

$I$  = ionic strength  
 $m$  = molality  
 $n$  = number of moles  
 $R$  = gas constant  
 $T$  = absolute temperature  
 $Z$  = charge on ion  
 $\alpha$  = special function defined in Equation 8  
 $\nu$  = number of ions  
 $\rho$  = special function defined in Equation 7  
 $\sigma(I^{1/2})$  = special function defined in ref. 10

#### SUPERSCRIPTS

° = standard state

#### SUBSCRIPTS

1 = solvent  
2 = solute  
+ = cation  
- = anion

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## Ternary-Phase Diagrams for Systems Pyridine, Water, and Some C<sub>6</sub> Hydrocarbons

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**Ternary-phase equilibrium data are reported for six liquid systems, each having pyridine and water as two of the three components. All of the measurements were made at atmospheric pressure, and the third component in the six systems was *n*-hexane, cyclohexene, 1-hexane, cyclohexane, 1-hexanol, and cyclohexanol. The solubility curve data were obtained by titrating known binary mixtures of hydrocarbon and water with pyridine to the point of homogeneity and the tie-line data were determined by titration of pyridine in hydrocarbon-, and water-rich phases with acid using an appropriate indicator.**

As an extension of some previous work (4), we had occasion to determine phase diagrams of the ternary systems comprised of water, pyridine and *n*-hexane, cyclohexane, 1-hexene, cyclohexene, 1-hexanol or cyclohexanol as the third component. The results illustrate the effect of a double bond or a hydroxyl group on the solubility relationships among water, pyridine, and solvents listed above.

#### EXPERIMENTAL

**Materials.** Reagent-grade pyridine, cyclohexane, and cyclohexanol were obtained from City Chemical Corp. Gas chromatographic grade *n*-hexane was obtained from J. T. Baker Chemical Co. and reagent-grade 1-hexene from Matheson, Coleman and Bell. The modified methyl orange indicator used for tie-line determination consisted of equal quantities of a 0.1% methyl orange indicator solution in water and 0.25% indigo carmine indicator solution in water.

**Procedure.** Binodal solubility curves were determined by titrating known mixtures of hydrocarbon and water with pyridine until a homogeneous solution was obtained (5). The titrations were cumulative, a series of points being determined by adding water or hydrocarbon in known amount after each end point and titrating again to a clear solution. End-point sharpness varied with the ratio of components in the usual way (3) being poor at either end of the binodal solubility curve for

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the first four systems but good over the entire curve for systems containing an alcohol. In determining phase diagrams for cyclohexanol and 1-hexanol, the equilibrium was approached from both sides of the phase diagram by conducting a series of titrations on alcohol-rich, water-poor solutions then conducting a second series on alcohol-poor, water-rich solutions. To study the alcohol-rich half of the binodal solubility curve, a 25-ml aliquot portion of the alcohol was placed in a flask containing a magnetic stirrer and known amounts of water were added. After each addition of water, the system was titrated to clarity with pyridine. The water-rich half of the curve was determined by starting with a 3-ml aliquot portion of the first four hydrocarbons mentioned above and 25-ml aliquots of the two alcohols.

Tie lines were determined by the method of Vreins and Medcalf (5). The weight of each component was not determined directly but was computed from the volume of that component and its density. In the cases of the first four hydrocarbons mentioned in the introduction, four ternary mixtures containing 20, 30, 40, and 50% by weight of pyridine were placed in separatory funnels, and equal parts of hydrocarbon and water were added to a total of 100 grams. All separated into two phases. In the case of the two alcohols, ternary mixtures were made up using much lower concentrations of pyridine because these hydrocarbons are miscible with water to some extent.

The mixtures, in all cases, were shaken for at least two full minutes and then placed in a water bath set at  $25 \pm 0.2^\circ\text{C}$  to reach equilibrium overnight (Figure 1). The resulting layers (four organic-rich and four water-rich) were separated by use of 25 or 50 ml pipets while the separatory funnels were still in the water bath. They were placed in 4-oz bottles and appropriate aliquots (20, 15, 10, 7.5, 5, 4, or 3 ml) were taken and placed in preweighed 50-ml Erlenmeyer flasks. The flask plus contents were then weighed and the aliquot was titrated with standardized 1N sulfuric acid using modified methyl orange indicator. The size of each aliquot was usually taken to yield readings in the range of 15–30 ml of 1N acid. With this titration data, the weight percent of pyridine in each layer was calculated. Because the color at the equivalence point depends slightly on the nature of the hydrocarbon present, standards were made up by titrating a known weight of pyridine in water or hydrocarbon to its theoretical stoichiometric equivalence point with the standardized 1N sulfuric acid and using the color of the indicator at that point as a color standard for the titrations of unknowns.

