Liquid-Liquid Equilibria for the Benzene–*n*-Heptane–Water System in the Critical Solution Region

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Liquid-liquid equilibria for the benzene–*n*-heptane–water system were measured in the critical solution region, 550° to 630° F. and 3600 to 4800 p.s.i.g. Equilibrium compositions are represented on binodal curves with tie lines on ternary phase diagrams. Beta values for the separation of benzene from *n*-heptane depend on benzene concentration in the water phase and range from 2 to 9, which are much lower than suggested from binary data.

WATER has been recognized for several years as a cheap and abundant solvent to separate aromatics from paraffins by extraction (*1, 4, 5*). However, in the ranges of temperature and pressure studies, 550° to 570° F. and up to 2700 p.s.i. the solubilities of the aromatics in water are low, and large volumes of water per volume of hydrocarbon were needed to obtain an aromatic product of better than 95% purity. No studies have been reported at higher temperatures and pressures.

Connolly recently measured solubilities of several hydrocarbons in water at 500° to 670° F. above 3000 p.s.i. and up to 10,000 p.s.i. (*3*). In these ranges the solubilities of aromatics increase markedly with temperature and pressure, whereas the solubilities of paraffins remain low. An interesting discovery was a maximum in the solubility-pressure isotherms at near critical temperatures and 3500 to 4500 p.s.i.

These effects warranted further investigation, to determine how the selectivities changed in a ternary system. Phase equilibria have therefore been measured for the benzene–*n*-heptane–water system at 3600 and 4800 p.s.i.g. and 550° to 630° F. Ratios of the distribution of benzene and heptane (*6*) have been calculated as quantitative measure of the selectivity of the solvent and have been designated as beta values, on a weight fraction basis.

MATERIALS AND APPARATUS

Benzene and *n*-heptane were Phillips research grade with less than 0.2% impurities as reported by Phillips. Water was distilled with no further purification.

A schematic diagram of the apparatus is shown in Figure 1. It consisted of twin facilities for pumping benzene–*n*-heptane mixtures and water through heated lines to an extractor immersed in a salt bath, and a mercury positive displacement system. All lines were high pressure tubing made of Type 316 stainless steel.

The extractor was a 100-ml. cylinder of Type 316 stainless steel. A disk magnet that was moved up and down by an external horseshoe magnet provided excellent agitation. The horseshoe magnet was moved by an adjustable crank and rod arrangement off a variable-speed motor drive.

