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Nonideality of Ammonia Solutions in *N,N*-Dimethylformamide

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Synopsis. Solutions of ammonia at 0—40 °C and 0.2—1.2 atm in *N,N*-dimethylformamide exhibit negative deviations from Raoult's Law and marked departures from Henry's Law. This behavior is shown to be consistent with predictions of a simple model for solute-solute hydrogen bonding.

At moderate temperatures and partial pressures ammonia exhibits a negative deviation from Raoult's Law and a marked departure from Henry's Law solubility in *N,N*-dimethylformamide.

Materials and Methods

Anhydrous ammonia was obtained from Matheson Gas Products Corp. and *N,N*-dimethylformamide (DMF) from Matheson Coleman & Bell Corp. Purities were verified by gas chromatographic analysis. Solubility data were obtained manometrically at 0—40 °C and at 0—1.2 atm. As a check on apparatus and procedures, similar solubility data were obtained with acetylene.

Results and Discussion

The solubility data for acetylene are in the expected good accord with Henry's Law:

$$C_a = k \cdot P_a \quad (1)$$

For this system the pressure-solubility curves are linear with an average correlation coefficient of 0.997. The indicated heat of solution, −4.6 (±0.5) kcal, is in excellent agreement with Ryutani's estimate of 3—5 kcal at higher pressures.[1]

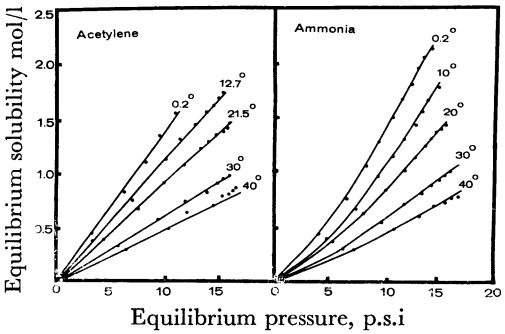

Fig. 1. Solubilities of acetylene and ammonia in *N,N*-dimethylformamide.

The corresponding data for ammonia describe a family of nonlinear curves (Fig. 1) inconsistent with Eq. (1). Under these conditions van der Waals corrections are very small. These data can be explained in terms of hydrogen bonding between solute ammonia molecules:

$$NH_{3(solute)} + NH_{3(solute)} \overset{K_d}{\rightleftharpoons} (NH_3)_{2(solute)} \quad (2)$$

Other calculations indicate a small amount of hydrogen-bonding dimerization in the gas phase;[2] the strength of the bridging bond is estimated to be 2.7—3.7 kcal.[3-5]

DMF, a very weak base,[6] is unlikely to be directly involved. A weak 1:1 ammonia–DMF complex has been detected in the solid state, but above its mp of −87 °C this is substantially dissociated.[7] Also this system shows a negative deviation from Raoult's Law, while ammonia at 0 °C shows marked positive deviations with hydrogen-bonding solvents.[8]

Taking dimerization as a simple model for solute-solute association, the total concentration of solute ammonia is:

$$\sum C = C_a + 2C_d \quad (3)$$

where C_a and C_d are the concentrations of ammonia and of ammonia dimer, respectively. From reaction 2,

$$C_d = K_d \cdot C_a^2 \quad (4)$$

Hence, by Eqs. (1), (3), and (4):

$$\sum C = k \cdot P_a + 2K_d \cdot k \cdot P_a^2 \quad (5)$$

This argument is supported by the good linearity of plots of $\sum C/P_a$ *vs.* P_a. The Henry's Law constant k is evaluated by the intercept of $\sum C/P_a$ at $P_a=0$. Estimates of k are shown in Table 1. The indicated heat of solution, 3.7 (±0.2) kcal, is consistent with those found for ammonia and the polar aprotic solvents adiponitrile (3.4 kcal)[9] and tributyl phosphate (2.5 kcal).[10]

Table 1. Equilibrium constants in *N,N*-dimethylformamide at 0.2—40.0 °C

T, °C	Henry's Law constant			Dimerization constant	
	k	stand. dev.	smoothed k[b,c]	K_d	smoothed K_d[b,d]
0.2	1.346	0.020 (8 df)	1.36	0.500	0.54
10.0	1.058	0.017 (8 df)	1.07	0.557	0.52
20.0	0.893	0.022 (8 df)	0.86	0.530	0.50
30.0	0.701	0.006 (6 df)	0.70	0.460	0.49
40.0	0.558	0.005 (5 df)	0.57	0.474	0.48

a) Calculated by the method of least squares from Eq. (5); k is in units of mol l^{-1} atm^{-1}; K_d is in units of 1 mol^{-1}.
b) By arithmetic average of five estimates using the least-squares temperature dependency.
c) The estimate of ΔH_{soln} from these data is −3.70 (±0.16) kcal.
d) The estimate of $\Delta G_{dimerization}$ from these data is −0.50(±0.40) kcal.

Under these conditions $K_d \simeq 0.5$ l mol^{-1}. Crudely, $\Delta G_{dimerization} \simeq -0.5$ (±0.4) kcal. We believe this to be the first showing of solute ammonia dimerization

at ambient temperatures and pressures.

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