Titrimetric determination of tie lines is inherently more accurate than refractive index or density methods. Pyridine gives a good colorimetric end point at the pH range covered by methyl orange and indigo carmine ( $\text{pH} = 4.1$ ).

One error source peculiar to these tie-line acid-base titrations is the color instability of modified methyl orange indicator in the organic-rich phase. Color standards, using a known amount of pyridine in all of the six hexane derivatives, when titrated with a stoichiometric amount of acid show an end-point color slightly different from the color in the water-rich phase at the end point. In addition, on standing, the color changes from a deep violet to light pink; therefore a freshly titrated solution was used as the standard for each sample. These effects were more pronounced for the unsaturated compounds and alcohols than for *n*-hexane or cyclohexane. The effect was much less pronounced in the water-rich phase where the color of the end point usually matched the color of a stable aqueous standard containing no organic component.

When the organic-rich mixture is titrated, two phases are formed during the titration. Pyridine is extracted from the organic-rich phase and neutralized in the acidic aqueous phase where the color change is observed. The two phases must come into intimate contact for an accurate end point. When titrating the water-rich solution, only one phase is present.

In the cyclohexanol–pyridine–water system, the end point was past the stoichiometric equivalence point. The discrep-

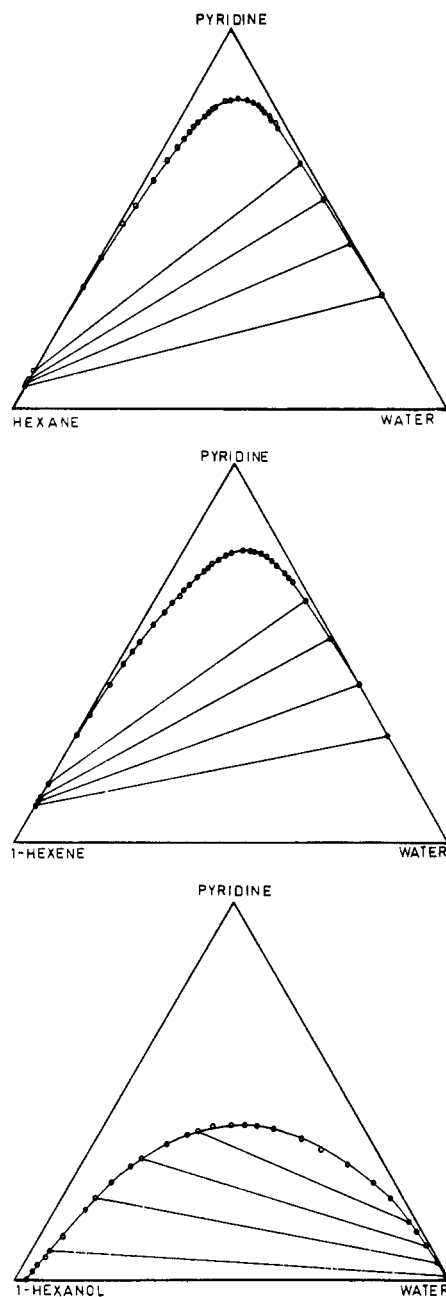


Figure 1 (Top). Phase diagram for system *n*-hexane–pyridine–water at  $25 \pm 0.2^\circ\text{C}$ . (Middle) Phase diagram for system 1-hexene–pyridine–water at  $25 \pm 0.2^\circ\text{C}$ . (Bottom) Phase diagram for system 1-hexanol–pyridine–water at  $25 \pm 0.2^\circ\text{C}$

ancy was greatest for the 5% pyridine tie line and least for the 25% pyridine tie line. The titrations of the water-rich phases did not show this discrepancy. In the 1-hexanol–pyridine–water system, this discrepancy was observed again but to a much smaller extent, once again primarily in the organic-rich phase of the 5% pyridine tie line. In the last two entries of Table I, uncorrected and corrected values are listed for the weight percent pyridine in the organic-rich phases. The corrected values are those which make the tie lines pass through the overall composition point computed from the amounts of components originally mixed. Tie lines for the *n*-hexane, cyclohexane, 1-hexene, and cyclohexene–pyridine–water systems passed through or came to within  $\pm 0.2\%$  of the respective overall composition points, and no correction was necessary.