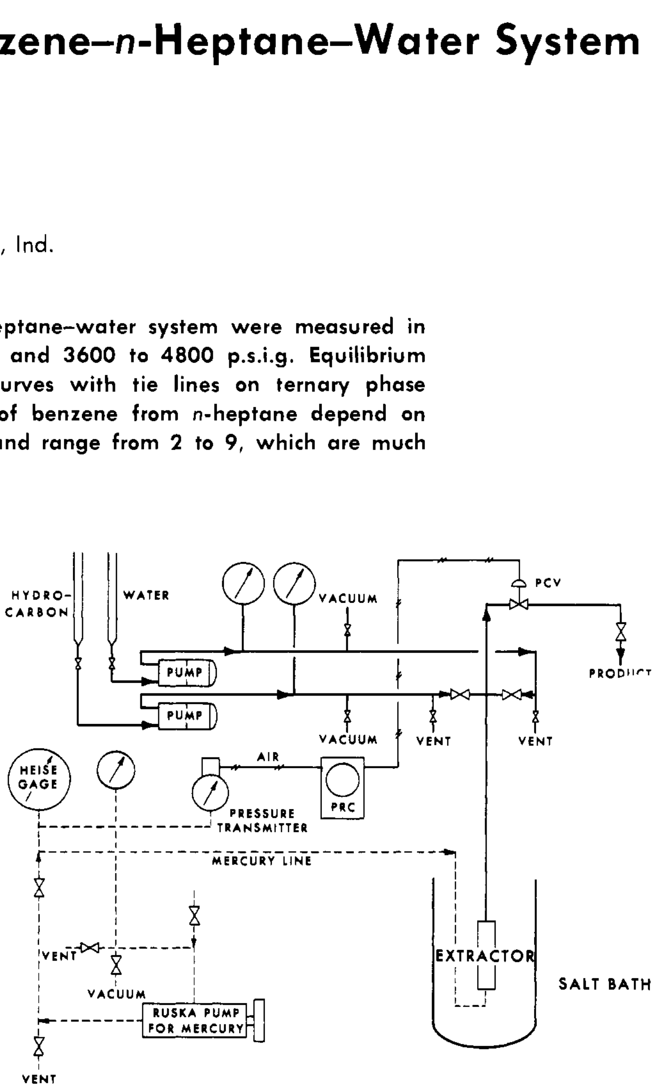

Figure 1. Batch extraction unit

The salt bath was a Schedule 30 carbon steel pipe with a dished bottom, raised and lowered on motor-driven screws, and containing Du Pont Hi-Tec heat transfer salt. Heat was supplied electrically from immersion elements and external wrap-around and bottom heaters. The molten salt was stirred with a propeller in an offset downdraft tube, an arrangement that produced a vertical circular movement.

Temperature was measured with a calibrated platinum resistance thermometer in the bath next to the extractor, and was controlled with a resistance thermometer and an immersion heater located in the downdraft tube.

Mercury was used to maintain constant pressure during a run and to displace equilibrated phases at constant pressure after a run. It was pumped into and from the bottom of the extractor through heated lines with a Ruska pump (manufactured by Ruska Instrument Corp., Houston, Tex.). Extraction pressure was measured with a Heise gage (calibrated with a dead weight pressure gage to ±10 p.s.i.) located on the mercury line to the extractor.

For maximum safety, the unit was housed in a concrete pressure cell with a blow-out panel in the back. Controls and instrumentation were located outside the cell. Instantaneous mercury vapor detectors were used both in and out of the cell, and general safety precautions for handling mercury were observed.

PROCEDURE

Measured amounts of water and hydrocarbon of known composition were pumped into the extractor and mixed for 1 or 2 hours. The phases were allowed to settle for about 2 hours; then the contents were slowly (1.5 ml. per minute) displaced at constant pressure with mercury.

The product was collected in 2- to 5-ml. cuts in burets with 0.1-ml. subdivisions. The hydrocarbon-water composition could be read directly. The amount of each phase in the extractor was known by change in the hydrocarbon-water composition of the product cuts. The benzene-heptane ratio of the oil phase was determined by gas chromatography. Weights were calculated from published water densities and measured densities of benzene-*n*-heptane mixtures at various ambient temperatures.

ACCURACY OF RESULTS

Temperature was maintained and measured with an error of less than 0.1° F. Pressure was controlled ±10 p.s.i.

The major errors occurred in composition measurements. Volumes of water and hydrocarbon were measured to ±0.02 ml. Density errors probably did not exceed 0.001 gram per ml.

Hydrocarbon concentrations by gas chromatography were determined to about ±0.1 weight %. Above 570° F. decomposition products of *n*-heptane amounted to concentrations no more than 0.1%. Material balances were all better than 98%, with most better than 99%. Maximum error in concentrations of components in the feed and equilibrated phases is therefore estimated to be about ±0.2%.

To determine the reproducibility and accuracy, runs were made with the benzene-water system for comparison with Connolly's data (*3*) at 549.5°, 560°, and 563° F. and 3000 to 4000 p.s.i.g. The results, plotted as points, fall along the solid curves representing Connolly's data in Figure 2, in excellent agreement, well within the limits of our experimental error. A bonus from these measurements was the equilibrium compositions of the benzene-rich phases, which could not be determined in the cloud-point apparatus. Gradual approach of the two sets of points illustrates approaching miscibility, reached between 563° and 572° F.

