

Physical Properties of Hydrocarbons

PART 34—Ethyamines

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THE ETHYLAMINES (monoethylamine, diethylamine and triethylamine) are produced largely by the reaction of ethyl alcohol and ammonia in the presence of alumina at 400° C and high pressure. They are used largely as intermediates in the production of specialty products.

Ethylenediamine is an important intermediate in the production of coatings and adhesives. It is extensively used in the textile and paper industries to increase wet strength and tensile strength. Approximately 50 million pounds were produced in 1966, largely by the reaction of ethylene dichloride and ammonia in the presence of caustic soda.

The physical properties of these compounds have been studied extensively below the boiling points.

Critical Properties and Vapor Pressures. The critical temperatures and pressures have been measured for the ethylamines.^{1,2,3} The critical densities are available for diethylamine and triethylamine.³ The critical densities of monoethylamine and ethylenediamine were calculated by the method of Vowles, with a probable error of 1-2 percent.³ Riedel's method was used to calculate the critical temperature and pressure of ethylenediamine.³

Stull reports the vapor pressures of monoethylamine and diethylamine up to the critical point and of triethylamine and ethylenediamine up to the boiling point. The vapor pressures of triethylamine and ethylenediamine above the boiling point were calculated by the method described in previous articles. This method gave results with an error of 1-3 percent for diethylamine.

Heat of Vaporization. Only the heats of vaporization at the boiling points have been experimentally determined.^{1,4} Kharbanda's nomograph has been used to calculate the heats of vaporization to the critical temperature.⁵

Heat Capacity. The vapor heat capacities have been calculated from the molecular structure.⁶

Hough and co-workers⁷ have determined the liquid heat capacity of ethylenediamine from 30-70° C. The heat capacities of the ethylamines were calculated by the method proposed by Johnson and Huang.³ This technique gave an error of less than 2 percent for ethylenediamine and about 6 percent for the methylamines. The data were extended over the -40 to +160° C range by the equation: heat capacity times density equals a constant.

Density. The orthobaric density of triethylamine has been reported from 0° C to the critical temperature.^{2,8} The densities of the other three compounds have been measured from 0-80° C.^{2,7,9} The Lydersen technique was used to calculate the densities up to the critical point.³ When compared with 13 experimental points, this method gave an average error of 0.8 percent and a maximum error of 2.4 percent. Fig. 34-6 shows the density of aqueous ethylenediamine solutions over the 10-90° C range.⁹

Viscosity. The vapor viscosities from 0-500° C were calculated by the equation proposed by Bromley and Wilke, with a probable error of 2-5 percent.

The liquid viscosity of monoethylamine has been determined at -33.5° C.⁸ Data are available on diethylamine from -35° C to +50° C,^{2,8,11} on triethylamine from -35° C to +80° C,^{2,8} and on ethylenediamine from 10 to 210° C.^{9,12} The method of Thomas was used to calculate the viscosities from -40° C to +160° C.³

TABLE 34-1—Physical Properties of Ethylamines

Compound	Abbreviation	Boiling Point, °C	Freezing Point, °C	Molecular Weight	Critical Properties		
					T _c , °C	P _c , psia	d _c , g/ml
Ethylamine.....	MEA	16.6	- 81.0	45.08	183.3	814	0.253*
Diethylamine....	DEA	55.9	- 59.0	73.14	223.5	536	0.246
Triethylamine....	TEA	88.8	-114.6	101.19	262.0	440	0.252
Ethylenediamine.	117.2	8.5	60.1	318*	916*	0.257*

* Estimated.

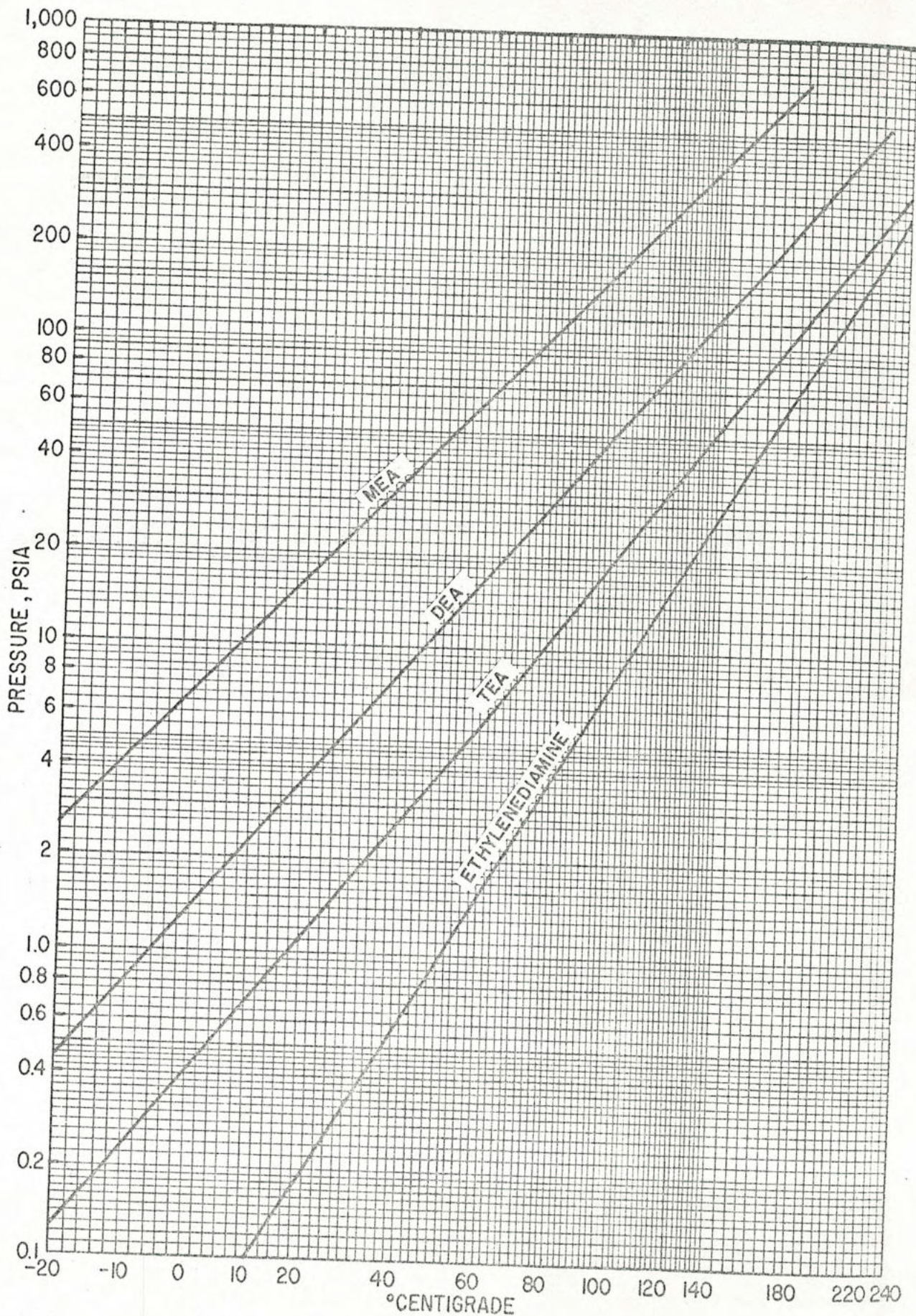


Fig. 34-1—Vapor pressure of ethylamines from -20° C to +240° C.

