Physical Properties of Hydrocarbons

Part 13—Ethylene Glycols

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As ONE OF THE EARLY MEMBERS of the petrochemical "billion pound per year club," ethylene glycol must be ranked as a major basic product of the chemical industry. Of the one and one-half billion pounds produced in 1965, almost 80 percent went into antifreeze. The remainder went largely into plasticizers, solvents, and glycol ethers. Diethylene glycol and triethylene glycol started out as unwanted byproducts of ethylene glycol production but have achieved a sizable market of their own as antifreeze additives, solvents, and plasticizers.

Probably no petrochemical can claim as many major producers as the ethylene glycols. The list of 11 producers include such giants as The Dow Chemical, Union Carbide, DuPont, and Allied Chemical. With more than adequate capacity, a slow growth rate, and no promising new outlets, ethylene glycol producers find themselves hoping that the future holds no revolutionary changes such as automobiles that do not need antifreeze or a new nonglycol antifreeze.

Because the ethylene glycols have been major products for a number of years, their physical properties have been extensively studied. Special attention has been given to the physical properties of the aqueous solutions since the glycols are generally encountered diluted in water. Experimental aqueous solution data have been included in the graphs in this article. A book on the manufacture and uses of glycols includes an excellent compilation of physical property data on ethylene glycol.[1] In addition, several product bulletins by producers contain extensive physical property data on all three ethylene glycols.[2,3]

Critical Properties. None of the critical properties of the ethylene glycols has been experimentally determined. Critical property measurements are impossible because the glycols begin decomposing even below their boiling points. Consequently, the critical property data presented in Table 13-1 have been estimated by the method proposed by Lydersen.[4] The error is probably ±5° C on the critical temperature; ± 60 psi on the critical pressure; and ± 0.01 grams/milliliter on the critical density.

Vapor Pressure. Because of decomposition, the vapor pressures of the ethylene glycols have not been determined above their boiling point. Commercially, plant distillations are carried out under high vacuum. Figures 13-1, 13-2 and 13-3 present the vapor pressure data up to 240° C for both the pure compounds and the aqueous solutions.[1,2,3]

Heat of Vaporization. Experimental data for ethylene glycol are available up to the boiling point.[1,5] The data were extended to the crticial temperature by use of the Watson equation.[4] The calculated values gave an average error of 1.3 percent when compared to four experimental values. The limited experimental data for diethylene glycol[3,6] and triethylene glycol[3] were also extended over the temperature range by the Watson equation.

Heat Capacity. There are no experimental vapor heat capacity data. Consequently, the method of Rihani and Doraiswamy[7] has been used. Although the method has not been tested on glycols, it gives excellent results on alcohols and ethers and should give equally good results on glycols since it is based only on the molecular structure.

The aqueous heat capacity of all three ethylene glycols

TABLE 13-1—Critical Property Data for Ethylene Glycols

	Boiling Point, °C	Melting Point, °C	Molecular Weight	Critical Properties °C T_c	psia P_c	g/ml d_c
Ethylene Glycol	197.3	−13.0	62.07	374*	1120*	0.333*
Diethylene Glycol	244.8	− 8.5	106.12	407*	680*	.336*
Triethylene Glycol	285.5	− 7.0	150.18	437*	486*	.337*

* Estimated.

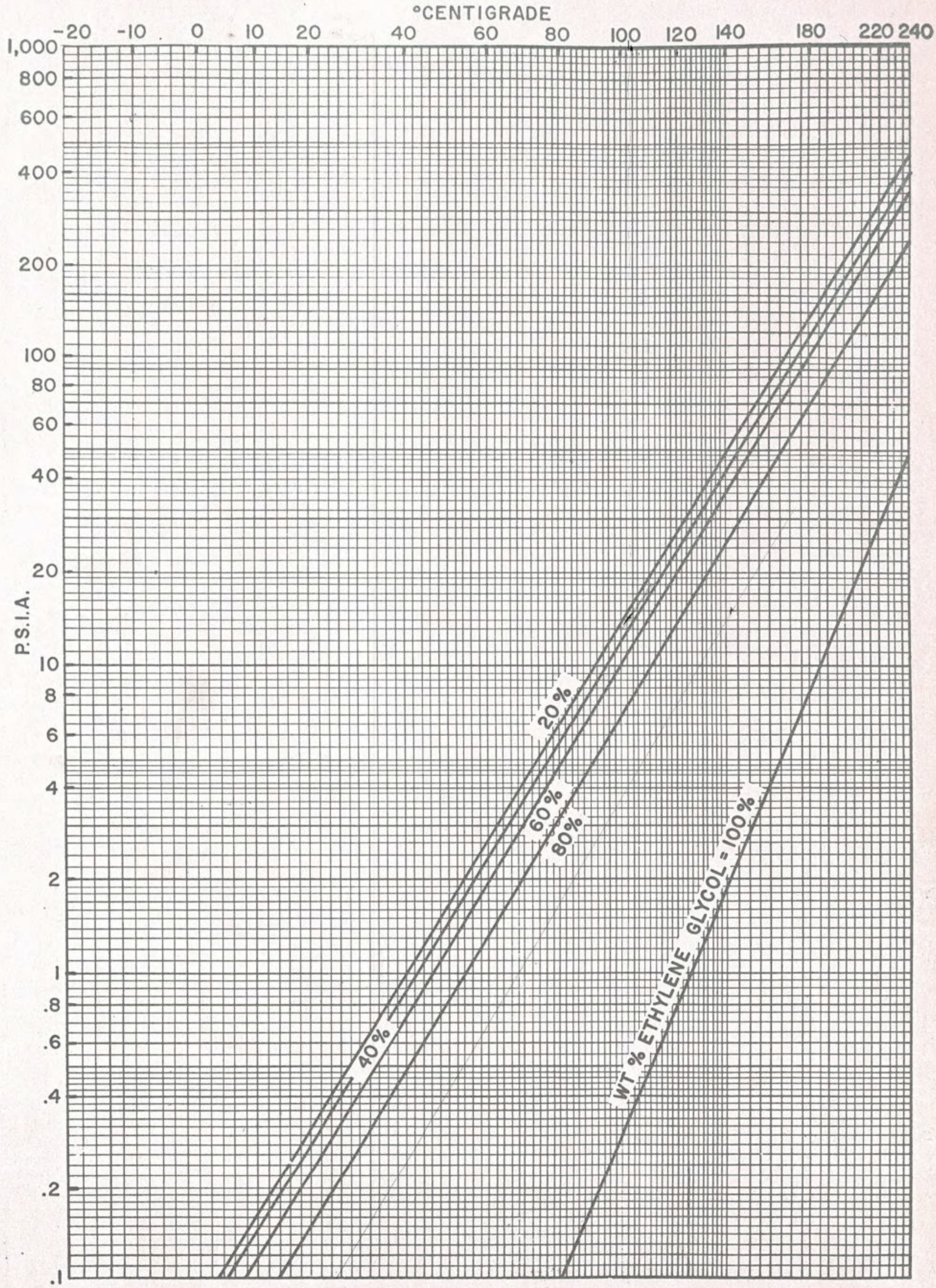

Fig. 13-1—Gives vapor pressure of aqueous ethylene glycol from 0° C to +240° C.

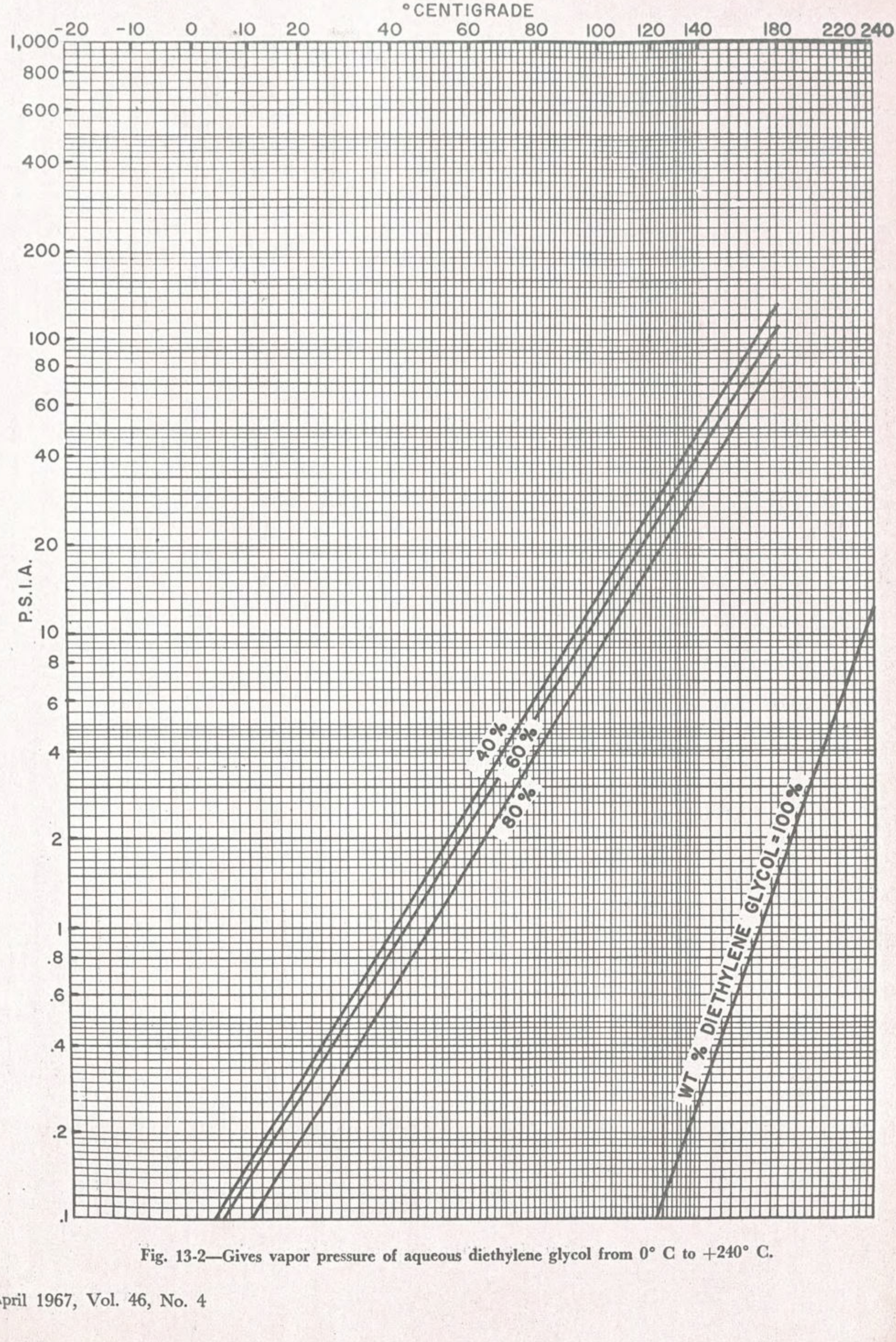

Fig. 13-2—Gives vapor pressure of aqueous diethylene glycol from 0° C to +240° C.

