CHAPTER - I

LITERATURE SURVEY OF 2-AMINO-2-ETHYL-1,3-PROPANEDIOL AND SCOPE OF THE STUDY
2-Amin-2-ethyl-1,3-propanediol, \((\text{CH}_2\text{OH})_2 \text{C(NH}_2)\text{CH}_2\text{CH}_3\), (shortly termed as AEPD), is one of the important compounds of unique series of alkanolamines (or) aliphatic hydroxy amines. The general method of preparation (54) of alkanolamines involves the reduction of nitro alcohols obtained by the condensation of nitro paraffins with formaldehyde. Literature survey has revealed that number of procedures have been adopted for the preparation of 2-amino-2-ethyl-1,3-propanediol. In earlier days, the preparation of alkanolamines in general and AEPD in particular was carried out by the reduction of nitro alcohols. Demuth and Meyer were the first to reduce nitro alcohols (1). With sodium amalgam as the reducing agent they obtained impure products. Henry (2) and Tordoir used tin and hydrochloric acid but reported low yields (4). Mousset (5) and Stienon employed aluminium amalgam and obtained yields of approximately 50% (3). Hass etal (6) and Kenneth Johnson etal (8) prepared 2-amino-2-ethyl-1,3-propanediol by carrying out the catalytic hydrogenation over Raney nickel of 2-ethyl-2-nitro-1,3-propanediol obtained by means of aldehyde-nitro paraffin condensation. They preferred catalytic hydrogenation for getting good yields over the simple reduction because of the fact that the nitro alcohols are found to be unstable under most reducing conditions. Murray Senkus (10) carried out catalytic reduction of 140 parts 5-nitro-5-ethyl-2-(1-ethyl-1-pentenyl)-1,3-dioxane in 300 parts methanol by hydrogenation for 3 hours at 60-70° and 150 lb. in the presence of 5 parts Raney nickel yielded 80 parts 5-amino-5-ethyl-2-(1-ethyl-1-pentenyl)-1,3-dioxane and its hydrolysis with dilute sulphuric acid yielded 2-amino-2-ethyl-1,3-propanediol.
Quantitative conversion of 2-nitro-2-ethyl-1,3-propanediol to 2-amino-2-ethyl-1,3-propanediol has been successfully carried out by iron reduction (13) in presence of FeSO₄ and H₂SO₄ and best results were obtained when the reduction was carried out at pH 3.0 to 3.5. 2-Amino-2-ethyl-1,3-propanediol was obtained also by electrolytic reduction (14) of corresponding nitro alcohol at lead cathode in presence of 10% hydrochloric acid or 25% sulphuric acid at temperature of 65-85 °C. Chikai et al (15) prepared AEPD by the reduction of nitro alcohol obtained by the condensation of nitro paraffins with formaldehyde in presence of basic catalysts. Simultaneous preparation of 2-amino-2-ethyl-1,3-propanediol and 2-amino-1-butanol was successfully achieved by the reduction of 1-nitropropane and formaldehyde over Raney nickel by John (31). Hydrogenation of (36) 2-nitro-2-ethyl-1,3-propanediol over 1% Ruthenium-Raney nickel gave 78-96% of 2-amino-2-ethyl-1,3-propanediol. Rignon et al (80) prepared AEPD through electro reduction of aliphatic nitro compound at a bimetallic electrode consists of copper support and zinc (or) cadmium as the active element.

Tindall (29) suggested a method for the purification of the title compound. The process was carried out by treating an aqueous solution of 16 wt% crude 2-amino-2-ethyl-1,3-propanediol with an adsorbant resin (a non-ionic; cross-linked copolymer of styrene and divinyl benzene). AEPD was passed upward through a resin column at an average rate of 4.5 ml/min. The effluent was collected in four fractions. The first and three fractions were of satisfactory qualities and were combined and distilled to liquid temperature of 150°/15mm. to remove low-boiling amines and alkanolamines.
2-Amino-2-ethyl-1,3-propanediol melts only slightly above the room temperature and usually contains some water in it may appear as pastes or semi solid rather than crystalline solid. Physical properties of the title compound are given (Table 1).

