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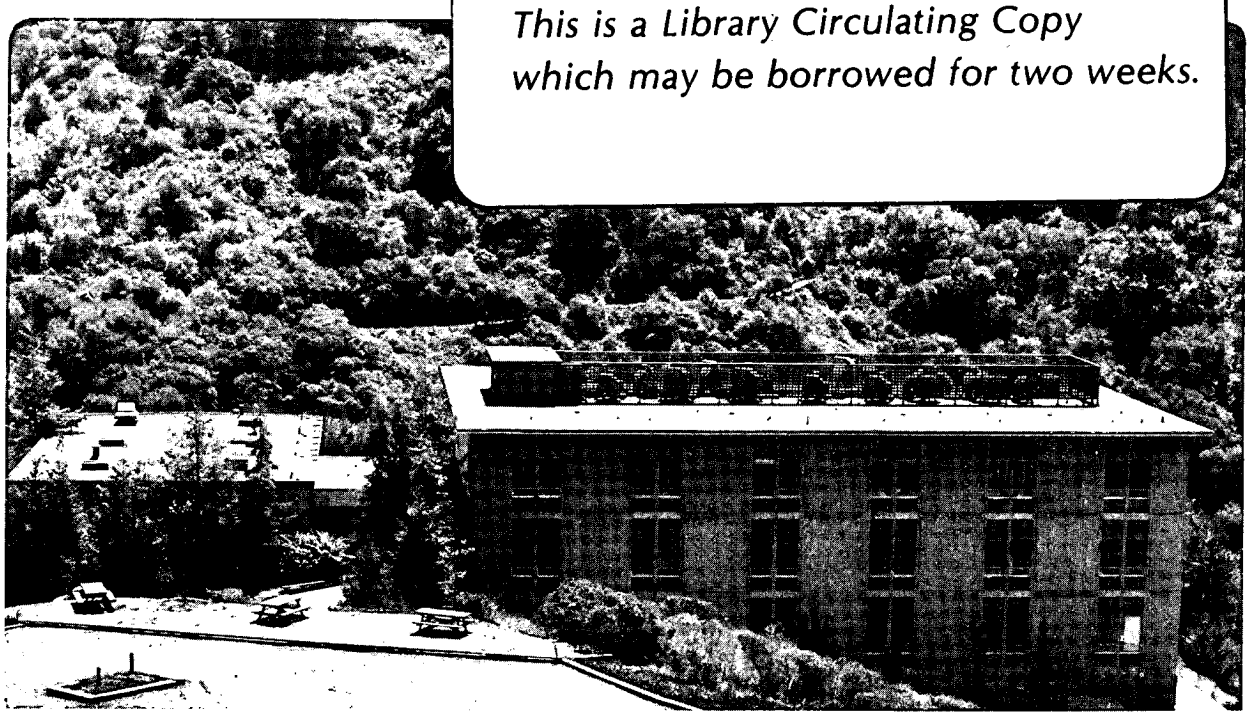

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High-Temperature Mutual Solubilities for Some Binary and Ternary Aqueous Mixtures Containing Aromatic and Chlorinated Hydrocarbons

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ABSTRACT

Mutual solubilities at the three-phase equilibrium pressure have been measured for binary mixtures of water with 1,2-dichloroethane and chlorobenzene in the temperature range 75 - 200°C. Liquid-liquid equilibria were measured for ternary aqueous mixtures containing toluene and phenol at 150 and 200°C, and for ternary aqueous mixtures containing thiophene and pyridine at 100 and 150°C. Results are given for equilibrium compositions of both liquid phases and for three-phase equilibrium pressures.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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Introduction

Water-hydrocarbon phase behavior is of fundamental interest in the chemical, petroleum, and synthetic-fuels industries. Mutual solubility data are required for design and operation of processes where there is contact between water and hydrocarbon or petrochemical streams. Often these processes are operated at elevated temperatures and pressures, where the organic-rich stream may contain many components, including water-soluble hydrocarbon derivatives. Mutual solubility data are especially important for design of water-pollution abatement processes.

While experimental solubility data are plentiful for binary water-hydrocarbon systems at near-ambient temperatures, few high-temperature data are available. Experimental data are scarce for aqueous ternary systems at temperatures exceeding 60°C. However, high-temperature solubility data are needed to test and extend the temperature range of existing molecular-thermodynamic correlations. Binary data are useful for establishing the temperature-dependence of water-hydrocarbon interaction parameters, while ternary data are needed to test the accuracy of solubility predictions based on binary data alone.

We report here mutual solubilities for binary aqueous mixtures containing chlorobenzene and 1,2-dichloroethane, for ternary mixtures containing water, toluene, and phenol, and for ternary mixtures of water, thiophene, and pyridine. All measurements were taken in the temperature range 75-200°C. Low-temperature solubility data have previously been reported for chlorobenzene/water and for 1,2-dichloroethane/water mixtures (1-2). Our measurements extend the temperature range of solubility data for both of these systems, and allow us to compare our results with published data at lower temperatures.

No previous measurements have been reported for the two ternary mixtures studied here. However, phase-equilibria data are available for each of the binary pairs in the two systems. The ternary data can thus be used to test predictions based on binary data alone.

Experimental

Equilibrium measurements were made in a recirculating static apparatus; details of the equipment and of the sampling procedure are given elsewhere (3). The upper temperature limit of the apparatus is 250°C (corresponding to the maximum rating of the sampling valves). Room conditions fix the lower-temperature limit.

Accurate sampling of water and hydrocarbon liquid phases is difficult because of low mutual solubilities. Trace contamination of one phase with small droplets or dispersions of the other phase can cause large errors (4). High-temperature measurements are especially prone to error because small perturbations during sampling (e.g., temperature or pressure drops) can cause phase separation and significantly alter sample compositions (5). Our apparatus is designed to minimize temperature and pressure gradients during sampling.

To measure binary mutual solubilities, approximately equal volumes of water and hydrocarbon are charged to the equilibrium cell and heated. The liquids are degassed by repeatedly venting the cell to low pressure until the mixture vapor pressure remains unchanged; the vapor in the cell occupies less than 5 percent of the 140 ml cell volume. Thorough mixing is accomplished by recirculating the upper liquid through the lower phase. At a fixed temperature, both liquid phases are sampled and analyzed at least three times. After obtaining consistent results for a given temperature, the cell is heated further and the sampling process is repeated.

For ternary mixtures, a range of overall cell compositions must be prepared at each temperature to study the entire liquid-liquid immiscibility region. Because the withdrawal of liquid-phase samples alters the overall cell composition, ternary tie lines are measured only once.

