We note in conclusion that Gorodtsov and Leonov [3] have used an alternative semiempirical theory of turbulent wall flow based on the model of a periodic viscous substrate to describe the motion of a viscoelastic fluid; their results are qualitatively consistent with those obtained in the present study.

NOTATION

u,v, longitudinal and transverse velocity components; u',v', fluctuation velocity components; l, mixing length; d, tube diameter; V, average (discharge) velocity in the tube; $u_\tau = \sqrt{\tau_0/\rho}$, dynamic velocity; μ, dynamic viscosity coefficient; ν, kinematic viscosity coefficient; θ_1, relaxation time; θ_2, retardation time; ρ, density; λ, coefficient of viscous friction; ω, cyclic frequency; $W = \theta V/d$, Weissenberg number; $E = \theta\nu/d^2$, elastic constant; $Re = Vd/\nu$, Reynolds number; ppm, weight concentration of the solution in polymer parts per million parts water.

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VISCOSITY OF BINARY LIQUID SYSTEMS

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UDC 532.13

A method is proposed for calculating the viscosity of binary liquid systems (solutions, mixtures) involving the concentrations and properties of initial components on the basis of the theory of generalized conductivity.

Formulation of the Problem

A significant number of formulas for calculating the viscosity of binary liquid systems are known at present. These systems are obtained either by generalizing the experimental data (empirical formulas) or on the basis of the molecular theory of the liquid state.

We note that empirical formulas that describe the isotherms of viscosity of some single systems do not completely satisfy the experimental data for other systems. At times, empirical formulas satisfactorily describe only a part of the isotherm of a significant number of systems (in most cases, the area with the less viscous component), but these formulas do not agree with the experimental isotherm throughout its whole range [1]. Despite the inadequacies of empirical formulas, they do have a definite advantage because of their simplicity and reliability. To use formulas of the second group we must know the experimental values of the viscosity of a single mixture and, even better, of some of its compounds. In the latter case the accuracy of determining the viscosity according to these formulas significantly increases [2].

In calculating the coefficients of thermal conductivity and electric conductivity of binary systems, we can successfully use methods of the theory of generalized conductivity that are applied to the structure of a mixture with interpenetrating components. Below we show the possibility of extending this method to the calculation of the viscosity of binary liquid systems.

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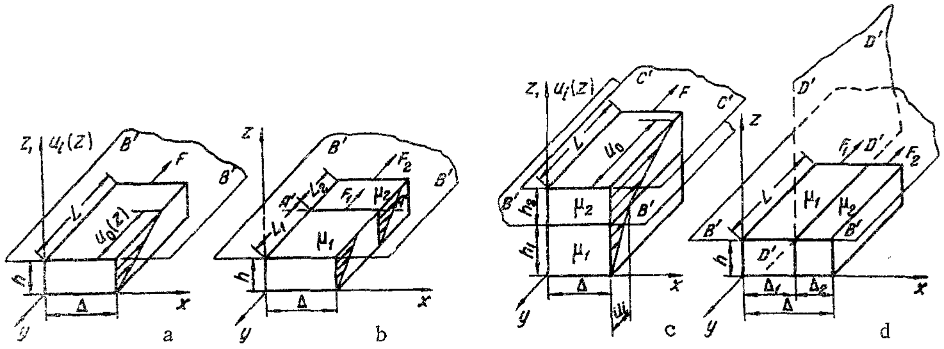

Fig. 1. Calculation of the viscosity of elementary liquid systems.

Viscosity of Elementary Binary Systems

We study a homogeneous liquid between two parallel planes (Fig. 1a), one of which (xy) is immoveable, and the other B'—B' moves under the action of the constant force F along the y axis with the constant velocity u_0. We assume that the frictional force between the plane and the liquid is the same as that between the moving layers in the liquid itself. A linear one-dimensional velocity field is established in the liquid, i.e.,

$$\frac{du}{dz} = -\frac{u_0}{h} = \text{const.} \tag{1}$$

We write Newton's law of friction as

$$F_i = -\frac{s_i}{\varkappa_i}\frac{du}{dz}, \quad \varkappa_i = \mu_i^{-1}, \quad s_i = L_i\Delta_i. \tag{2}$$

After substituting (1) into (2), we obtain the equation for the force f_i per unit width Δ_i of a layer of the liquid:

$$f_i = \frac{F_i}{\Delta_i} = \frac{L_i}{h_i\varkappa_i}u_0. \tag{3}$$

We study the motion of the binary liquid, the components of which are located as shown in Fig. 1b. We draw a conditional infinitely thin vertical plane A'—A' that separates the first component from the second. As above, we assume that the motion is one-dimensional.

