Heats of Mixing of C_4 Hydrocarbons in Water-Acetone Solvent

DAN E. NICHOLSON
Humble Oil & Refining Co., Baytown, Tex.

IN CONJUNCTION with research on extractive distillation it has become customary to calculate heats of mixing from phase equilibrium measurements (*2*, *3*). If sufficient vapor-liquid equilibrium data are available, the differential heats of mixing are obtainable from the variation of the activity coefficient with temperature. The determination of the partial molar heat of mixing from the relationship $d\ln \gamma / d\,(1/T) = \Delta H_m/R$ places stringent requirements on both the quantity and accuracy of the phase-equilibrium measurements. This investigation was undertaken to obtain reliable data for the energy changes attendant to the solution of several liquid C_4 hydrocarbons in the water-acetone solvent currently in use in the production of the butenes. The calorimeter designed for this purpose is described here and the data are compared with those of previous investigators.

EXPERIMENTAL

Starting Materials. The C_4 hydrocarbons were research grade materials purchased from the Phillips Petroleum Co. Baker's reagent grade acetone, carbon tetrachloride, and chloroform were used without further purification. The liquid hydrocarbons were transferred directly from the inverted cylinders into a reservoir from which they passed into the calorimeter. Compression of the samples indicated clearly the absence of many permanent gases in the connecting lines and the reserviors. Eastman white label 2-furaldehyde was distilled shortly before use under reduced pressure and stored in dark bottles under an atmosphere of nitrogen. Water in the reagent grade acetone was measured by the Karl Fisher titration.

The Calorimeter and Appurtenances. In the calorimeter and jacket (Figure 1), thermowells *A* and *B* housed Leeds & Northrup 25-ohm platinum resistance thermometers, helium-filled and sheathed in platinum to permit rapid response to temperature changes. A 10-junction Chromel P-Constantan thermocouple (No. 32 B. & S. gage wire) having double glass fiber insulation was located on the inner walls of the jacket, *G*. Thermocouple junction, at *D* and *D'* and elsewhere, were spaced to cover areas approximately equal, thereby giving a properly integrated temperature. One set of the cold junctions was located externally in a thick-walled copper tube for immersion in melting ice.

The enveloping cylinder, *G*, was machined from an aluminum casting 9 inches in diameter; it was equipped with an electric heater capable of delivering 180 watts and energized by a Kepco Model 500-R direct current stabilized power supply. The jacket heating element consisted of 308 feet of No. 30 B. & S. gage Nichrome wire with double glass fiber insulation; the heater wire was distributed over the outer surface, *T*, *S*, and *G*, uniformly to prevent the development of hot spots on the inner walls of the aluminum jacket. Copper tubing (1/8-inch) was wound on the jacket at position *U* and in the corresponding space at the bottom to facilitate cooling of the entire assembly in adjustment of temperature levels prior to experiments. The enveloping cylinder was surrounded by 2.5 inches of glass fiber.

The cover, *V*, of the jacket was held firmly in place by 12 bolts, *W*, and contains preheat coils, *H*, to ensure that the solute was brought to the temperature of the calorimeter vessel, *M*, before passage through the throttle valve, *J*. The calorimeter proper had a free volume of approximately 300 ml., and was constructed of stainless steel. It was equipped with a 1-mm. stainless steel tube, *Q*, to allow introduction of solvent and emptying the calorimeter contents at the completion of a run. The solute inlet tube, *P*, also connected to the throttle valve, an integral part of the pressure vessel. The copper internal heater tube, *I*, contained 4.9 feet of No. 32 B. & S. gage Constantan wire, noninductively wound, an insulated resistor in helical form. The resistor was embedded in magnesia. Copper vanes, *X*, channeled the liquid circulated by a propeller-type stirrer, *K*. The stirrer was magnetically coupled to the shaft, *O*, by cylindrical Alnico V magnets, *L*. Thermocouple junctions located at *E* and *F* indicated equality in temperatures within ±0.003° C. when 100 watts of electrical power were supplied to the jacket heater, showing uniformity of heat transfer and absence of thermal lag. Three Bakelite cleats at position *N* supported the calorimeter within its jacket and contributed a negligible amount to the total heat transfer.

