RELATION OF THE VISCOSITY OF A LIQUID TO ITS THERMAL PROPERTIES

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It is shown that all points on an $\eta-\rho$ diagram for a liquid must lie on a single curve, and the curves of constant viscosity in P–T coordinates are straight lines.

By applying Newton's hypothesis on the tangential stresses in a viscous liquid the law of conservation of momentum for a homogeneous isotropic medium [1] can be written in the form

$$\frac{dW_i}{d\tau} = -\frac{1}{\rho}\cdot\frac{\partial P}{\partial x_i} + \frac{4}{3}\cdot\frac{\eta}{\rho}\cdot\frac{\partial \varphi}{\partial x_i}, \qquad (1)$$

where

$$\varphi = -\frac{1}{\rho}\cdot\frac{d\rho}{d\tau}.$$

In deriving (1) Frenkel's hypothesis on the potential nature of fluctuating flows [2, 6] was used. Although there are no reliable experimental data on relaxation times in liquids the validity of this hypothesis is confirmed in first approximation by the existence of the Bernoulli, Cauchy, and Bernoulli–Euler integrals [1].

Assuming that momentum is propagated so rapidly that the process can be considered adiabatic, we replace the operator $\partial/\partial x_i$ by $(\partial\rho/\partial x_i)\partial/\partial\rho$. Then it follows from (1) that

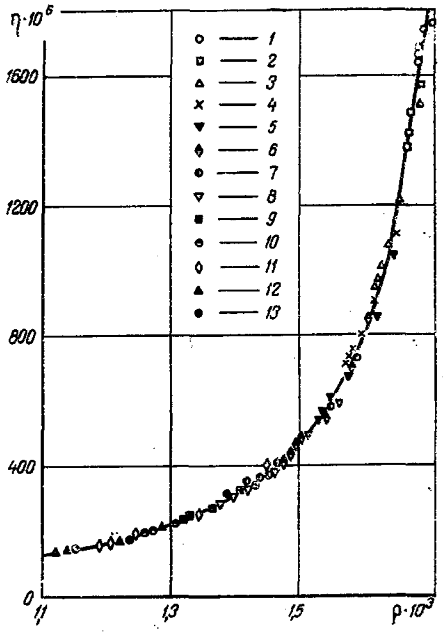

Fig. 1. Generalized relation of the viscosity of Freon-113: 1) 242.95; 2) 251.45; 3) 273.15; 4) 292.75; 5) 313.95; 6) 334.15; 7) 351.90; 8) 372.05; 9) 392.95; 10) 413.15; 11) 433.30; 12) 452.15; 13) 472.70°K.

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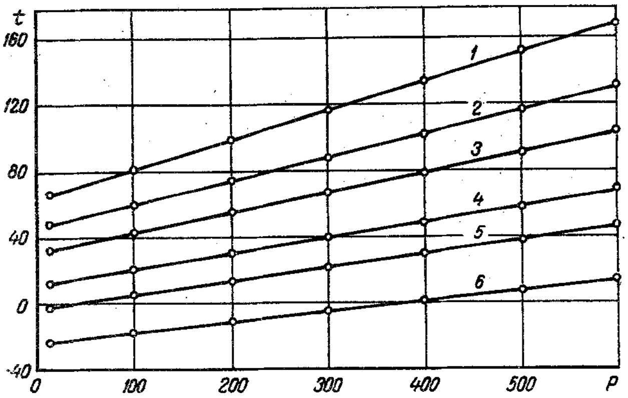

Fig. 2. Lines of constant viscosity for Freon-113. 1) 400; 2) 500; 3) 600; 4) 800; 5) 1000; 6) $1500 \cdot 10^{-6}$ N sec/m^2; t in °C; P in bars.

$$\frac{dW_i}{d\tau} = -\left[\left(\frac{\partial P}{\partial \rho}\right)_s - \frac{4}{3}\eta\left(\frac{\partial \varphi}{\partial \rho}\right)_s\right]\frac{\partial(\ln \rho)}{\partial x_i}. \tag{2}$$

According to Stokes' hypothesis on the impossibility of observing forces of normal extension or compression we have from the viscoelastic model for small strains [3]

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \frac{2}{3}\cdot\frac{\eta}{\tau_{\text{M}}\rho}. \tag{3}$$

In investigating the relation between transport and thermal properties we have used the Hadamard, Riemann, and Huygens method of "identical conditions" [1] which permits an analysis of the differential equations of state and hydrodynamics without integration. By applying this method we obtain

$$G = \left(\frac{\partial P}{\partial \rho}\right)_s - \frac{4}{3}\eta\left(\frac{\partial \varphi}{\partial \rho}\right)_s. \tag{4}$$

Substituting the value of $(\partial P/\partial \rho)_s$ from (3) into (4) we find the viscosity in the form

$$\eta = \frac{3}{2}\cdot\frac{G\tau_{\text{M}}}{v - 2\dfrac{\partial \varphi}{\partial \rho}\tau_{\text{M}}}. \tag{5}$$

Equation (5) can be considered as a qualitative analog of the well-known Batchinsky formula [4], but it clearly can give better quantitative results since the values of the coefficient in (5) can be found as functions of the pressure and temperature.