Successive tie-line determinations had a relative average deviation of about  $\pm 0.2\%$ . The solubility data involving mix-

**Table I. Liquid-Liquid Equilibrium Data for Six Ternary Systems Involving Pyridine and Water at  $25 \pm 0.2^\circ\text{C}$**

Pyridine-Water- <i>n</i> -Hexane, Wt %			Pyridine-Water-Cyclohexane, Wt % (Contd.)		
<i>n</i> -Hexane	Pyridine	Water	Cyclohexane	Pyridine	Water
67.4	32.2	0.4	2.3	72.2	25.5
59.1	40.0	0.7	2.1	71.2	26.7
49.8	49.0	1.2			
44.4	54.0	1.6			
37.1	60.6	2.3			
31.4	65.7	2.9			
27.4	69.2	3.4			
24.6	71.6	3.8			
22.5	73.4	4.1			
20.8	74.8	4.4			
19.8	75.9	4.7			
17.3	77.4	5.3			
15.7	78.5	5.8			
14.5	79.3	6.2			
13.4	79.9	6.8			
10.6	81.4	8.0			
9.1	81.8	9.1			
7.1	82.2	10.7			
5.9	82.2	11.9			
5.2	81.8	13.0			
4.2	81.1	14.7			
3.5	80.4	16.1			
2.9	79.4	17.7			
2.5	78.5	19.0			
2.2	77.5	20.3			
2.0	76.4	21.6			
1.7	75.5	22.8			
1.6	74.5	23.9			

Pyridine-Water-1-Hexene, Wt %		
1-Hexene	Pyridine	Water
71.3	28.3	0.4
65.3	33.9	0.8
56.8	41.9	1.3
51.2	47.0	1.8
47.5	50.2	2.3
44.6	52.8	2.6
39.0	57.5	3.5
35.1	60.7	4.2
32.2	63.0	4.8
29.7	65.0	5.3
27.7	66.6	5.7
25.9	68.0	6.1
23.1	70.1	6.8
20.9	71.7	7.4
19.2	72.9	7.9
17.8	73.8	8.4
15.7	75.0	9.3
13.9	75.7	10.4
11.7	76.6	11.7
9.1	77.2	13.7
7.6	77.2	15.2
6.6	76.9	16.5
5.3	76.2	18.5
4.5	75.4	20.1
3.7	74.2	22.1
3.2	73.1	23.7
2.6	71.3	26.1
2.2	69.8	28.0
2.0	68.5	29.5

Tie Lines, Wt % Pyridine		
In original mixture	In <i>n</i> -hexane-rich phase	In water-rich phase
20.0	6.1	30.0
30.0	6.9	43.7
40.0	8.0	55.3
50.0	9.9	64.9

Pyridine-Water-Cyclohexane, Wt %		
Cyclohexane	Pyridine	Water
70.6	29.0	0.4
64.2	35.1	0.7
56.6	42.2	1.2
52.2	46.2	1.6
45.6	52.0	2.4
40.1	56.8	3.1
36.3	60.0	3.7
33.2	62.5	4.3
30.6	64.6	4.8
28.5	66.3	5.2
26.8	67.7	5.5
25.2	68.9	5.9
23.9	69.9	6.2
21.7	71.6	6.7
20.1	72.7	7.2
18.7	73.6	7.7
18.3	73.8	7.9
16.5	75.0	8.5
14.9	75.9	9.2
12.3	77.1	10.6
9.5	78.3	12.2
8.0	78.3	13.7
6.2	77.8	16.0
5.1	77.3	17.6
4.4	76.6	19.0
3.9	75.8	20.3
3.4	75.0	21.6
3.0	74.1	22.9
2.6	73.1	24.3

Tie Lines, Wt % Pyridine		
In original mixture	In 1-hexene-rich phase	In water-rich phase
20.0	9.5	28.2
30.0	10.9	42.0
40.0	12.4	54.0
50.0	15.4	63.8

Pyridine-Water-Cyclohexene, Wt %		
Cyclohexene	Pyridine	Water
81.4	18.2	0.4
76.4	22.8	0.8
66.0	32.7	1.3
60.7	37.5	1.8
57.0	40.8	2.2
53.9	43.4	2.7
48.3	48.1	3.6
44.5	51.1	4.4
38.8	55.5	5.7
34.7	58.5	6.8
31.5	60.8	7.7
27.6	63.2	9.2
24.5	65.3	10.2
19.5	68.3	12.2
16.5	69.8	13.7
12.9	71.0	16.1
10.8	71.4	17.8
9.3	71.4	19.3

(Continued on next page)

Table I. (Continued)