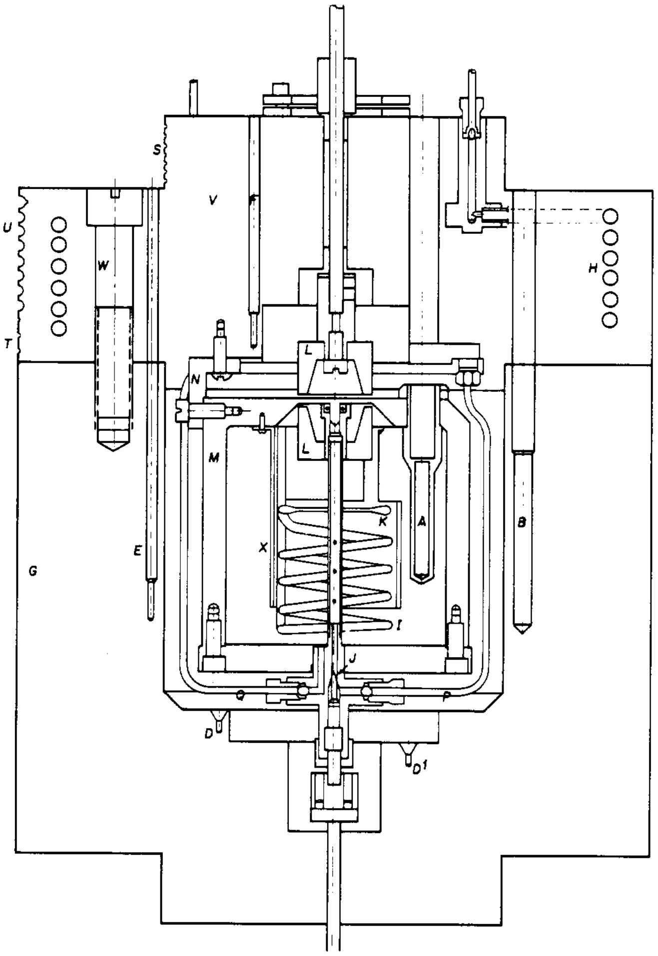

Figure 1. The calorimeter and jacket

Accessory Apparatus. The thermoregulator was selected with the objectives of allowing the calorimeter to be operated with an isothermal jacket and, of allowing the jacket to follow the calorimeter temperature in an exothermic process. Electronic equipment consisted of five items: a Leeds & Northrup No. 60614-H1-Q1-779 Model S Speedomax Type G indicating and recording controller, L. & N. No. 9835-B stabilized direct current indicating amplifier, L. & N. No. 10874 position adjusting type electric control unit (Series 60), L. & N. No. 10262-60 electric drive mechanism, and Kepco Laboratories Model 500-R direct current power supply. These or similar components have been incorporated, with some modifications, in a precision adiabatic calorimeter designed by Ginnings and West (*4, 5*). For adiabatic operation, the electronic system accepts a d.c. signal from the thermopile, amplifies and records the voltage, and turns the shaft of a control mechanism so as to match the temperature of one body with that of another. A first 10-junction thermopile was built into the calorimeter with the reference and measuring junctions situated on the inner wall of the jacket and the outer wall of the calorimeter; this arrangement allowed study of the rate at which the jacket would follow the pressure vessel for an exothermic process. Using a second 10-junction thermopile, a bucking voltage was applied to the thermal electromotive force output so that no signal was fed to the linear amplifier when the calorimeter and jacket were in thermal equilibrium. In this second arrangement a set of measuring junctions was spaced over the inner wall of the jacket and the reference junctions were located in an ice bath. The experiments reported here were made holding the jacket at constant temperature, letting the calorimeter cool when the liquids are mixed, and evaluating the heat transfer between the calorimeter and its jacket. The calorimeter heater, *I*, was used to evaluate the heat capacity of the calorimeter (and contents). A mercury cell was used in the circuit to supply the constant voltage for this purpose. With a single adjustment of the bucking voltage every hour or so it was possible to maintain the jacket temperature constant to ±0.002° C. Thermoregulator provided for three different types of temperature control: proportional, automatic reset, and rate action. For isothermal operation of the jacket the controller-regulator settings were, of course, not nearly so critical as for operation of an adiabatic calorimeter. With an isothermal jacket, the following instrument parameters were satisfactory to yield temperature regulation to ±0.002° C.: 20% proportional band, 0.06 automatic reset, 0.1-0.5 rate action, and a scale multiplier on the linear amplifier of 0.1.

