Physical Properties of Hydrocarbons

PART 29–Acetates

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

VINYL ACETATE is the most important commercial ester, with sales of close to 500 million pounds a year in 1966. One-half of this goes into polyvinyl acetate. The rest goes into such polymers as polyvinyl alcohol, polyvinyl-butyral, and polyvinyl chloride copolymers.

Ethyl acetate and butyl acetate find wide usage as solvents for nitrocellulose, lacquers, and resins. Ethyl acetate is considered the least toxic of all industrial organic solvents. The market for these two solvents has leveled out at a little over 100 million pounds for ethyl acetate and about 50 million pounds a year for butyl acetate. Longer term, they may suffer the same fate as methyl acetate, which has been largely displaced by other solvents.

These esters are generally made by the reaction of an alcohol with an organic acid in the presence of a catalyst such as sulfuric acid or paratoluenesulfonic acid.

Extensive physical property data are available on methyl and ethyl acetate. Almost no experimental data are reported on vinyl acetate.

Critical Properties and Vapor Pressure. The critical properties of methyl acetate and ethyl acetate have been reported in the literature.[1,2] Estimation methods were used to calculate the critical properties of butyl and vinyl acetate.[3] The probable error is ± 4° C on the critical temperature, 15-25 psi on the critical pressure, and 0.002 grams/milliliter on the critical density.

The vapor pressures have been measured up to the boiling point on all four compounds and up to the critical point for methyl and ethyl acetate.[1,2,4] Previously described methods were used to estimate the vapor pressure above the boiling point for butyl and vinyl acetate.

Heat of Vaporization. Giacalone's method[3] was used to calculate the heat of vaporization at the boiling point for vinyl acetate. Marsden[4] and Timmermans[1] report experimental data on the other three compounds at the boiling point. The data were extended over a wide temperature range by use of Kharbanda's nomograph.[5]

Heat Capacity. The method proposed by Rihani and Doraiswamy was used to calculate the vapor heat capacities.[6] The probable error is 2-4 percent.

Liquid heat capacities have been determined only up to room temperature.[1,4] The heat capacity of vinyl acetate at 20° C was calculated by the method of Johnson and Huang.[3] This method yielded an error of less than 1 percent for ethyl and butyl acetate. The data were extrapolated over the –40° C to 160° C range by the equation, heat capacity times density equals a constant. The probable error is about 5 percent.

Density. Timmermans reports data for the density of methyl and ethyl acetate up to the critical point.[1] The additive method of Shroeder[3] was used to calculate the density of vinyl acetate at the boiling point. This method gave an error of less than 1 percent for ethyl acetate. The density of butyl acetate has been measured at room temperature. The density at other temperatures for butyl and vinyl acetate was calculated by the method of Lyderson and co-workers.[3] This method gave an average error of about 2 percent for methyl and ethyl acetate.

Viscosity. The vapor viscosity has been measured from 100-200° C for methyl acetate[7] and 0-325° C for ethyl acetate.[3,7] Bromley and Wilkes[7] method was used to estimate the vapor viscosity from 0° C to 500° C.[8] The error is normally about 3 percent.

Experimental data have been reported on methyl acetate from 0-140° C, on ethyl acetate from 0-190° C, and on butyl acetate at 25° C.[1,3,4,7] The liquid viscosities of butyl and vinyl acetate were estimated by the method proposed by Thomas,[3] with a probable error of 5-10 percent.

Fig. 29-8 shows the effect of pressure on the liquid viscosity of ethyl acetate at 30° C and 75° C.[7]

Surface Tension. Experimental data have been published on the surface tension of methyl and ethyl acetate from 0° C to the critical point.[7] Sugden's method was used to calculate the surface tension of butyl and vinyl acetate.[9] Up to the boiling point, this method gives errors of only a few percent.

Thermal Conductivity. The vapor thermal conductivities were estimated by the method developed by Owens and Thodos.[10] Owens and Thodos report the quasi-critical thermal conductivities of methyl and ethyl acetate. Consequently, the error on these two compounds should only be a few percent. This parameter had to be estimated for butyl and vinyl acetate, with a probable error of about 10 percent.

Mason has measured the liquid thermal conductivities of ethyl and butyl acetate from 0-100°C.[11] The method of Robbins and Kingrea was used to estimate the thermal conductivities of methyl and vinyl acetate.[12] This method gave an average error of 3.8 percent for eight experimental values of ethyl and butyl acetate.

LITERATURE CITED

[1] Timmermans, J., "Physical-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York (1950).
[2] Stull, D. H., *Industrial and Engineering Chemistry* 39, pp. 517-550 (April, 1947).

TABLE 29-1—Physical Properties of Acetates

Compound	Boiling Point, °C	Freezing Point, °C	Molecular Weight	Critical Properties		
				T_c °C	P_c psia	d_c g/ml
Methyl Acetate.	57.8	−98.7	74.08	233.7	666	0.3252
Ethyl Acetate...	77.1	−83.6	88.10	250.1	557	0.3077
Butyl Acetate...	126.1	−73.5	116.16	306	442*	0.294*
Vinyl Acetate...	72.5	......	86.10	252*	609*	0.324*

* Estimated.

