Physical Properties of Hydrocarbons

Part 14—Propylene Glycols and Glycerine

Robert W. Gallant
The Dow Chemical Co., Plaquemine, La.

ONE OF THE FACTS of the chemical industry is that if a product derived from ethylene has a large volume market, then the analogous propylene-based product will also be valuable but on a considerably smaller scale. None of the C_3 glycols approaches the billion pound per year usage of ethylene glycol. However, propylene glycol continues to enjoy a strong 10 percent per year growth, a rate that would be most welcome by ethylene glycol. Of the 260 million pounds of propylene glycol consumed in 1965, almost two-thirds went into polyesters and cellophane. Dipropylene glycol usage is largely confined to specialty markets as a solvent or plasticizer.

Glycerine has been an important commercial product for many years. Until Shell Chemical pioneered synthetic glycerine via allyl chloride, all glycerine was produced as a byproduct of soap manufacture. More recently, glycerine has been synthetically produced by oxidation of propylene. Today, Shell Chemical and Dow Chemical are the major glycerine producers. In the next few years, synthetic glycerine will reach a milestone—more pounds of synthetic glycerine will be sold than natural glycerine. With glycerine usage spread fairly even over such mature markets as alkyd resins, cellophane, pharmaceuticals, and tobacco, synthetic glycerine's growth above its present 140 million pounds per year will be slow. What glycerine really needs is new process technology that would enable it to sell at 15 cents/pound.

Because of its wide usage, extensive experimental data are available on glycerine. There are three excellent compilations of these data available.[1,2,3] Glycerine, like the glycols, is generally used as an aqueous solution. Whenever aqueous solution properties were reported in the literature, they have been included in these data.

Critical Properties. Neither the glycols or glycerine are ever used near their critical points. Because the critical points are very high and decomposition begins well below these temperatures, the critical properties have not been experimentally determined. Consequently, they have been estimated from the structure of the molecules, using the method of Lydersen.[4]

Vapor Pressure. The major interest in the vapor pressures of these compounds has centered on the aqueous solutions in the 0-150° C range. Figures 14-1, 14-2, and 14-3 present the vapor pressures for both the pure and aqueous solutions up to 240° C for propylene glycol,[5,6,7] dipropylene glycol,[5,6] and glycerine.[1,2,8]

Heat of Vaporization. The heat of vaporization of propylene glycol has been experimentally determined up to 187° C.[7] The only data available on dipropyl glycol is at the boiling point.[6] Glycerine data are available up to 200° C.[1,9] The data for all three compounds have been extrapolated to the critical point by the Watson method.[4] When compared with experimental data in the 100-200° C range, the error averaged 2.2 percent. Near the critical temperature, the error is probably 5-10 percent.

Heat Capacity. In the absence of any data, the vapor capacities have been calculated from the molecular structures by the method of Rihani and Doraiswamy.[10]

The aqueous heat capacities of the glycols are avail-

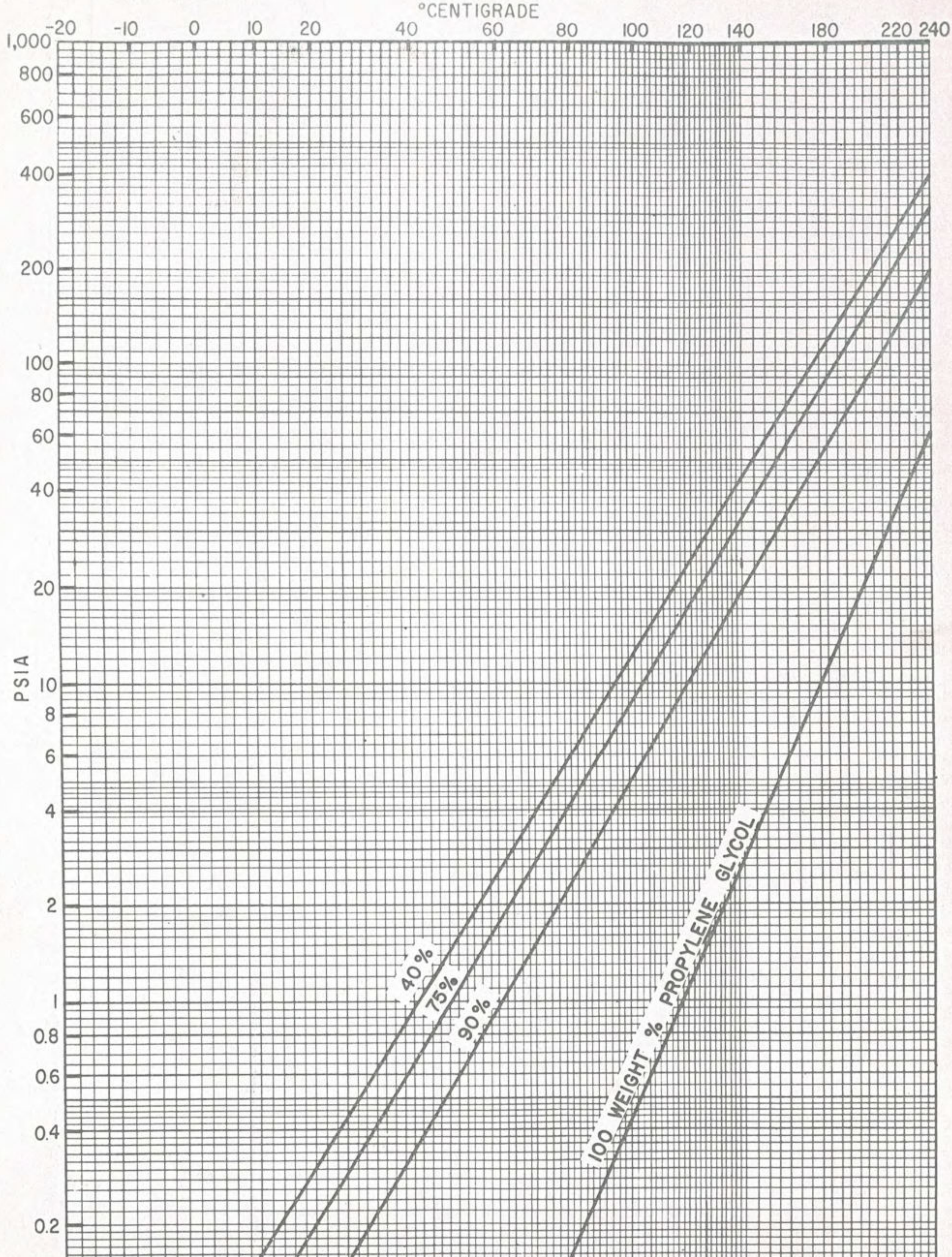


Fig. 14-1—Gives vapor pressure of aqueous propylene glycol from 0° C to +240° C.

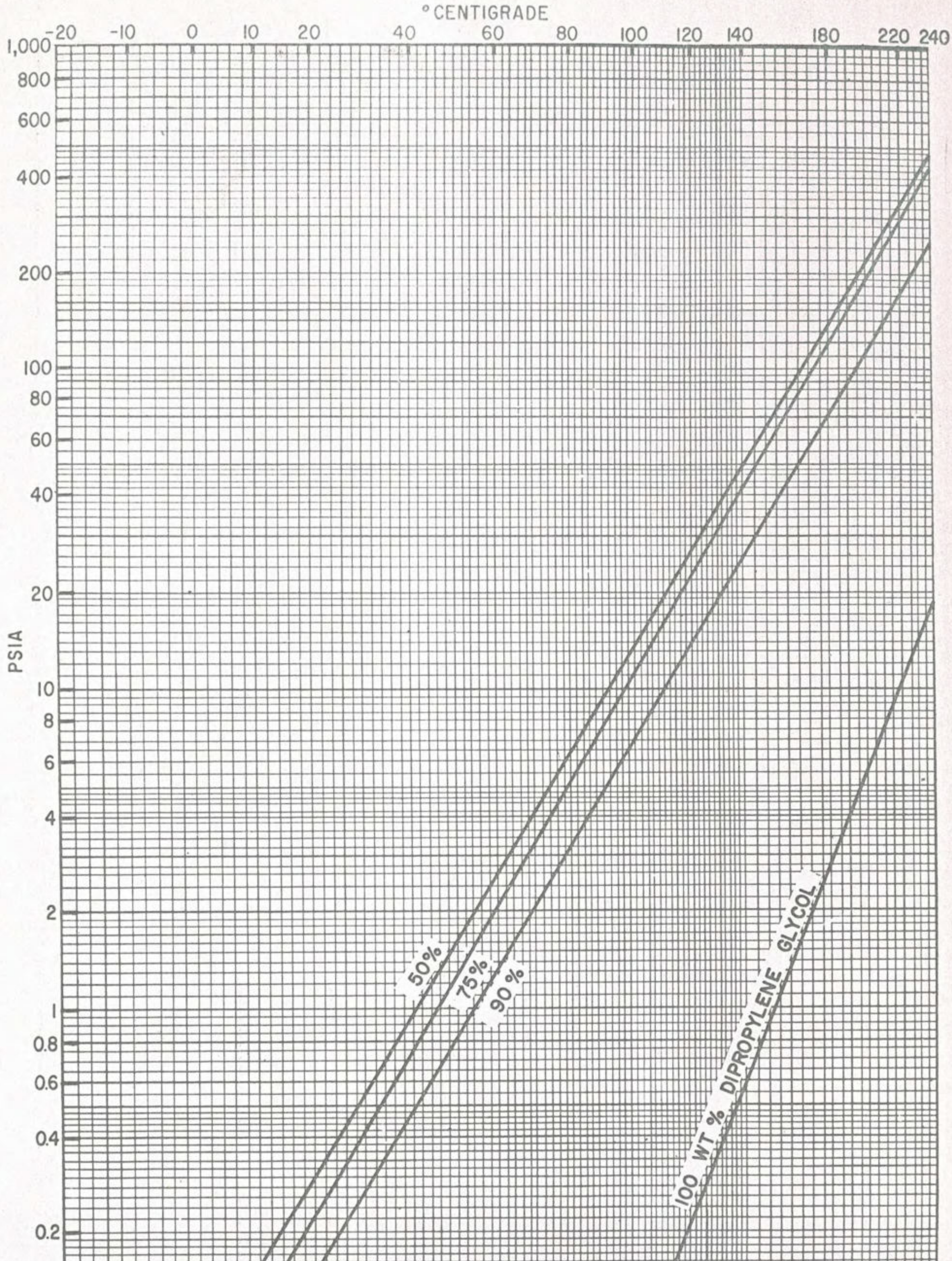


Fig. 14-2—Gives vapor pressure of aqueous dipropylene glycol from 0° C to +240° C.