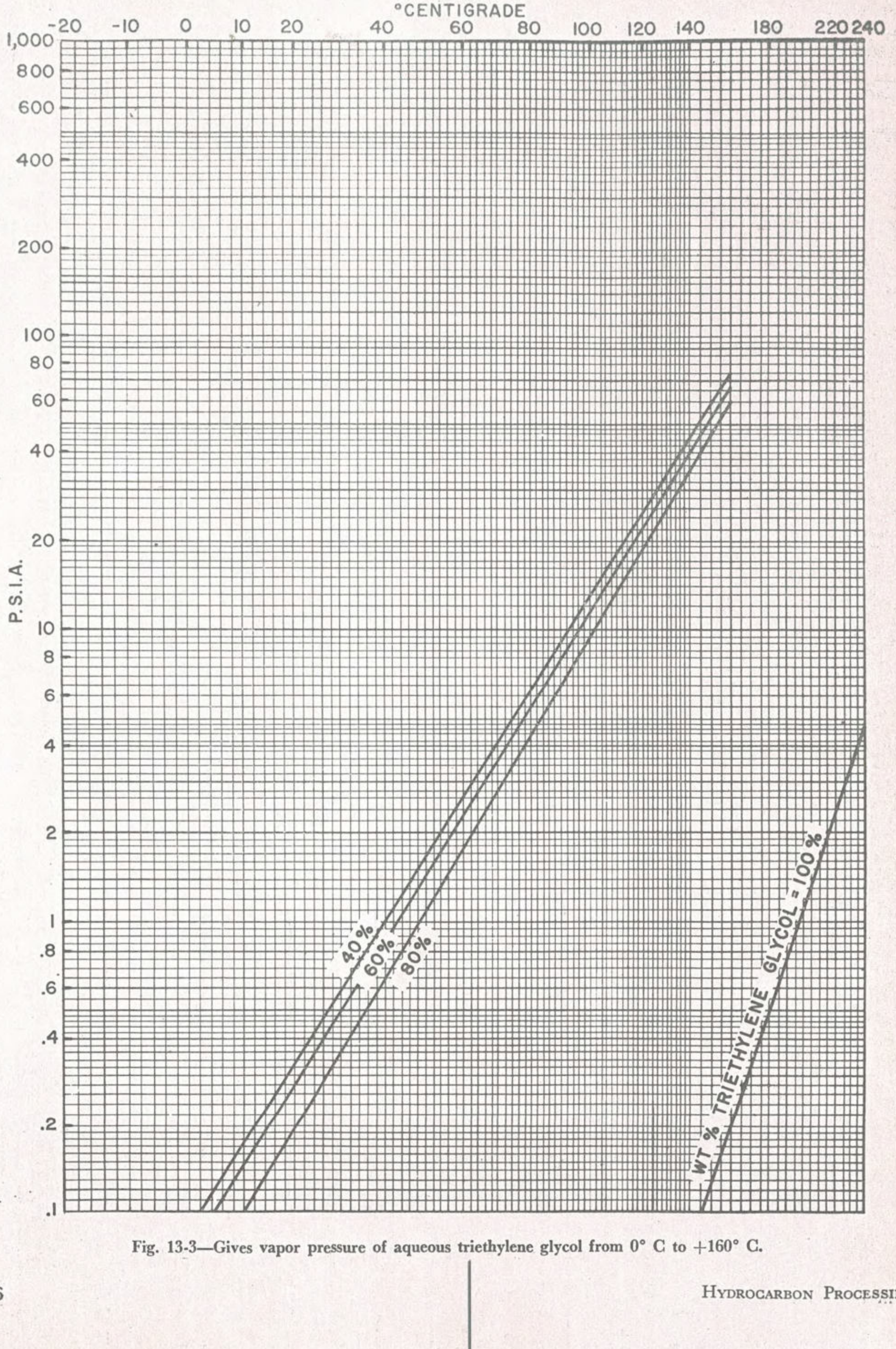

Fig. 13-3—Gives vapor pressure of aqueous triethylene glycol from 0° C to +160° C.

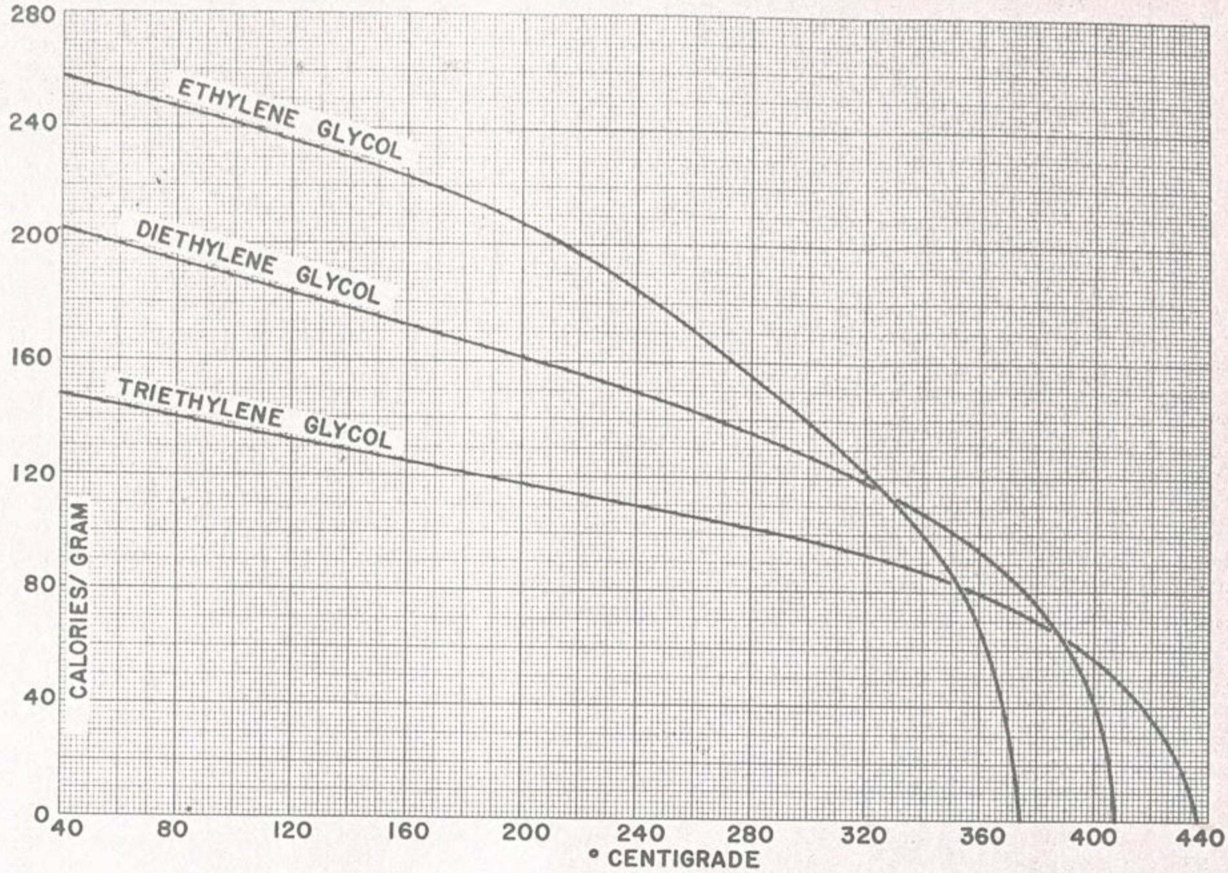

Fig. 13-4—Shows heat of vaporization of ethylene glycols from 40° C to 440° C.

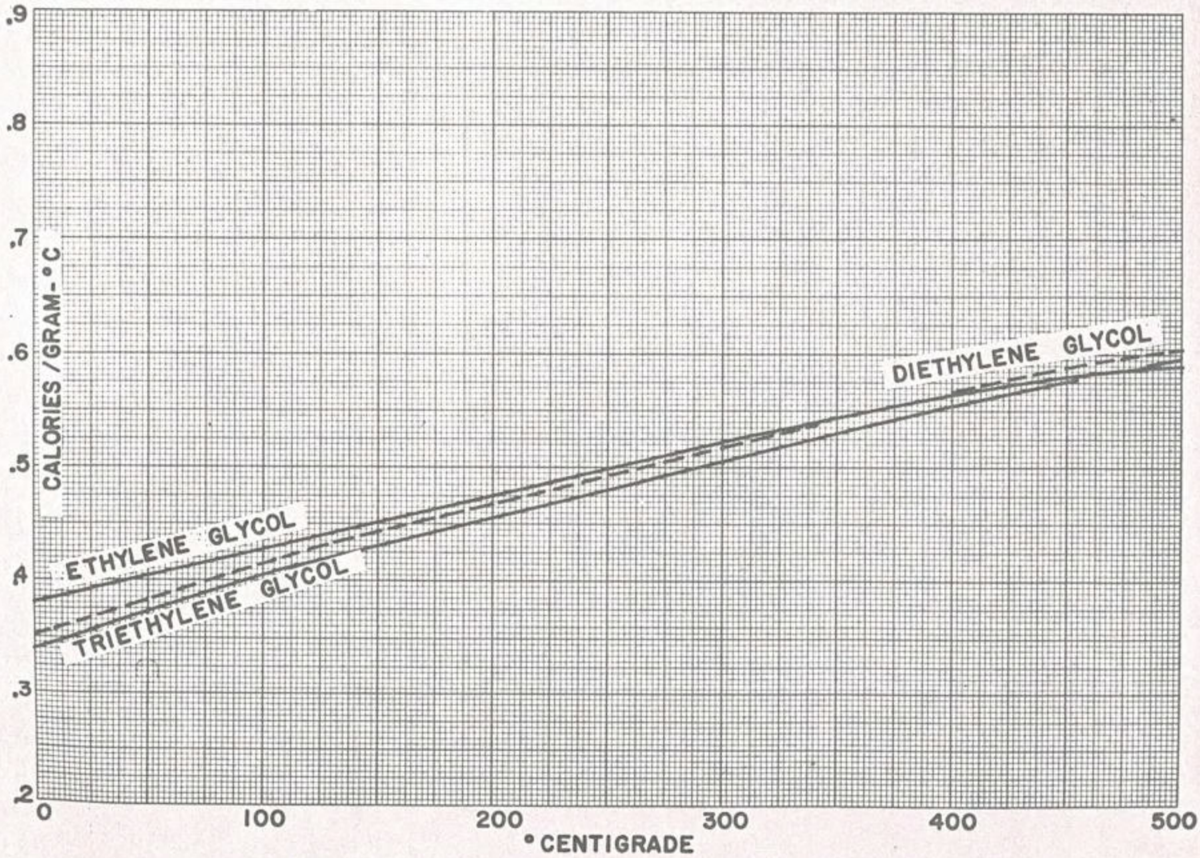

Fig. 13-5—Shows vapor heat capacity of ethylene glycols from 0° C to 500° C.