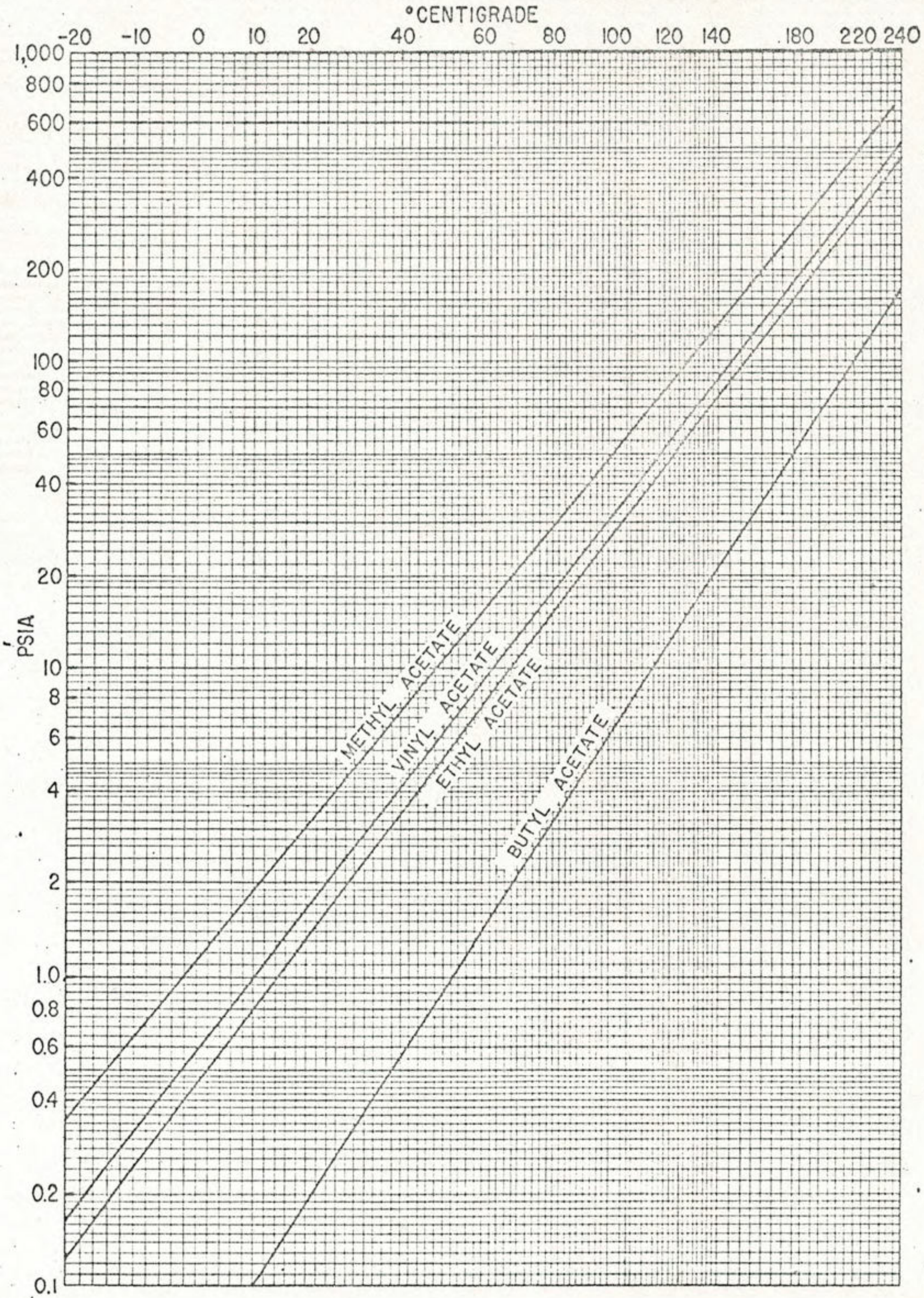

Fig. 29-1—Gives vapor pressure of acetates from —20° C to +240° C.

[3] Reid, R. C., and Sherwood, T. K., "The Properties of Gases and Liquids." McGraw-Hill Book Co., New York (1958).
[4] Marsden, C., and Mann, S., "Solvents Guide." Interscience Publishers, New York (1963).
[5] Kharbanda, P. O., *The Industrial Chemist*, pp. 124-7 (March, 1955).
[6] Rihani, D. N., and Doraiswamy, L. K., *Industrial and Engineering Chemistry Fundamentals* 4 (1), pp. 17-21 (1965).
[7] "International Critical Tables," McGraw-Hill Book Co., Inc. (1926).
[8] Bromley, L. A., and Wilkes, C. R., *Industrial and Engineering Chemistry* 43 (7), pp. 1641-8 (1951).
[9] Gambill, W. R., *Chemical Engineering*, pp. 146-50 (April, 1958).
[10] Owens, E. J., and Thodos, G., *AIChE Journal* 6 (4), pp. 676-81 (1960).
[11] Mason, H. L., *Transactions of The ASME*, pp. 817-21 (July, 1954).
[12] Robbins, L. A., and Kingrea, C. L., *American Petroleum Institute, Division of Refining* 42 (III), pp. 52-61 (1961).

Indexing Terms: Butyl Acetate-9, Computations-4, Ethyl Acetate-9, Heat-7, Liquid Phase-5, Methyl Acetate-9, Physical Properties-7, Pressure-6, Properties/Characteristics-7, Temperature-6, Vapor Phase-5, Vinyl Acetate-9.