Chemicals

Water was filtered and purified through a Millipore system before use, and spectral-grade purity toluene was purchased from Mallinkrodt Co. All other chemicals were purchased from Aldrich Chemical Co. with specified purities of 99+%.

Analysis

Water-rich and hydrocarbon-rich samples are both analyzed on a Varian Model 3700 gas chromatograph with a thermal-conductivity detector. Binary mixtures containing water with chlorobenzene or 1,2-dichloroethane are separated on a Chromosorb 104 packed column. Water-toluene-phenol mixtures are separated on a Chromosorb 105 column, and Chromosorb 103 provides the best separation for water-thiophene-pyridine mixtures. All columns are 1/8-inch x 6-ft stainless-steel, and Chromosorb packing material is 80/100 mesh.

Relative responses of the mixture components are calibrated against samples of known composition for each system studied. Details of the calibration procedure are given by Anderson (3). Samples to be analyzed (whether from the cell or for calibration) are vaporized into evacuated 1-liter stainless-steel cylinders. The cylinders are heated (in the sampling oven) above the atmospheric boiling point of the least volatile component. Each sample is analyzed at least three times.

For the binary systems, relative responses on the chromatograph are reproducible to better than ±2%. Responses for all components in the water/thiophene/pyridine ternary can be replicated to ±1%. Results for water/toluene/phenol mixtures are less precise. In the non-aqueous phase, relative responses for all components are reproducible to better than ±2%. In the aqueous phase, analyses for phenol and toluene are reproducible to ±5%, while water response can be replicated to ±1%.

Results

Tables 1 and 2 present mutual solubility data and vapor pressures for water/chlorobenzene and water/1,2-dichloroethane mixtures. The standard deviation for repeated measurements generally decreases with increasing solubilities, except for the water/chlorobenzene solubility measurements at 150°C which were only reproducible to ±6%. Measurements for water/1,2-dichloroethane were discontinued at 125°C due to an apparent chemical reaction. After equilibrating the mixture overnight at 125°C, a green color was observed in the aqueous phase; this effect was reproduced with fresh liquid samples.

Figure 1 shows water/chlorobenzene mutual solubility data from this work along with earlier published measurements at temperatures below 100°C. The new data agree well with the lower temperature data for both water-rich and chlorobenzene-rich phases. Figure 2 compares new mutual solubility data for water and 1,2-dichloroethane with previous measurements below 75°C. Again, the data from this work appear to extrapolate well to the lower-temperature results.

Tables 3 and 4 present mutual solubilities for water/toluene/phenol mixtures at 150 and 200°C, and mutual solubilities for water/thiophene/pyridine mixtures at 100 and 150°C. The measured three-phase equilibrium pressures are also reported. In a ternary mixture, this pressure depends not only on temperature, but also on liquid-phase compositions. We control the overall cell composition which, at a given temperature, fixes the liquid-phase compositions and the three-phase pressure.

Figures 3 and 4 show ternary phase diagrams for water, toluene and phenol at 150 and 200°C. Tie lines were measured over the entire two-phase region, coming as close to the plait point as possible. While no ternary data are available for comparison, our results approach the correct limit at low phenol concentrations as determined by the mutual solubilities of toluene and water. The water-rich region of the ternary diagrams is expanded in Figure 5. Again, the correct boundary condition appears to be met at low phenol concentrations.

Figure 6 presents the distribution of phenol between water-rich and organic-rich phases for the two temperatures studied. At all concentrations, phenol partitions more heavily into the organic-rich phase at 150°C than at 200°C.

Figures 7 and 8 show ternary diagrams for water/thiophene/pyridine mixtures at 100 and 150°C; the aqueous region of these diagrams is expanded in Figure 9. No ternary data are available for comparison with our results. Mutual solubilities for water and thiophene have been measured at 150°C (5), but not at 100°C. The measured binodal curve at 150°C appears to approach the boundary conditions given by the binary mutual solubility data.

Figure 10 illustrates the temperature dependence of pyridine distribution between the water-rich and the organic-rich phases. As the temperature rises from 100 to 150°C, the liquid-liquid immiscibility region decreases, and the tie-line slopes become less steep. Thus, pyridine partitions less into the organic-rich phase

at 150°C than at 100°C.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. One of us, S.M., gratefully acknowledges the Henrich-Hertz-Foundation (West Germany) for the grant of a fellowship.

Literature Cited

(1) Horvath, A.L., and F.W. Getzen, "Halogenated Benzenes, Toluenes and Phenols with Water," IUPAC Solubility Data Series, Vol. 20 (1985).

(2) Sorensen, J.M., and W. Arlt, Liquid-Liquid Equilibrium Data Collection, DECHEMA Chemistry Data Series, Vol. 5, Part 1, Deutsche Gesellschaft für Chemisches Apparatewesen, Frankfurt/Main West Germany (1979).

(3) Anderson, F.E., PhD Dissertation, University of California, Berkeley (1985).

(4) Tsonopoulos, C., and W. Wilson, "High-Temperature Mutual Solubilities of Hydrocarbons and Water," *AIChE J.*, **29** (11), 990 (1983).

(5) Anderson, F.E., and J.M. Prausnitz, "Mutual Solubilities and Vapor Pressures for Binary and Ternary Aqueous Systems Containing Benzene, Toluene, m-Xylene, Thiophene and Pyridine in the Region 100-200°C," *Fluid Phase Equilibria,* **32**, 63 (1986).

(6) Filippov, T.S., and A.A. Furman, *Zh. Prikl. Khim.*, **25**, 895 (1952).

(7) Kisarov, V.M., *Zh. Prikl. Khim.*, **35**, 2347 (1962).

(8) Udovenko, V.V, and L.G. Fatkulina, *Zh. Fiz. Khim.*, **26**, 892 (1952).

(9) Van Arkel, A.E., and S.E. Vles, *Recl. Trav. Chim. Pays-Bas.*, **55**, 407 (1936).