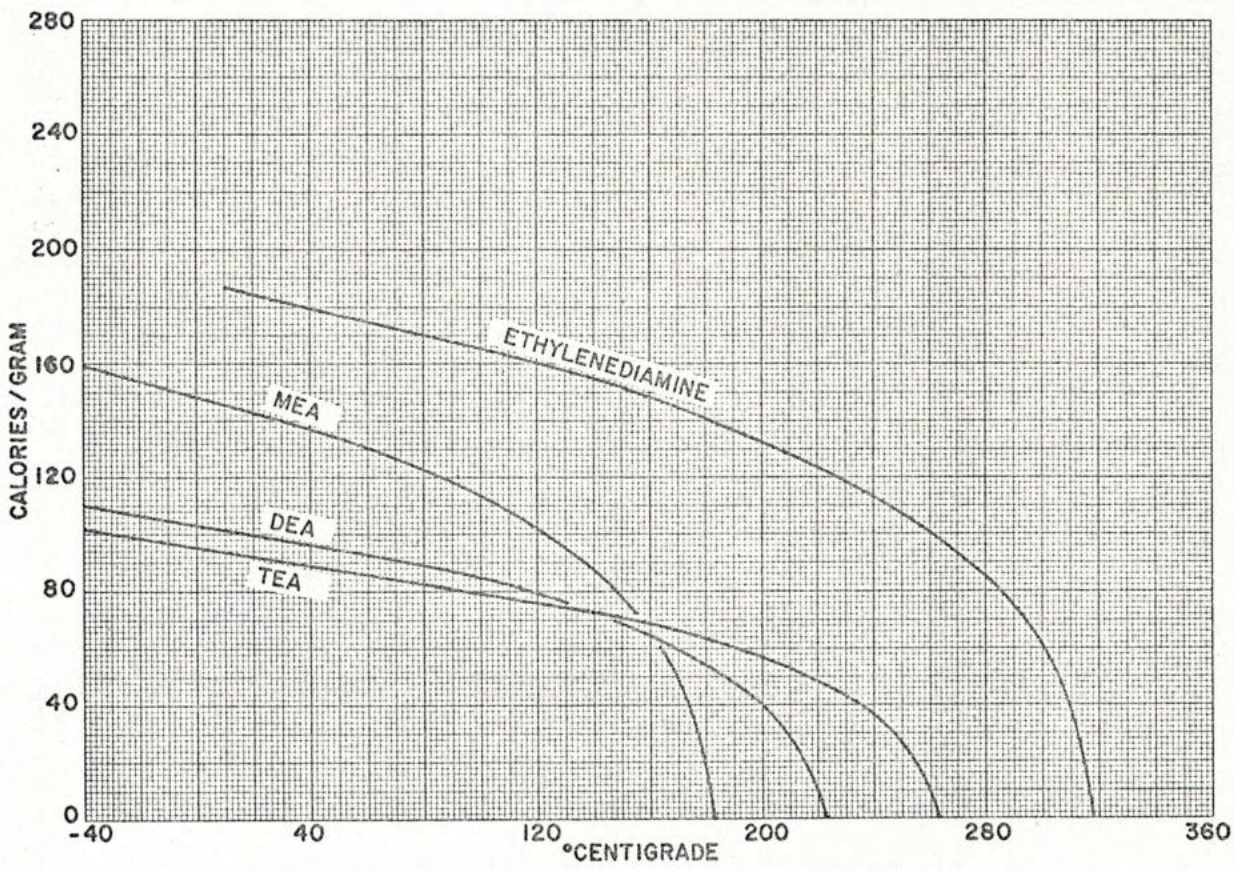


Fig. 34-2—Heat of vaporization of ethylamines from -40° C to +320° C.

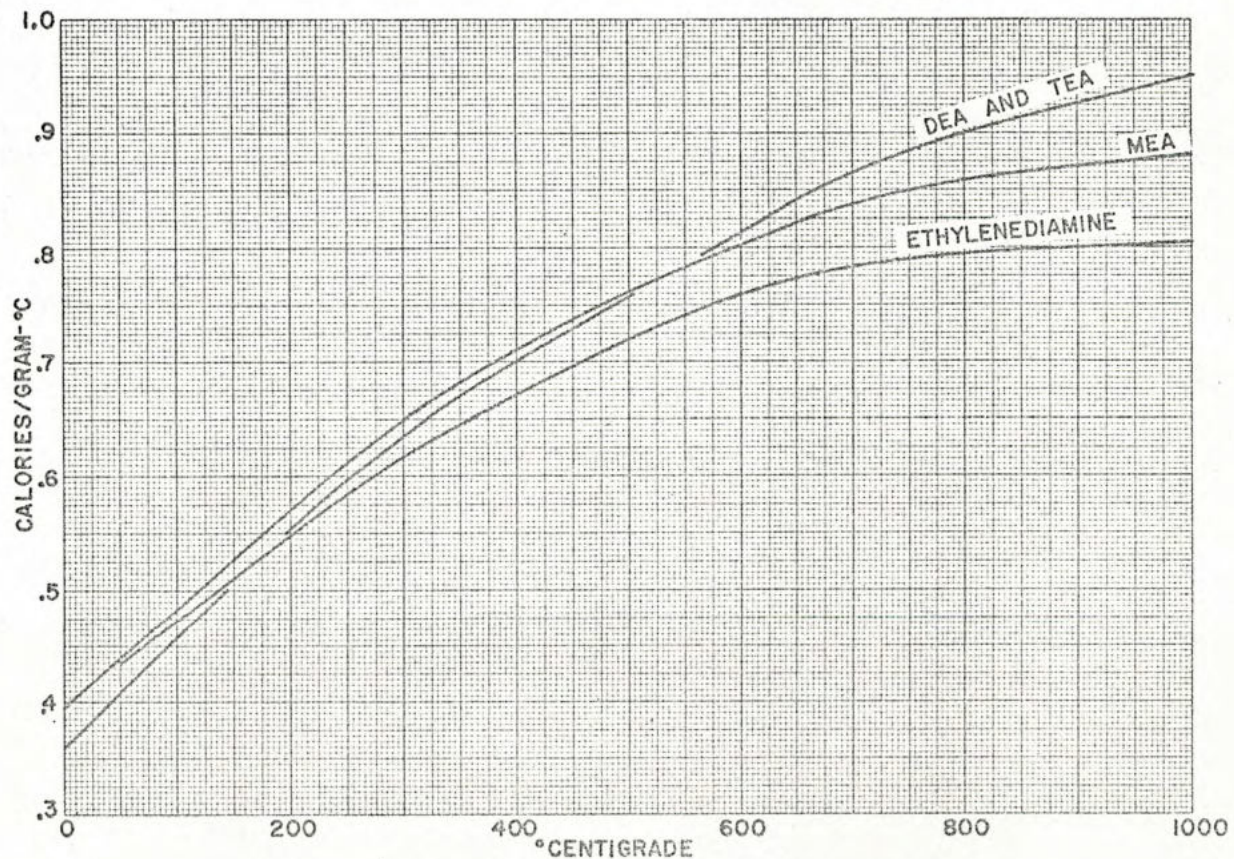


Fig. 34-3—Vapor heat capacity of ethylamines from 0° C to 1,000° C.

