Enthalpy of Two Ternary Mixtures of Benzene–Octane–Tetralin

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The results of enthalpy measurements of two ternary mixtures of benzene–*n*-octane–tetralin are reported for the temperature range 280–600°F, with pressures extending to 1400 psia.

This measurement study was undertaken to determine how the addition of the heavy aromatic tetralin would change the enthalpy values of an equimolar mixture of the close-boiling nonideal system benzene with *n*-octane. Two mixtures were examined—one with 10 mol % tetralin, and one with 33.3 mol % tetralin. Measurements for the binary mixture benzene with *n*-octane have already been reported (*5*).

The measurements were made with a flow calorimeter that has been used over a five-year period. Accuracy has been frequently established as within 1.5 Btu/lb by measuring values of *n*-pentane and liquid water, and by comparing the results with published literature values (*2*, *9*). The calorimeter measures isobarically the enthalpy difference relative to 75°F and the pressure of measurement. The description of the calorimeter with operating procedure has been described (*6*). The results of 271 measurements have been tabulated and are deposited with the ACS Microfilm Depository Service. Compositions are presented in Table I, both as mole and weight percent.

The mixtures were prepared by weighing the pure components for samples of 5000 grams. All the hydrocarbons were obtained from the Phillips Petroleum Co., with the benzene and *n*-octane used as received. The benzene density was 0.8730 g/cc at 75°F, with refractive index $\eta^{20}{}_{D} = 1.50030$, and a purity determined by chromatographic analysis to be 99.87%. The *n*-octane had a density of 0.7000 g/cc at 75°F, a refractive index of $\eta^{20}{}_{D} = 1.50030$, and a stated purity exceeding 99.0%. The tetralin (1,2,3,4-tetrahydronaphthalene) was purified by using an Oldershaw laboratory fractionating column containing about 20 theoretical stages and using a 40–1 reflux ratio. The selected pure tetralin portion had a refractive index of 1.5410 $\eta^{20}{}_{D}$ and a density of 0.9691 at 60°F.

Table I. Properties of Liquid Phase at 75°F and 1 Atm Pressure

Material	Wt %	Liquid density, g/cc	Heat of mixing, Btu/lb	Enthalpy[a] to add, Btu/lb
45.0 Mol % benzene	35.2			
44.9 Mol % *n*-octane	51.5	0.7803	4.4	107.0
10.1 Mol % tetralin	13.3			
33.3 Mol % benzene	24.0			
33.4 Mol % *n*-octane	35.3	0.8329	2.9	102.1
33.3 Mol % tetralin	33.3			

[a] Needed enthalpy to convert measurements relative to 75°F and the saturated liquid state to the −200°F enthalpy basis.

The measured enthalpies were converted to a basis of −200°F and the saturated liquid state of the pure components, in agreement with the base level used by the American Petroleum Institute data book (*1*). As a first step in making this conversion, the measurements were corrected for the change in enthalpy in the liquid state at 75°F as the pressure changes. This correction was made using the thermodynamic equation of state (*6*) and resulted in small changes that never exceeded 3.3 Btu/lb. These changes were computed with preciseness that exceeded the accuracy of measurement. The numbers needed to correct the pure component enthalpies from 75° to −200°F in the liquid were previously established as 88.1 for benzene (*5*), 115.3 for *n*-octane (*7*), and 91.7 for tetralin (*4*). The enthalpy addition required to convert the mixture measurements from 75° to −200°F was computed as a weight average of the pure component conversion values plus the heat of mixing at 75°F.

Table I lists the densities, the heats of mixing, and the numbers needed to convert the measurements. The heat of mixing was computed using the procedure of Tsao and Smith (*10*) from the binary heat of mixing values presented by Lundberg (*8*). The enthalpy values converted to the −200°F basis were then cross-plotted on large-scale paper. Smoothed results obtained are presented in Tables II and III. The values presented at 75°F show the computed difference between the enthalpy at 75°F and measured pressure and the −200°F base level. These smoothed values deviate from the measured quantities by a standard error of estimation of 1.2 Btu/lb.