Pyridine-Water-Cyclohexane, Wt % (Contd.)			Tie Lines, Wt % Pyridine			
Cyclohexane	Pyridine	Water	In original mixture	In 1-hexanol-rich phase		In water-rich phase
7.5	70.8	21.7	5.0	Corr	Uncorr	
5.9	69.6	24.5	15.0	8.0	8.6	1.3
			25.0	21.9	21.9	4.6
			35.0	32.3	32.3	9.0
				39.1	39.3	15.4
Tie Lines, Wt % Pyridine			Pyridine-Water-Cyclohexanol, Wt %			
In original mixture	In cyclohexene-rich phase	In water-rich phase	Cyclohexanol	Pyridine	Water	
20.0	13.1	25.8	92.0	0	9.5	
30.0	14.9	40.1	89.6	0.7	9.7	
40.0	17.0	52.2	84.0	5.1	10.9	
50.0	20.9	62.0	79.6	8.4	12.0	
			75.0	12.0	13.0	
			68.2	17.0	15.2	
			59.9	21.9	18.2	
			52.2	25.2	22.6	
			43.5	28.3	28.2	
			37.9	29.4	32.7	
			33.8	29.6	36.6	
			30.8	29.2	40.0	
			26.0	28.0	46.0	
			20.5	25.3	54.2	
			17.7	23.7	58.6	
			14.5	21.4	64.1	
			10.7	18.2	71.1	
			8.6	16.0	75.4	
			6.9	14.2	78.9	
			5.3	12.0	82.7	
			4.2	10.1	85.7	
			3.4	7.1	89.5	
			2.9	0.8	96.3	
			2.6	0	97.1	
Pyridine-Water-1-Hexanol, Wt %			Tie Lines, Wt % Pyridine			
1-Hexanol	Pyridine	Water	In original mixture	In cyclohexanol-rich phase		In water-rich phase
97.6	0	2.8	5.0	Corr	Uncorr	
96.6	0.5	2.9	10.0	7.4	8.6	1.4
94.4	2.3	3.3	15.0	14.4	16.1	2.9
92.3	4.0	3.7	20.0	20.2	21.9	4.7
89.5	6.1	4.4	25.0	24.7	26.1	6.7
82.4	11.5	6.1		28.1	29.1	9.3
74.3	18.4	7.3				
64.7	25.7	9.6				
58.4	30.0	11.6				
54.8	31.7	13.5				
46.8	35.9	17.3				
41.2	38.4	20.4				
34.1	40.6	25.3				
29.6	41.2	29.2				
26.3	41.2	32.5				
23.5	40.8	35.7				
20.3	39.8	39.9				
15.6	37.1	47.3				
12.2	34.7	53.1				
8.0	30.7	61.3				
4.5	26.1	69.4				
2.5	22.0	75.5				
1.4	16.6	82.0				
0.9	13.1	86.0				
0.3	0	99.7				

tures near the plait point had a relative average deviation of about  $\pm 0.3\%$  while at the extreme ends of the curve, the average deviation was about  $\pm 0.7\%$ . The entire method—solubility-curve determination and tie-line determination—was tested by determining the water-pyridine-benzene and water-pyridine-toluene-phase diagrams. Evidently accumulation of error, to be expected from the procedure used to determine the solubility curves, was insignificant, as comparison with published data ( $\delta$ ) was excellent.

## RESULTS AND DISCUSSION

The peaks of the solubility curves come at 82.2% pyridine for *n*-hexane, 78.3% pyridine for cyclohexane, 77.2% for 1-hexene, and 71.4% for cyclohexene. This effect shows that the amounts of pyridine needed to solubilize these four solvents with water decrease when the structure is changed from straight chain to cyclic or from alkane to alkene. The closeness in percent pyridine necessary to solubilize cyclohexane and 1-hexene shows that going from a straight chain to a cyclic structure is almost as effective in reducing the pyridine peak height as going from a straight-chain aliphatic compound to a straight-chain olefin.

Tie-line slope for these four systems is about the same. Pyridine is much more soluble in the water-rich phase. In

going from *n*-hexane through cyclohexane and 1-hexene to cyclohexene, pyridine becomes relatively more soluble in the organic-rich phase. The shift is slight, however, just as the peak height of the solubility curves for these systems changes only slightly.

Since all four of these hexane derivatives have the same number of carbon atoms and almost the same number of hydrogen atoms, we may compare their subtle differences in solubility in structural terms. Not all are insoluble in water to the same extent. One source (*1*) gives cyclohexene as very slightly soluble in water, whereas the other three solvents were listed as insoluble. This is in agreement with the data we have accumulated showing that the cyclohexene-pyridine-water system has the lowest peak in its solubility curve among the first four systems. Second, with regard to the straight chain as compared to cyclic structure, greater solubilizing properties of pyridine on the cyclic vs. straight-chain solvents suggest an association between pyridine and the cyclic compounds which is stronger than that between pyridine and the corresponding straight-chain molecules. Third, the double bond compounds contrast with those without double bonds in the extra source of  $\pi$  electrons which evidently help pyridine to solubilize the alkene by  $\pi$ -dipole attraction which is absent in the alkane.

