PREPARATION OF ANHYDROUS ETHYLENEDIAMINE

A Report Prepared for the International Union of Pure and Applied Chemistry by the Commission on Electroanalytical Chemistry

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY

PREPARATION OF ANHYDROUS ETHYLENEDIAMINE

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INTRODUCTION

Ethylenediamine (EDA) was discovered by Cloëz[1] in 1853. It is a colourless, water-soluble liquid with an ammoniacal odour. (Detailed properties of EDA are given in Appendix.) It is extremely hygroscopic and forms a solid carbamate[2] (m.p. 170°) with carbon dioxide. Thus, two common impurities in EDA are water and carbon dioxide, while the presence of other impurities in the commercial product is determined chiefly by the method of preparation employed. EDA can be prepared by reacting ethylenedichloride with alcoholic[3b] or aqueous[4] ammonia. The latter is a high-pressure reaction and is reported to give low conversion of ammonia and large amounts of by-products. EDA has also been prepared from ethylenedibromide by phthalimide synthesis[5]. Certain organic chlorides such as ethylenedichloride, if present as contaminants, are known to react with the solvent (at 100°) to produce secondary amines and secondary amine hydrochlorides[6]. Likely impurities produced as by-products during the manufacture of EDA include piperazine and similar cyclic materials, 2-ethylpyrazine and higher polyethylene amines, e.g. diethylenetriamine, triethylenetetramine and tetraethylenepentamine.

In the United States the principal suppliers of EDA are Eastman–Kodak Co., Dow Chemical Co., Union Carbide Corporation, Fisher Scientific Co., and Matheson, Coleman and Bell. Some of the above suppliers purchase the EDA from the original manufacturers (Eastman from Dow, Fisher from Union Carbide), and it is not clear if further purification of EDA is performed before re-packaging. The manufacturing process used is based on the high-pressure reaction between ethylenedichloride and ammonia mentioned above. The specifications of some of the suppliers are:

Dow (EDA Assay: > 98 per cent; no water content specified)

Union Carbide (EDA: 98 per cent; water: <2 per cent)

Fisher (EDA: >98 per cent; water: 0·02 per cent)

Matheson, Coleman and Bell (EDA: 99·8 per cent; water: 0·2 per cent).

PURIFICATION

EDA cannot be dried by fractional distillation because it forms a constant boiling (b.p. 118·5°) fraction containing ~15 per cent by weight of water[7]. Details of the methods which have been used for the purification of EDA are given below.

Historical

Hoffmann[3a] first recommended dehydration of EDA with sodium metal. Current practice involves the treatment of EDA with solid alkali (e.g., NaOH or KOH), followed by refluxing over molten sodium metal and, finally, fractional distillation in an inert atmosphere (N$_2$ or H$_2$).

Several modifications of the above procedure exist. White and Morgan[8] purified their EDA by three successive distillations from sodium. Putnam and Kobe[9] treated their sample (70 per cent EDA) with a large excess of sodium hydroxide over a steam bath. The EDA layer separating out at 60° was decanted off and treated again with sodium hydroxide and subsequently refluxed with sodium shavings and fractionated. Bromley and Luder[10] stored their starting material (95 per cent EDA) over a mixture of sodium hydroxide and barium oxide for several days, contacted with sodium at room temperature for a day, fractionally distilled from a mixture of activated alumina and sodium hydroxide and finally fractionated two more times from alumina. Clarke and Bloat[11] obtained "100 per cent EDA" by heating the 70 per cent commercial sample with sodium hydroxide, followed by re-fluxing with 2–3 per cent by weight of sodium for two hours; the purity was estimated by titration with hydrochloric acid using methyl red as an indicator. Schmidt and coworkers[12] refluxed over lithium metal for several days and then used a double fractional distillation from sodium metal. In one instance[13] they used calcium hydride as a substitute for sodium metal. Siefkar[14] refluxed commercial EDA twice over sodium metal followed each time by a fractional distillation (25 cm Hg; b.p. 85°) in a current of pure nitrogen; the first 10 per cent of the distillate was discarded in each distillation. This procedure seemed to have removed a polarographic impurity [$E_{1/2}$ = 0·15 volt vs. saturated Zn(Hg)/ZnCl$_2$(s), LiCl(s) reference electrode] present in the starting material.

Schöber and Gutmann[15] have demonstrated that detectable quantities of impurities may be leached from glassware by EDA. They obtained successively smaller specific conductances for their EDA by repeated (5×) distillation from sodium metal into vessels previously "steamed" with EDA vapour for several hours. Alternatively, receptacles were pre-soaked in EDA for two (or three) days. Their lowest reported specific conductance (9 × 10^{-9} ohm^{-1} cm^{-1}) is one-tenth of that reported by other workers[10].

Using lithium metal instead of sodium, Schöber and Gutmann found that a larger number of distillations were needed to produce the same specific conductance. On heating to 100° with potassium metal, detectable amounts of ammonia are produced along with a dark-black, highly viscous residue insoluble in water, ethanol, and diethyl ether.

