

Ullmann's Encyclopedia of Industrial Chemistry

Volume A10:
Ethanolamines to Fibers, 4. Synthetic Organic

Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 10:

Ethanolamines to Fibers, 4. Synthetic Organic

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Symbols and Units

Symbols and units agree with SI standards (for conversion factors see p. VIII–IX). The following list gives the most important symbols used in the encyclopedia. Articles with many specific units and symbols have a similar list as front matter.

Symbol	Unit	Physical Quantity
a_B		activity of substance B
A_r		relative atomic mass (atomic weight)
A	m^2	area
c_B	mol/m^3 , mol/L (M)	concentration of substance B
C	C/V	electric capacity
c_p , c_v	$J\text{ kg}^{-1}K^{-1}$	specific heat capacity
d	cm, m	diameter
d		relative density (ρ/ρ_{water})
D	m^2/s	diffusion coefficient
e		elementary charge
E	J	energy
E	V/m	electric field strength
E	V	electromotive force
E_A	J	activation energy
f		activity coefficient
F	C/mol	Faraday constant
F	N	force
g	m/s^2	acceleration due to gravity
G	J	Gibbs free energy
h	m	height
h	$W \cdot s^2$	Planck constant
H	J	enthalpy
I	A	electric current
I	cd	luminous intensity
k	(variable)	rate constant of a chemical reaction
k	J/K	Boltzmann constant
K	(variable)	equilibrium constant
l	m	length
m	g, kg, t	mass
M_r		relative molecular mass (molecular weight)
n_D^{20}		refractive index (sodium D-light, 20 °C)
n	mol	amount of substance
N_A	mol^{-1}	Avogadro constant ($6.023 \times 10^{23} \text{ mol}^{-1}$)
p	Pa; bar*	pressure
Q	J	quantity of heat
r	m	radius
R	$J\text{ K}^{-1}\text{mol}^{-1}$	gas constant
R	Ω	electric resistance
S	J/K	entropy
t	s, min, h, d, month, a	time
t	°C	temperature
T	K	absolute temperature
u	m/s	velocity
U	V	electric potential

* The official unit of the pressure is the Pascal (Pa).

Symbols and units (continued from p. VII)

Symbol	Unit	Physical Quantity
U	J	internal energy
V	m ³ , L, mL	volume
w		mass fraction
W	J	work
x_B		mole fraction of substance B
α		cubic expansion coefficient
α	W m ⁻² K ⁻¹	heat transfer coefficient (heat transfer number)
α		degree of dissociation of electrolyte
$[\alpha]$	10 ⁻² deg cm ² g ⁻¹	specific rotation
η	Pa · s	dynamic viscosity
θ	°C	temperature
κ		c_p/c_v
λ	W m ⁻¹ K ⁻¹	thermal conductivity
λ	nm, m	wavelength
μ		chemical potential
ν	Hz; s ⁻¹	frequency
ν	m ² /s	kinematic viscosity (η/ρ)
π	Pa	osmotic pressure
ρ	g/cm ³	density
σ	N/m	surface tension
τ	Pa (N/m ²)	shear stress
φ		volume fraction
χ	Pa ⁻¹ (m ² /N)	compressibility

Conversion Factors

SI unit	Non-SI unit	From SI to non-SI multiply by
Mass		
kg	pound (avoirdupois)	2.205
kg	ton (long)	9.842×10^{-4}
kg	ton (short)	1.102×10^{-3}
Volume		
m ³	cubic inch	6.102×10^4
m ³	cubic foot	35.315
m ³	gallon (U.S., liquid)	2.642×10^2
m ³	gallon (Imperial)	2.200×10^2
Temperature		
°C	°F	°C × 1.8 + 32
Force		
N	dyne	1.0×10^5

Conversion factors (continued from p. VIII)

SI unit	Non-SI unit	From SI to non-SI multiply by
<i>Energy, Work</i>		
J	Btu (int.)	9.480×10^{-4}
J	cal (int.)	2.389×10^{-1}
J	eV	6.242×10^{18}
J	erg	1.0×10^7
J	kW · h	2.778×10^{-7}
J	kp · m	1.020×10^{-1}
<i>Pressure</i>		
MPa	at	10.20
MPa	atm	9.869
MPa	bar	10
kPa	mbar	10
kPa	mm Hg	7.502
kPa	psi	0.145
kPa	torr	7.502