All precision temperature measurements were taken with two 25-ohm four-lead potential terminal calorimetric type resistance thermometers. The thermometers were calibrated by the National Bureau of Standards at the fixed points of ice, steam, and boiling sulfur. Resistance readings were based on values indicated by a Leeds & Northrup G2 Mueller bridge, calibrated in this laboratory. The equivalent heat capacity of the calorimeter and contents was established by applying a known voltage, determined by a Leeds & Northrup K2 potentiometer, across the calorimeter resistor for a specified length of time. The resistance of the calibrating heater was 23.188 absolute ohms at 90° C. The power developed in the lead wires between the calorimeter heater (junction of the current and potential wires with the heater) and the jacket was approximately 0.064% of the total power. No further accounting for this power was made other than to establish that it was negligible in relation to over-all experimental uncertainties in measuring heats of mixing. Potential standards consisted of three recently certified Eppley standard cells which were intercompared frequently. The assembly of high capacity lead storage cells to supply power for the calorimeter heater were maintained at about 70% of full charge. The battery was discharged for 1/2 to 1 hour through a 23-ohm resistor before switching rapidly to the calorimeter resistor in all series of measurements. A standard laboratory timer was employed to determine the length of heating periods.

Solvent and solute were introduced into the calorimeter through two gage glasses by means of mercury displacement from a common volumetric pump. One revolution of the pump wheel handle corresponded to 3 ml. of liquid. In practice, volumes could be estimated to approximately ±0.005 ml. The smallest quantity of liquid hydrocarbon metered was approximately 10 ml. The gage glass containing the solvent was not thermostated because, in general, the solvent was added to the calorimeter at least 2 hours before experiments were initiated. The reservior for solute was housed in a thermostated oil bath held at a temperature within about 1° of that of the calorimeter. Final preheating of the liquid was afforded by the stainless steel coils in the calorimeter cover. An extended series of trial runs established that very small changes in temperature—i.e., ±0.003° C.—occured when volumes of liquid greater than 50 ml. were forced quickly into the pressure vessel through the coiled tubing in the aluminum jacket. Time-temperature measurements were ordinarily taken during a 3-hour period in the completion of a set of heat-of-mixing measurements. This time interval included the fore period, the mixing and after periods, and electrical calibration to establish precisely the thermal leakage modulus and power input due to stirring under the conditions of the experiment.

RESULTS

The reliability of the calorimeter was confirmed by reproducing the heats of mixing of carbon tetrachloride and chloroform reported by Cheesman and Whitaker (*1*) within ±0.5%. The thermal leakage modulus, *K*, defined by Newton's law and its formulation in the First Geophysical Method, was computed to be −0.0042 and −0.0063° C. per minute per degree of thermal head at 35° and 90° C., respectively. The energy input due to the mechanical stirrer, *w*, at 60 r.p.m. was equivalent to a temperature rise of 0.00030° C. per minute. Between 35° and 90° C. the heat capacity of the calorimeter was 296.3 calories per degree. The most accurate value for a heat of mixing was obtained by calculating *K* and *w* for that particular experiment. No vapor space existed within the calorimeter after mixing of the liquids was completed. Sufficient pressure was always applied in forcing liquefied hydrocarbon into the calorimeter to ensure that only a liquid phase was present. Corrections were applied, however, for the heat evolved in condensing the solvent from the gaseous to liquid state upon addition of the hydrocarbon solute under pressure. This correction was of the order of 1 to 4% of the intregral heat of mixing for the C_4 hydrocarbons.

