NOTATION

x, r, longitudinal and transverse coordinates; u, v, axial and radial components of the velocity vector; ΔT, excess temperature above the environmental; a, thermal diffusivity coefficient; K_0, momentum; Q_0, heat flux; c_p, specific heat at constant pressure; C, value of the impurity concentration; ρ, density; F, symbol for the hypergeometric function; Pr, Prandtl number; Re, Reynolds number; Sc, Schmidt number; u_0, value of the mean discharge velocity; C_0, value of the initial methane impurity concentration.

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VISCOUS FLOW OF LIQUID GLYCERIN—POLYETHYLENE GLYCOL—WATER MIXTURES

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The viscous flow of liquid water—glycerin mixtures is analyzed within the framework of free volume theory and thermodynamic reaction-rate theory.

Nonflammable liquids based on water—glycerin mixtures are currently widely used in industry and transportation [1]. These mixtures have the designations PGV, P-20, P-20M1, and P-20M2. The percentage content of the main components is shown in Table 1.

Measurements of the dynamic viscosity of these mixtures have been made in experiments for a broad range of temperatures and pressures [2]. Study of such mixtures is interesting first of all from the point of view of learning more about the intermolecular hydrogen bonds [3]. The molecules of all three components contain OH groups which form H-bonds between adjacent molecules. The high degree of molecular association resulting from this is the reason for the appreciable delay in transfer processes (diffusion, viscous flow, etc.) compared to nonassociated liquids of the same molecular weight.

Unfortunately, interpretation of experimental data in this case is complicated by the fact that the three-component mixture has a very complicated and nonuniform structure. Also, there are various additives ranging from 3 to 7% in the investigated mixtures, which may also affect the validity of any conclusions made. Finally, the interval of concentrations of the components in these mixtures is too narrow to obtain sufficiently reliable conclusions and recommendations as to the composition of mixtures with certain properties.

To analytically represent the empirical data, we will use a semiempirical relation linking the viscosity and density of the liquid and based on free volume theory [4]. Analysis of the data shows that it can be described satisfactorily if the empirical dependence of the specific volume of the "incompressible" nuclei on temperature is determined.

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TABLE 1. Percentage Composition of the Investigated Mixtures

Component	PGV	P-20	P-20M1	P-20M2
	TU6-02.761–78	TU-6-02.1140–78		
Glycerin	37	32	26	43
Water	33	31	42	33
Polyethylene glycol	23 (PEG -35)	34 (PEG-35)	27 (PEG-115)	19(GIDROPOL- -200)
Additives	7	3	5	5

Note. Polyethylene glycol was replaced in the P-20M2 mixture by a similar compound (GIDROPOL-200) which is a copolymer of ethylene oxide and propylene oxide in an 80:20 ratio.

Table 2 shows values of the parameters of an interpolational equation of the type

$$\ln\eta/\eta_0 = \{1-\rho\,[K_0-\varkappa(T-293)]\}^{-1}-\{1-\rho_0\,[K_0-\varkappa(T-293)]\}^{-1} \tag{1}$$

for all of the mixtures investigated.

Equation (1) satisfactorily interpolates data on the viscosity of the mixtures in relation to temperature and pressure in the intervals 233 < T < 353°K and 0 < P < 120 MPa, respectively. The standard deviation of the empirical values from those calculated with Eq. (1) varies within the range 1-10%. The resulting deviations are comparable to the experimental errors, so we would hardly be justified in complicating Eq. (1) by increasing the number of adjustment constants.

