ACKNOWLEDGMENT

The authors express their appreciation to the University of Kentucky Computing Center for the use of their computer and to Donald E. Sands for his assistance with computer programs.

NOMENCLATURE

A, B, D = constants in Equation 1
α, β, γ = constants in Equation 2
a, b = constants in Equation 4
d = density, grams/ml. or grams/cc.
E_{vis} = activation energy of viscous flow, cal./mole
η = viscosity, cp.
ϵ = dielectric constant
n_D = refractive index (sodium D line)
R = molar gas constant, cal./(mole deg.)
T = temperature, ° K.
W_W = weight fraction of water
X_W = mole fraction of water

LITERATURE CITED

(1) Conner, W.P., Clarke, R.P., Smyth, C.P., *J. Am. Chem. Soc.* **64**, 1379 (1942).
(2) Cowie, J.M.G., Toporowski, P.M., *Can. J. Chem.* **39**, 2240 (1961).
(3) Critchfield, F.E., Gibson, J.A., Hall, J.L., *J. Am. Chem. Soc.* **75**, 1991 (1953).
(4) Denny, D.J., Cole, R.H., *J. Chem. Phys.* **23**, 1767 (1955).
(5) Girifalco, L.A., *Ibid.*, **23**, 2446 (1955).
(6) Leader, G.R., *J. Am. Chem. Soc.* **73**, 856 (1951).
(7) LeBel, R.G., Goring, D.A.I., J. CHEM. ENG. DATA **7**, 100 (1960).
(8) Lohr, L.J., *J. Phys. Chem.* **62**, 1150 (1958).
(9) Malmberg, C.G., Maryott, A.A., *J. Res. Natl. Bur. Std.* **56**, 1 (1956).
(10) Misra, B.N., Varshni, Y.P., J. CHEM. ENG. DATA **6**, 194 (1961).
(11) Moore, D.W., Burkardt, L.A., McEwan, W.S., *J. Chem. Phys.* **25**, 1235 (1956).
(12) Petersen, R.C., *J. Phys. Chem.* **64**, 184 (1960).
(13) Sears, P.G., Siegfried, W.D., Sands, D.E., J. CHEM. ENG. DATA **9**, 261 (1964).
(14) Varshni, Y.P., Srivastava, S.N., *J. Phys. Chem.* **62**, 706 (1958).
(15) Vaughn, J.W., Sears, P.G., *Ibid.*, **62**, 183 (1958).

RECEIVED for review July 27, 1964. Resubmitted February 1, 1966. Accepted February 11, 1966.

Flow Calorimeter Measurements of Binary Heats of Mixing for Liquid Normal, Primary Alcohols in Normal Alkanes

VINCENT C. ROSE[1] and T. S. STORVICK
University of Missouri, Columbia, Mo.

A steady-flow calorimeter assembled to measure the heats of mixing of binary mixtures is described. Its performance is compared to the batch and semibatch procedures conventionally used. The data in the 0.1- to 0.9-volume fraction range were determined and compared to literature values. An accuracy of ±5% is obtained and the data reported are satisfactory for most engineering calculations. Heats of mixing data for 1-hexanol–*n*-heptane, 1-decanol–*n*-heptane, 1-butanol–*n*-undecane, and 1-hexanol–*n*-undecane binaries at 35° and 45° C. are reported.

HEATS of mixing data for nonideal liquid systems are useful for design calculations and for the information they provide concerning the structure of the liquid phase. Since the theory of the liquid phase is comparatively incomplete, a common basis for reliable predictive procedures for estimating heats of mixing has not been developed. It appears that empirical methods to extend available data should be based on a systematic study of similar compounds.

To obtain systematic data to develop an empirical procedure, the heats of mixing of several binary mixtures of primary, normal alcohols in normal alkanes were measured in a flow calorimeter (*7*), at 35° and 45° C. and atmospheric pressure. Recent measurements reported by Savini, Winterhalter, and Van Ness (*9*) on 1-propanol, 1-butanol, and 1-butanol and 1-hexanol in *n*-hexane were duplicated in this work and provide a comparison for the data obtained with the flow calorimeter. The heats of mixing data on the 1-hexanol and 1-decanol in *n*-heptane systems and the 1-butanol and 1-hexanol in *n*-undecane systems are reported.