Prefixes for Powers of Ten

T (tera) 10^{12}	k (kilo) 10^3	d (deci) 10^{-1}	μ (micro) 10^{-6}
G (giga) 10^9	h (hecto) 10^2	c (centi) 10^{-2}	n (nano) 10^{-9}
M (mega) 10^6		m (milli) 10^{-3}	p (pico) 10^{-12}

Abbreviations

The following is a list of the abbreviations used in the text. Common terms, the names of publications and institutions, and legal agreements are included along with their full identities. Other abbreviations will be defined wherever they first occur in an article. For further abbreviations, see p. VII (Symbols and Units), p. XIV (Companies and Country Codes in Patent References). The names of periodical publications are abbreviated exactly as done by Chemical Abstracts Service.

abs.	absolute		and all national waterways of the countries concerned)
a.c.	alternating current		
ACGIH	American Conference of Governmental Industrial Hygienists	ADR	accord européen relatif au transport international des marchandises dangereuses par route (European agreement concerning the international transportation of dangerous goods by road)
ACS	American Chemical Society		
ADI	acceptable daily intake		
ADN	accord européen relatif au transport international des marchandises dangereuses par voie de navigation intérieure (European agreement concerning the international transportation of dangerous goods by inland waterways)	AEC	Atomic Energy Commission (United States)
		AICbE	American Institute of Chemical Engineers
ADNR	ADN par le Rhin (regulation concerning the transportation of dangerous goods on the Rhine)	AIME	American Institute of Mining, Metallurgical, and Petroleum Engineers

APhA	American Pharmaceutical Association	dil.	dilute, diluted
ASTM	American Society for Testing and Materials	DIN	Deutsche Industrie Norm (Federal Republic of Germany)
BAM	Bundesanstalt für Materialprüfung (Federal Republic of Germany)	DOE	Department of Energy (United States)
BAT	Biologischer Arbeitsstoff-Toleranzwert (biological tolerance value for a working material, established by MAK commission, see MAK)	DOT	Department of Transportation – Materials Transportation Bureau (United States)
Beilstein	Beilstein's Handbook of Organic Chemistry, Springer, Berlin-Heidelberg-New York	DTA	differential thermal analysis
BET	Brunauer-Emmett-Teller	ed.	editor, editors, edition, edited
BGBI.	Bundesgesetzblatt (Federal Republic of Germany)	EEC	European Economic Community
BIOS	British Intelligence Objectives Subcommittee Report (see also FIAT)	e.g.	for example
BOD	biological oxygen demand	emf	electromotive force
<i>bp</i>	boiling point	EPA	Environmental Protection Agency (United States)
B.P.	British Pharmacopeia	EPR	electron paramagnetic resonance
BS	British Standard	Eq.	equation
ca.	circa	ESCA	electron spectroscopy for chemical analysis
calcd.	calculated	esp.	especially
CAS	Chemical Abstracts Service	ESR	electron spin resonance
cat.	catalyst; catalyzed	Et	ethyl substituent ($-C_2H_5$)
cf.	compare	et al.	and others
CFR	Code of Federal Regulations (United States)	etc.	et cetera
Chap.	chapter	EVO	Eisenbahnverkehrsordnung (Federal Republic of Germany)
ChemG	Chemikaliengesetz (Federal Republic of Germany)	exp (. . .)	$e^{-(\dots)}$, mathematical exponent
C.I.	Colour Index	FAO	Food and Agriculture Organization (United Nations)
CIOS	Combined Intelligence Objectives Subcommittee Report (see also FIAT)	FDA	Food and Drug Administration (United States)
CNS	Central Nervous System	FD & C	Food, Drug and Cosmetic Act (United States)
Co.	Company	FHSA	Federal Hazardous Substances Act (United States)
COD	chemical oxygen demand	FIAT	Field Information Agency, Technical (United States reports on the chemical industry in Germany, 1945)
conc.	concentrated	Fig.	figure
const.	constant	<i>fp</i>	freezing point
Corp.	Corporation	Friedländer	P. Friedländer, Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige, Vol. 1–25, Springer, Berlin 1888–1942
crit.	critical	FT	Fourier transform
CTFA	The Cosmetic, Toiletry and Fragrance Association (United States)	(g)	gas, gaseous
DAB 9	Deutsches Arzneibuch, 9th ed., Deutscher Apotheker-Verlag, Stuttgart 1986	GC	gas chromatography
d.c.	direct current	GGVE	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit der Eisenbahn (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by rail)
decomp.	decompose, decomposition		
DFG	Deutsche Forschungsgemeinschaft (German Science Foundation)		