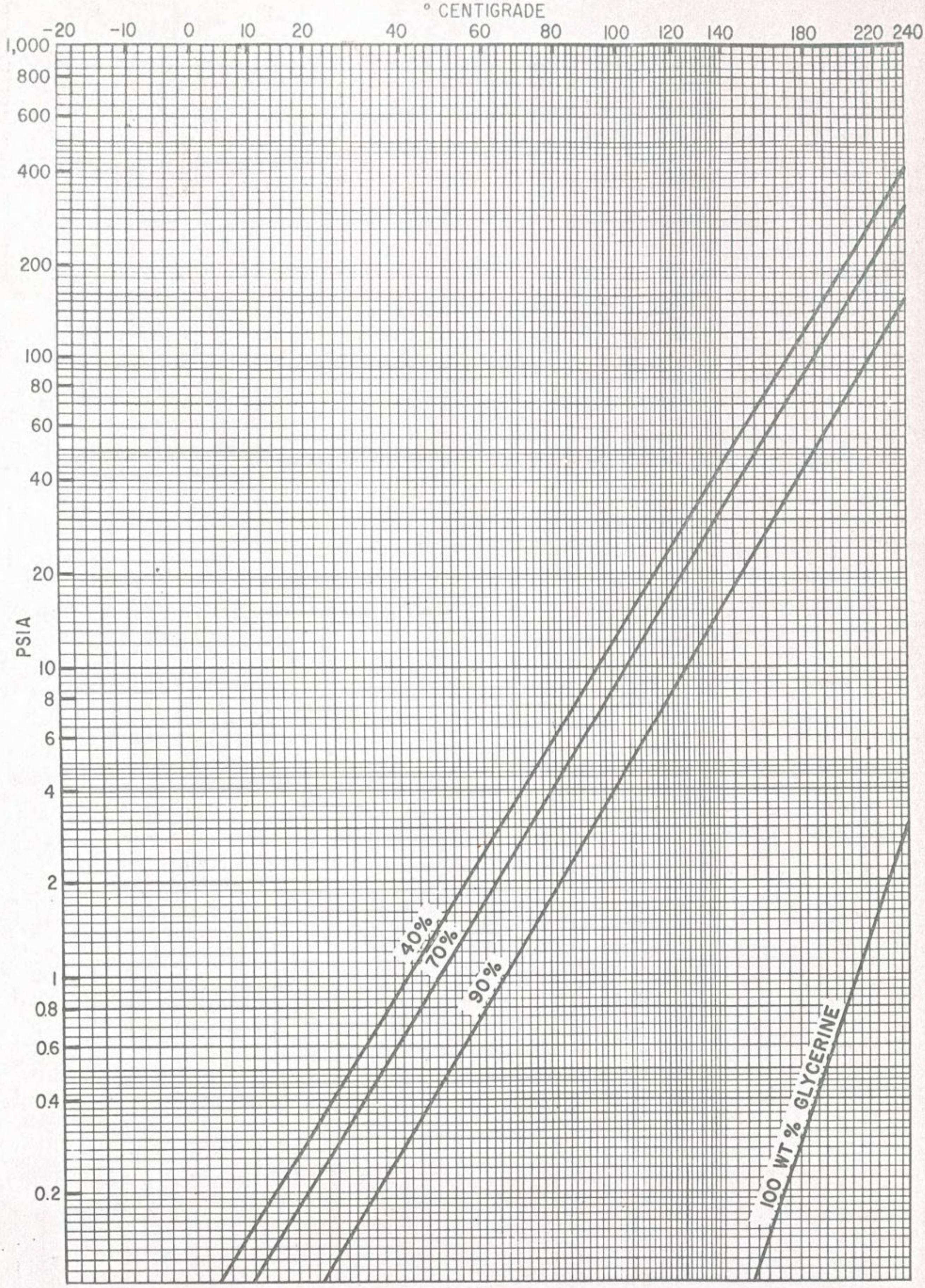


Fig. 14-3—Gives vapor pressure of aqueous glycerine from 0° C to +240° C.

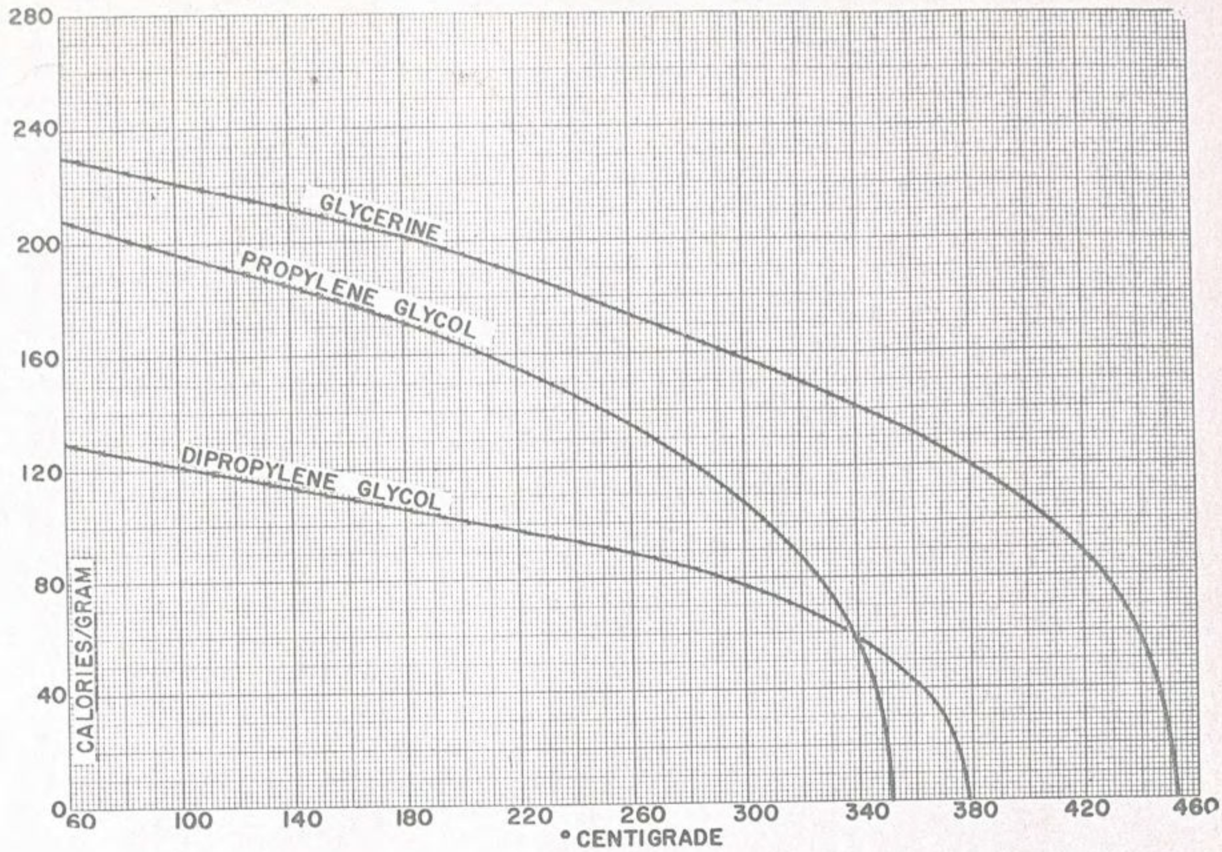


Fig. 14-4—Gives heat of vaporization of propylene glycols and glycerine from 60° C to 450° C.

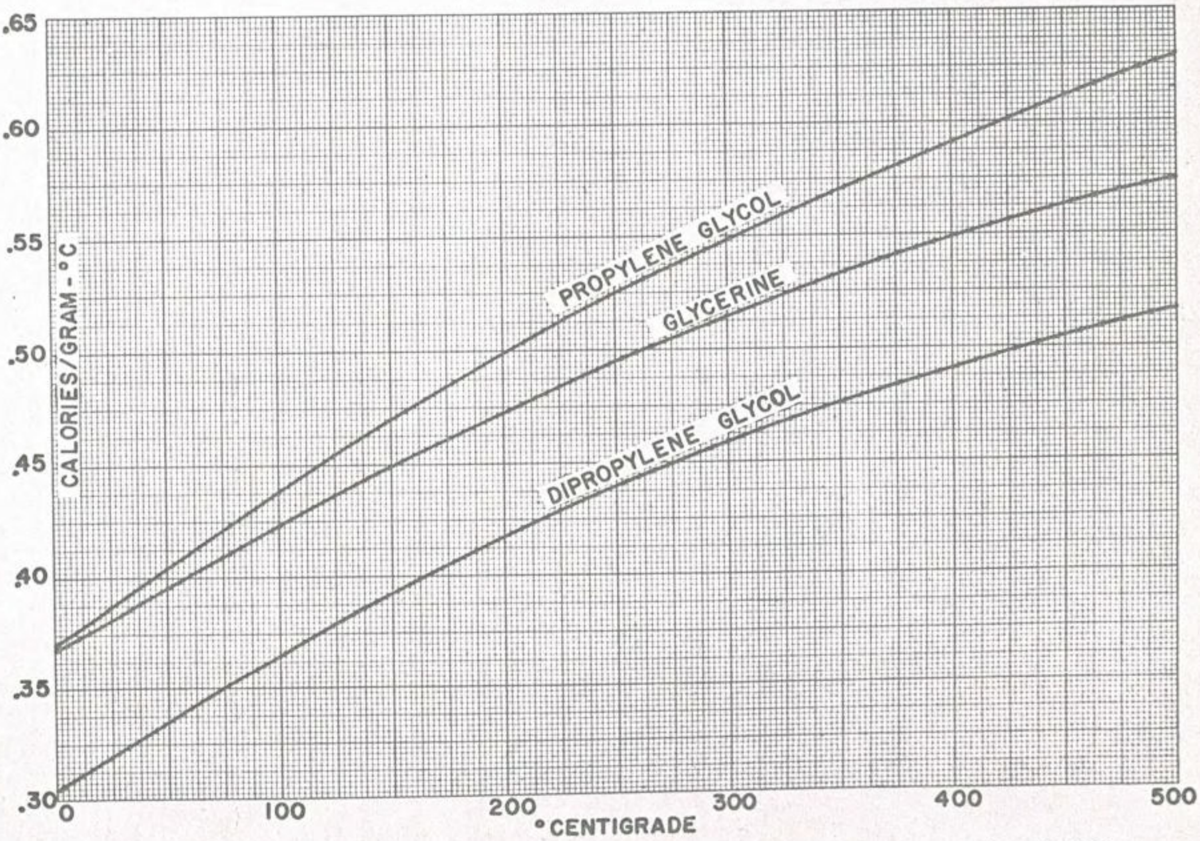


Fig. 14-5—Gives vapor heat capacity of propylene glycols and glycerine from 0° C to 500° C.