More graphs on following pages

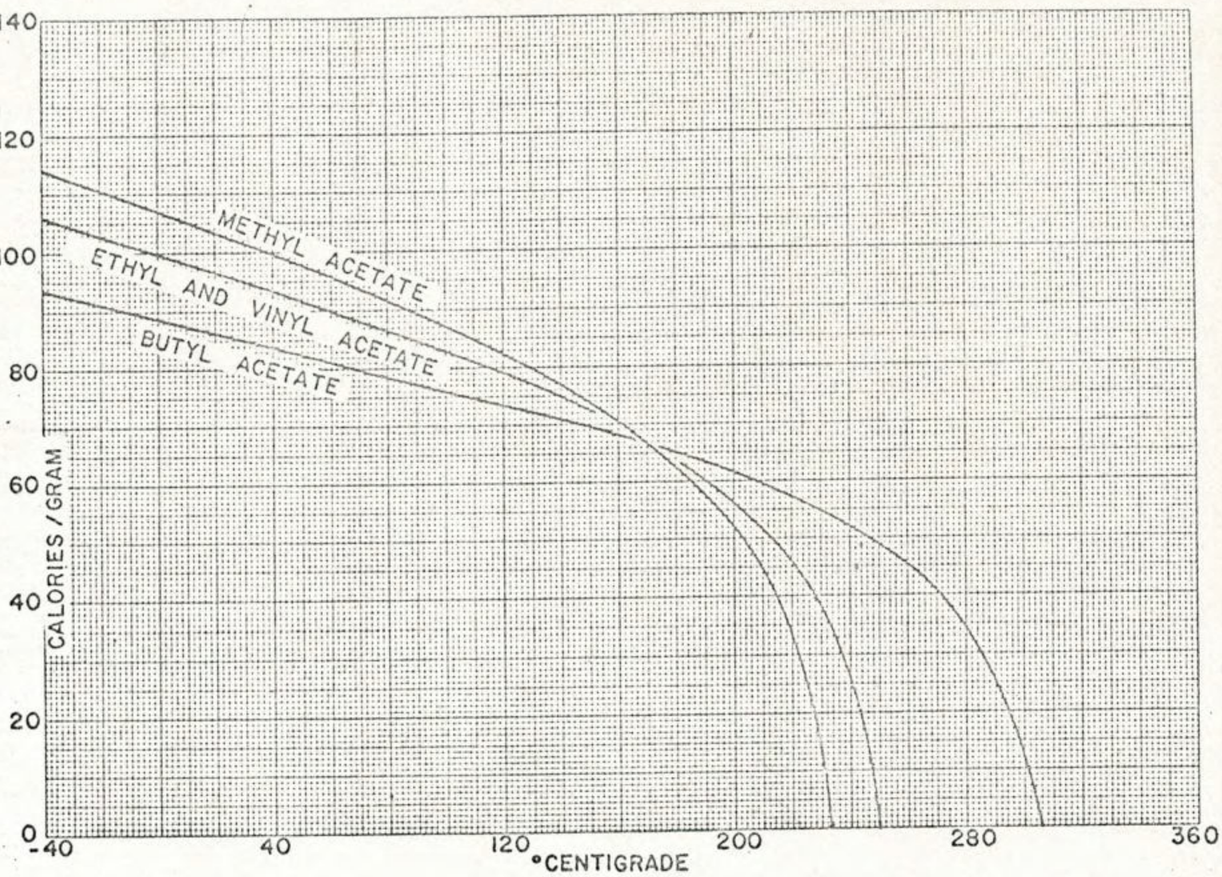

Fig. 29-2—Gives heat of vaporization of acetates from −40° C to +300° C.

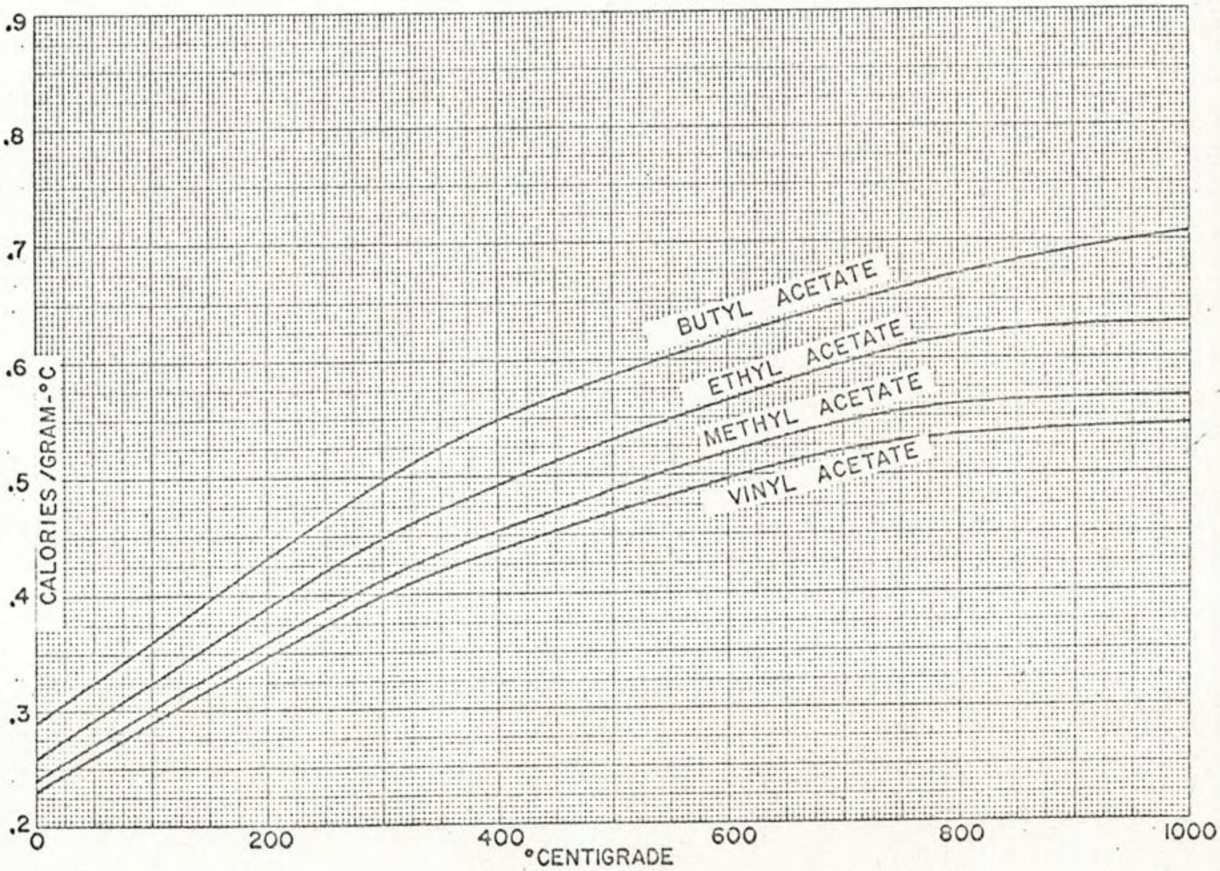

Fig. 29-3—Gives vapor heat capacity of acetates from 0° C to 1,000° C.