Usually 2-amino-2-ethyl-1,3-propanediol is irritating to the eyes and should be washed out immediately on contact and it is only mildly irritating to the skin. Glasstone and Alfred (12) determined the basic dissociation constants of AEPD from pH measurements with a glass electrode and found to be pKb = 5.20. They also showed that the introduction of an hydroxyl group into aliphatic amine decreased the basic strength. The first OH groups increases pKb by 1.3 the second by 1 and the third by about 0.75. Migration of 2-amino-2-ethyl-1,3-propanediol on Whatman No.1 paper has been studied, the $R_f$ values reported and variations in migration rates with structural characteristics of amino alcohols have been discussed by Zimmerman (19). Donald Milton Smith (9) estimated AEPD by esterfication procedure employing BF$_3$ as the esterfication catalyst using Karl Fischer reagent.

A perusal of literature revealed that 2-amino-2-ethyl-1,3-propanediol and its derivatives have innumerable applications in various important fields. A compound derived from AEPD and thiazolidine carboxylic acid is useful for the treatment of liver diseases and can be administered orally (or) parenterally (26). A salt of 2-amino-2-ethyl-1,3-propanediol and hydrocortisone 21-hemisuccinate has been employed as corticoid hormone derivative which is suitable for intravenous (or) parenteral administration in emergency conditions (16). Heteropolycyclic aromatic derivative of 2-amino-2-ethyl-1,3-propanediol was
used as antitumor agent (85). A new class of antitumour DNA intercalators have been prepared from amino alcohols which include AEPD also (85). Oxazoline derivatives of AEPD helped to decrease in blood cholesterol level and in blood triglycerides level (43). Labrude (59) studied relative effectiveness of solutions of 2-amino-2-ethyl-1,3-propanediol and 27 related compounds in protecting Hemoglobin during freeze-drying. The unprotonated forms of the buffers are responsible for the enhancement of GABA uptake and this is a result of the removal of protons from a membrane site in such a manner as to allow the GABA transporter to function (73). Roberts (75) studied the composition of AEPD and other alkanolamines for use in promoting nerve regeneration. The composition further comprises proton withdrawing substances to inhibit growth of glial tissue by increasing the pH at the site of nerve injury. Competition for binding site within the oxygen-evolving complex between various amines including AEPD was examined (76). Fluoranthene derivatives of AEPD and other alkanolamines have been prepared and tested for their antitumour, antiviral, antifungal, antibacterial activities by Bair Kenneth (81). Sandusky (82) and his co-worker carried out steady-state kinetic analysis of the inhibition of $H_2O_2$ oxidation in presence of AEPD and other alkanolamines towards chloride-depleted thylakoid membranes. The dissolution behaviour of two different resins obtained by condensing epoxy compound with 2-amino-2-ethyl-1,3-propanediol in various acidic buffer solutions and their pharmaceutical dosage forms were studied (30). The concentration of amine in these resins and pH as well as ionic strength of the buffer solutions had a significant effect on the dissolution of the resins. Trichlorophenoxy aceticacid ester of 2-amino-2-ethyl-
1,3-propanediol is useful in herbicidal application (32).

The alkanolamines being similar can often be utilized interchangeably. More often, however, a specific choice is dictated by physical or chemical properties or cost considerations. The fatty acid soaps of alkanolamines have long been utilized as emulsifying agents in floor polishes, mineral oil emulsions and insecticide emulsions (54).