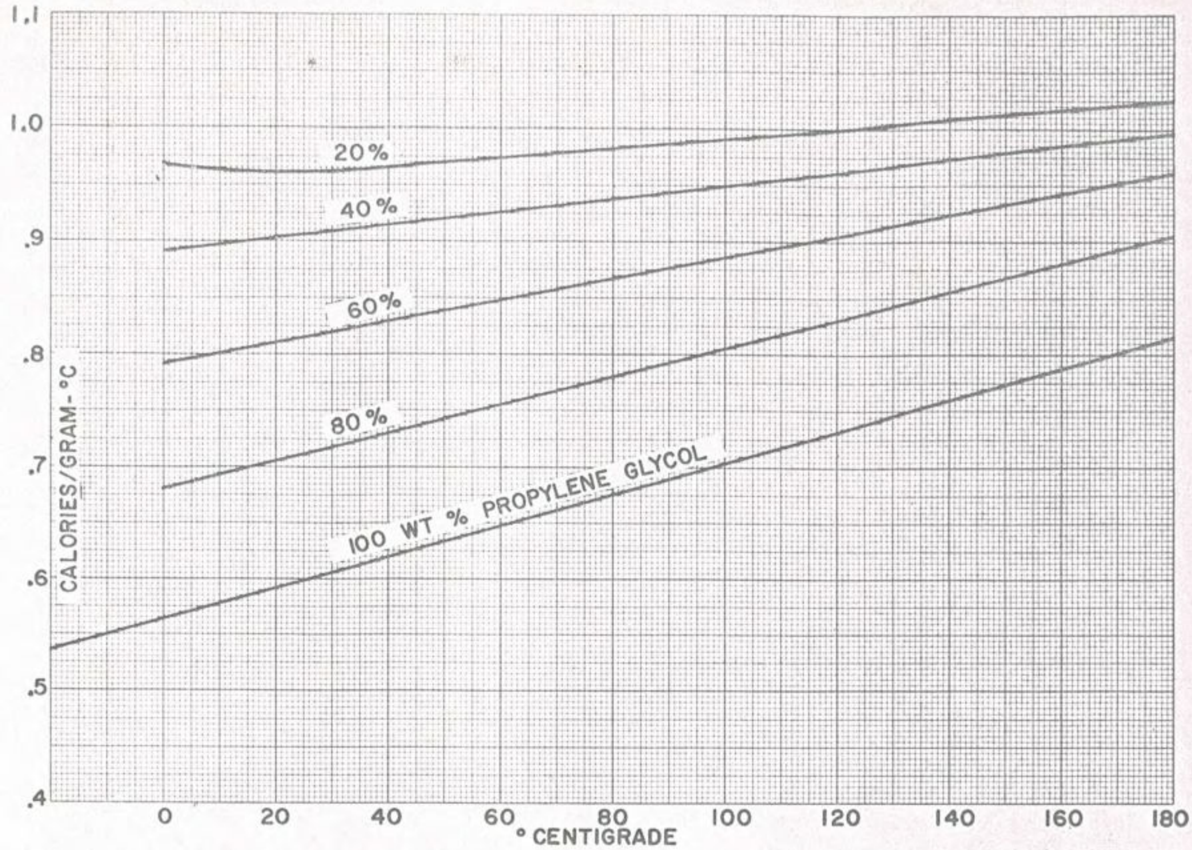


Fig. 14-6—Gives aqueous heat capacity of propylene glycol from −20° C to +180° C.

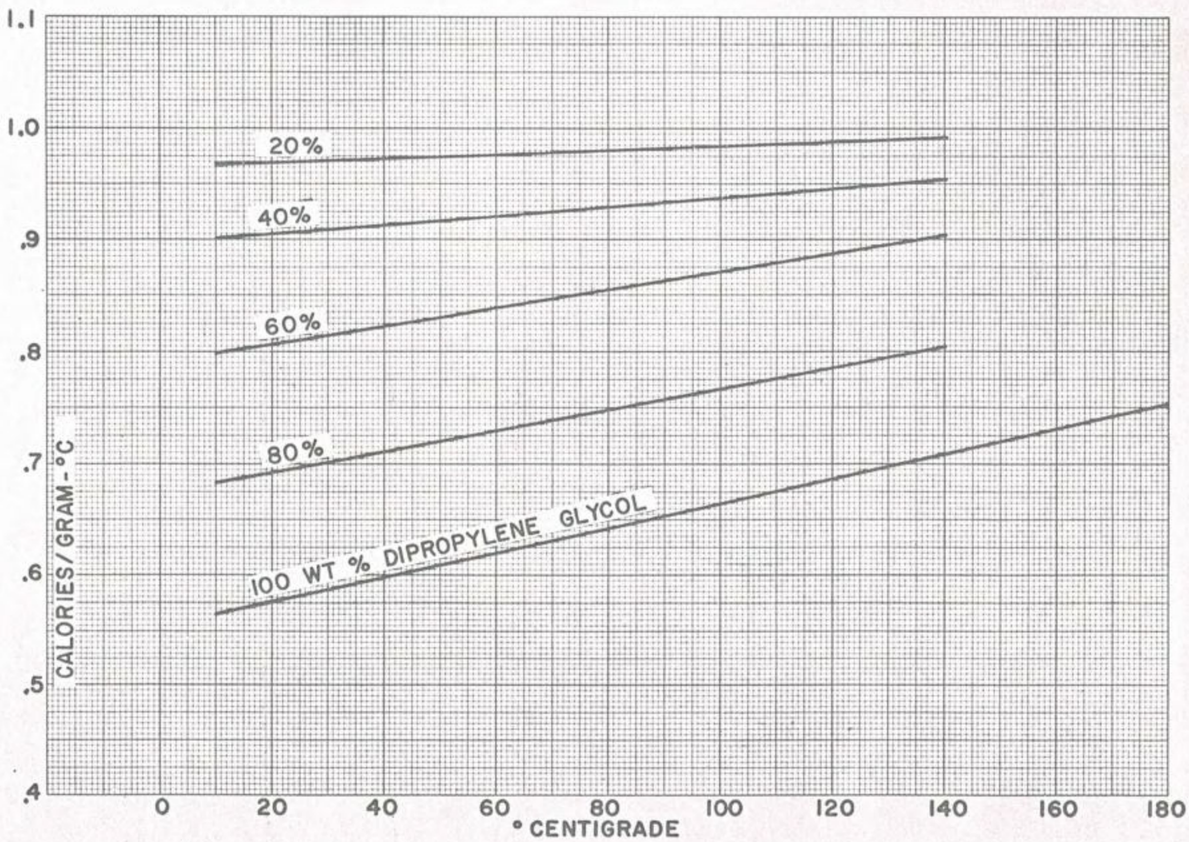


Fig. 14-7—Gives aqueous heat capacity of dipropylene glycol from −20° C to +140° C.

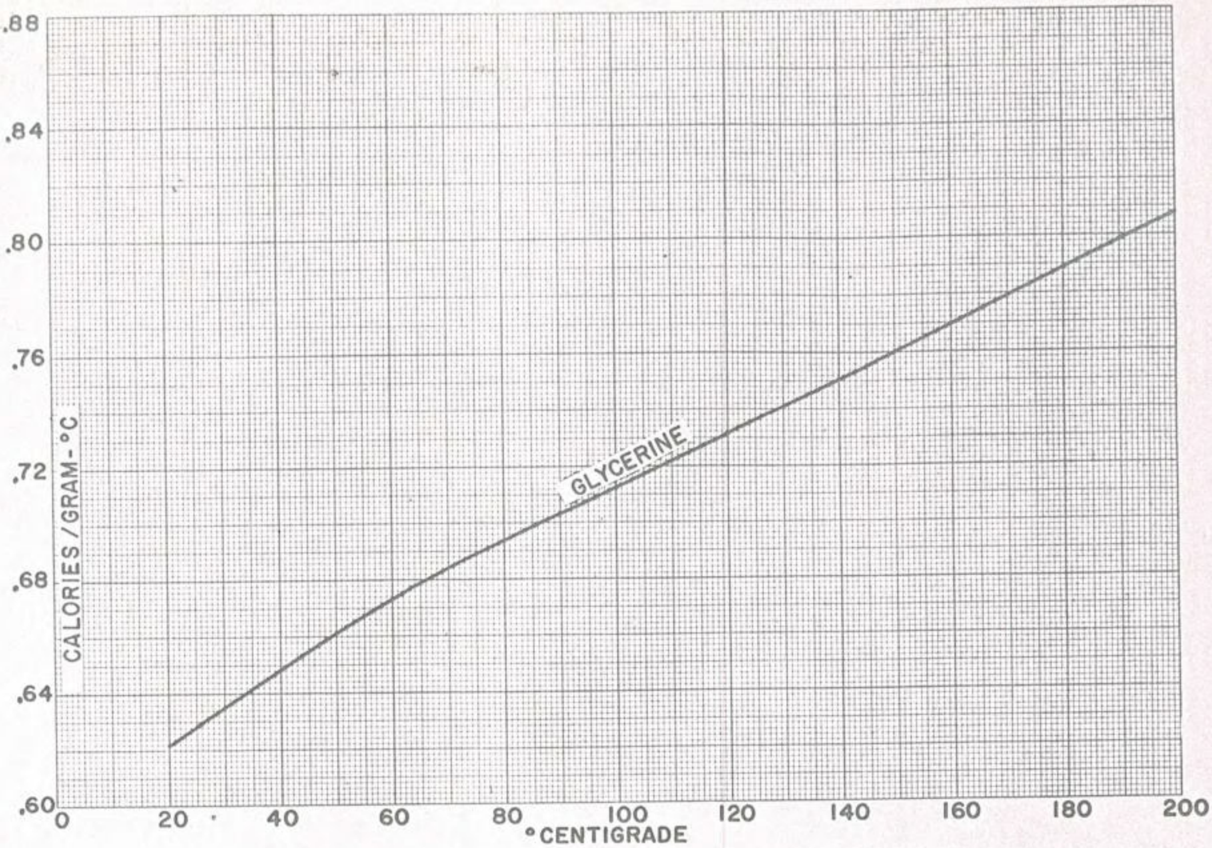


Fig. 14-8—Gives liquid heat capacity of glycerine from 20° C to 200° C.