GGVS	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter auf der Straße (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by road)	(l)	liquid
GGVSee	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit Seeschiffen (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by sea-going vessels)	Landolt-Börnstein	Zahlenwerte u. Funktionen aus Physik, Chemie, Astronomie, Geophysik u. Technik. Springer, Heidelberg 1950-1980; Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie, Springer, Heidelberg, since 1961
GLC	gas-liquid chromatography	LC ₅₀	lethal concentration
Gmelin	Gmelin's Handbook of Inorganic Chemistry, 8th ed., Springer, Berlin-Heidelberg-New York	LCLo	lowest published lethal concentration
GRAS	generally recognized as safe	LD ₅₀	lethal dose
Hal	halogen substituent (-F, -Cl, -Br, -I)	LDLo	lowest published lethal dose
Houben-Weyl	Methoden der organischen Chemie, 4th ed., Georg Thieme Verlag, Stuttgart	ln	logarithm (base e)
HPLC	high performance liquid chromatography	LNG	liquefied natural gas
IARC	International Agency for Research on Cancer, Lyon, France	log	logarithm (base 10)
IAEA	International Atomic Energy Agency	LPG	liquefied petroleum gas
IATA-DGR	International Air Transport Association, Dangerous Goods Regulations	M	mol/L
i.e.	that is	M	metal (in chemical formulas)
i.m.	intramuscular	MAK	Maximale Arbeitsplatz-Konzentration (maximum concentration at the workplace in the Federal Republic of Germany); cf. Deutsche Forschungsgemeinschaft (ed.): Maximale Arbeitsplatzkonzentrationen (MAK) und Biologische Arbeitsstoff-Toleranzwerte (BAT), VCH Verlagsgesellschaft, Weinheim (published annually)
IMDG	International Maritime Dangerous Goods Code	max.	maximum
IMO	Inter-Governmental Maritime Consultative Organization (in the past: IMCO)	MCA	Manufacturing Chemists Association (United States)
Inst.	Institute	Me	methyl substituent (-CH ₃)
i.p.	intraperitoneal	Methodicum	Methodicum Chemicum, Georg Thieme Verlag, Stuttgart
IR	infrared	Chemicum	Chemicum
ISO	International Organization for Standardization	MIK	maximale Immissionskonzentration (maximum immission concentration)
IUPAC	International Union of Pure and Applied Chemistry	min.	minimum
i.v.	intravenous	mp	melting point
Kirk-Othmer	Encyclopedia of Chemical Technology, 3rd ed., J. Wiley & Sons, New York-Chichester-Brisbane-Toronto 1978-1984	MS	mass spectrum, mass spectrometry
		NAS	National Academy of Sciences (United States)
		NASA	National Aeronautics and Space Administration (United States)
		NBS	National Bureau of Standards (United States)
		NCTC	National Collection of Type Cultures (United States)
		NIH	National Institutes of Health (United States)