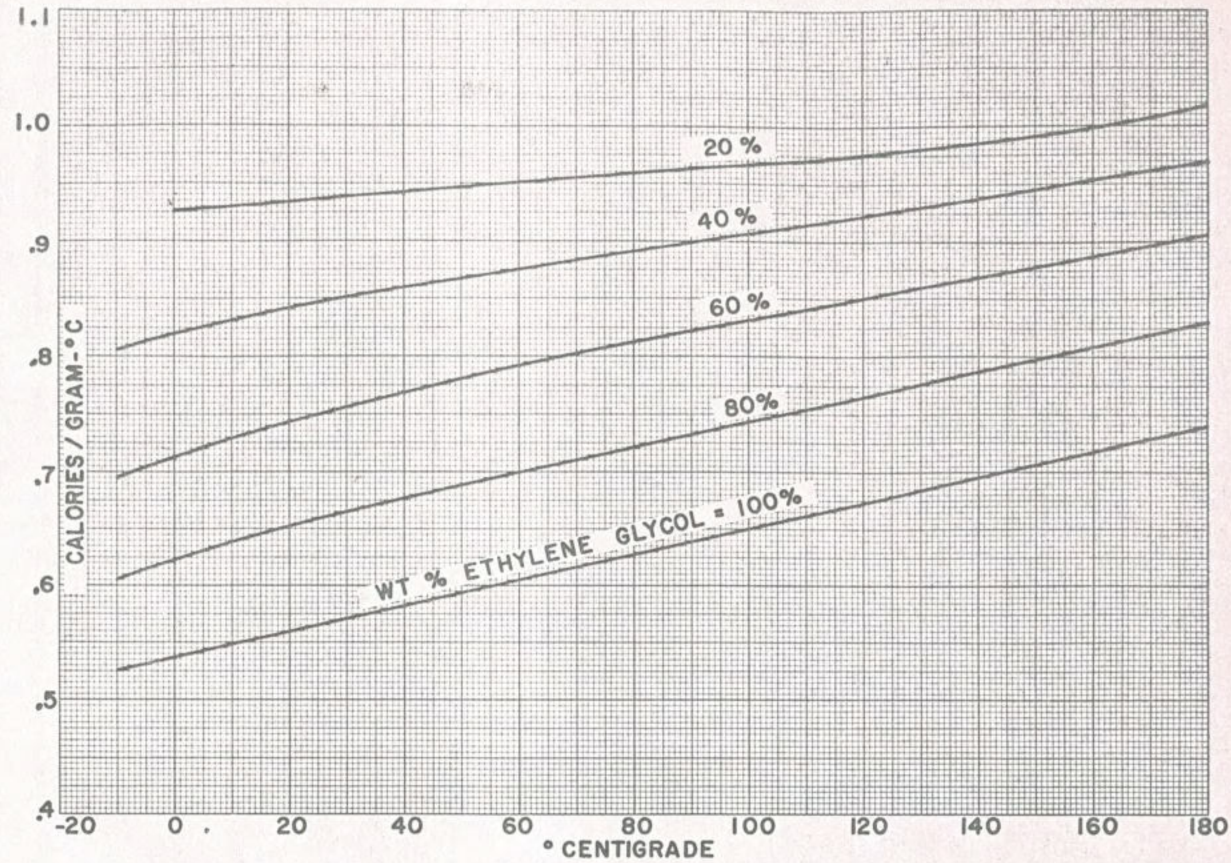

Fig. 13-6—Shows aqueous heat capacity of ethylene glycol from −10° C to +180° C.

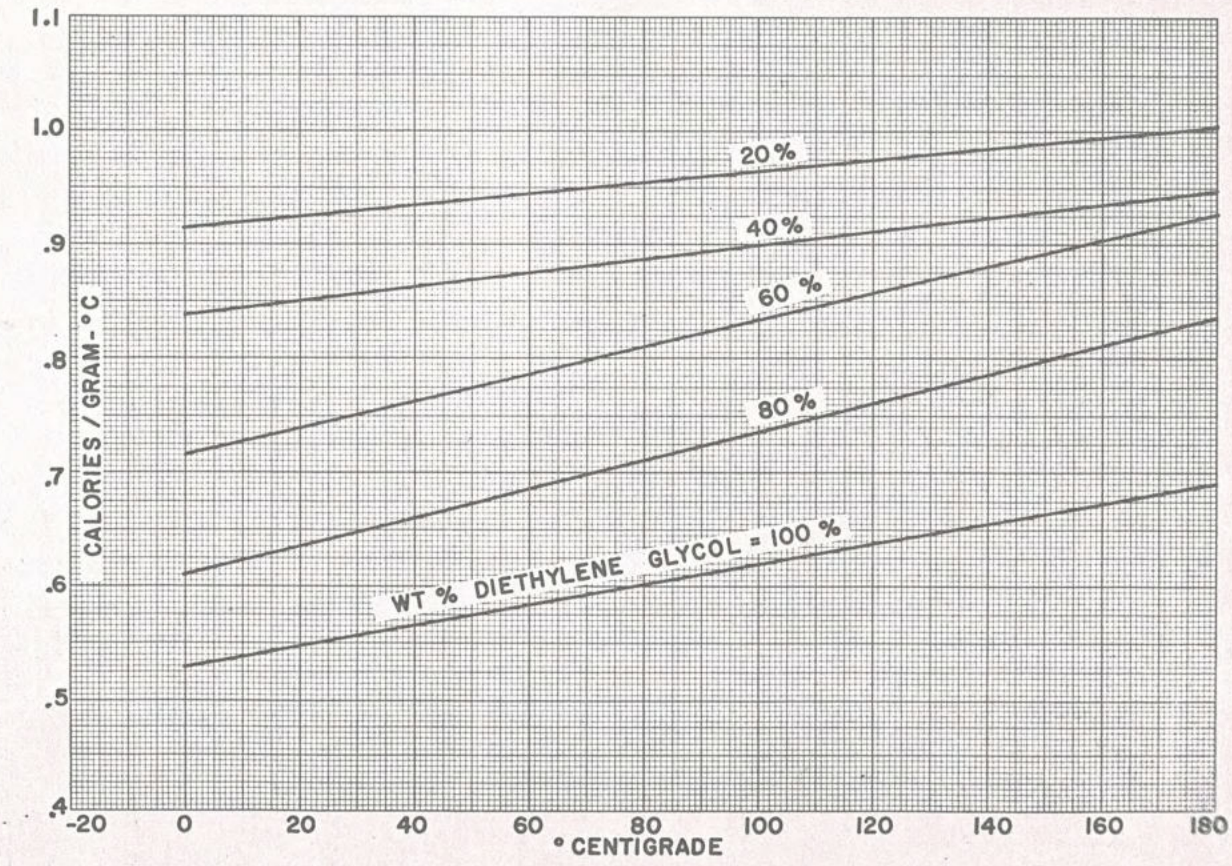

Fig. 13-7—Shows aqueous heat capacity of diethylene glycol from 0° C to 180° C.

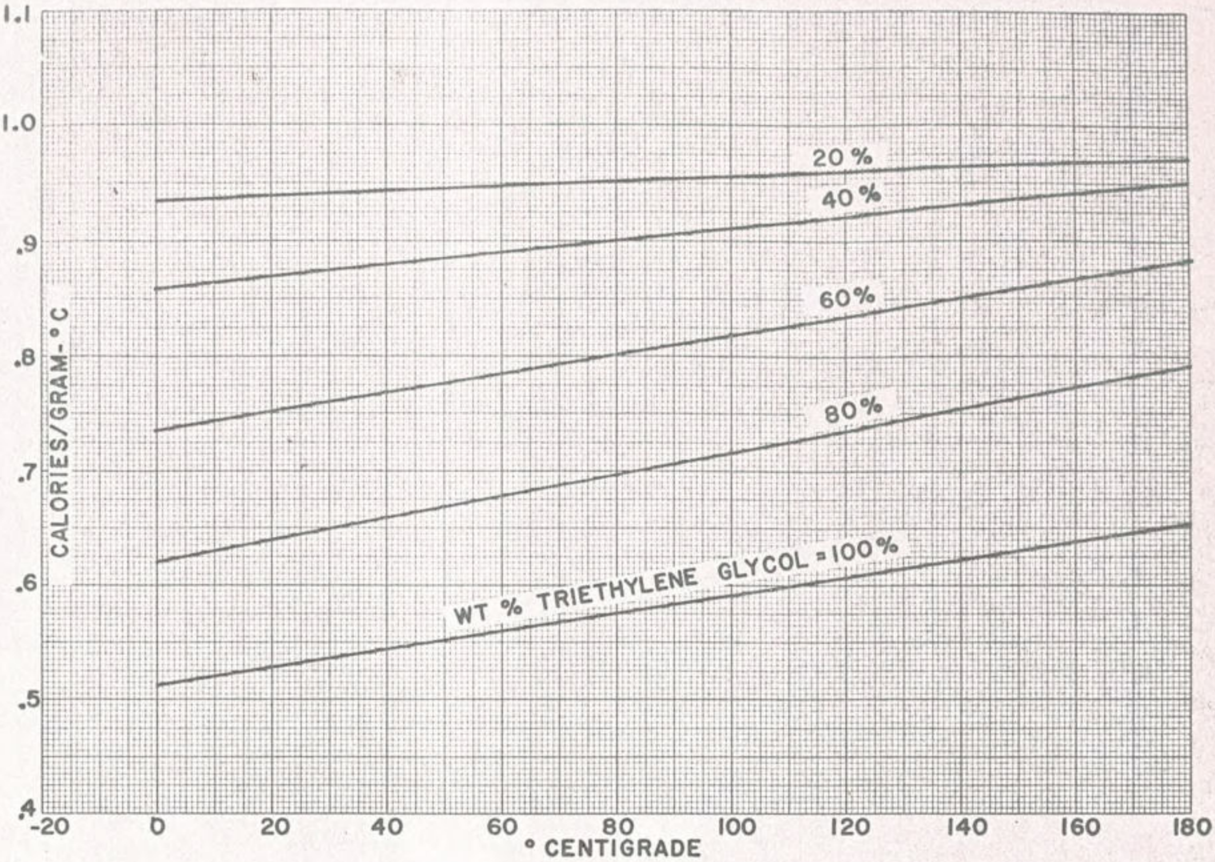

Fig. 13-8—Shows aqueous heat capacity of triethylene glycol from 0° C to 180° C.

