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# INFLUENCE OF EXCITED MOLECULES ON THE PROCESS OF FRICTIONAL FLOW OF NONASSOCIATED LIQUIDS

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It is shown that the viscosity of various nonassociated liquids can be described adequately by taking into account both the influence of the rate of the straight-line formation of holes' volume caused by irregular jumpings of excited molecules and the increase in the number of bimolecular collisions which is connected with intramolecular conformational transitions in the liquid phase. The proposed equations allow the calculation of this transport property at different temperatures.

*Keywords:* Viscosity; Nonassociated liquids; Excited molecules

## 1. INTRODUCTION

It has been shown in the work [1] that the viscosity  $\eta$  of near-boiling nonassociated liquids can be described adequately by means of the following equation:

$$\eta = \xi\sigma(m/T)^{1/2}G(N)[1 - \exp(-g\sigma V^{2/3}/T)], \quad (1)$$

where  $\sigma$ ,  $V$  and  $m$  are, respectively, surface tension, molar volume and molecular mass of a liquid considered at its absolute temperature  $T$ .  $\xi$  and  $g$  are the constants, whose numerical values equal to  $4.352 \times 10^{-2}$  ( $\text{s K}^{1/2} \text{m}^{-1}$ ) and  $9.35 \times 10^6$  ( $\text{J}^{-1} \text{K mol}^{2/3}$ ), respectively (at the pressure  $P=0.1$  MPa).  $G(N)$  is the function (see [2]), taking into account the influence of intramolecular conformational transitions on  $\eta$ . These transitions occur among one-particle energetically degenerate (or quasi-degenerate) conformational states, whose number is equal to  $N$ .

For different nonassociated liquids Eq. (1) fits for the adequate calculation of  $\eta$ , if their temperatures are near their normal boiling points. However, when the quantity  $T$  is near the middle of the investigated liquid range (at  $P=0.1$  MPa), the values of  $\eta$

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calculated by means of Eq. (1) become greater than the corresponding experimental ones (see [1]).

Thus, bearing in mind the above-mentioned circumstances, the aim of the present work is to find an equation, which describes the viscosity of nonassociated liquids taken near the middle of their liquid range.

## 2. THEORY

First of all we shall consider the molecules of the investigated liquid phase as spherical particles due to their fast mutual reorientations. The value of  $T$  is supposed to be high enough for such a consideration to be valid.

Further, let us consider two parallel neighbouring molecular layers of unit area. The velocity gradient of this liquid phase is supposed to be unity and normal to their planes. At the time zero let only the first layer be involved in the process of the frictional flow of the investigated liquid. At this moment the second layer is considered as motionless. Thus, it is about the involvement of the second layer into this process. On all these conditions the quantity of  $\eta$  will be numerically equal to the quantity  $P$  of the impulsive moment which is passed by bimolecular collisions from the molecules of the first layer to the molecules of the second one (per unit time).

The molecules of the second layer (and, therefore, the molecules of the motionless liquid phase) take part in vibrational and translational motions. Their spatial translations have the form of irregular jumpings. The average energy of these jumping molecules is greater than that of the vibrating ones. In its turn, this fact means that the relative share of the irregular jumping (excited) molecules will be essentially less than that of the vibrating ones (especially near the middle of the liquid range of the investigated liquid).

Passing to the first layer, we shall have the following situation. The regular jumping molecules of the first layer will correspond to the above vibrating molecules of the second one. Their regular jumpings will occur in the direction of the frictional flow under consideration. At the same time some part of the molecules of the first layer will belong to the above-mentioned irregular jumping (excited) molecules. In its turn, the interaction between the molecules of the first layer and the molecules of the second one is being realized by means of their bimolecular collisions.

