ALKANOLAMINES FROM OLEFIN OXIDES AND AMMONIA

1. Introduction

Ethylene oxide [75-21-8], propylene oxide [75-56-9], or butylene oxide [106-88-7] react with ammonia to produce alkanolamines (Table 1). Ethanolamines, $NH_{3-n}(C_2H_4OH)_n$ ($n = 1, 2, 3$, mono-, di-, and tri-), are derived from the reaction of ammonia with ethylene oxide. Isopropanolamines, $NH_{3-n}(CH_2CHOHCH_3)_n$ (mono-, di-, and tri-), result from the reaction of ammonia with propylene oxide. Secondary butanolamines, $NH_{3-n}(CH_2CHOHCH_2CH_3)_n$ (mono-, di-, and tri-), are the result of the reaction of ammonia with butylene oxide. Mixed alkanolamines can be produced from a mixture of oxides reacting with ammonia.

Ethanolamines have been commercially available for over 50 years and isopropanolamines, for over 40 years. *sec*-Butanolamines have been prepared in research quantities, but are not available commercially. Primary butanolamines, eg, 2-amino-1-butanol [96-20-8] are made by a different chemical route (see ALKANOLAMINES FROM NITROALCOHOLS).

A variety of substituted alkanolamines are also available commercially, but have not reached the volume popularity of the ethanolamines and isopropanolamines (see Table 2).

2. Physical Properties

The freezing points of alkanolamines are moderately high as shown in Tables 1 and 2. The ethanolamines, monoisopropanolamine and mono-*sec*-butanolamine, are colorless liquids at or near room temperature. Di- and triisopropanolamine and di- and tri-*sec*-butanolamine are white solids at room temperature.

All the ethanolamines and isopropanolamines except monoisopropanolamine are available in low freezing grades, to provide liquid handling at room temperature.

Alkanolamines have a mild ammoniacal odor and are extremely hygroscopic (1). The mono- and dialkanolamines have a basicity similar to aqueous ammonia; the trialkanolamines are slightly weaker bases.

Table 1. **Physical Properties of Alkanolamines Prepared from Ammonia and Olefin Oxides**

Common name	Molecular formula	CAS Registry Number	Chemical Abstracts name	Structural formula	Freezing point, °C	Boiling point[a], °C	Water solubility[b], g/100 g	*n*-Heptane solubility[b], g/100 g	Viscosity[b], mPa·s (= cP)
monoethanolamine (MEA)	C_2H_7NO	[141-43-5]	2-aminoethanol	$NH_2C_2H_4OH$	10	171	∞	0.06	19
diethanolamine (DEA)	$C_4H_{11}NO_2$	[111-42-2]	2,2′-iminobisethanol	$NH(C_2H_4OH)_2$	28	268	∞	0.01	54 (60°C)
triethanolamine (TEA)	$C_6H_{15}NO_3$	[102-71-6]	2,2′,2″-nitrilotrisethanol	$N(C_2H_4OH)_3$	21	340	∞	0.02	600
monoisopropanolamine (MIPA)	C_3H_9NO	[78-96-6]	1-amino-2-propanol	$NH_2CH_2CHOHCH_3$	3[c]	159	∞	0.4	23
diisopropanolamine (DIPA)	$C_6H_{15}NO_2$	[110-97-4]	1,1′-iminodi-2-propanol	$NH(CH_2CHOHCH_3)_2$	44[c]	249	1200	0.1	86 (54°C)
triisopropanolamine (TIPA)	$C_9H_{21}NO_3$	[122-20-3]	1,1′,1″-nitrilotris-2-propanol	$N(CH_2CHOHCH_3)_3$	44[c]	306	>500	3.4	100 (60°C)
mono-*sec*-butanolamine	$C_4H_{11}NO$	[13552-21-1]	1-amino-2-butanol	$NH_2CH_2CHOHC_2H_5$	3	169	∞	0.04	29
di-*sec*-butanolamine	$C_8H_{19}NO_2$	[21838-75-5]	1,1′-iminodi-2-butanol	$NH(CH_2CHOHC_2H_5)_2$	68–70	256	∞	4.7	890
tri-*sec*-butanolamine	$C_{12}H_{27}NO_3$	[2421-02-5]	1,1′,1″-nitrilotris-2-butanol	$N(CH_2CHOHC_2H_5)_3$	41–47	310	ca 7	>100	ca 6000

[a] At 101.3 kPa = 1 atm.

[b] Approximate, at 25°C unless otherwise noted.

[c] Supercools; freezing points may show variation.

Table 2. **Physical Properties of Substituted Alkanolamines**

Common name	Molecular formula	CAS Registry Number	Chemical Abstracts name	Freezing point, °C	Boiling point[a], °C	Water solubility[b], g/100 g[a]	Viscosity[c], mPa·s (= cP)
dimethylethanolamine	$C_4H_{11}NO$	[108-01-0]	2-dimethylaminoethanol	−59	135	∞	3
diethylethanolamine	$C_6H_{15}NO$	[100-37-8]	2-diethylaminoethanol		162	∞	4
aminoethylethanolamine	$C_4H_{12}N_2O$	[111-41-1]	2-(2-aminoethylamino)ethanol	−38[d]	244	∞	141
(AEEA)			2-methylaminoethanol	−4.5	160	∞	13
methylethanolamine	C_3H_9NO	[109-83-1]	2-butylaminoethanol	−2	199	∞	20
butylethanolamine	$C_6H_{15}NO$	[111-75-1]	*N*-2-hydroxyethyl	16	decompn	∞	203
N-acetylethanolamine	$C_4H_9NO_2$	[142-26-7]	acetamide				
phenylethanolamine	$C_8H_{11}NO$	[122-98-5]	2-anilinoethanol	11	285	4.6	101
dibutylethanolamine	$C_{10}H_{23}NO$	[102-81-8]	2-dibutylaminoethanol	−75[e]	229	0.4	8
diisopropylethanolamine	$C_8H_{19}NO$	[96-80-0]	2-diisopropylaminoethanol	−39	191	1.2	8
phenylethylethanolamine	$C_{10}H_{15}NO$	[92-50-2]	2-*N*-ethylanilinoethanol	37[f]	decompn	0.2	
methyldiethanolamine	$C_5H_{13}NO_2$	[105-59-9]	2,2′-(methylimino)diethanol	−21	247	∞	101
ethyldiethanolamine	$C_6H_{15}NO_2$	[139-87-7]	2,2′-(ethylimino)diethanol	44e	253	∞	87
phenyldiethanolamine	$C_{10}H_{15}NO_2$	[120-07-0]	2,2′-(phenylimino)diethanol	57d		2.8	119 (60°C)
dimethylisopropanolamine	$C_5H_{13}NO$	[108-61-7]	1-dimethylamino-2-propanol	−85[e]	126		
N-(2-hydroxypropyl)ethylenediamine	$C_5H_{14}N_2O$	[123-84-2]	1-(2-aminoethylamino)-2-propanol	−50[e]	155[g]	∞	112 (25°C)

[a] At 101.3 kPa = 1 atm unless otherwise noted.