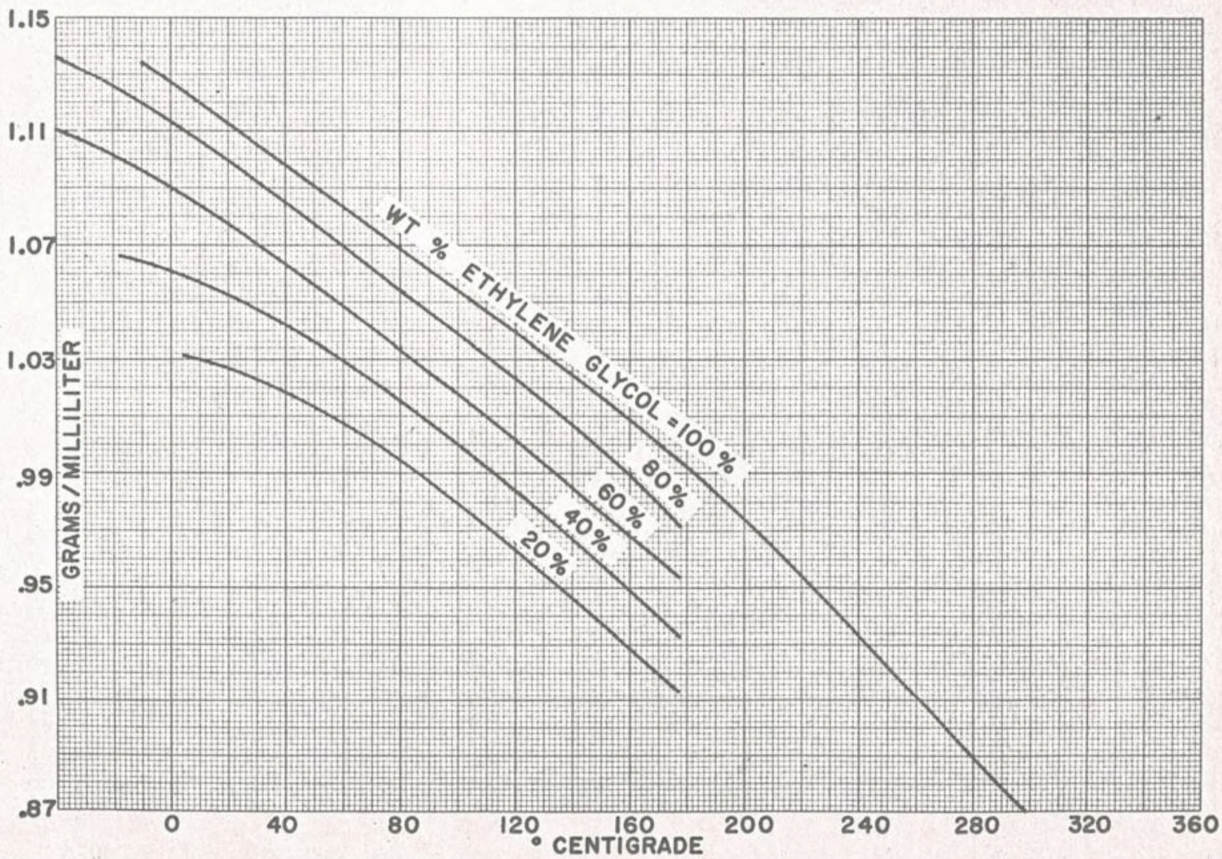

Fig. 13-9—Shows aqueous density of ethylene glycol from −40° C to +180° C.

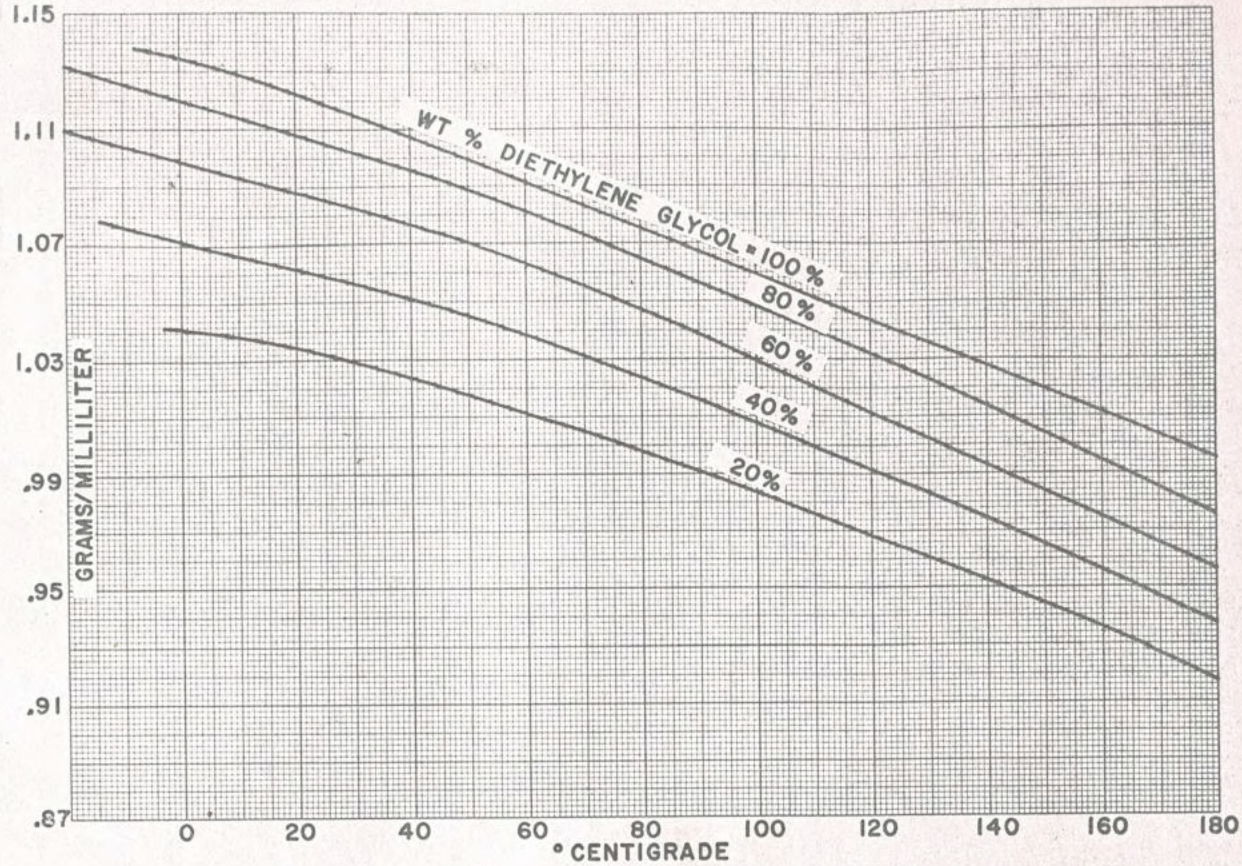

Fig. 13-10—Shows aqueous density of diethylene glycol from —20° C to +180° C.