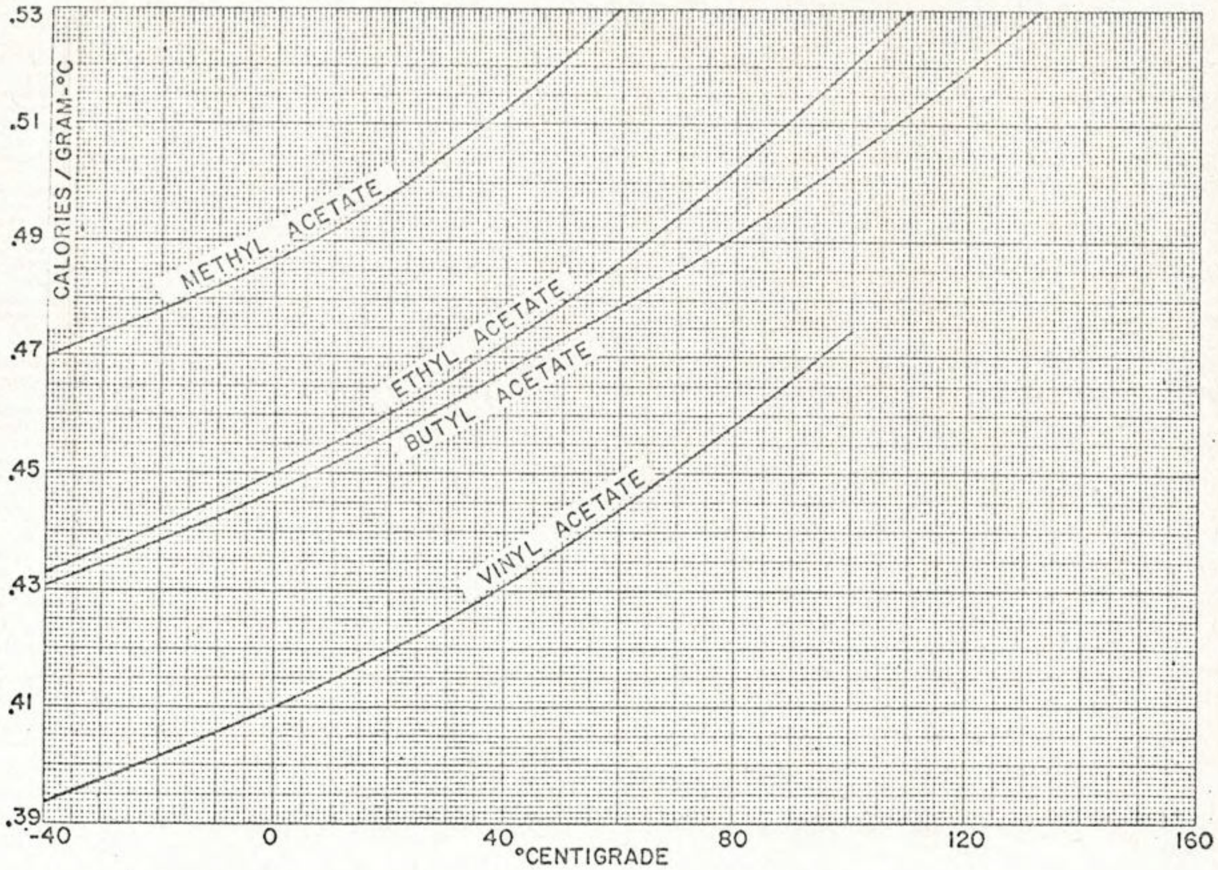

Fig. 29-4—Gives liquid heat capacity of acetates from —40° C to +130° C.