[b] Approximate, at 25°C.

[c] At 20°C unless otherwise noted.

[d] Pour point.

[e] Sets to a glasslike solid below this temperature.

[f] Melting point.

[g] At 8 kPa (60 mm Hg).

All the alkanolamines, except tri-*sec*-butanolamine, are completely miscible in water and polar solvents. Solubility in nonpolar solvents varies, as noted in Tables 1 and 2.

3. Chemical Reactions

Alkanolamines are bifunctional molecules because of the alcohol and the amine functional groups in the same compound. This allows them to react in a wide variety of ways, with similarities to primary, secondary, and tertiary amines, and primary and secondary alcohols.

3.1. Reaction with Acids. Under anhydrous conditions, mono- and diethanolamines and isopropanolamines form carbamates with carbon dioxide (2,3).

$$2HOCHRCH_2NH_2 + CO_2 \longrightarrow HOCHRCH_2NHCOOH{\cdot}H_2NCH_2CHROH \qquad (1)$$

Trialkanolamines, lacking an amine hydrogen, do not undergo the carbamate reaction.

Alkanolamines in aqueous solution react with carbon dioxide and hydrogen sulfide to yield salts, important to gas conditioning reactions. The dissociation of the salts upon heating results in recovery of the original starting material. These reactions form the basis of an important industrial application, ie, the "sweetening" of natural gas.

$$HOCHRCH_2NH_2 + CO_2 + H_2O \overset{\Delta}{\rightleftharpoons} HOCHRCH_2NH_2{\cdot}H_2CO_3 \qquad (2)$$

$$HOCHRCH_2NH_2 + H_2S \overset{\Delta}{\rightleftharpoons} HOCHRCH_2NH_2{\cdot}H_2S\} \qquad (3)$$

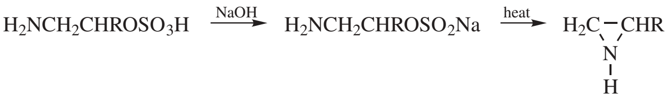
Halogen acids and strong organic acids, such as *p*-nitrobenzoic acid and trichloroacetic acid, form crystalline salts (4), with alkanolamines.

$$HOCHRCH_2NH_2 + HCl \longrightarrow HOCHRCH_2NH^{+}{}_3Cl^{-} \qquad (4)$$

Heating with sulfuric acid gives bisulfates (5).

$$H_2NCH_2CHROH + H_2SO_4 \xrightarrow{\Delta} H_2NCH_2CHROSO_3H + H_2O \qquad (5)$$

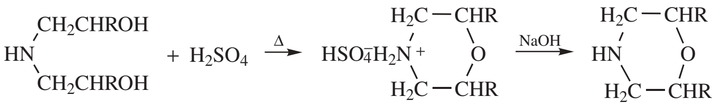
These can be cyclized by heating in the presence of sodium hydroxide to give a dehydration product. Thus monoalkanolamines form 2-alkylaziridines.



$$H_2NCH_2CHROSO_3H \xrightarrow{\text{NaOH}} H_2NCH_2CHROSO_2Na \xrightarrow{\text{heat}} \underset{\substack{\diagdown\;\diagup\\ N\\ |\\ H}}{H_2C-CHR}$$

(6)

In a similar manner, diethanolamine and diisopropanolamine can be cyclized to give morpholines (6).


(7)

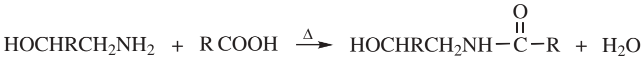
Nitric acid gives nitrates and concentrated (48%) hydrobromic acid gives olefins, upon reaction with alkanolamines.

$$R_2NCH_2CHROH \xrightarrow{HBr} R_2NCH{=}CHR + H_2O \qquad (8)$$

3.2. Reaction with Fatty Acids and Esters.

Alkanolamines and long-chain fatty acids react at room temperature to give neutral alkanolamine soaps, which are waxy, noncrystalline materials with widespread commercial applications as emulsifiers. At elevated temperatures, 140–160°C, *N*-alkanolamides are the main products, at a 1:1 reaction ratio (7,8).

$$HOCHRCH_2NH_2 + C_{17}H_{35}COOH \longrightarrow HOCHRCH_2NH_2{\cdot}HOOCC_{17}H_{35} \qquad (9)$$


(10)

$$HOCHRCH_2NH_2 + RCOOH \xrightarrow{\Delta} HOCHRCH_2NH{-}\overset{O}{\overset{\|}{C}}{-}R + H_2O \qquad (10)$$

Significant quantities of amine and amide esters are formed by side reactions (9). In addition, with dialkanolamines, amide diesters, morpholines, and piperazines can be obtained, depending on the starting material. Reaction of dialkanolamines with fatty acids in a 2:1 ratio, at 140–160°C, produces a second major type of alkanolamide. These products, in contrast to the 1:1 alkanolamides, are water soluble; they are complex mixtures of *N*-alkanolamides, amine esters, and diesters, and still contain a considerable amount of unreacted dialkanolamine, accounting for the water solubility of the product. Both the 1:1 and the 2:1 alkanolamides are of commercial importance in detergents.

Trialkanolamines cannot form amides, but they do give esters at temperatures sufficiently high to eliminate water.

$$(HOCHRCH_2)_3N + 3R'COOH \longrightarrow N(CH_2CHROOCR')_3 + 3H_2O \qquad (11)$$

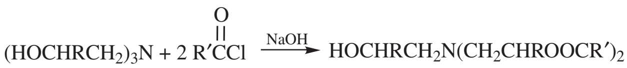
3.3. Reaction with Acyl Halides.

Acyl halides react at room temperature with mono- and dialkanolamines to give amides (10,11).


(12)

$$2\,HOCHRCH_2NH_2 + R'\overset{O}{\overset{\|}{C}}Cl \longrightarrow HOCHRCH_2NH\overset{O}{\overset{\|}{C}}R' + HOCHRCH_2NH_3^{+}Cl^{-} \qquad (12)$$

At elevated temperatures, in the presence of alkali, mono-, di-, and trialkanolamines produce esters.