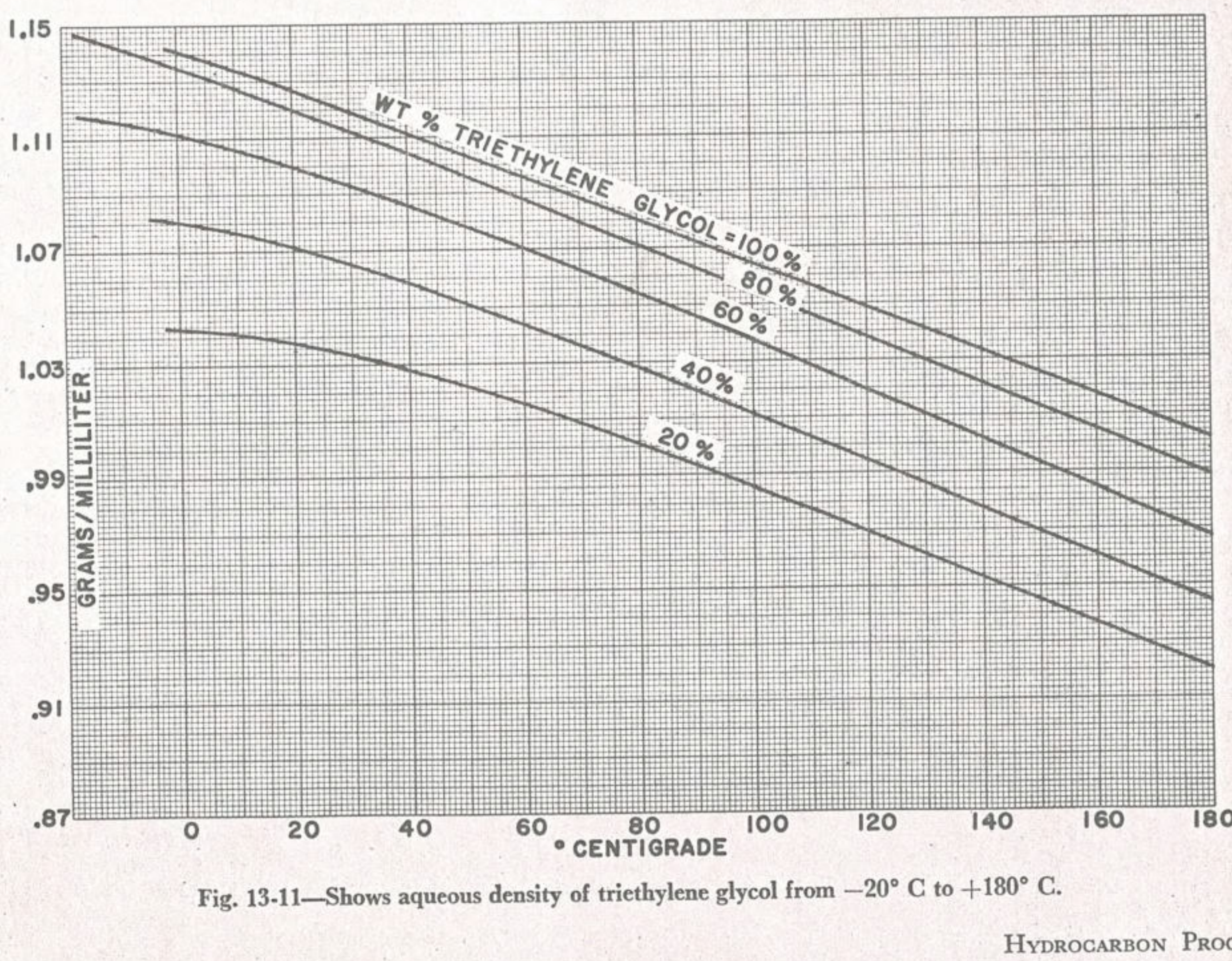

Fig. 13-11—Shows aqueous density of triethylene glycol from —20° C to +180° C.

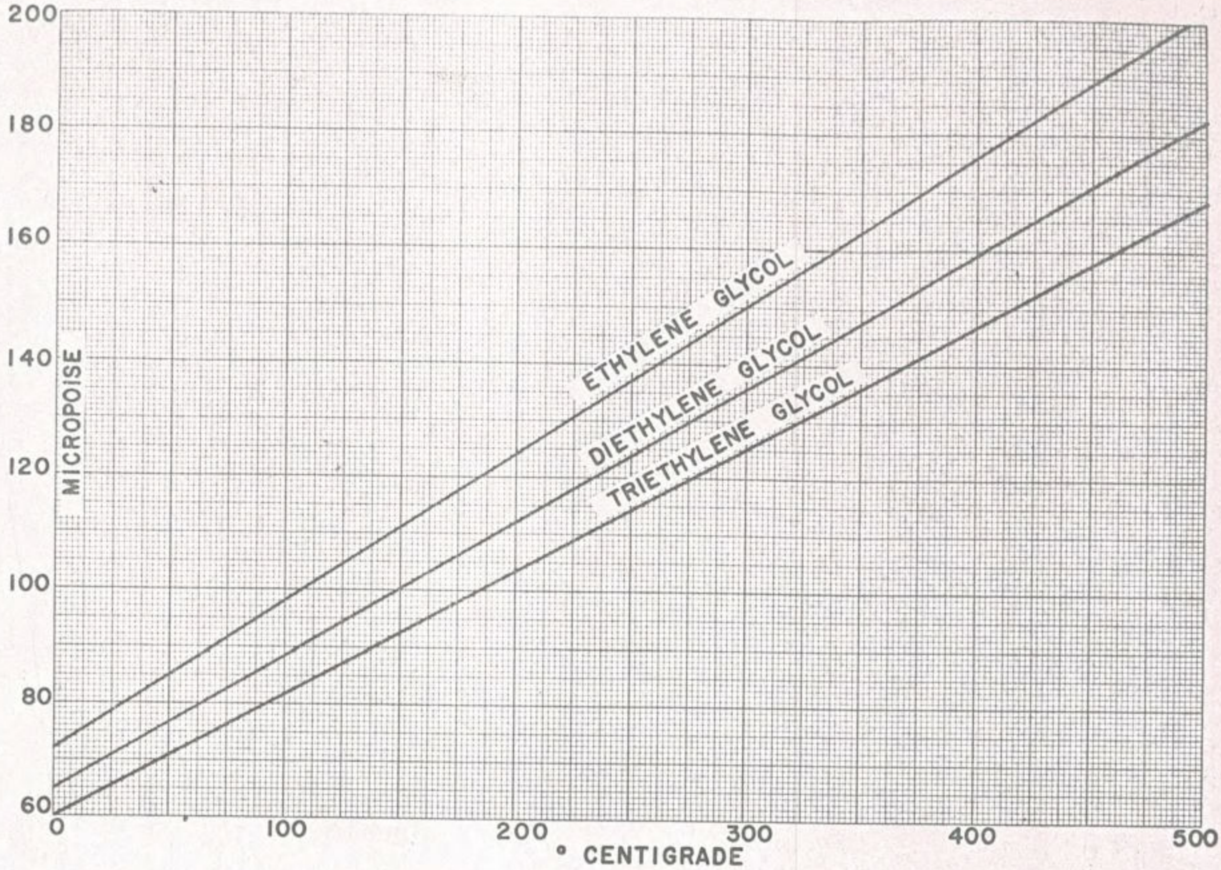

Fig. 13-12—Shows vapor viscosity of ethylene glycols from 0° C to 500° C.

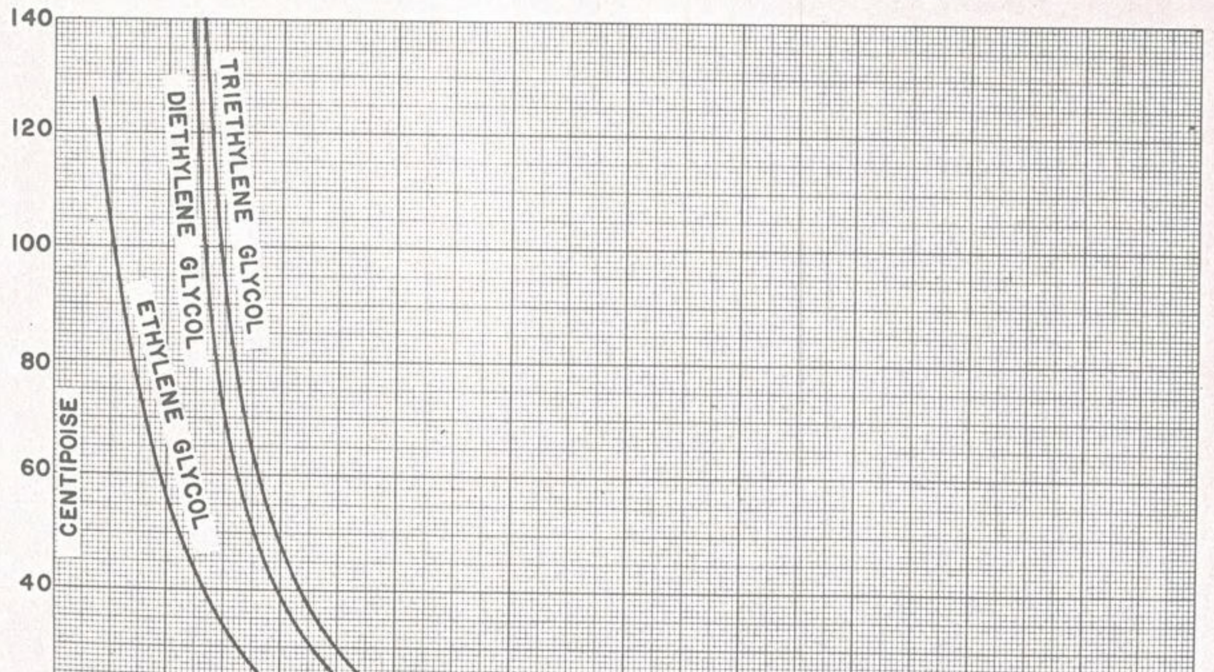

Fig. 13-13—Shows liquid viscosity of ethylene glycols from −10° C to +180° C.

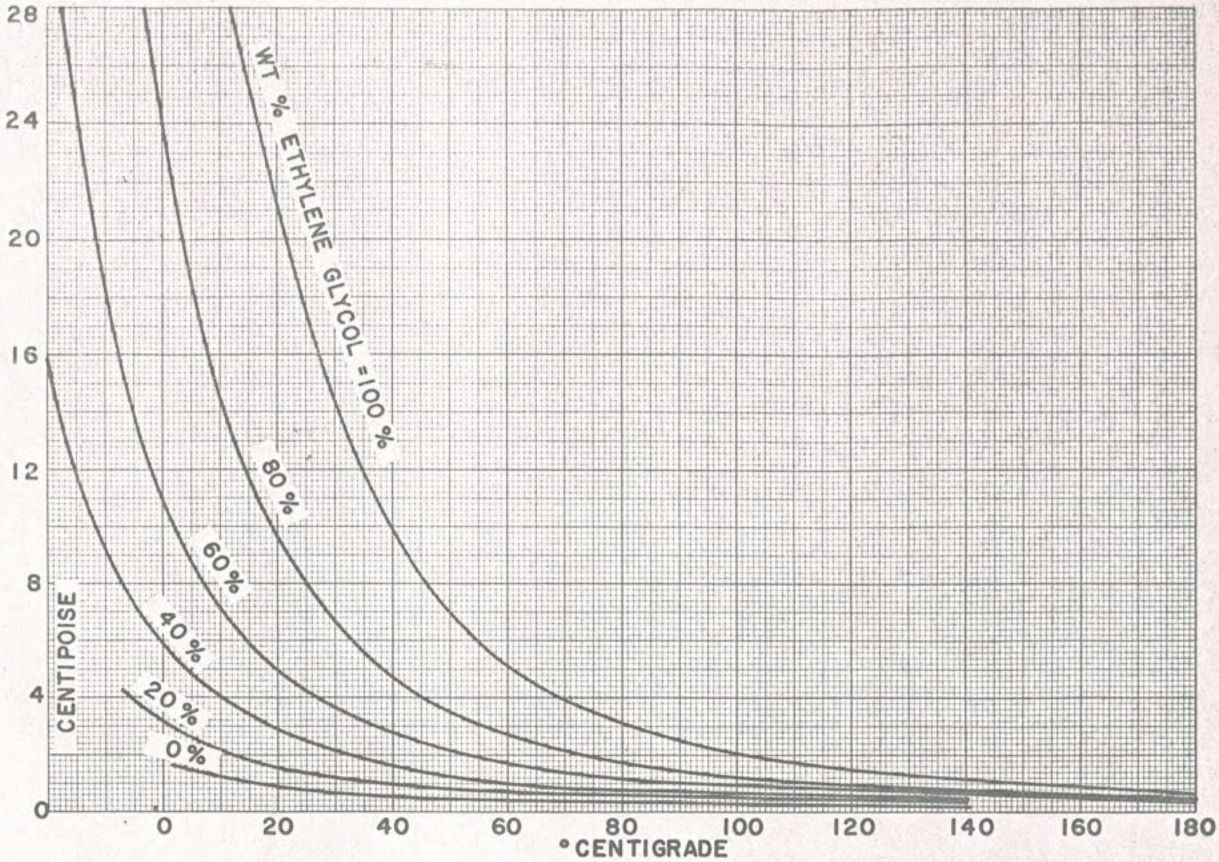

Fig. 13-14—Shows aqueous viscosity of ethylene glycol from −20° C to +180° C.