NIOSH	National Institute for Occupational Safety and Health (United States)	SIMS	secondary ion mass spectrometry
NMR	nuclear magnetic resonance	STEL	Short Term Exposure Limit (see TLV)
no.	number	STP	standard temperature and pressure (0°C, 101.325 kPa)
NRC	Nuclear Regulatory Commission (United States)	T _g	glass transition temperature
NRDC	National Research Development Corporation (United States)	TA Luft	Technische Anleitung zur Reinhaltung der Luft (clean air regulation in Federal Republic of Germany)
NSC	National Service Center (United States)	TA Lärm	Technische Anleitung zum Schutz gegen Lärm (low noise regulation in Federal Republic of Germany)
NSF	National Science Foundation (United States)	tan	tangent
NTSB	National Transportation Safety Board (United States)	TDLo	lowest published toxic dose
OECD	Organization for Economic Cooperation and Development	TLC	thin layer chromatography
OSHA	Occupational Safety and Health Administration (United States)	TLV	Threshold Limit Value (TWA and STEL); published annually by the American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, Ohio
p., pp.	page, pages	TOD	total oxygen demand
Patty	G. D. Clayton, F. E. Clayton (ed.): Patty's Industrial Hygiene and Toxicology, 3rd ed., Wiley-Interscience, New York	TRK	Technische Richtkonzentration (lowest technically feasible level)
PB report	Publication Board Report (U.S. Department of Commerce, Scientific and Industrial Reports)	TSCA	Toxic Substances Control Act (United States)
PEL	permitted exposure limit	TWA	Time Weighted Average
Ph	phenyl substituent ($-C_6H_5$)	Ullmann	Ullmanns Encyklopädie der Technischen Chemie, 4th ed., Verlag Chemie, Weinheim 1972-1984;
Ph. Eur.	European Pharmacopoeia, 2nd. ed., Council of Europe, Strasbourg 1981 -		3rd ed., Urban und Schwarzenberg, München 1951-1970
q. v.	which see (quod vide)	USAEC	United States Atomic Energy Commission
ref.	refer, reference	USAN	United States Adopted Names
resp.	respectively	USD	United States Dispensatory
R _f	retention factor (TLC)	USDA	United States Department of Agriculture
R. H.	relative humidity	U.S.P.	United States Pharmacopoeia
RID	règlement international concernant le transport des marchandises dangereuses par chemin de fer (international convention concerning the transportation of dangerous goods by rail)	UV	ultraviolet
rpm	revolutions per minute	UVV	Unfallverhütungsvorschriften der Berufsgenossenschaft (workplace safety regulations in the Federal Republic of Germany)
RTECS	Registry of Toxic Effects of Chemical Substances, edited by the National Institute of Occupational Safety and Health (United States)	VbF	Verordnung in der Bundesrepublik Deutschland über die Errichtung und den Betrieb von Anlagen zur Lagerung, Abfüllung und Beförderung brennbarer Flüssigkeiten (regulation in the Federal Republic of Germany concerning the construction and operation of plants)
(s)	solid		
SAE	Society of Automotive Engineers (United States)		
s.c.	subcutaneous		
SI	International System of Units		

	for storage, filling, and transportation of flammable liquids; classification according to the flash point of liquids, recently in accordance with the classification in the United States)	VO	Verordnung
VDE	Verband Deutscher Elektrotechniker (Federal Republic of Germany)	vol	volume
		- vol.	volume (of a series of books)
		vs.	versus
VDI	Verein Deutscher Ingenieure (Federal Republic of Germany)	WHO	World Health Organization (United Nations)
		Winnacker-Kühler	Chemische Technologie, Carl Hanser Verlag, München
		wt	weight
		\$	U.S. dollar, unless otherwise stated

Abbreviations for the Names of Frequently Cited Companies

Air Products	Air Products and Chemicals	ICI	Imperial Chemical Industries
Akzo	Algemene Koninklijke Zout Organon	INCO	International Nickel Company
Alcoa	Aluminum Company of America	3M	Minnesota Mining and Manu- facturing Company
Allied	Allied Corporation	Mitsubishi	Mitsubishi Chemical
Amer.	American Cyanamid	Chemical	Industries
Cyanamid	Company	Monsanto	Monsanto Company
BASF	BASF Aktiengesellschaft	Nippon	Nippon Shokubai Kagaku
Bayer	Bayer AG	Shokubai	Kogyo
Celanese	Celanese Corporation	PCUK	Pechiney Ugine Kuhlmann
Daicel	Daicel Chemical Industries	PPG	Pittsburg Plate Glass Industries
Dainippon	Dainippon Ink and Chemicals Inc.	Searle	G.D. Searle & Company
Dow Chemical	The Dow Chemical Company	SKF	Smith Kline & French Laboratories
DSM	Dutch Staats Mijnen	SNAM	Società Nazionale Metandotti
Du Pont	E.I. du Pont de Nemours & Company	Sohio	Standard Oil of Ohio
Exxon	Exxon Corporation	Stauffer	Stauffer Chemical Company
FMC	Food Machinery & Chemical Corporation	Sumitomo	Sumitomo Chemical Company
GAF	General Aniline & Film Corporation	Toray	Toray Industries Inc.
W.R. Grace	W.R. Grace & Company	UCB	Union Chimique Belge
Hoechst	Hoechst Aktiengesellschaft	Union Carbide	Union Carbide Corporation
IBM	International Business Machines Corporation	UOP	Universal Oil Products Company
		VEBA	Vereinigte Elektrizitäts- und Bergwerks-AG
		Wacker	Wacker Chemie GmbH