TABLE 1

Water(1)/chlorobenzene(2) mutual solubility data in mole percent

Number of replicated measurements	T(°C)	P(bar)	Water-rich phase		Organic-rich phase	
			(2) in (1)	standard deviation	(1) in (2)	standard deviation
5	99.8	1.64	0.040	0.0019 (4.7%)	2.51	0.061 (2.4%)
6	124.8	3.60	0.059	0.0017 (2.9%)	4.10	0.077 (1.9%)
5	150.1	6.69	0.088	0.0053 (6.0%)	6.56	0.404 (6.2%)
3	174.9	12.2	0.132	0.0016 (1.2%)	10.0	0.088 (0.9%)
3	199.8	21.4	0.239	0.0004 (0.2%)	15.2	0.056 (0.4%)

TABLE 2

Water(1)/1,2-dichloroethane(2) mutual solubility data in mole percent

Number of replicated measurements	T(°C)	P(bar)	Water-rich phase		Organic-rich phase	
			(2) in (1)	standard deviation	(1) in (2)	standard deviation
4	74.9	*	0.272	0.0030 (1.1%)	3.21	0.168 (5.2%)
3	100.0	2.55	0.419	0.0068 (1.9%)	5.89	0.152 (2.6%)
1	124.8	5.62	0.804		11.0	

*Pressure too low to measure

TABLE 3

Water(1)/toluene(2)/phenol(3) mutual solubilities in mole percent

		Water-rich phase			Organic-rich phase		
T(°C)	P(bar)	(1)	(2)	(3)	(1)	(2)	(3)
149.9	7.09	99.22	0.09	0.69	7.39	84.67	7.94
149.9	6.82	98.68	0.12	1.20	11.78	72.39	15.82
149.8	6.82	97.75	0.15	2.09	20.83	53.48	25.69
150.0	6.58	97.22	0.20	2.58	28.43	41.99	29.58
150.0	6.65	96.09	0.28	3.63	41.75	26.08	32.16
149.7	6.62	95.21	0.37	4.42	50.62	18.08	31.30
150.0	6.41	94.56	0.44	5.00	54.88	15.13	29.99
200.0	22.3	99.05	0.33	0.62	17.22	76.86	5.92
200.4	22.3	98.26	0.62	1.12	20.27	70.07	9.66
199.4	21.6	97.93	0.56	1.51	22.32	64.77	12.91
200.0	21.4	96.96	0.69	2.35	28.76	53.55	17.69
199.7	21.4	96.02	0.71	3.27	35.59	43.30	21.12
199.8	21.2	95.02	0.92	4.06	40.16	37.25	22.59
200.4	21.8	92.76	1.36	5.88	52.92	23.94	23.14
200.3	21.7	91.82	1.61	6.57	55.14	21.84	23.01

TABLE 4

Water(1)/thiophene(2)/pyridine(3) mutual solubilities in mole percent

		Water-rich phase			Organic-rich phase		
T(°C)	P(bar)	(1)	(2)	(3)	(1)	(2)	(3)
100.2	3.02	98.95	0.21	0.84	5.93	77.83	16.24
99.6	2.89	98.33	0.22	1.45	10.51	66.40	23.09
99.8	3.26	97.44	0.25	2.31	20.58	49.64	29.78
100.2	2.62	96.09	0.33	3.58	30.12	37.24	32.64
100.0	2.62	94.55	0.45	5.00	40.54	26.94	32.52
100.3	3.50	89.77	0.98	9.25	56.55	15.21	28.24
149.7	10.1	98.95	0.43	0.62	11.78	77.19	11.03
149.9	9.29	97.79	0.51	1.70	20.87	57.84	21.29
149.7	9.56	96.49	0.64	2.87	32.53	42.15	25.32
150.0	8.89	93.46	0.98	5.56	49.13	24.12	26.75
150.1	8.68	91.04	1.32	7.64	56.44	17.99	25.57
150.0	8.99	86.04	2.33	11.63	69.41	10.30	20.29

List of Figure Captions

Figure 1: Mutual Solubilities of Water and Chlorobenzene

Figure 2: Mutual Solubilities of Water and 1,2-Dichloroethane

Figure 3: Liquid-Liquid Equilibria for Water/Toluene/Phenol Mixtures at 150°C

Figure 4: Liquid-Liquid Equilibria for Water/Toluene/Phenol Mixtures at 200°C

Figure 5: Water-Rich Compositions for Water/Toluene/Phenol Mixtures at 150 and 200°C

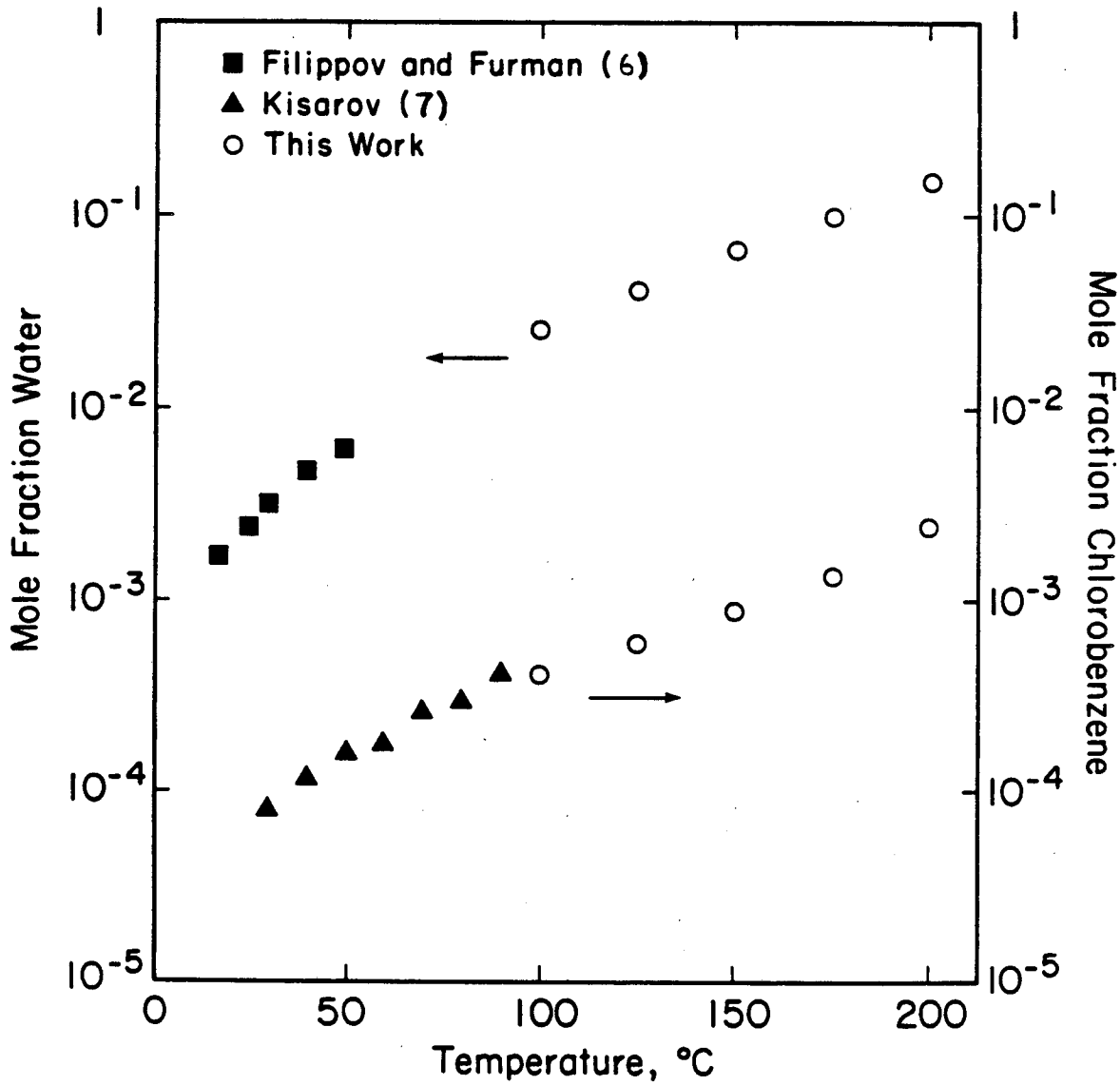
Figure 6: Distribution of Phenol Between Water-Rich Phase and Organic-Rich Phase at 150 and 200°C