APPARATUS

The problems associated with the design of a calorimeter to measure heats of mixing have been discussed by White (*13*), Weissberger (*12*), Rossini (*8*), and Skinner (*11*). Although both nonisothermal and isothermal calorimetry have been extensively used, the latter offers the advantage of direct measurement of the heats of mixing. If the systems under study are endothermic, energy can be added to the mixture. Constant temperature can be maintained by adjusting either the energy input or the rate of addition of pure components.

Mrazek and Van Ness (*4*) have developed an isothermal calorimeter that allows rapid determination of the heats of mixing. The mixing chamber contains an initial charge of one component. The second component is added at a variable rate just to compensate the constant rate of electrical energy input. Simultaneous readings of the energy input and the amount of component added yield the heats of mixing data. Evaporation and condensation effects were eliminated by using an expandable mixing chamber to eliminate the vapor space. The data obtained were of excellent quality and compared favorably with the best literature values.

---

[1] Present address: College of Engineering, University of Rhode Island, Kingston, R. I.

Continuous flow calorimeters have seldom been used for determination of heats of mixing. Pratt (*6*) used a nonisothermal flow system to study heats of dilution. The continuous flow, isothermal device used in this work was suggested by Mueller and Lewis (*5*). The troublesome vapor space was eliminated by injecting the two components into a mixing chamber and adding energy through a resistance heater to balance the endothermic mixing energy.

A schematic diagram of the flow calorimeter used in this work is shown in Figure 1.

Two stainless steel positive displacement pumps, *A*, each of 435-ml. capacity, forced mercury into the feed tanks, *B*. The mercury displaced the mixture components into the calorimeter, *F*, through coiled transfer lines *C*, which provided heat exchange with the constant temperature bath. The feed tanks were charged at *D* by reversing the pumps. The calorimeter was surrounded by a vacuum jacket, *G*, which kept the calorimeter body from contact with the constant temperature bath fluid. This jacket was evacuated at *I* to reduce heat losses from the calorimeter. The electrical leads extended through the vacuum line at *H*. The mixture from the calorimeter was collected in a tank, *J*, which was vented to the atmosphere at *K*. Provisions for siphoning the contents of this container were provided at *L*.

All of the equipment shown in Figure 1 was submerged in a constant temperature bath controlled to ±0.05° C. of the isothermal temperature at which data were taken. The bath temperature was measured with a platinum resistance thermometer calibrated by the National Bureau of Standards.

The positive displacement pump cylinders were precision-ground and calibrated by weighing the quantity of mercury displaced per revolution of the drive screw. This displacement was 1.3740 and 1.3749 cc. per revolution with a standard deviation of 0.00256 cc. per revolution based on nearly 200 weighings of mercury displaced. The piston position or the number of turns had no perceptible influence on the discharge per turn of either pump. The mixture composition was controlled by selecting the desired speed ratio through a system of spur gears, sprockets, and chains driven by a three-phase induction motor.

Details of the calorimeter are shown in Figure 2. Pure components entered the mixing chamber, *A*, at a rate of 0.2 ml. per second through 1/8-inch copper tubing, *B* and *C*. Two 10-cm. lengths of 3/16-inch copper tubing lined with No. 10 A.W.G. Teflon spaghetti were joined with a brass compression tee, *D*, to form the section for measuring the heats of mixing, *E*, and the heat capacity of the mixture, *F*. The heaters, *G*, were made from No. 36 B and S gage Cupron wire and had a resistance of of 0.105 ± 0.002 and 0.252 ± 0.002 ohm, respectively. The temperatures of the mixture and one of the pure components were measured by three thermistors located at *H*. The thermistors had a nominal resistance of 100 ohms at 25° C. They were calibrated in place with the platinum resistance thermometer and the constant temperature bath described above.

The brass compression fittings were all lined with Teflon sleeves which served as a thermal barrier and as electrical insulation for the heater and thermistor lead wires. Figure 3 shows the design of the seals on the lead wires. A Kel-F button was machined to fit the bottom of the brass fitting. Holes in the button were provided for each lead wire. Four slots were cut in the brass fitting at 90° to provide the lead wire exits. A Kel-F disk was placed over the button and a brass plug follower advanced with the compression fitting nut. Plastic deformation of the Kel-F provided the pressure seal. Care was required to avoid electrical grounding of the lead wires with the compression fitting. No problems were encountered after assembly was completed and the system pressure tested.

