vior of the 500-p.s.i.a. isobar for octane, the mixtures, and pentane (*3*), showing the progressive decrease in enthalpy as the octane content increases.

ACKNOWLEDGMENT

Gratitude is expressed to the American Petroleum Institute, which provided funds for the enthalpy measurement of these mixtures.

NOMENCLATURE

H = enthalpy, B.t.u. per lb.
P = pressure, p.s.i.a.
V = specific volume, cu. ft. per lb.
T = temperature, Rankine

LITERATURE CITED

(1) American Petroleum Institute, Division of Refining, "Technical Data Book—Petroleum Refining," Section 7A1.3, New York, 1966.
(2) Das, T. R., Kuloor, N. R., *Indian J. Technol.* 5 (2), 51 (1967).
(3) Lenoir, J. M., Robinson, D. R., Hipkin, H. G., J. CHEM. ENG. DATA 15, 23 (1970).
(4) McKay, R. A., Sage, B. H., *Ibid.*, 5, 21 (1960).

RECEIVED for review April 1, 1969. Accepted July 14, 1969. For supplementary material, order NAPS Document NAPS 00624 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y., 10001, remitting $1.00 for microfiche or $3.00 for photocopies.

Solubility of Some Ammonium, Copper, Iron, Potassium, and Zinc Salts in Formamide

BROOKS BECKER[1]
Kansas City Laboratory, Gulf Research and Development Co., Merriam, Kan. 66204

Solubilities of 21 compounds in formamide were determined. Most compounds were considerably less soluble in formamide than in water. Zinc oxide proved to be more soluble in formamide than in water.

FORMAMIDE, like water, is a polar solvent with a high dielectric constant. The solubility of inorganic salts tends to be high in formamide because of solvation. Gopal and Husain (*4*) reported that the solubilities of the alkali and alkaline earth halides in formamide are less than the corresponding values in water, whereas the reverse is true for lead salts. Colton and Brooker (2) determined the solubility of a variety of alkali metal salts, but reported their data as grams of salt per liter of solution, which is not a very useful unit without density data. Consequently, some of their measurements were repeated and the data are reported here in more suitable units.

Most of the present data are for solutions of copper, iron, and zinc salts in formamide. Such solutions may be useful as liquid fertilizers, rich in both nitrogen and trace elements essential for proper plant growth (*1*, *7*). No solubility data for copper, iron, or zinc salts in formamide have been reported in the literature.

EXPERIMENTAL

Matheson, Coleman and Bell formamide, 99%, was used in all solubility studies. This formamide melts at 2.5° ± 0.1° C., which is in good agreement with the literature value of 2.55° C. (*8*). All salts were reagent grade chemicals and were used without purification. Hygroscopic salts were stored in a dry box.

Formamide and an excess of the salt were weighed into a 100-ml. volumetric flask, in amounts such that the flask was about half full. The formamide was exposed to the air only briefly during addition, and all hygroscopic salts were added in the dry box. The flasks were closed with glass stoppers and attached to a shaker arm so that all of the flask except the top of the neck was immersed in a stirred constant-temperature water bath maintained at 25° ± 1° C. All samples were shaken for at least 48 hours, after which the mixtures were filtered rapidly in air at 25° C. A weighed aliquot of the filtrate was taken for analysis. Two or three separate solubility determinations were made for each compound.

Both water and air temperatures were determined with an Anschutz precision thermometer with a range of –5° to +55° C., and 0.2° C. divisions. This thermometer had been checked previously at the ice point and against a calibrated copper-constantan thermocouple. The copper-constantan thermocouple, in conjunction with a Leeds and Northrup K-2 potentiometer, was used to measure the melting point of formamide.

Bath temperature was controlled with a Fisher immersion-type thermoregulator, which controlled an immersion heater in the bath. The heater worked against a cooling coil cooled with tap water. Air temperature was thermostatically controlled at 25° C.