Figure 7: Liquid-Liquid Equilibria for Water/Thiophene/Pyridine Mixtures at 100°C

Figure 8: Liquid-Liquid Equilibria for Water/Thiophene/Pyridine Mixtures at 150°C

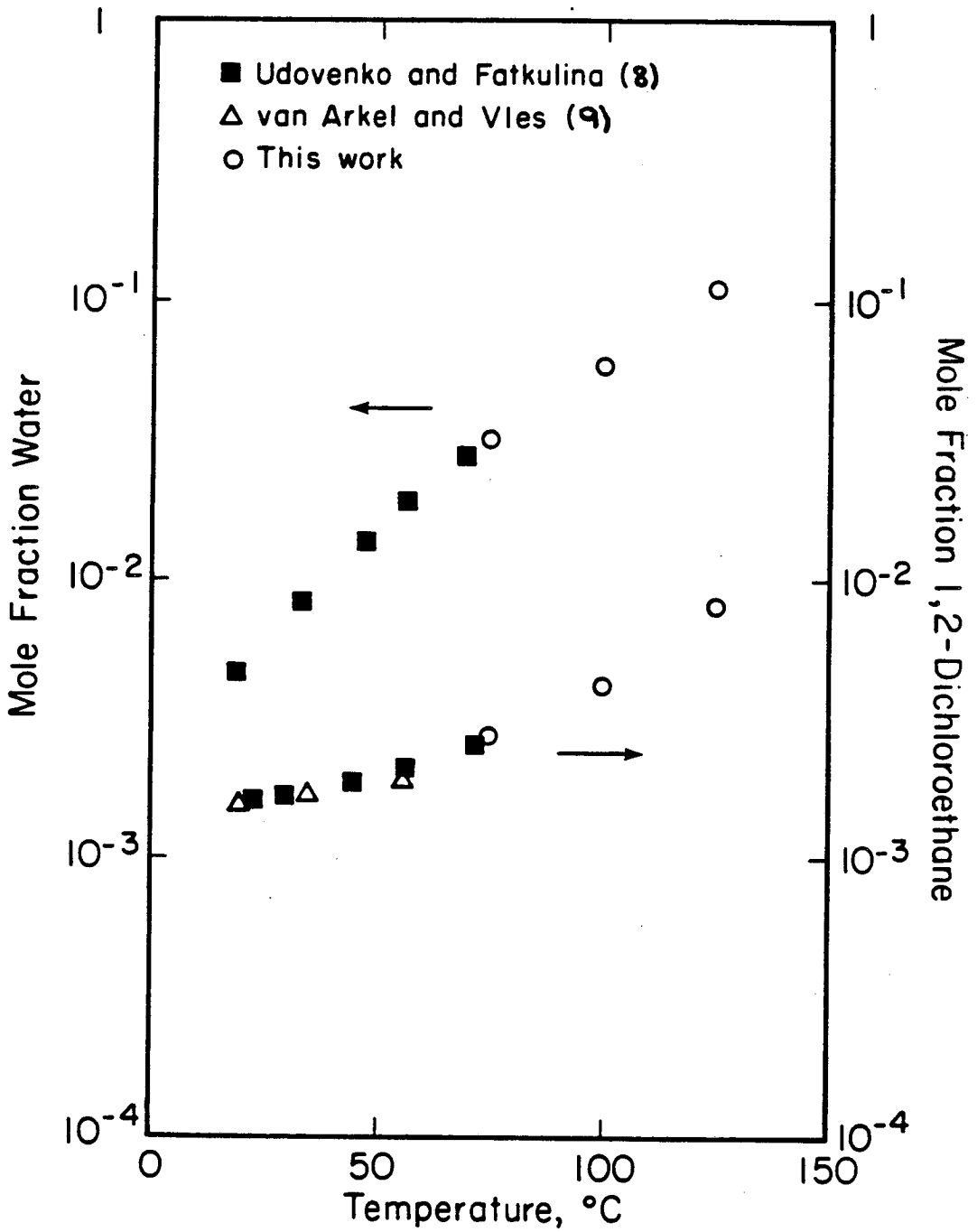
Figure 9: Water-Rich Compositions for Water/Thiophene/Pyridine Mixtures at 100 and 150°C

Figure 10: Distribution of Pyridine Between Water-Rich Phase and Organic-Rich Phase at 100 and 150°C



