pounds of water and 0.6 pound of methyl ethyl ketone, the other containing 99.4 pounds of methyl ethyl ketone and 2.0 pounds of water. Thus approximately 90% of the water content would be removed from the methyl ethyl ketone with a loss of about 0.6% of the solvent.

The major operating cost for such a process appears to be the cost for the recompression of the recycled ethylene.

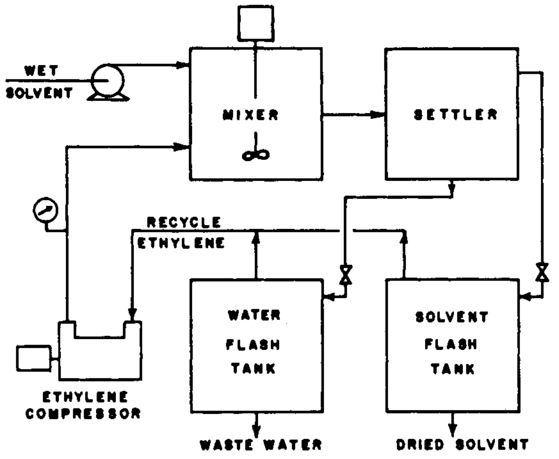

Figure 16. Schematic flowsheet for ethylene dehydration of solvents

For this example, the theoretical work of isothermal compression required to supply the necessary amount of ethylene (40 pounds) at the system pressure (515 p.s.i.a.) is 1.5 kw.-hr. Applying conservative values of compressor efficiency (25%) and power cost (1.0 cent per kw.-hr.) to this figure, one arrives at a magnitude for this portion of the operating cost of about 6 cents per 100 pounds of methyl ethyl ketone processed. This cost is approximately equal to the value of the methyl ethyl ketone lost with the discarded water. Undoubtedly dehydration to remarkably small water contents can be achieved by this method by suitable adjustment of temperature and pressure conditions.

ACKNOWLEDGMENT

The authors express their grateful appreciation to the Dreyfus Foundation, Inc., for a grant-in-aid to Princeton University which provided partial support for the conduct of the research investigations on which this paper is based.

NOMENCLATURE

F = fluid phase existing above critical pressure of ethylene-solvent binary at temperature of diagram
L = single liquid phase existing over entire range of water-solvent compositions, usually at low ethylene concentrations
L_1 = water-rich or more dense liquid phase
L_2 = solvent-rich or less dense liquid phase
P_1 = low pressure, about 1 to 5 atm.
P_2 = moderate pressure, below critical pressure of ethylene-solvent binary
P_3 = high pressure, above critical pressure of ethylene-solvent binary
S = solvent component of system: ethylene, water, solvent
V = vapor (or gas) phase, essentially pure ethylene

REFERENCES

(1) Carson, D. B., Katz, D. L., *Trans. AIME* **146**, 150 (1941).
(2) Diepen, G. A. M., Scheffer, F. E. C., *J. Am. Chem. Soc.* **70**, 4081, 4085 (1948).
(3) Diepen, G. A. M., Scheffer, F. E. C., *Rec. trav. chim.* **69**, 593, 604 (1950).
(4) Ewell, R. H., Harrison, J. M., Berg, L., *Ind. Eng. Chem.* **36**, 871 (1944).
(5) Gottschlich, C., M. S. E. thesis, Department of Chemical Engineering, Princeton University, Princeton, N. J., 1952.
(6) Hammerschmidt, E. G., *Ind. Eng. Chem.* **26**, 851 (1934).
(7) Jaglom, J., M. S. E. thesis, Department of Chemical Engineering, Princeton University, Princeton, N. J., 1951.
(8) Meter, D. M., *Ibid.*, 1955.
(9) Sykes, H. B., *Ibid.*, 1948.
(10) Taylor, H. S., "Treatise on Physical Chemistry," vol. 1, p. 449, Van Nostrand, New York, 1925.
(11) Todd, D. B., Ph. D. dissertation, Department of Chemical Engineering, Princeton University, Princeton, N. J., 1951.

Received for review April 22, 1958. Accepted August 25, 1958.