The electrical circuit used to make the power measurements is shown in Figure 4. Power was supplied to the heats of mixing section by a 6-volt storage battery. A 10-ohm

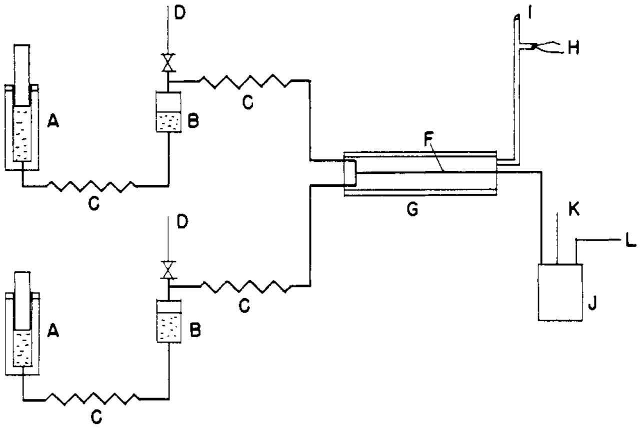

Figure 1. Schematic diagram of calorimeter assembly

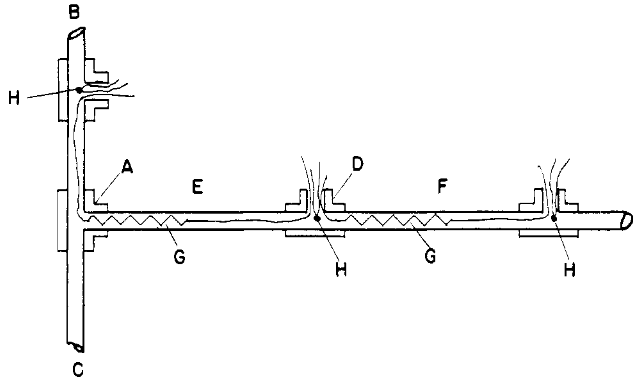

Figure 2. Detailed schematic diagram of calorimeter

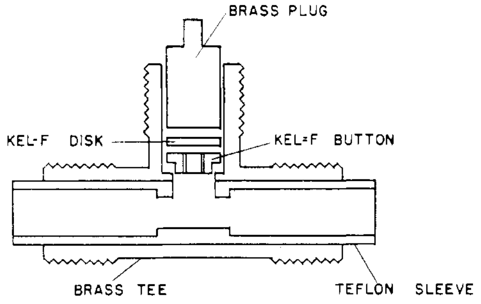

Figure 3. Lead-wire seal assembly

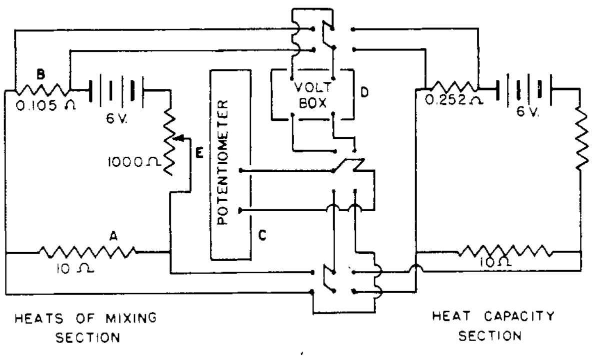

Figure 4. Wiring diagram for energy input measurements

Advance wire standard resistor, *A*, was connected in series with the calorimeter heater, *B*. The potential drop across the standard resistor and the heater was measured by a precision potentiometer, *C*. Voltages were reduced to the range of the potentiometer with a volt box, *D*. A 1000-ohm decade resistance box, *E*, which could be adjusted in steps of 0.1 ohm was placed in series with heater *B* to control the energy input.

The heat capacity section was assembled in the same manner as the heats of mixing section. A 50-ohm resistor was placed in series with the heater to keep the temperature rise of the fluid below 0.5° C. at the design flow rate of 0.2 cc. per second. Initial tests of the equipment indicated erratic performance of the thermistor downstream from the heat capacity section. No data were obtained from this part of the apparatus.