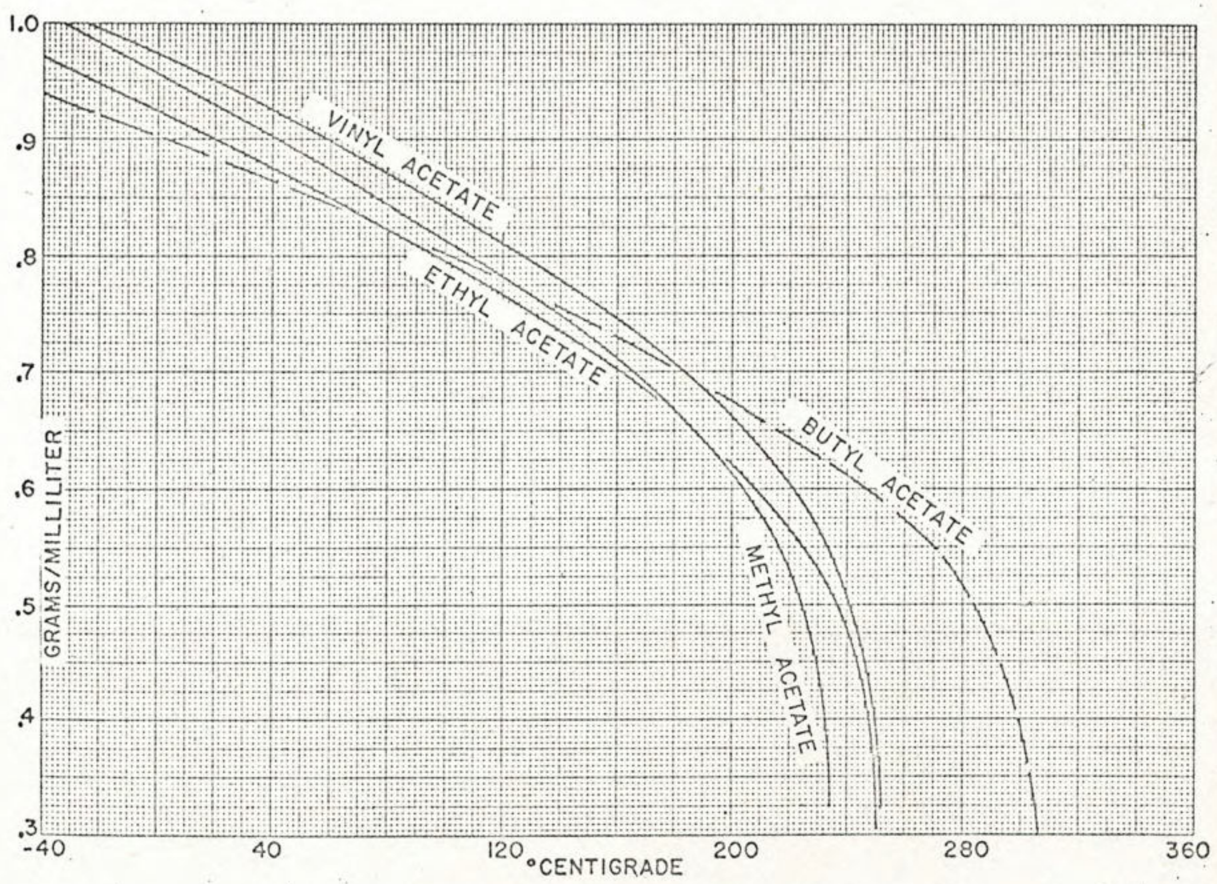

Fig. 29-5—Gives liquid density of acetates from —40° C to +300° C.

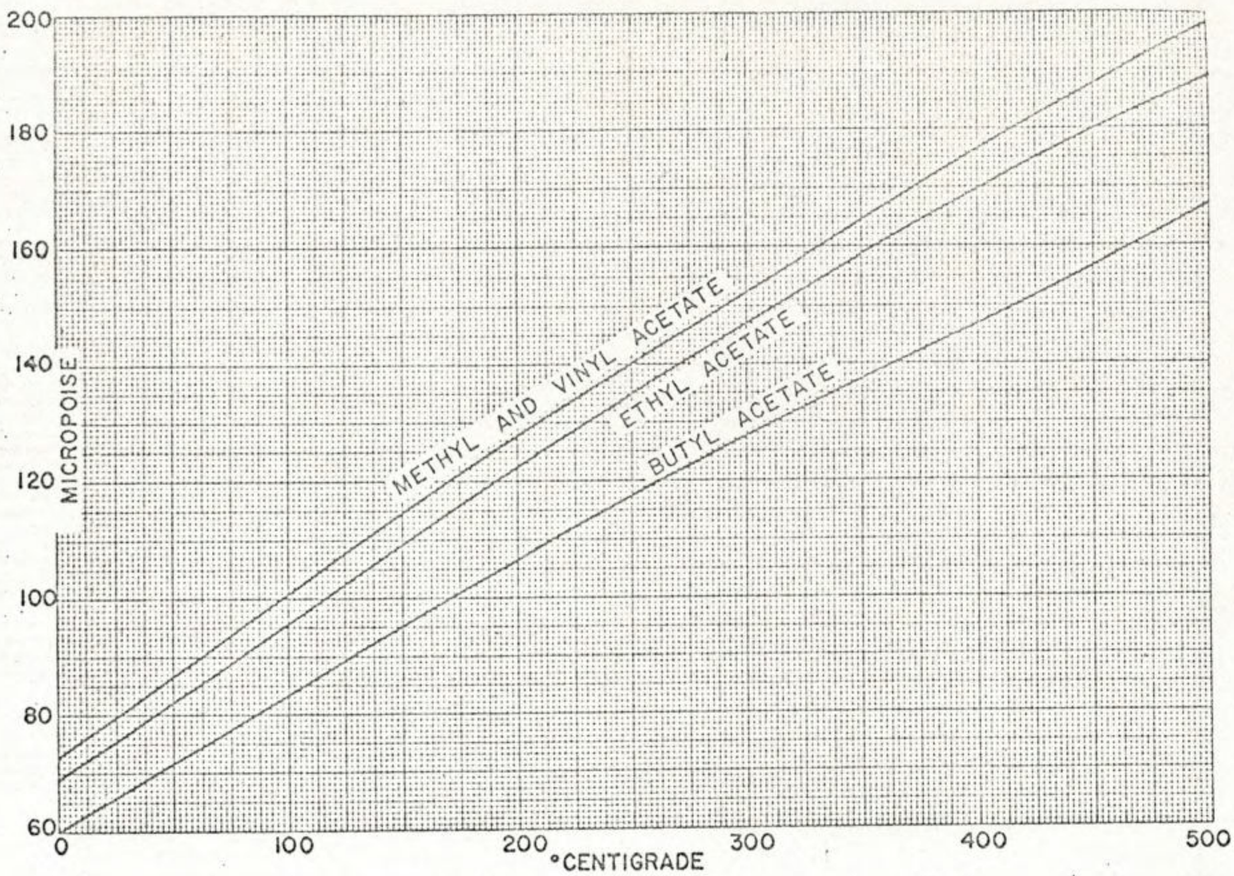

Fig. 29-6—Gives vapor viscosity of acetates from 0° C to 500° C.

