Heats of Mixing of Binary Mixtures of *N*-Methylpyrrolidone, Ethanolamine, *n*-Heptane, Cyclohexane, and Benzene by Differential Flow Calorimetry

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Heats of mixing of binary mixtures of benzene, *n*-heptane, *N*-methylpyrrolidone, and ethanolamine at 25° and 40°C, cyclohexane–*N*-methylpyrrolidone at 25°C were obtained with a flow calorimeter. The apparatus was tested on the system benzene–carbon tetrachloride at 25°C. For two-phase systems, heats of mixing are given at least at the equilibrium concentrations.

Heats of mixing of binary liquid mixtures were measured to complement vapor-liquid equilibria data at about 25°C. A method to measure rapidly and accurately the heat of mixing of liquids applicable to difficult systems was developed by use of the isothermal flow microcalorimeter LKB 10700.

Experimental

The heat produced by mixing two continuous liquid flows is measured in a mixing cell consisting of a T tubing where the two incoming streams merge and a long narrow channel where the mixture exchanges heat with an isothermal air bath through an electric heat-flux meter. The liquid flow rates are set to allow the liquid to reach the bath temperature before leaving the mixing cell.

The incoming liquids are brought to the bath temperature through a heat exchanger.

Viscous flow heat evolution is reproduced by circulating the liquid in a reference cell. The corresponding heat effect is subtracted from the heat effect in the mixing cell. Both cells are provided with calibration heaters.

The heat flux detector consists of a thermocouple assembly soldered to the cell and a heat sink kept at the bath temperature. The electric power is linearly related to the heat flux transmitted to the heat sink. The electric signal is amplified by a Keithley 150 B amplifier and recorded. The measurement is obtained by comparing the base line shift of the recorder on mixing to the deviation produced by a known current applied in one calibration heater while the liquids are pumped. The calibration cell is chosen to reduce the base line shift on mixing, and the current is set to produce a heat effect close to that of mixing.

Tacussel "electroburap" BC/VRE Syringe pumps, equipped with 10-cm^3 syringes were set at flow rates ranging from 0.01 to 0.4 cm^3/min. Flow rates were obtained with a precision of 0.2% and calibrated by weighing. The use of a step-by-step electric motor did not produce any fluctuation of the recorder response.

Degassing of pure liquids was found necessary because the solubility of air is lower in mixtures than in pure liquids. Bubble growth in the mixing cell caused instability of the recorder response. Air concentration should be reduced below its solubility in the mixture. The liquids were frozen under vacuum during 20 min. Before pumping was started, atmospheric pressure was established with argon which has a low concentration-independent solubility in liquids.

Results

Materials. Benzene was Rhône-Poulenc cryoscopy grade; carbon tetrachloride was Merck spectroscopy grade. *N*-methylpyrrolidone (NMP) was Lurgi Gmbh, dried by low-pressure azeotropic distillation with benzene. Ethanolamine was Prolabo or Merck, dried over 4Å molecular sieves. *n*-Heptane was Philips Petroleum Co., ASTM lot No. 1359. Cyclohexane was Rhône-Poulenc pure grade.

Test System. The method was tested by measuring the heat of mixing of the system benzene-carbon tetrachloride at 25°C which is of the order of magnitude of other measured values.

Appreciation of the validity of measurements is provided by examination of Figure 1 where differences between measured and calculated values with Equation 1 repre-

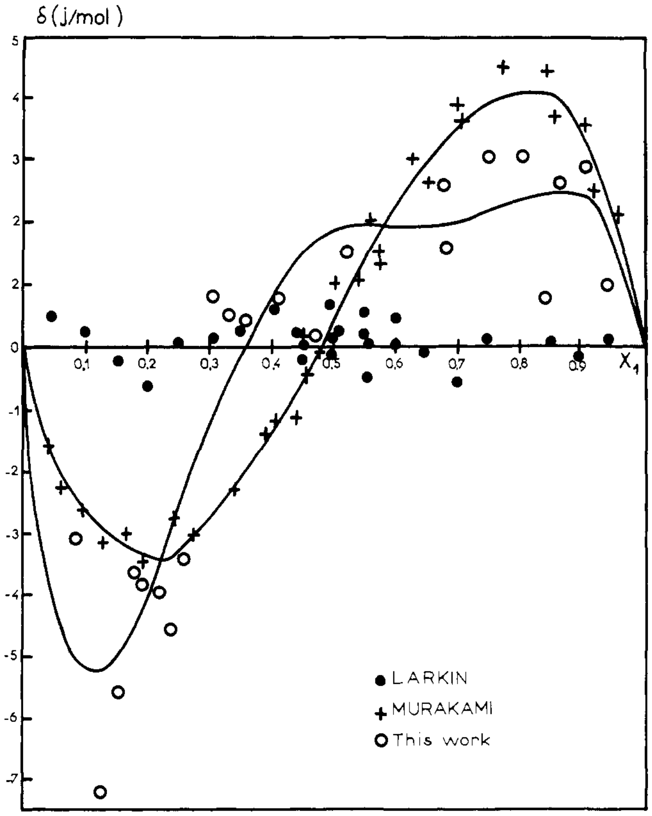

Figure 1. Comparison of experimental data for the system benzene(1)–carbon tetrachloride at 25°C