Country Codes

The following list contains a selection of standard country codes used in the patent references.

AT	Austria	ID	Indonesia
AU	Australia	IL	Israel
BE	Belgium	IT	Italy
BG	Bulgaria	JP	Japan *
BR	Brazil	LU	Luxembourg
CA	Canada	MA	Morocco
CH	Switzerland	NL	Netherlands *
CS	Czechoslovakia	NO	Norway
DD	German Democratic Republic	NZ	New Zealand
DE	Federal Republic of Germany (and Germany before 1949) *	PL	Poland
DK	Denmark	PT	Portugal
ES	Spain	SE	Sweden
FI	Finland	SU	Soviet Union
FR	France	US	United States of America
GB	United Kingdom	YU	Yugoslavia
GR	Greece	ZA	South Africa
HU	Hungary	EP	European Patent Office *
		WO	World Intellectual Property Organization

* For Europe, Federal Republic of Germany, Japan, and the Netherlands, the type of patent is specified: EP (patent), EP-A (application), DE (patent), DE-OS (Offenlegungsschrift), DE-AS (Auslegeschrift), JP (patent), JP-Kokai (Kokai tokkyo koho), NL (patent), and NL-A (application).

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Cross References

Ethyl Alcohol → Ethanol	Extraction, treated in the B-Series
Ethyl Cellulose → Cellulose Ethers	Fatty Amines → Amines, Aliphatic
Ethyl Chloride → Chlorinated Hydrocarbons	Feldspar → Silicates
Ethylene Chlorohydrin → Chlorohydrins	Fermentation → Biotechnology
Ethylene Polymers → Polyolefins	Fermium → Transuranium Elements
Ethylene - Propene Rubber	Ferrites → Magnetic Materials
→ Rubber, Synthetic	Ferroboron → Boron and Boron Alloys
Ethylenimine → Aziridines	Ferrochromium → Chromium and Chromium
Ethyl Ether → Ethers, Aliphatic	Alloys
Europium → Rare-Earth Elements	Ferromanganese → Manganese and Manganese
Eutrophication → Detergents	Alloys
Evaporators, treated in the B-Series	Ferrotitanium → Titanium and Titanium Alloys
Exhaust Control → Automobile Exhaust	Ferrotungsten → Tungsten and Tungsten
Control	Compounds
Expectorants → Cough Remedies	Ferrovanadium → Vanadium and Vanadium
Explosive Cladding → Metals, Cladding and	Compounds
Lining	Fiber Glass → Fibers, 5. Synthetic Inorganic

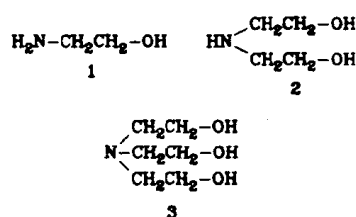
Ethanolamines and Propanolamines

HANS HAMMER (Chap. 1), WOLFGANG KÖRNIG (Chaps. 2 and 4–6),
THEODOR WEBER (Chap. 3), HEINZ KIECZKA (Chap. 7), BASF Aktiengesellschaft, Ludwigshafen/Rhein,
Federal Republic of Germany

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Amino alcohols have been prepared industrially since the 1930s. However, large-scale production started only after 1945, when alkoxylation with ethylene oxide and propylene oxide replaced the older chlorohydrin route. In industry, amino alcohols are usually designated as alkanolamines. Ethanolamines (aminoethanols) and propanolamines (aminopropanols) are by far the most important compounds of this group. Both are used widely in the manufacture of surfactants and in gas purification [1]–[6].

amine [102-71-6] (3) (TEA; 2,2,2'-nitriolo-triethanol) can be regarded as derivatives of ammonia in which one, two, or three hydrogen atoms have been replaced by a $-\text{CH}_2\text{CH}_2-\text{OH}$ group.



