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A Note on Viscosity as a Function of Volume and Temperature of Oils

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The viscosity-volume data of Kleinschmidt and Dow have been examined at various pressures and temperatures for lard, sperm and Pennsylvania medium oil. The viscosity-volume isotherms at 25°, 40° and 75°C are not identical for any of the oils studied, indicating that viscosity cannot be a function of the specific volume alone. The viscosity-volume curve for lard oil at 25° departs from the one at 75° by an amount sufficient to change the viscosity by a factor of 2.3 at a volume of 0.99, and by a factor of 3.2 at a volume of 0.93. Similar curves for Pennsylvania medium oil at the same temperatures are even more relatively displaced; the discrepancy in viscosity varies from a factor of 3.8 at a volume of 0.99 to 7.6 at 0.94. The three oils do not obey Batschinski's equation at atmospheric and higher pressures up to 4000 kg/cm^2.

COMPARATIVELY little is known of the physical properties of lubricating oils at high hydrostatic pressures. Among the nonthermodynamic properties of lubricants at high pressures, viscosity has been most extensively studied because of its significance for thick film lubrication. The experiments of Hyde[1] and, more recently, those of Hersey and Shore,[2] and Kleinschmidt,[3] have shown that the coefficient of viscosity of a mineral oil at ordinary temperatures increases by a factor of about 20 with an initial increase of pressure of 1000 kg/cm,[2] this increase being several times greater than that observed for pure liquids[4] or mixtures of liquids[5] through the same range of pressure. With the recent study of some of the thermodynamic properties of similar oils,[6] sufficient data are available for an examination of the viscosity of oils as a function of volume.

In addition to the practical usefulness of viscosity-volume data taken at various pressures and temperatures, there is theoretical interest in the functional relation between viscosity and volume. Consequently, this communication presents the viscosity-volume-temperature relations for three lubricating oils and includes a discussion of the theoretical relationship.

DATA

Table I contains the log relative viscosities and volumes at various pressures and temperatures for lard, sperm and Pennsylvania medium oil, respectively, the data being taken from the papers of Kleinschmidt[3] and Dow.[6] The density of each oil at atmospheric pressure and 40°C is given in order that the specific volumes may be computed directly from the table of volumes by division. The log relative viscosities are expressed as $\log_{10} t/t_0$, t being the time of fall of a weight in a viscometer at a certain pressure and tempera-

TABLE I. *Relative viscosity and volume.*

PRESSURE KG/CM^2	$\log_{10}$ RELATIVE VISCOSITY			VOLUME		
	25°	40°	75°	25°	40°	75°
			Lard oil $\rho_{40}=0.9009$ g/cm^3			
1	0	$\bar{1}.770$	$\bar{1}.370$	0.9902	1.0000	1.0190
100	0.079	.845		.9844	.9936	
250	.183	.938	.500	.9763	.9850	1.0051
500	.345	0.082	.628	.9647	.9721	.9921
750	.499	.220	.742	.9550	.9615	.9800
1000	.642	.351	.855	.9461	.9523	.9697
1500	.920	.607	0.070	.9299	.9366	.9522
2000		.835	.262		.9229	.9374
2500		1.052	.441		.9111	.9240
3000			.615			.9120
4000			.962			.8927
			Sperm oil $\rho_{40}=0.8945$ g/cm^3			
1	0	$\bar{1}.720$	$\bar{1}.256$	0.9894	1.0000	1.0227
100	0.079	.792	.374	.9835	.9934	
200	.150			.9781	.9876	1.0099
300	.220	.920		.9730	.9818	
400	.289	.981		.9685	.9768	
500		0.040	.531		.9722	.9925
750		.181	.649		.9618	.9794
1000		.318	.757		.9525	.9684
1500			.959		.9437	.9510
2000			0.149			.9368
2500			.327			.9241
3000			.481			.9127
4000			.792			.8926
			Pennsylvania oil $\rho_{40}=0.8524$ g/cm^3			
1	0	$\bar{1}.660$	$\bar{1}.020$*	0.9901	1.0000	1.0178
100	0.119	.761		.9839	.9934	
250	.280	.904	.235*	.9752	.9841	1.0040
500	.536	0.131	.420*	.9632	.9711	.9908
750	.777	.346	.594*	.9529	.9599	.9786
1000	1.008	.551	.760*	.9440	.9504	.9672
1500		.955	0.070		.9340	.9485
2000		1.341	.369		.9196	.9330
2500			.661			.9196
3000			.953			.9082
4000			1.511			.8891

* Extrapolated.