(13)

$$(HOCHRCH_2)_3N + 2\,R'\overset{O}{\overset{\|}{C}}Cl \xrightarrow{NaOH} HOCHRCH_2N(CH_2CHROOCR')_2 \qquad (13)$$

3.4. Reaction with Acid Anhydrides.

Below room temperature, acid anhydrides react with alkanolamines to produce amides, which partially rearrange to esters on warming to room temperature or slightly above.

$$\mathrm{HOCHRCH_2NH_2} + \mathrm{O(\overset{O}{\overset{\|}{C}}R')_2} \longrightarrow \mathrm{HOCHRCH_2NH{-}\overset{O}{\overset{\|}{C}}{-}R'} \xrightarrow{\Delta} \mathrm{R'COOCHRCH_2NH_2} \tag{14}$$

A 2:1 molar ratio of alkanolamine and fatty acid anhydride, at room temperature, gives a mixture of amide and alkanolamine soap.

$$2\,\mathrm{HOCHRCH_2NH_2} + \mathrm{R\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}R} \longrightarrow \mathrm{HOCHRCH_2NH\overset{O}{\overset{\|}{C}}R} + \mathrm{HOCHRCH_2NH_2{\cdot}HOOCR} \tag{15}$$

3.5. Reaction with Aldehydes and Ketones.

Formaldehyde combines with primary and secondary alkanolamines in the presence of alkali to give methylol derivatives. For the reaction of monoethanolamine with formaldehyde (12), the reaction scheme shown in Figure 1 occurs.

Primary alkanolamines react with aliphatic and aromatic aldehydes or ketones (other than formaldehyde) to give Schiff bases.

$$\mathrm{HOCHRCH_2NH_2} + \mathrm{R'R''C{=\!=}O} \longrightarrow \mathrm{HOCHRCH_2N{=\!=}CR'R''} + \mathrm{H_2O} \tag{16}$$

The Schiff bases can be catalytically hydrogenated to the corresponding saturated derivatives. More severe conditions cause cyclization to oxazolidines.

With secondary alkanolamines, aldehydes in the presence of K_2CO_3 yield di-tertiary amines, which, on distillation, break down into α,β-unsaturated

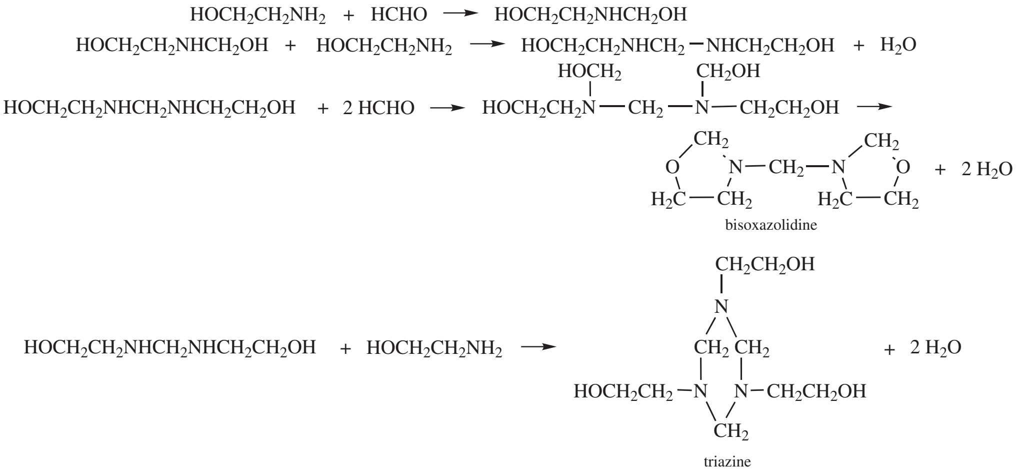
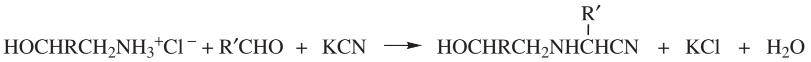


Fig. 1. Reaction of formaldehyde with monoethanolamine. If two moles of monoethanolamine react with three moles of formaldehyde, the bisoxazolidine is the only product isolated. A 1:1 mole ratio of monoethanolamine to formaldehyde produces a mixture of the triazine and the bisoxazolidine.

amines and secondary amines. With a mono- or dialkanolamine, an alkali metal cyanide, and an aldehyde or ketone, aminoacetonitriles are formed.



$$HOCHRCH_2NH_3^+Cl^- + R'CHO + KCN \longrightarrow HOCHRCH_2NH\underset{}{\overset{R'}{\overset{|}{C}}}HCN + KCl + H_2O \qquad (17)$$

These nitriles can be saponified to the corresponding acids.

3.6. Reaction with Alkyl and Aralkyl Halides. Alkyl halides form *N*-alkyl derivatives of alkanolamines.

$$HOCHRCH_2NH_2 + R'Cl \longrightarrow HOCHRCH_2NHR' + HCl \qquad (18)$$

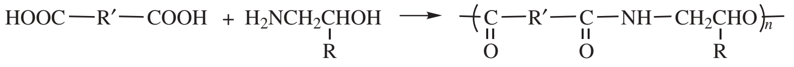
Aralkyl halides (R′ either phenyl or naphthyl) give disubstituted products.

$$HOCHRCH_2NH_2 + 2R'CH_2Cl \longrightarrow HOCHRCH_2N(CH_2R')_2{\cdot}HCl + HCl \qquad (19)$$

Mono- and dialkyl derivatives can also be prepared using alkyl sulfates. Aryl chlorides are usually inert, unless activated by an electron-withdrawing group. Conversion to alkoxides allows formation of ethers.

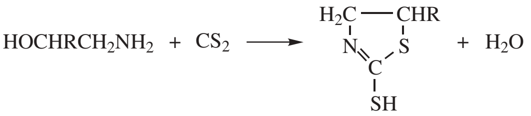
$$HOCH_2CH_2NH_2 \xrightarrow{NaOH} NaOCH_2CH_2NH_2 \xrightarrow{RCl} ROCH_2CH_2NH_2 + NaCl \qquad (20)$$

3.7. Other Reactions. Polyester polyamides can be formed from dicarboxylic acids (13).

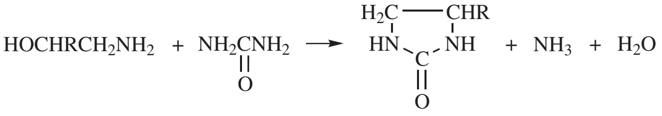


$$HOOC{-}R'{-}COOH + H_2NCH_2\underset{R}{\underset{|}{C}}HOH \longrightarrow \left(\underset{O}{\underset{\|}{C}}{-}R'{-}\underset{O}{\underset{\|}{C}}{-}NH{-}CH_2\underset{R}{\underset{|}{C}}HO \right)_n \qquad (21)$$

Monoalkanolamines are converted by carbon disulfide into 2-mercaptothiazolines. Ethyleneurea (2-imidazolidinone) can be prepared by heating a mixture of monoethanolamine and urea for several hours.



