USE OF THE THEORY OF SIMILARITY IN DETERMINING THE VISCOSITY OF FLUIDS FROM MOLECULAR DATA

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Inzhenerno-Fizicheskii Zhurnal, Vol. 15, No. 1, pp. 139–145, 1968

UDC 530.17:532.133

An approximate method is proposed for determining the viscosity of one-component fluids on the saturation line. This method involves the use of the theory of similarity and the molecular data of the substance investigated.

Lack of information on the structure of fluids makes it impossible to determine their properties by purely analytic means using the apparatus of modern mathematics. The empirical method of investigating physical constants has only a limited potential, since the data of one experiment cannot be extended to other substances. The method based on the theory of similarity and dimensional analysis is free of this disadvantage.

The problem of determining physical constants from the law of corresponding states was comprehensively examined in [8]. In [9] one section includes a determination of the viscosity of fluids on the saturation line, where the concept of a standard is introduced. The study of fluid parameters has also attracted much attention among foreign authors, for example, [10]. In particular, in [10] there is a short section on the determination of viscosity. L. P. Filippov [11, 12] and others have written many papers on the investigation of fluid parameters.

The dimensionless relative variables, by means of which the quantitative relation between the primary quantities is expressed, are obtained on the basis of the system of differential equations characterizing the phenomenon in question. The absence of a complete system of equations describing the properties of a fluid prevents the direct application of the theory of similarity. Consequently, there remains for obtaining the relative variables the second component of the method of generalized variables [1]—dimensional analysis. This paper is concerned with a method of analyzing experimental data which, in some degree, makes it possible to express the individual properties of fluids in terms of their molecular data. This method is a further development of the ideas advanced in [6] and [7].

One of the authors previously obtained several generalized variables on the basis of dimensional analysis [6]. If we supplement this system with the compressibility

$$K_z = \frac{pv}{RT},$$

experimentally we can obtain a simple criterial relation for determining the viscosity on the saturation line

$$K_\mu = f(K_z) \tag{1}$$

or in developed form

$$\frac{N}{M}\,\frac{l}{p}\,\mu^2 = f\left(\frac{pv}{RT}\right). \tag{1a}$$

In Eq. (1a) the characteristic dimension l must somehow express the properties of the fluid.

To increase the volume of information expressed by the characteristic dimension, the following formula is proposed:

$$l = \sqrt{\frac{M(\Sigma E)}{(\Sigma C)(\Sigma Z)}}. \tag{2}$$

The radicand in (2) was selected on the basis of its property of approximately expressing the compactness of the molecule. Consequently, the characteristic dimension is a quantity inversely proportional to the nominal diameter of the molecule, since the specific volume and density are related by the expression

$$\rho v = 1.$$

For a molecule consisting of several atoms of different kinds the individual characteristics are defined as follows:

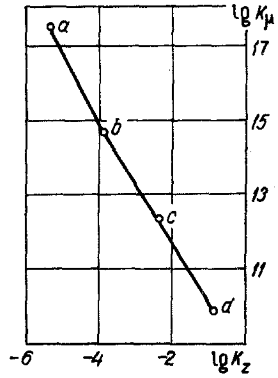
$$\Sigma C = \sum_1^m (n_A \Sigma C_A), \quad \Sigma Z = \sum_1^m n_A Z_A,$$

$$\Sigma E = \sum_1^m n_A E_A. \tag{3}$$

Thus, the characteristic dimension expresses the individual properties of a substance in terms of its molecular data. In order to obtain a specific form of criterial equation (1) we used the thermophysical data for water from [2] and [3]. Water is a substance that is anomalous in certain respects. However, its properties have been closely studied, and for this reason it was selected as a standard. The relation between K_μ and K_Z for water is presented in a logarithmic coordinate system in the figure. The graph shows the presence of three clearly expressed regions. For the first region with

$$K_z = 4.91 \cdot 10^{-6} - 1.323 \cdot 10^{-4}$$

analysis of the experimental data gives the following criterial equation:



Dimensionless viscosity K_μ as a function of the compressibility K_z.

$$K_\mu = \frac{7.85\cdot 10^7}{K_z^{1.775}}, \tag{4}$$

which corresponds to the equation in general form

$$K_\mu = c\,(K_z)^n. \tag{5}$$

For the second region with

$$K_z = 1.323\cdot 10^{-4} - 4.34\cdot 10^{-3}$$

we obtain the equation

$$K_\mu = \frac{1.5\cdot 10^8}{K_z^{1.705}}. \tag{6}$$

For the third region with

$$K_z = 4.34\cdot 10^{-3} - 1.577\cdot 10^{-1}$$

the relation between the variables has the form

$$K_\mu = \frac{5.57\cdot 10^8}{K_z^{1.471}}. \tag{7}$$

The graphical construction of relation (1) for a number of liquids (benzene, ethyl alcohol, etc.) shows that the family of curves obtained possesses approximate similarity. Here, in accordance with [1], similarity is used in a broader sense than elementary geometric similarity. This means that the coordinates of the standard curve can be obtained by multiplying the coordinates of the test fluid by the conversion factors K_x and K_y.