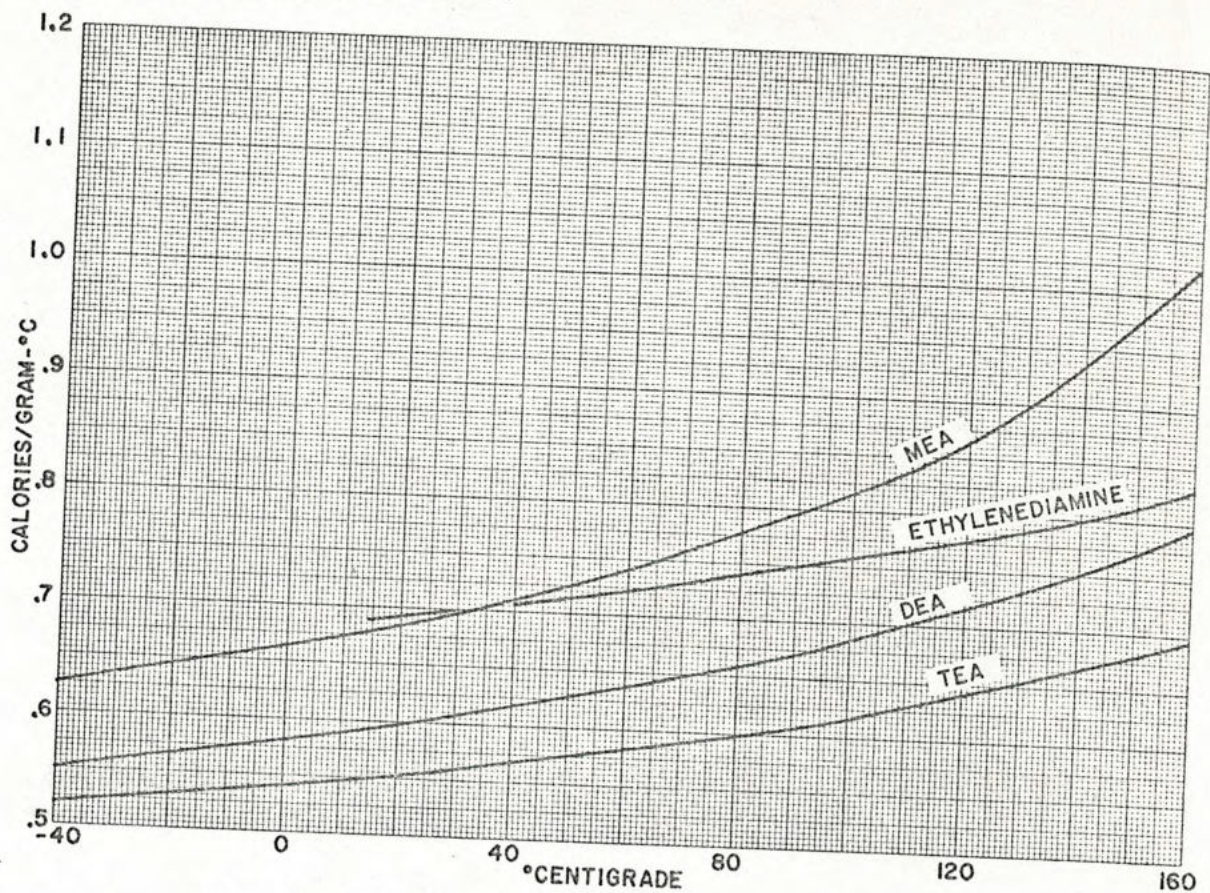


Fig. 34-4—Liquid heat capacity of ethylamines from -40° C to +160° C.

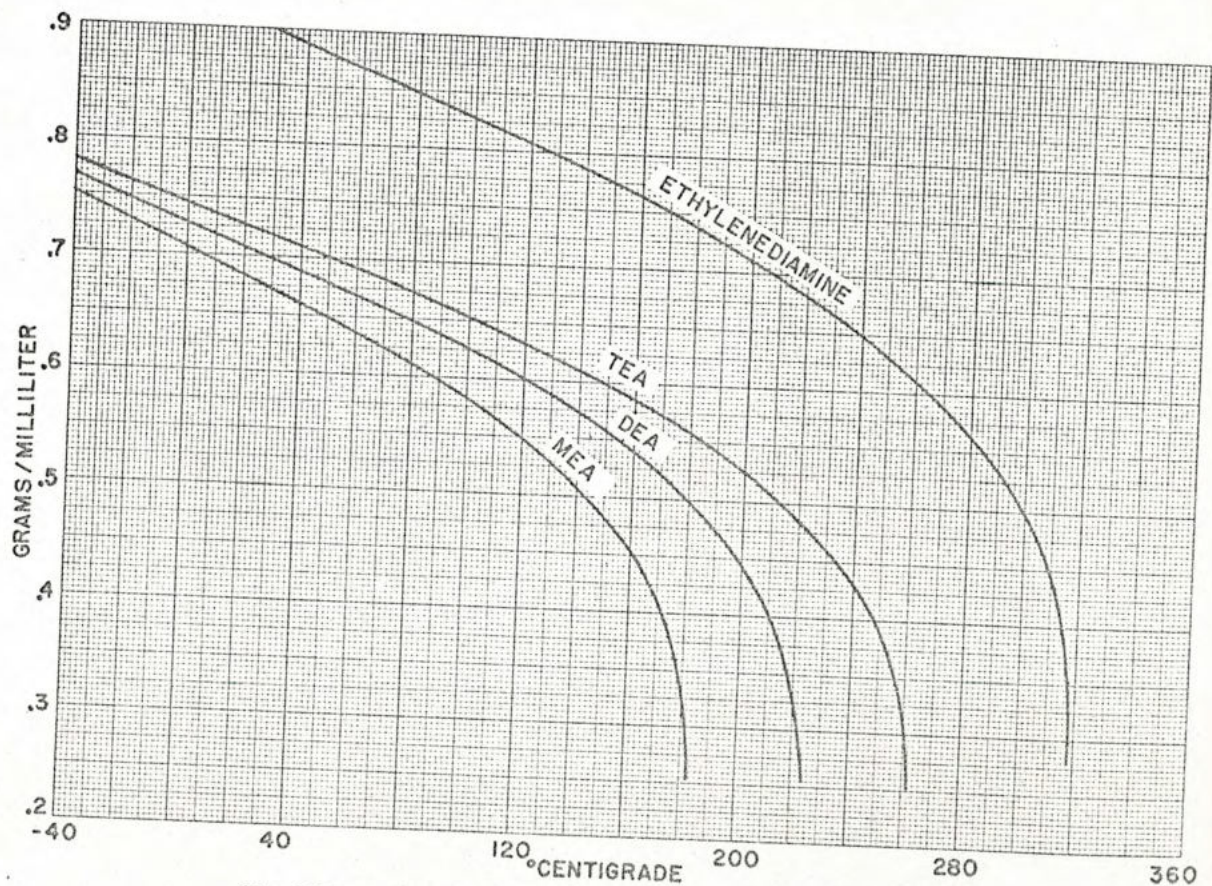


Fig. 34-5—Liquid density of ethylamines from -40° C to +320° C.