Phase Behavior of the System UO_2SO_4-$CuSO_4$-H_2SO_4-H_2O at Elevated Temperatures

F. E. CLARK,[1] J. S. GILL, RUTH SLUSHER, and C. H. SECOY
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

The fuel solution proposed for use in the second homogeneous reactor experiment at Oak Ridge was a heavy water solution, 0.04 molal in uranyl sulfate and 0.005 molal in copper sulfate. The purpose of the copper sulfate was to provide for the liquid-phase catalysis (*1*) of the deuterium-oxygen recombination reaction, thus eliminating problems associated with handling large volumes of an explosive mixture of radiolytic gas in the reactor system. Earlier experience with dilute uranyl sulfate solutions had indicated that increases in temperature promoted hydrolysis of the uranyl ion to such an extent that basic salts or hydrated oxides of uranium precipitated. In concentration regions where a hydrolytic precipitate was not encountered, the temperature limit of homogeneity was fixed by the appearance of a second liquid phase (*3*). Posnjak and Tunell (*2*) have reported studies of the copper sulfate system to 200°C. in which analogous promotion of hydrolysis by increased temperatures was indicated, the predominant solid phase encountered being the basic copper sulfate, $3CuO.SO_3.2H_2O$.

The addition of sulfuric acid to such solutions would be expected to oppose and retard the hydrolysis reaction. Furthermore, the addition of acid to uranyl sulfate solutions was known to cause the liquid miscibility gap (two-liquid phase region) to shrink in scope. The effect of sulfuric acid in either case was to elevate the temperature ceiling on the region of one liquid phase homogeneity. However, use of an excessive amount of acid in the reactor system was objectionable primarily because it would increase the corrosiveness of the solution and secondarily because it would increase the neutron losses in the reactor. The work reported here is a systematic determination of this temperature ceiling for a single liquid phase homogeneity as a function of the copper sulfate concentration, the uranyl sulfate

---

[1] Present address, National Carbon Research Laboratories, P. O. Box 6116, Cleveland, Ohio.

Table I. Second Liquid Phase Temperatures, °C.

Master solutions. 17.17% $CuSo_4$, 0.00 mole % excess H_2SO_4; 47.64% UO_2SO_4, 0.00 mole % excess H_2SO_4

Weight Ratio, Solution/H_2O	Weight Ratio, $CuSO_4/UO_2SO_4$									
	8/2	7/3	6/4	5½/4½	5/5	4/6	3/7	2/8	1/9	0/10
10/0		^{a}	^{a}	287	287	287	287.5	288.5	289.5	291
9/1			^{a}	^{a}	286	286		287		290
8/2			^{a}	^{a}	285.5	285.5		286		289
7/3				^{a}	^{a}	285		285.5		288
6/4					^{a}	284.5		285		287
5/5					^{a}	285		285		287
4/6					^{a}	286		286		287.5
3/7					^{a}	288 + ^{b}		289		289.5
2/8				^{a}	^{a}	292.5 + ^{b}		292.5 + ^{b}		293
1/9	^{a}				^{a}	^{a}and^b		302 + ^{b}		302.7
0.75/9.25						^{a}	^{b}	^{b}		^{b}
0.5/9.5						^{a}and^b	^{b}	^{b}	^{b}	312
0.25/9.75							^{b}	^{b}	^{b}	^{b}

^{a}Blue-green solid.
^{b}Red-yellow solid.

Table II. Second Liquid Phase Temperatures, °C.

Master solutions. 17.24% $CuSO_4$, 9.91 mole % excess H_2SO_4;
47.05% UO_2SO_4, 9.91 mole % excess H_2SO_4

Weight Ratio, Solution/H_2O	Weight Ratio, $CuSO_4/UO_2SO_4$								
	8/2	7/3	6/4	5/5	4/6	3/7	2/8	1/9	0/10
10/0	^{a}	306.5	305.5	305	304.5	305	305.5	307	308.5
9/1		305		303					305.5
8/2	^{a}		301.5		300.5		301		303
7/3		301.5		300					300.5
6/4			299.5		297.5		297.5		298.5
5/5		^{a}		297.5					297.5
4/6			300		297		296.5		297
3/7				299.5					298
2/8			^{a}		302		300.5		300.5
1/9	^{a}	^{a}	^{a}	^{a}	311		309.5		309
0.75/9.25	^{a}	^{a}	^{a}	^{a}	313	313	313	313	313
0.5/9.5	^{a}	^{a}	^{a}	^{a}	321	320	319	319	319
0.25/9.75	^{a}	^{a}	^{a}	^{a}	332	332	331	331	

^{a}Blue-green solid.

concentration, and the sulfuric acid concentration. Although emphasis was placed on solutions of low concentration, the study was intended to include all concentrations which might be of interest in any reactor considerations now or in the future. The solvent used in all cases was distilled natural water rather than heavy water.