(22)

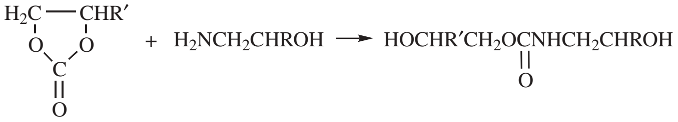


(23)

With acrylonitrile, mono- and dialkanolamines undergo a Michael addition to give the β-aminonitrile.

$$NH(CH_2\overset{CH_3}{\overset{|}{C}}HOH)_2 + CH_2{=}CHCN \longrightarrow (HO\overset{CH_3}{\overset{|}{C}}HCH_2)_2NCH_2CH_2CN \qquad (24)$$

Mono- and dialkanolamines react readily with ethylene or propylene carbonates to yield carbamates.



(25)

Alkanolamines can be oxidized with various oxidizing agents. With acidic potassium permanganate or excess potassium hydroxide, the potassium salts of the corresponding amino acid are obtained.

$$NH(CH_2CH_2OH)_2 \xrightarrow[200-300^\circ C]{KOH} NH(CH_2COOK)_2 + 3H_2 \qquad (26)$$

Mono- and diethanolamine are converted to formaldehyde and ammonia by acidic periodates.

Numerous patents exist for the production ofnitrilotriacetic acid [139-13-9] and its salts from triethanolamine (14–16).

$$N(CH_2CH_2OH)_3 \xrightarrow{O_2} N(CH_2COOH)_3 \qquad (27)$$

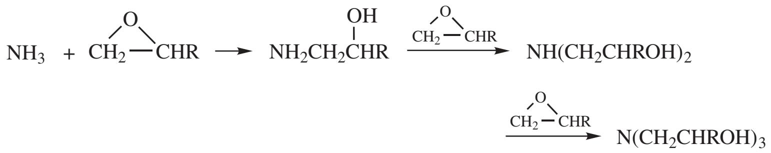
In certain cases, alkanolamines function as reducing agents. For example, monoethanolamine reduces anthraquinone to anthranols, acetone to 2-propanol, and azobenzene to aniline (17). The reduction reaction depends on the decomposition of the alkanolamine into ammonia and an aldehyde. Similarly, diethanolamine converts *o*-chloronitrobenzene to 2,2′-dichloroazobenzene and *m*-dinitrobenzene to 3,3′-diaminoazobenzene.

Monoethanolamine can also be reduced catalytically with hydrogen and ammonia over Raney nickel at 200°C and 20.7 MPa (3000 psig) to produce ethylenediamine [107-15-3] (18,19).

$$NH_2CH_2OHOH + NH_3 \xrightarrow[\text{Raney Ni}]{H_2} NH_2CH_2CH_2NH_2 + H_2O \qquad (28)$$

4. Manufacture

Alkanolamines are manufactured from the corresponding oxide and ammonia. Anhydrous or aqueous ammonia may be used, although anhydrous ammonia is typically used to favor monoalkanolamine production and requires high temperature and pressure (20). Mono-, di-, and trialkanolamines are produced in the reactor and sent to downstream columns for separation (Fig. 2).



where R = H, CH_3, C_2H_5

The reaction is exothermic; reaction rates decrease with increased carbon number of the oxide (ethylene oxide > propylene oxide > butylene oxide). The

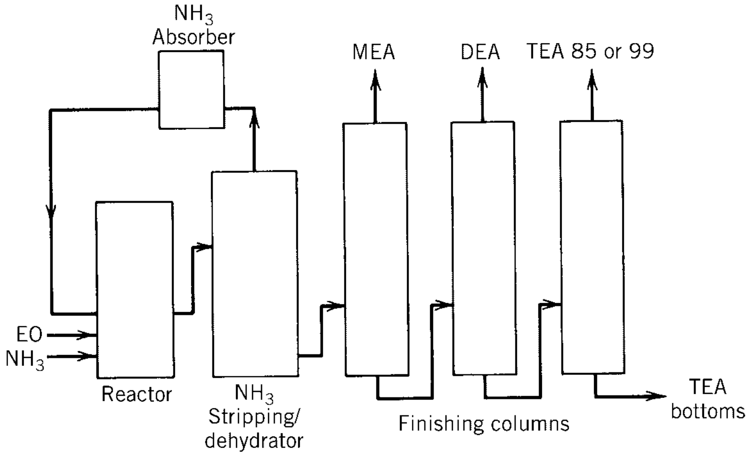


Fig. 2. Flow sheet for ethanolamine production. EO = ethylene oxide; MEA, DEA, and TEA are defined in Table 1.

ammonia–oxide ratio determines the product split among the mono-, di-, and trialkanolamines. A high ammonia to oxide ratio favors mono- production; a low ammonia to oxide ratio favors trialkanolamine production. Mono- and dialkanolamines can also be recycled to the reactor to increase di- or trialkanolamine production. Mono- and dialkanolamines can also be converted to trialkanolamines by reaction of the mono- and di- with oxide in batch reactors. In all cases, the reaction is run with excess ammonia to prevent unreacted oxide from leaving the reactor.

A variety of substituted alkanolamines (Table 2) can also be made by reaction of oxide with the appropriate amine. Aminoethylethanolamine is made from the reaction of ethylenediamine [107-15-3] and ethylene oxide. Methyldiethanolamine is made from the reaction of ethylene oxide andmethylamine [74-89-5]. Diethylethanolamine is made by the reaction of diethylamine [109-87-7] and ethylene oxide.

5. Economic Aspects

U.S. capacity of the ethanolamines in 1989, almost one-half of global capacity, was estimated to be 379,000 t. Global capacity for 1989 was estimated at 692,000 t. Estimated annual U.S. production figures are listed in Table 3 (21). U.S. consumption of ethanolamines for various applications is shown in Table 4.