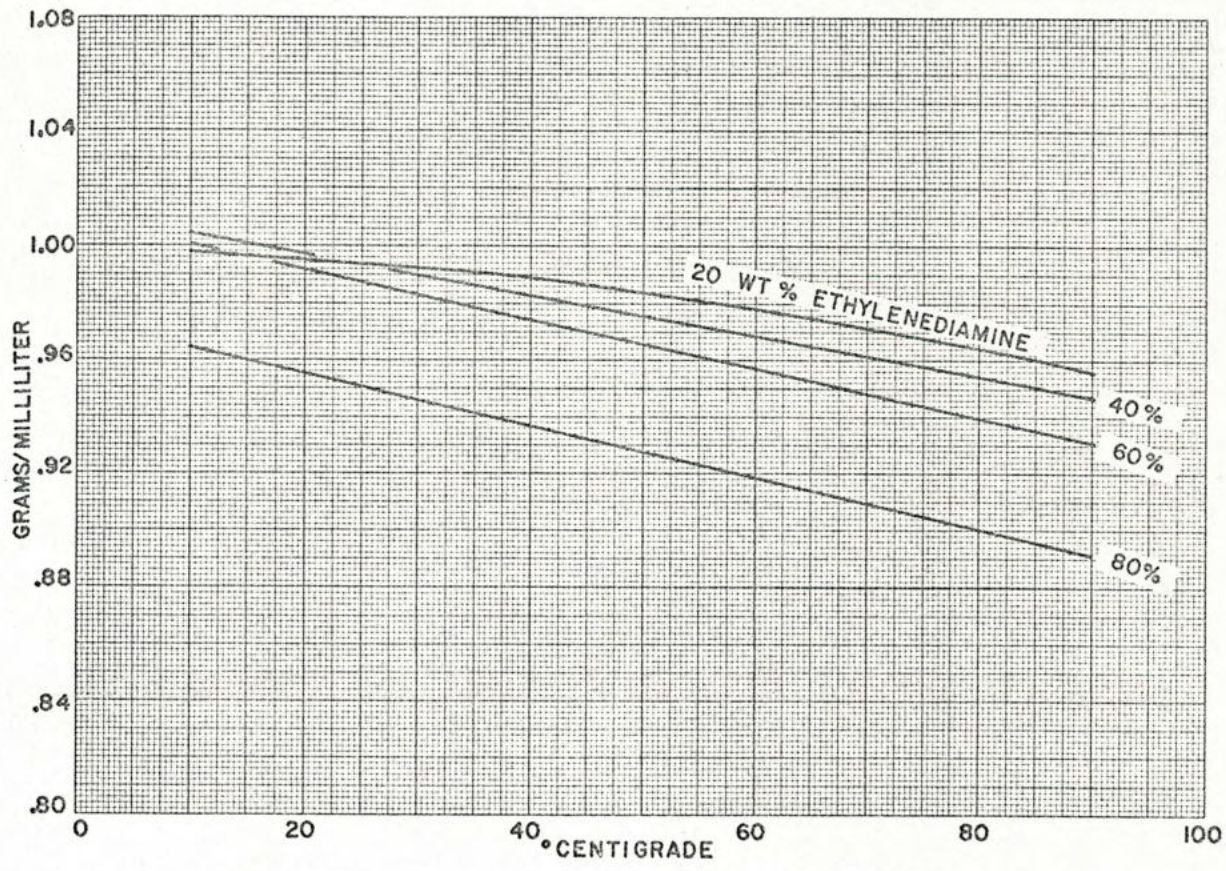


Fig. 34-6—Liquid density of aqueous ethylenediamine from 0° C to 90° C.