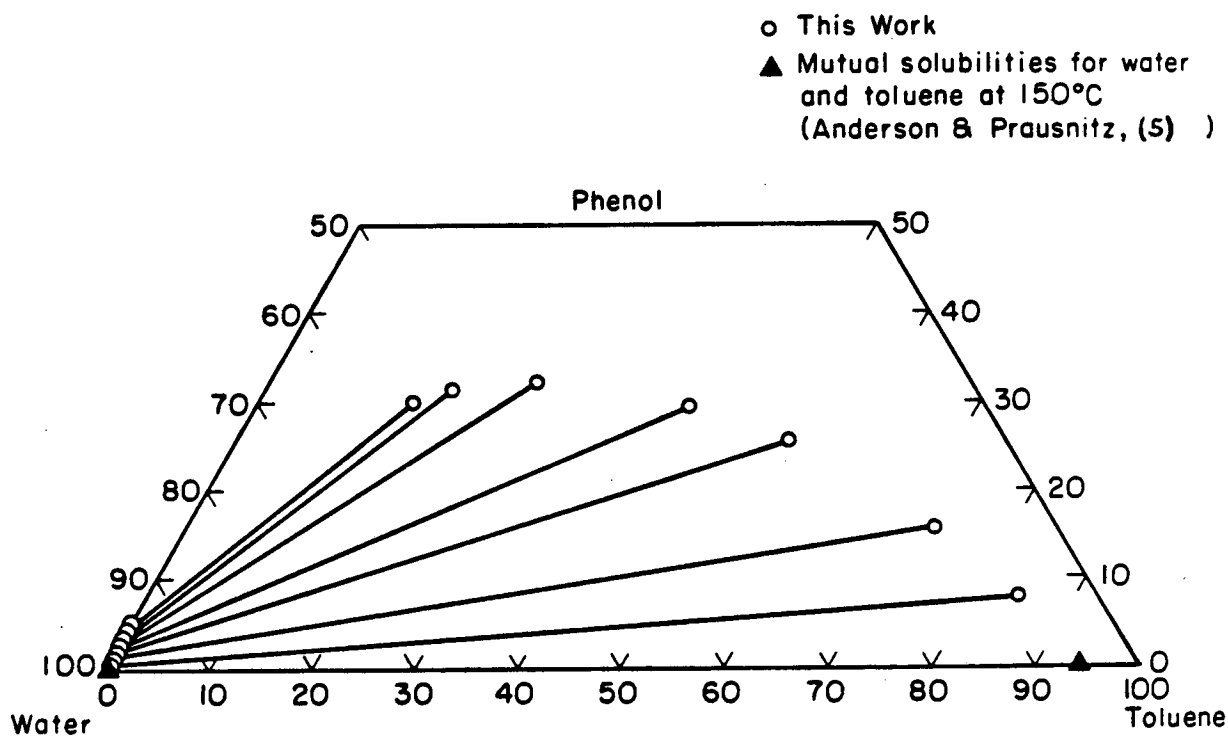
MUTUAL SOLUBILITIES OF WATER AND CHLOROBENZENE

Figure 1



MUTUAL SOLUBILITIES OF WATER AND 1,2-DICHLOROETHANE

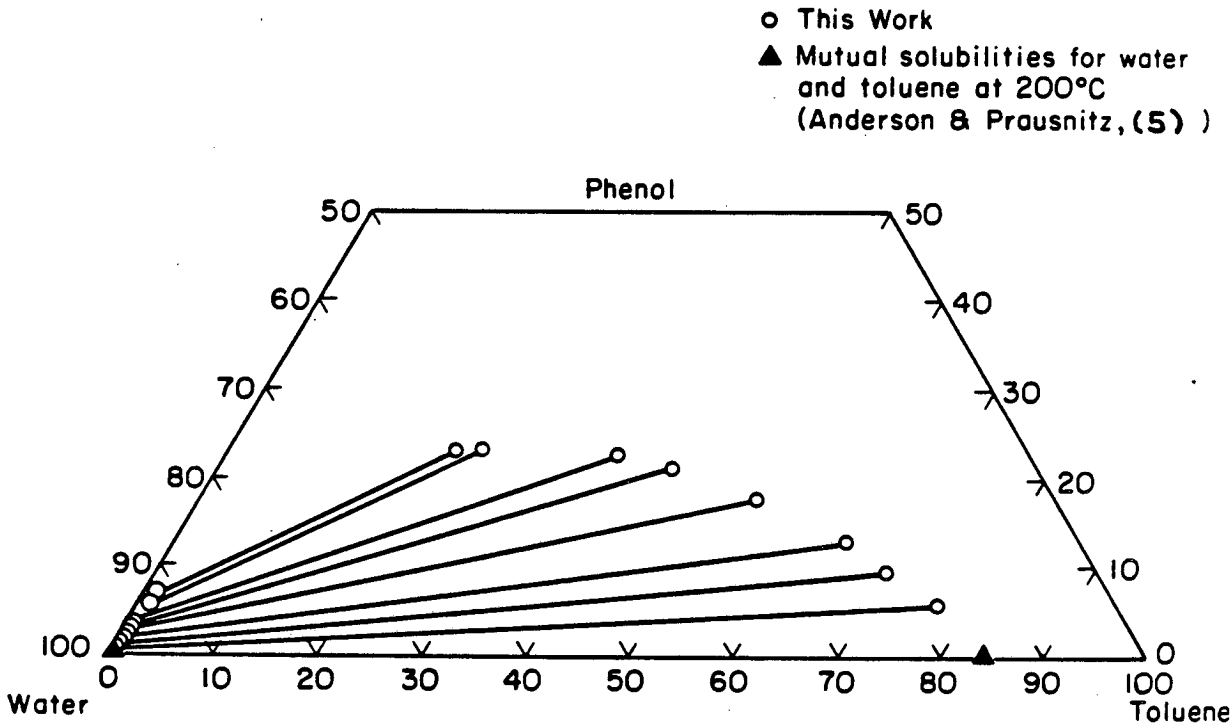
Figure 2



Liquid-Liquid Equilibria for Water/Toluene/Phenol Mixtures at 150°C

(Compositions in mole percent)