Let us analyze the viscous flow of the liquid mixtures on a molecular level using concepts of the thermodynamic theory of absolute reaction rates or the theory of activated complexes. In accordance with this theory [5]:

$$\eta = \frac{hN}{V}\exp\left(\Delta\Phi_\eta^{\neq}/RT\right). \tag{2}$$

Equation (2) also allows us to calculate several thermodynamic activation parameters of the viscous flow, such as the activation enthalpy $\Delta H_\eta^{\neq}$ and the activation volume $\Delta V_\eta^{\neq}$. Calculation of these quantities can appreciably help to illuminate the molecular mechanism of viscous flow. We obtain the following formulas for such calculations from familar thermodynamic relations:

$$\Delta H_\eta^{\neq} = R\,[\partial\ln\eta/\partial(1/T)-\alpha T^2]\,P, \tag{3}$$

$$\Delta V_\mu^{\neq} = RT\,(\partial\ln\eta/\partial P)\,T, \tag{4}$$

where

$$\alpha = (1/V)(\partial V/\partial T)\,P.$$

Table 3 shows the values of $\Delta H_\eta^{\neq}$ for all four mixtures. The calculations were performed by graphically differentiating the functions $\ln\eta=f(1/T)$.

Despite the considerable difference in the viscosities, the activation enthalpies are the same and are independent of the composition of the mixture. All of the mixtures are characterized by the presence of intermolecular hydrogen bonds, creating a three-dimensional network in the liquid. It may therefore be suggested that viscous flow takes place in all of the mixtures mainly as a result of elementary processes, including the breaking of H-bonds. Independent measurements of the energy of the H-bonds [3] give values of 25-40 kJ/mole, which agrees well with the data in Table 3. The number of H-bonds decreases with an increase in temperature, and associations which include only a small number of molecules appear. Thus, the contribution of H-bond breakage in the overall elementary process of viscous flow is somewhat reduced. Conversely, the number of H-bonds becomes so great at low temperatures that there are more than one such bond per molecule. Accordingly, $\Delta H_\eta^{\neq}$ increases with a decrease in temperature. A similar effect is seen with an increase in pressure.

The activation energy (enthalpy) of viscous flow is an important characteristic of the liquid, determining how much viscosity will change with temperature. The lower the activation energy for viscous flow, the less strong the dependence of viscous flow on temperature.

Table 4 shows the temperature and pressure dependences of the activation volume $\Delta V_\eta^{\neq}$ of viscous flow for the investigated mixtures. Within the limits of the experiment error,

TABLE 2. Parameters of Eq. (1) for the Investigated Mixtures

Mixture	$10^3 \cdot K_0$, m^3/kg	$10^4 \cdot \varkappa$, K^{-1}
PGV	0,665	7,5
P-20	0,70	3,3
P-20M1	0,66	5,5
P-20M2	0,64	7,5

TABLE 3. Temperature and Pressure Dependence of Activation Enthalpy of Viscous Flow for the Investigated Mixtures

T, K	$\Delta H_\eta^{\neq}$, kJ/mole at P, MPa		
	0	60	120
233	83	93	103
263	53	60	66
293	42	55	60
323	32	37	42
353	27	30	35

TABLE 4. Temperature and Pressure Dependence of Activation Volume of Viscous Flow for the Investigated Mixtures

T, K	$10^6 \cdot \Delta V_\eta^{\neq}$, m^3/mole at P, MPa		
	5	50	110
233	23	18	16
263	13	12	9,5
293	10	10	9
323	12	9	9
353	8,5	8	9

$\Delta V_\eta^{\neq}$ is also the same for these mixtures. Worth noting is the very low value of $\Delta V_\eta^{\neq}$, amounting to only $(1-2) \cdot 10^{-5}$ m^3/mole. It should be pointed out that the gram molecular volume of PÉG-35 is about $1.3 \cdot 10^{-3}$ m^3/mole, while the corresponding value for PÉG-115 is $4.4 \cdot 10^{-3}$ m^3/mole. Even the relatively small molecules of ethylene glycol and glycerin have gram molecular volumes of 5.6 and $7.3 \cdot 10^{-5}$ m^3/mole, respectively. Comparison of the activation volume $\Delta V_\eta^{\neq}$ of viscous flow of the mixtures with the gram molecular volumes of the chemical compounds entering into them allows us to make the following conclusion.