A typical set of time-temperature profiles is shown in Table I. From these data it can be shown that the true temperature drop due to the addition of *n*-butane to the water-acetone solvent is −0.5436° C.; the true temperature rise of the calorimeter due to the addition of heat energy during the calibration period is +0.7455° C.; and the integral heat of mixing of the components indicated to yield a mixture containing 4.52 weight % hydrocarbon is 1322 calories per mole of dissolved *n*-butane. A plot of the time-temperature data is given in Figure 1.

The principle calorimetric data derived from the current study are for the energy change accompanying the solution of the liquid hydrocarbons in a water-acetone solvent (12.86 weight % water, 87.14 weight % acetone). These results are summarized in Table II and Figure 2. The heat effects are endothermic and large, in some cases being of the order of one third of the heat of vaporization for the compounds studied. Thus, the energy of mixing for *n*-butane is about

Table I. Time-Temperature Profiles for the Heat of Mixing of n-Butane in Water-Acetone Solvent

Weight of hydrocarbon. 11.345 grams
Weight of acetone-water solvent. 239.85 grams
Electrical power added via calorimeter heater. 329.0 calories

Time, Min.	Jacket Temp., ° C.	Calorimeter Temp., ° C.	Time, Min.	Jacket Temp., ° C.	Calorimeter Temp., ° C.
0	90.463	90.534	100	90.484	90.173
10	90.439	90.527	110	90.480	90.189
20	90.446	90.519	115 Heat on		
23	n-C_4H_{10}		130 Heat off	90.435	90.912
24	added		140	90.422	90.864
25	90.560	89.978	150	90.435	90.821
30	90.529	89.995	160	90.437	90.787
40	90.513	90.024	170	90.437	90.749
50	90.500	90.057	180	90.442	90.717
60	90.491	90.085	190	90.448	90.689
70	90.489	90.111			

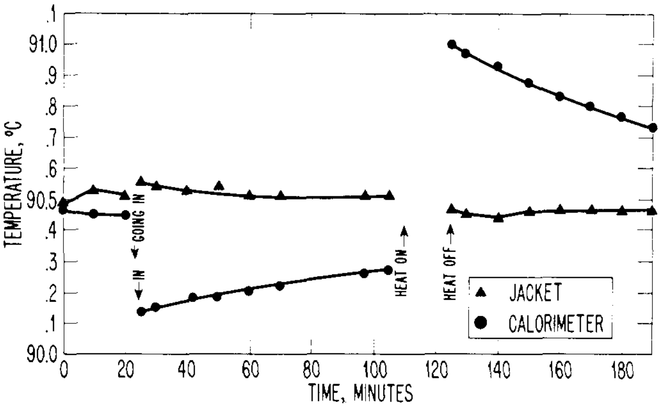

Figure 2. Time-temperature profile for the mixing of n-butane with water-acetone solvent at 90° C.

0.01005 mole fraction n-butane

1430 calories per mole of dissolved hydrocarbon (mole fraction of approximately 0.026). The molar integral heats of mixing show marked dependence upon the concentration of the respective hydrocarbons in solution, and the systems are rather complex. For example, the integral heat of mixing of n-butane first increases as concentration of n-butane in the solvent increases, reaches a maximum, and then decreases—the curve (ΔH_m *vs.* concentration) is concave toward the concentration axis. 2-Methylpropane, *cis*-2-butene, and 1-butene exhibit a type of behavior more frequently encountered; the molar heat effect first decreases regularly with increasing concentration as the solvent becomes more nearly like the solute. The heat of mixing for 2-methylpropane is less dependent upon hydrocarbon content in the solvent than are the heat of mixing values for the other three C_4 hydrocarbons. The heats of mixing (Table II) are estimated to be accurate to ±2%.

Table II. Experimental Values for the Endothermic Integral Heats of Mixing of C_4 Hydrocarbons in Water-Acetone Solvent at 90° C.