MATERIALS

The materials used in this work and the specifications provided by the supplier are:

Compound	Specifications
n-Hexane	Purity, 99 mole % min. Boiling point, 155.8° F. Sp. g. 20/4, 0.660
n-Heptane	Purity, 99 mole % min. Boiling point, 209.1° F. Sp. g. 20/4, 0.6838
n-Undecane	Purity, 99 mole % min. Boiling point, 384.0° F. Sp. g. 60/60, 0.745
Benzene	Thiophene-free Boiling range, 79.5° to 81.0° C. Sulfur, 0.005% Water, 0.02%
Methanol	Purity, 99.5 mole % min. Boiling range, 64.6–64.8° C. Sp. g. at 25° C., 0.7886
1-Butanol	Boiling range, 117.4–117.9° C. Aldehydes and ketones, 0.05%
1-Hexanol	Boiling range, 153° to 160° C. Sp. g. 20/20, 0.819 to 0.823
1-Decanol	Melting range, 5.5° to 6.5° C. Sp. g. 20/4, 0.830

All of the chemicals were used as received, except the 1-hexanol, which contained 3 to 5% 2-ethylbenzene and was purified by vacuum distillation in a Todd precise fractionation assembly. The distilled material was eluted through a 5-foot Apiezon J gas chromatographic column maintained at 85° C. Only trace impurities were detected. These were not identified.

The 1-decanol was used without purification, even though the melting point indicates the presence of impurities. The separation of the isomers from 1-decanol is difficult, and since a large quantity of this material was required it was not attempted.

PROCEDURE

The constant temperature bath was set at the run temperature and controlled to ±0.05° C. of the set point. The feed tanks were filled with solvent and about 4 hours allowed to establish thermal equilibrium with the bath. The mixture composition was selected by adjusting the pump drive gear ratio. A run was started when the temperatures of the solvents to the calorimeter were the same as the bath temperature. The power to the calorimeter heater was adjusted until the temperature of the mixture from the calorimeter was the same as the inlet solvent temperature. The voltages across the heater and the standard resistor were recorded and the run was terminated if these measurements remained constant when the readings were repeated. The heat of mixing was calculated and plotted as each value was obtained and any questionable value was rerun.

The feed tanks provided enough materials for measuring several points without refilling. Care was taken to avoid contamination of the feed by other components. The feed tanks and calorimeter were flushed several times with solvent when a new system was measured.

The data for one binary at one temperature could be obtained in one day. This included repeating a major portion of the points in addition to any points that appeared incorrect at the time the data were taken.

Solvent volatility and failure of the lead wire seals precluded measurements at 55° C. Modified design of the lead wires and backpressure control on the mixture accumulation tank would allow operation of this calorimeter at any pressure in the liquid range.

A complete description of the apparatus and the operating procedure is given by Rose (*7*).

EXPERIMENTAL RESULTS

Accuracy of Data. The vaporization condensation effects associated with a vapor space in a heat of mixing calorimeter have been eliminated by the design of the flow calorimeter. The volume of the hydrocarbon and alcohol pumped was known to ±1.1% when one component was pumped at a very low rate. This combined with the errors assigned to the current-voltage measurements indicates that the heats of mixing values are accurate to ±2.75% at dilute concentrations. The data were reproducible to ±1.0%. These estimates apply to systems with heats of mixing greater than 2 joules per cc.

To check the accuracy of the apparatus, values of the heat capacity of benzene at 35° C. were measured. A value of 1.77 joules/gram ° C. was obtained, which is within 2% of the literature value, 1.752 joules/gram ° C. (*3*). A benzene heat capacity of 2.03 joules/gram ° C. was obtained from the heat capacity section, indicating a malfunction. No data were obtained from this section.

The heats of mixing of methonol-benzene were obtained at 35° C. in order to compare the calorimeter performance with the large number of reported data for this system. This work has been reviewed in detail by Mrazek and Van Ness (*4*). In Figure 5 the smoothed data of Mrazek and Van Ness, experimental values of Brown and Fock (*1*), and this work are compared. All data agree within 2% over the full composition range. This is excellent agreement, considering that three experimental techniques were used to obtain the data.

The data for 1-octanol in *n*-heptane system obtained by Savini, Winterhalter, and Van Ness (*9*) were about 25% higher than the values obtained with the flow calorimeter at 45° C. This error occurred at a volume fraction of 0.6 to 0.7 1-octanol and decreased at higher and lower alcohol concentrations. The same trend was noted for the 1-propanol and 1-butanol in *n*-heptane systems, but the maximum error was about 5% for these systems. This error may have been due to incomplete mixing in the calorimeter section, and suggests that the accuracy of the data reported probably decreases as the solvents become more viscous.