Equation (3) for segments 1 and 2 takes the form

$$f_1 = \frac{L_1}{h\varkappa_1}u_0, \quad f_2 = \frac{L_2}{h\varkappa_2}u_0. \tag{4}$$

The total force F that acts on the surface $s = \Delta(L_1 + L_2) = \Delta L$ is equal to

$$F = \Delta f = \Delta(f_1 + f_2). \tag{5}$$

After substituting f_1 and f_2 from (4) into (5), we find

$$f = \left(\frac{L_1}{\varkappa_1} + \frac{L_2}{\varkappa_2}\right)\frac{u_0}{h}. \tag{6}$$

On the other side, f can be represented as

$$f = \frac{L}{\varkappa}\frac{u_0}{h}, \tag{7}$$

where κ is the fluidity of the binary liquid system. Equations (6) and (7) yield

$$\frac{L}{h\varkappa}=\frac{L_1}{h\varkappa_1}+\frac{L_2}{h\varkappa_2}. \tag{8}$$

We now study a binary system whose components are located as shown in Fig. 1c. We assume that the components are divided by an infinitely thin plane B'—B' that separates one component from the other. The character of the motion is as above. If the plane C'—C' moves with the velocity u_0, then in the plane B'—B' the motion of the layers of the liquid will originate with the velocity u_1. The velocity profile is shown in Fig. 1c (for the case $\kappa_1 > \kappa_2$). On segments 1 and 2, Eq. (3) takes the form

$$f_1=\frac{L}{\varkappa_1}\frac{u_1}{h_1},\quad f_2=\frac{L}{\varkappa_2}\frac{u_0-u_1}{h_2}. \tag{9}$$

We transform the equations obtained:

$$\frac{f_1\varkappa_1h_1}{L}=u_1,\qquad \frac{f_2\varkappa_2h_2}{L}=u_0-u_1. \tag{10}$$

The force f_2 acts on the upper boundary and in the liquid itself on segment 2, and it equals the force f_1 on the lower boundary, i.e., $f_1 = f_2$. The velocity of the liquid of each of the segments on the boundary is identical in magnitude (since the layers move without slippage), and the gradient undergoes a stepwise variation. Thus, by combining both equations of (10) and considering that $f_1 = f_2 = f$, we find

$$f=\frac{Lu_0}{h_1\varkappa_1+h_2\varkappa_2}. \tag{11}$$

After using (7), we obtain

$$\frac{Lu_0}{\varkappa h}=\frac{Lu_0}{\varkappa_1h_1+\varkappa_2h_2}, \tag{12}$$

from which

$$h\varkappa=h_1\varkappa_1+h_2\varkappa_2.$$

We study the system of two components in Fig. 1d. We draw a vertical infinitely thin plane D'—D' that separates the components so that their motion occurs independently (the plane of zero friction), i.e., the boundary of the first segment moves with the velocity u_{01} and the boundary of the second segment moves with the velocity u_{02}. The motion remains one-dimensional as in the previous cases. We apply the force F_1 to the first segment and the force F_2 to the second segment. The total force F that acts on the entire system is $F = F_1 + F_2$. The forces per unit width on the separate segments are equal to each other and are equal to the total force referred to the width of the entire system:

$$f_1=f_2=f=\frac{F}{\Delta}. \tag{13}$$

Equation (13) denotes that the external action on the separate components of the system is identical, and the difference in the properties of the components is shown by the different reaction of the various segments to the external action. In the present case the liquid layers in segments 1 and 2 will move with different velocities because of the different viscosities in them. On segments 1 and 2 we have the following from Eq. (3):

$$\Delta_1u_{01}=\Delta_1\frac{h\varkappa_1}{L}f_1,\qquad \Delta_2u_{02}=\Delta_2\frac{h\varkappa_2}{L}f_2. \tag{14}$$