1. Ethanolamines

Monoethanolamine [141-43-5] (1) (MEA; 2-aminoethanol), diethanolamine [111-42-2] (2) (DEA; 2,2'-iminodiethanol), and triethanol-

Ethanolamines were prepared in 1860 by WURTZ from ethylene chlorohydrin and aqueous ammonia [7]. It was only toward the end of the 19th century that an ethanolamine mixture was separated into its mono-, di-, and triethanol-

amine components; this was achieved by fractional distillation.

Ethanolamines were not available commercially before the early 1930s; they assumed steadily growing commercial importance as intermediates only after 1945, because of the large-scale production of ethylene oxide. Since the mid-1970s, production of very pure, colorless triethanolamine in industrial quantities has been possible. All ethanolamines can now be obtained economically in very pure form.

The most important uses of ethanolamines are in the production of emulsifiers, detergent raw materials, and textile chemicals; in gas purification processes; and in cement production, as milling additives. Monoethanolamine is an important feedstock for the production of ethylenediamine and ethylenimine.

1.1. Properties

1.1.1. Physical Properties

Monoethanolamine and triethanolamine are viscous, colorless, clear, hygroscopic liquids at room temperature; diethanolamine is a crystalline solid. All ethanolamines absorb water and carbon dioxide from the air, and are infinitely miscible with water and alcohols. The freezing points of all ethanolamines can be lowered considerably by the addition of water. Some physical properties of ethanolamines are listed in Table 1.

1.1.2. Chemical Properties

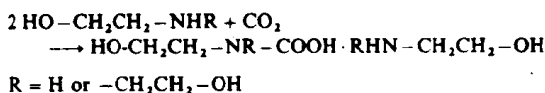
Because of their basic nitrogen atom and the hydroxyl group, ethanolamines have chemical properties resembling those of both amines and alcohols. They form salts with acids, and the hydroxyl group permits ester formation. When mono- and diethanolamine react with organic acids, salt formation always takes place in preference to ester formation. With weak inorganic acids, e.g., H_2S and CO_2 , thermally unstable salts are formed in aqueous solution. This reaction of ethanolamines is the basis for their application in the purification of acidic natural gas, refinery gas, and synthesis gas [1], [8]. In the absence of water, monoethanolamine and diethanolamine react with CO_2 to form car-

Table 1. Physical properties of ethanolamines

Compound	M_r	$m.p.$, °C	$b.p.$ (101.3 kPa), °C	ρ (20 °C), g/cm ³	Heat of vaporiza- tion (101.3 kPa), kJ/kg	Specific heat c_p , kJ kg ⁻¹ K ⁻¹	Cubic ex- pansion coefficient, K ⁻¹	Viscosity (20 °C), mPa · s	n_D^{20}	Surface tension (20 °C), N/m	Flash point ^a , °C	Ignition tempera- ture ^b , °C	Tem- pera- ture class ^c
Monoethanolamine	61.08	10.53	170.3	1.0157	848.1	2.72	7.78×10^{-4}	23.2	1.4544	0.049	94.5	410	T2
Diethanolamine	105.1	27.4	268.5	1.0912 (30 °C)	638.4	2.73	5.86×10^{-4}	389 (30 °C)	1.4747	0.0477	176.0	365	T2
Triethanolamine	149.2	21.6	336.1	1.1248	517.8	2.33	4.82×10^{-4}	930	1.4852	0.0484	192	325	T2

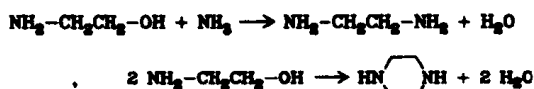
^a According to DIN 51 738. ^b According to DIN 51 794. ^c According to VDE 0165. Ethanolamines do not belong to any hazard class according to VbF (regulation governing flammable liquids).

bamates:

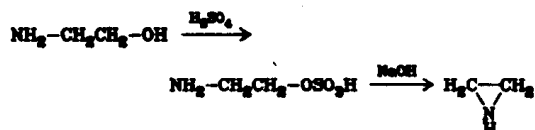


Triethanolamine does not form a carbamate.