(12.86 wt. % water, 87.14 wt. % acetone)

Wt. % n-Butane	Mole-Fraction n-Butane	Heat of Mixing, Cal./Mole of Dissolved n-Butane	Wt. % *cis*-2-Butene	Mole-Fraction *cis*-2-Butene	Heat of Mixing, Cal./Mole of Dissolved *cis*-2-Butene
2.46	0.0192	1113	3.30	0.0267	1120
2.90	0.0227	1178	3.34	0.0270	1119
4.09	0.0321	1321	5.97	0.0486	947
4.12	0.0323	1270	9.75	0.0800	866
4.52	0.0355	1321	15.45	0.1282	1001
4.78	0.0376	1271	15.50	0.1286	1008
5.60	0.0441	1354	...	...	...
5.64	0.0444	1337	...	...	...
7.30	0.0577	1434	...	...	...
9.06	0.0718	1492	...	...	...
9.17	0.0728	1416	...	...	...
13.65	0.1094	1250	...	...	...
13.71	0.1099	1236	...	...	...
2-Methyl-propane	2-Methyl-propane	Cal./Mole of Dissolved 2-Methyl-propane	1-Butene	1-Butene	Cal./Mole of Dissolved 1-Butene
2.74	0.0214	1174	4.13	0.0335	813
4.95	0.0389	1101	4.57	0.0371	739
8.77	0.0695	1007	4.60	0.0374	741
14.08	0.1131	1054	9.24	0.0757	641
14.10	0.1135	1058	9.30	0.0762	637
...	...	....	15.58	0.1349	968
...	...	....	15.61	0.1351	975

DISCUSSION

The *a priori* prediction of heats of mixing of multicomponent nonideal systems in which hydrogen bonding is prevalent is not feasible at this time. Comparisons have been made, however, of the results of this investigation with energy data derived from the phase-equilibria study of Ewanchyna and Ambridge (2). In general, the divergence in integral heats of solution based on the current study and the work of Ewanchyna and Ambridge is appreciable, but not unexpected in view of the fundamental differences in the methods employed. A portion of the data bearing on certain comparisons is reproduced in Table III. The deviation in the values of the heats of mixing determined calorimetrically and those calculated from activity coefficients differ by about 10 to 30%. The calculated energies of mixing are not uniformly lower or higher numerically than the experimental energies of mixing. There is no basis for the discrepancies from any approximations introduced in the thermodynamic derivations leading to the operational equations; it is not practicable to measure the activity coefficients at varying temperatures with the accuracy which would be required to permit energies of mixing to be reliable within ±2%.

The factors leading to the convex and concave shapes of the heat-of-mixing *vs.* concentration curves are not understood at this time. It is possible, however, that the terminal activity coefficients which describe adequately the vapor-liquid equilibria may not be of sufficient number and accuracy to calculate the integral heats of solution—the computation of these may require some very complex equations. If such is the case, one is justified in representing the data by curves of the type drawn in Figure 3. It is conceivable that the solvent is changing structure upon the

Table III. Calorimetric and Vapor-Liquid Eqilibria Values for Integral Heats of Mixing of C_4 Hydrocarbons in Water-Acetone Solvent

Compound	Mole Fraction Hydrocarbor in Solvent	Integral Heat of Mixing, Cal./Mole of Dissolved Hydrocarbon: This study	Integral Heat of Mixing, Cal./Mole of Dissolved Hydrocarbon: Phase-equilibria
n-Butane	0.020	1170	1395
2-Methylpropane	0.020	1170	1408
cis-2-Butene	0.027	1120	758

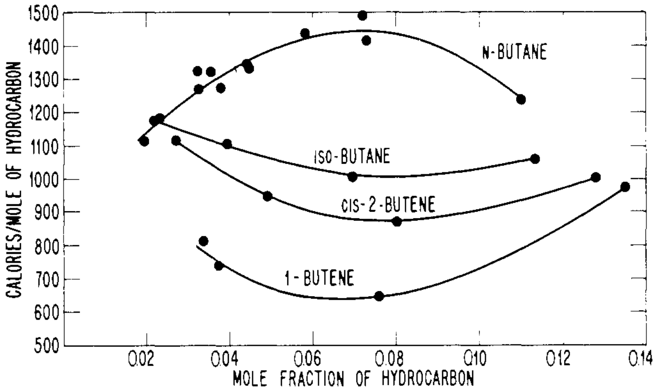

Figure 3. Intregal heats of mixing of C_4 hydrocarbons in water-acetone solvent

addition of *n*-butane to it in some manner which differs from the change found when the other three C_4 hydrocarbons are added.