A product obtained by a reaction of 1 mole stearic acid and 1 mole AEPD was condensed with 40 moles ethylene oxide is useful as levelling agent, dispersing agent and post treating agent for dyeing cellulose or synthetic fibres (34). Derivatives of AEPD and other primary amines have been used in the preparation of highly elastic polyurethane foams of improved deformability (35). 2-Amino-2-ethyl-1,3-propanediol salts of long chain sulphates and carboxylates have been employed in the preparation of foams and foam stabilizers (39). Jerry (44) prepared 2-amino-2-ethyl-1,3-propanediol-amino tris (hydroxy-methyl) methane isophthalic acid copolymer ammonium salt and used it as levelling agent in emulsion waxes for linoleum tiles. Alkanolamines are recommended [50,95] as a hair fixatives which are sold as styling gels and as aqueous or alcoholic solutions. Oxazoline derivatives of 2-amino-2-ethyl-1,3-propanediol and other alkanolamines were prepared by Elmar Harry et al and used as antioxidants for polypropylene (60). A compound obtained from cyclohexanone and AEPD was used as the haze inhibitor for lubricating oils and acts as a chelating agent for contaminant metals (67). 2-Amino-2-ethyl-1,3-propanediol was employed in hair dye preparations along with N-substituted O-nitroanilines glycidol and an alkalimetal or ammonium bisulfite. The resul-
tinting gel was applied to human hair for 30 minutes and dried. An ash, bright, brown nuance was obtained (68,71). Aminoalcohols including AEPD were evaluated as neutralizers for carboxylic hairspray resin. All appeared adequately comparable and could be used as mixtures without harmful effects [37,101]. Kokai (69) recommended Aliphatic amino alcohols for cleaning composition for metal molds for rubber. Amino hydroxy compounds such as 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol and Tris were evaluated as formaldehyde scavengers in textile finishing baths of resin-finished fabrics (77). AEPD along with number of polar group and polar bond compounds was suggested in a thermal printing with excellent thermal transfer characteristics upon a great number of paper surfaces, that can be used for multiple copy productions (79). Coating compositions forming metal working lubricants of alkanolamines were used as films for drawing heavy gage metals (24). AEPD was also used as Aircraft lubricant (11). Esters of alkanolamines from gels in alcoholic water solutions, so that they can be mixed in liquid form to have binders for refractories [25,94] Charles recommended AEPD as foaming agent for galvanizing fluxes (7). The enzyme deactivation by chlorine fabric laundering in water was prevented by using a detergent composition containing 2-amino-2-ethyl-1,3-propanediol as chlorine scavenger (40,46).

The title compound is used in the preparation of Thermosetting polyester-amino plastic coatings (41). Combination of AEPD and water-dispersed coating compounds of short oil alkyd resin has been employed to improve flexibility without significant loss of hardness (55). Fluxes prepared from AEPD and other alkanolamines are used for solde-
ring and metal coatings (17). The compounds are found to be superior to the usual zinc chloride fluxes. The substance consists of AEPD combined with a halogenated aromatic hydroxy compound is used in the preparation of masking coatings for heat-sensitive marking sheets (21). Besides 2-Amino-2-ethyl-1,3-Propanediol other alknaolamines such as Tris, 2-amino-2-methyl-1-propanol and 2-dimethylamino-2-methyl-1-propanol are employed in production of water-based coatings (87). Heat curable water-based coatings were prepared where only a minor amount of AEPD used to solubilize the carboxyl-containing polymers was released on heating. It is hard, clear and gloss coating with good adhesion was cast on glass, mild steel and tin plate dried and cured (57). Heat-curable resins prepared from phenol, formaldehyde, dimethylo propionic acid and AEPD are useful in paper coating compositions and in metal finishes, textile crease-proofing agents (38). Storage stable resins were manufactured by condensing a lower aliphatic aldehyde and urea in presence of 2,2-bis(hydroxymethyl)propionic acid and AEPD (42). The resulting resins were suitable for the preparation of baked coatings and the coated paper was oil and water resistant free from brittleness, and remained porous to the passage of air. Compounds prepared by Jurisch obtained from the reaction of AEPD with acrolein gave Vinyl oxazolidine derivatives which are useful as dispersing agents for H2O-based paints (49). 2-Amino-2-ethyl-1,3-propanediol is used in the preparation of paint emulsions of improved water and scrub resistance (22). Compositions containing AEPD along with sodium hydroxide, ethylene glycol were employed for removing acrylic paint coating applied to steel plates (33). Alkanolamines were treated with oilicica oil, gave dispersing agents for water-based paints [56,96,97].
Combination of 2-amino-2-ethyl-1,3-propanediol and organometallic compounds of Magnesium, Aluminium or Zinc was used to polymerize alkylene oxides to Crys inability regular products (45). The dispersion of polymer containing acrylic acid or hydroxy alkyl acrylate is neutralized with alkanolamines, acylamines or arylamines. The adhesive is useful for bonding building materials and smooth surfaces (83). Thus, 40 parts 45% aq. dispersion of ethyl acrylate-2-hydroxyethyl acrylate-vinyl chloride polymer was partially neutralized with 3 parts AEPD to give a thixotropic paste for smoothing concrete surfaces. A high strength water resistant fiber board is prepared from a cellulosic filler and polymerizable binder containing oxazoline oil which was the reaction product of AEPD with formaldehyde and fatty acid in varying proportions (28). The board formed was flexible and hardened with age. The presence of 2-amino-2-ethyl-1,3-propanediol has improved the viscosity stability, gel temperature and life stability of water-resistant corrugating adhesives (51). Alkanolamines particularly AEPD and poly ethylene poly amines are used as corrosion inhibitors in boilers fixed with S-contg oil to prevent sulphuric acid corrosion of cold-end steel surfaces [61,89]. The derivatives of 2-amino-2-ethyl-1,3-propanediol namely mono and bicyclic oxazolidines are used as additives for functional fluids (63). Metal complexes prepared by the reaction of poly alkenyl succinic anhydride with AEPD in presence of metal salt were recommended as lubricant and fuel additives [64,99]. Reactive adhesives are prepared (72) by heating methacrylonitrile with the appropriate alkanolamine in presence of catalysts.