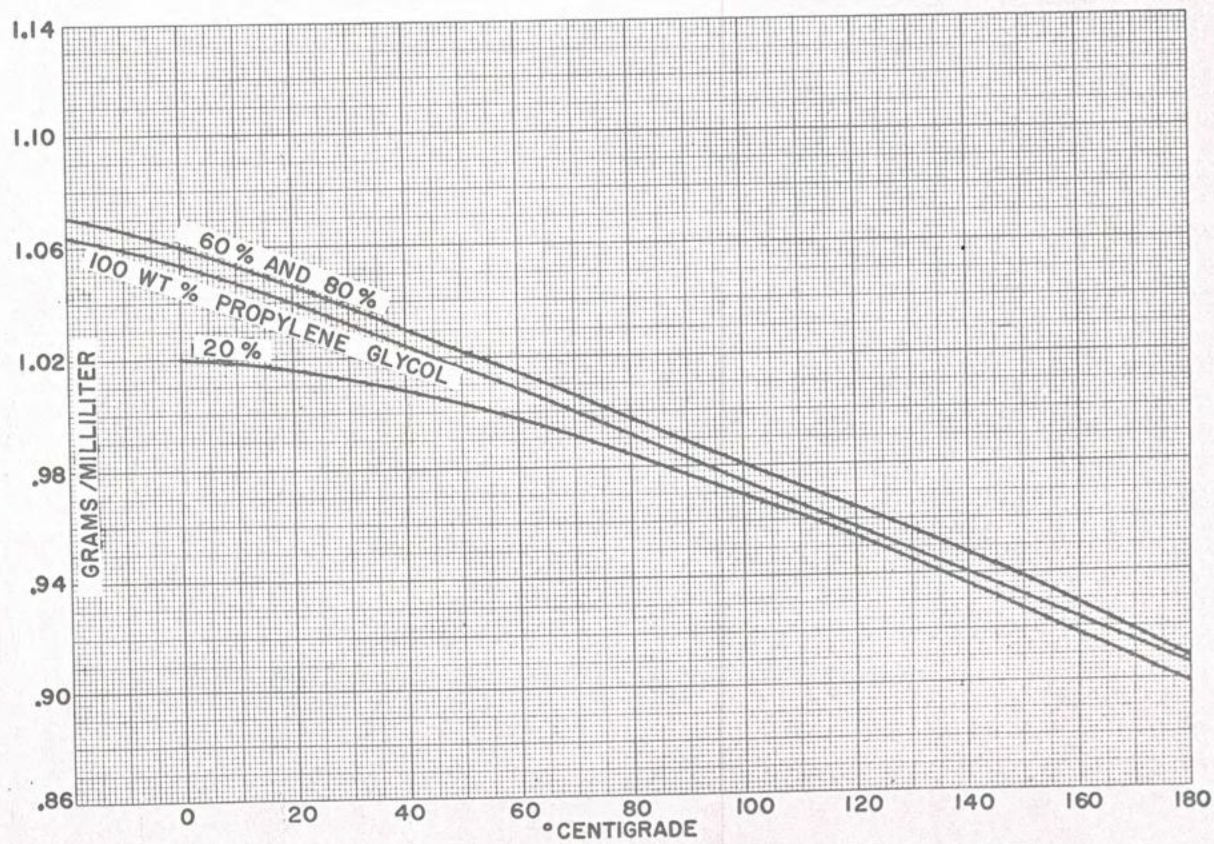


Fig. 14-9—Gives aqueous density of propylene glycol from −20° C to +180° C.

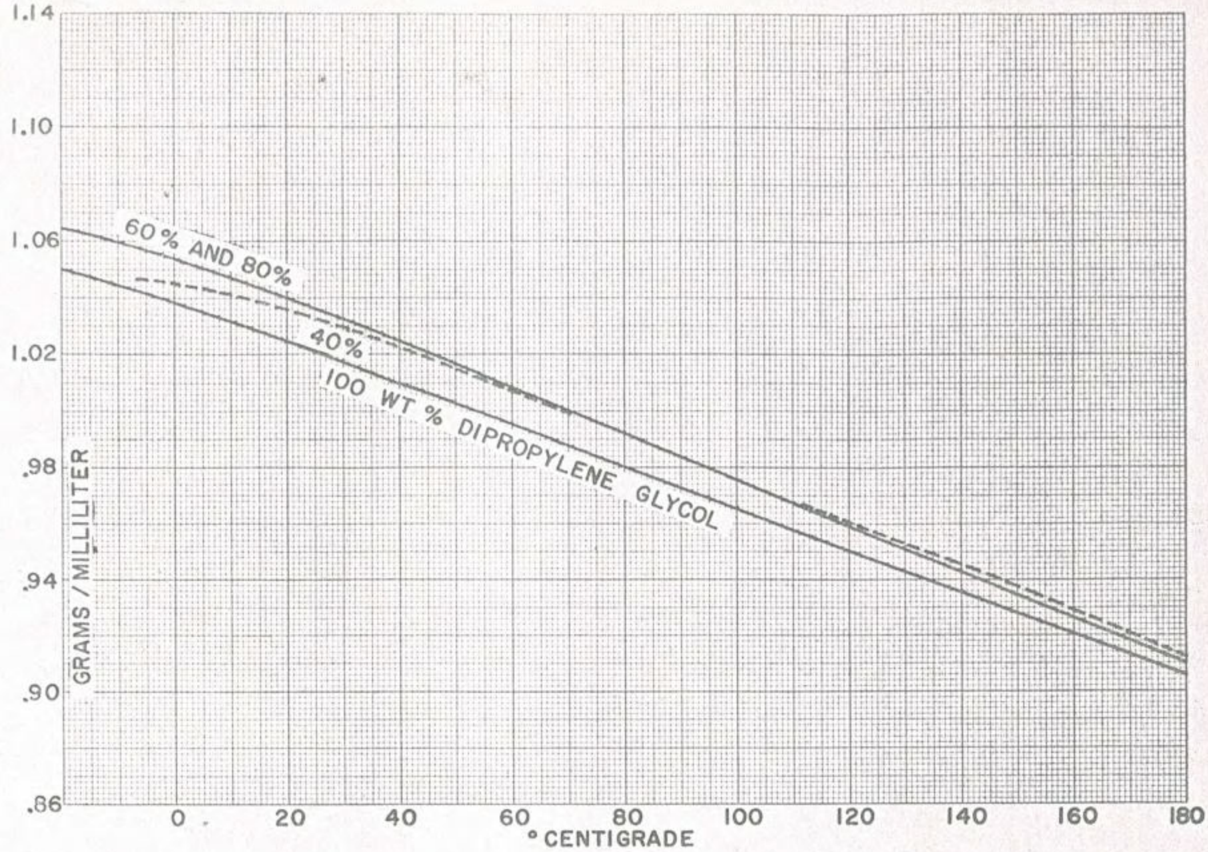


Fig. 14-10—Gives aqueous density of dipropylene glycol from −20° C to +180° C.

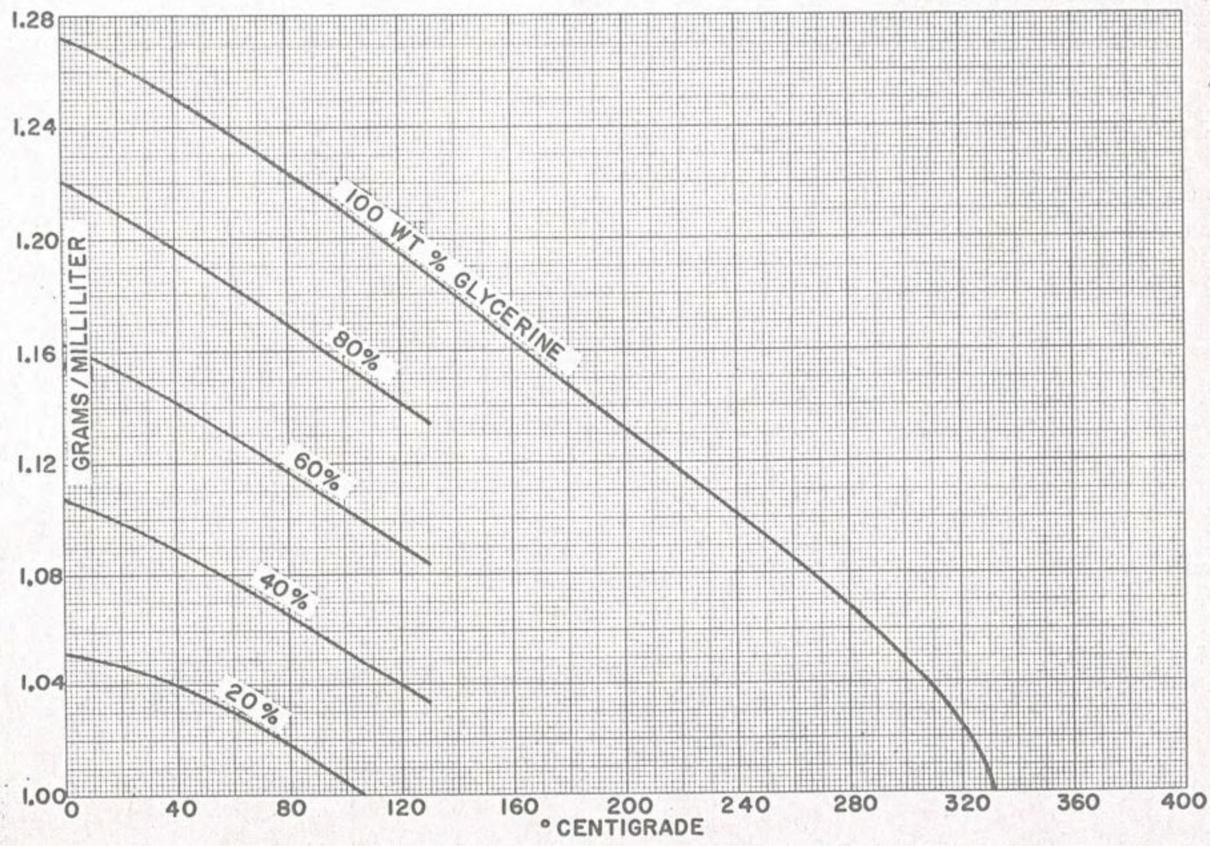


Fig. 14-11—Gives aqueous density of glycerine from 0° C to 130° C.

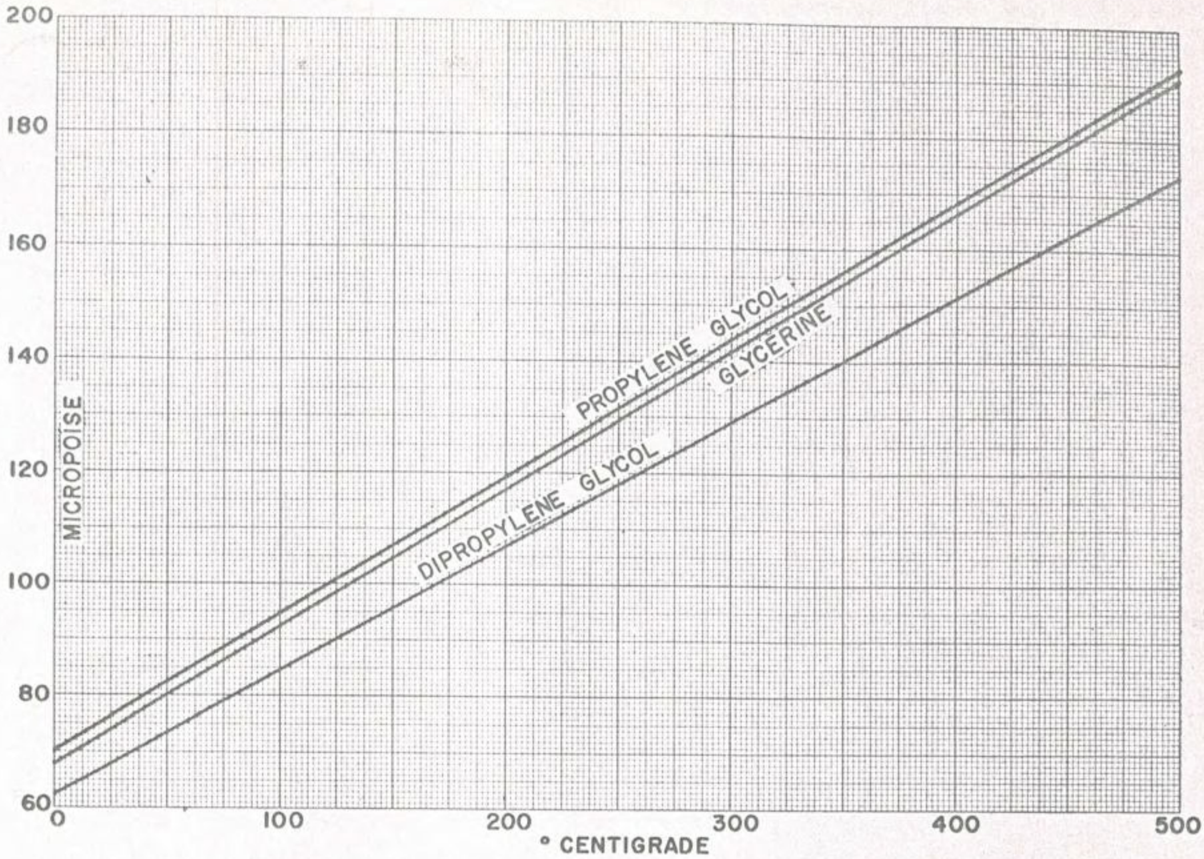


Fig. 14-12—Gives vapor viscosity of propylene glycols and glycerine from 0° C to 500° C.