Figure 1 illustrates the dependency of enthalpy with pres-

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Table II. Enthalpy Values for Mixture 35.2 Wt % Benzene, 51.5 Wt % *n*-Octane, and 13.3 Wt % Tetralin

Units: Btu per lb. Base level: pure saturated liquid components at −200°F

Temp, °F	Psia 0	40	100	200	300	400	450	1000	1400
75		107.1	107.3	107.5	107.7	108.0	108.2	109.5	110.5
277		211.3[a]							
300		285.3	255.3						
320		335.2	237.7						
340		369.8	250.1						
346		377.8[a]							
360		385.2	262.9						
361			263.4[a]						
380		394.9	321.9	275.7					

(*Continued on next page*)

Table II. *(Continued)*

Units: Btu per lb. Base level: pure saturated liquid components at −200°F

Temp, °F	Psia 0	40	100	200	300	400	450	1000	1400
400		404.4	372.0	288.7				288.8	
420	419	414.7	405.7	301.5				301.5	
425			409.2[a]						
434.3				311.0[a]					
440	429.0	425.1	418.1	321.1	314.8			314.8	314.8
460	439.8	436.1	429.6	375.9	328.8			328.7	328.5
480	450.8	447.5	441.7	420.2	342.7			341.7	341.4
487.7					348.0[a]				
494.3				437.6[a]					
500	462.0	459.0	453.6	441.8	370.0	356.8		355.2	354.8
520	473.0	470.2	465.4	456.7	425.1	371.0		369.2	367.9
527.8						377.6[a]			
535.8					455.0[a]				
540	484.0	481.5	477.1	470.0	459.0	406.0	386.2	383.3	381.4
548.8						428.0	393.0[a]		
560	495.0	492.8	489.0	482.8	474.2	452.9	419.2	397.8	395.2
570					480.8	468.8[a]	444.5	405.2	402.1
580	506.0	504.0	500.6	494.7	487.0	477.7	464.4	413.1	409.1
584.6							472.0[a]		
590					493.1	484.9	477.3	421.0	416.1
600	517.1	515.0	512.2	506.1	499.1	491.5	485.9	429.0	423.1

Temp, °F	Psia 500	600	610	650	700
560	402.3				
568	409.0[a]				
570	413.1	410.7			
580	440.8	420.3	419.9	419.1	416.1
590	461.0	430.7	430.0	428.1	424.3
598.8	472.3[a]				
600	473.5	443.8	442.0	437.4	432.6

[a] Enthalpy values on two-phase boundary.

Table III. Enthalpy Values for Mixture 24.0 Wt % Benzene, 35.3 Wt % *n*-Octane, and 33.2 Wt % Tetralin

Units: Btu per lb. Base level: Pure saturated liquid components at −200°F

Temp, °F	Psia 0	40	100	200	300	350	400	500	1400
75		102.2	102.3	102.6	102.9	103.0	103.1	103.4	105.7
280		204.3							205.8
300		215.6[a]							216.7
320		250.6	226.9						227.9
340		285.3	238.5						239.4
360		318.6	250.2						250.9
380		351.5	262.4						262.6
392.8			270.2[a]						
400		382.8	283.3	274.7					274.4
414		404.7[a]							
420		407.8	318.8	287.0					286.5
440	420.8	417.8	353.9	299.1					298.4
460	430.9	427.9	386.6	311.8					310.7
470				317.9[a]					
480	441.2	438.3	415.9	331.4	324.4				322.9
500	451.9	448.9	439.2	362.7	337.4				335.3
507.3			446.8[a]						
520	463.1	460.0	454.3	398.3	350.9				348.5
534.3					360.6[a]				
540	474.2	471.4	466.0	432.8	371.0	364.7			362.0
559.1						378.7[a]			
560	485.7	482.8	477.9	459.2	405.7	379.8	379.1		376.4
570			483.9	470.9	421.6	394.9	386.6		383.8
575.7				477.7[a]					
580	496.9	494.1	489.8	480.6	436.9	411.8	394.0[a]		391.0
590	502.7	499.8	495.8	486.9	452.4	429.7	410.6	401.6	398.7
600	508.5	505.6	501.6	493.7				409.4	406.1

[a] Enthalpy values on two-phase boundary.