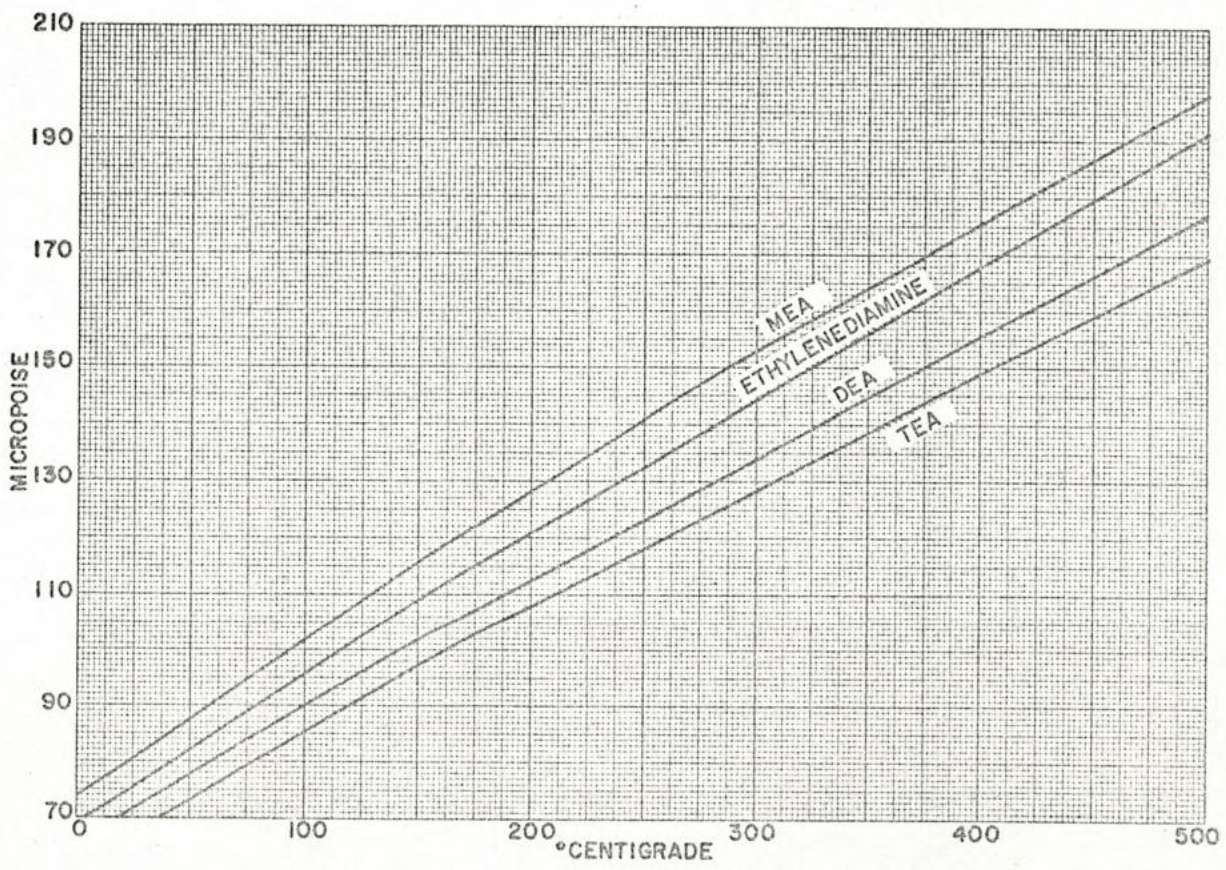


Fig. 34-7—Vapor viscosity of ethylamines from 0° C to 500° C.

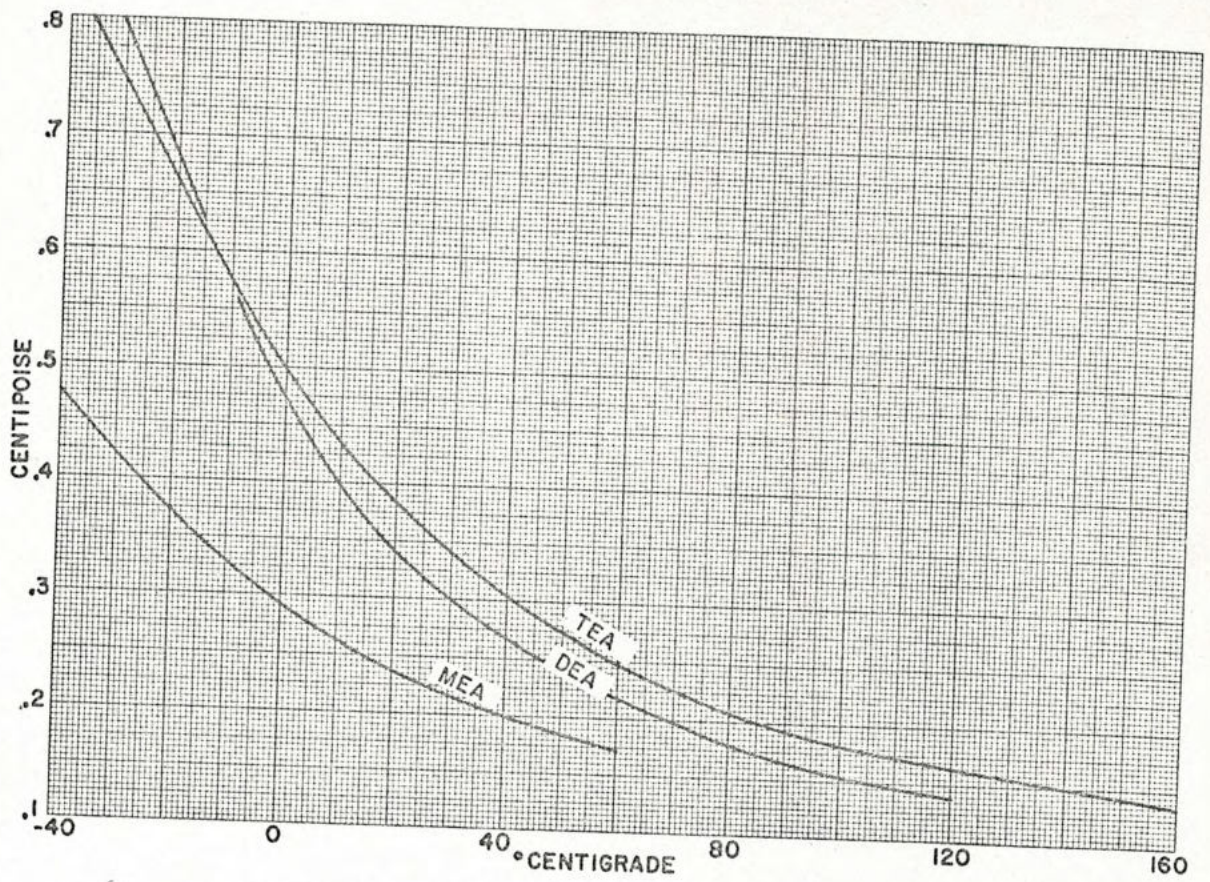


Fig. 34-8—Liquid viscosity of ethylamines from -40° C to +160° C.