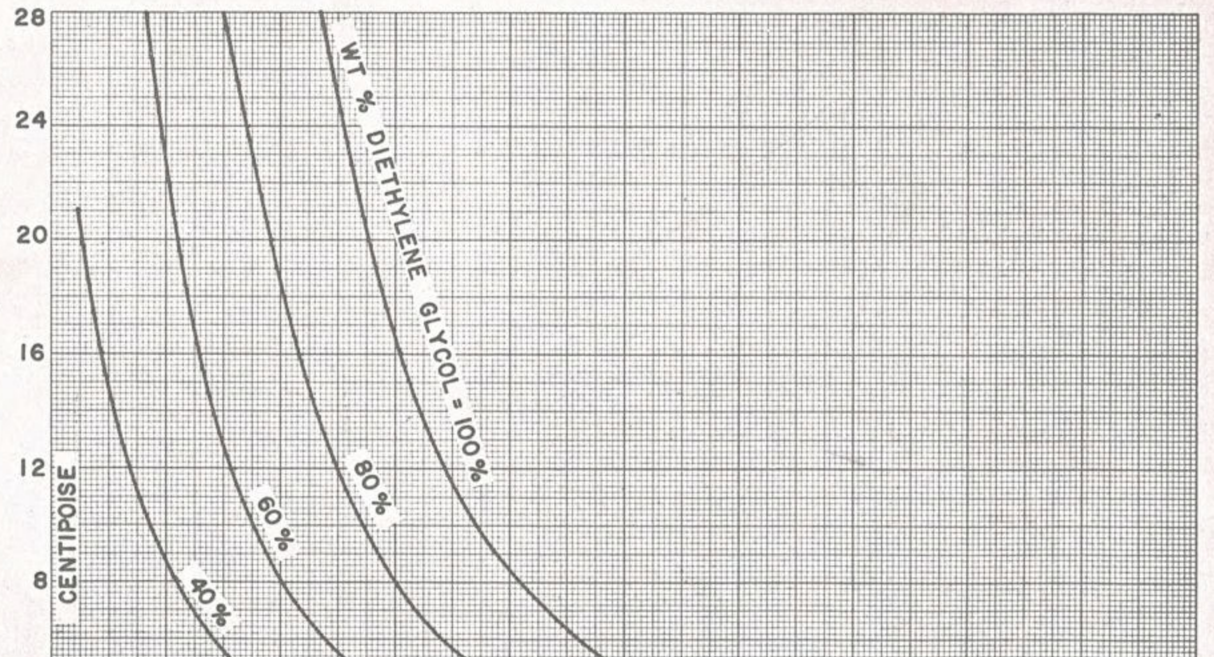

Fig. 13-15—Shows aqueous viscosity of diethylene glycol from −15° C to +180° C.

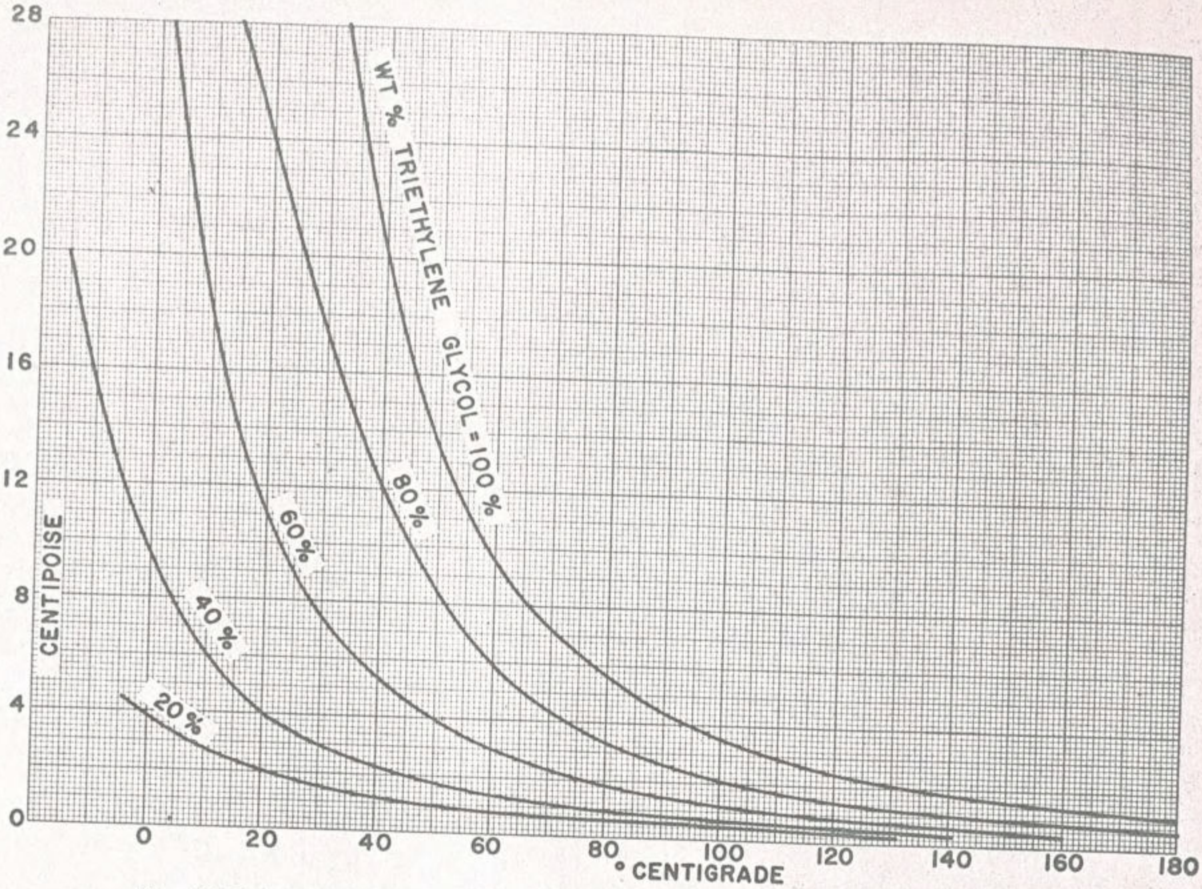

Fig. 13-16—Shows aqueous viscosity of triethylene glycol from −15° C to +180° C.

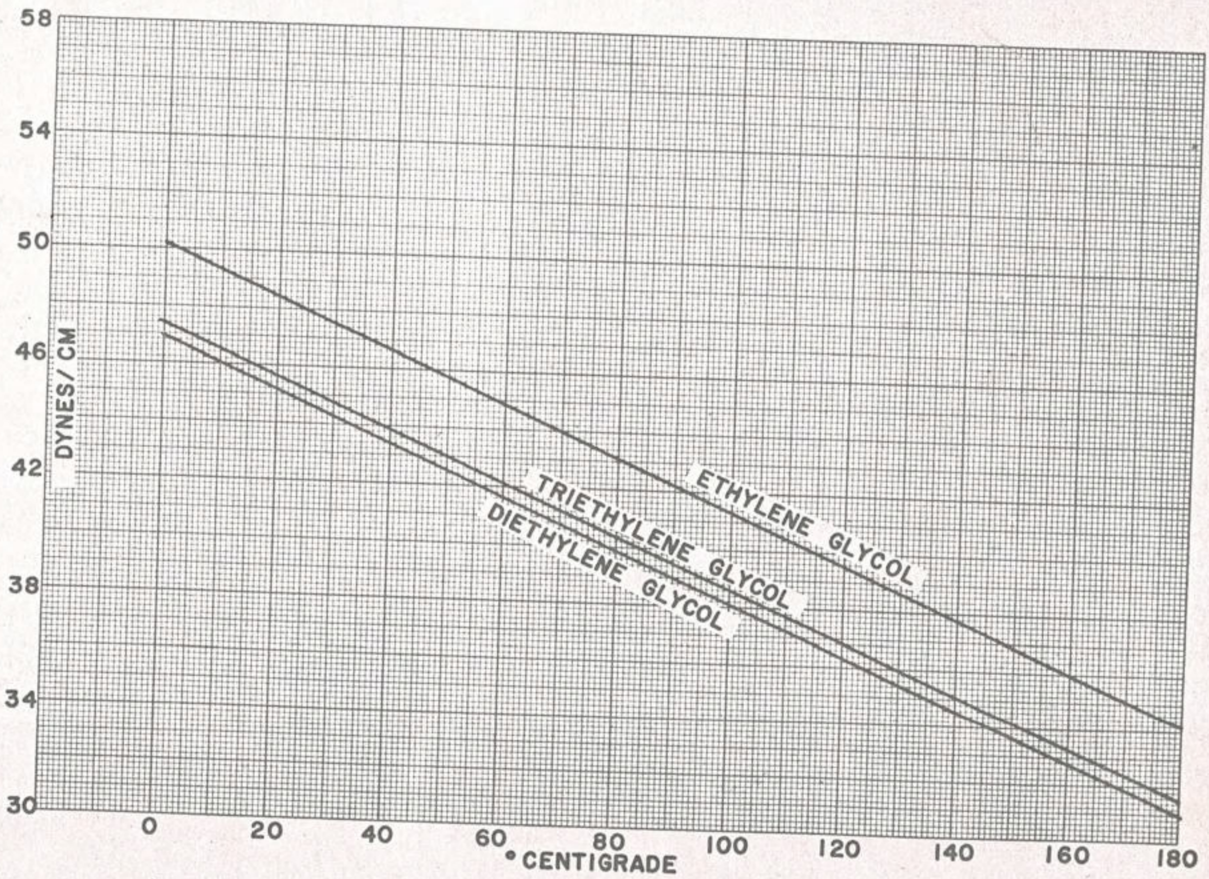

Fig. 13-17—Shows surface tension of ethylene glycols from 0° C to 180° C.