An analysis of the experimental data shows that in the given case K_x and K_y are not equal (for most points). Therefore in order to employ criterial equations (4), (6), and (7) it is necessary to determine the corresponding (similar) points expressing similar states of the standard and the test substance. To determine the limits of applicability of the criterial equation to the test substance we introduce the dimensionless parameter

$$\Pi = \frac{T}{T_{cr}} + \frac{p}{p_{cr}} + \frac{v}{v_{cr}}. \tag{8}$$

The parameter Π contains fuller information than any of its components. Quantitatively, the same thermodynamic state is characterized differently by each of these simplexes T/T_{cr}, v/v_{cr}, p/p_{cr}. The order of magnitude of these variables and their rate of change on transition from one state to another sometimes differ considerably.

The introduction of the parameter Π smooths out this difference and reduces the scatter of the points (as compared with the simplexes). The use of this parameter accelerates the calculations, since even at small values of p, v, and T it takes values close to unity. For water at the point b the quantity $\Pi = 0.83$ and at the point c, $\Pi = 1.062$. Consequently, Eq. (4) is applicable at $\Pi < 0.83$ and Eqs. (6) and (7) at $\Pi = 0.83–1.062$ and $\Pi > 1.062$, respectively.

We can now employ the following method of extending the criterial equations for water (4), (6), and (7) to other fluids.

For the standard in general form we have

$$K_\mu^{st} = c\,(K_z^{st})^n. \tag{9}$$

Here, it is assumed that K_μ and K_z for the standard are expressed in terms of the same quantities for the test fluid:

$$K_\mu^{st} = K_\mu^t K_y,$$
$$K_z^{st} = K_z^t K_x. \tag{9a}$$

Using (9a), we obtain

$$K_\mu^t K_y = c\,(K_z^t K_x)^n. \tag{9b}$$

For our conditions from Eq. (9b) (considering that the exponents in (4), (6), and (7) are negative)

$$K_\mu^t = \frac{1}{K_y (K_x)^n}\,\frac{c}{(K_z^t)^n} \tag{10}$$

follows directly.

In the general case, in accordance with [1], the quantities K_y and K_x are functions of the independent variables

$$K_y (K_x)^n = f\,(K_z,\ K_\mu,\ \Pi). \tag{11}$$

An analysis of the experimental data shows that relation (11) can be approximately reduced to the following simple formulas: a) for $0 < \Pi < 2$

$$\frac{1}{K_y (K_x)^n} \cong (\Pi_{cr} - \Pi)^2, \tag{12}$$

where $\Pi_{cr} = 3$ is the dimensionless parameter Π in the critical state;

b) for $\Pi \geq 2$

$$\frac{1}{K_y (K_x)^n} \cong 1. \tag{13}$$

To check the applicability of the formulas obtained we compared the experimental viscosity data of [2, 3] with the values calculated from (10). The substances concerned, propane, benzene, carbon tetrachloride, ethyl alcohol, and diborane, have distinctly different physical properties.

The molecular characteristics of these substances are presented in Table 1.

Table 2 shows how the calculated values differ from the experimental viscosities. At present, when experi-