Further, let us apply the law of conservation of energy to the process of the above intermolecular interaction between both the layers under consideration. This law applied to the above bimolecular collisions leads to the following equality:

$$Pv/2 = \eta v/2 = \chi nu, \quad (2)$$

where  $v$  is some average value of the velocity of the translational motion of all the molecules of the first layer,  $u$  is some average value of the one-particle energy barrier which exists for the vibrating molecules of the second one in the direction of the frictional flow.  $n$  is the total number of the latter molecules situated on the unit surface of the second layer.  $\chi$  is some coefficient of proportionality which describes the relative share of the vibrating molecules which can be displaced from their equilibrium positions per unit time, when the velocity gradient is unit. On these conditions  $\chi$  is constant for

various nonassociated liquids considered at different temperatures (see [1]). In its turn,  $\chi n$  is the number of the vibrating molecules of the second layer which are being involved in the process of the frictional flow due to their bimolecular collisions with all the molecules of the first one. This process is being accompanied by the transfer of the kinetic energy  $\eta v/2$ . The quantity  $\eta v/2$  is the total kinetic energy taken over all the molecules of the first layer which take part in the above collisions (per unit time).

Here the following circumstance is to be noted. Writing the law of conservation of energy in the form of Eq. (2), we suppose that, when the vibrating molecules of the second layer become free, their following displacement in the direction of the frictional flow requires some negligible (as compared with their total potential energy) quantity of the kinetic energy of the molecules of the first layer. The same situation takes place for the corresponding simultaneous displacement of the irregular jumping molecules of the second layer.

For the molecules, whose translational motion is being realized in the form of molecular jumpings, their one-particle energy is greater than or equal to some critical value  $E$  [3]. In its turn, the energy of any vibrating molecule is lower than  $E$ . Then the number  $n$  in Eq. (2) may be found by means of Boltzmann statistics. In the two-dimensional case considered this gives (see [3]) the following equation:

$$n = N_s[1 - \exp(-E/kT)], \quad (3)$$

where  $k$  is the Boltzmann's constant and  $N_s$  is the total number of molecules situated on the unit area of the second layer.

It has been shown in the work [4] that the following equation holds for the quantity  $E$ :

$$E = j\pi r^2 \sigma, \quad (4)$$

where  $\sigma$  is surface tension of a liquid,  $r$  is effective radius of its molecules and  $j$  is some coefficient of proportionality which is constant for various nonassociated liquids. As  $N_s$  is equal to  $1/\pi r^2$ , so we have for  $n$ :

$$n = (\pi r^2)^{-1}[1 - \exp(-j\pi r^2 \sigma/kT)]. \quad (5)$$

Supposing that for different nonassociated liquids their average one-particle energy barrier  $u$  is some constant share of their critical energy  $E$ , we shall have for the quantity  $u$ :

$$u = \alpha E, \quad (6)$$

where  $\alpha$  is some coefficient of proportionality which does not depend on the nature of the investigated nonassociated liquid.

Using Eqs. (4)–(6) in Eq. (2), we can write for the quantity  $\eta$ :

$$\eta = 2\alpha j \chi \sigma v^{-1}[1 - \exp(-j\pi r^2 \sigma/kT)]. \quad (7)$$

In order to define the quantity  $v$  in Eq. (7), let us consider the molecules of the first layer which are situated on some straight-line segment of unit length. This segment is

in the plane of the given layer and is oriented along the direction of the frictional flow under investigation. The above segment will contain both the regular jumping molecules and the irregular jumping (excited) ones of the first layer. As the regular jumping molecules, belonging to this segment, move along its length, its irregular jumping (excited) ones can abandon it, forming the corresponding vacancies (holes) around their former equilibrium positions. Here we consider that all the molecules of the first layer can vibrate around their temporal equilibrium positions during some part of their time (between their jumpings).