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Table I. Measured Heats of Mixing (J/mol)

25°C		40°C	
Mole fraction, x_1	h^E, J/mol	x_1	h^E, J/mol
	Benzene (1)-NMP (2)		
0.1196	−187.4	0.1196	−186.8
0.2132	−300.7	0.2132	−293.3
0.2891	−369.1	0.2891	−368.0
0.3517	−436.0	0.3517	−424.8
0.4042	−460.8	0.4042	−464.1
0.4486	−483.7	0.4486	−476.8
0.4870	−496.3	0.4870	−493.8
0.5535	−506.4	0.5204	−499.2
0.5913	−498.7	0.5535	−491.3
0.6344	−481.5	0.5913	−484.8
0.6846	−463.8	0.6344	−472.0
0.7430	−414.5	0.6846	−438.9
0.8128	−317.9	0.7430	−392.6
0.8970	−202.3	0.8970	−206.8
	NMP (1)-Ethanolamine (2)		
0.0939	258.9	0.0854	236.4
0.1721	386.8	0.1109	295.1
0.2379	488.6	0.1388	366.6
0.2379	485.6	0.1721	428.3
0.2937	588.3	0.1721	428.8
0.3421	633.6	0.2379	555.9
0.3426	618.1	0.2937	637.8
0.4280	740.0	0.3426	719.5
0.4834	781.5	0.4041	805.6
0.5550	833.9	0.4383	841.2
0.6515	842.3	0.5334	918.4
0.7138	838.7	0.5996	933.6
0.7893	771.3	0.6515	921.8
0.8332	670.3	0.7137	865.1
0.8332	674.7	0.7688	798.8
0.8620	601.8	0.8332	695.3
		0.8620	607.9
	Benzene (1)-Ethanolamine (2)		
0.1277	507	0.0855	372.0
0.9925	200	0.1517	595.0
		0.9833	315.0
		0.9854	255.4
	n-Heptane (1)-NMP (2)		
0.0758	566.0	0.0758	577.5
0.1438	880.0	0.1102	750.4
0.9170	820.0	0.1415	877.1
		0.2166	1126.0
		0.8584	1152.0
	n-Heptane (1)-Ethanolamine (2)		
0.00108	22.50	0.00250	23.62
0.99804	6.21	0.99664	44.95
	Cyclohexane (1)-NMP (2)		
0.1005	628.9		
0.1821	944.9		
0.2506	1185.8		
0.3085	1261.6		
0.3581	1313.8		
0.4008	1335.2		
0.4384	1350.7		
0.4715	1360.3		
0.5048	1355.4		
0.5433	1352.8		
0.5879	1335.4		
0.6409	1345.6		
0.7038	1300.8		
0.7811	1162.5		
0.8775	896.9		

Table II. Liquid-Liquid Equilibria[a]

t, °C	x_{11}	x_{12}
	n-Heptane (1)-NMP (2)	
25	0.9170	0.1438
30	0.9019	0.1628
35	0.8846	0.1873
40	0.8584	0.2166
45	0.8097	0.2574
50	0.7652	0.3290
	Benzene (1)-Ethanolamine (2)	
25	0.9925	0.1277
30	0.9896	0.1355
35	0.9864	0.1435
40	0.9833	0.1517
45	0.9801	0.1607
50	0.9769	0.1702
	n-Heptane (1)-Ethanolamine (2)	
25	0.99804	0.00108
30	0.99758	0.00150
35	0.99710	0.00195
40	0.99664	0.00250
45	0.99615	0.00282
50	0.99566	0.00330

[a] x_{ij} = mole fraction of component *i* in phase *j*.

senting the results of Larkin and McGlashan *(1)* are plotted.

$$h^E = x_1(1 - x_1)\,[C_1 + C_2(1 - 2x_1) + C_3(1 - 2x_1)^2 + C_4(1 - 2x_1)^3] \quad (1)$$

Our results show more dispersion [root mean square (rms) dev of 1 J/mol] than those of Larkin and McGlashan *(1)* and Murakami and Benson *(2)* (rms dev of 0.3 J/mol). This can be explained by the manual exploitation of recorded electric signal; a numerical integration of it should give results of improved accuracy.

The deviations between sets of data are largest around $x_1 = 0.25$ and $x_1 = 0.75$ where the heat of mixing varies quickly with concentration; this suggests that deviation is mainly due to errors in determination of the concentrations. Deviations between measurements of the two other authors are of the same order as deviation between ours and each of theirs.

New Systems. Heats of mixing of new binary systems are given in Table I.