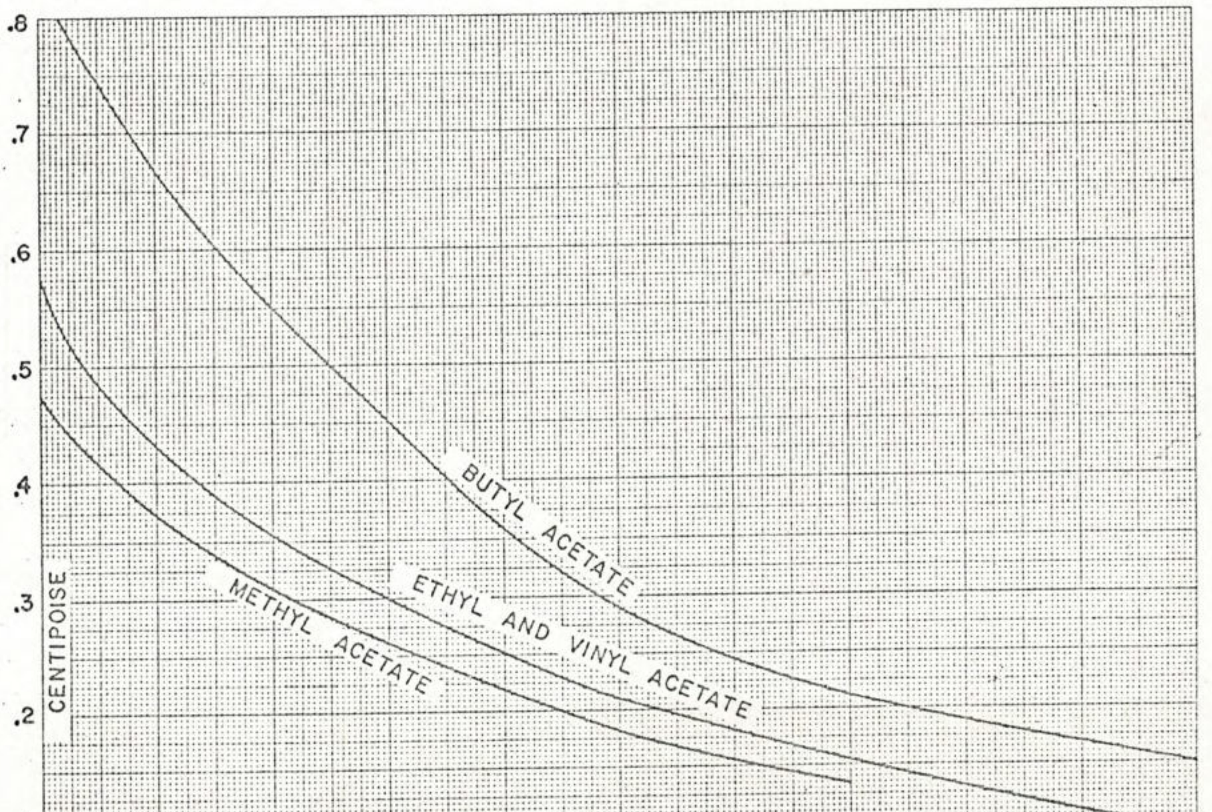

Fig. 29-7—Gives liquid viscosity of acetates from 0° C to 200° C.

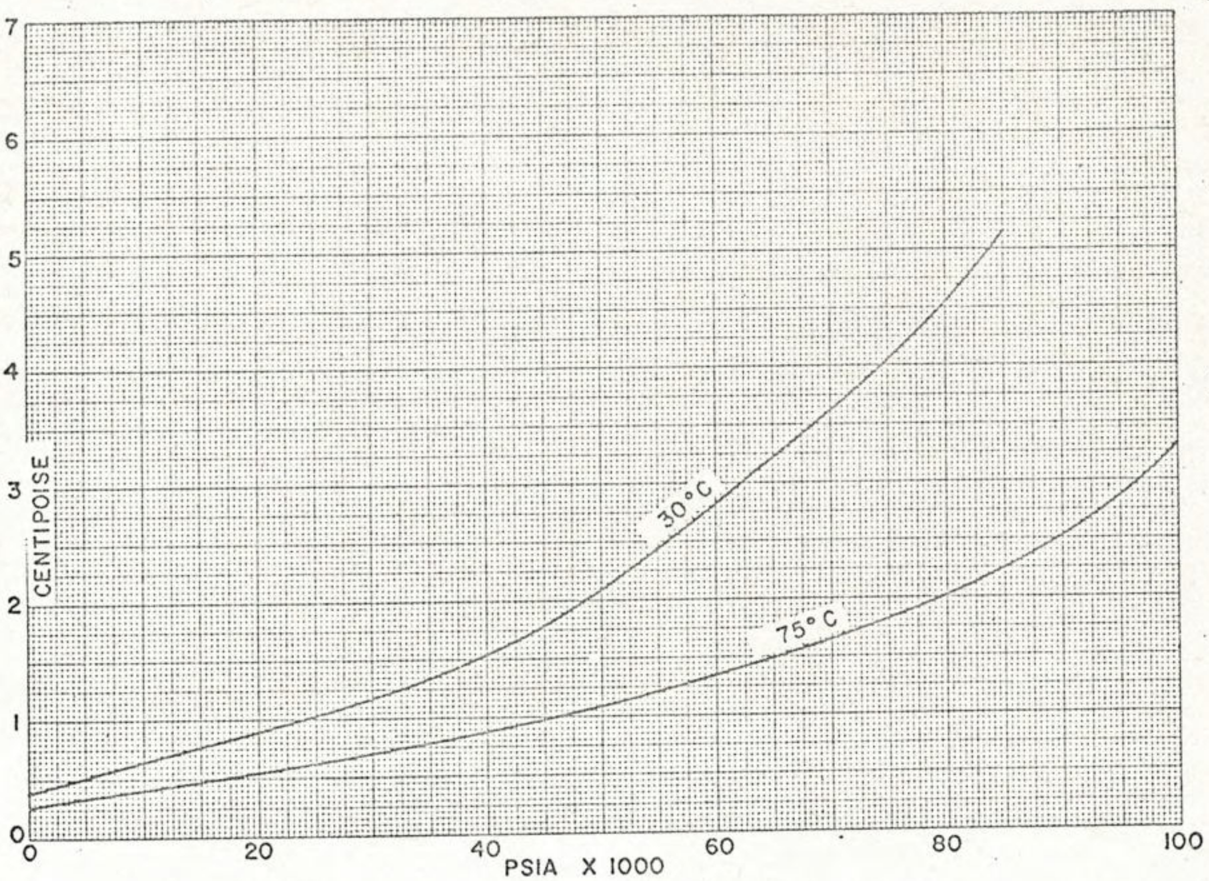

Fig. 29-8—Gives effect of pressure on ethyl acetate liquid viscosity.