EXPERIMENTAL

The method was a synthetic one in which solutions of known composition were sealed in short sections of 1-mm. quartz tubing and heated in either an aluminum block furnace or a liquid bath. The bath liquid was a eutectic mixture of the nitrates of sodium, potassium, and lithium. Agitation was obtained by attaching the tubes to a Vibratool operated through a time clock so that alternate periods of oscillation and rest were obtained. The frequency and amplitude of the Vibratool were such that the contents of the tube were rather violently mixed. Temperature was measured by a calibrated iron-Constantan thermocouple. Visual observation of the tubes during heating was augmented by the use of a modified Bausch & Lomb Baliscope. This instrument was equipped with eyepieces to give magnifications of 10×, 20×, and 60×, respectively. It was modified to give a large field and to have a working distance of about 4 feet.

All solutions used were prepared from two master solutions, one a nearly saturated copper sulfate solution and the other a nearly saturated uranyl sulfate solution. Five sets of submaster solutions were prepared from these, each set having a selected mole per cent excess of sulfuric acid added to it. By analysis followed by adjustment of the acid content, the mole per cent excess acid for the copper sulfate solutions was made precisely the same as that of the corresponding uranyl sulfate solution. Weight aliquots

Table III. Second Liquid Phase Temperatures, °C.

Master solutions. 16.90% $CuSO_4$, 19.25 mole % excess H_2SO_4; 46.29% UO_2SO_4, 19.25 mole % excess H_2SO_4

Weight Ratio, Solution/H_2O	Weight Ratio, $CuSO_4/UO_2SO_4$													
	9/1	8½/1½	8/2	7½/2½	7/3	6½/3½	6/4	5½/4½	5/5	4/6	3/7	2/8	1/9	0/10
10/0	326	324.5	323	322.5	321.5	320	320	321	320	321	321.5	324	324.5	327
9/1	323		320		318.5		317			316.5				322
8/2	^{a}	319	318				314		313.5					317
7/3		^{a}		314	313			312.5		310.5				313.5
6/4	^{a}		314.5		311.5		310		309					310
5/5				311.5	310.5			309.5		307				307.5
4/6	^{a}		^{a}				308		306.5					308.5
3/7				^{a}	311			309.5		306				306.5
2/8	^{a}				^{a}		312		309.5	309				310.5
1/9				^{a}		^{a}	319		317.5	316				315
0.75/9.25	^{a}		^{a}		^{a}		^{a}		320	319	318	317	317	317
0.5/9.5	^{a}		^{a}		^{a}		^{a}		325	325	325	323	322	322
0.25/9.75	^{a}		^{a}		^{a}		^{a}		337	335	335	333	334	334

^{a}Blue-green solid.

of the two solutions and of water could then be mixed to give any desired copper to uranium ratio and any desired dilution. The constancy of the mole ratio of excess sulfuric acid to the total copper sulfate plus uranyl sulfate was not affected by mixing or dilution errors. Nominal values for excess acid for the five sets, respectively, were 0, 10, 20, 30, and 40 mole per cent. The use of weight aliquots in a systematic pattern with constant acid-salt mole ratio permits interpolation within the limits of any phase region to yield a valid prediction of the temperature limit for any specified concentration.

DATA AND DISCUSSION

The composition of solutions used and the experimentally observed temperatures at which a second liquid phase appeared are reported in Tables I to V. The compositions are expressed in terms of the compositions of the master solutions and the weight aliquots, from which the true composition in terms of either weight per cent or mole per cent may be readily calculated for any specific solution. These compositions are those of the solutions at room temperature and are not the true compositions at the temperature of the phase transition. This fact introduces no difficulty in the use of the data, as there is point-to-point correspondence in the phase behavior and the room temperature composition.

Temperatures are not reported in those instances in which a solid phase appeared at temperatures below the two-liquid phase region. It was found impossible to determine these temperatures with any reasonable certainty because of the slowness with which equilibrium seemed to be established. However, in nearly all cases the temperature of appearance of the solids, at least the blue-green solid, was far below (100° C. or more) the two-liquid phase region. The solid crystals could readily be classified by color into two groups, blue-green solids and red-yellow solids. Each class was obtained only in a specific region of the composition diagram: the blue-green solids from solutions with high copper-uranium ratio and the red-yellow solids with low copper-uranium ratio. An increase in sulfuric acid content reduced the scope of both regions.

Efforts to isolate crystals of the solids for further study produced no reliable information. In most cases the amount of solid available from a specific tube was very small, being scarcely visible without the aid of a microscope. Furthermore, the stability of the solids when removed from the conditions of formation was not certain. As a result of the visual observations, however, it is believed that there are at least two solid phases in each of the color regions and that one of the blue-green solids is probably the well known basic copper sulfate, $3CuO.SO_3.2H_2O$.