Isopropanolamine global capacity for 1989 was estimated at 37,000 t. U.S. capacities for isopropanolamine (IPA), aminoethylethanolamine (AEEA), and methyldiethanolamine (MDEA) are as follows:

Akanolamine	U.S. capacity, 10^3 t
IPA	23,000
AEEA	9,000
MDEA	20,000

Table 3. **Estimated Annual U.S. Production of Ethanolamines, 10^3 t**

Year	Total	MEA	DEA	TEA
1955	36	12	14	10
1960	57	20	24	13
1965	91	31	35	25
1970	120	40	42	38
1975	118	38	39	41
1980	171	59	56	56
1985	245	98	76	71
1988	278	103	86	89
1990	302	113	91	98
1995	362	137	106	119

Consumption of ethanolamines in the United States has changed dramatically since the 1960s. Consumption in gas conditioning applications has peaked and chemical processing intermediates (captive use for ethyleneamine and surfactant applications) has increased significantly.

U.S. production of ethanolamines grew at just under 8% during the 1980s. Export of ethanolamines has contributed significantly to the increased production. Exports have averaged 11% growth per year during the 1980s. U.S. sales consumption have grown an average of 6% a year since 1970.

List pricing (22) has ranged from ~45/kg in the 1960s, to a low of 33¢/kg in the early 1970s. In the mid-1970s, the price increased to over 65¢/kg to peak in the early 1980s at over $1.10/kg. Prices decreased again in the mid-1980s to peak again at $1.43/kg in 1989 for bulk quantities.

6. Specifications

Specifications for the most commonly used alkanolamines are listed in Table 5. Special grades of products have been developed as needed by the customer. *National Formulary* grade meets the specifications in the *U.S. Pharmacopeia*. Low iron and electronic grades have particular specifications for iron and other metals. Low freezing grades were developed because of the high freezing points of most of the product. Generally, the addition of 15% water, by weight, significantly reduces the freezing point to a manageable level.

Table 4. **U.S. Consumption by Use of Ethanolamines, 10^3 t**

Use	1950	1960	1970	1980	1990
surfactants, detergents, and personal care products	5.9	25.4	43	60	95
gas purification	1.8	13.2	23	35	30
textiles	1.8	9.1	6	4	5
agricultural products	2.7	1.1	2	4	4
cement and concrete			3	5	7
metal working	1.8	3.6	5	6	7
chemical processing intermediate			6	8	42
other	1.4	4.5	4	5	5

Table 5. **Typical Specifications of Alkanolamines**[a]

Compound	Assay[b], min %	Apparent[c] equivalent weight	APHA[d] color max	Water, max %
MEA, CG[e]	99	61–62	15	0.3
DEA, CG[e]	99	104–106	15	0.15
TEA 85[f]	85	140–145	40	0.20
TEA 99	99	148–150	50	0.2
MIPA	99	75–76	20	0.5
DIPA, CG[e]	98	132–134	40	0.5
TIPA 99	99	190–192	50	0.3
AEEA	99.6		25	0.2

[a] Specification values and items may vary with different manufacturers. Analytical methods may be obtained from manufacturers.

[b] Assay determined by gas chromatography.

[c] Apparent equivalent weight determined by titration with hydrochloric acid.

[d] APHA color determined by ASTM D1209, platinum–cobalt method.

[e] CG = commercial grade.

[f] Contains approximately 15% DEA.

7. Analytical Test Methods

Generally, alkanolamines are analyzed by gas chromatography or wet test methods. Details on gas chromatography conditions are available in the literature (1) for packed or glass capillary columns.

Apparent equivalent weight can be determined by titration with hydrochloric acid using a bromocresol green indicator. Calculations give the equivalent weight of total amines and are not specific for the mono-, di- or trialkanolamines.

APHA color is determined using ASTM D1209; percent water is determined by Karl Fischer titration following ASTM E203. Detailed analytical procedures are available in the literature (1) or from producers.

8. Storage and Handling

Stainless steel, 316L and 304L, is the preferred material of construction for shipment and storage of alkanolamines, if product quality is of importance. Aluminum can be used for short term transport, at temperatures below 60°C, for the pure amines. Plastic liners have not been found acceptable for all alkanolamines. Phosphatized-lined steel drums are used for transport of ethanlomaines and isopropanolamines, except MEA, which is shipped in high density polyethylene drums to maintain low product color. Monoethanolamine and monoisopropanolamine are classified as DOT corrosive liquids.

Polyethylene, polypropylene, and Teflon resins have been found to be acceptable in contact with all of the alkanolamines at low temperatures. Lined tanks have not been found to successfully withstand monoethanolamine and monoisopropanolamine. These two alkanolamines degrade all linings tested. Extensive testing of any lined tank or piping should be initiated before being used in any alkanolamine service. Some producers use only stainless steel in handling, storage, and shipping of their alkanolamines.

Mild steel can be used for transport and storage if product discoloration is not a problem, such as in gas conditioning applications. Contact with copper, brass, and other copper alloys may cause corrosion of the metal.

Storage tanks, lines, and pumps should be heat traced and insulated to enable product handling. Temperature control is required to prevent product degradation because of color; alkanolamines have poor heat transfer properties. Exposure to air will also cause product discoloration. Storage tanks should be nitrogen-padded if low color product is required.

Normally, centrifugal pumps, made of stainless steel, are used to transfer amines to maintain good product quality. Carbon steel or black iron pumps can be used if quality is unimportant. Heat tracing the pumps may also be required if exposure to cold weather is a possibility. Teflon gaskets and Teflon tape can be used for applications under 200°C. Graphite-filled gaskets can also be used. Graphite packing or mechanical seals with Teflon resins are also suggested. Alkanolamines can leach conventional pipe dope.

Reactions of monoethanolamine with mild steel are referenced in the literature (23). The complex formed, identified as trisethanolamino–iron, can decompose in air to pyrophoric iron, with the potential to cause a fire, if contacted with combustible materials.

9. Health and Safety Factors

A brief summary of safety and health hazards follows; detailed health hazards, however, should be obtained from producers by requesting Material Safety Data Sheets. Proper protective equipment and exposure hazards should be noted before handling any alkanolamine. Detailed toxicological testing is found in the CTFA Chemical Ingredient Review Board Reports on ethanolamines and isopropanolamines (24).

9.1. Oral Toxicity. Alkanolamines generally have low acute oral toxicity, but swallowing substantial quantities could have serious toxic effects, including injury to mouth, throat, and digestive tract.