RESULTS AND DISCUSSION

The binodal curves for the benzene–*n*-heptane–water system at 3600 p.s.i.g. and 550° to 630° F. are shown in Figures 3 to 8. The equilibrium compositions are summarized in Table I. For obvious reasons the tie lines are not shown for the composite of curves in Figure 3. Tie lines are shown in the other figures for each temperature.

Plait points (critical mixing points, where the compositions of the two phases in equilibrium are identical) for continuous binodal curves at 570° F. and above were estimated graphically (*7*). Equilibrium compositions of the hydrocarbon-rich (raffinate) phase are to the left of the plait point, while those of the water-rich (extract) phase are to the right. Tie lines connect the compositions of the two phases in equilibrium.

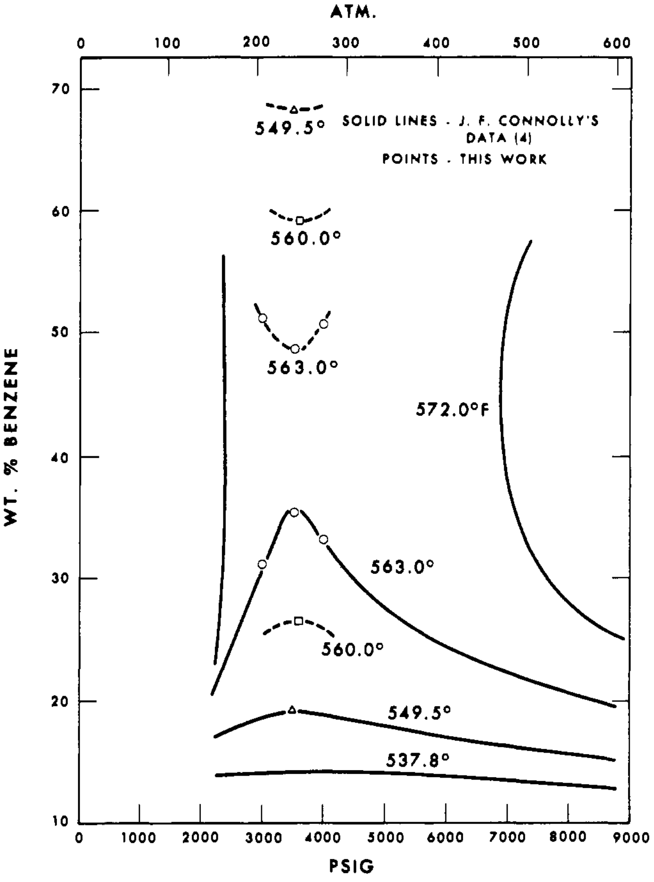

Figure 2. Benzene-water

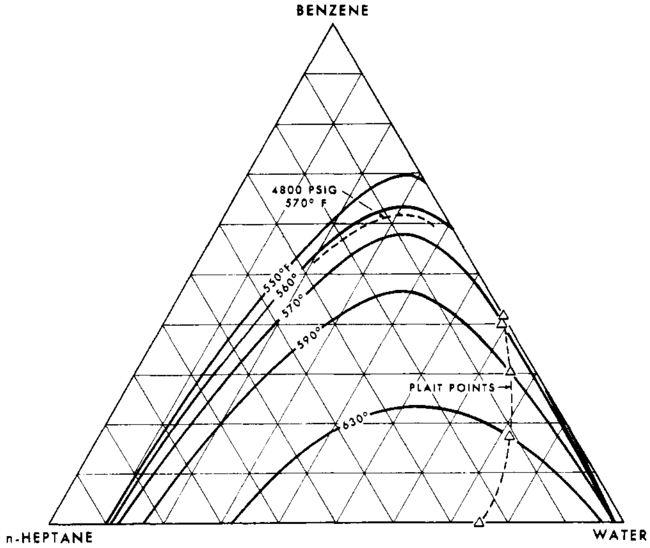

Figure 3. Benzene–*n*-heptane–water
3600 p.s.i.g.