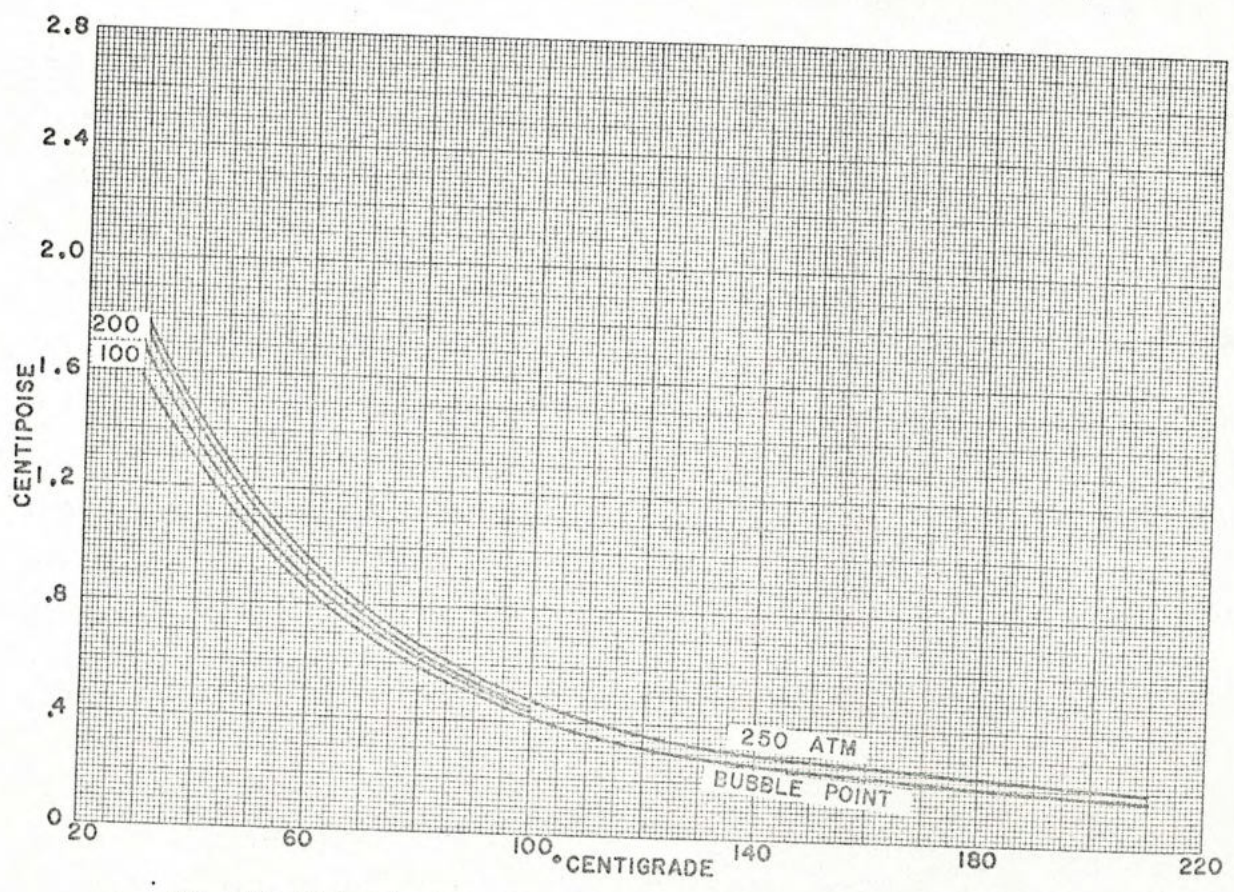


Fig. 34-9—Ethylenediamine liquid viscosity effect of pressure from 20° C to 220° C.

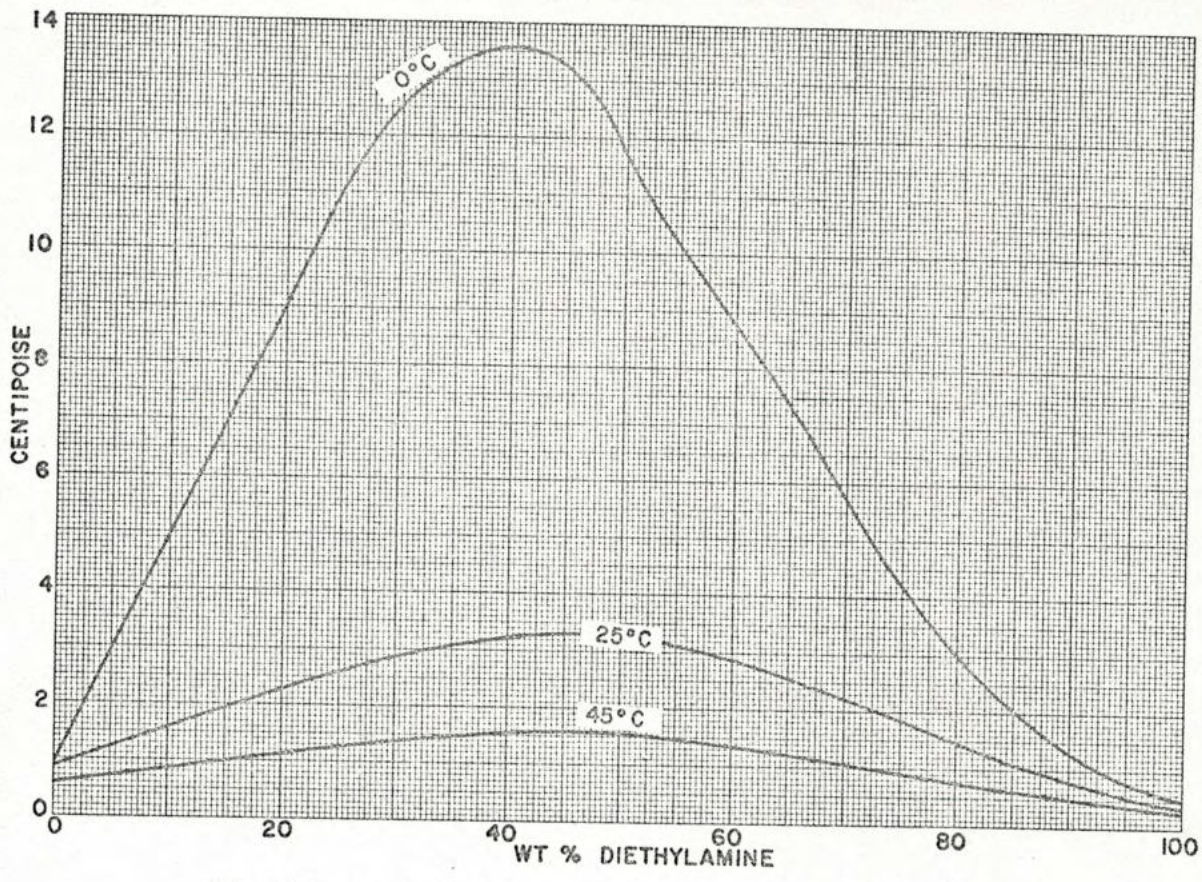


Fig. 34-10—Liquid viscosity of aqueous diethylamine from 0° C to 45° C.