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[1] J. H. Hyde, Proc. Roy. Soc. **A97**, 240 (1920).
[2] M. D. Hersey and H. Shore, Mech. Eng. **50**, 221 (1928).
[3] R. V. Kleinschmidt, Trans. A.S.M.E. APM-50-4 (1928).
[4] P. W. Bridgman, Proc. Am. Acad. **61**, 57 (1926).
[5] R. B. Dow, Physics **6**, 71 (1935).
[6] R. B. Dow, J. Wash. Acad. Sci. **24**, 516 (1934).

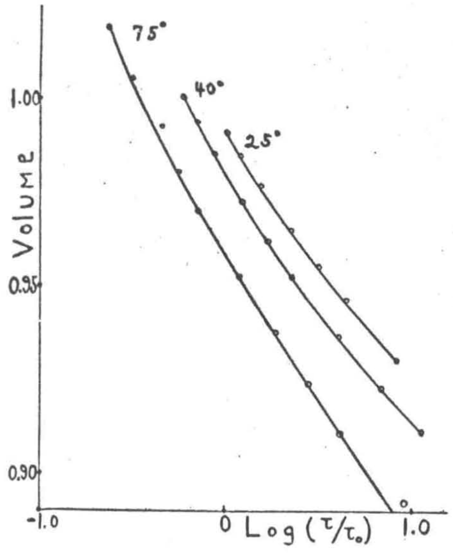

FIG. 1. Relative viscosity of lard oil as a function of volume.

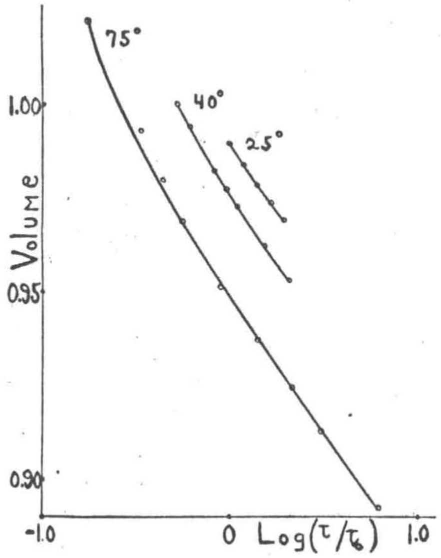

FIG. 2. Relative viscosity of sperm oil as a function of volume.

ture and t_0 the time of fall at atmospheric pressure at 25°. The reader is referred to the original papers for details of method and computation.

DISCUSSION

It is apparent at once on inspection of Figs. 1, 2, and 3, which are drawn from the data of Table I, that the relative viscosity increases greatly with comparatively small decrease of volume. Inasmuch as the figures are drawn from data of different observers, as mentioned previously, there is some doubt as to the experimental accuracy of the viscosity-volume curves. However, the writer's acquaintance with the method used by Kleinschmidt for the viscosity determinations leads him to estimate the inaccuracy of the curves to be not more than a few percent, which does not seriously limit their applicability. The lack of serious deviation of the points representing the experimental values from the smooth curves of the figures gives an indication of the probable degree of accuracy of the data.

An interesting feature of the figures is the relative displacements of the viscosity-volume curves at 25°, 40° and 75°C. If viscosity were a function of volume only, the curves for each oil would coincide at all three temperatures. The figures show that this requirement is not satisfied in any case. The viscosity-volume curve for lard oil at 25° departs from the curve at 75° by an amount sufficient to change the viscosity by a factor of 2.3 at a volume of 0.99, and by a factor of 3.2 at a volume of 0.93. Similar curves for the Pennsylvania oil at 25° and 75° are even more relatively displaced; the discrepancy in viscosity varies from a factor of 3.8 at a volume of 0.99 to 7.6 at 0.94.