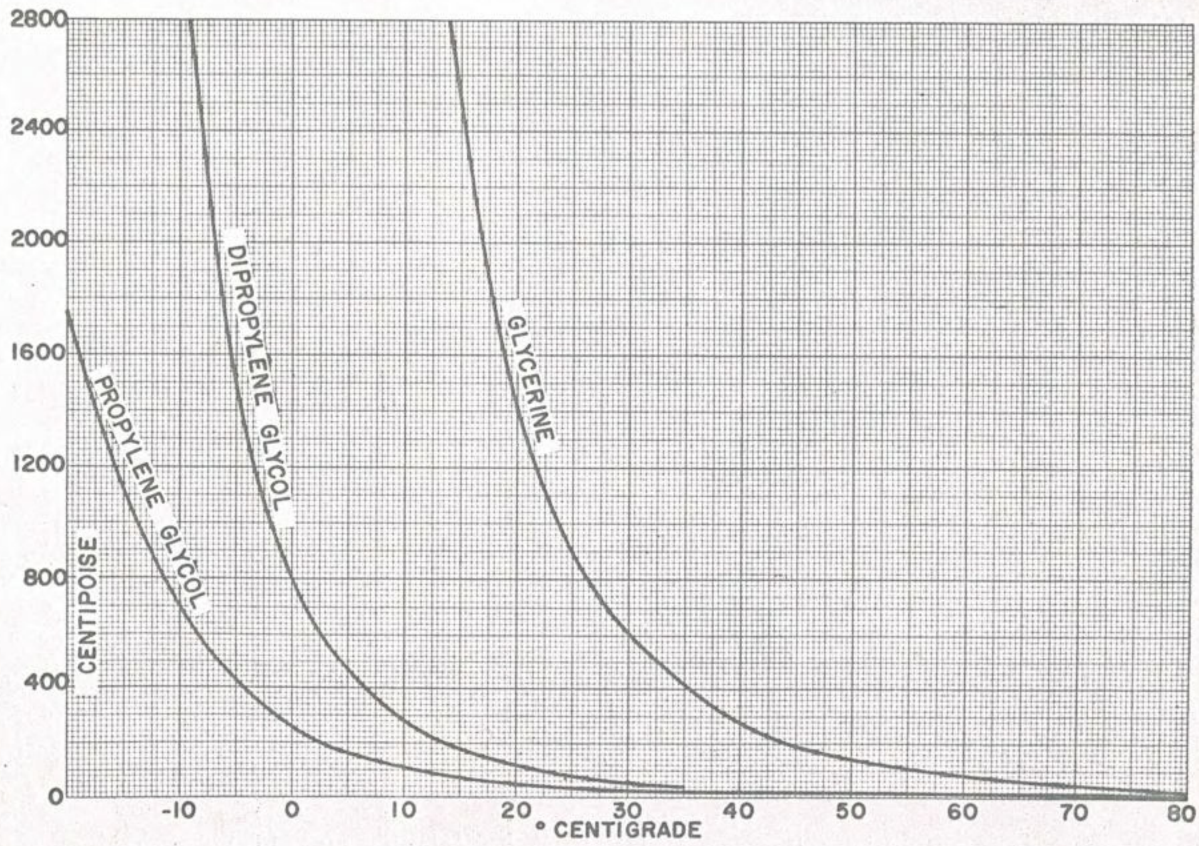


Fig. 14-13—Gives liquid viscosity of propylene glycols and glycerine from −20° C to +80° C.

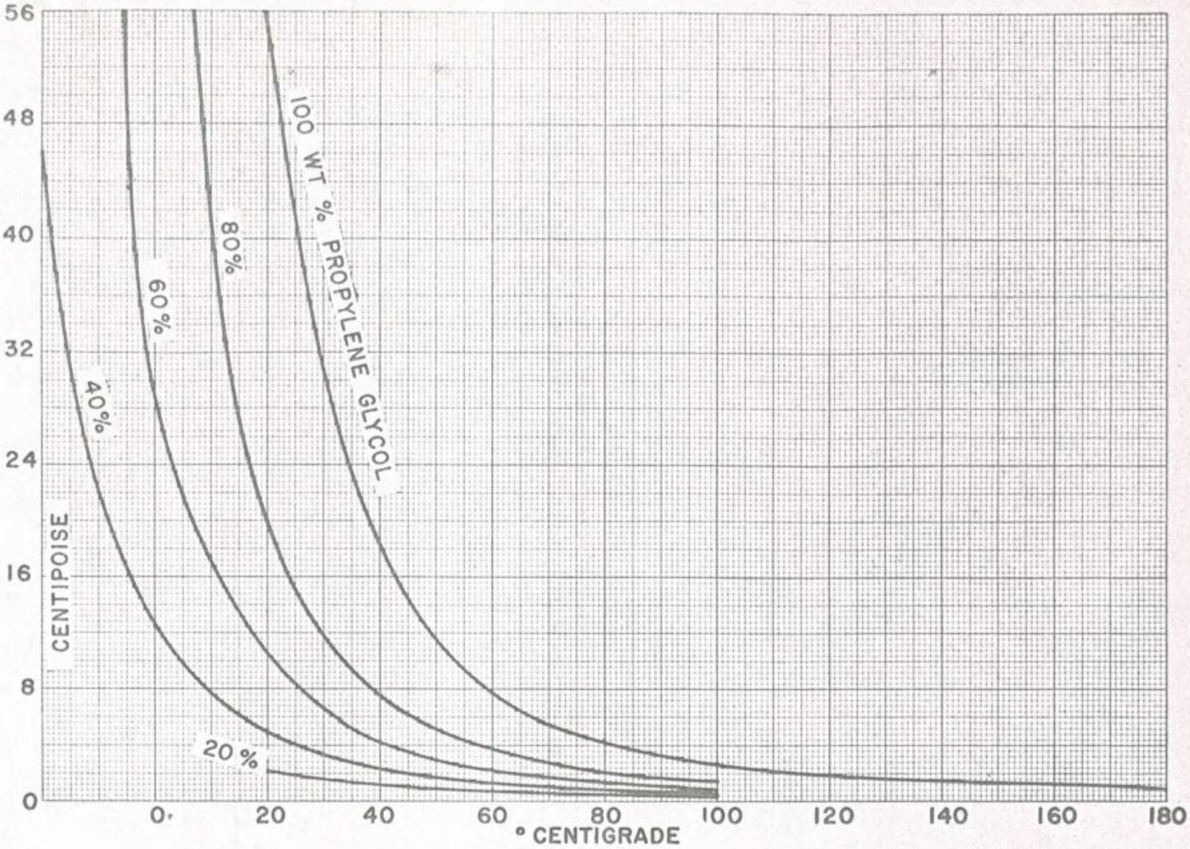


Fig. 14-14—Gives aqueous viscosity of propylene glycol from −20° C to +100° C.

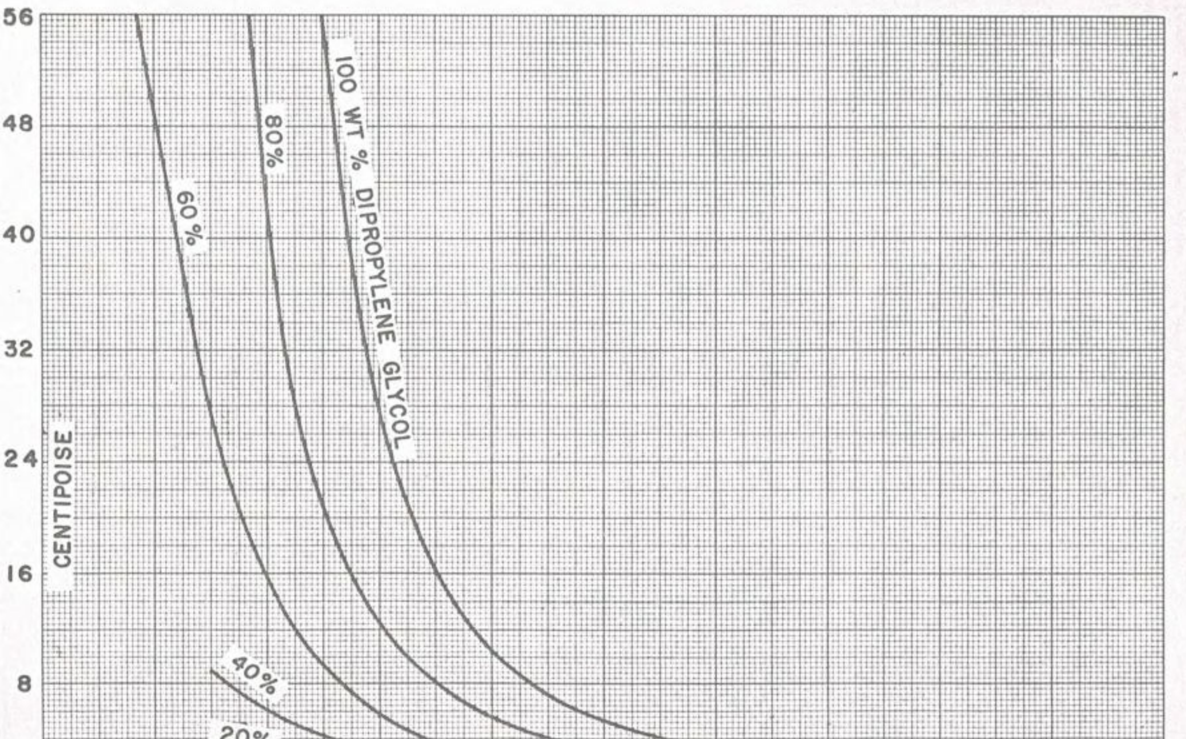


Fig. 14-15—Gives aqueous viscosity of dipropylene glycol from 0° C to 100° C.