The height of the solubility curves for the last two systems is greatly reduced, having a pyridine peak of 41.2% for 1-hexanol and 29.6% for cyclohexanol. Cyclohexanol and 1-

hexanol are partially soluble in water [0.6 part/100 water for 1-hexanol and 3.6 parts for cyclohexanol at 20°C (2)]. Both cyclohexanol and 1-hexanol have some ability to form hydrogen bonds with water. Again, the cyclic structure is more soluble in water than the straight chain.

Tie lines in the last two systems slope in the opposite direction to the first four systems described. Both cyclohexanol and 1-hexanol have OH groups. Pyridine, being an organic dipole, can associate both with the hydrophilic OH group in the alcohols and with their hydrophobic hydrocarbon chains making cyclohexanol and 1-hexanol better competitors for pyridine than water.

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ing which time these results were prepared for publication. The authors also wish to acknowledge the preliminary data gathered by D. L. Thompson in this laboratory on the systems pyridine-water-*n*-hexane and pyridine-water-cyclohexane.

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## Enthalpy of Molybdenum and Tantalum from 298–1400K

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**High-temperature enthalpies from 298–1400K for molybdenum and tantalum have been determined by a copper block drop calorimeter of the isoperibol type. Agreement between these experimental results and certain compilations in the literature is satisfactory.**

During the course of investigating the high-temperature thermodynamic properties of nuclear materials, it was necessary to encapsulate certain of these nuclear materials with either molybdenum or tantalum so that the materials would be compatible with the high-temperature drop calorimetric experiments.

It was therefore necessary to correct the experimental enthalpy measurements for the enthalpy of the encapsulating material. Examination of the enthalpy data available on either molybdenum or tantalum revealed that several choices were possible for the respective enthalpies, differing by several percent. Because of the need for comparatively accurate enthalpy values for the encapsulating materials in order to define accurately the enthalpy of the specific material being investigated, enthalpies of both molybdenum and tantalum in our calorimeter were determined.

#### EXPERIMENTAL

**Calorimeter.** The calorimeter used for these enthalpy measurements was a copper block drop calorimeter of the isoperibol type where the enthalpies measured were relative to 25°C (298.15°K). The furnace was a platinum 10% rhodium resistance type where the limiting factor for the highest attainable temperature was the melting point of the furnace resistance winding, 1650°C. The apparatus is operated in an air environment necessitating the outermost capsule to be platinum. It is the incompatibility of certain nuclear materials with platinum at the higher temperatures that requires additional encapsulation of molybdenum or tantalum. The detailed description of this apparatus, as well as the calculation of the temperature rise of the calorimeter, may be found elsewhere (?). The reliability of the calorimeter was periodically

checked by measurements on the calorimetric standard, aluminum oxide. The standard deviation of these Al<sub>2</sub>O<sub>3</sub> enthalpy results was not more than ±0.2% from those reported by the National Bureau of Standards (?).

**Materials.** The molybdenum and tantalum used in this study were in the form of hollow closed cylinders where the tops and bottoms were attached by electron beam welding. The size of these metal cylinders was such that they would slip-fit into a platinum capsule (2.5 cm high; 2 cm o.d.; 0.025 cm wall thickness) which, in turn, was sealed under 200-torr helium pressure by heliarc oxygen-acetylene welding. The molybdenum and tantalum capsules also had a wall thickness of 0.025 cm and weighed 9.2283 grams and 11.5739 grams, respectively.

Emission spectrographic analyses, capable of detecting some 40 metallic elements, as well as oxygen, carbon, and nitrogen, indicated 199 ppm of impurities for molybdenum and 186 ppm of impurities for tantalum. Enthalpy corrections for the impurities were not made on either sample; therefore, both metals were considered to be 100% pure, although in actuality both had a purity of 99.98%. There is no significant error involved in not making the enthalpy correction for the impurities.

#### RESULTS

A total of 11 drop experiments were taken on molybdenum over the temperature range of 696.36–1380.70°K (all temperatures are based on IPTS-1968). Eight drop experiments were taken on tantalum over the temperature range of 533.76–1383.37°K. The experimental molar enthalpy results are given in Table I (cal = 4.184 J) as well as the smoothed enthalpy results at each experimental temperature. The smoothed results are taken from the Shomate equation (8) which connects the high temperature data with existing thermo-