Bruckenstein and Mukherjee[16] noted that the commercially available EDA, both Dow (98 per cent) and the Eastman–Kodak (95–100 per cent) contained impurity(ies) absorbing at 260, 265–270, and 310–312 mμ in 95 per cent ethanol. The commercial liquids as such did not transmit appreciable light at wavelengths below 340 mμ. Several methods of purification investigated by Bruckenstein and Mukherjee are described below.

In the first method, EDA was fractionally distilled from sodium and the 114–117·5° fraction was shaken overnight with freshly activated F20 ALCOA alumina (∼20 g/litre); the alumina was allowed to settle and the supernatant liquid fractionally distilled in the presence of another batch of alumina. All distillations were carried out in nitrogen atmosphere using a reflux ratio of 1:24. The fraction boiling at a constant temperature of 117·2° (760 mm Hg) showed the presence of a minimum of the ultraviolet absorbing impurity mentioned. In the second method, commercial EDA (Dow 98 per cent) was shaken with Linde molecular sieve (Type 5A—1/16 in. pellets—∼70 g/litre) and then with a mixture of 15 g potassium hydroxide and 50 g calcium oxide per litre of the solvent. This was followed by a fractional distillation of the supernatant EDA from a batch of freshly activated molecular sieve in an atmosphere of pure nitrogen. The fraction boiling at 117·2° (760 mm Hg) was collected. The water content (as determined by Karl–Fischer method) of this molecular sieve-treated sample was considerably lower (∼0·05 M vs. ∼0·015 M) than that obtained from the sodium treatment described above[17].

Siefkar[14] noted a polarographic wave in commercial EDA [$E_{1/2}$ = 0·15 v. vs. saturated Zn(Hg)/ZnCl₂(s), LiCl(s) electrode] which was removed by two distillations at reduced pressure over sodium. In the molecular sieve-treated EDA we have observed[18] two polarographic waves at −1·65 v. (I) and −1·83 v. (II) vs. the aqueous saturated calomel electrode. We calculate these waves to occur at +0·040 v. (I) and −0·140 v. (II) vs. the saturated Zn(Hg)/ZnCl₂(s), LiCl(s) reference electrode of Schaap et al.[19]. A single fractional distillation of the molecular sieve-treated material from sodium metal completely removed the second impurity; however, distillation over calcium hydride almost doubled the wave height due to this particular impurity. Both sodium and calcium hydride did not appear to have any effect on the first wave. Moreover, changes in ultraviolet absorption at ∼340 mμ paralleled the polarographic observations in the present case. Also, no further change in water content could be noted after distillation of the molecular sieve-treated sample from either sodium or calcium hydride.

We have also fractionally distilled commercial EDA a number of times from sodium metal. Each successive distillation improves the ultraviolet spectrum.

Multiple extractions[17] of the sodium-distilled EDA with fresh batches of purified cyclohexane showed that the ultraviolet absorbing impurity(ies) was extractable with cyclohexane. However, the following procedures did

not produce any improvement in the ultraviolet spectrum of the sodium-treated solvent: (i) fractional crystallization, and (ii) treatment with sodium borohydride, sodium hydride, cation- and anion-exchange resins, silica gel, and subsequent distillation.

Azeotropic distillation has been used by Creamer and Chambers[20] for the removal of water from EDA. These authors added benzene or isopropyl ether to form a low-boiling azeotrope with water. Benzene removes water faster than isopropyl ether. This method yielded products of at least 99·5 per cent purity with a specific conductance of no more than $1·0 \times 10^{-5}$ ohm^{-1} cm^{-1}.

Recommended Purification Procedure

A recommended procedure for obtaining pure EDA is:

(1) Shake commercial sample (98 per cent EDA) with activated molecular sieves (Linde Type 5A—70 g/litre) for approximately 12 hours.

(2) Decant supernatant from (1) and shake it for about 12 hours with a mixture of calcium oxide (50 g/litre) and potassium hydroxide (15 g/litre).

(3) Fractionally distil (1:20 reflux ratio) supernatant liquid obtained from (2) in the presence of freshly activated molecular sieves. Collect the fraction

boiling at 117·2° (760 mm Hg) $\left(\dfrac{\partial T}{\partial P} = 0·041°C/mm\ Hg \right)$.

(4) The distillate obtained from (3) should be fractionally distilled at least once from sodium metal. All distillations should be carried out in an atmosphere of pure nitrogen.