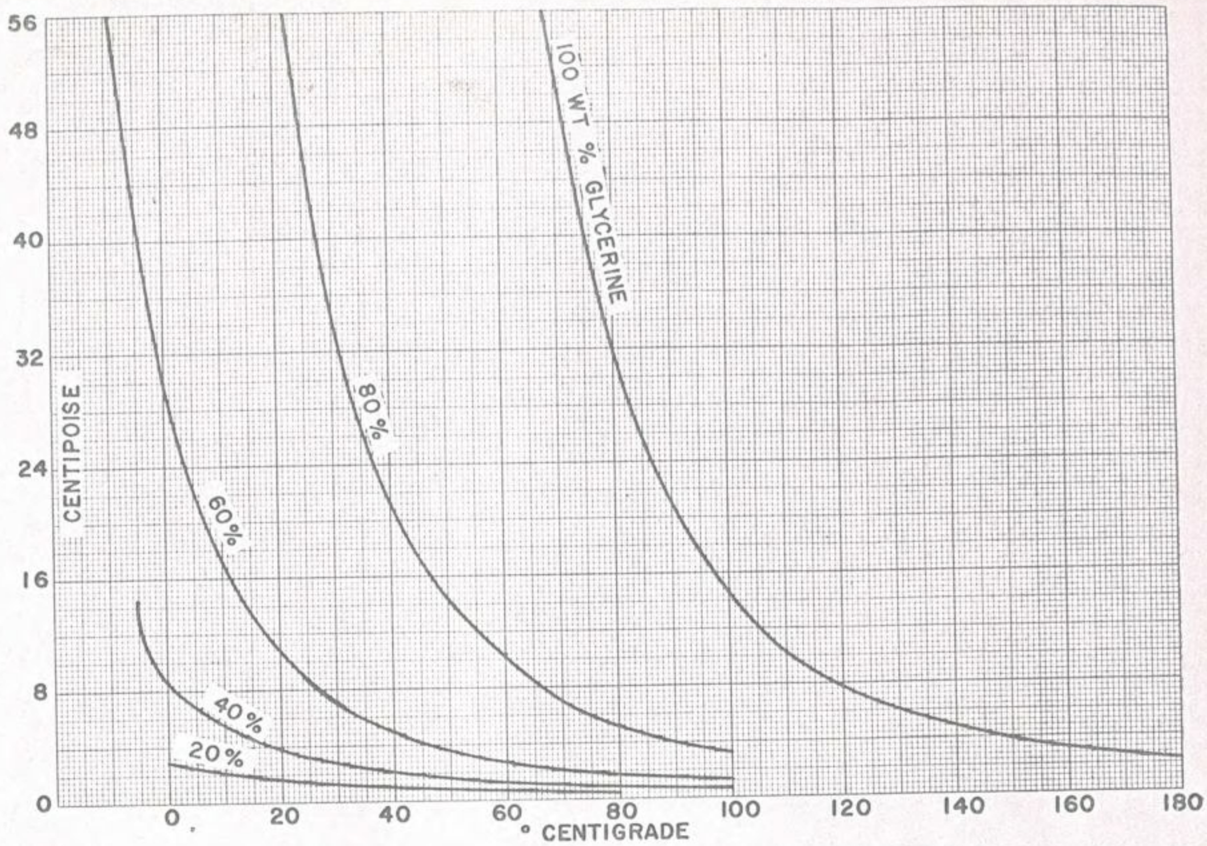


Fig. 14-16—Gives aqueous viscosity of glycerine from 0° C to 100° C.

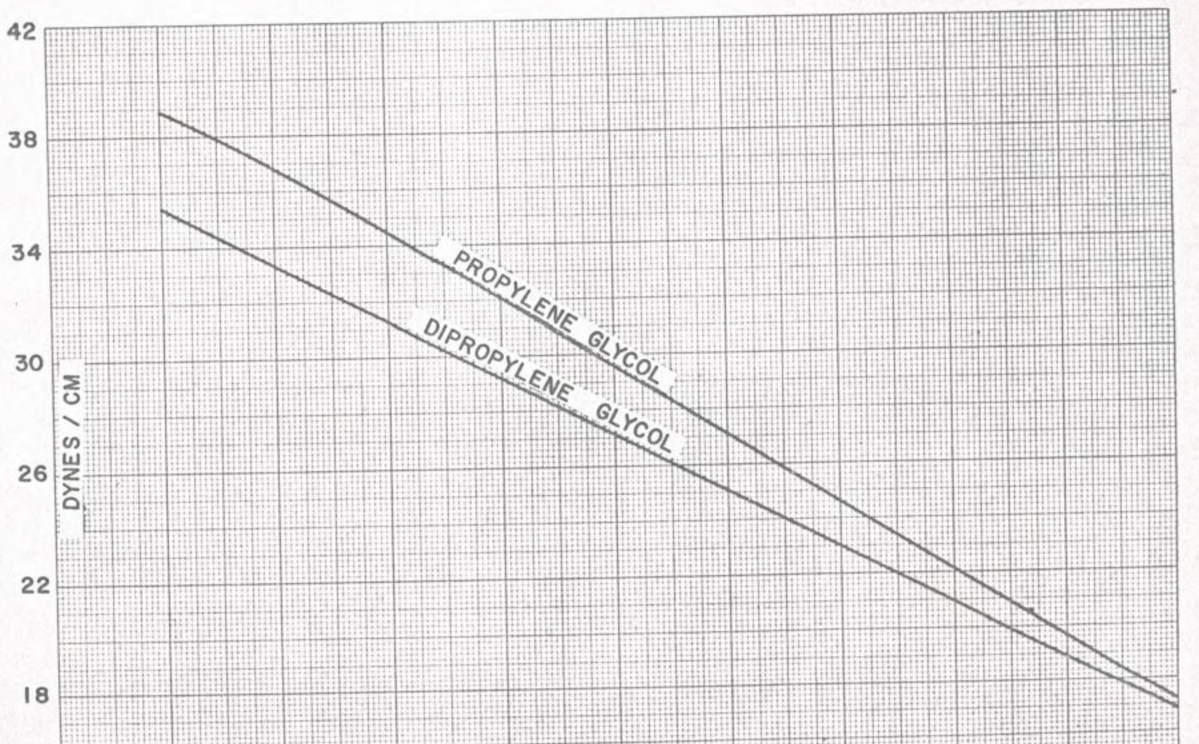


Fig. 14-17—Gives surface tension of propylene glycols from −20° C to +180° C.

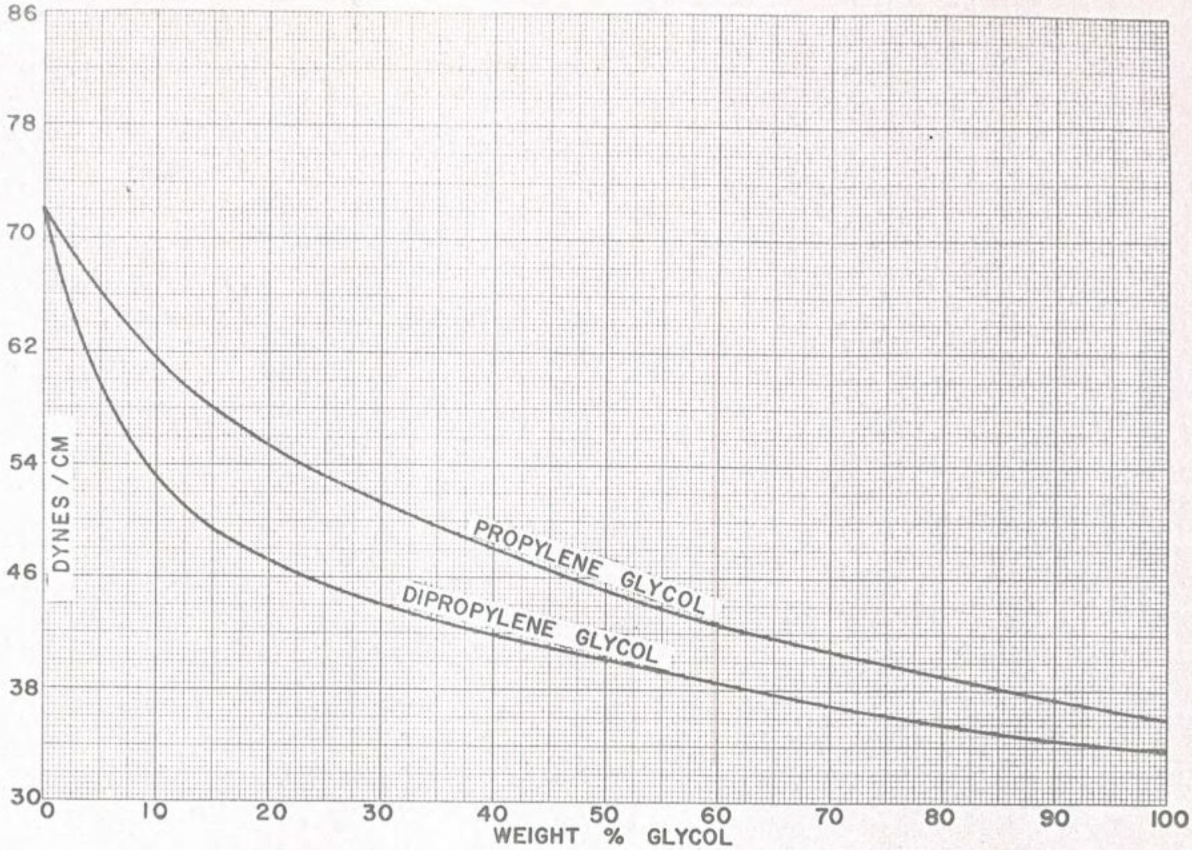


Fig. 14-18—Gives surface tension at 25° C for aqueous propylene glycols.