Expressions $\Delta_1\dot{u}_{01}$ and Δ_2u_{02} (m^2/sec) can be interpreted as the surface flow in segments 1 and 2. Thus, the total flow in the entire system is equal to

$$\Delta_1 u_{01} + \Delta_2 u_{02} = \frac{h}{L} f(\varkappa_1 \Delta_1 + \varkappa_2 \Delta_2). \tag{15}$$

The latter equation can be rewritten as

$$\Delta_1 u_{01} + \Delta_2 u_{02} = \frac{h}{L} f \Delta\varkappa. \tag{16}$$

By equating the last two expressions, we obtain

$$\frac{h\Delta\varkappa}{L} = \frac{h\Delta_1\varkappa_1}{L} + \frac{h\Delta_2\varkappa_2}{L}. \tag{17}$$

We determine the thermal and electric resistances R_t and R_e:

$$R_t = \frac{L}{h\Delta\lambda}, \quad R_e = \frac{L}{h\Delta\sigma} \tag{18}$$

and use a similar concept for the viscous resistance R_μ:

$$R_\mu = \frac{L}{h\Delta\varkappa}. \tag{19}$$

Here Eq. (8) is an example of series-connected viscous resistances $R_\mu = R_{\mu 1} + R_{\mu 2}$, and Eqs. (12) and (17) are an example of parallel-connected viscous resistances, i.e., $R_\mu^{-1} = R_{\mu 1}^{-1} + R_{\mu 2}^{-1}$.

Thus, as follows from the above examples, the Kirchhoff laws are valid in calculating the viscous resistance of a heterogeneous liquid system.

Viscosity of a System with Interpenetrating Components

In [3, 4] a model of a structure in the form of a set of two space lattices with interpenetrating components is used to study a binary system consisting of normal liquids. It is assumed that the initial thermal conductivity of the components does not vary with the concentration (noninteracting components). Thermal resistances in the form of (18) are used to obtain equations for the effective thermal conductivity of the binary liquid system. Thus, we can directly use the results obtained in [3, 4] and for the effective fluidity κ of the binary liquid system we can write an equation similar to the Dul'nev formula for the effective thermal conductivity of binary liquid systems:

$$\varkappa = \varkappa_1 \left[c^2 + \nu(1-c)^2 + \frac{2\nu c(1-c)}{\nu c + (1-c)} \right], \qquad \nu = \frac{\varkappa_2}{\varkappa_1}, \tag{20}$$

in which the parameter c is related to the bulk concentration of the second component m_2 by the equation

$$2c^3 - 3c^2 + 1 = m_2, \tag{21}$$

the solution of which is presented in [3].

After replacing the fluidity with the viscosity in (20), we obtain the following equation for the effective viscosity of the binary liquid system:

$$\mu = \mu_1 \left[c^2 + \frac{(1-c)^2}{\nu'} + \frac{2c(1-c)}{(1-c)\nu' + c} \right]^{-1}, \qquad \nu' = \frac{\mu_2}{\mu_1}. \tag{22}$$

To verify Eq. (22) quantitatively, the calculated values of the effective viscosity are compared with the experimental data in [5, 6] for 33 binary systems with normal components (110 points in all), and a composite bar graph for the discrepancies between the calculation and the experiment is constructed. The form of the graph is close to the curve of the normal distribution with dispersion $a \approx 3.8\%$ and with mean arithmetic deviation $b \approx -0.74\%$.

The obtained equation (22) describes the concentrated behavior of the isotherms of the viscosity of binary liquid systems consisting of normal fluids, when it is possible to neglect the effect of the component interaction on the effective viscosity of the system.

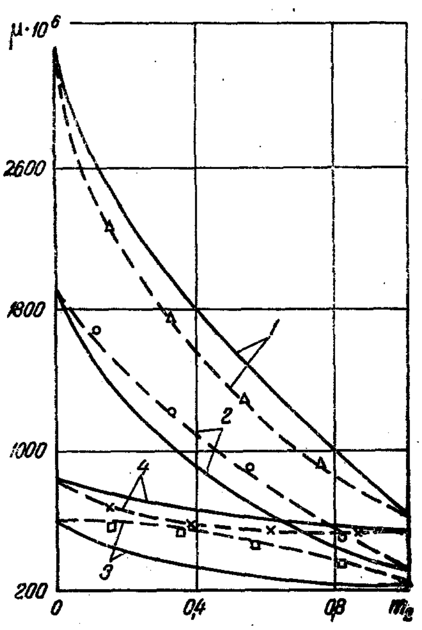

Fig. 2. Effective viscosity of binary systems: solid line corresponds to calculation with interaction disregarded; broken line, with interaction taken into account; 1) amyl alcohol—benzene; 2) bromoform—acetone; 3) chloroform—ethyl alcohol; 4) cyclohexanetoluene; μ, N•sec/m².