2-Amino-2-ethyl-1,3-propanediol-hydrochloride was used as catalyst in presence of aqueous solution of urea and formaldehyde
in the manufacture of pressed particle board and laminated wood articles (47). Methyl heptenone was prepared from prenyl mesityloxide in presence of AEPD as catalyst (58). Richard employed alkanolamines as amine catalysts in the preparation of poly urethane foams (74). AEPD was employed in controlling the curing rate of silicone elastomers (20). Electrophotographic plate obtained from the condensation of AEPD with polyoxypropylene-2,2-bis (4-hydroxyphenyl) propane, fumaric acid in presence of hydroquinone yielded 20,000 sharp copies (48). Durable antistatic film laminates obtained from unsaturated acid copolymers and alkanolamines. The film thus obtained gave a laminate attracting no dust when rubbed with a cloth (78). Background-free image on an electrophotographic plate was produced whose base material is non metallic, when an intermediate coating of an amino alcohol (AEPD) is placed between the base e.g. paper and the light-sensitive layer. By incorporating a fluorescent material e.g.; Zns, Cu**, or Co**, in the amino alcohol coating, the plates are made useful for electroradiography (23). The intensification of photographic silver images have been carried out in presence of developers prepared from amino borane, boran hydride, alkanolamine and Group IB or VII metal salt (52). Derivative of an alkanolamine such as methylated polyoxazolines was employed as a prime coating in the production of glass sealed metal products (53). Yoneda developed corrosion-inhibiting agents for metal-cutting fluids which consist of AEPD, sodium nitrite, and water (65). An ion-selective electrode is described for CO\textsubscript{2} determination in biological fluids which consists of a support which has sequential layers of a metal conductive zone, a metal
halide zone, an electrolyte zone, a membrane zone contg. an ionophore, a hydrophilic binder and an alkanolamine in sufficient amount to provide a pH in the range 7.5 - 9.5 with micro quantity of the sample (66). Bates reviewed the use of AEPD and other alkanolamines as buffers for pH control. Buffer capacity, pH range, solution values, temperature coefficient and salt effects are being considered (18). An important object of a cutting oil besides cooling is to prevent corrosion of both the working surface and the cutting tool. This object is attained by an oil which contains a base of mineral lubricating oil plus an oil-solution prepared from AEPD and other compounds (27). Anti-corrosive agents for condensed water systems have been obtained from alkanolamines (88). Cathodic electrocoating compositions are prepared by the reaction of epoxide groups of epoxy resins with acid esters of dicarboxylic acids and oxazolidines, the derivatives of AEPD and neutralizing the products with acids. Coatings from this composition on steel, baked 30 min. at 160° showed no visible change after 380h in water at 40°(70).