The temperatures reported for the appearance of a second liquid phase were obtained with both rising and falling temperature and were readily reproducible. The transition is sharp and easy to observe. These temperatures are believed to be accurate to the nearest degree. Plotting the temperature data along any one of the dilution paths

Table IV. Second Liquid Phase Temperatures, °C.

Master solutions. 16.64% $CuSO_4$, 29.11 mole % excess H_2SO_4; 45.63% UO_2SO_4, 29.11 mole % excess H_2SO_4

Weight Ratio, Solution/H_2O	Weight Ratio, $CuSO_4/UO_2SO_4$													
	10/0	9½/½	9/1	8½/1½	8/2	7½/2½	7/3	6/4	5/5	4/6	3/7	2/8	1/9	0/10
10/0	347.5	342.5	341.7	339	338	337	337	334	335	336	336	336.5	339.5	343.5
9/1	342.2		337		335.5		332	330.5	329.5	329.5				334
8/2	340		334		331.5		328.5	326	325	325				329
7/3	338.2		332		328		325	323	322	321				324
6/4	[a]	332.2	330		325.5		322	320.2	319	318.2				319
5/5		[a]	328.5	324.5	323.5		320.5	318	316.5	315.5				316
4/6			327	323.5	322.5		319.5	316	315	314				313.5
3/7			[a]	323.5	322		319	316	315	313.5				312.2
2/8				[a]	323.5		318.5	316.5	313.5	313.5				313
1/9			[a]		[a]		[a]	323	318	318				318.5
0.75/9.25			[a]		[a]		[a]	327	327	325	325	322	320	320
0.5/9.5			[a]		[a]		[a]	331	331	331	329	329	327	327
0.25/9.75			[a]		[a]		[a]	[a]	339	339	339	339	340	339

[a] Blue-green solid.

Table V. Second Liquid Phase Temperatures, °C.

Master solutions. 16.53% $CuSO_4$, 38.75 mole % excess H_2SO_4; 45.36% UO_2SO_4, 38.75 mole % excess H_2SO_4

Weight Ratio, Solution/H_2O	Weight Ratio, $CuSO_4/UO_2SO_4$										
	10/0	9/1	8/2	7/3	6/4	5/5	4/6	3/7	2/8	1/9	0/10
10/1	361	355	351.5	350.2	349	349.5	349	350.5	352.5	355	358
9/1	357.5	351		345	344			343.5	345		353.5
8/2	355	348	344			338		338	339		347
7/3	352	345		336.5	335						338.5
6/4	349.5	341.5	337.5			329.5		328	328.5		331.5
5/5	347	339		330.5	327.5	326					327.5
4/6	345	336.5	332	328.5	325.5	323.5		321.5	321		324
3/7	344	335.5	331	327	324	322		320	319.5		321.5
2/8	[a]	[a]	332	328	325	322.5		320.5	320		320
1/9	[a]	[a]	336.5	333.5	330	328		326	325		324.5
0.75/9.25		[a]	[a]	334	330	330	328	327	326	326	326
0.5/9.5		[a]	[a]	339	336	336	333	332	332	330	330
0.25/9.75		[a]	[a]	[a]	347	343	343	342	342	340	340

[a] Blue-green solid.