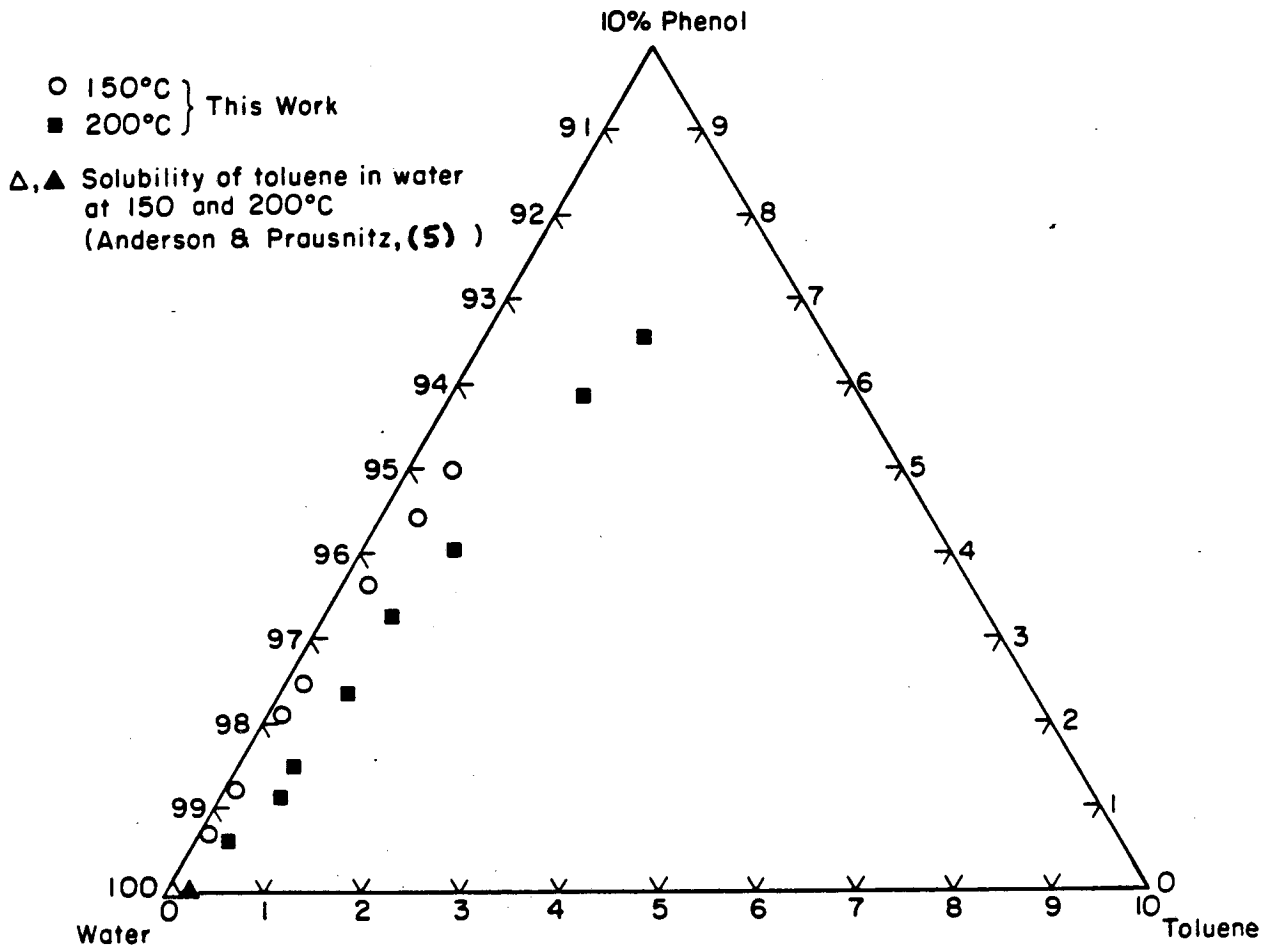
Figure 3



Liquid-Liquid Equilibria for Water/Toluene/Phenol Mixtures at 200°C

(Compositions in mole percent)