Plait points are shown in Figure 3 as a function of temperature. The intersections of the plait points at the benzene-water and *n*-heptane–water lines, which represent these binary systems, very closely correspond to the estimated compositions at the critical solution temperatures (*3*).

The effect of increasing temperature is remarkably similar to the effect of increasing morpholine concentration when morpholine-water is the solvent (*2*): Solubilities increase and selectivities decrease at nearly the same values.

A measure of selectivity in extraction processes is the beta value, which is analogous to relative volatility in dis-

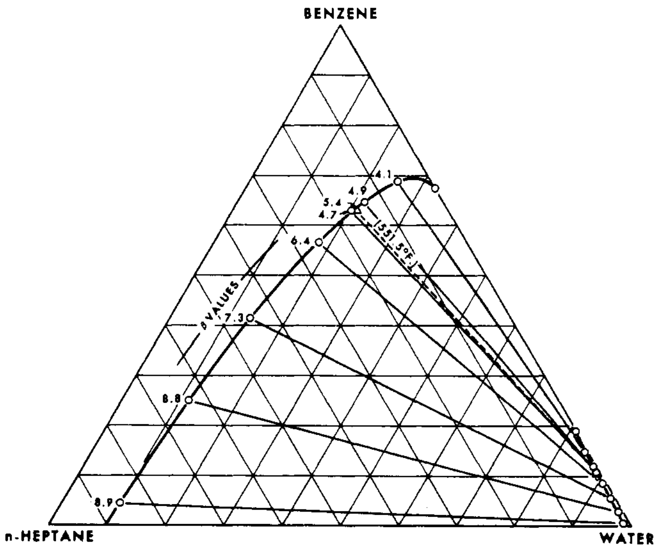

Figure 4. Benzene–*n*-heptane–water
550° F., 3600 p.s.i.g.

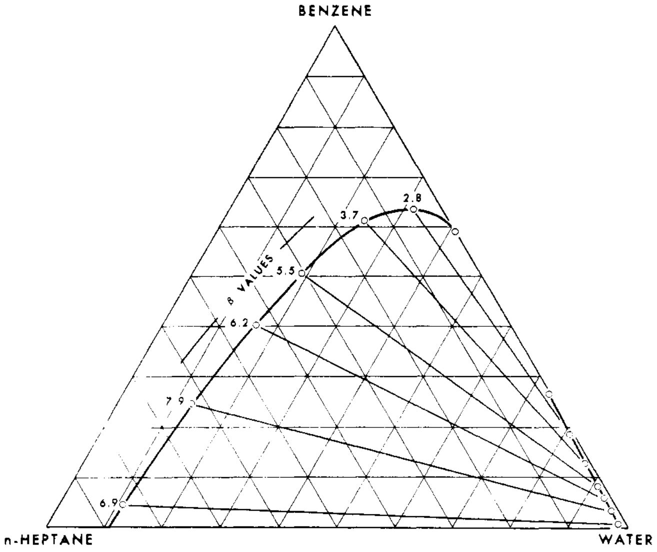

Figure 5. Benzene–*n*-heptane–water
560° F., 3600 p.s.i.g.