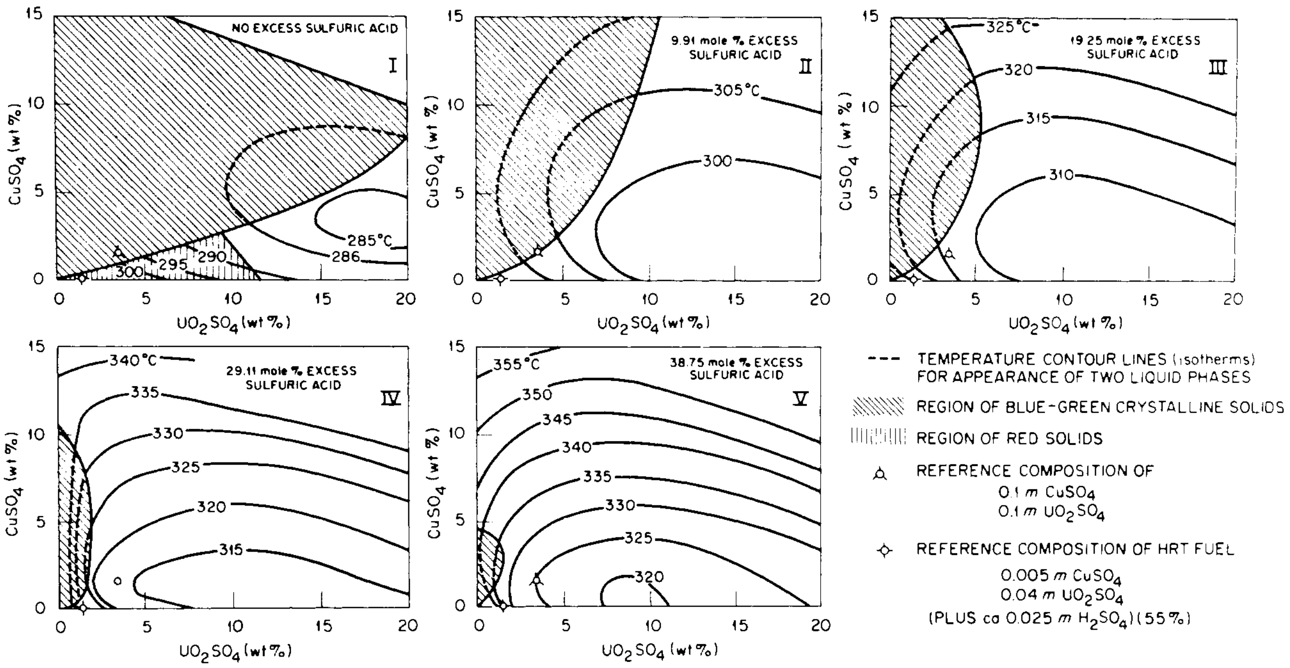

Figure 1. Phase-transition temperatures in solutions containing cupric sulfate, uranyl sulfate, and sulfuric acid

against one of the composition variables yields smooth curves from which interpolation values may be obtained. Figure 1 shows temperature contour plots obtained in this manner for each of the five acidity values. The regions in which solid phases were encountered are indicated. A comparison shows that as the amount of excess sulfuric acid is increased the scope of the precipitation regions shrinks and that the temperature at which liquid phase separation occurs for a specific concentration is elevated. If sufficient acid is present to prevent precipitation of a solid, pure copper sulfate-sulfuric acid solutions will yield a second liquid phase in a manner completely analogous to the behavior or uranyl sulfate solutions.

Solution compositions falling within the precipitation regions are probably of no interest for reactor use, because of the temperature limitation. The data in the two-liquid phase region provide an upper temperature limit for reactor use for any composition within the scope of this study. Relying on past experimental data (*4*), the two liquid phase appearance temperatures for the heavy water system are expected to be of the order of 5° to 10°C. lower than for the corresponding ordinary water system.

LITERATURE CITED

(1) McDuffie, H. F., Compere, E. L., Stone, H. H., Woo, L. F., Secoy, C. H., "Homogeneous Catalysis for Homogeneous Reactors. Catalysis of the Reaction Between Hydrogen and Oxygen," Southwide Chemical Conference, ACS, Memphis, Tenn., Dec. 6, 1956.

(2) Posnjak, E., Tunell, G., *Am. J. Sci.* **218**, 1-34 (1929).

(3) Secoy, C. H., *J. Am. Chem. Soc.* **72**, 3343 (1950).

(4) Secoy, C. H., others, "The Reactor Handbook AECD-3646," Vol. 2, 1st ed., Chap. 4.3, p. 559, Technical Information Service, U. S. Atomic Energy Commission, Oak Ridge, Tenn., May 1955.

Received for review May 24, 1958. Accepted October 9, 1958. Division of Industrial and Engineering Chemistry, Symposium on Chemistry and Reprocessing of Circulating Nuclear Reactor Fuels, 133rd meeting, ACS, San Francisco, Calif., April 1958. Based on work performed at Oak Ridge National Laboratory, operated by Union Carbide Corp. for the Atomic Energy Commission. Other articles from this symposium will be published in the February 1959 issue of *Industrial and Engineering Chemistry*.

Diffusion Coefficients in Hydrocarbon Systems. Methane in the Liquid Phase of the Methane-Santa Fe Springs Crude Oil System

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

Little experimental work is available concerning the molecular transport of methane in the liquid phase of hydrocarbons except the earlier work of Pomeroy (*10*) and of Lacey and others (*1*, *4*, *5*, *7*). More recently, interest in this field has revived and at the present time some information is available concerning the transport of methane in binary systems made up of this hydrocarbon and the paraffin hydrocarbons from propane through *n*-decane, with the exception of octane and nonane (*11*, *13-16*). Kirkwood (*6*) has set forth some of the basic relationships of molecular transport and these have been extended to a number of situations of particular interest to petroleum production (*9*).

The work of Drickamer has made a marked contribution to an understanding of transport in liquid and gas phases at elevated pressures. His studies, directed toward an understanding of the behavior at a gas-liquid interface (*24*, *25*),