Viscosity of Systems with Interacting Components

We can characterize the interaction of the components in a liquid system by the quantity of heat in the liquid solution. The heat of the mixture is the basic energy characteristic of the solution; its quantity is directly related to the energy of the intermolecular interaction in the liquid phase. Actually, the specific heat of the mixture of liquid systems with normal components of an equimolal concentration varies in order of magnitude from unity to tenths of cal/mole, and in systems with associated components it varies from tenths to hundredths of cal/mole. The heat escapes or is absorbed during the formation of the solution, and we can qualitatively estimate the character of the interaction between the heterogeneous molecules and relate this to the viscosity of the system. The heat escape testifies to the fact that the proximity between the heterogeneous molecules is energetically more suitable. The viscosity of the binary system increases in comparison to the viscosity of the solution with the noninteracting components. If heat must be supplied to form the solution, then its components become isolated and its viscosity decreases in comparison to the viscosity of the solution with the noninteracting components.

We denote the integral heat of the mixture in terms of δH and use the system of signs commonly used in the literature: if $\delta H > 0$, then absorption occurs, and if $\delta H < 0$, then the heat escapes. An analysis of the experimental data for the viscosity of binary liquid systems shows that both positive $\mu_{exp} - \mu > 0$ and negative $\mu_{exp} - \mu < 0$ deviations (Fig. 2) are observed on the curve $\mu = f(m_2)$. In this connection, if $\delta H > 0$, the heterogeneous molecules become isolated and $\delta\mu < 0$, and if $\delta H < 0$, then the affinity between the heterogeneous molecules is stronger than between the homogeneous molecules, and $\delta\mu > 0$ [7].

We then determine the quantitative effect of the heat of the solution δH on the quantity μ. For this we use the da Andrade formula [8, 9] that determines the temperature function of the viscosity of a pure liquid:

$$\mu_i = A_i \exp\left(\frac{B_i}{RT}\right), \tag{23}$$

where A_i = const, and B_i is the energy of activation (cal/mole) [10]. In the solution the individual energy of activation B_i' is equal to

$$B_i' = N_i B_i + N_j B_{ij}, \quad i \neq j, \tag{24}$$

where N_i and N_j are the molal concentrations of the i-th and j-th components; B_{ij} is the mutual energy of activation. If we assume that the heat of the mixture δH is uniformly distributed among the molecules, then B_{ij} can be represented as

$$B_{ij} = B_i \mp \delta H. \tag{25}$$

TABLE 1. Comparison of Calculated Values of Effective Viscosity with Experiment

Components of the solution and viscosity μ, $(N\cdot sec/m^2)\cdot 10^6$	Bulk concentration of second component m_2	Heat of solution δH, cal/mole	Discrepancy in % $[(\mu_{exp}-\mu)/\mu_{exp}]\cdot 100$	
			interaction disregarded	interaction taken into account
Isopropyl alcohol (2590)—benzene (603)	0,184	130	—14	—1,2
	0,357	230	—22	0,5
	0,572	310	—30	—1,9
	0,783	290	—26	0,6
Ethyl alcohol (1180)—acetone (346)	0,25	170	—17	2,7
	0,50	260	—24	3,2
	0,75	200	—19	3,5
Isopropyl alcohol (2020)—acetone (308)	0,18	260	—24	4,0
	0,50	407	—43	—2,2
	0,70	306	—36	—0,3
Cyclohexane (1260)—benzene (812)	0,18	240	—20	0,1
	0,47	350	—25	9,0
	0,89	160	—9,2	3,5
Bromoform (1890)—acetone (305)	0,20	—220	26,0	4,0
	0,40	—330	20,0	—3,0
	0,60	—300	21,0	—2,7
	0,80	—200	13,0	+2,3
Pentachloroethane (3730)—ethyl ether (228)	0,27	—560	39,0	1,0
	0,46	—714	40,0	—7,0
	0,72	—430	28,0	2,0

Taking Eqs. (24) and (25) into account, we write Eq. (23) as follows:

$$\mu_i' = \mu_i \exp(\mp N_j \delta H/RT), \qquad (26)$$

where μ_i' is the viscosity of the individual liquid in the solution.

