Reviews of Environmental Contamination & Toxicology

Reviews of Environmental Contamination and Toxicology

Continuation of Residue Reviews

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George W. Ware

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Coordinating Board of Editors

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Foreword

International concern in scientific, industrial, and governmental communities over traces of xenobiotics in foods and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published research papers and progress reports, and archival documentations. These three international publications are integrated and scheduled to provide the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. This series is reserved exclusively for the diversified literature on "toxic" chemicals in our food, our feeds, our homes, recreational and working surroundings, our domestic animals, our wildlife and ourselves. Tremendous efforts worldwide have been mobilized to evaluate the nature, presence, magnitude, fate, and toxicology of the chemicals loosed upon the earth. Among the sequelae of this broad new emphasis is an undeniable need for an articulated set of authoritative publications, where one can find the latest important world literature produced by these emerging areas of science together with documentation of pertinent ancillary legislation.

Research directors and legislative or administrative advisers do not have the time to scan the escalating number of technical publications that may contain articles important to current responsibility. Rather, these individuals need the background provided by detailed reviews and the assurance that the latest information is made available to them, all with minimal literature searching. Similarly, the scientist assigned or attracted to a new problem is required to glean all literature pertinent to the task, to publish new developments or important new experimental details quickly, to inform others of findings that might alter their own efforts, and eventually to publish all his/her supporting data and conclusions for archival purposes.

In the fields of environmental contamination and toxicology, the sum of these concerns and responsibilities is decisively addressed by the uniform, encompassing, and timely publication format of the Springer-Verlag (Heidelberg and New York) triumvirate:

Reviews of Environmental Contamination and Toxicology [Vol. 1 through 97 (1962–1986) as Residue Reviews] for detailed review articles concerned with any aspects of chemical contaminants, including pesticides, in the total environment with toxicological considerations and consequences.

Bulletin of Environmental Contamination and Toxicology (Vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

Archives of Environmental Contamination and Toxicology (Vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

Manuscripts for *Reviews* and the *Archives* are in identical formats and are peer reviewed by scientists in the field for adequacy and value; manuscripts for the *Bulletin* are also reviewed, but are published by photo-offset from camera-ready copy to provide the latest results with minimum delay. The individual editors of these three publications comprise the joint Coordinating Board of Editors with referral within the Board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

Coordinating Board of Editors

Preface

Thanks to our news media, today's lay person may be familiar with such environmental topics as ozone depletion, global warming, greenhouse effect, nuclear and toxic waste disposal, massive marine oil spills, acid rain resulting from atmospheric SO_2 and NO_x, contamination of the marine commons, deforestation, radioactive leaks from nuclear power generators, free chlorine and CFC (chlorofluorocarbon) effects on the ozone layer, mad cow disease, pesticide residues in foods, green chemistry or green technology, volatile organic compounds (VOCs), hormone- or endocrine-disrupting chemicals, declining sperm counts, and immune system suppression by pesticides, just to cite a few. Some of the more current, and perhaps less familiar, additions include *xenobiotic transport, solute transport, Tiers 1 and 2, USEPA to cabinet status, and zero-discharge.* These are only the most prevalent topics of national interest. In more localized settings, residents are faced with leaking underground fuel tanks, movement of nitrates and industrial solvents into groundwater, air pollution and "stay-indoors" alerts in our major cities, radon seepage into homes, poor indoor air quality, chemical spills from overturned railroad tank cars, suspected health effects from living near high-voltage transmission lines, and food contamination by "flesh-eating" bacteria and other fungal or bacterial toxins.

It should then come as no surprise that the '90s generation is the first of mankind to have become afflicted with *chemophobia*, the pervasive and acute fear of chemicals.

There is abundant evidence, however, that virtually all organic chemicals are degraded or dissipated in our not-so-fragile environment, despite efforts by environmental ethicists and the media to persuade us otherwise. However, for most scientists involved in environmental contaminant reduction, there is indeed room for improvement in all spheres.

Environmentalism is the newest global political force, resulting in the emergence of multi-national consortia to control pollution and the evolution of the environmental ethic. Will the new politics of the 21st century be a consortium of technologists and environmentalists or a progressive confrontation? These matters are of genuine concern to governmental agencies and legislative bodies around the world, for many serious chemical incidents have resulted from accidents and improper use.

