The Systems Potassium Chloride–Formamide–Water, Potassium Nitrate–Formamide–Water, and Monopotassium Phosphate–Formamide–Water

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The ternary solid-liquid equilibrium diagrams at 25° C. were determined for potassium chloride, potassium nitrate, and monopotassium phosphate with water and formamide. In all three cases, the pure salt was the only solid phase.

FORMAMIDE is a solvent much like water. That is, it is a polar solvent with a high dielectric constant. Because of solvation, the solubility of inorganic salts tends to be high in formamide. Nevertheless, salt solubilities in formamide are generally less than in water (*1*), although the reverse is true for some lead salts (*2*). Since formamide is potentially useful as a liquid nitrogen-containing fertilizer (*3*), the study of the solubility of some common potassium and phosphorus compounds in the formamide-water system was of interest. The salts chosen were KCl, KNO_3, and KH_2PO_4. The ternary systems of each of these salts with formamide and water at 25° C. are described.

EXPERIMENTAL

Fresh reagent-grade salts were used without further purification. Matheson, Coleman and Bell 99% formamide

Table I. Starting Compositions and Analyses of the Ternary Systems

Initial Composition, Wt. %			Saturated Liquid Phase, Wt. %[a]		
KCl	Formamide	Water	KCl	Formamide	Water
30.5	14.4	55.1	21.7	16.3	62.0
42.6	20.4	36.9	18.5	29.1	52.4
33.2	33.6	33.2	15.1	42.6	42.4
37.2	37.7	25.1	12.8	53.8	33.4
25.4	59.6	15.0	9.4	71.9	18.7
41.4	47.1	11.5	9.3	72.8	17.9
31.8	61.0	7.2	7.8	82.4	9.8
40	60	0	6.4	93.6	0
KNO_3			KNO_3		
33.2	20.0	46.8	23.0	22.4	54.6
28.5	35.7	35.7	19.5	40.3	40.2
44.3	33.2	22.5	17.6	48.0	34.4
22.0	50.5	27.5	18.1	53.1	28.8
35.2	52.9	11.9	14.9	68.9	16.2
34.4	60.3	5.3	14.3	78.0	7.7
40	60	0	13.3	86.7	0
KH_2PO_4			KH_2PO_4		
40.7	7.6	51.7	15.2	10.9	73.9
29.8	20.3	49.9	10.3	25.6	64.1
32.9	33.6	33.5	5.8	46.5	47.7
28.6	43.0	28.4	3.9	58.4	37.7
32.2	49.5	18.3	2.7	71.0	26.3
29.6	59.7	10.7	1.6	82.7	15.7
...	...	...	1.6	85.1	13.3
20.0	74.0	6.0	0.9	91.4	7.5
...	...	...	1.0	95.1	3.9
40	60	0	1.0	99.0	0

[a] At 25° C.

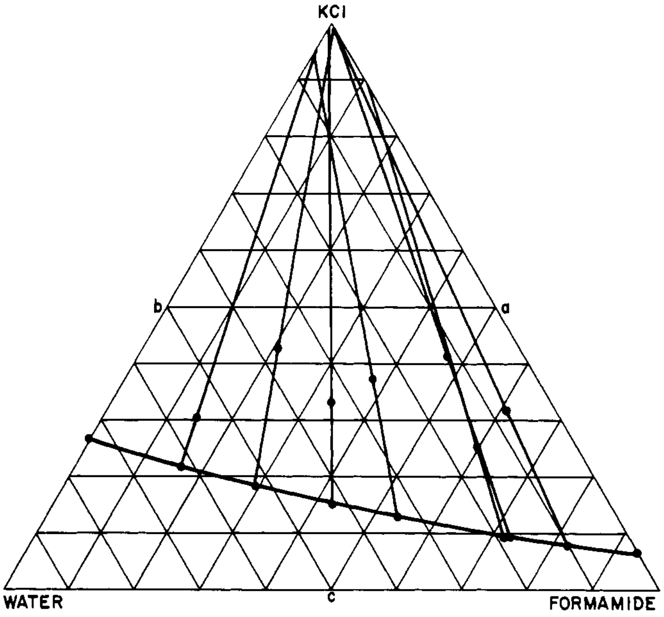

Figure 1. System formamide–H_2O–KCl at 25° C. (weight %)

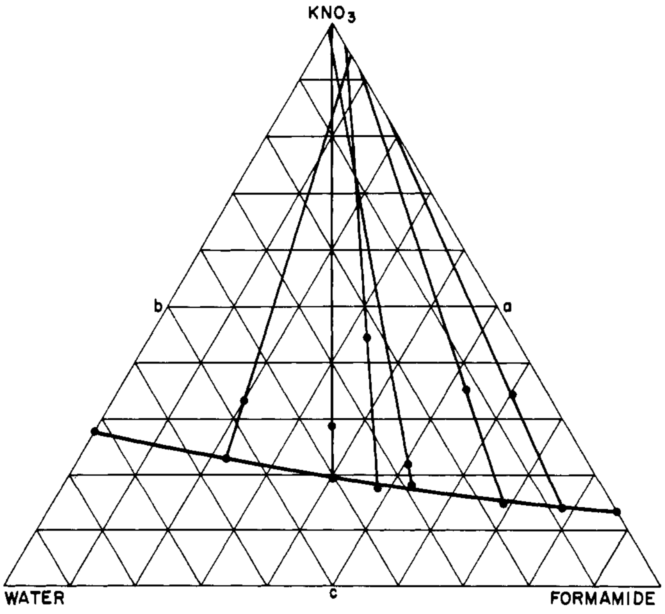

Figure 2. System formamide–H_2O–KNO_3 at 25° C. (weight %)