The heats of mixing data for the nine alcohol-hydrocarbon systems were smoothed by plotting $\Delta H/\phi_1\phi_2$ *vs.* ϕ_1 and $\phi_1\phi_2/\Delta H$ *vs.* ϕ_1. The volume fractions ϕ_1 for the alcohol and ϕ_2 for the hydrocarbon represent the fraction of the volume actually displaced by the feed pump for each component. Figures 6 and 7 show these plots for the 1-butanol-*n*-hexane system. The data of Brown, Fock, and Smith (*2*) are included for comparison. The heats of mxing at infinite dilution can be obtained by extrapolating the curves to a volume fraction of 0 and 1. Since the measured values are relatively

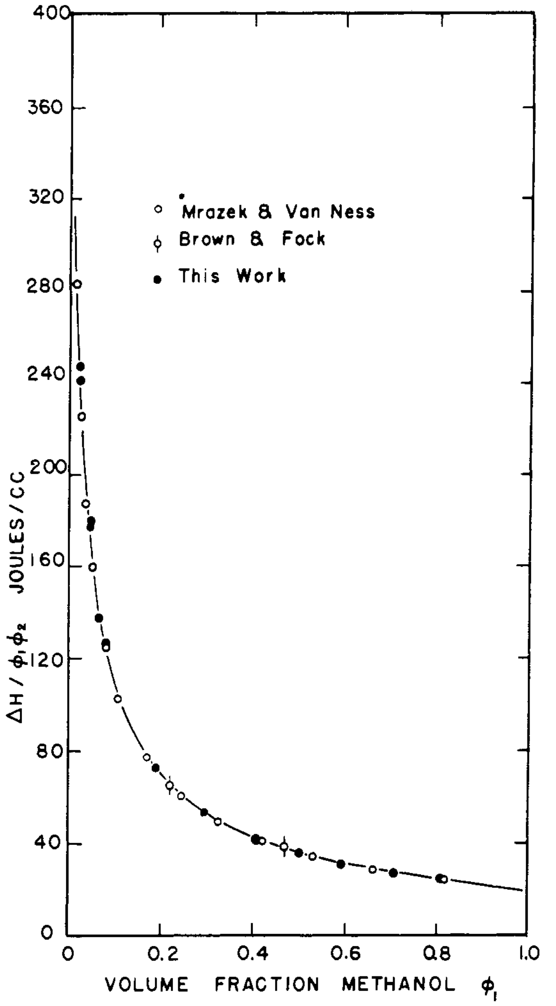

Figure 5. Heats of mixing for methanol-benzene system

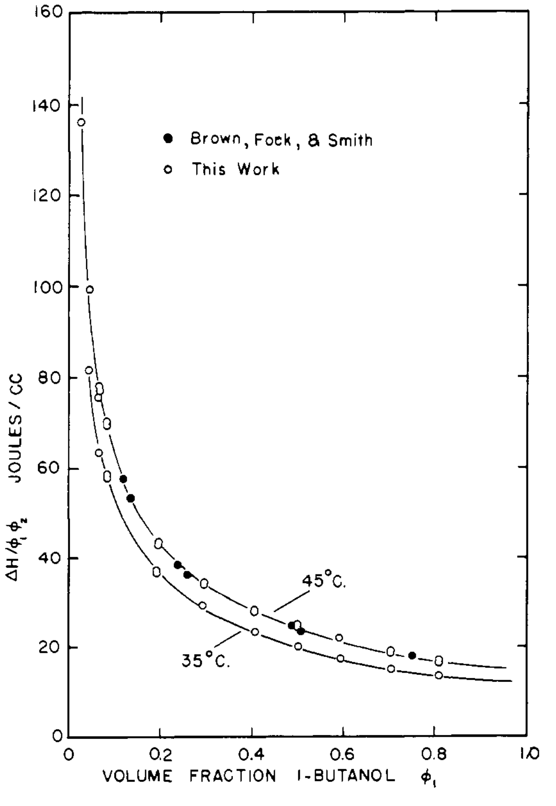

Figure 6. Heats of mixing for 1-butanol–*n*-hexane system

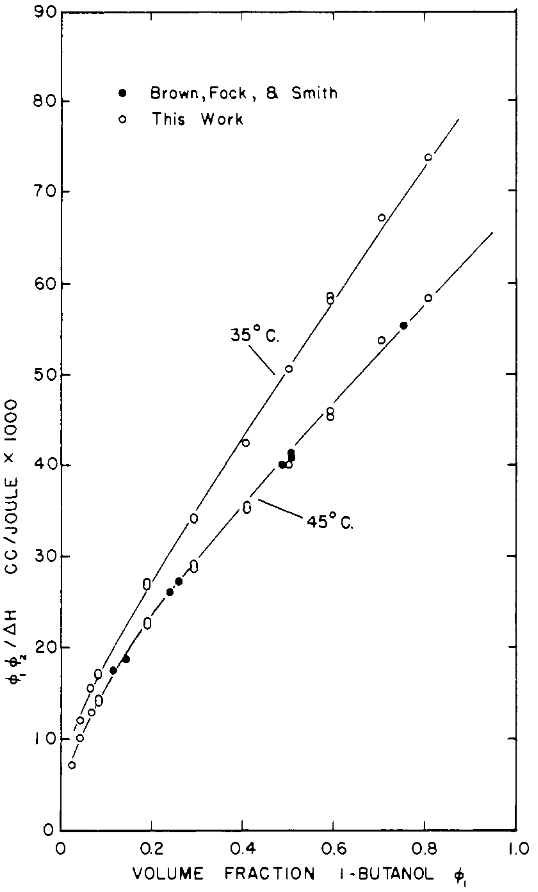

Figure 7. Reciprocal heats of mxing for 1-butanol–*n*-hexane system

Table I. Smoothed Heats of Mixing for *n*-Alcohol–*n*-Alkane Systems Tabulated as $(\Delta H)/\phi_1\phi_2$ Joules per Cc.

	1-Hexanol *n*-Heptane		1-Decanol *n*-Heptane		1-Butanol *n*-Undecane		1-Hexanol *n*-Undecane	
ϕ_1	35° C.	45° C.	35° C.	45° C.	35° C.	45° C.	35° C.	45° C.
0.9	9.2	13.0	5.6	7.4	10.8		5.1	
0.8	10.3	13.6	6.1	7.9	11.3	14.0	5.4	
0.7	11.6	14.3	6.9	8.7	12.3	15.0	5.0	13.8
0.6	13.3	15.4	7.8	9.8	13.9	16.7	7.0	14.9
0.5	15.8	17.5	9.2	11.6	16.0	19.2	8.5	16.5
0.4	18.2	20.8	11.2	14.	19.0		11.0	
0.3	21.8	25.8	13.8	18.4	23.4		14.6	
0.2	29.0	33.9	19.9	25.6	31.2		21.1	
0.1	44.5	51.8	33.5	40.2	48.4		37.5	

inaccurate at the extreme concentrations, the infinite dilution values could be in error and are not reported here.