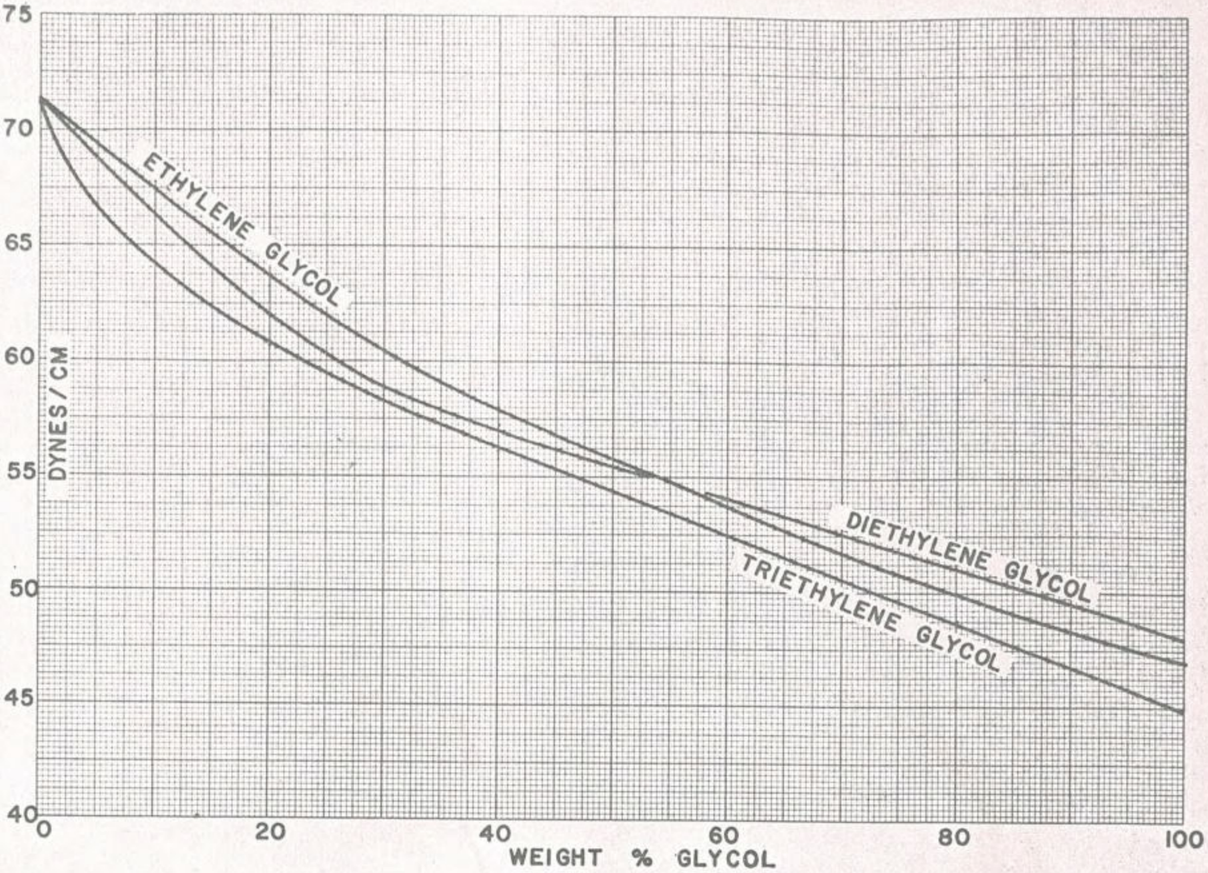

Fig. 13-18—Shows surface tension at 25° C of aqueous ethylene glycols.

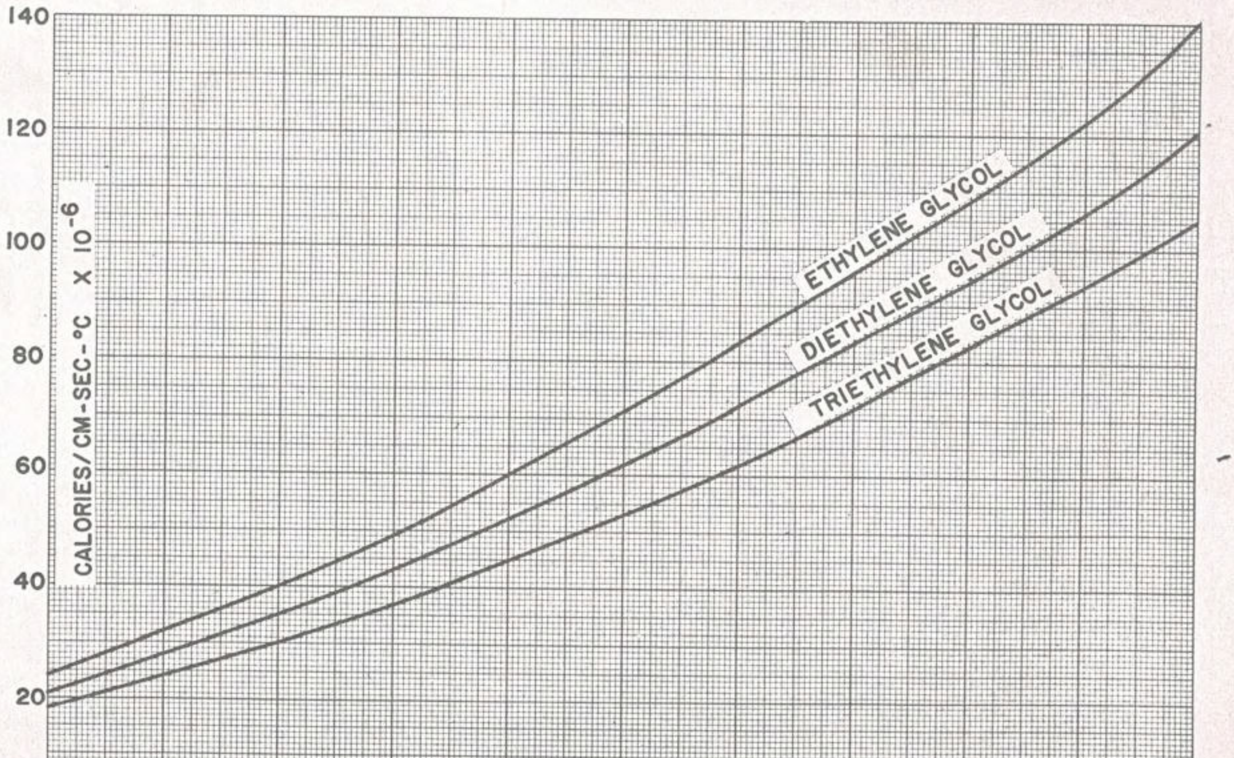

Fig. 13-19—Shows vapor thermal conductivity of ethylene glycols from 0° C to 500° C.

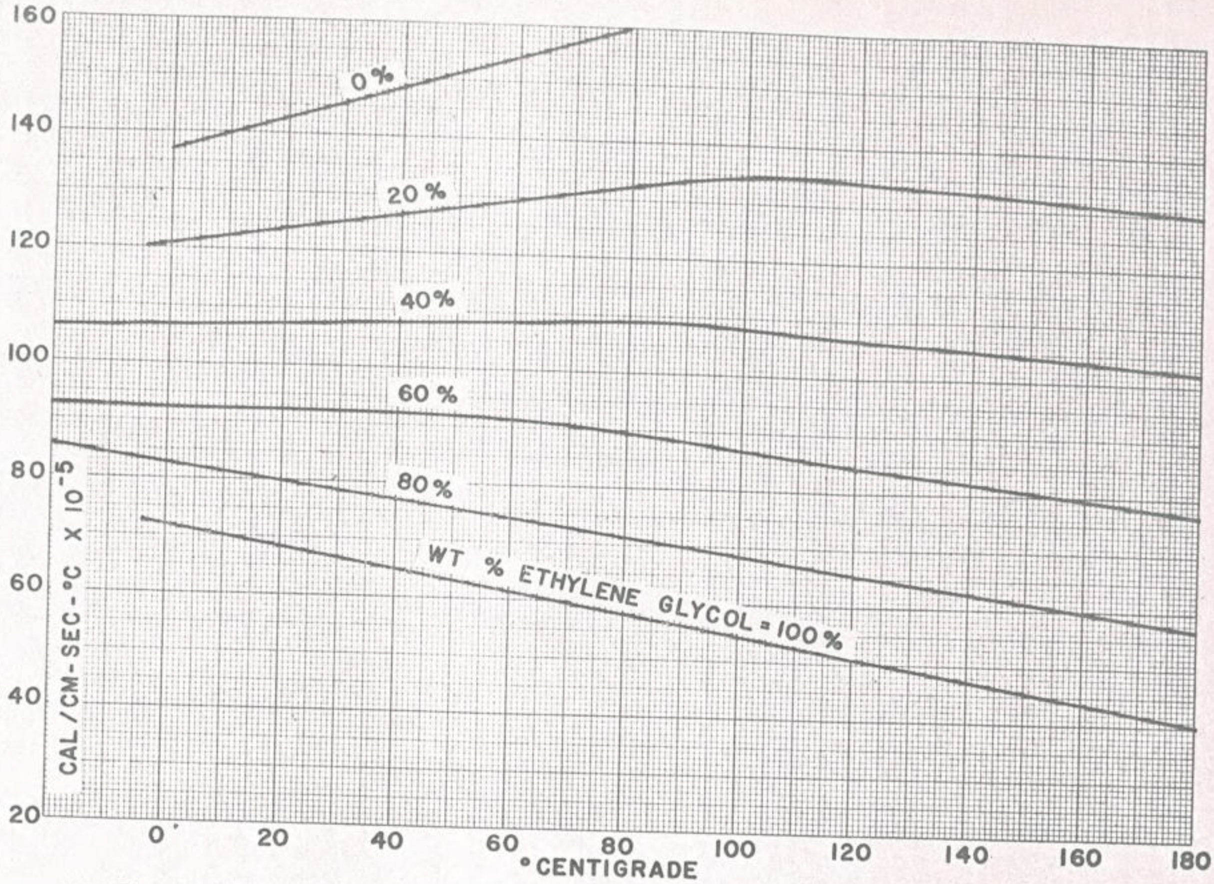

Fig. 13-20—Shows thermal conductivity of aqueous ethylene glycol from −20° C to +180° C.