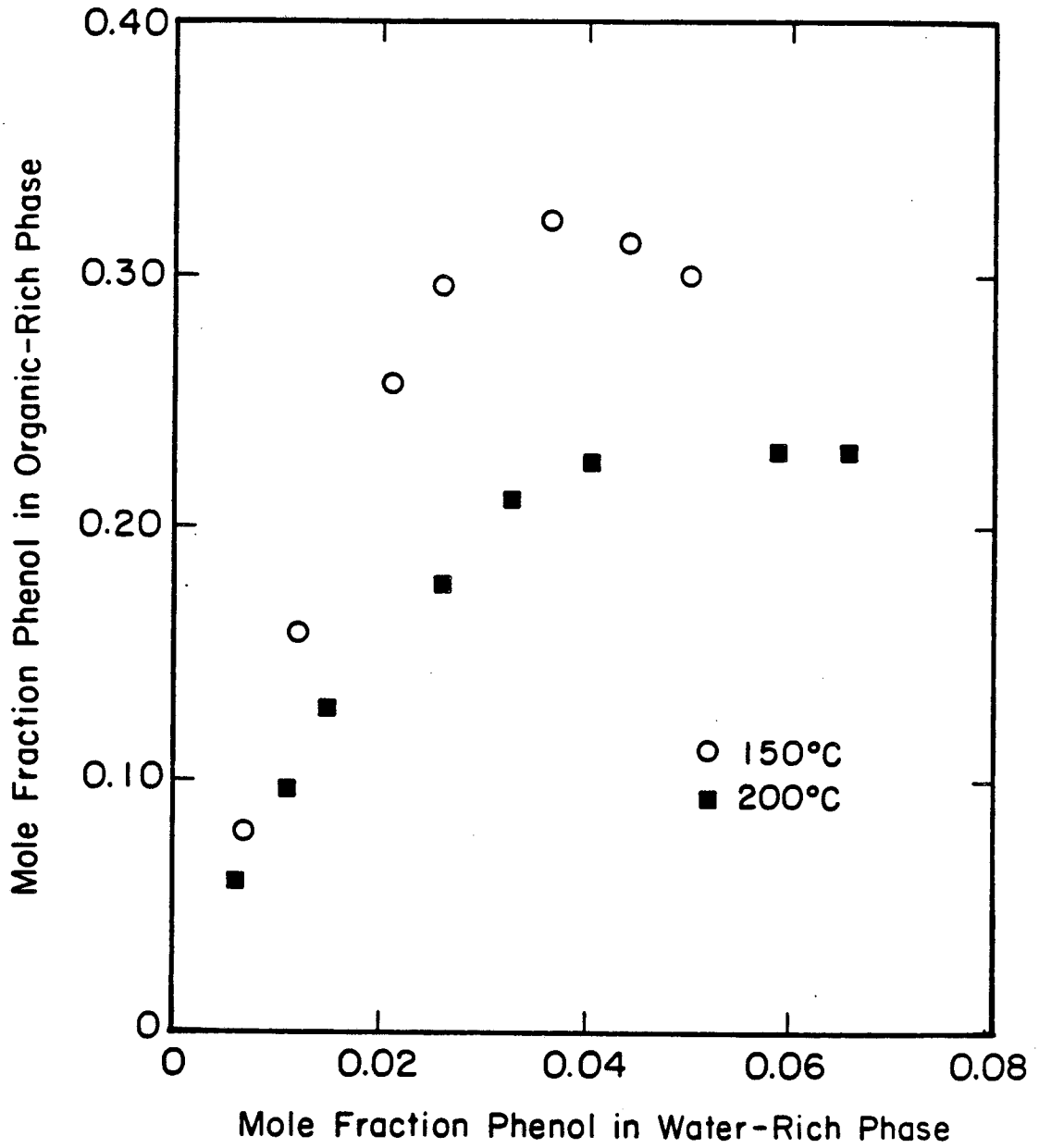
Figure 4



Water-Rich Compositions for Water/Toluene/Phenol Mixtures at 150 and 200°C

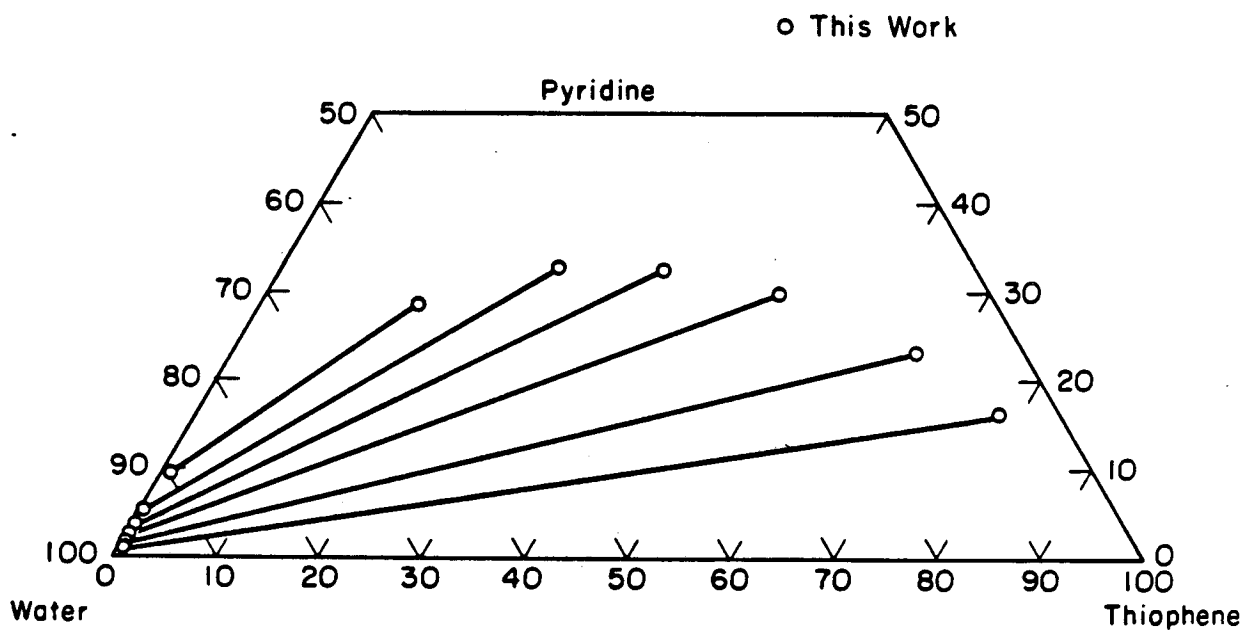
(Compositions in mole percent)

Figure 5



Distribution of Phenol Between Water-Rich Phase and Organic-Rich Phase at 150 and 200°C

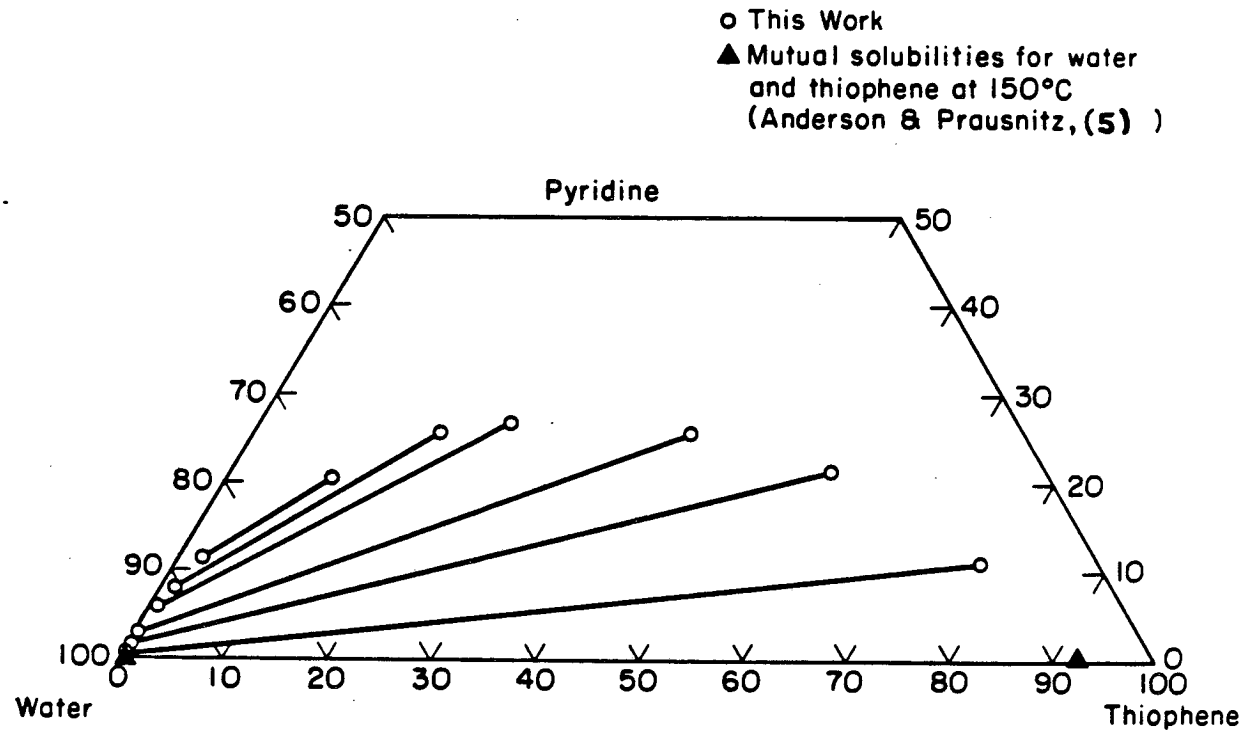
Figure 6



Liquid-Liquid Equilibria for Water/Thiophene/Pyridine Mixtures at 100°C

(Compositions in mole percent)