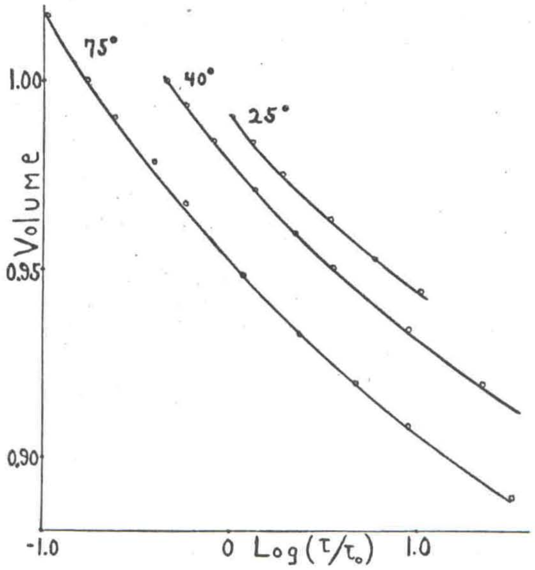

FIG. 3. Relative viscosity of Pennsylvania medium oil as a function of volume.

Of the theoretical relationships that have been proposed for viscosity as a function of volume, that of Batschinski[7] has been the most useful. His equation states that viscosity is related to the specific volume in the following way

$$\eta = c/v - \omega.$$

c and ω are characteristic constants of the liquid. Batschinski showed that if the change of fluidity of normal liquids, such as benzene and ethyl ether, was expressed with change of volume caused by change of either temperature or pressure, a linear relation resulted as demanded by his equation. But the data on viscosity and volume as functions of pressure were so limited in range of pressure available at that time, that both quantities could be fairly well expressed as linear functions of pressure. It is well known that such functions do not remain linear through the range of pressure now available.

Batschinski's equation has been used lately by Bingham and Brown,[8] Bingham and Coombs,[9] and Lederer[10] in deducing theories of viscosity. Although there is little experimental information concerning lubricants in this respect, R. N. J. Saal[11] in discussing the influence of pressure on the viscosity of a nonplastic, asphaltic bitumen, considered that his experimental data showed that the decrease of viscosity as the temperature rose was due to the effect of thermal expansion. Thus in addition to what has already been established without any assumption as to theory, namely, that viscosity is not a function of volume only, it is desirable to call attention to the failure of Batschinski' equation at high pressures, for this limitation does not seem to have been generaly established.

Bridgman[4, 12] has published viscosity-volume data for several normal liquids. His results gave curves similar to the figures of this paper. An examination of Batschinski's equation by substitution of Bridgman's data gives a general result that in no case is a linear relation obtained between fluidity and specific volume. Benzene, ethyl ether, pentane, etc., obey the Batschinski equation at atmospheric pressure, that is when the equation is applied for change of temperature, but at higher pressures the invalidity of the equation is beyond experimental error.

Consequently, on referring to Figs. 1, 2, and 3 again, it is not unexpected that the fluidity curves would not bear a linear relation to the volume, and the observed displacements of the curves show that the viscosity, or fluidity, is also a function of temperature. Accordingly, the constants c and ω of Batschinski's equation vary with pressure and temperature for these three oils. These data establish a point of much theoretical interest, namely that pressure and temperature changes affect viscosity differently.

Bridgman[13] in a recent paper on some of the theoretical aspects of high pressure phenomena has discussed the effects of temperature and pressure on the energy of solids, showing that in the case of NaCl the change of energy internal to the atom is nearly three times as great when a definite change of volume is brought about by a change of pressure as when brought about by a change of temperature. His explanation considers a compressible atom as demanded by a theorem of Schottky. It is likely that the fundamentals of the situation apply to liquids and give a possible explanation of the different effects of pressure and temperature on viscosity, although the problem remains to be treated quantitatively. The experimental evidence for the compressible atom is uncontrovertible to such an extent that Batschinski's conception of atomic volume constants cannot be valid over a wide experimental range. It is the desire of the author to call attention to these serious limitations of Batschinski's theory as demanded by the experimental data, rather than to question the usefulness of the relation at atmospheric pressure.

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[8] E. C. Bingham and D. F. Brown, J. Rheol. **3**, 95 (1932).

[9] E. C. Bingham and C. E. Coombs, Physics (New York Meeting).

[10] E. L. Lederer, Kolloid-Bei. **34–35**, 270 (1932).

[11] R. N. J. Saal, Proc. Wor. Pet. Congress, London, 521 (1934).

[12] P. W. Bridgman, Proc. Am. Acad. **66**, 185 (1931).

[13] P. W. Bridgman, Rev. Mod. Phys. **7**, 6 (1935).