Concentrated monoethanolamine and monoisopropanolamine can cause severe local irritation or even burns to the mouth, throat, and digestive tract. If monoethanolamine and monoisopropanolamine are swallowed, large volumes of milk or water should be administered immediately. If diethanolamine, triethanolamine, diisopropanolamine, or triisopropanolamine are swallowed, vomiting should be induced after drinking two glasses of water.

9.2. Vapor Toxicity. Laboratory exposure data indicate that vapor inhalation of alkanolamines presents low hazards at ordinary temperatures (generally, alkanolamines have low vapor pressures). Heated material may cause generation of sufficient vapors to cause adverse effects, including eye and nose irritation. If inhalation exposure is likely, approved respirators are suggested. Monoethanolamine and diethanolamine have OSHA TLVs of 3 ppm.

9.3. Eye Irritation. Exposure of the eye to undiluted alkanolamines can cause serious injury. Solutions as dilute as 1% of monoethanolamine and monoisopropanolamine can cause some eye irritation.

Diethanolamine, diisopropanolamine, and isopropanolamine mixtures are also irritating to the eyes, even diluted, but less so than monoethanolamine and monoisopropanolamine. Undiluted triethanolamine and triisopropanolamine and concentrated solutions have an irritating action on the eyes, but only slight transient or no corneal injury would be expected. Proper protective equipment, as detailed in the Material Safety Data Sheets should be used. Chemical workers' goggles or the equivalent, and suitable facilities for washing the eyes should be readily available. If any of the amines contact the eyes, the eyes should be flushed thoroughly with flowing water for 30 min for monoethanolamines and isopropanolamines, and 15 min for di- and triethanolamines, and di- and triisopropanolamines.

9.4. Skin Irritation. Monoethanolamine and monoisopropanolamine, being strongly alkaline, are skin irritants, capable of producing serious injury in concentrations of 10% or higher upon repeated or prolonged contact. Occasional short contact, assuming the material is thoroughly washed off, should have little adverse effect.

Diethanolamine, diisopropanolamine, and isopropanolamine mixtures are less irritating to the skin than MEA and MIPA; however, any one of them may produce severe skin irritation, even mild burns, if contact is prolonged or frequently repeated. Occasional short contact should not result in more than slight irritation. Undiluted triethanolamine and triisopropanolamine are slightly to moderately irritating to the skin. A burn may result from prolonged and repeated contact. Short occasional contact and solutions of less than 10% concentration are unlikely to cause more than very slight irritation, if any.

Monoethanolamine and monoisopropanolamine may be moderately toxic by absorption through the skin. The other amines are low in toxicity by this route and are not likely to be absorbed in acutely toxic amounts. In the event of skin contact, clothing and shoes should be removed promptly, and the skin thoroughly washed with water. Contaminated clothing should be thoroughly cleaned before reuse; shoes and leather products should be discarded.

9.5. Special Precautions. Use of sodium nitrite or other nitrosating agents in formulations containing alkanolamines could lead to formation of suspected cancer-causing nitrosamines.

Strong oxidizers and strong acids are incompatible with alkanolamines. Reactions, generating temperature and/or pressure increases, may occur with halogenated organic compounds. Alkanolamines are corrosive to copper and brass and may react. Contact with aluminum by alkanolamines, particularly when wet or at elevated temperatures (60°C), should be avoided.

Spills and leaks should be cleaned up with alkanolamine-compatible absorbents or sands. Local, state, and federal requirements should be followed for disposal. Incineration in an approved facility is suggested for final disposal.

10. Uses

Alkanolamines and their derivatives are used in a wide variety of household and industrial applications. Nonionic surfactants (alkanolamides) can be formed by the reaction of alkanolamines with fatty acids, at elevated temperatures (eq. 10). The amides can be liquid, water-soluble materials as produced from a 2:1 ratio, or solid, poorly water-soluble materials, or "super" amides as produced from a 1:1 ratio of reactants. These products are useful as foam stabilizers, and aid cleaning in laundry detergents, dishwashing liquids, shampoos, and cosmetics. They are also used as antistatic agents, glass coatings, fuel gelling agents, drilling mud stabilizers, demulsifiers, and in mining flotation. Reaction of alkanolamines with a fatty acid at room temperature produces neutral alkanolamine soaps (eq. 9). Alkanolamine soaps are found in cosmetics, polishes, metalworking fluids, textile applications, agricultural products, household cleaners, and pharmaceuticals.

Alkanolamine salts are anionic surfactants (qv) formed from the reaction of alkanolamines and the acids of synthetic detergents, such as alkylarylsulfonates, alcohol sulfates, and alcohol ether sulfates. These add to the surfactants line used in detergents, cosmetics, textiles, polishes, agricultural sprays, household cleaners, pharmaceutical ointments, and metalworking compounds. Salts of alkanolamines and inorganic acids are useful chemical intermediates (eq. 4), and are also used in corrosion inhibitors, antistatic agents, glass coatings, electroplating, high octane fuels, inks, metalworking, dust control in mining, and in textiles.

10.1. Adhesives.

Alkanolamines are used in hot melt adhesives for binding nonpervious materials to polyolefins (25). Diethanolamine and triethanolamine have been used in the area of phenol formaldehyde adhesives to improve bond strengths (26,27), improve storage stability (28–30), and to increase water dispersibility (31). Starch-based adhesives have increased stability, viscosity, and gel temperature with the addition of monoethanolamine or diethanolamine to Mannich reaction products (32,33). Asphalt compositions have increased bonding to the aggregate in the emulsion when monoethanolamine is added (34,35). Refractory binder formulations, ceramics, and molds are improved by alkanolamine usage for stimulating gel formation (36–38). Anaerobic adhesive sheets, useful in adhering to ABS resin sheets, are made from the combination of diethanolamine, epoxidized polybutadiene, and peroxide (39).

10.2. Cement and Concrete.

Low concentrations of triethanolamine or its salts are added to cement clinkers to increase the efficiency of the grinding mill by reducing particle agglomeration (40). The resulting cement is more free-flowing and pack-set is reduced. The mechanism is presumed to be due to the dispersing capability of the triethanolamine, creating a uniform particle dispersion throughout the mixture.

In concrete, triethanolamine accelerates set time and increases early set strength (41–43). These are often formulated as admixtures (44), for later addition to the concrete mixtures. Compared to calcium chloride, another common set accelerator, triethanolamine is less corrosive to steel-reinforcing materials, and gives a concrete that is more resistant to creep under stress (45). Triethanolamine can also neutralize any acid in the concrete and forms a salt with chlorides. Improvement of mechanical properties, whiteness, and more even distribution of iron impurities in the mixture of portland cements, can be effected by addition of 2% triethanolamine (46). Triethanolamine bottoms and alkanolamine soaps can also be used in these type applications. Waterproofing or sealing concrete can be accomplished by using formulations containing triethanolamine (47,48).

