# Solubility of Potassium Methylamide in Aminomethane

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**The solubility of potassium methylamide in aminomethane is measured over the temperature range −78° to 40°C. The solubility is 39 ± 3 g K/kg amine at −78°C and decreases with increasing temperature. The solubility of potassium ethylamide in aminomethane increases markedly with temperature and is approximately 90 g K/kg amine at −40°C. Potassium also dissolves in and reacts with 1-aminopropane, 1,2-diaminopropane, and 1,2-diaminoethane.**

The exchange of deuterium between hydrogen gas and liquid aminomethane is the basis of a new process being developed for the production of heavy water (*1*). The exchange reaction

$$CH_3NH_2 + HD \rightleftarrows CH_3NHD + H_2 \qquad (1)$$

occurs in the liquid phase and is catalyzed by potassium methylamide with the rate being dependent on the concentration of amide (*2, 6*). This work was undertaken to determine the limits of solubility of the amide in aminomethane at temperatures being considered for use in a bithermal exchange process. In addition, preliminary information was obtained on the preparation and solubility of potassium metal alkylamides of other amines which have some potential as substitutes for aminomethane in an amine-hydrogen exchange process.

## Experimental

***Purification of amines.*** Ammonia, aminomethane, and aminoethane were obtained from Matheson of Canada. Water impurity was removed by contacting them as liquids for at least 5 hr with freshly cut lithium metal. Lithium readily dissolved in the liquid amines to form dark blue solutions and reacted with water to form lithium hydroxide. Simple flash distillation was subsequently used to provide a middle fraction of purified amine.

The amines which are normally liquids at room temperature were contacted with 4A molecular sieves for at least 10 hr prior to contacting with lithium and distilling.

***Preparation of amide solutions.*** Several possible preparative methods are available (*3*), the most attractive being the direct reaction of liquid amine with alkali metal dissolved in the amine. Traces of metals, such as iron, silver, nickel, or platinum may catalyze this reaction. Ferric oxide has been used as a catalyst for the preparation of potassium ethylamide (*2*), and ferric chloride for the preparation of potassium methylamide (*6*).

Solutions of potassium methylamide in aminomethane were prepared by contacting metallic potassium with liquid aminomethane in the presence of a small amount of ferric oxide in an atmosphere of dry helium or argon. Potassium dissolves in the amine, even at −78°C, to form a deep blue solution. The rate of solution is relatively slow and increases with an increase in temperature. The dissolved potassium subsequently reacts to form the amide

$$K + CH_3NH_2 \rightarrow CH_3NHK + \tfrac{1}{2} H_2 \qquad (2)$$

The rate of reaction is also temperature dependent and is negligible at temperatures below −60°C. Most solutions were prepared at approximately −6°C. The evolution of hydrogen is an indication that the reaction is proceeding, and as the reaction progresses, the color of the solution changes from deep blue to a pale yellow. The yellow color was more intense at higher temperatures, and the amide solution was almost colorless at −78°C.

The time to complete the reaction also depended on the amount of ferric oxide catalyst employed. Approximately 10 mg were used when dissolving and reacting 4–5 grams of potassium in 150 ml of aminomethane, and the reaction time varied from 7 to 15 hr.

A glass reaction vessel was used for studies at and below the normal boiling point of the amine, and a stainless-steel reactor was employed at higher temperatures. Temperature was controlled by immersing the reactor in a refrigerated, controlled-temperature bath.

Samples of amide solutions were removed at constant pressure through a 10–20-$\mu$ sintered filter. Samples of known volume were removed from the low-pressure reactor, whereas samples of known weight were removed from the high-pressure reactor.

***Analysis.*** Samples of amine solutions containing dissolved amide were hydrolyzed by contacting them with deoxygenated distilled water. The resulting solutions were taken to dryness, and the solid, which was expected to be KOH, was redissolved in distilled water. The amount of potassium in these solutions was then determined with atomic absorption spectrophotometry.

## Results

***Potassium methylamide in aminomethane.*** At saturation, potassium methylamide precipitated as a fine white solid. White needle-like crystals, 3–5 mm long, were present for a few runs. An inverse solubility was observed in that solid, which had precipitated at higher temperatures, redissolved on cooling the solutions.

The effect of temperature, over the range −78° to 40°C, on the solubility of amide, reported as grams of potassium per kilogram of amine (g K/kg amine), is shown in Figure 1. Results for eight different runs are given in Table I. Each solubility reported is an average of values obtained for duplicate samples. The precision for any given solubility determination was generally better than ±4%. However, an uncertainty of up to ±9% occurs when data for different runs are compared. Solubility data obtained from the low-pressure apparatus were actually determined as g K/l. solution. The units were converted by use of density data for aminomethane (*4*), as information on the density of potassium methylamide-aminomethane solutions was not available.