The smoothed data are tabulated in Table I. The units of joules per cubic centimeter are used, since these units represent the measured energy input per unit volume of the two fluids displaced by the pumps. These data may readily be converted to the more familiar units of energy per unit mass of solution by multiplying the table entry by $(\phi_1\phi_2)/(\phi_1\rho_1 + \phi_2\rho_2)$, where ρ is the density of the pure components in grams per cubic centimeter. The most familiar units of energy per mole of solution can be obtained from the expression $(\Delta H)/x_1x_2 = (\Delta H)/\phi_1\phi_2\,[V_1 - \phi_1\,(V_1 - V_2)]$, where ΔH is the heat of mixing per mole of solution, x is the mole fraction, and V is the molar volume.

DISCUSSION

An isothermal flow calorimeter, designed to measure the heats of mixing of hydrocarbon-alcohol systems, gives rapid determination of the data, ease of operation, and an accuracy of ±5% or better in the composition range between 0.1 and 0.9 volume fractions. This accuracy is sufficient for most engineering calculations and could be increased by improving the instrumentation and providing a better mixing section. The major advantage of the flow calorimeter is that it can be easily modified to operate at elevated pressure.

The flow calorimeter has two distinct disadvantages. It requires a large quantity of pure components which are usually difficult and expensive to obtain. In addition, the precision of the measurements is least reliable at low concentrations, the very region where precision data would be most valuable for comparison with the theories of liquid structure. Although design improvements can reduce these errors, very high precision batch or semibatch calorimeters will be required to eliminate both of these shortcomings. Such an instrument has been perfected by Van Ness and coworkers (*4*, *9*).

ACKNOWLEDGMENT

The authors acknowledge the graduate fellowship support received from the Texaco Co. and the Shell Oil Co. Financial assistance from the Engineering Experiment Station at the University of Missouri provided special equipment and the chemicals required for this project.