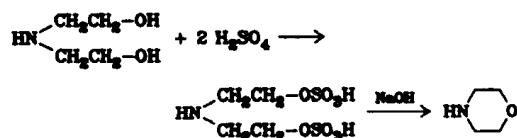
By reaction with ammonia in the presence of hydrogen, the hydroxyl group of monoethanolamine can be replaced by an amine group to form ethylenediamine [107-15-3] and piperazine [110-85-0] [9], [10]:



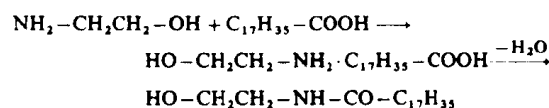
Considerable quantities of monoethanolamine are converted into ethylenimine (aziridine [151-56-4]) by adding sulfuric acid and cyclizing the hydrogen sulfate with sodium hydroxide (\rightarrow Aziridines, A 3, p. 241) [11], [12]:



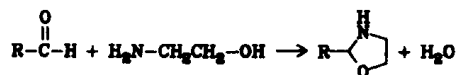
In a similar manner, morpholine [110-91-8] is formed from diethanolamine (\rightarrow Amines, Aliphatic, A 2, p. 15) [13]:



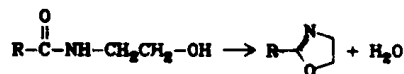
As primary and secondary amines, monoethanolamine and diethanolamine also react with acids or acid chlorides to form amides. The amine first reacts with the acid, e.g., stearic acid, to form a salt, which can be dehydrated to the amide by heating:



The action of aromatic aldehydes on monoethanolamine yields oxazolidines in accordance with the following reaction [14]:

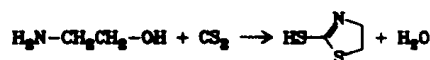


On the other hand, oxazolidines are formed when ethanalamides of fatty acids are heated at fairly high temperature with simultaneous removal of water [15]:

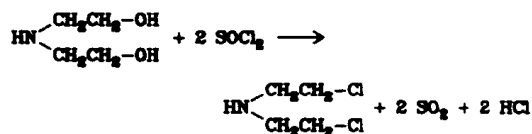


Formaldehyde reacts with monoethanolamine and diethanolamine to form hydroxymethyl compounds, which can be reduced to the *N*-methyl derivatives [16] (see Section 2.2).

Monoethanolamine reacts with carbon disulfide to form 2-mercaptothiazoline [96-53-7] [17]:

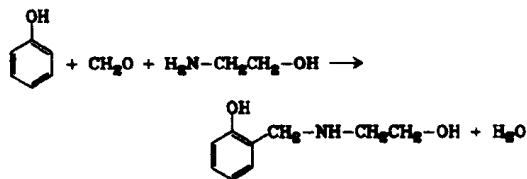


The hydroxyl groups of ethanalamines can be replaced with chlorine by reaction with thionyl chloride or phosphorus pentachloride. The chloroethylamines formed are hazardous because of their skin toxicity. For example, tris(2-chloroethyl)amine has been used as a gas in warfare. Bis(2-chloroethyl)amine is obtained in good yield by reaction of diethanolamine with thionyl chloride:



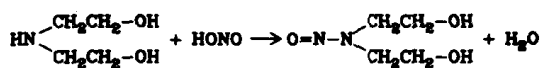
Reaction of triethanolamine with ethylene oxide gives unstable alkaline quaternary compounds and the corresponding stable ethers. For example, undistilled triethanolamine prepared from mono- or diethanolamine always contains some triethanolamine monoglycol ether [18].

Mono- or diethanolamine can also be used as the amine component in aminoalkylation, the so-called Mannich reaction, which is very important in the biosynthesis of many alkaloids [19].



