

Table III. Properties at the Unique States in the *n*-Butane-*n*-Decane System

Mole Fraction <i>n</i> -Butane	Critical		Maxcondentherm		Maximum Press.	
	Press. P.S.I.A.	Temp., ° F.	Press. P.S.I.A.	Temp., ° F.	Press. P.S.I.A.	Temp., ° F.
0.0 ^a	304.0	655.0	304.0	655.0	304.0	655.0
0.1	362.0	631.7	338.3	635.3	363.2	630.0
0.2	423.0	608.3	371.5	616.0	424.7	605.2
0.3	486.0	584.7	403.0	596.8	488.5	580.3
0.4	553.8	560.0	432.5	578.0	557.2	554.0
0.5	621.5	533.7 ^b	461.2	558.3	625.7	526.8 ^c
0.6	683.3	505.2	490.2	536.6	685.5	499.7
0.7	710.8	474.3	520.0	510.2 ^b	711.2	471.7
0.8	710.8	434.0	547.2	476.0	711.2	437.0
0.9	674.0	378.5	565.0	410.7	680.0	389.7
1.0 ^c	550.7	305.6	550.7	305.6	550.7	305.6

^aCritical state of *n*-decane (1). ^bValues at this and higher temperatures are subject to greater uncertainty. ^cCritical state of *n*-butane (1).

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Benzene-Methanol-Copper (II) Chloride System at 30.0°C.

Properties of $\text{CuCl}_2 \cdot \text{CH}_3\text{OH}$

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The phase diagram for the system CuCl_2 -methanol-benzene at 30.0°C. was determined by the wet residue method. The solid component in the two-phase region of the diagram was $\text{CuCl}_2 \cdot \text{CH}_3\text{OH}$.

ALTHOUGH CONSIDERABLE work has been done on systems of the type inorganic solid-water-organic liquid, (1, 2, 3, 6) few ternary diagrams with the water replaced by another organic liquid have been published. The results reported here are the first of a planned study on systems of this type.

EXPERIMENTAL PROCEDURE

The Schreinemaker wet residue (4) method was employed.

Reagents. Fisher reagent grade benzene, methanol, and anhydrous copper (II) chloride were used without further purification, except for drying the CuCl_2 at 170°C. The Cl-Cu ratio was greater than 1.99 for the CuCl_2 .

Mixture Preparation. Mixtures of CuCl_2 , methanol, and benzene were prepared in 8-ounces glass bottles, fitted with caps containing polyethylene liners. The CuCl_2 was added to the bottles in a dry box (or very quickly in the open). Each bottle contained a Teflon-coated magnetic stirring bar. The composition of each batch of samples was adjusted (by trial and error) so that the amount of solid phase was

sufficient for a wet residue analysis, but not so great as to make the mixtures too viscous to stir. The mixtures were sealed tightly, stirred for about 10 minutes at 35° to 40°C., placed in a 30.0°C. bath, and allowed to stand. Once or more daily during this equilibration period the mixtures were stirred at 30–31°C. All mixtures were equilibrated for a week or more.

Sampling Procedure. After equilibration, a sample of the liquid phase was removed (by oral suction through a coarse filter stick) into a sample bulb. Care was taken to prevent moisture from entering the sample and to prevent evaporation. Part of this sample was poured into a conical weighing bottle, and the per cent CuCl_2 determined. The remaining part was placed in a distillation flask. A sample of wet residue of the desired consistency (determined by trial and error in a number of runs) was put into a weighed flat-bottomed distillation flask (which had a 24/40 or a 19/24 G.S. neck so that a powder funnel could be admitted) and the weight of the wet residue was then determined.

Analyses. The EDTA method for copper was used to determine the CuCl_2 percentages in the liquid phase and wet residue. The distillation flask containing the liquid

phase was fitted with a receiving flask and chilled in an acetone-dry ice bath. The liquid was recovered by reduced pressure distillation and the per cent benzene determined from the refractive index and a previously prepared calibration curve. The wet residue flask was treated in the same manner; in this case, a CuCl_2 analysis was done on the solid remaining in the flat-bottomed flask.

RESULTS AND INTERPRETATION

Computation and Data Display. The data obtained were converted to percentages of CuCl_2 , CH_3OH , and C_6H_6 in the liquid phase and in the wet residue. (The CuCl_2 percentages were obtained directly. From the percentages of benzene in the recovered liquids, the over-all liquid percentages were obtained.) The data in Table I are representative of a large number of trials. Duplicate, and in some cases, triplicate values were obtained for all points shown.