NOMENCLATURE

ΔH = heat of mixing, joules/cc., joules/mass
V = molar volume, cc./g.-mole
x = mole fraction
ϕ = volume fraction
ρ = density, g./ml., g. mole/cc.

SUBSCRIPTS

1 = alcohol
2 = hydrocarbon solvent

LITERATURE CITED

(1) Brown, I., Fock, W., *Australian J. Chem.* **14**, 387 (1961).
(2) Brown, I., Fock, W., Smith, F., *Ibid.*, **17**, 1106 (1964).
(3) "International Critical Tables," Vol. **5**, p. 86, McGraw-Hill, New York, 1929.
(4) Mrazek, R.V., Van Ness, H.C., *A.I.Ch.E. J.* **7**, 190 (1961).
(5) Mueller, C.R., Lewis, J.E., *J. Chem. Phys.* **25**, 1166 (1956).
(6) Pratt, F.R., *J. Franklin Inst.* **185**, 663 (1918).
(7) Rose, V.C., Ph.D. dissertation, University of Missouri, January 1965.
(8) Rossini, F.D., ed., "Experimental Thermochemistry," pp. 237–86, Interscience, New York, 1956.
(9) Savini, C.G., Winterhalter, D.R., Van Ness, H.C., J. CHEM. ENG. DATA **10**, 168 (1965).
(10) Sieg. L., *Chem.-Eng.-Tech.* **23**, 112 (1951).
(11) Skinner, H.A., ed., "Experimental Thermochemistry," Wiley, New York, 1962.
(12) Weissberger, A., ed., "Physical Methods of Organic Chemistry," 3rd ed., Part I, Interscience, New York, 1959.
(13) White, W.P., "Modern Calorimeter," Chemical Catalog Co., New York, 1928.

RECEIVED for review October 5, 1964. Accepted November 26, 1965.

Isobaric Vapor-Liquid Equilibrium of *n*-Heptane–*n*-Butanol System

S. V. VIJAYARAGHAVAN, P. K. DESHPANDE, and N. R. KULOOR
Department of Chemical Engineering, Indian Institute of Science, Bangalore-12, India

Vapor-liquid equilibrium data for the system *n*-heptane–*n*-butanol have been reported. The thermodynamic consistency of the data was tested with Chao's modified Redlich-Kister equation and Tao's method.

VAPOR-LIQUID equilibrium data for the system *n*-heptane–*n*-butanol are available only at isothermal conditions (*6*). Therefore, the system has been studied under isobaric conditions at 684 ± 5 mm. of Hg.

EXPERIMENTAL

The equilibrium still used has been described (*8*), and it is a modified Ellis and Garbett (*2*) still. The still was operated without stirrers for 3 hours to attain equilibrium, and then samples were drawn for analysis.

Both *n*-heptane and *n*-butanol of British Drug House laboratory reagent grade were used. The density and refractive index of reagents and also the literature values are given in Table I.

Samples were analyzed by determination of density and viscosity. The viscosity was determined using Hoppler's falling ball viscometer. A calibration chart was initially constructed from the data of known composition.

THERMODYNAMIC CONSISTENCY

The experimental vapor-liquid equilibrium data are presented in Table II. Liquid phase activity coefficients are calculated from the equation,

Table I. Properties of Pure Components

	Density, at 20° C.		Refractive Index, at 20° C.	
Compound	Exptl.	Lit. (*3*)	Exptl.	Lit. (*3*)
1. *n*-Heptane	0.68380	0.68376	1.3880	1.3876
2. *n*-Butanol	0.80986	0.80978	1.3988	1.3991

Table II. Vapor-Liquid Equilibrium Data (Pressure 684 ± 5 mm.)

		Mole % of *n*-Heptane			
No.	Temp., ° C.	Liquid	Vapor	γ_1	γ_2
1	103.8	5.7	37.0	4.995	1.007
2	98.2	14.2	54.4	3.469	1.013
3	95.2	22.1	62.1	2.790	1.043
4	92.2	32.9	69.3	2.282	1.108
5	90.2	43.4	73.0	1.941	1.259
6	89.5	55.2	75.8	1.622	1.471
7	89.0	61.4	77.4	1.510	1.627
8	88.8	73.8	79.5	1.296	2.190
9	89.3	91.1	84.6	1.100	4.984
10	93.4	98.0	93.5	1.001	7.532