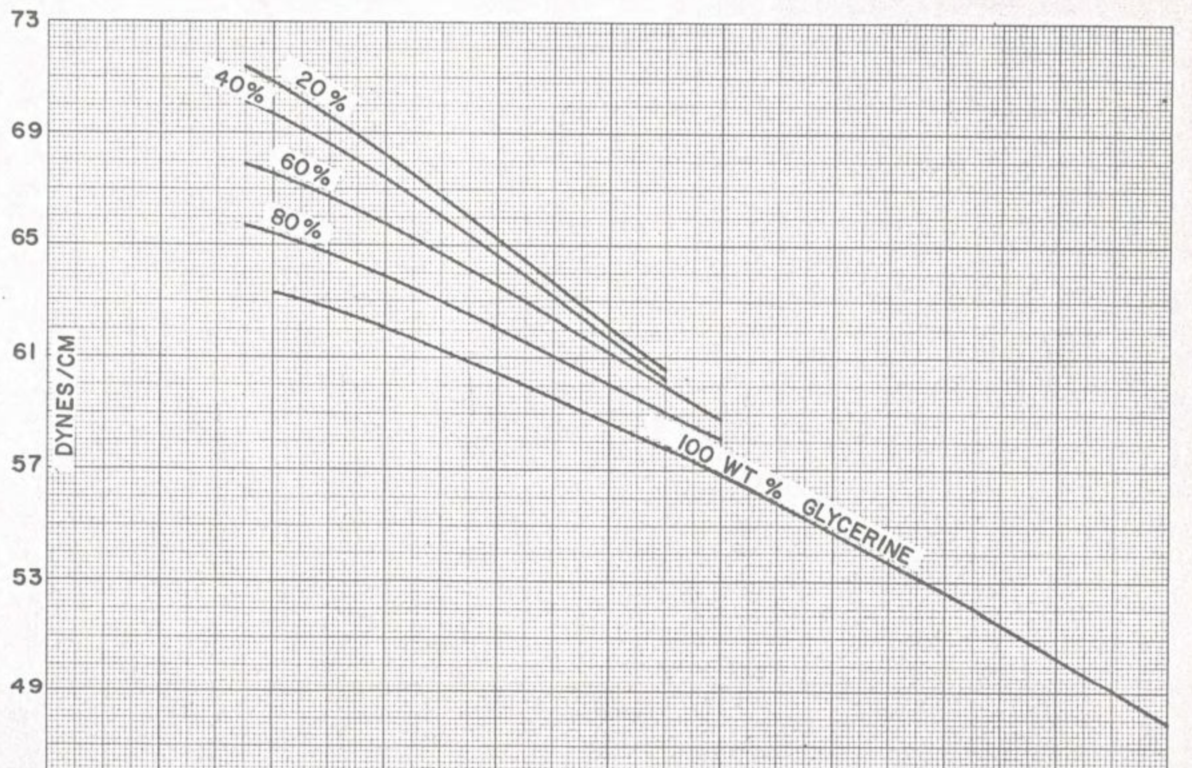


Fig. 14-19—Gives aqueous surface tension for glycerine from 20° C to 100° C.

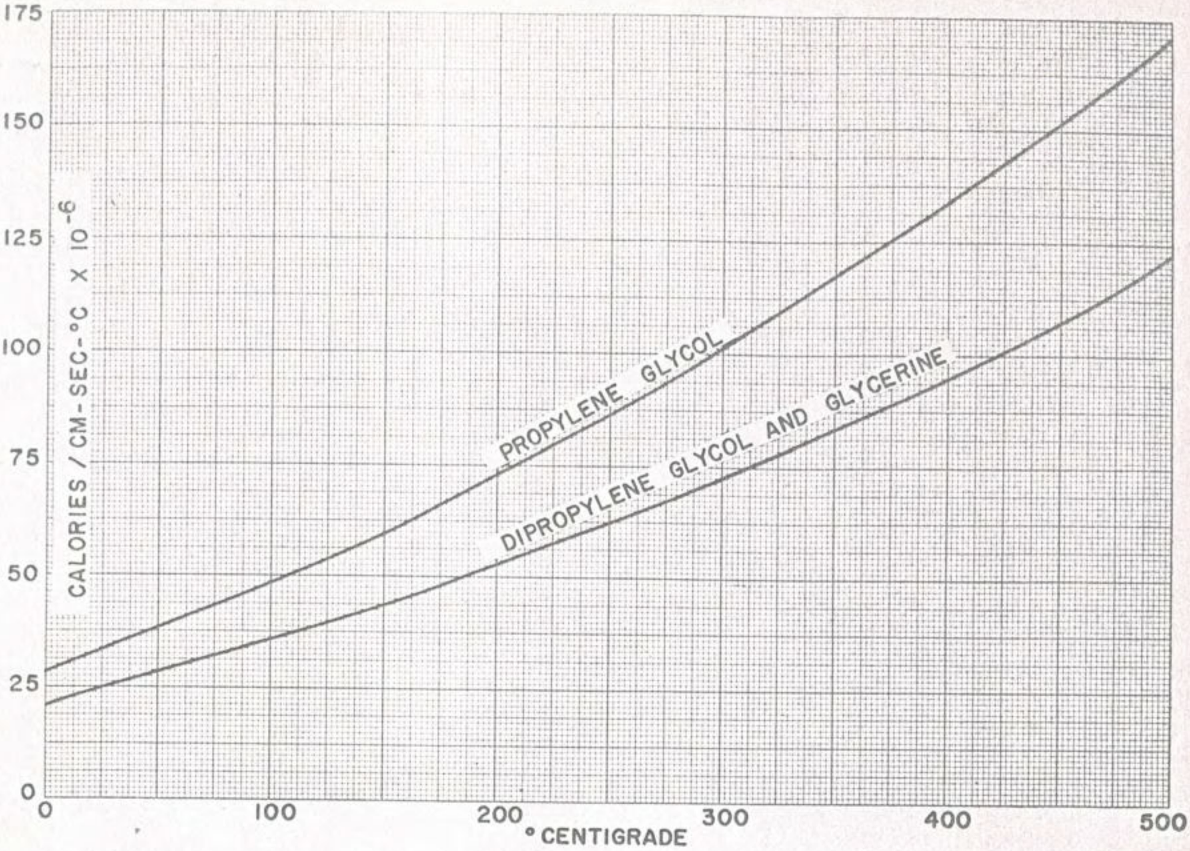


Fig. 14-20—Gives vapor thermal conductivity for propylene glycols and glycerine from 0° C to 500° C.

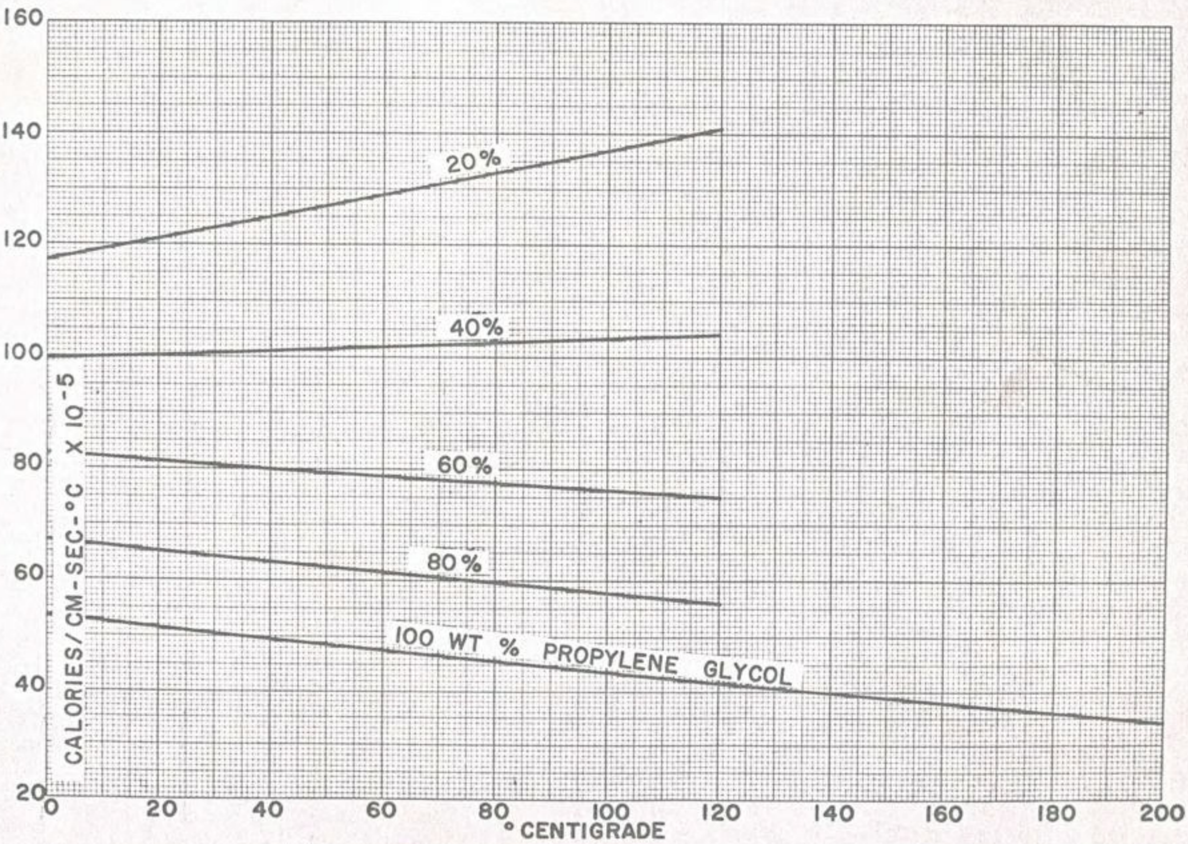


Fig. 14-21—Gives liquid thermal conductivity for aqueous propylene glycol from 0° C to 120° C.

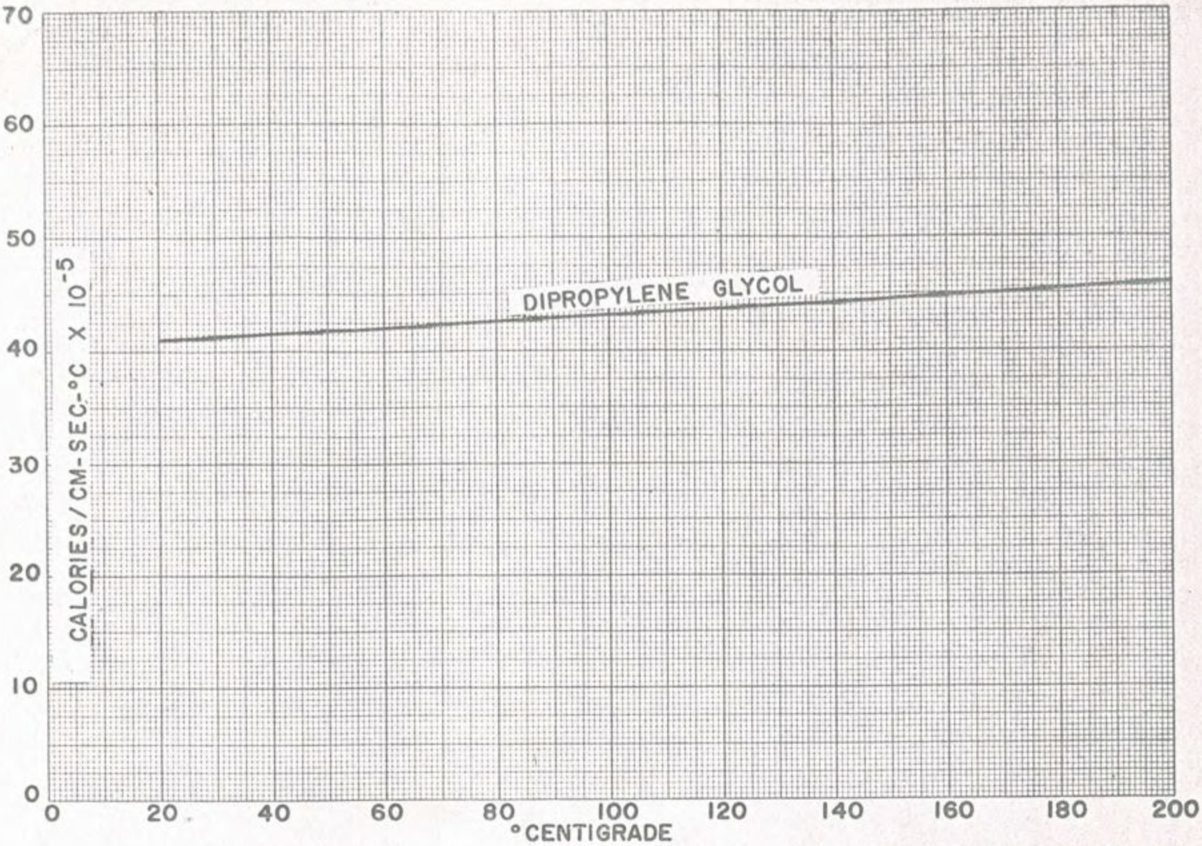


Fig. 14-22—Gives liquid thermal conductivity for dipropylene glycol from 20° C to 200° C.

able from the literature.[5,7] For glycerine, only the low temperature (below 0° C) heat capacities have been determined for the aqueous solutions. For pure glycerine, Omelchenko[11] has determined the heat capacity up to 250° C.