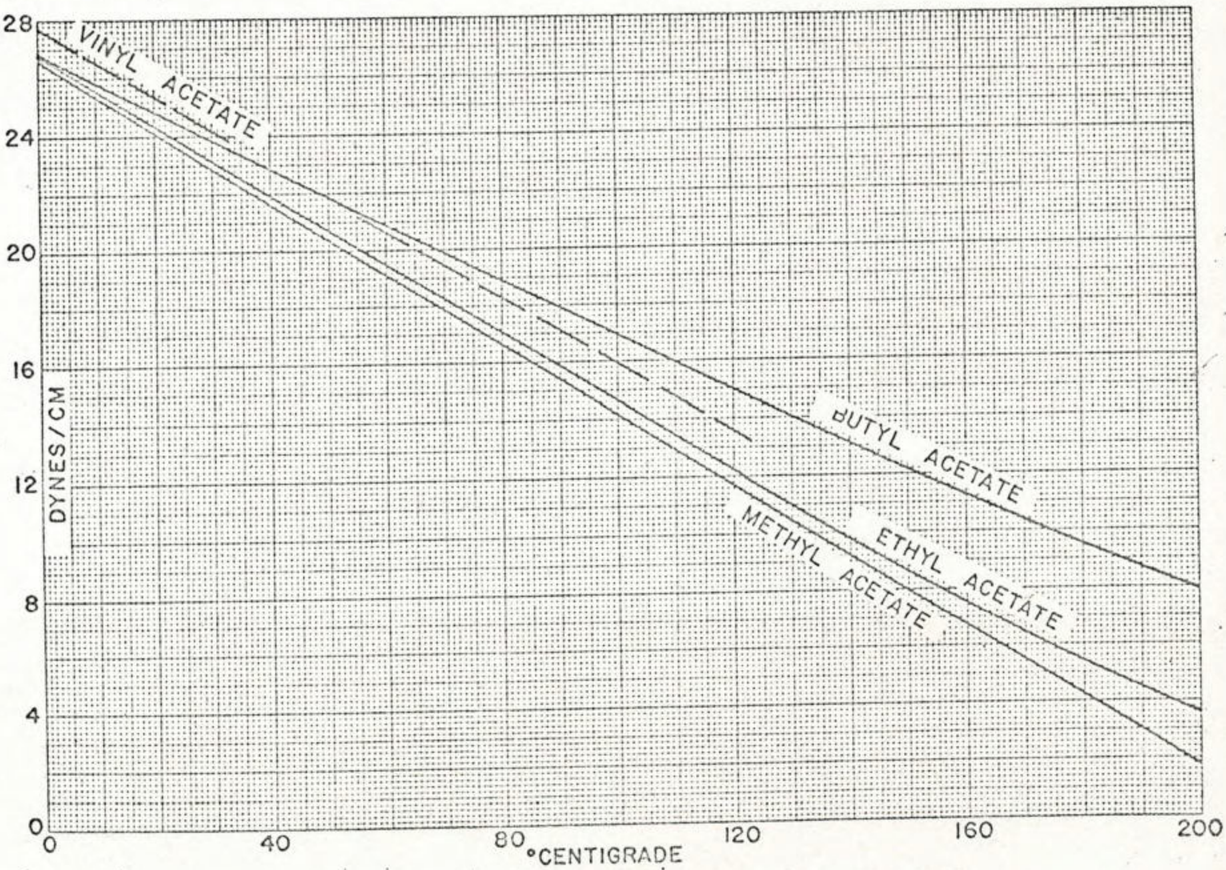

Fig. 29-9—Gives surface tension of acetates from 0° C to 200° C.