Before analysis, formamide was removed by evaporating an aqueous solution of the sample to dryness. Copper was

---

[1] Present address: Gulf Research and Development Co., P. O. Drawer 2038, Pittsburgh, Pa. 15230

Table I. Solubility of Salts in Formamide at 25° C.

Salt	Grams of Anhydrous Salt/100 Grams Formamide[a]	Grams of Anhydrous Salt/100 Grams Water (5)	Salt	Grams of Salt/100 Grams Formamide[a]	Grams of Anhydrous Salt/100 Grams Water (5)
$NH_4H_2PO_4$	1.3	41.8	$K_3Fe(CN)_6$	14.7	48.8
$(NH_4)_2HPO_4$	0.18	71.9	$K_4Fe(CN)_6$	2.69	31.6
$CuCl_2 \cdot 2H_2O$	4.6	77.3	KH_2PO_4	1.2	25
$CuSO_4 \cdot 5H_2O$	4.3	22.7	K_2HPO_4	4.1	168
$Cu(NO_3)_2 \cdot 3H_2O$	79	150.5	K_3PO_4	4.5	106
$Cu(C_2H_3O_2)_2 \cdot H_2O$	0.9	7.28	KSCN	88.6	239
$CuSO_4$	1.4	22.7	$ZnCl_2$	43.1	432
CuO	<0.01	2×10^{-4}	ZnO	0.8	2×10^{-4}
$Fe(NO_3)_3 \cdot 9H_2O$	1.3	87.3	ZnS	<0.001	10^{-8}
$FeSO_4 \cdot 7H_2O$	2.6	29.6			
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	3.7	25.0			
$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	0.5	...			

[a] Each value is the mean of two or three determinations. Density of formamide at 25° C. is 1.130.

then determined iodometrically, iron was measured by titration with potassium dichromate, and zinc was precipitated and weighed as zinc ammonium phosphate (*3*). Potassium was determined by the Perrin method (*6*). Phosphorus was analyzed gravimetrically by the quinoline molybdate method.

DISCUSSION

In nearly all cases, the salt solubility is considerably less in formamide than in water. A large difference in solubility is shown by diammonium orthophosphate; in formamide, the value is about 1/400 of that in water. On the other hand, potassium ferricyanide has a solubility in formamide nearly one third of that in water. Zinc oxide does not follow the trend; it is more soluble in formamide than in water. In contrast to the order in water, monoammonium phosphate is more soluble in formamide than diammonium phosphate. Tripotassium orthophosphate proved to be the most soluble of the three orthophosphates in formamide, whereas dipotassium orthophosphate is the most soluble in water. The data are presented in Table I, together with literature values for the solubility of the anhydrous salts in water. In the case of hydrated salts, the data represent not only the solubility of the hydrated salt in formamide, but also a point in the ternary system formamide-water-salt. Unfortunately, hydration numbers were not determined for the hydrates. Thus, data for the hydrates could be subject to some error if the nominal hydration number is not the true hydration number.

LITERATURE CITED

(1) Brown, B. E., Reid, F. R., *Soil Sci.* **43**, 341-7 (1937).
(2) Colton, E., Brooker, R. E., *J. Phys. Chem.* **62**, 1595-6 (1958).
(3) Furman, N. H., "Scott's Standard Methods of Chemical Analysis," 6th ed., Vol. **1**, pp. 404-5, 542-3, 1232, Van Nostrand, New York, 1962.
(4) Gopal, R., Husain, M. M., *J. Indian Chem. Soc.* **40**, 272-4 (1963).
(5) Linke, W. F., Seidell, A., "Solubilities. Inorganic and Metal-Organic Compounds," Van Nostrand, New York, 1958.
(6) Perrin, C. H., *Anal. Chem.* **21**, 948 (1949).
(7) Rehling, C. J., Taylor, J. R., Jr., *J. Am. Soc. Agron.* **29**, 134-44 (1937).
(8) Smith, G. F., *J. Chem. Soc.* **1931**, 3257.

RECEIVED for review January 15, 1969. Accepted November 25, 1969