Thus, depending on the heat escape or absorption during the formation of the solution, an increase or decrease occurs in the viscosity of the initial components and, consequently, an increase or decrease in the viscosity of the solution.

According to the scheme indicated we can calculate the effective viscosity of various binary systems with normal as well as associated components. The values of the quantities for the heat of the mixture are taken from [11]. The comparison of the calculated values of the effective viscosity with the experimental data of [5] are presented in Fig. 2 and Table 1.

As we see, the suggested method allows us to calculate the viscosity of various binary liquid mixtures with sufficient accuracy.

NOTATION

x, y, z, coordinate axes; F, force; f, force per unit width; $u(u_0, u_{01}, u_{02}, u_1)$, velocity; μ, dynamic viscosity; $\kappa = \mu^{-1}$, fluidity; h, Δ, L, thickness, width, and length of liquid layer; $s = \Delta L$, area of the liquid surface layer; R_μ, R_t, R_e, viscous, thermal, and electrical resistances; λ, thermal conductivity; σ, electrical conductivity; c, parameter; m_2, bulk concentration of the second component; a, dispersion; b, mean arithmetic deviation; A_i, constant; B_i, B_{ij}, B_i', energy of activation, mutual energy of activation, energy of activation of liquid i in solution; N_i, N_j, molal concentrations of components i and j; R, gas constant; T, absolute temperature; δH, heat of solution.

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EQUATION OF STATE OF A DENSE GAS IN A QUASICLASSICAL APPROXIMATION

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UDC 536.71

We obtain an equation of state for a dense monatomic gas involving the first quantum correction for thermodynamic functions.

The equilibrium theory of a classical fluid that has been intensively developed in recent years enables us at present to quantitatively describe the thermodynamic properties of a liquid and a dense gas consisting of monatomic particles that interact additively [1-4]. Further progress in fluid theory is related to the consideration of quantum and nonadditive effects, and also to the nonspherical nature of complex molecules.

The influence of small quantum effects on the thermodynamic properties of a fluid is studied in [5-8]. In [5-7] equations are used that require knowledge of the binary correlation function (or some integral of it) [6-7] of a classical system which is calculated by methods of molecular dynamics or the Monte Carlo method. The necessary calculations are carried out only for the Lennard-Jones potential (12-6) which does not adequately describe the intermolecular interaction and, in addition, does so only for low temperatures (referred to the characteristic energy of interaction), which conditions the application of these equations only for neon and argon [5-7].

The equation obtained by perturbation theory [8] is also valid for high temperatures. It has little accuracy, however, which is possibly due to the unsuccessful choice of the intermolecular potential. Another inadequacy in the equation obtained in [8] is the necessity of integrating a binary correlation function for the distribution of solid spheres that is given in table form for each temperature and density. Since we must solve an interpolation problem to obtain thermodynamic functions at a fixed pressure, this equation is practically inapplicable for engine ring calculations.

1. Presentation of the Quantum Correction for the Equation of State at High Temperature

At temperatures for which we can disregard the nonadditive interactions (shown by the example of three-particle interactions) of the monatomic sphericosymmetric neutral particles [9, 10], the free energy of the system of N particles contained in volume V takes the following form with accuracy up to the first nonzero quantum correction [11]:

$$F = F_{\mathrm{cl}} + \frac{h^2 (\rho N_{\mathrm{A}})^2 V}{24\pi mkT} \int_0^\infty g(R)\, \nabla^2 u(R)\, R^2 dR = F_{\mathrm{cl}} + F_{\mathrm{qu}}. \tag{1}$$

Here $g(R) = \exp[-u(R)/kT]y(R)$ is the radial function of the classical system of particles that interact additively with the force $-du(R)/dR$.

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