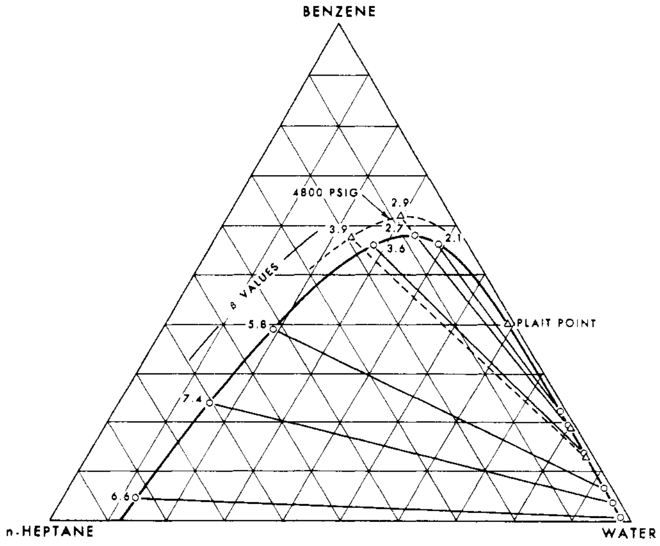

Figure 6. Benzene–*n*-heptane–water
570° F., 3600 to 4800 p.s.i.g.

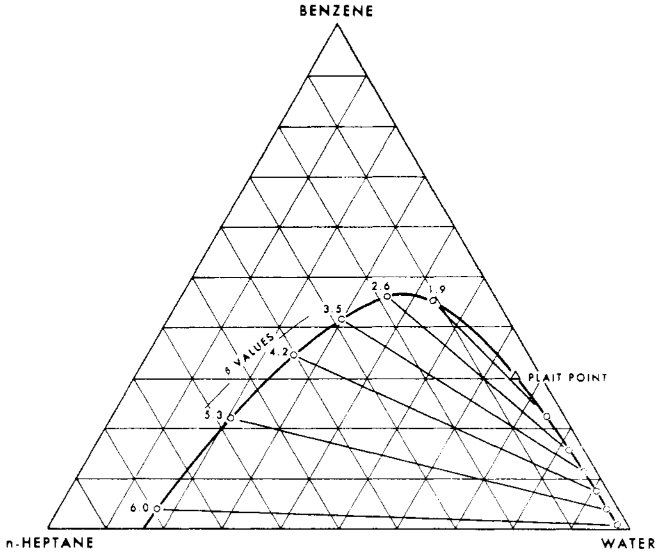

Figure 7. Benzene–*n*-heptane–water
590° F., 3600 p.s.i.g.

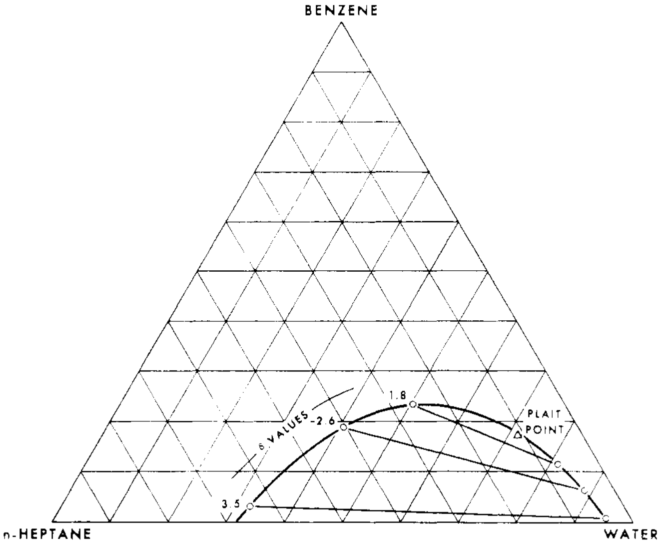

Figure 8. Benzene–*n*-heptane–water
630° F., 3600 p.s.i.g.

tillation. Beta is the ratio of the distributions of the two partially miscible components (in this case, benzene and *n*-heptane) in the two phases at equilibrium. Distribution is described by a distribution coefficient, *k*, which is the ratio of the concentrations of a component in each phase. Beta is expressed as follows:

$$\beta = \frac{k_B}{k_H}$$

$$k_B = \frac{\text{concentration of benzene in water-rich phase}}{\text{concentration of benzene in oil-rich phase}} = \frac{x_{BW}}{x_{BO}}$$

$$k_H = \frac{\text{concentration of } n\text{-heptane in water-rich phase}}{\text{concentration of } n\text{-heptane in oil-rich phase}} = \frac{x_{HW}}{x_{HO}}$$

$$\beta = \frac{\dfrac{x_{BW}}{x_{BO}}}{\dfrac{x_{HW}}{x_{HO}}} = \frac{x_{BW}}{x_{HW}}\,\frac{x_{HO}}{x_{BO}}$$

