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Solubility in the System $CO(NH_2)_2$–NH_3–H_3PO_4–H_2O at 0, 25, and 50 °C

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The quaternary system $CO(NH_2)_2$–NH_3–H_3PO_4–H_2O was studied at 0, 25, and 50 °C to determine the solubility isotherms in the pH range 1–7. No interaction occurred between urea and the ammonium phosphates, but at low pH the urea–phosphoric acid adduct formed. The solid phase contained urea and mono- or diammonium phosphate throughout most of the pH range studied. An equation was developed to predict P_2O_5 and N solubility over the pH range 2–5.5 and temperature range 0–50 °C.

Introduction

Several papers concerning the solubility of urea in ammonium orthophosphate solutions (*1–4*), as well as its solubility in ammonium polyphosphate solutions (*5*), have appeared in the literature. In the present report the phase relationships in the system urea–ammonia–orthophosphoric acid–water at 0, 25, and 50 °C over a wide pH range (1–7) are reported. This system provides an excellent liquid fertilizer with a high content of plant nutrients.

Experimental Section

Reagent-grade mono- and diammonium phosphate and recrystallized reagent urea were employed in the study. Saturated solutions of mono- and diammonium phosphate were prepared. The solutions were adjusted to the desired pH by adding H_3PO_4 or anhydrous ammonia and then saturating with urea. This saturation was performed at 5 °C above the experimental temperature to assure that the solid phase contained well-formed crystals when the solutions were adjusted to the desired temperature. The solutions (in plastic bottles) were rotated at 4 rpm in a water bath at 25 ± 0.05 °C. The approach to equilibrium was followed by periodic petrographic examination of the solid phase. When it was determined that a salt was absent, a few grams of the missing salt was added and equilibration continued. When all the expected solid phases were present, the liquid phase was sampled for composition and pH. This was repeated at 1-week intervals until two consecutive samplings produced the same results. The 0 °C data were obtained from solutions stored in a cold room at 0.0 ± 0.5 °C and agitated manually at various intervals. The sampling at 50 ± 0.1 °C was at 1-week intervals, except for those solutions at low pH (<3) where hydrolysis began to occur. Here, sampling was conducted daily until consecutive duplicate results were obtained.

Table I. Solubility of Urea in Ammonium Orthophosphate

solution no.	pH	liquid-phase composition, % total N	 urea N	 NH_3 N	 P_2O_5	solid phases[a]
			0 °C			
1	2.04	19.0	17.6	1.4	17.28	A, D
2	2.21	19.7	18.4	1.3	17.12	A, C, D
3	2.80	19.0	17.6	1.4	12.30	A, C
4	3.15	19.0	17.5	1.5	10.55	A, C
5	4.87	18.7	17.0	1.7	8.36	A, C
6	5.42	18.5	16.4	2.1	9.14	A, C
7	6.23	16.1	10.2	5.9	20.15	A, B, C
8	7.24	17.4	13.6	3.8	11.16	B, C
			25 °C			
1	1.86	23.8	22.7	1.1	21.87	A, D
2	2.17	24.2	22.6	1.6	19.01	A, C, D
3	2.59	23.8	22.3	1.5	15.19	A, C
4	3.08	23.9	22.1	1.8	11.19	A, C
5	4.67	23.9	22.0	1.9	9.13	A, C
6	5.24	23.7	21.7	2.0	9.73	A, C
7	6.05	20.5	15.3	5.2	18.90	A, B, C
8	7.02	23.1	19.4	3.7	8.93	B, C
			50 °C			
1	1.42	25.2	24.3	0.9	25.76	A, D
2	1.93	27.1	25.6	1.5	21.21	A, C, D
3	2.10	27.9	26.3	1.6	19.03	A, C
4	2.45	28.1	26.1	2.0	16.07	A, C
5	2.81	28.2	26.3	1.9	13.29	A, C
6	3.22	28.8	26.9	1.9	11.67	A, C
7	4.07	28.2	26.2	2.0	10.23	A, C
8	4.96	29.1	26.9	2.2	9.97	A, C
9	5.21	28.8	26.4	2.4	10.53	A, C
10	5.35	28.9	26.6	2.3	10.78	A, C
11	6.09	26.3	22.1	4.1	16.52	A, B, C
12	7.09	30.1	28.4	1.7	5.43	B, C

[a] A = $NH_4H_2PO_4$; B = $(NH_4)_2HPO_4$; C = $CO(NH_2)_2$; D = $CO(NH_2)_2 \cdot H_3PO_4$.