Density. The aqueous densities of all three compounds have been experimentally determined.[1,2,3,5,6,7] Costello and Bowden[12] have experimentally determined the high temperature density of glycerine.

Viscosity. As in the previous articles viscosity has been estimated by the method of Bromley and Wilke.[4]

At temperatures below 80° C, the glycols and glycerine are very viscous. Figure 14-13 shows the high viscosity range for the pure compounds. Figures 14-14, 14-15, and 14-16 are plots of the viscosities of the aqueous solutions.[1,2,5,7,13]

Surface Tension. The surface tension of pure propylene glycol and dipropylene glycol is available only at 25° C. These data have been extrapolated over the 0-180° C range by Kharbanda's nomograph for the variation of surface tension with temperature.[14] The error should be less than 5 percent. Figure 14-18 is a plot of the surface tension of the aqueous glycols at 25° C.[5] The surface tension of aqueous glycerine solutions have been determined in the 20-100° C range. The surface tension of pure glycerine is available up to 200° C.[1,2] The difficulty of obtaining a highly purified glycerine has resulted in some variation in results among various experimenters.

Thermal Conductivity. The previously mentioned method of Owens and Thodos[15] has been used to calculate the vapor thermal conductivities.

Figure 14-21 is a plot of the thermal conductivity of aqueous solutions of propylene glycol.[6,16,17] Because no data are available for dipropylene glycol, the thermal conductivity for the pure liquid has been calculated by the method of Robbins and Kingrea.[18] The error is probably less than 5 percent. The data of Bates[19] for the thermal conductivity of aqueous glycerine are shown in Figure 14-23. A number of investigators have studied the thermal conductivity of pure glycerine.[17,19,20,21,22] In addition to the problems normally encountered in measuring liquid thermal conductivity, the purity of the glycerine is a major factor in the results. Even a few percent moisture can give significantly different

TABLE 14-1—Propylene Glycols and Glycerine

	Boiling Point, °C	Melting Point, °C	Molecular Weight	CRITICAL PROPERTIES °C T_c	psia P_c	g/ml d_c
1, 2-Propylene Glycol.....	187.3	−60	76.10	351*	884*	0.321*
Dipropylene Glycol.......	231.0	......	134.18	378*	520*	.321*
Glycerine................	290	18.2	92.09	452*	965*	.361*

* Estimated.

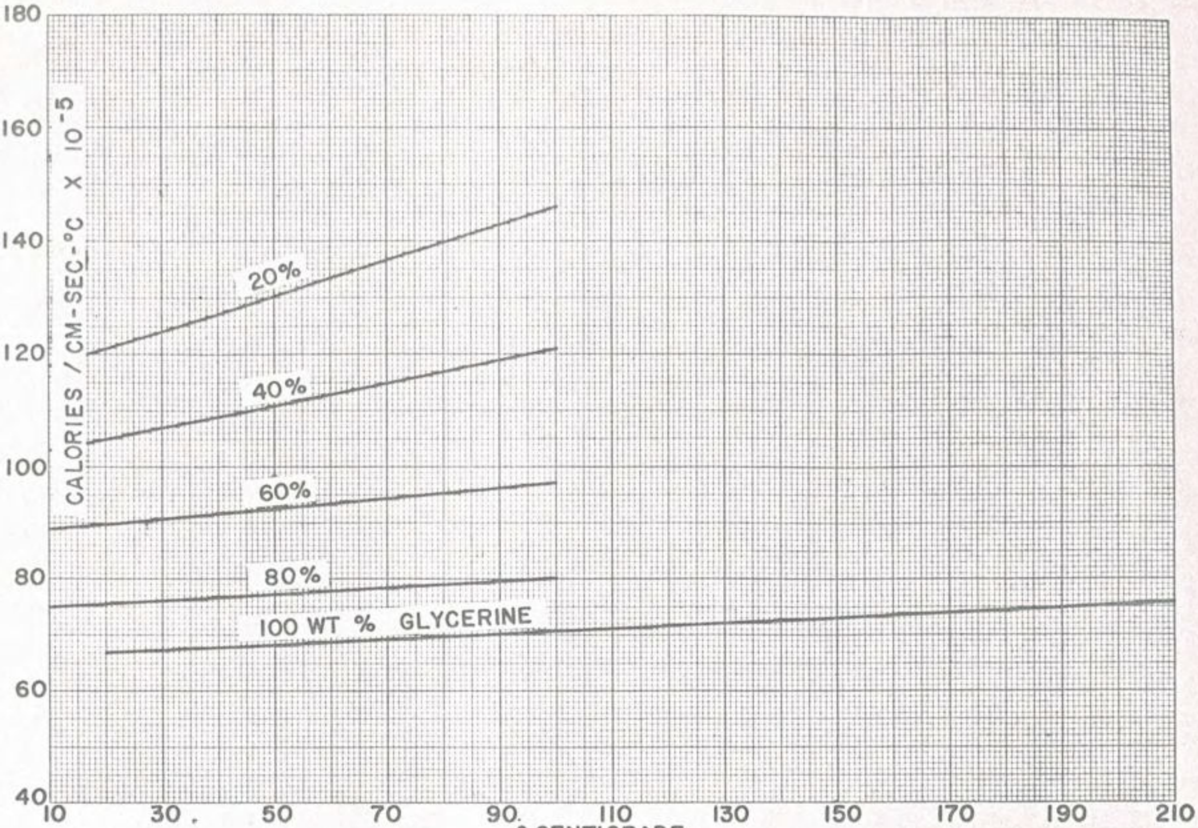
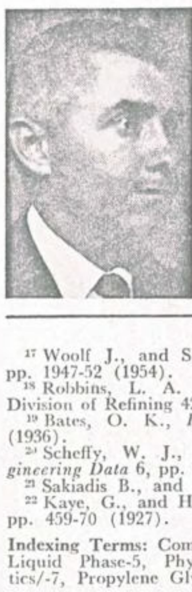


Fig. 14-23—Gives aqueous thermal conductivity for glycerine from 10° C to 100° C.

results. Consequently, there is a wide spread in the experimental data obtained by various investigators. The data presented in Figure 14-23 represents the best curve that could be drawn through the various data points.

LITERATURE CITED

[1] Miner, C. S., "Glycerol." Reinhold Publishing Corp., New York (1953).
[2] "Physical Properties of Glycerine and Its Solutions," The Soap and Detergent Association, New York.
[3] "Glycerine—Properties, Reactions, Performance," Glycerine Producers' Association, New York.
[4] Reid, R. C. and Sherwood, T. K., "The Properties of Gases and Liquids," McGraw-Hill Book Co., New York (1958).
[5] "Glycols: Properties and Uses," The Dow Chemical Co. Product Bulletin.
[6] "Glycols," Union Carbide Chemicals Co. Product Bulletin.
[7] Curme, G. P., "Glycols," Reinhold Publishing Corp., New York (1953).
[8] Ross, G. R. and Heideger, W. J., *Journal of Chemical and Engineering Data* 7, Part 1, pp. 505-7 (1962).
[9] Stedman, D. F., Transactions, Faraday Society 24, pp. 289-98 (1928).
[10] Rihani, D. N. and Doraiswamy, L. K., *Industrial and Engineering Chemistry Fundamentals* 4 (1), pp. 17-21 (February 1965).
[11] Omelchenko, F. D., *Izv. Vysshikh Uchebn Zayedenii, Pischevaya Tekhnol* 1962 (3), pp. 97-98.
[12] Costello, J. M., and Bowden, S. T., *Recueil* 77, pp. 36-46 (1958).
[13] Segur, J. B. and Oberstar H., *Industrial and Engineering Chemistry* 43, pp. 2117-20 (1951).
[14] Kharbanda, P. O., *The Industrial Chemist*, pp. 187-92 (April 1955).
[15] Owens, E. J. and Thodos, G., *AIChE Journal* 6 (4), pp. 676-681 (December 1960).
[16] Bates, O. K., and Hazzard, G., *Industrial and Engineering Chemistry* 37, pp. 193-5 (1945).
[17] Woolf J., and Sibbert, W., *Industrial and Engineering Chemistry* 46, pp. 1947-52 (1954).
[18] Robbins, L. A. and Kingrea, C. L., American Petroleum Institute, Division of Refining 42 (III), pp. 52-61 (1962).
[19] Bates, O. K., *Industrial and Engineering Chemistry* 28, pp. 494-98 (1936).
[20] Scheffy, W. J., and Johnson, E. F., *Journal of Chemical and Engineering Data* 6, pp. 245-9 (1961).
[21] Sakiadis B., and Coates, J., *AIChE Journal* 1, pp. 275-81 (1955).
[22] Kaye, G., and Higgins, W., Proceedings Royal Society (London) A 117, pp. 459-70 (1927).



About the author

R. W. GALLANT *is a group leader in the research and development department of The Dow Chemical Co., Plaquemine, La. His duties include process design, production plant trouble-shooting, pilot plant operations, product development, and process development. Mr. Gallant received a B.S. in chemical engineering from the University of Florida.*

Indexing Terms: Computations-4, Dipropylene Glycol-9, Glycerine-9, Heat-7, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties/Characteristics/-7, Propylene Glycol-9, Temperature-6, Vapor Phase-5.

Future Installments of Physical Properties of Hydrocarbons series will include . . .

Part 15—C_5-C_8 Alkanes
Part 16—C_5-C_8 Alkenes
Part 17—C_4-C_5 Branched Hydrocarbons
Part 18—C_6-C_8 Branched Hydrocarbons
Part 19—Chlorinated C_2's
Part 20—Halogenated Methanes
Part 21—Halogenated Hydrocarbons
Part 22—Fluorinated Hydrocarbons