Figure 1 shows the ternary diagram constructed from the results. The percentage CuCl_2 at which the tie line crossed the CH_3OH - CuCl_2 axis was determined analytically, using a modification of the procedure devised by Schott (5). The

last column in the table shows the analytically determined values.

Solid Phase. Of major interest on the diagram is the convergence of the tie lines at 80.7% CuCl_2 on the copper (II) chloride-methanol axis. Thus, the compound $\text{CuCl}_2 \cdot \text{CH}_3\text{OH}$ (80.7% CuCl_2) is the stable solid phase in the two phase region. No evidence of a previously reported dimethanolate (3) was found. Work in the low benzene (0 to 4%) part of the two-phase region of the diagram is subject to large experimental error, because of the small differences in the refractive indices of the recovered liquids from the liquid phase and the wet residue but analyses of the dried solid from saturated solutions of CH_3OH and CuCl_2 indicate the presence of the monomethanolate.

Several attempts have been made to isolate the compound $\text{CuCl}_2 \cdot \text{CH}_3\text{OH}$. In the method here the wet residue was placed in a small sintered glass funnel, filtered by suction, and placed in a dry box with P_2O_{10} or anhydrous CuCl_2 as a desiccant. The compound was removed from the funnel and pressed with filter paper to absorb excess solvent. The remained in the dry box for various lengths of time. Samples were removed in a weighing bottle, and the CuCl_2 percentages determined by EDTA analysis for the copper (II) ion.

Eight determinations were made with CuCl_2 as a desiccant. In all cases, the wet residue was derived from a saturated solution of CuCl_2 and methanol. In five determinations, the pressed material appeared to be free of excess solvent; for these samples CuCl_2 percentages between 80.3 and 80.5% were obtained. The drying periods ranged from less than an hour to 12 hours. In three determinations, samples were removed that were not powdery and appeared to contain excess solvent. These samples were removed immediately from the dry box after being pressed with filter paper. The CuCl_2 percentages ranged from 77.2 to 80.0%.

The results obtained using P_2O_{10} as a drying agent showed a marked dependence on the drying period. No CuCl_2 percentages below 70% were obtained for any samples. The lower values were obtained for samples that were pressed with filter paper a few times and quickly removed from the dry box. In one series of five samples, portions of the dried solid were placed in weighing bottles at intervals beginning after 15 minutes of drying (when the solid first appeared free of excess methanol). The last sample was removed after 35 minutes. The analyses ranged from 80.1 to 81.0% CuCl_2 on these samples. On other runs, longer drying periods resulted in higher CuCl_2 percentages and were accompanied by visible appearance of the brown CuCl_2 .

The CuCl_2 percentage in the dimethanolate would be 67.72, so that the results on the samples that were pressed free of excess solvent (and not allowed to dry after pressing) are strong evidence against the existence of this compound.

The compound $\text{CuCl}_2 \cdot \text{CH}_3\text{OH}$ is light yellow-green in color and is highly hygroscopic; tinges of blue appear almost immediately on the surface of this compound when it is exposed to moist air.

Liquid Phase. The only invariant point was pure benzene in equilibrium with CuCl_2 and $\text{CuCl}_2 \cdot \text{CH}_3\text{OH}$. This was checked from two directions. First, samples of CH_3OH , CuCl_2 , and C_6H_6 were prepared in which insufficient CH_3OH was present to solvate all of the CuCl_2 . Second, benzene-washed wet residue from a high benzene mixture was equilibrated with benzene. In both cases, the refractive index of the (clear) liquid phase was found to be that of pure benzene.

The color of the saturated liquid was dark green (similar to concentrated H_2O solution of CuCl_2) in the high methanol region and a lighter yellow green in the high benzene region.

The saturated solution of CuCl_2 in methanol at 30.0°C. contained 37.82% CuCl_2 . The value 37.5% has been reported previously (3).

Liquid Phase, %		Wet Residue, %		CuCl ₂ at which Tie Line Intersects the CuCl ₂ -CH ₃ OH Axis, %
Methanol	CuCl ₂	Methanol	CuCl ₂	
62.18	37.82
60.25	36.51	57.79	39.17	79.6
57.68	33.70	51.19	41.70	79.4
54.93	31.76	51.46	36.39	79.3
51.50	28.57	48.48	33.23	80.0
43.77	21.28	40.50	29.23	80.2
40.03	18.88	37.85	25.50	80.2
34.50	15.65	33.18	21.06	81.6
24.94	9.97	24.44	16.00	80.9
12.63	3.57	13.23	11.18	81.2
5.54	1.07	6.73	7.71	80.2
0.15	0.025	2.19	8.97	80.5
0.00	0.00	0.67	7.85	92