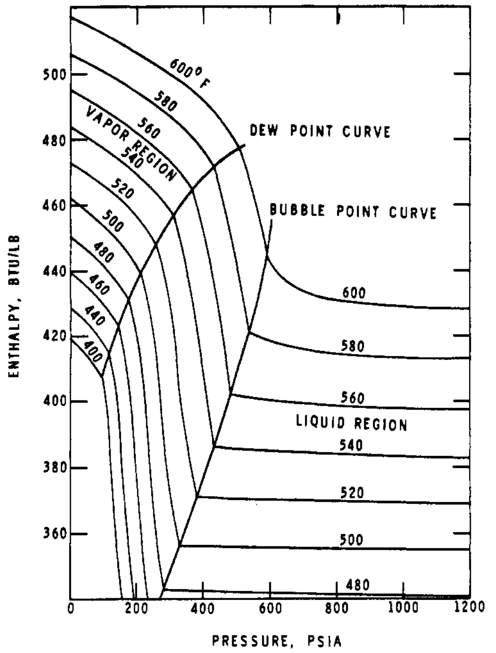

Figure 1. Enthalpy of the mixture 35.2 wt % benzene, 51.5 wt % octane, and 13.3 wt % tetralin

sure and temperature for the mixture with 10 mol % tetralin, with a cricondentherm computed to be 612°F (*3*). The cricondentherm for the case of the $33\frac{1}{3}$ mol % tetralin mixture is estimated to be 685°F, and without tetralin, it is determined (*5*) to be 556°F. The two-phase region enlarges as the tetralin content increases. The difference in the gas phase between the measured enthalpy and the ideal gas state enthalpy becomes progressively larger as the tetralin content increases. In the liquid phase, the addition of tetralin decreases the enthalpy. These changes are not linearly dependent on tetralin mole fraction or weight fraction, and illustrate that the mixture of benzene-octane-tetralin does not exhibit simple behavior.

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Separation of Scandium and Calcium by Liquid-Liquid Extraction Using Tri-*n*-butyl Phosphate as Solvent

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The separation of scandium from calcium by solvent extraction at trace-level concentrations has been studied by several investigators. In the isolation of carrier-free calcium from fast-neutron-irradiated scandium from HCl solutions using tri-*n*-butyl phosphate (hereafter TBP) as the solvent, the maximum distribution coefficient for scandium was in 8*N* HCl solutions (*4*). In solutions with a constant, high-chloride-ion concentration (e.g., 11*N* LiCl and HCl), the scandium distribution coefficient was independent of acid concentration. In 7-9*N* HCl solutions, the degree of extraction of scandium was much greater than that of calcium; in fact, the ratio of distribution coefficients was of the order of 200.

When extracting scandium with TBP from $CaCl_2$ and HCl solutions, Romanova et al. (*6*) found that increasing the concentration of $CaCl_2$ increased the amount of scandium extracted. They concluded that scandium can be extracted with high yield both from neutral and acidic solutions. Data for the extraction of scandium and the rare earths distributed between TBP and aqueous solutions containing 3-8*M* HCl have been reported by Peppard et al. (*5*).

Although the distribution coefficients of elements are lower for the TBP-nitrate systems as compared with the TBP-HCl system (*2*), the former system is more selective for certain elements.

Separation and purification of scandium and some actinide and lanthanide elements using the solvent TBP to extract the metal values from nitrate solutions of relatively high acidity look promising. The purpose of this study was to obtain distribution coefficient and separation factor data at concentrations greater than trace level so that these data can be used in the recovery of scandium from a slag which results during the preparation of very pure scandium metal from its oxide.

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