The elementary event of viscous flow is accompanied in the investigated mixtures only by a small change in a local volume comprising an insignificant part of the whole molecule. In fact, each elementary event of viscous flow is accompanied by the displacement of only a small part of the molecule (e.g., the $-CH_2-$ unit). We should also point out the important role that the water molecules probably play in these mixtures.

Since the gram molecular volume of water is $1.8 \cdot 10^{-5}$ m^3/mole, it may be assumed that the displacement of H_2O molecules makes a large contribution to the mean activation volume of viscous flow of the mixture.

For comparison, we calculated the values of $\Delta H_\eta^{\neq}$ and $\Delta V_\eta^{\neq}$ for spindle oil AU, consisting of paraffin-naphthene and aromatic hydrocarbons. Experimental values of $\eta(P, T)$ were obtained earlier [6] for the temperature interval 282-363°K and pressure interval 0-60 MPa. It turned out that the values of $\Delta H_\eta^{\neq}$ for the spindle oil were nearly the same as the analogous values for the PGV mixtures, but the activation volumes $\Delta V_\eta^{\neq}$ were roughly five times greater than the corresponding values for PGV, reaching $(5-6) \cdot 10^{-5}$ m^3/mole. Similar values of $\Delta V_\eta^{\neq}$ were seen for all of the oils of mineral or organic origin that were investigated, as well as for polymethylsiloxanes and other organosilicon liquids. The elementary event of viscous flow is accompanied in such liquids by a local thinning which is sufficient for the displacement of a relatively large part of the molecule [4].

On the other hand, monohydric aliphatic alcohols exhibit a slight dependence of viscosity on pressure [7]. Since the physicochemical properties of alcohols and their molecular structure — as for the PGV mixtures — are determined by OH groups and hydrogen bonds, it is natural to suggest that intermolecular hydrogen bonding plays the decisive role. All of the above leads us to the following conclusion: liquids with intermolecular hydrogen bonds are characterized by low rates of increase in viscosity with pressure, while the temperature derivatives of their viscosity are comparable to the analogous values for liquids in which intermolecular hydrogen bonds are absent.

NOTATION

P, pressure; T, temperature; N, Avogadro's number; R, universal gas constant; V, molar volume; h, Planck's constant; η and η_0, dynamic viscosity of liquid at elevated and atmospheric pressure, respectively; ρ and ρ_0, density of liquid at elevated and atmospheric pressure, respectively; K_0, specific volume of "incompressible" nuclei; $\varkappa$, linear temperature coefficient of specific volume of incompressible nuclei; $\Delta\Phi_\eta^{\neq}$, free activation energy of viscous flow; $\Delta H_\eta^{\neq}$, activation enthalpy; $\Delta V_\eta^{\neq}$, activation volume; α, isobaric coefficient of cubical expansion.

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VARIOUS CASES OF MUTUAL DISPLACEMENT OF IMMISCIBLE FLUIDS IN POROUS MEDIA

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All possible solutions to the problem of mutual displacement of immiscible fluids are obtained for the case of one-dimensional filtration with piecewise-uniform initial conditions.

Displacement of crude oil or natural gas from a porous medium by water plays an important role in oil and gas extraction. This process is basic in application of secondary methods of oil extraction as well as in the tapping of underground basins formed in water-bearing bedrocks.

For evaluating the effectiveness with which crude oil or natural gas is displaced by an immiscible fluid, one must know how the saturation of one of the phases in the bedrock varies. During the displacement process there forms a zone of concurrent flow of both fluids, the displacing fluid flowing through some pores and the displaced fluid flowing through others. Accordingly, the displacement of immiscible fluids can be treated as a process of two-phase filtration.

In the case of uniform flow of incompressible fluids, when the surface tension between the two phases is small and the capillary pressure as well as the effects of gravity are negligible, the displacement process is amenable to a simple mathematical description [1] such as that given by Buckley and Leverett. In this formulation, the problem was subsequently analyzed by several authors. In one study [2], the general properties of the saturation

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