For those who make the decisions about how our planet is managed, there is an ongoing need for continual surveillance and intelligent controls to avoid endangering the environment, the public health, and wildlife. Ensuring safety-in-use of the many chemicals involved in our highly industrialized culture is a dynamic challenge, for the old, established materials are continually being displaced by newly developed molecules more acceptable to federal and state regulatory agencies, public health officials, and environmentalists.

Adequate safety-in-use evaluations of all chemicals persistent in our air, foodstuffs, and drinking water are not simple matters, and they incorporate the judgments of many individuals highly trained in a variety of complex biological, chemical, food technological, medical, pharmacological, and toxicological disciplines.

Reviews of Environmental Contamination and Toxicology continues to serve as an integrating factor both in focusing attention on those matters requiring further study and in collating for variously trained readers current knowledge in specific important areas involved with chemical contaminants in the total environment. Previous volumes of *Reviews* illustrate these objectives.

Because manuscripts are published in the order in which they are received in final form, it may seem that some important aspects of analytical chemistry, bioaccumulation, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology have been neglected at times. However, these apparent omissions are recognized, and pertinent manuscripts are in preparation. The field is so very large and the interests in it are so varied that the Editor and the Editorial Board earnestly solicit authors and suggestions of underrepresented topics to make this international book series yet more useful and worthwhile.

Reviews of Environmental Contamination and Toxicology attempts to provide concise, critical reviews of timely advances, philosophy, and significant areas of accomplished or needed endeavor in the total field of xenobiotics in any segment of the environment, as well as toxicological implications. These reviews can be either general or specific, but properly they may lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology. Certain affairs in food technology concerned specifically with pesticide and other food-additive problems are also appropriate subjects.

Justification for the preparation of any review for this book series is that it deals with some aspect of the many real problems arising from the presence of any foreign chemical in our surroundings. Thus, manuscripts may encompass case studies from any country. Added plant or animal pest-control chemicals or their metabolites that may persist into food and animal feeds are within this scope. Food additives (substances deliberately added to foods for flavor, odor, appearance, and preservation, as well as those inadvertently added during manufacture, packing, distribution, and storage) are also considered suitable review material. Additionally, chemical contamination in any manner of air, water, soil, or plant or animal life is within these objectives and their purview.

Normally, manuscripts are contributed by invitation, but suggested topics are welcome. Preliminary communication with the Editor is recommended before volunteered review manuscripts are submitted.

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G.W.W.

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Toxicology of Mono-, Di-, and Triethanolamine

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I. Introduction

The family of ethanolamines, including monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA), offers a broad spectrum of application opportunities because they combine the properties of amines and alcohols. Ethanolamines exhibit the unique capability of undergoing reactions common to both groups. As amines, they are mildly alkaline and react with acids to form salts or soaps. As alcohols, they are hygroscopic and can be esterified. Thus, since their introduction in the late 1920s, the ethanolamines have found uses in such diverse areas as gas sweetening, where they remove carbon dioxide and hydrogen sulfide; metalworking, in which they act as corrosion inhibitors in synthetic fluids; textile processing, where they serve as intermediates for cationic softening agents, durable press fabric finishes, dye leveling agents, lubricants, and scouring agents; detergent and specialty cleaner formulations, in which they are used to form various amine salts and to control pH; and a slew of other applications ranging from concrete admixtures to flexible urethane foam catalysts to pharmaceuticals to agricultural chemicals and photographic emulsions (Dow Chemical 1988; Howe-Grant 1992; OCC 1995).

Since the ethanolamines receive widespread applications in various industries and consumer products, they may present a significant potential for human exposure. A considerable number of experimental studies have been conducted over the years to understand the potential hazards of the ethanolamines. These studies evaluate the toxicity of the ethanolamines from single and repeated exposures, including their potential to cause mutation, birth defects, and tumors. These extensive toxicology data have been exhaustively compiled, fully annotated, and critically reviewed in this comprehensive paper.

II. Physical and Chemical Properties

The physical and chemical properties of the ethanolamines are summarized in Table 1. Pure ethanolamines are colorless liquids possessing a mild ammoniacal odor. Their chemical and physical properties exhibit properties of their two functional groups, alcohol and amines. Figure 1 gives their structures. The ethanolamines are soluble in most polar solvents (e.g., water, alcohol, etc.) but have limited solubility in organic solvents such as *n*-heptane (<0.06 g/100 g). Triethanolamine is the most polar, with its three -OH groups, followed by DEA and MEA. All three solvents are viscous at low temperatures, with MEA being considerably less viscous than

Table 1. Physical and chemical properties of the alkanolamines.