Binders giving good bath stability and strong films, are prepared by mixing 85-95% cationic, film-forming resin and 15.5% alkanolamine derivative of oxazolidine.

Gum and sediment formation in liquid hydrocarbon mediums are inhibited by adding to the medium a branched or straight chain amino alcohols such as AEPD, Tris etc. The compound has particular advantage in distillate fuels such as in blended diesel fuels [91].
Mechanism of irreversible inhibition of $O_2^-$ evolution in photosystem by AEPD was studied by Sears et al. [92]. In photographic processing AEPD derivative has been used for silver-complex diffusion transfer reversal process [90]. Non-foaming, non-viscous, alcohol free water based, pressurized hair spray products have been prepared from AEPD [100]. Carbon dioxide is removed from a combustion gas using a mixed aqueous solution of 100 parts by wt. of alkanolamines which include AEPD also [98].

Literature survey revealed that not much work has been carried out in establishing the complexing ability of AEPD towards metal ions. Even the available few references on metal complexes of AEPD not fully established the coordinating ability of AEPD towards metals, but only emphasized the application of those complexes as lubricants and fuel additives. Reaction carried out by Sheldon et al (64) with zinc acetate, polypropenyl succinic anhydride and AEPD yielded a metal complex which has been used as lubricant and fuel additive. Competition between chloride ion and Ammonia (or) alkano-lamines for binding site within the Oxygen-evolving Manganese complex of spinach photo system has examined. This competition was a general inhibiting property of amines and was released to their nucleophilicity which suggests that the binding site was associated with a metal (76,84). Werner coordination complexes (62) prepared by reacting a benzotriazole with a mono epoxide to form a mixture of 1- and 2-hydroxy alkyl benzotriazoles and esterfying mixture with an a alkenyl succinic anhydride to form a mono ester and converting
the mono ester to a salt of metal selected from IB, IIB, IVB and VII of the periodic table and complexing the salt with alkanolamines including AEPD to form a chelate. The chelate thus obtained was employed as detergent and anti wear additive for lubricants. Synthesis, structural characteristics and magnetic properties of Molybdenum (VI) and copper (II) Schiffbase complexes derived from AEPD have been studied by Catherine et al (93).
SCOPE OF THE STUDY

Above cited literature survey reveals that alkanolamines are having important applications in many fields. Perusal of literature also suggests that the coordination chemistry of AEPD towards metal ions is not extensively studied. Further, the ligand under consideration has not been employed in polarographic investigation of metal ions. Keeping all these facts in view the author in the present investigations used AEPD as ligand to study its complexing ability towards various metal ions and extended the studies to determine ligand number, stability constants and kinetic parameters like $\ln K^0_{f,h}$ values. Thus, the aim of the study is to enrich the none too existing literature on AEPD as far as polarographic behaviour of metal-AEPD systems are concerned.
<table>
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<th>Name of the compound</th>
<th>Molecular weight</th>
<th>Boiling point</th>
<th>Melting point</th>
<th>Density</th>
<th>Refractive index</th>
<th>pH of 0.1 aqueous solution</th>
<th>Solubility in water at 20°C g/100 ml</th>
<th>Spectral data</th>
<th>IR</th>
<th>NMR</th>
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<td>2-Amino-2-ethyl-1,3-propanediol</td>
<td>119.16</td>
<td>152-153°C</td>
<td>37.5-38.5°C</td>
<td>1.099</td>
<td>1.490</td>
<td>10.8</td>
<td>Completely miscible</td>
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