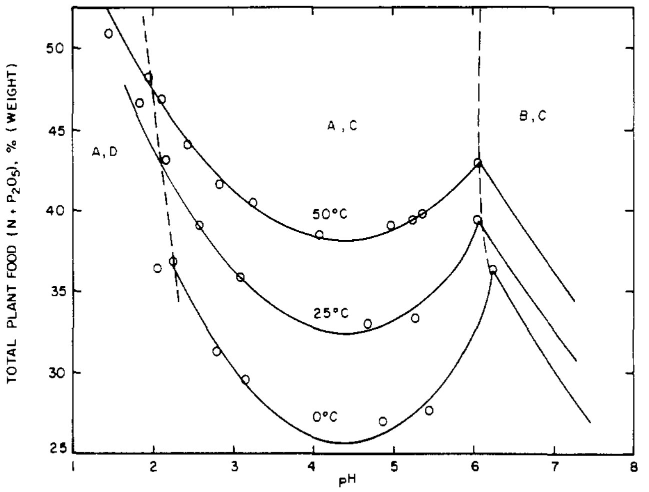

Figure 1. Solubility diagram in urea-ammonium orthophosphate solutions. Saturating salts: A = $NH_4H_2PO_4$, B = $(NH_4)_2 \cdot HPO_4$, C = $CO(NH_2)_2$, D = $CO(NH_2)_2 \cdot H_3PO_4$.

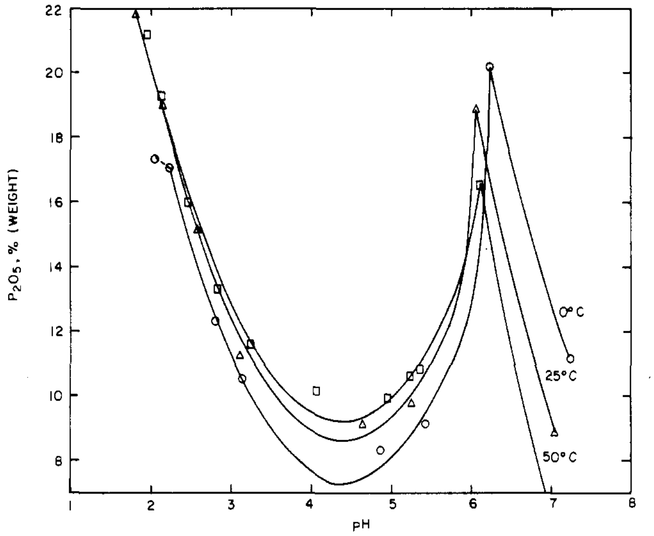

Figure 2. Solubility of P_2O_5 in urea-ammonium phosphate.

The phosphorus pentoxide content was determined gravimetrically as quinolinium molybdophosphate (*6*); total nitrogen was determined by the Kjeldahl method; ammoniacal nitrogen was determined by the reduced-pressure method; urea nitrogen was calculated by difference; and pH was determined with a glass electrode.

Results and Discussion

Data in Table I show the composition of the solutions and the solid phases present. The composition of two invariant solutions of the system was determined at 0, 25, and 50 °C. The higher pH invariant solution contained $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $CO(NH_2)_2$ as solid phases, while the lower pH invariant solution contained solid $NH_4H_2PO_4$, $CO(NH_2)_2$, and $CO(NH_2)_2 \cdot H_3PO_4$.

The coordinates of Figure 1 were chosen to demonstrate the total plant nutrient contents (total % N + P_2O_5) of the saturated solutions as a function of pH. The isotherms for the three temperatures show two branches. There is only a minor break in the isotherms at the low pH invariant point at 25 and 50 °C; however, there is a distinct downward break in the 0 °C isotherm at this point. The solution with the maximum total plant food in the high pH zone (>4) is at the invariant point. In the low pH zone (<4) the total plant food continues to increase with decreasing pH.