EDA thus purified has the following characteristics:

Boiling point (760 mm Hg)   117·2° ± 0·1

*Freezing point   11·3°

*Heat of Fusion   64·5 ± 0·6 cal g^{-1} at 11·3°

*Freezing point depression constant 2·43 ± 0·02°C mole^{-1} kg^{-1}

Ultraviolet Absorption $\left\{ \begin{array}{l} \text{Peak at 310–330 m}\mu\text{: absorbance (1 cm light} \\ \quad \text{path)} = 0·25 \\ \text{Cut-off: } \sim 280 \text{ m}\mu. \end{array} \right.$

Polarographic impurity $\left\{ \begin{array}{l} E_{\frac{1}{2}} = +0·04 \text{ v. } vs \text{ Zn(Hg)/ZnCl}_2 \text{ (s), LiCl(s)} \\ \quad \text{reference electrode}[19]; i_d = 2 \text{ micro amp in} \\ \quad \text{saturated LiCl as a supporting electrolyte.} \end{array} \right.$

Water content $\sim 0·015\ M$

*EDA purified by molecular sieve treatment (steps 1 to 3 above) was used. Cryoscopic measurements[21] showed that the total impurity content of the molecular sieve–treated EDA was 0·030 M; half of this was due to water ($\sim 0·015\ M$). Most of the remaining impurity probably was dissolved nitrogen gas.

APPENDIX

PROPERTIES OF ETHYLENEDIAMINE

Formula weight $\qquad$ 60·10

Freezing point (°C) $\qquad$ $\begin{cases} 11·0^a \text{ (ref. 9)} \\ 11·3^b \text{ (ref. 21)} \end{cases}$

Heat of fusion $\qquad$ 64·5 ± 0·6 (ref. 21)
(cal g^{-1} at 11·3°C—Cryoscopic)

Freezing point depression constant $\qquad$ 2·43 ± 0·02 (ref. 21)
(°C mole^{-1} kg^{-1})

Boiling point (°C) $\qquad$ $\begin{cases} *116·9^a \text{ (ref. 22)} \\ 116·2^a \text{ (ref. 9)} \\ *117·6^a \text{ (ref. 11)} \\ 117·2 \text{ (ref. 23)} \\ *117·2 ± 0·1^{a,b} \text{ (ref. 16)} \end{cases}$

Vapour pressure (mm Hg at 21·5°C) $\qquad$ 10·0 (ref. 24)

Heat of vaporization $\qquad$ 11·2^a (ref. 9)
(kcal mole^{-1} at 20°C)

Density, ρ (g c.c.$^{-1}$) $\qquad$ $\begin{cases} 0·893^a \text{ at } 25°C \text{ (ref. 22)} \\ 0·898 \text{ at } 25°C \text{ (ref. 25)} \\ 0·897^a \text{ at } 19·9°C \text{ (ref. 8)} \\ 0·891^a \text{ at } 25°C \text{ (ref. 9)} \end{cases}$

$\dfrac{\partial \rho}{\partial T}$ (g c.c.$^{-1}$ °C^{-1}) $\qquad$ $\begin{cases} 0·001^a \text{ (ref. 22)} \\ 0·00088^a \text{ (ref. 9)} \end{cases}$

Refractive index, n_D $\qquad$ $\begin{cases} 1·45400^a \text{ at } 26·1°C \text{ (ref. 22)} \\ 1·4513^a \text{ at } 30°C \text{ (ref. 11)} \\ 1·4532^a \text{ at } 20°C \text{ (ref. 15)} \end{cases}$

Molar refraction, R $\qquad$ 18·22^a at 26·1°C (ref. 22)

Dielectric constant, D $\qquad$ $\begin{cases} 12·9^a \text{ at } 25°C \text{ (cf. ref. 10)} \\ 12·4^a \text{ at } 25°C \text{ (ref. 14)} \\ 13·5^a \text{ at } 26·5°C \text{ (100 kc) (ref. 8)} \end{cases}$

Viscosity, η (cp at 25°) $\qquad$ $\begin{cases} 1·54 \text{ (ref. 25)} \\ \eta_{\text{relative}} 1·725^a \text{ (ref. 9)} \end{cases}$

Sp. conductance, σ (ohm^{-1} cm^{-1}) $\qquad$ $\begin{cases} {}^a1·4 \times 10^{-6} \text{ at } 25°C \text{ (ref. 9)} \\ {}^a9·0 \times 10^{-8} \text{ at } 25°C \text{ (ref. 10)} \\ {}^a2·0 \times 10^{-7} \text{ at } 25°C \text{ (ref. 12)} \\ {}^a9·0 \times 10^{-9} \text{ at } 20°C \text{ (ref. 15)} \\ {}^a4·6 \times 10^{-7} \text{ at } 30°C \text{ (ref. 26)} \end{cases}$

Autoprotolysis constant, K_s, at 25°C $\qquad$ $\begin{cases} \sim 10^{-12} \text{ (ref. 17)} \\ 5 \times 10^{-16} \text{ (ref. 19)} \end{cases}$

Dissociation constant, K_b, in water at 25°C $\qquad$ $\begin{cases} 7·1 \times 10^{-5} \text{ (ref. 27)} \\ 8·5 \times 10^{-5} \text{ (ref. 23)} \end{cases}$

Equivalent conductance at infinite $\qquad$ 242 (ref. 27)
dilution at 25°C

^{a} Some form of sodium treatment.
^{b} Moleculer sieve treatment.

*At 760 mm Hg

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