This conversion assumes that there is a negligible volume change when the amide is dissolved in aminomethane. Data obtained from the high-pressure apparatus were in terms of grams of potassium per kilogram of solution and were converted to a basis of unit weight of amine by assuming all potassium existed in solution as the amide.

***Other amines.*** A preliminary investigation was made on the preparation and solubility of the potassium alkylamides of aminoethane, 1-aminopropane, 1,2-diaminopropane, and 1,2-diaminoethane.

Generally, 5–6 grams of potassium reacted with 180 ml of aminoethane in the presence of ferric oxide cata-

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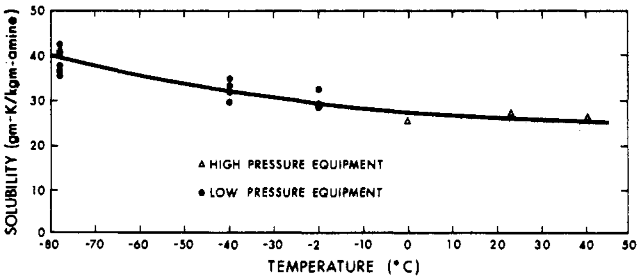

Figure 1. Solubility of potassium methylamide in aminomethane

**Table I. Solubility of Potassium Methylamide in Aminomethane**

| Temp, ±0.1°C | Solubility, g K/kg amine |
|---|---|
| −20 | 29.1 |
| −78 | 37.6 |
| −20 | 32.2 |
| −78 | 36.7 |
| −40 | 29.5 |
| −40 | 31.8 |
| −78 | 40.4 |
| −20 | 28.5 |
| −40 | 34.9 |
| −78 | 42.4 |
| −40 | 33.2 |
| −78 | 35.9 |
| 23 | 26.9[a] |
| 0 | 25.6[a] |
| −78 | 41.2[a] |
| 40 | 26.1[a] |

[a] Determined in high-pressure apparatus.

lyst at 14.5°C in a time varying from 10 to 20 hr to produce a clear, pale yellow solution. The solubility of potassium ethylamide in aminoethane is relatively high, and the system is similar to the potassium amide–ammonia system (5) in that the solubility increases markedly with temperature. Solutions containing 90 g K/kg amine as amide have a saturation temperature close to −40°C, and the solubility at −78°C is at least 25 g K/kg amine.

The rate of solution of potassium in 1-aminopropane was slow at room temperature and appeared to control the rate of amide formation. An unsaturated solution containing 10 g K/l. solution as amide was prepared at 22°C.

Potassium readily dissolves in 1,2-diaminopropane and 1,2-diaminoethane to form intense blue solutions. Appreciable reaction between potassium and 1,2-diaminopropane only occurred after the addition of ferric oxide catalyst. Potassium reacted with 1,2-diaminoethane in the absence of catalyst. As the reactions progressed, the solutions gradually turned reddish brown and became viscous. The potassium amides of the diamines seem to be unstable and to readily decompose at room temperature and to evolve hydrogen and form low-molecular-weight polymers. Thus, attempts to obtain reliable values for amide solubilities of saturated solutions were unsuccessful.

## Discussion

The effect of temperature on the solubility of potassium methylamide in aminomethane is surprising in that the solubility decreases with temperature over the range −78° to 40°C. The effect is unexpected, particularly, since the solubility of potassium amide in ammonia and of potassium ethylamide in aminoethane increases markedly with increasing temperature over the same range. The observed temperature effect indicates that the enthalpy change on solution is negative. It is not possible to obtain an exact value of the enthalpy of solution because of the uncertainty as to the activity of the solute. An order of magnitude value can be obtained from the following form of the Gibbs-Helmholtz equation:

$$\Delta H = -R \frac{d \ln x_2}{d\, 1/T} \qquad (3)$$

where $x_2$ is the mole fraction of solute, $R$ is the gas constant, and $T$ is the absolute temperature. The value of $\Delta H$ estimated from the measured solubilities is −0.5 kcal/g-mol.

Alkali metal alkylamides are white crystalline solids with relatively high melting points, and in general, they react vigorously with oxygen, carbon dioxide, water, and alcohols.

Potassium methylamide and potassium ethylamide react explosively with air and spontaneously ignite. Solutions of these amides in their respective amines are also sensitive to air and moisture. Care must be taken to remove all impurities such as $CO_2$, $O_2$, and $H_2O$ if reliable solubility data are to be obtained. The amides may be safely destroyed by reacting them with amyl alcohol. There is considerable scope for additional work to elucidate the chemistry and physical properties of alkali metal alkylamide–amine systems.

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