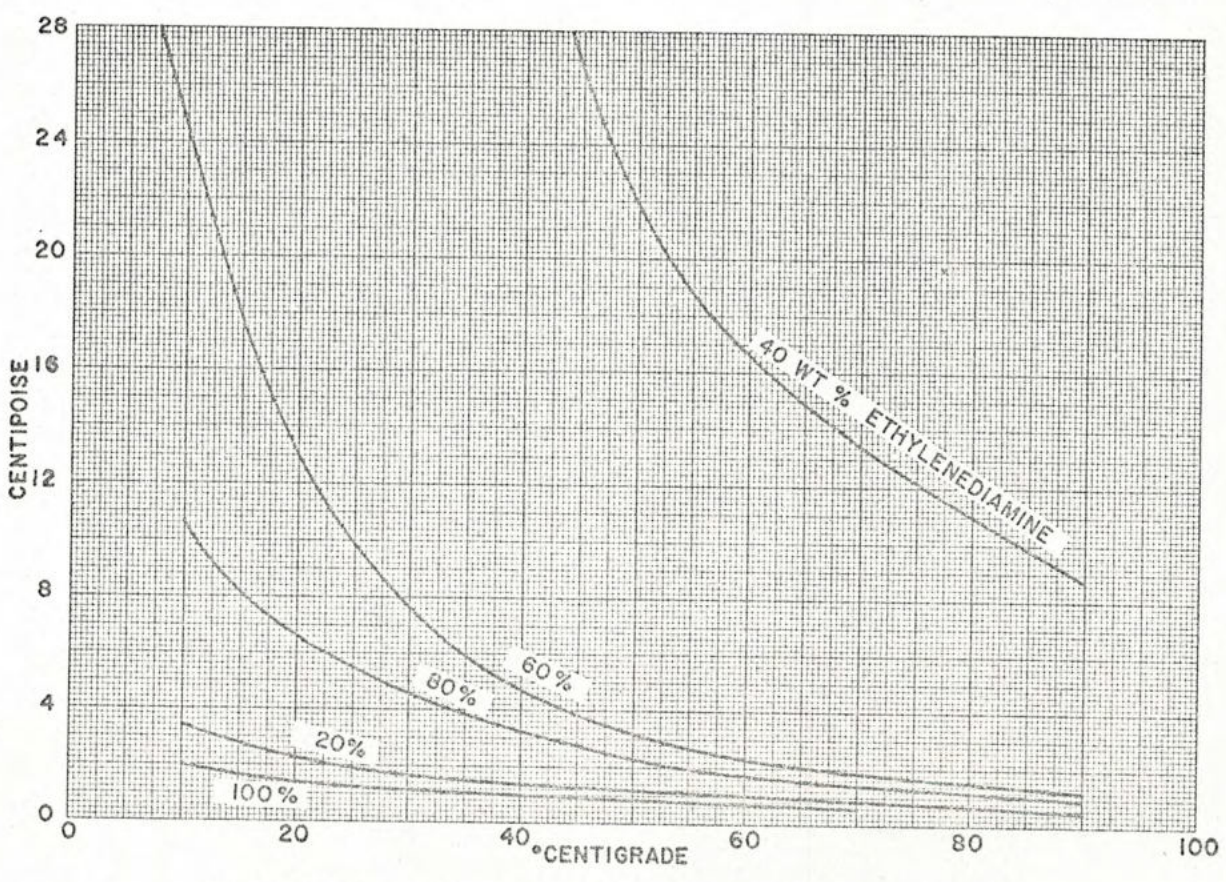


Fig. 34-11—Liquid viscosity of aqueous ethylenediamine from 0° C to 90° C.

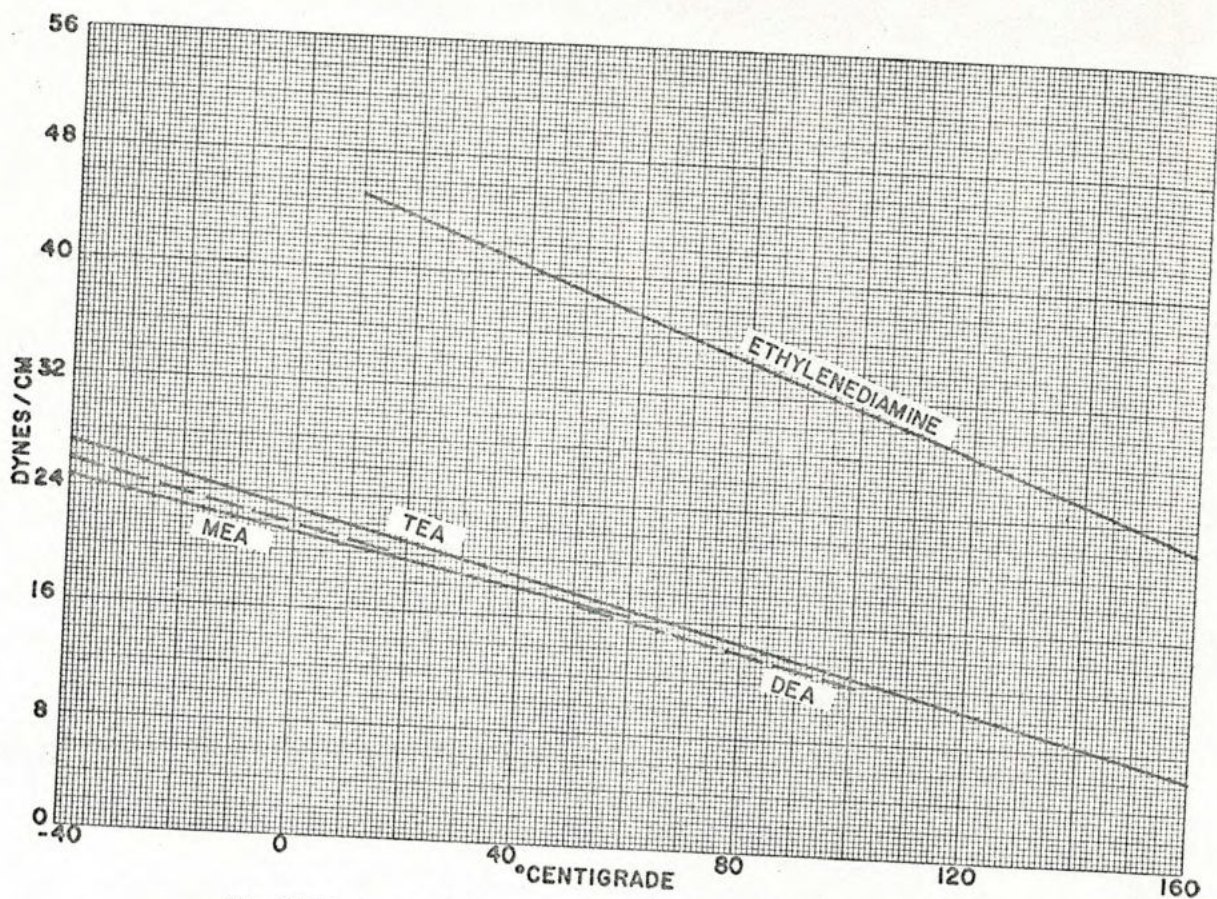


Fig. 34-12—Surface tension of ethylamines from -40°C to $+160^{\circ}\text{C}$.