Property	Monoethanolamine	Diethanolamine	Triethanolamine
CAS Number	141-43-5	111-42-2	102-71-6
Chemical name	Ethanol, 2-amino	Ethanol, 2,2-iminobis	Ethanol, 2,2,2 nitrilo tris
Molecular weight	61.08	105.13	149.18
Physical state (25°C)	Liquid above 10.5°C	Liquid above 28°C	Liquid above 20.5°C
Melting point (°C)	10.5	28.0	20.5
Boiling point (°C)	171	268.8	335.4
Density (g/cm^3)	1.0180 at 20°C	1.0966 at 20°C	1.1242 at 20°C
Refractive index	1.4542 at 20°C	1.4776 at 20°C	1.4853 at 20°C
Solubility	Water, alcohol, ethanol, benzene, chloroform, glycerol, ligroin	Water, alcohol, ethanol, benzene	Water, alcohol, ethanol, benzene, chloroform, ligroin
pK_a	9.5 at 25°C	8.88 at 25°C	7.76 at 25°C
Mass spectrum, NIST	34160	34166	4612
m/e dominant species	61.05	105.08	149.11
IR reference	ALIRS 5776	COB 5638	COB 6371

CAS, Chemical Abstracts Service; NIST, U. S. National Institute of Standards and Technology; ALIRS, Aldrich Library of Infrared Spectra, Ed. III. Aldrich Chemical Co., Milwaukee, WI; COB, COBLENTZ Collection, Joint Committee on Atomic and Molecular Physical Data; Evaluated IR Spectra, BioRad Laboratories, Stadtler Division, Philadelphia, PA.

Properties from Lange's Handbook of Chemistry, 14th ed. McGraw-Hill Inc., New York, 1992.

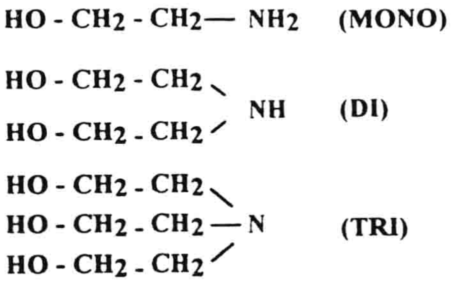


Fig. 1. Structure of mono-, di-, and triethanolamines.

DEA or TEA. Their melting points range from 10.5° to 28 °C, with MEA having the lowest melting point, DEA the highest, and TEA falling in between at 20.5 °C; DEA is a white crystalline solid at room temperature.

All three alkanolamines are alkaline, having pH values ranging from 10.0 to 12.5. MEA is the most alkaline and is similar in strength to aqueous ammonia. The ethanolamines boil at elevated temperatures ranging from 171° to 335.4 °C, with MEA having the lowest and TEA the highest boiling point. Although ethanolamines have relatively high freezing points, they are warmed to decrease their viscosity during transport and handling. The alkanolamines are unstable in the presence of reactive metals and water at elevated temperatures, reacting to produce colored products, and under extreme conditions react to liberate hydrogen. Because of their instability at higher temperatures, flammability limits are hard to determine. Their flash point lies between 190 °F for MEA and 400 °F for TEA. APHA (American Public Health Association) color is determined using an ASTM (American Society for Testing Materials) D1209 cobalt-platinum method. MEA is generally water-white to off-white in color. DEA has a specification limit of 50 APHA, or slightly yellow. TEA can range from off-white to dark amber in color (250 APHA) depending on the manner in which it was produced and stored. Detailed analytical procedures are available in the literature (Dow Chemical 1988) or from individual manufacturers.