The excess enthalpy of the system benzene-NMP is negative, showing a complexation. Systems *n*-heptane-NMP, *n*-heptane-ethanolamine, and benzene-ethanolamine exhibit low mutual solubility. Liquid-liquid equilibria were measured between 25° and 50°C by the cloud point method. Mutual solubilities are given in Table II.

Heats of mixing for the equilibrium concentrations at 25° and 40°C were obtained by extrapolating the straight line h^E vs. x_1 obtained in the two-phase region, to the equilibrium concentrations. The excess enthalpies of totally miscible systems were fitted with Equation 1. Constants C_i and mean square deviation σ are given in Table III.

Conclusion

The use of an isothermal flow microcalorimeter is convenient for a quick and simple measurement of heats of mixing. (Ten points for one system at one temperature are obtained in two days.) It is a convenient tool to complement information on phase equilibria for the design of separation processes or fundamental investigation of the

Table III. Adjusted Values of Parameters C in Equation 1

System	C_1	C_2	C_3	C_4	σ/(J/mol)
Benzene–NMP (25°C)	−1989.8	410.5	−0.389	−292.4	5.38
Benzene–NMP (40°C)	−1956.3	273.7	−0.389	+64.239	5.46
NMP–Ethanolamine (25°C)	3168.5	−1602.2	1441.8	77.866	10
NMP–Ethanolamine (40°C)	3556.0	−1366.7	905.8	−114.07	8.1
Cyclohexane–NMP (25°C)	5443.0	44.028	3711.8	−1809.9	13.15

effect of molecular structure on excess properties of mixtures.

Acknowledgment

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Determination of Solubilities of Light Hydrocarbons in Di-2-ethylhexyl Sebacate by Saturation of a Gas-Liquid Chromatographic Column

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The solubilities of propane, isobutane, neopentane, and *cis*-2-butene in di-2-ethylhexyl sebacate at low concentrations have been determined by measuring the amount of hydrocarbon sample required to saturate all the liquid in a chromatographic column. The method does not depend upon the progress of a peak conforming to a particular mathematical model of the chromatographic process and therefore is generally applicable. The solubilities at 55°C were: propane 0.182, isobutane 0.090, neopentane 0.057, and cis-2-butene 0.045, expressed as (mol/cm^3 in gas)/(mol/cm^3 in liquid).

Numerous investigators have measured the solubility of volatile compounds in relatively nonvolatile compounds by gas–liquid chromatography *(4, 5, 6, 9)*. Newman and Prausnitz *(8)* have used the method to measure the solubility of volatiles in polymers.

The determinations of solubility have generally used ordinary isothermal analytical chromatographs. A column containing a known amount of nonvolatile liquid is prepared and installed in the chromatograph oven. Carrier gas flow is adjusted to a known rate and a pulse of volatile material is injected into the carrier stream. The times for the sample peak and for an air peak to appear at the detector are measured. The retention volume is calculated from these time measurements and used in other equations to deduce the solubility (or activity coefficient). The calculations are described by Kuchhal and Mallik *(7)* and Newman and Prausnitz *(8)*.

To the extent that the physical situation existing in the column is described by the equations, this method is sound and accurate. The principal limitations are that the solubility of the volatile compound follow Henry's law, that there be no absorption of volatile on the solid support, that mass transfer rates be relatively high, and that axial dispersion in the column not affect the position of the maxima of the peaks.

A convenient method which is not subject to these limitations, for determining the solubility of volatiles in nonvolatile compounds, is based on completely saturating the liquid of a chromatographic column with a volatile material. It has been used to determine the solubility of propane, isobutane, neopentane, and *cis*-2-butene in di-2-ethylhexyl sebacate.

Method and Apparatus

Figure 1 is a schematic diagram of the apparatus. A column (*A*), containing a known weight of di-2-ethylhexyl sebacate on the packing was prepared. The packing was prepared by dissolving the di-2-ethylhexyl sebacate in acetone, mixing the solution with the support in an evaporating dish and, with continuous stirring, evaporating off the acetone over a water bath. The packing was dried to constant weight in a vacuum oven at 100°C. The amount of di-2-ethylhexyl sebacate on the packing was determined by extracting a weighed sample of the packing with ether for 24 hr and drying the extracted packing to constant weight.

Flow-through type thermistor detectors (B,B') were mounted at the inlet and outlet of the column. Three gas streams (C,C',C'') measured by critical orifices (D,D',D'') were fed to the system continuously. Streams C and C' were pure carrier gas streams. Stream C'' was sample gas. Depending upon the position of a switch connected to solenoid valves E and E', either the carrier gas stream (C') or the sample gas stream (C'') was fed to the column, the other stream being vented. The sample gases were solutions of argon or one of the hydrocarbons in helium.

The pressure at the column outlet as indicated by absolute pressure manometer *F* was maintained constant by regulator *G* attached to surge tank *H*. The total flow through the column was maintained constant by regulator

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