Table 2

Comparative Data on the Determination of Viscosity by Different Methods

Substance	$p_{cr}\cdot 10^{-4}$, N/m²	$v_{cr}\cdot 10^{3}$ m³/kg	T_{cr}, °K	$p\cdot 10^{-4}$, N/m²	$v\cdot 10^{3}$, m³/kg	T, °K	$\mu_{exp}\cdot 10^{6}$, N·sec/m²	Viscosity according to Souders $\mu\cdot 10^{6}$, N··sec/m²	Error according to Souders in % $((\mu_{exp}-\mu)/\mu_{exp})\cdot 100$	Viscosity according to Thomas $\mu\cdot 10^{6}$, N·sec/m²	Error according to Thomas in % $((\mu_{exp}-\mu)/\mu_{exp})\cdot 100$	Π	Viscosity according to Eq. (10) $\mu\cdot 10^{6}$, N·sec/m²	Error according to Eq. (10) in % $((\mu_{exp}-\mu)/\mu_{exp})\cdot 100$
C_3H_8	388	6.02	370	117.2	2.08	306.9	87	133	— 51,2	106,5	—19,4	1,477	65,5	24,7
				238	2·3	333	61.8	112	— 81	85	—38,2	1,897	60,6	1,93
				350	2·785	356.9	46	109,5	—138	73,5	—60	2,37	43,7	5
C_6H_6	477	3.29	563	10.15	1.225	353	314,5	100	+ 68	252	+19,2	1,025	309	+1,72
				182,5	1.525	487	98.1	100	0	118	—14	1,712	104	—6
				445	2.28	554	41.5	100	—136,5	72	—73,8	2,608	52	—25,3
CCl_4	456	2.06	556	0,436	6.12	273	1353	3310	—145	1285	+5,07	0,789	1035	+23,5
				18.8	6·98	373	380	428	—10,4	389	—0,25	1,011	295	+22,3
				102	8.0	456	197	195	+1,97	210	—5,4	1,433	154	+22,0
B_2H_6	412,5	4.45	290	0·896	2.15	145,6	240	—	—	—	—	0,988	320	—33,3
				3.67	2·24	164	173·8	—	—	—	—	1,079	183,5	— 5,65
				30.45	2·5	204	95.8	—	—	—	—	2,016	60,8	+36,5
C_2H_5OH	640	3.57	516	10.15	1·36	358	440	492	—11,6	188	+63	1,087	584	—31,8
				79.4	1·51	414	179·5	235,8	—31,1	136	+24,3	1,357	274	—52
				528	2.3	504	63·1	113	—78	84	—33	2,445	56	+11,3

Table 1

Molecular Characteristics of Fluids

Substance	M	ΣC	$\Sigma 3$	ΣE	l
C_3H_8	44	14	26	20	1.343
C_6H_6	78	18	42	30	1.451
C_2H_5OH	46	12	26	20	1.434
B_2H_6	27.7	10	16	12	1.275
CCl_4	154	14	74	32	1.68

mental data are lacking, fluid viscosities are generally determined by either the Souders or the Thomas method [4,5]. Accordingly, we decided to compare the data obtained with the corresponding Souders and Thomas viscosities. The Souders formula [4] is

$$\lg(\lg 10\mu) = m\rho - 2.9, \tag{14}$$

where μ is the viscosity in centipoise, ρ is the density in g/cm³, m = I/M = const, and I the structural constant [4].

Thomas's formula is

$$\lg \frac{8.569\mu}{\sqrt{\rho}} = \theta\left(\frac{T_{cr}}{T} - 1\right). \tag{15}$$

Here, θ, the structural component, is determined from the data tabulated in [4]. The calculated values of the viscosity for all three methods are compared with the experimental values in Table 2, which shows, on average, the error is least when formula (10) is employed. Moreover, the Thomas and Souders formulas are limited to the extent that they are valid only for organic liquids. Consequently, the methods of [4] cannot be used to calculate the viscosity of diborane.

The proposed method of determining viscosity has its advantages and disadvantages. Among the latter is the need to know in advance the critical parameters and the specific volume, as well as a certain clumsiness. Its advantages are as follows.

1. The universality of the method, since there is no apparent reason for not using Eq. (10) to calculate the viscosity of any fluid.
2. The wide range of the basic formulas. They embrace practically all values of the independent variables—pressure and temperature of liquid phase—up to the critical values.
3. The possibility of estimating the viscosity of substances not yet created, which is important for producing fluids with predetermined properties (on the basis of the molecular data and critical parameters, for estimating which a number of methods exist).

NOTATION

$K_\mu = (N/M)(l/p)\mu^2$ is the generalized variable from [6]; T is the fluid temperature on the saturation line; p is the pressure; b is the specific volume; R is the gas constant; N is Avogadro's number for a kilomole; M is the molecular mass; μ is the dynamic viscosity; l is the characteristic dimension; A is the symbol of the chemical element; n_a is the number of atoms of the element A; ΣC is the sum of electron shells of all atoms of the molecule; ΣE is the sum of valences of all atoms of the molecule according to the Mendeleev periodic system; st, t are indices denoting standard and test substance, respectively; Z_A is the charge of element A; m is the number of atoms of different kinds in the molecule; ΣC_A is the sum of electron shells in an atom of element A; E_A is the group number of element A in the periodic table.

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22 November 1967

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