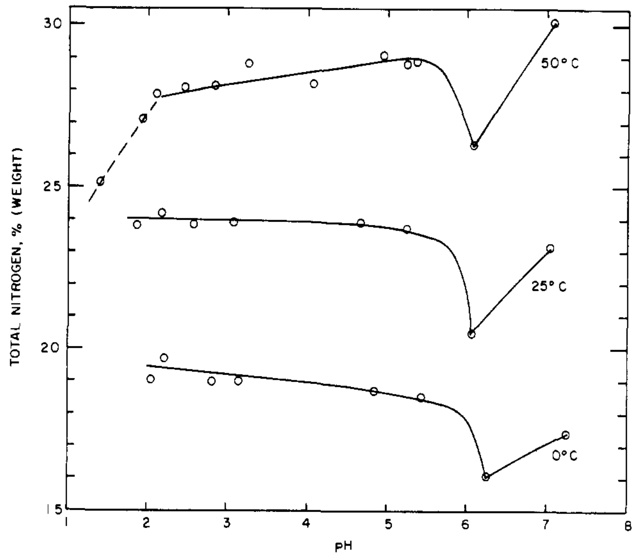

Figure 3. Solubility of total nitrogen in urea-ammonium phosphate.

Table II. Coefficients of the Solubility Equation

	%		
	N + P_2O_5	P_2O_5	N
a_0	72.335 06	47.475 85	19.537 36
a_1	−21.298 23	−18.309 58	0
a_2	0	0	0.203 82
a_{11}	2.427 05	2.085 18	−0.036 79
a_{22}	−0.000 761	−0.000 536	−0.001 276
a_{12}	0.129 16	0.028 39	0
a_{112}	−0.014 458	−0.003 085	0
a_{122}	0	0	0.000 261
R^2 [a]	0.994	0.988	0.996
SE [b]	0.542	0.510	0.295

[a] R^2 = square of the multiple correlation coefficient.
[b] SE = standard error.

From Table I it is noted that the total nitrogen in solution was almost constant at each temperature, the major exception being at the higher pH invariant point where the total nitrogen decrease was coupled with a P_2O_5 increase. At this point the P_2O_5 solubility varies inversely with temperature. The % P_2O_5 in solution is 20.15, 18.90, and 16.52% at 0, 25, and 50 °C, respectively. Figures 2 and 3 show the solution P_2O_5 and N concentration over the pH range 1–7.

Since the isotherms for total plant food (N + P_2O_5) concentration, P_2O_5 concentration, and N concentration change smoothly in the pH range 2–5.5, stepwise regression analysis (*7*) was used to fit the data in terms of temperature and pH, according to the following equation:

$$\text{solubility, wt \%} = a_0 + a_1(\text{pH}) + a_2T + a_{11}(\text{pH})^2 + a_{22}T^2 + a_{12}(\text{pH})T + a_{112}(\text{pH})^2T + a_{122}(\text{pH})T^2 \quad (1)$$

where T is temperature of solution in degrees Celsius and a_i is the coefficient of the term. The coefficients of the terms significant at the 90% confidence level are listed in Table II. As demonstrated by a small difference between observed and predicted solubility, the above equation can predict the solubility of total nitrogen, P_2O_5, and a combination of N and P_2O_5 over the pH range 2–5.5 and the temperature range 0–50 °C. The curves of Figures 1–3 were calculated from the above equation (except for data outside the pH range 2–5.5).

These data show that it is possible to produce a plant food solution stable at 0 °C of 16–20–0 grade at pH 6 or a 19–17–0 grade solution at pH 2. Solutions with pH between 2 and 6 would contain less total plant food than these samples.

Registry No. Urea, 57-13-6; ammonia, 7664-41-7; H_3PO_4, 7664-38-2.

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Use of Mixing Rules in the Analysis of Data for Binary Liquid Mixtures

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The binary mixture data of density and refractive index published earlier are further analyzed to test the validity of refractive index mixing rules. It is found that the Lorentz-Lorenz (LL), Gladstone-Dale (GD), Weiner, and Arago-Biot (AB) relations perform considerably well within the experimental precision. For the experimental systems studied here Heller's relation proved unsatisfactory.