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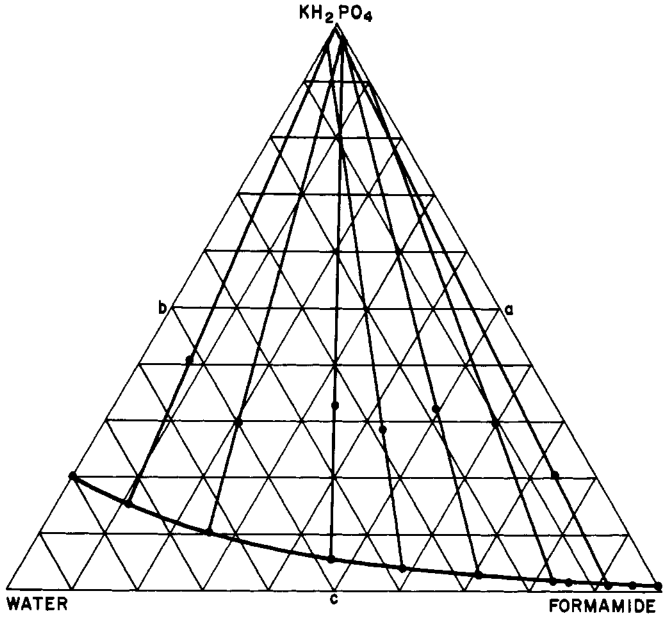

Figure 3. System formamide–H_2O–KH_2PO_4 at 25° C. (weight %)

was used without further purification, since it had a melting point of 2.5° ± 0.1° C., which was in good agreement with the literature value of 2.55° C. (*5*).

A known excess of salt was added to a selected mixture of water and formamide in a 100-ml. volumetric flask. Each flask was attached to the arm of a mechanical shaker and immersed in a water bath which was maintained at 25° C. After vigorous shaking for at least 24 hours, the saturated liquid phase was removed through a fine fritted glass filter on the end of a tube by applying a slight pressure to the system.

Amide nitrogen was determined by the Kjeldahl procedure. After the formamide had been removed by evaporating an aqueous solution of the sample to dryness, potassium was determined by the Perrin method and phosphorus was determined gravimetrically by the quinoline molybdate method. Water was calculated by difference.

RESULTS AND DISCUSSION

The complete system was determined for each of the following salts: KCl, KNO_3, and KH_2PO_4. The data are listed in Table I. The salt itself is the only solid phase in each of these systems at 25° C. The solubility of both potassium chloride and potassium nitrate decreased almost linearly with addition of formamide (Figures 1 and 2). The solubility of monopotassium phosphate decreased somewhat more rapidly at low formamide concentrations (Figure 3). Tie lines were established from the known initial composition and the analysis of the saturated liquid phase. The wet residue was not analyzed. This method was sufficiently accurate, since the systems were relatively simple and none of the solutions were unduly viscous. The data of Linke and Seidell (*4*) were used for the solubility of the pure salts in water—26.4, 27.5, and 20.0 grams per 100 grams of saturated solution of KCl, KNO_3, and KH_2PO_4, respectively.

LITERATURE CITED

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Vapor-Liquid Equilibria of 1,3-Butadiene Systems

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Vapor-liquid equilibrium data at 25° C. are reported for solutions of 1,3-butadiene in benzene, ethyl acetate, ethyl ether, carbon tetrachloride, carbon disulfide, dichloromethane, and nitromethane at concentrations up to 20 to 30% butadiene in the liquid. Measurements were made by a static technique. The results are compared with several expressions for excess Gibbs energy.

VAPOR-LIQUID equilibrium data are useful not only in the design of separation processes, but also as a key to the understanding of intermolecular forces in solution. The authors report experimental results for the interactions of a conjugated π-bond structure, 1,3-butadiene, with seven varied solvents.

Although many experimenters use circulation stills for direct measurements of vapor-liquid equilibria (*3*), they usually obtain isobaric data which are inadequate for rigorous thermodynamic analysis without information on the heat of mixing. In this work, a static technique was used to obtain isothermal vapor pressures of butadiene solutions. This method avoided the necessity of sampling either phase, thus eliminating one frequent source of error, but it did require precautions to prevent condensation of the vapor outside the cell and adequate degassing of solvents. Recently, other authors have reported using similar techniques (*2, 18*).

EXPERIMENTAL

Reagents used were:

Benzene, Baker, thiophene-free spectrophotometric reagent.
n-Butane, Phillips Petroleum, research grade, purity >99.90%.
1,3-Butadiene, Phillips Petroleum, research grade, purity >99.97%.