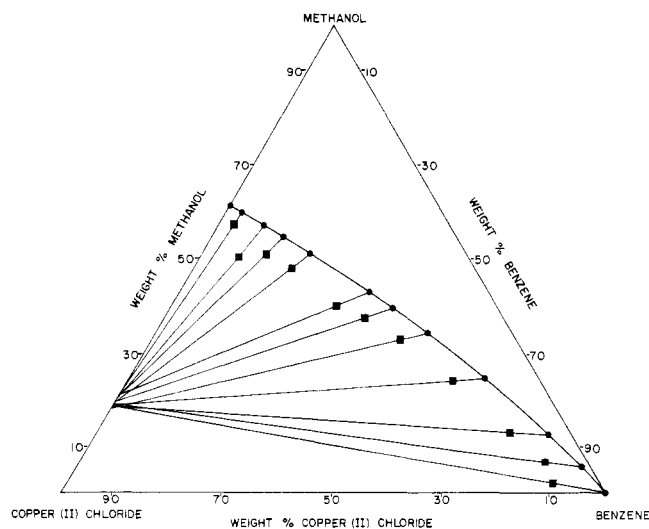


Figure 1. Ternary phase diagram for the system CuCl_2 - CH_3OH - C_6H_6 at 30°C.

- liquid points
- wet residue points

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Vapor-Liquid Equilibrium of the Methane-*n*-Butane-Carbon Dioxide System at Low Temperatures and Elevated Pressures

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The effect of carbon dioxide on the vapor-liquid equilibrium of hydrocarbons at low temperatures and elevated pressures was studied. The temperature range was from -140 to 100° F., and the pressure range was from 400 to 1700 p.s.i.a. The experimental data are presented as the isotherms on pressure-composition plots and as isobars on temperature-composition plots. *K*-values are also presented.

CARBON DIOXIDE is found in varying percentages in many petroleum reservoir fluids. In recent years, the increasing interest in secondary recovery techniques has brought greater interest in the investigations of its presence. A knowledge of the effect of carbon dioxide on the vapor-liquid equilibrium of hydrocarbon systems would provide useful information.

Reliable data on the phase equilibrium relationship of ternary systems involving carbon dioxide and hydrocarbon at low temperatures are very scarce. Clark and Din (1), studied the carbon dioxide-ethane-ethylene system at low temperatures and at subatmospheric pressures.

EXPERIMENTAL

The equilibrium apparatus was essentially a windowed equilibrium cell contained in a constant temperature liquid bath. Circulation of the fluid in the cell was accomplished by a positive displacement magnetic pump which took vapor from the top of the cell, passed it through the pump, and coolers where the vapor was cooled to cell temperature, and injected into the bottom of the equilibrium cell to bubble through the liquid. Eight hours of circulation and two hours for phase separation were allowed before the phases were sampled for analyses.

The liquid bath consisted of a 10-gallon Dewar flask surrounded by vermiculite insulation all of which was enclosed in a metal box constructed of 1/16-inch aluminum

plate. Cell contents were viewed through slits cut in the box and insulation at positions corresponding to 1-inch wide unsilvered strips located on opposite sides of the Dewar.

Water was used as the liquid bath medium at 100° and 40° F. Freon Refrigerant-11 was used down to -140° F.

The temperature of the liquid bath was controlled using a precision temperature controller with a sensitivity of ±0.002° F. The temperature of the cell and the liquid bath was measured using three copper-constantan thermocouples. Pressures were read on Heise Bourdon tube gages which were calibrated, using a dead-weight gage, after each isotherm was completed. No change in calibration was noted during the entire project. Details of the equipment, operation, and analytical procedure are available (3).

Analytical. Each equilibrium phase was sampled for analysis. The vapor and liquid samples were withdrawn from the equilibrium cell into stainless steel, high pressure tubing connected to the cell proper. The pressure was carefully maintained in the equilibrium cell by adding mercury to the pressure control cylinder as the samples were withdrawn. Samples were analyzed using a Beckman GC-2 gas chromatograph, and occasional checks were made using a mass spectrometer. The analyses with these two methods never disagreed more than 0.10 mole %.

Materials Used. The methane and *n*-butane used in this work were Phillips Petroleum Co. research grade hydrocarbons with a 99.9 mole % minimum purity. The carbon dioxide was Matheson Co. bone dry grade with 99.8 mole % minimum purity.

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