Introduction

The literature dealing with the study of binary liquid mixtures has been extensive since the development of refractive index mixing rules (*1*). Among these, the most widely used relations are those of Lorentz-Lorenz (LL) and Galdstone-Dale (GD). These theoretical mixing rules have in common that they are based upon the electromagnetic theory of light with the implicit restriction that the molecules may be considered as dipoles or assemblies of dipoles induced by an external field. A series of failures of specific ones of these mixing rules reported in the literature is due to this restriction having been overlooked; others are due to the fact that other restrictions (homogeneous, undistorted electromagnetic field) had not been considered. The details of the relative merits and interrelations of a few mixing rules have been elegantly discussed by Heller (*1*).

One of the serious drawbacks of most of the mixing rules, however, is their inability to account for changes in volume and refractivity during mixing. A recent theory by Aminabhavi and Munk (*2*) provides an answer to this problem wherein the changes in volume and refractivity were adequately treated for six binary liquid mixtures from both density and refractive index data. In this work, as a part of the ongoing research program dealing with binary liquid mixtures, an attempt has been made to test several of the mixing rules using density and refractive index data published earlier (*3*).

Mixing Rules

One of the most frequently used mixing rules in the analysis of refractive index and density data of mixtures is due to Lorentz-Lorenz

$$\frac{n_{12}^2-1}{n_{12}^2+2} = \phi_1\left[\frac{n_1^2-1}{n_1^2+2}\right] + \phi_2\left[\frac{n_2^2-1}{n_2^2+2}\right] \qquad (1)$$

Here, n_{12}, n_1, and n_2 are the refractive indices of mixtures, solvent 1, and solvent 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the respective components in the mixture. The volume fraction ϕ_i of the i-th component in the mixture is defined as $\phi_i \equiv C_i/\rho_i$ where C_i is the concentration (g/mL) and ρ_i is the density of the i-th component. Alternatively, $\phi_i = w_i\rho_{ij}/\rho_i$, where w_i is the weight fraction of the i-th component and ρ_{ij} is the density of the mixture.

The Gladstone-Dale (GD) relation has the following form:

$$n_{12} - 1 = \phi_1(n_1 - 1) + \phi_2(n_2 - 1) \qquad (2)$$

Several alternative forms of eq 1 and 2 have been given in the literature. However, the most frequently used relations are in terms of specific refractions (mL/g). In such a case, eq 1 and 2 take the following forms:

$$\left[\frac{n_{12}^2-1}{n_{12}^2+2}\right]\frac{1}{\rho_{12}} = \left[\frac{n_1^2-1}{n_1^2+2}\right]\frac{w_1}{\rho_1} + \left[\frac{n_2^2-1}{n_2^2+2}\right]\frac{w_2}{\rho_2} \qquad (3)$$

$$\frac{n_{12}-1}{\rho_{12}} = \left[\frac{n_1-1}{\rho_1}\right]w_1 + \left[\frac{n_2-1}{\rho_2}\right]w_2 \qquad (4)$$

Weiner's relation which applies to isotropic bodies of spherically symmetric shape and which presupposes volume additivity is given in the following form:

$$\frac{n_{12}^2-n_1^2}{n_{12}^2+2n_1^2} = \phi_2\left[\frac{n_2^2-n_1^2}{n_2^2+2n_1^2}\right] \qquad (5)$$

Heller's relation which assumes the equivalence of the light scattering equations of Debye and Rayleigh has the following form:

$$\frac{n_{12}-n_1}{n_1} = \tfrac{3}{2}\phi_2\left[\frac{m^2-1}{m^2+2}\right] \qquad (6)$$

where $m = n_2/n_1$. Eq 5 and 6 differ from others by the absence of ϕ_1 in the formulation. They can therefore be strictly valid only in the case of volume additivity, i.e., if $\phi_1 = v_1^0/(v_1^0 + v_2^0)$, $\phi_2 = v_2^0/(v_1^0 + v_2^0)$ where superscript zero refers to volume of the components before mixing.

One other relation due to Arago and Biot (AB) has the following form:

$$n_{12} = \phi_1 n_1 + \phi_2 n_2 \qquad (7)$$

It should be noted that the fundamental difference between eq