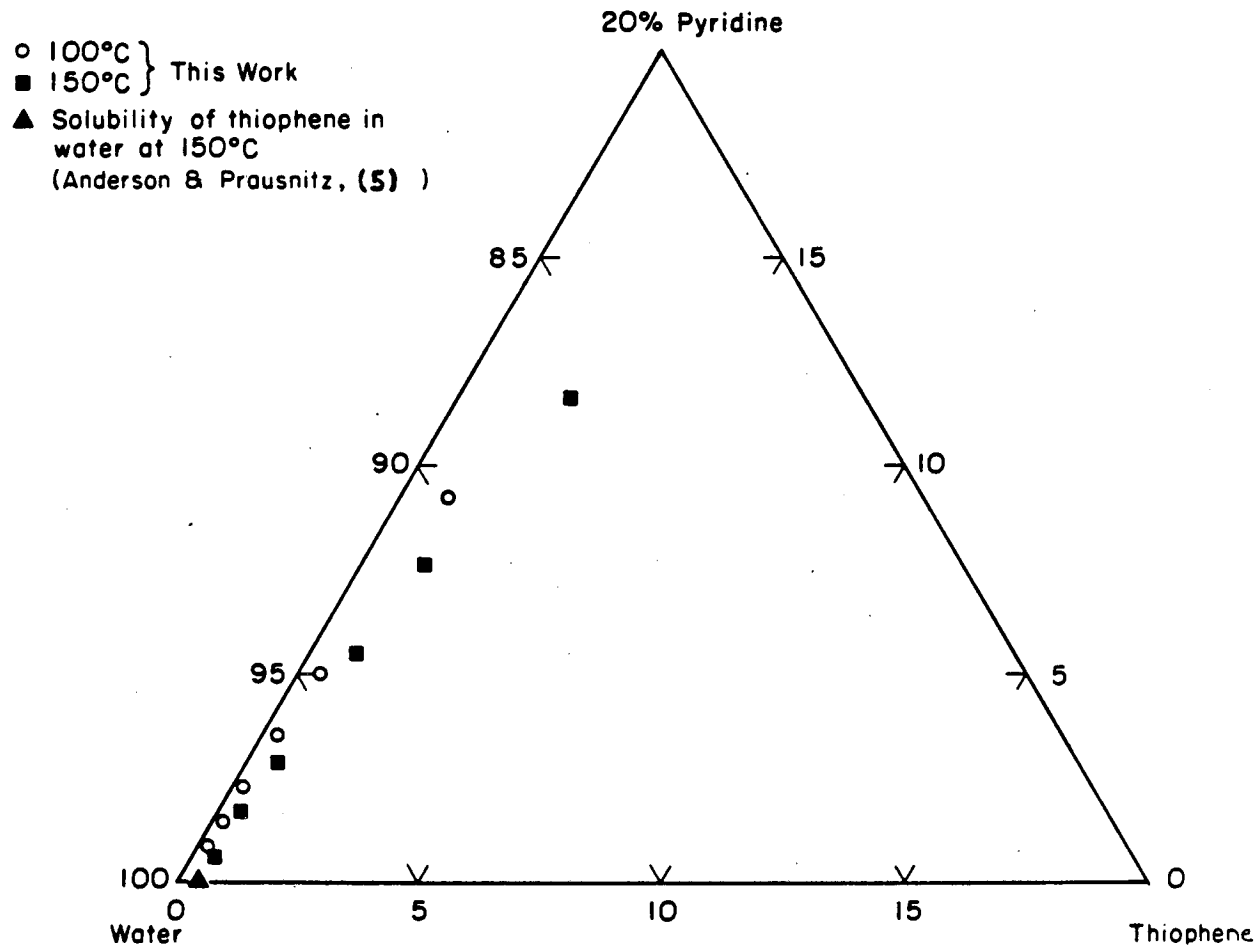
Figure 7



Liquid-Liquid Equilibria for Water/Thiophene/Pyridine Mixtures at 150°C

(Compositions in mole percent)

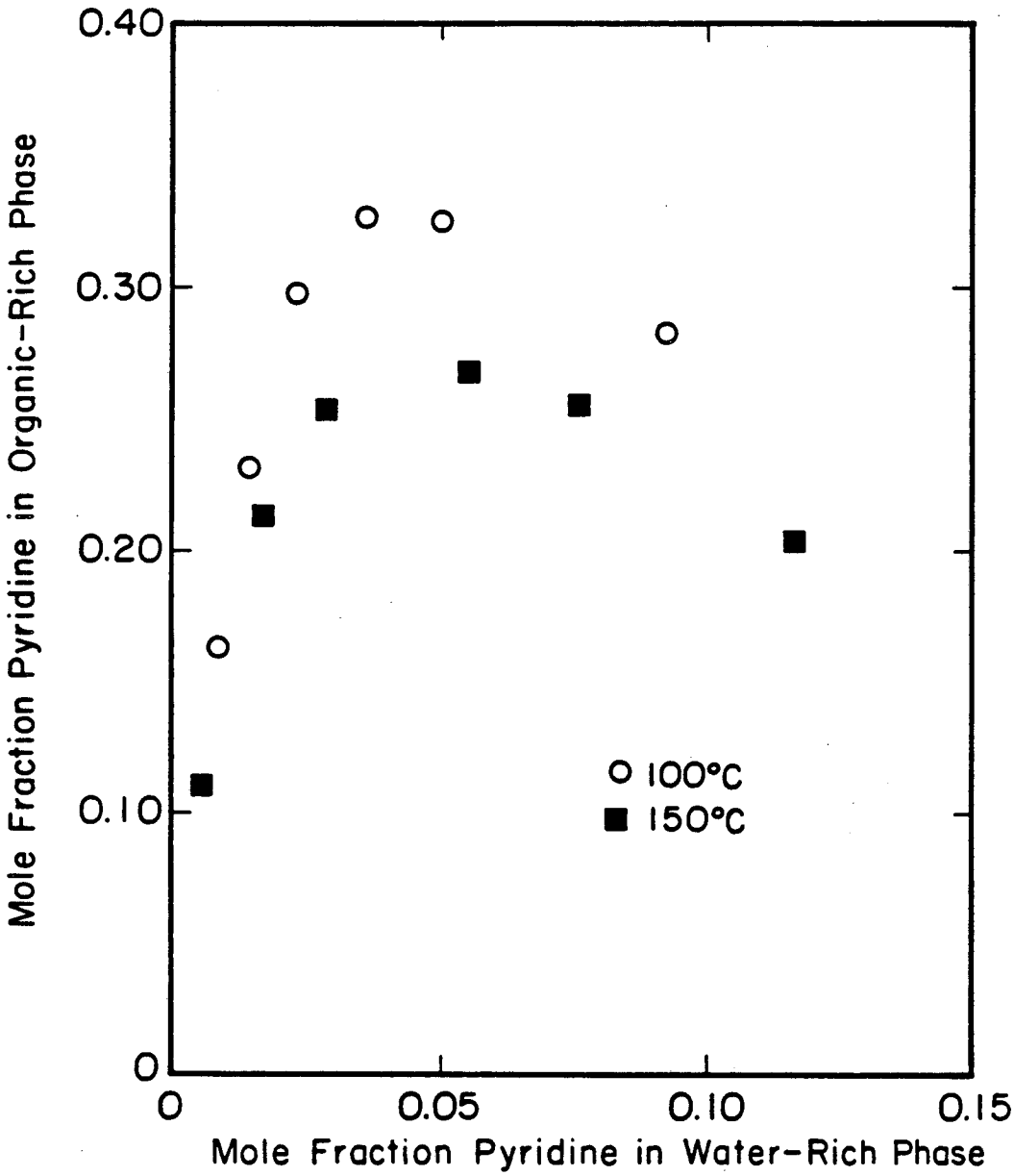
Figure 8



Water-Rich Compositions for Water/Thiophene/Pyridine Mixtures at 100 and 150°C

(Compositions in mole percent)

Figure 9



Distribution of Pyridine Between Water-Rich Phase and Organic-Rich Phase at 100 and 150°C

Figure 10

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