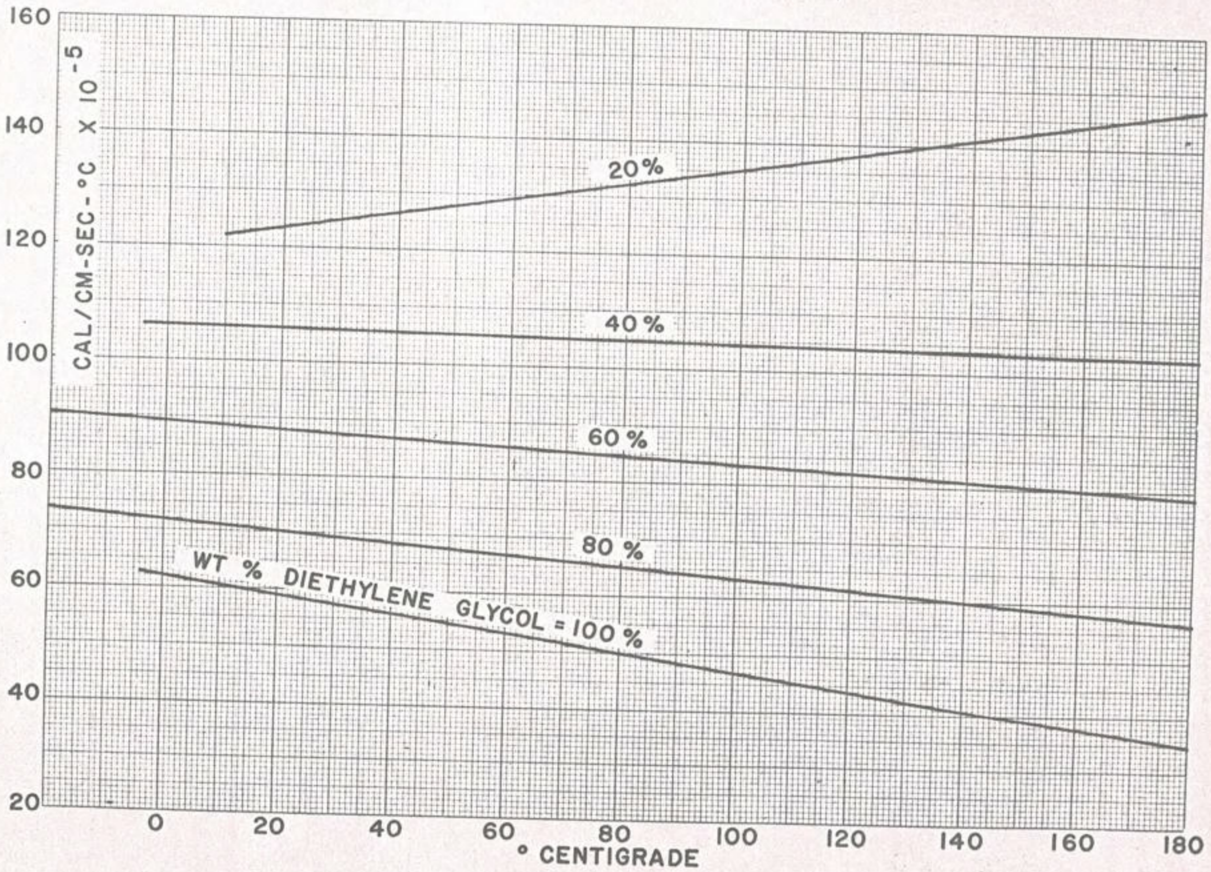

Fig. 13-21—Shows thermal conductivity of aqueous diethylene glycol from −20° C to +180° C.

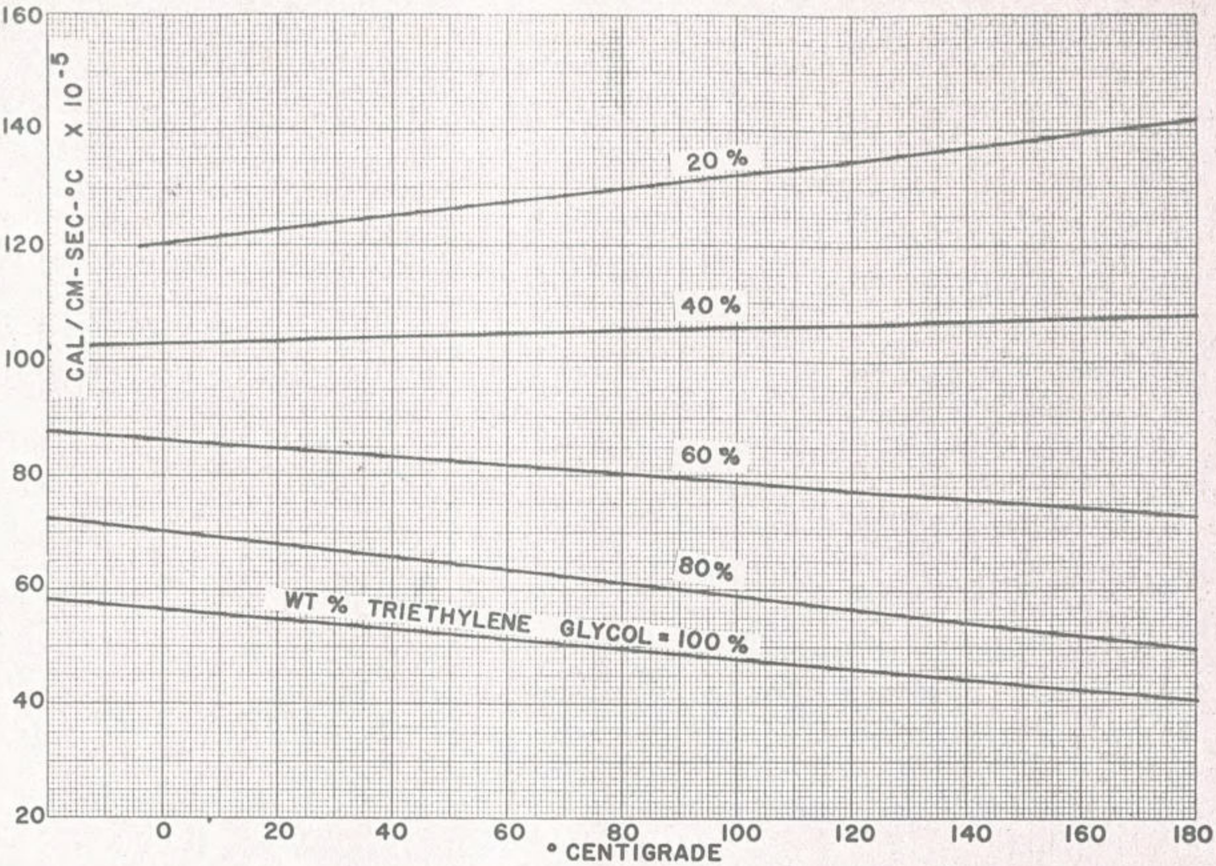

Fig. 12-22—Shows thermal conductivity of aqueous triethylene glycol from —20° C to +180° C.

has been experimentally determined[1,2] and is presented in Figures 13-6, 13-7, and 13-8 over the temperature range of —20 to +180° C.

Density. The density of pure ethylene glycol has been experimentally determined from its freezing point up to 280° C.[1,8] The densities of pure diethylene glycol, triethylene glycol and the aqueous solutions of all three glycols are available in the literature up to 180° C.[1,2,3]

Viscosity. As with the other vapor phase properties of the glycols, no experimental data are available. Consequently, the vapor viscosity has been estimated by the method of Bromley and Wilke.[4] Although the error is normally only a few percent, it should be noted that this method uses the crtical properties. Since these were also estimated, any error in estimating the critical properties will affect the accuracy of the viscosity estimation. The over-all error should still be less than 5 percent.

About the author

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Extensive data are available for the liquid viscosity of the pure glycols and their aqueous solutions.[1,2,8,9] The high viscosities of the pure glycols are an important reason for normally using the glycols as aqueous solutions.

Surface Tension. Gallaugher and Hibbert[10] have determined the surface tension of all three glycols up to 160° C. No extensive data are available on the surface tension of the aqueous solutions. However, Figure 13-18 does show the aqueous surface tension of all three glycols at 25° C.

Thermal Conductivity. The vapor thermal conductivities have been estimated by the methods of Owens and Thodos.[11] This method is also dependent on the critical properties. The error should be less than 10 percent.

The thermal conductivities of the pure compounds and their aqueous solutions are available from the literature.[1,3]

LITERATURE CITED

1 Curme, G. O., "Glycols," Reinhold Publishing Corp. (1953).
2 "Glycols: Properties and Uses," The Dow Chemical Co., product bulletin.
3 "Glycols," Union Carbide Chemicals Co. product bulletin.
4 Reid, R. C., and Sherwood, T. K., "The Properties of Gases and Liquids," McGraw-Hill Book Co., New York (1958).
5 Coolidge, A. S., *Journal of The American Chemical Society* 52, pp. 1874-1887 (1930).
6 Veneraki, I. E., *Gazoyaya Promyshlennost* 9, (3), pp. 30-32 (1964).
7 Rihani D. N. and Doraiswamy, L. K., *Industrial and Engineering Chemistry Fundamentals* 4, (1), pp. 17-21 (February 1965).
8 Costello, J. M. and Bowden, S. T., *Recueil* 77, pp. 36-46 (1958).
9 Meissner, W., *Zeitschrift Fuer Angewandte Physik* 1, pp. 75-8 (1948).
10 Gallaugher, A. F., and Hibbert, H., *Journal of the American Chemical Society* 59, pp. 2514-21 (1937).
11 Owens, E. J. and Thodos, G., *AIChE Journal* 6, (4) pp. 676-681 (December 1960).

Indexing Terms: Computations-4, Ethylene Glycol-9, Diethylene Glycol-9, Heat-7, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics/-7, Temperature-6, Triethylene Glycol-9, Vapor Phase-5.

Part 14, "Propylene glycols and glycerine," will appear in an early issue.