Assuming that $(\partial P/\partial \rho)_s \gg (4/3)\eta(\partial \varphi/\partial \rho)_s$ for a liquid it follows from (4) that

$$G = \left(\frac{\partial P}{\partial \rho}\right)_s. \tag{6}$$

Since according to (5)

$$\tau_{\text{M}} = A\frac{\eta}{K}, \tag{7}$$

where

$$K = -\frac{1}{\dfrac{1}{v}\left(\dfrac{\partial v}{\partial P}\right)_s}.$$

we obtain from (5), (6), and (7)

$$\eta = -\frac{1}{4.4}\cdot\frac{v^2}{\left(\dfrac{\partial \varphi}{\partial \rho}\right)_s}\left(\frac{\partial P}{\partial v}\right)_T\frac{C_p}{C_v}. \tag{8}$$

Since $C_p/C_v \approx$ const for a liquid over a rather wide range of temperatures and pressures it follows from Eq. (8) that in the range of parameters where it is accurate enough to consider the density on the isotherms as a linear function of the pressure, i.e., $(\partial P/\partial v)_T$ = const, all points on an $\eta-\rho$ diagram must lie on a single curve since $(\partial \varphi/\partial \rho)_s$ is a function of the density only. In addition since the values of $(\partial P/\partial v)_T$ on neighboring isotherms in a liquid are very close to one another, differences with respect to isotherms in the region of moderate densities will not be noticed in quite accurate experimental data on viscosity.

As an example Fig. 1 shows the $\eta-\rho$ diagram of Freon-113 (trichlorotrifluoroethane) in the liquid phase. The values of the viscosity were obtained with an accuracy of ±1.5% [7] by the capillary viscosimeter method at temperatures from −30 to +200°C and pressures up to 600 bars. The deviations of the experimental data from the generalized relation lie within the limits of experimental error. A similar result was reported in [8] for the experimental data on the viscosity of normal hydrocarbons and certain other liquids. It appears that the divergences occurring in the high density region can be explained by the fact that in this range of parameters the assumptions made in the analysis of Eq. (8) are no longer valid.

From (8) it is easy to obtain the relation

$$F=\frac{\left[\frac{\partial}{\partial P}(\ln v^2)\right]_T-\left\{\frac{\partial}{\partial P}\left[\ln\left(\frac{\partial v}{\partial P}\right)_T\right]\right\}_T-\left\{\frac{\partial}{\partial P}\left[\ln\left(\frac{\partial \varphi}{\partial \rho}\right)_s\right]\right\}_T}{\left[\frac{\partial}{\partial T}(\ln v^2)\right]_P-\left\{\frac{\partial}{\partial T}\left[\ln\left(\frac{\partial v}{\partial P}\right)_T\right]\right\}_p-\left\{\frac{\partial}{\partial T}\left[\ln\left(\frac{\partial \varphi}{\partial \rho}\right)_s\right]\right\}_p}, \tag{9}$$

where

$$F=\frac{\left(\frac{\partial\eta}{\partial P}\right)_T}{\left(\frac{\partial\eta}{\partial T}\right)_p}.$$

Since η is a single valued function of the density in the region considered, in the analysis of Eq. (9) it is necessary to differentiate it with respect to v. Since $(\partial v/\partial P)_T$ is small in a liquid except near the critical region, it follows from an analysis of dF/dv that F = const.

Writing the equation of state for viscosity in the form $\psi(P, T, \eta) = 0$ we obtain

$$\frac{\left(\frac{\partial\eta}{\partial P}\right)_T}{\left(\frac{\partial\eta}{\partial T}\right)_P}=-\left(\frac{\partial T}{\partial P}\right)_\eta. \tag{10}$$

Thus in the range of parameters under discussion the curves of constant viscosity on a P–T diagram are straight lines.

This conclusion was verified with the experimental data for water, carbon dioxide, ammonia, benzene, toluene, a number of saturated hydrocarbons, and certain Freons. Figure 2 shows the lines of constant viscosity for Freon-113 according to the data of [7].

It should be noted that this characteristic behavior of the viscosity of a liquid was first observed by Rivkin et al., [5] and used to describe the experimental values of η for ordinary and heavy water.

NOTATION

W_i	is the i-th component of velocity;
x_i	is the coordinate;
G	is the function of the state parameters;
P	is the pressure;
ρ	is the density;
η	is the coefficient of dynamic viscosity;
τ	is the time;
τ_M	is the Maxwellian relaxation time;
v	is the specific volume;
K	is the bulk modulus;
T	is the temperature;
A, B	are the constants.

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