In conjunction with comparisons between the energies of mixing established directly through calorimetry and from vapor liquid equilibria, other systems were investigated. The molar integral heat of mixing of *n*-butane in furfural was found to be 1298 calories per mole at the 0.010 mole fraction level of hydrocarbon. From vapor-liquid equilibria Mertes and Colburn (*1*) concluded the value to be 1668 calories per mole. Likewise, the calorimetric and calculated values for the heat of mixing of 2-methylpropane are 1234 and 1659 calories per mole, respectively; for 1-butene the quantities are 1199 and 1094 calories per mole.

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Supersaturation in Hydrocarbon Systems

n-Pentane–Silica

H. H. REAMER and B. H. SAGE
California Institute of Technology, Pasadena, Calif.

NICHOLS RECENTLY reviewed the experimental work associated with the supersaturation of hydrocarbon liquids (*9*). Silvey and coworkers studied supersaturation in the methane-*n*-decane system (*14*). Kennedy and Olson (*5*) established that it was possible to maintain hydrocarbon liquids at pressures markedly below bubble point for short periods of time. Marboe and Weyl (*8*) made some investigations of the influence of solid surfaces upon the duration of a specified degree of supersaturation in liquids.

The molecular theory of liquids (*3, 6, 7*) is based upon the concept that significant local fluctuations in the state variables are to be expected at a point as a function of time. Such fluctuations result in marked differences in the time during which a thermodynamic system may be maintained in a strained condition at an invariant macroscopic state. This time of strain is random in time (*4, 9*) and follows Poisson's distribution (*9*). A reconnaissance study has been made of the *n*-pentane-silica system at 160° F. Regression analysis of the experimental information substantiates in part that the time of strain is random with respect to time. No review of the statistics (*4, 9*) will be given here. The methods of regression analysis set forth by Nichols (*9*) will be employed in the analysis of the results.

METHODS AND EQUIPMENT

In principle, the method involved placing a quantity of *n*-pentane and silica in a spherical, isochoric vessel and adjusting the temperature so that the system was maintained under a desired strain. The time required for the formation of the first bubble was noted. Measurements using this equipment were first made with *n*-pentane alone and later with a mixture of *n*-pentane and a substantial quantity of finely divided silica. The primary objective was to establish the order of magnitude of the effect of silica upon the time of strain for a particular degree of supersaturation.

Figure 1 portrays the details of the arrangement of the isochoric pressure vessel. It is constructed of 347 stainless steel and was provided with a slack diaphragm which permitted the pressure in the system to be measured with a pressure balance (*13*). In the case of most of the results reported here for the *n*-pentane-silica system, the isochoric vessel was connected also by means of a stainless steel tube 0.070 inch in diameter to a mercury U-tube to permit the pressure variations within the system to be measured as a function of time. The other arm of the mercury U-tube was connected to a manostat which has been described (*10*). This manostat, which involved a slack diaphragm and an isochoric vessel filled with nitrogen, made it possible to determine readily variations in pressure of the order of 0.01 p.s.i. The variations in pressure with time of the strained system were recorded upon a conventional strip-recorder.

The temperature of the system was known within 0.01° F. in relation to the international platinum scale (*1*). Pressures were measured within 0.1 p.s.i. relative to the vapor pressure of carbon dioxide at the ice point (*2*).

The net volume of the isochoric vessel, with no silica present, at a temperature of 160° F. and a pressure corresponding to the vapor pressure of *n*-pentane was 0.008541 cubic foot. The details of the equipment have been published (*13*). The interior surface of the vessel was 0.25 square foot. This included the area of two steel balls approximately 0.75 inch in diameter which were used to agitate the *n*-pentane and the *n*-pentane-silica systems