10.3. Cleaners. Properties, such as foaming and detergency (qv), make alkanolamines useful in cleaning formulations. Monoethanolamine is particularly effective in wax removal formulations because of its ability to penetrate films. Cleaners that involve skin contact use triethanolamine because of its mildness. Derivatives of the amines (49,50) as well as the free alkanolamines (51–53), may be formulated into cleaning products.

10.4. Coatings. A wide variety of applications have been reported in coatings technology. The alkanolamines are added to neutralize polyester, epoxy (54–56), polyamide, and urethane (57) resin coatings to enhance dispersibility (58–60). In metal-coating preparations, the alkanolamines serve as complexing agents, neutralizers, promoters, modifiers, corrosion inhibitors, and electrophoretic bath components (61,62). Alkanolamines assist in improving adhesion, curing resins, complexing metals, improving storage stability, and improving both fresh and salt water resistance for some types of coatings (63–67).

Alkanolamines are used in urethane coatings for glass shatter proofing (68) and have been utilized as amides, salts, or free amines in providing antifrosting, antifogging, and dirt-resistant films on glass and plastics (69–72).

Triethanolamine and diethanolamine are accelerators for photopolymerization coatings (73–75). Diethanolamine is the most commonly used alkanolamine in the preparation of cationic polymers for electrophoretic coatings. The use of acrylate–amine–isocyanate–anhydride copolymers provides electrodeposited coatings that can be cured with uv light (76,77). All of the ethanolamines are effective in improving thermal properties and reducing cracking in prepared wire coatings (78–82).

10.5. Corrosion Inhibitors. Alkanolamines inhibit corrosion of ferrous metals (83). These can be used in a wide variety of applications, such as coolant systems, lubricating oils (84,85), metal working fluids, petroleum antifouling (86), and drilling needs (87). Monoethanolamine is most often used in applications requiring free base, and triethanolamine as a salt with organic and inorganic acids. Fatty acid salts are used in lubricating and metal working fluids (88), whereas inorganic salts, the phosphate or borate, are used in aqueous or mixed-solvent systems such as glycol antifreeze (89). Corrosion inhibitors for aluminum, containing alkanolamines, are also detailed in the literature (90).

Alkanolamines are also used in formulations for corrosion prevention. Triethanolamine-containing formulations can be used to coat stainless steel to prevent high temperature oxidation (91). Short term anticorrosion protection for metal parts during quenching can be accomplished by using triethanolamine salts of phosphoric acid esters (92,93). Rusted steel surfaces can be stabilized before painting, using triethanolamine-containing formulations in the prime paint (94).

It should be noted that corrosion inhibitors and protection systems are generally designed for specific conditions, and the effectiveness of the inhibitor can change with conditions.

10.6. Cosmetics and Personal Care Products. Alkanolamines are important raw materials in the manufacture of creams (95–97), lotions, shampoos, soaps, and cosmetics. Soaps (98) formed from triethanolamine and fatty acids are mild, with low alkalinity and excellent detergency. Triethanolamine lauryl sulfate is a common base for shampoos (99–101) and offers significant mildness over sodium lauryl sulfate. Diethanolamine lauryl sulfate and fatty acid soaps of mono- and triethanolamine can also be used in shampoos and bubble bath formulations. Chemistry similar to that used in soluble oils and other emulsifiers is applicable to cleansing creams and lotions (102, 103). Alkanolamides or salts are added to the shampoo base to give a smooth, dense foam (104).

10.7. Detergents. Alkanolamines, alkanolamine fatty acid soaps, and alkanolamides, with their mild alkalinity and excellent detergency characteristics, are used extensively in soaps and detergents. An alkanolamine salt of LAS (linear alkylbenzene sulfonate) forms the anionic surfactant component of many liquid laundry detergents (105). Monoalkanolamides have very limited water solubility and excellent alkaline resistance, resulting in widespread use in heavy-duty powder detergents as foam stabilizers and rinse improvers (106). Dialkanolamides are used in light-duty liquid detergents, where high alkalinity is not needed and high solubility is required.

The new liquid laundry detergents, with no phosphates, have developed a use for alkanolamines. In nonenzyme formulations, they contribute alkalinity, pH control, and enhanced product stability. In enzyme products, alkanolamines contribute to the stability of the enzyme in water solutions (107).

10.8. Electroplating, Electroless Plating and Stripping. Alkanolamines form complexes with many metal ions, and are consequently useful in electrolytic and chemical plating to improve coating properties. Diethanolamine is used in baths for electroplating palladium (108), triethanolamine in electroless baths for coating copper (109), and monoethanolamine in electrodeposition baths for zinc (110). Various coating formulations also contain alkanolamines, such as diethanolamine in cationic electrophoretic coatings (111), monoethanolamine in photoresist developers (112), and triethanolamine in formulations to protect electric switches and contact elements (113).

Alkanolamines are also used in formulations for removing photoresists (114,115) and cleaning printed-circuit boards (116). Formulations containing diethanolamine are used for electrodip coating of substrates (117).

Various documents relate to the use of formulations containing triethanolamine as flux for a variety of metals (118,119), for solders (120), for soldering pastes (121, 122), and for low corrosion solder pastes (123).

10.9. Gas Purification. In the “sweetening” of natural gas, aqueous ethanolamine reacts with the hydrogen sulfide, carbon dioxide, or other acid constituents of the gas to give a water-soluble salt. The amine is then regenerated by steam stripping. Generally, monoethanolamine is used because of its low equivalent weight. Diethanolamine must be used, however, if there is a significant quantity of carbonyl sulfide in the gas, since this forms an unregenerable complex with monoethanolamine. The advantages of diethanolamine and monoethanolamine in treating refinery gases include low vapor pressure and hydrocarbon solubility (124).

Work continues on improving the efficiency of this process, such as for freeing the alkanolamine from heat-stable salts that can form (125). Formulations have been developed which inhibit degradation of mono- and diethanolamine in processing (126). Models (127), computer programs (128), and kinetics and enthalpies (129–136) have been developed to help determine equilibria of the acid gas–alkanolamine–water system. Additional references relate to the use of tertiary alkanolamines, such as triethanolamine, for gas conditioning (137–139).

Extensive work has been done on corrosion inhibitors (140), activated carbon use (141–144), multiple absorption zones and packed columns (145,146), and selective absorption and desorption of gas components (147,148). Alkanolamines can also be used for acid gas removal in ammonia plants (149).