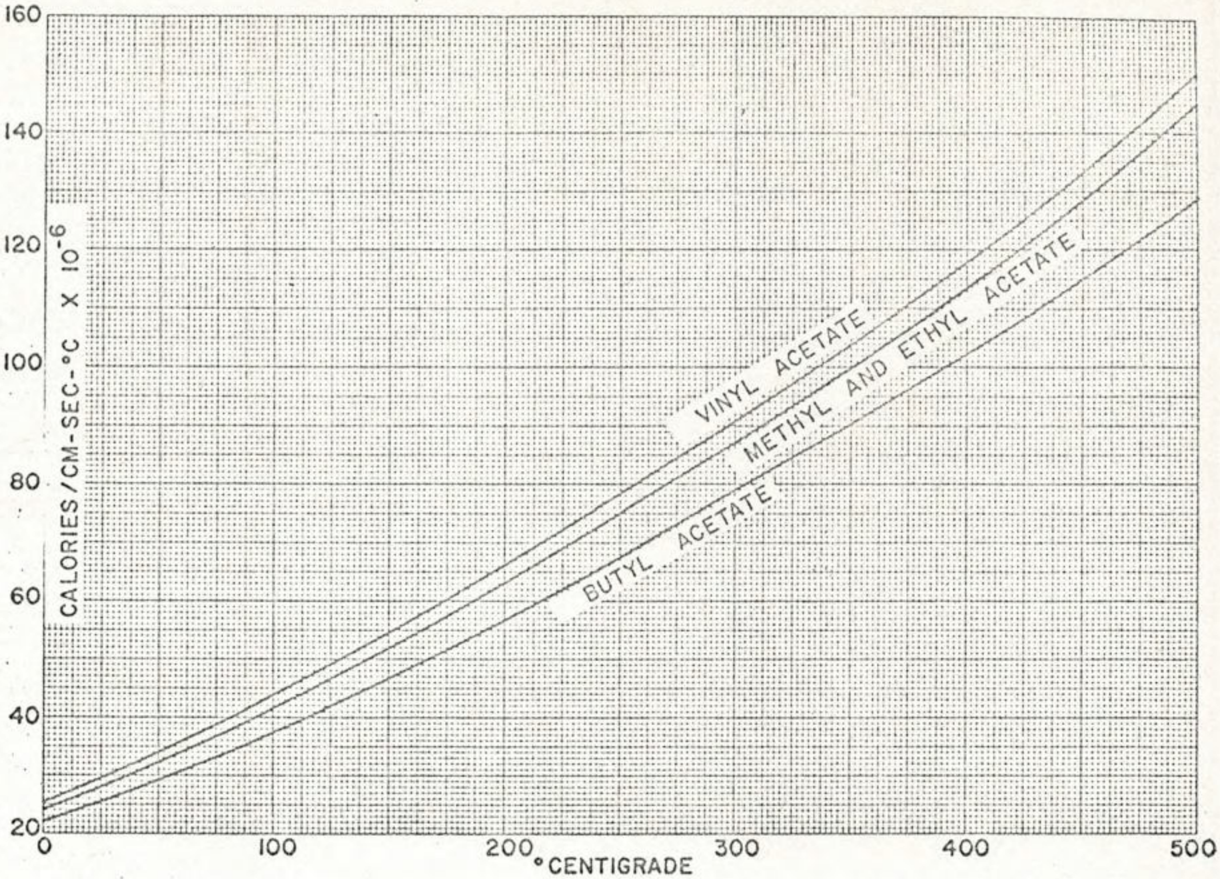

Fig. 29-10—Gives vapor thermal conductivity of acetates from 0° C to 500° C.

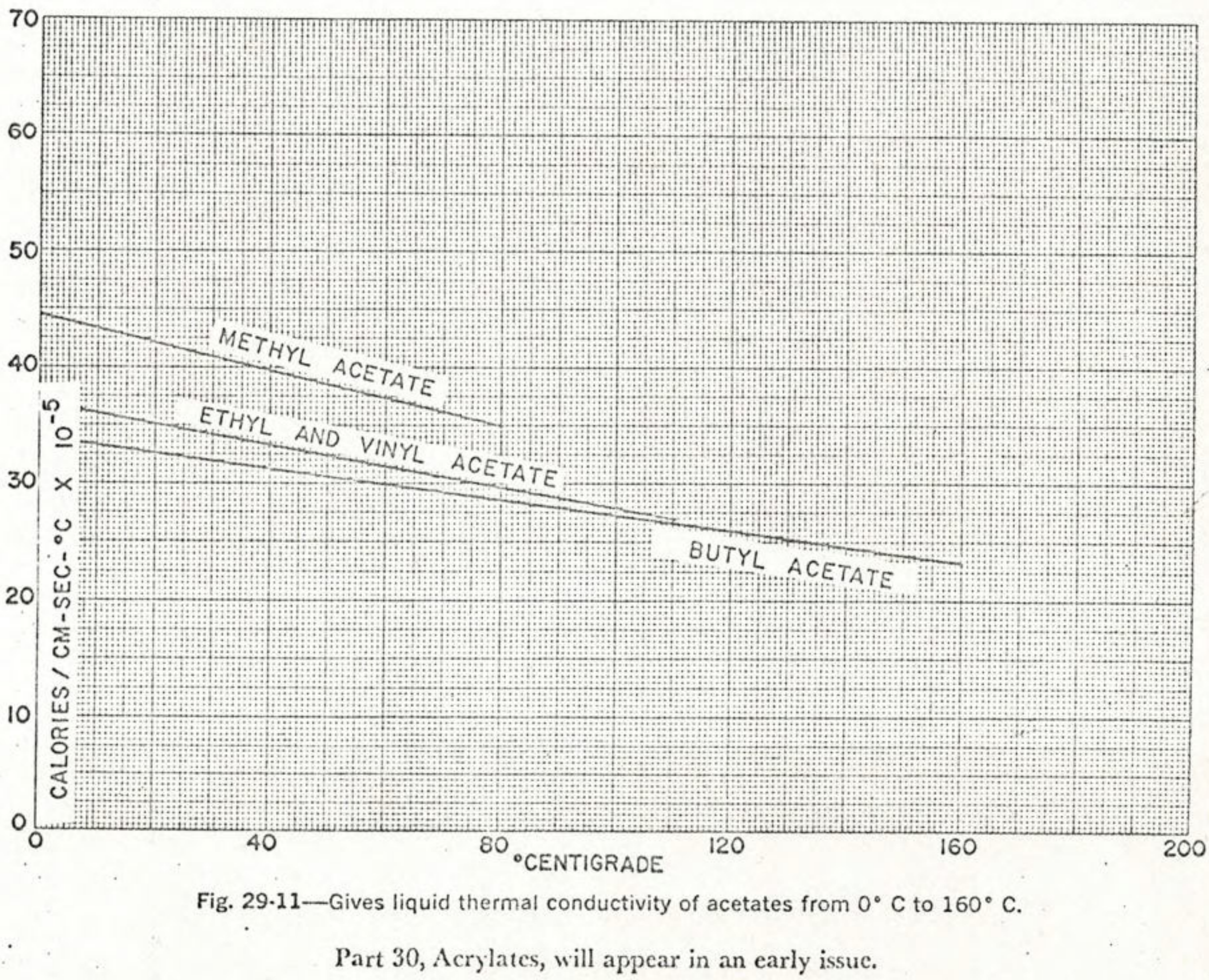

Fig. 29-11—Gives liquid thermal conductivity of acetates from 0° C to 160° C.

Part 30, Acrylates, will appear in an early issue.