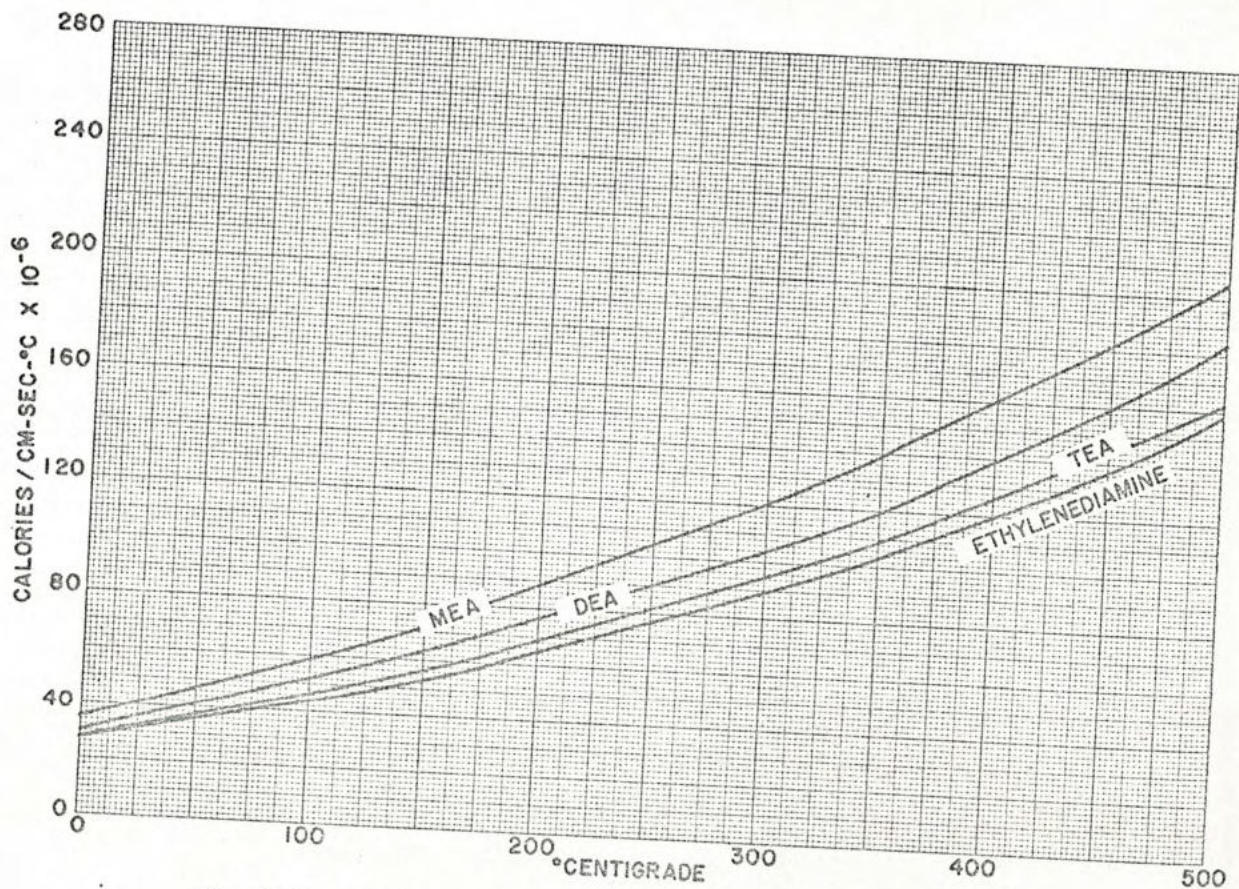


Fig. 34-13—Vapor thermal conductivity of ethylamines from 0°C to 500°C .

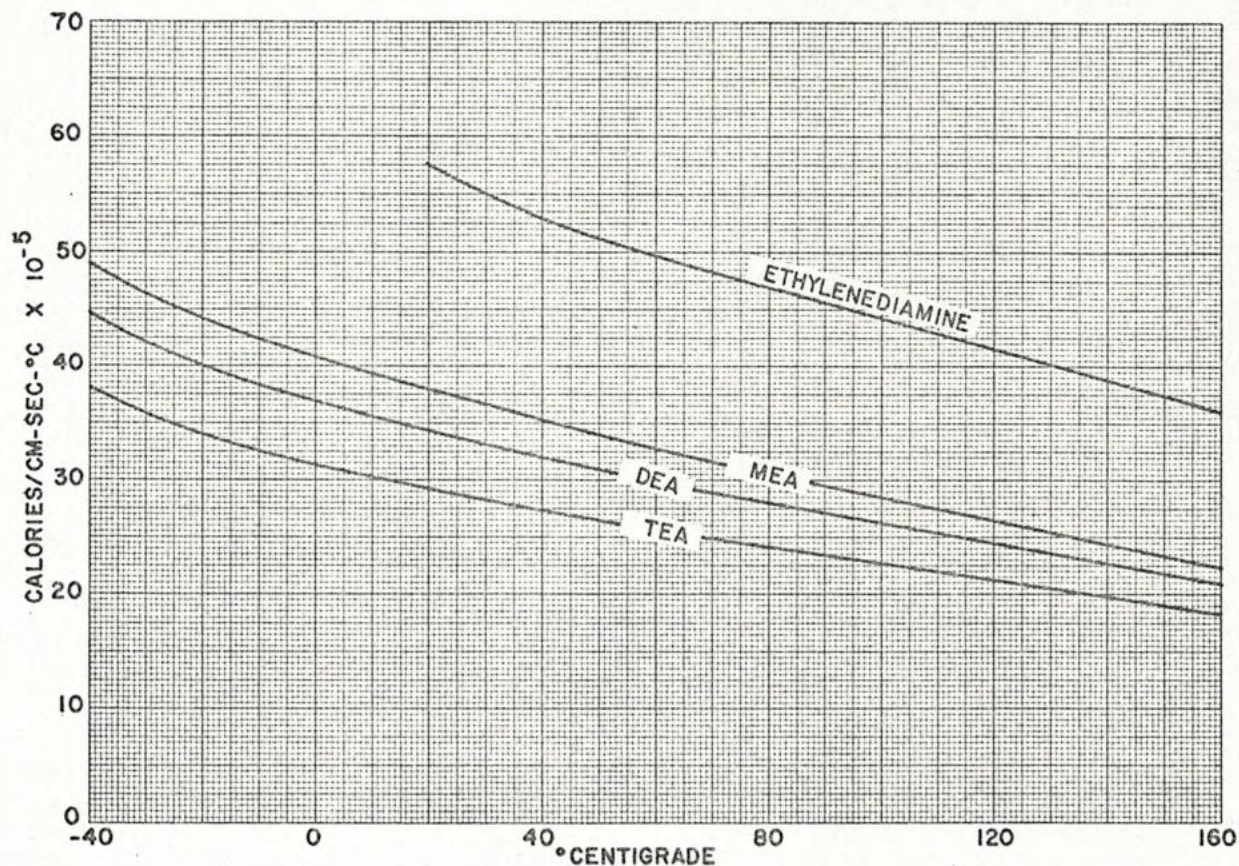


Fig. 34-14—Liquid thermal conductivity of ethylamines from -40° C to +160° C.

Barfield has measured the aqueous solution viscosities of diethylamine.¹¹ These data are presented in Fig. 34-10.

Mason has studied the effect of pressure on the liquid viscosity of ethylenediamine.¹² Fig. 34-9 shows these results. As can be seen from the graph, viscosity is only slightly affected by pressure. At 250 atmospheres, the viscosity is only about 10 percent higher than the viscosity at atmospheric pressure.

Fig. 34-11 shows the effect of temperature on the aqueous solution viscosities of ethylenediamine.⁹

Surface Tension. The surface tension has been measured from -74° C to +35° C for ethylamine,^{8,13} from 10° to 56° C for diethylamine,^{8,13} and from 0 to 90° C for triethylamine.^{8,13} These data have been extended from -40° C to +160° C by the equation relating surface ten-

sion to density, molecular weight, and parachor.¹⁴ This method was used to calculate the entire curve for ethylenediamine.

Thermal Conductivity. Vines and Bennett have measured the vapor thermal conductivities of diethylamine and triethylamine from 80° to 150° C.¹⁵ The method of Owens and Thodos was used to calculate the vapor thermal conductivities over the 0-500° C range.¹⁶

The liquid thermal conductivities were calculated by the method proposed by Robbins and Kingrea.¹⁷

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Indexing Terms: Computations-4, Ethylamine-9, Ethylenediamine-9, Diethylamine-9, Heat-7, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Temperature-6, Triethylamine-9, Vapor Phase-3.

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