Table I. Benzene–*n*-Heptane–Water Equilibrium Compositions

Temp., °F.	Pressure, P.S.I.G.	Hydrocarbon Phase, Wt. %			Water Phase, Wt. %		
		Water	Benzene	*n*-Heptane	Water	Benzene	*n*-Heptane
550	3600	10.0	4.4	85.6	98.4	0.5	1.1
		11.5	25.1	63.4	96.4	2.8	0.8
		13.8	41.4	44.8	93.8	5.4	0.8
		18.1	56.5	25.4	90.8	8.6	0.6
		20.5	63.0	16.5	88.7	10.7	0.6
		21.9	64.7	13.4	87.6	11.9	0.5
		25.4	68.9	5.7	84.8	14.9	0.3
		32.6	67.4	...	81.0	19.0	...
551.5	3600	21.4	62.9	15.7	88.7	10.8	0.5
560	3600	11.1	4.5	84.4	98.5	0.4	1.1
		13.0	24.6	62.4	95.9	3.1	1.0
		16.2	40.1	43.7	93.3	5.7	1.0
		19.0	50.4	30.6	91.0	8.1	0.9
		24.6	61.0	14.4	86.6	12.6	0.8
		31.9	63.3	4.8	81.1	18.4	0.5
		41.0	59.0	...	73.7	26.3	...
570	3600	12.6	4.5	82.9	98.1	0.5	1.4
		15.7	23.9	60.4	95.3	3.5	1.2
		19.1	38.9	42.0	92.4	6.4	1.2
		34.2	57.8	8.0	79.8	19.2	1.0
		39.1	56.0	4.9	77.1	22.0	0.9
Plait pt.		59.0	40.1	0.9	59.0	40.1	0.9
570	4800	23.5	57.4	19.1	86.1	12.8	1.1
		29.8	61.6	8.6	80.3	18.8	0.9
590	3600	16.9	3.9	79.2	97.8	0.5	1.7
		20.6	22.1	57.3	94.2	3.9	1.9
		25.1	34.6	40.3	90.8	7.2	2.0
		30.0	42.6	27.4	86.6	11.3	2.1
		35.6	46.2	18.2	82.0	15.6	2.4
		43.9	45.2	10.9	74.9	22.2	2.9
Plait pt.		65.4	30.4	4.2	65.4	30.4	4.2
630	3600	32.6	3.1	64.3	95.1	0.7	4.2
		40.9	18.9	40.2	88.7	6.2	5.1
		50.6	23.4	26.0	81.6	11.4	7.0
Plait pt.		71.7	17.4	10.9	71.7	17.4	10.9

Practical extraction processes require betas much greater than 1, to minimize the number of stages and reflux ratios required.

Betas are given in Figures 4 to 8; most lie between 2 and 9. In all cases they decrease with increasing concentrations of benzene in the oil phase and with increasing temperature.

Figure 6 shows that increasing the pressure to 4800 p.s.i.g. at 570° F. increases the selectivity only slightly. Moreover, since the solubility relationships in the binary systems (*3*) are about the same at 2800 and 4800 p.s.i.g., similar results could be expected at the lower pressure.

In all cases the distribution coefficient (*6*) for benzene is less than 1, which means benzene is always more concentrated in the raffinate phase. A distribution coefficient greater than 1, or decreasing less rapidly at higher benzene concentrations, would have been more desirable. Beta would have been higher, and would have decreased with increasing benzene concentration in both phases. Since the distribution coefficient is a measure of the slope of the tie lines, less slope or an opposite slope would have been more encouraging for a practical process.

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