III. Production, Use, and Chemistry

A. Production and Use

MEA is produced by reacting 1 mole of ethylene oxide (EO) with 1 mole of ammonia (NH_3). The addition of 2 and 3 moles of EO to 1 mole of ammonia will produce DEA and TEA, while additional EO will continue to react to produce higher EO adducts of TEA. In a typical production facility, EO is reacted with ammonia in a batch process to produce a crude mixture of roughly one-third each MEA, DEA, and TEA. The crude is stored and then separated by distillation (Dow Chemical 1988; OCC 1995). Because they have similar properties, the alkanolamines are used interchangeably or in combination with each other. Stainless steel, 316 L and 304 L, is the preferred material for constructing shipping and storage tanks. Table 2 lists the current uses of the ethanolamines as a group, while Table 3 gives the individual uses for each ethanolamine. The total worldwide production capacity for ethanolamines in 1992 was estimated at 300,000 metric tons. Of this demand, 145,450 tons was exported, 7727 tons was imported from foreign producers, and 45,455–54,545 tons was consumed in internal operations (OCC 1995). In 1995, the annual U.S. production capacity for ethanolamines was estimated to be 447,727 metric tons (SRI 1995).

Table 2. Major uses of the alkanolamines.

Applications	Percent of production	Action	
Exports	39		
Surfactants	13	Anionics (sulfonic acids):	Nonionics (fatty acids):
Gas processing	11	remove carbon dioxide	remove H_2S
Ethyleneamines	10		
Corrosion inhibitors	9	Salts of phosphoric acid	Salts of sulfuric acid:
Miscellaneous	7	Plasticizers	Corrosion inhibitors
Concrete/cement	6	Grinding aid Air entrainer	Drying accelerator
Textiles	5	Anionic fiber treatment: Acid acceptor Alkaline additives	UV light fade inhibitor: Anti-static agents Humectants/lubricants
Detergents	4	Heavy duty (industrial applications)	Light duty (dishwashing)
Agricultural chemicals	1	Herbicides	
Personal care products	1		

From OCC (1995).

B. Chemistry

1. Soaps, Surfactants, and Salts. Ethanolamines function as important intermediates in the production of surfactants because of their dual functional groups (Davidson and Milwidsky, 1968; Howe-Grant 1992; Jungerman and Tabor 1967; OCC 1995). At elevated temperatures, MEA and DEA react in a 2 : 1 ratio with long-chain fatty acids to produce Kritchevsky-type or regular ethanolamides. Regular ethanolamides consist of a viscous slurry of 60%–70% ethanolamide and lesser yields of unreacted ethanolamine and amide and amine esters according to Eq. (1).

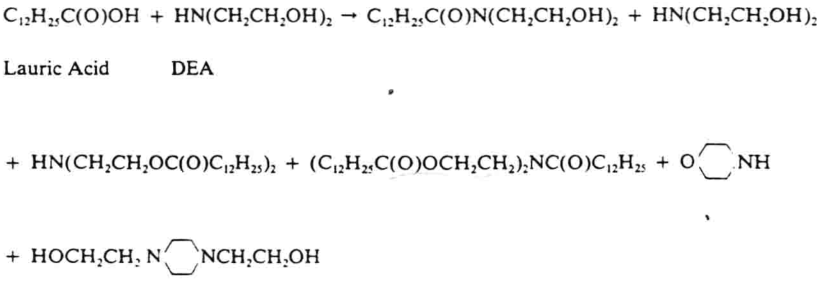
$$\begin{aligned}&\underset{\text{Stearic Acid}}{C_{17}H_{35}C(O)OH} + \underset{\text{MEA}}{2\,H_2NCH_2CH_2OH} \rightarrow C_{17}H_{35}C(O)NHCH_2CH_2OH + H_2NCH_2CH_2OH \\ &+ C_{17}H_{35}C(O)OCH_2CH_2NH_2 + C_{17}H_{35}C(O)OCH_2CH_2NHC(O)C_{17}H_{35}\end{aligned} \tag{1}$$

Table 3. Major uses of mono-, di-, and triethanolamines.

Applications	Percent of production
Monoethanolamine market	
Ethyleneamines	40
Gas purification	25
Surfactants	12
Detergents	10
Miscellaneous	7
Metalworking fluids	2
Cosmetics	2
Textile processing	2
Diethanolamine market	
Surfactants	39
Gas purification	30
Textile processing	15
Metalworking fluids	10
Miscellaneous	8
Laundry detergents	2
Agricultural chemicals	2
Triethanolamine market	
Metalworking fluids	33
Concrete/cement	25
Surfactants	20
Textile processing	8
Miscellaneous	6
Agricultural chemicals	3
Cosmetics	2

From OCC (1995).

When DEA is used in the production of ethanolamides, amine and amide diesters and some morpholine and piperazine derivatives are produced, as shown in Eq. (2).



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