene to 25° C. from above the normal melting point yields a value of 125.9 ml. per mole (*4*). The calculated liquid molar volume is uncertain to ±0.1 ml. per mole at temperatures in the region moderately above the normal freezing point (*4*), and the uncertainty is quite indefinite at 25° C.

Lumsden (*5*) reported 124.25 ml. per mole for naphthalene dissolved in toluene at 25° C. at a single solute mole fraction of 0.09. The value was determined by density measurement, assuming ideal behavior. His additional results (*5*) for naphthalene dissolved in toluene, xylene, and benzene at 15° C., at solute mole fractions of 0.05, 0.10, and 0.20 in each system, indicate that the single value at 25° C. should be considered uncertain to approximately 0.3 to 0.4 ml. per mole.

This note reports the molar volume of supercooled naphthalene, based on a series of density measurements of naphthalene-ethylbenzene solutions. The solubility of naphthalene in ethylbenzene is about 95% of the ideal value (*2*) at 25° C. Moreover, refractive indices in this system are additive in mole fraction at 25° C. (*3*), again indicating near-ideality, as well as near-equal molar volumes for these components as liquids at this temperature. This should be a more reliable value of the molar volume of supercooled naphthalene than presently available.

EXPERIMENTAL

Material. Naphthalene was Baker reagent grade, recrystallized from alcohol. Previous work has shown that further recrystallization causes no measurable change in properties in these mixtures (*2*), so the material was used as received. Ethylbenzene was MCB Spectroquality grade, purified by distillation through a 4-foot-long vacuum-jacketed column at a recovery rate of about 1 ml. per minute. Calcium hydride was used as a drying agent. Only the middle half of the distillate was recovered. For the purified product, the refractive index (sodium D-line at 25.00° ± 0.01° C.) was 1.49300 [lit., 1.49320 (*1*)].

Equipment. Densities were determined with a 25-ml. Weld pycnometer. The pycnometer was calibrated with degassed distilled water to a standard error of ±0.002 ml. Weighings were made with a Mettler single-pan balance with certified weights. Temperature equilibrium was reached in a Sargent Thermonitor-controlled bath at 25.000° ± 0.005° C. Replication indicated an uncertainty in density equivalent to 0.02 ml. in molar volume.

RESULTS AND DISCUSSION

The experimental molar volumes, V°, of the solvent and four mixtures are given in Column 2 of Table I. Assuming ideality

$$V^\circ = x_1 V_1^\circ + x_2 V_2^\circ \qquad (1)$$

where x is the mole fraction, and the subscripts 1 and 2 refer, respectively, to solvent (ethylbenzene) and solute (naphthalene). By rearrangement of Equation 1 into

$$V^\circ = V_1^\circ + (V_2^\circ - V_1^\circ)x_2$$

$V_2^\circ - V_1^\circ$, and thus V_2°, may be evaluated as the slope

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