N-Nitrosamines can be formed by reacting diethanolamine or, under suitable conditions, triethanolamine with nitrous acid, nitrites, or oxides of nitrogen. Animal experiments have

shown that *N*-nitrosamines are carcinogenic [20].



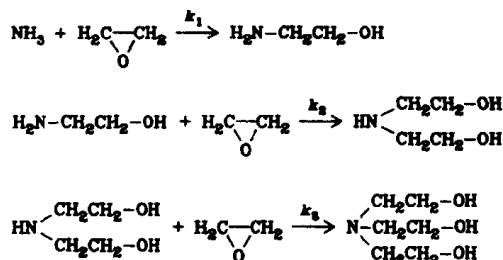
Monoethanolamine can form complexes with heavy-metal ions (e.g., copper, nickel, and iron); some of these complexes are water-soluble.

1.2. Production

Today, ethanolamines are produced on an industrial scale exclusively by reaction of ethylene oxide with excess ammonia, this excess being considerable in some cases [21].

The reaction of ethylene oxide with ammonia takes place slowly and is accelerated by water. An anhydrous procedure employs a fixed-bed catalyst consisting of an ion-exchange resin [22].

In all conventional processes, reaction takes place in the liquid phase, and the reactor pressure must be sufficiently large to prevent vaporization of ammonia at the reaction temperature. In current procedures, ammonia concentrations in water between 50 and 100%, pressures up to 16 MPa (160 bar), reaction temperatures up to 150 °C, and an excess up to 40 mol of ammonia per mole of ethylene oxide are used. The reaction is highly exothermic; the enthalpy of reaction is about 125 kJ per mole of ethylene oxide [23]. The following competing reactions occur:



Further possible reactions to tetraethanolammonium hydroxide or the monoglycol ether of triethanolamine do not play any role in the synthesis. The kinetics of these reactions have been studied [24].

All the reaction steps have about the same activation energy and show a roughly quadratic dependence of the reaction rate on the water content of the ammonia-water mixture used. Therefore, product composition depends solely on the

molar excess of ammonia and not on water content, reaction temperature, or pressure [25]. The product distribution as a function of the molar ratio of the reactants is shown in Figure 1 [26].

Unconsumed ammonia and water fed in as a catalyst are separated from the end products in a distillation line downstream of the reactor and are recycled. In large-scale continuous single-line plants, the requirement for low energy use (i.e., operation with minimum steam consumption) determines both the transport of heat from the reactor and the design of the thermally integrated distillation line. The ethanolamine mixture is worked up in vacuum distillation columns to give the pure products (Fig. 2).

Product distribution of the three ethanolamines can be controlled by appropriate choice of the ammonia:ethylene oxide ratio. A higher diethanolamine or triethanolamine content can also be obtained by recycling monoethanolamine or diethanolamine to the reactor or by reacting them with ethylene oxide in a separate unit.

For safety reasons, ethylene oxide must be metered into the ammonia stream; in the reverse procedure, ammonia or amines may cause ethylene oxide to undergo an explosive polymerization reaction.

In all large-scale processes, virtually complete conversion to the three ethanolamines, without significant formation of byproducts, is achieved. Therefore, feedstock costs are inde-

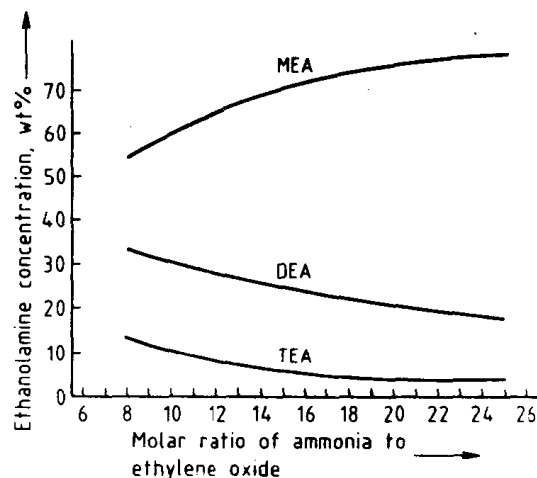


Figure 1. Product distribution of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) as a function of the molar ratio of ammonia to ethylene oxide (concentration of the aqueous ammonia solution ca. 85%)