Methyldiethanolamine (MDEA) and solutions of MDEA have increased in use for gas treating (150,151). Additional gas treating capacity can often be obtained with the same working equipment, because of the higher amine concentrations that can be used.

The Sulfinol gas conditioning process of Shell uses diisopropanolamine in a sulfolane solvent system. This system also increases gas capacity with improved efficiencies (152).

10.10. Metal Working, Cleaning, and Lubricating. Alkanolamines find wide use in the metal working industry, in formulations used for cutting fluids, lubricating oils, and cleaning solutions. The literature cites diethanolamine and triethanolamine as contributing biostatic effectiveness and high corrosion resistance (153). Triethanolamine derivatives, reacted with fatty acids, are formulated in emulsifiable oils, cutting fluids, and water-soluble cutting fluids (154–157). Triethanolamine is an excellent chelating agent in basic solutions. This chelating ability makes triethanolamine particularly useful in metal cleaning (158,159). Lubricants and coolants containing triethanolamine can increase the life of the cutting tool (160), increase the efficiency of the process (161), reduce surface roughness of the cutting tool (162), and reduce bactericidal concentrations (163).

10.11. Mining. Numerous patents have advocated the use of alkanolamines in mining applications. Triethanolamine has been used as a depressent in the flotation of copper (164), in the electrotwinning of gold (165), and as an aid in the froth flotation of nickel ores. Phosphate ore flotation has been improved through the use of a fatty acid condensate with ethanolamine (166). Beneficiation of tin ore has been accomplished using fatty acid alkanolamides (167).

10.12. Petroleum and Coal. The alkanolamines have found wide use in the petroleum industry. The ethanolamines are used as lubricants and stabilizers in drilling muds. Reaction products of the ethanolamines and fatty acids are used as emulsion stabilizers, chemical washes, and bore cleaners (168). Oil recovery has been enhanced through the use of ethanolamine petroleum sulfonates (169–174). Oil–water emulsions pumped from wells have been demulsified through the addition of triethanolamine derivatives. Alkanolamines have been used in recovering coal in aqueous slurries and as coal–oil mix stabilizers (175–177).

10.13. Polymers. Because of their polyfunctionality, alkanolamines are used as additives in polyurethanes, polycarbonates, epoxy resins, polyesters, and other various resins and rubbers. Triethanolamine and triisopropanolamine are cited in the literature as cross-linking agents and curing agents in injection-molding formulations, contributing stability, strength, good impact, heat, and flame resistance (178–182) for urethanes. In polyester formulations, triethanolamine-based formulations give good physical and mechanical properties (183), form good coatings for concrete floors (184), and decrease molding pressure (185).

Monoethanolamine-containing formulations can be used to make polycarbonate molds with good dyeability and crack resistance (186). Monoethanolamine, diethanolamine, and triethanolamine have been cited in formulations for epoxy resins compounds (187–192).

Triisopropanolamine is used in natural rubber cross-linking and as a color stabilizer for polyethylene formulations. Chain termination of polybutadiene with triisopropanolamine gives improved cold-flow properties.

Alkanolamines can also be used to improve thermal stability in PVC copolymers and polystyrene.

10.14. Textiles. Alkanolamines are used in many stages in the production of textiles, from fiber manufacture, fiber lubrication, and fabric bleaching to fiber dyeing, and finishing. The alkanolamine fatty acid soaps and salts are used to lend antistatic properties to the fibers (193–195). Soluble oils can be formulated for easy removal from the fabric. Fabric lubrication can be accomplished with alkanolamine derivatives or alkanolamine-containing formulations (196, 197). Ethanolamines can improve dyeing in a number of fabrics, including cotton (198), triacetate textiles (199), polyester-cellulosic fibers (200), acrylic fibers (201), polycarbonates (202), and leather (203). Quarternary alkanolamines can improve the dye stability (204), and act as fabric softeners as part of a formulation (205,206). Treatment of wool with a dilute solution of monoethanolamine, followed by steaming, imparts a durable crease (207) and sizing (208).

10.15. Pigment Dispersion. The alkanolamines and their derivatives are useful in dispersing titanium dioxide and other pigments (209). Monoisopropanolamine and triethanolamine are particularly effective in aiding titanium dioxide dispersion in the production of TiO_2 and in water-based paints (210). The alkanolamines are also an aid in the grinding of titanium dioxide (211).

10.16. Wood Pulping. Numerous patents have appeared in recent years regarding the use of alkanolamines in wood pulping. Pretreatment of wood chips with monoethanolamine has resulted in increasing yields from the alkaline pulping process (212). Monoethanolamine has also been used as an aid to increase pulp (qv) strength and brightness (213). Monoethanolamine has been used to impregnate wood to a more dense configuration (214). Combinations of an aqueous lignin slurry with monoethanolamine have produced a lignin salt that is suitable for printing compositions (215).

10.17. Chemical Processing Intermediates and Other Applications. Monoethanolamine can be used as a raw material to produce ethylenediamine. This technology has some advantages over the ethylene dichloride process in that salts are not a by-product. Additional reactions are required to produce the higher ethyleneamines that are normally produced in the ethylene dichloride process.

Alkanolamines are used in the manufacture of a variety of pharmaceutical compounds. Some of these products include antitumor agents, anti-inflammatory and allergy agents, and anticonvulsants. The literature reports ethanolamine derivatives in the treatment of Alzheimer's disease (216), the treatment of cerebral psychoorganic syndromes (217), and veterinary drugs (218).

The major use of alkanolamines in agricultural products is as a neutralizer for acidic herbicides. They also contribute increased water solubility, reduced volatility, and more uniform solutions. Various ethanolamines are reported in formulations to improve potato tuber size (219) and enhance the resistance to salt of some crops (220).

A variety of applications, including photography, employ alkanolamines for pH control. Reports have described formulations including monoethanolamine and triethanolamine in films and processing (221–224).

Diethanolamine can be used in the manufacture of morpholine (eq. 7).

10.18. Alkylalkanolamines. Aminoethylethanolamine and its derivatives are used in textiles, detergents, fabric softeners, chelating agents, water treating, petroleum, oil field and gas conditioning products, agricultural and pharmaceutical products, emulsifiers, mining chemicals, corrosion inhibitors, and surfactants for cosmetics (225).

Dimethylethanolamine, diethylethanolamine, and their derivatives are used in pesticides, corrosion inhibitors, drugs and pharmaceuticals, emulsification, paints and coatings, metal fabrication and finishing, petroleum and petroleum products, and plastics and resins (226).

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