In its turn, the translational motion of the regular jumping molecules of the above segment will occur by their displacement into the above vacancies. Here it is to be noted that some part of the irregular jumping molecules of this segment may occupy these vacancies again. However, taking into account both the above-mentioned low relative share of these excited molecules and the nearly absolute spatial irregularity of their jumpings which, in its turn, diminishes the corresponding occupation probability, we shall consider that the displacement of the regular jumping molecules of the given segment into these vacancies will be the predominant form of the molecular translational motion which occurs along this segment in the direction of the frictional flow. This displacement is energetically more preferable than the formation of the vacancies (see [3]). Due to this fact this displacement will be essentially faster than the above formation of the vacancies. Thus, the formation of the vacancies will be the most slow-speed stage of all the process under investigation; and, therefore, will determine the value of  $\nu$ . It means that the greater the total volume of all the vacancies (the holes) formed on the unit segment per unit time, the higher is the quantity of  $\nu$ .

Bearing in mind all the above reasons, we shall suppose that the average velocity  $\nu$  of the translational motion of the molecules of the first layer will be proportional to the rate  $W$  of the above straight-line formation of the total volume of these vacancies. The given formation takes place on the considered segment of unit length due to all the excited (irregular jumping) molecules situated on this length. Thus, we shall have for the quantity  $\nu$ :

$$\nu = \tau W, \quad (8)$$

where  $\tau$  is some coefficient of proportionality which may depend on  $T$ . Its quantity is supposed to be constant for different nonassociated liquids, when their  $T$  is constant.

Let  $\nu$  and  $A$  be, respectively, some average values of frequency and amplitude of vibrations of the excited molecules, belonging to the first layer. Further, let the number of these molecules situated on the above segment of unit length be  $N_1$ . Supposing that the average frequency of their irregular jumpings is proportional to  $\nu$  and taking into account that the average volume of one vacancy equals to  $4\pi A^3/3$ , we can write the following equation for the rate  $W$ :

$$W = \mu \nu N_1 (4\pi A^3/3), \quad (9)$$

where  $\mu$  is some coefficient of proportionality which is supposed to be constant for various nonassociated liquids considered at different temperatures.

In order to find  $N_1$ , let us consider one mole of the investigated nonassociated liquid. In this case the number of its excited irregular jumping molecules, whose

energy  $E$  is greater than  $j\pi r^2\sigma$  (see Eq. (4)) may be defined on the basis of Boltzmann statistics (see [3]) and is equal to  $N_A \exp(-j\pi r^2\sigma/kT)$ , where  $N_A$  is Avogadro number. Their number per unit volume (their volume concentration) equals to  $(N_A/V) \times \exp(-j\pi r^2\sigma/kT)$ , where  $V$  is the molar volume of the given liquid taken at its absolute temperature  $T$ . Then the following equation holds for the number  $N_1$ :

$$N_1 = [(N_A/V) \exp(-j\pi r^2\sigma/kT)]^{1/3}. \quad (10)$$

Further, for any excited molecule of the first layer considered during the time interval of its vibrations the frequency  $\nu$  in Eq. (9) may be received by means of Eq. (11) which holds for any vibrational degree of freedom of this molecule considered as a three-dimensional oscillator:

$$2(\pi\nu A)^2 m = kT, \quad (11)$$

where  $kT$  is the average energy of the vibrational motion of this molecule along one of space axes (see [3]),  $m$  is its molecular mass. It follows from Eq. (11) that

$$\nu = (\pi A)^{-1} (kT/2m)^{1/2}. \quad (12)$$

It has been shown in the work [4] that for different nonassociated liquids the amplitude  $A$  of vibrations of their excited molecules may be described as:

$$A = q(V_c^{1/3} - V^{1/3}), \quad (13)$$

where  $V_c$  is molar critical volume of a liquid and  $q$  is coefficient of proportionality which is constant for various nonassociated liquids [4].

Using Eqs. (8)–(10) and (12), (13) in Eq. (7) and taking into account that the quantity  $r$  is proportional to  $V^{1/3}$ , we obtain for  $\eta$ :

$$\eta = \varphi\sigma(m/T)^{1/2}(V_c^{1/3} - V^{1/3})^{-2}(V/z)^{1/3}(1 - z), \quad (14)$$

where

$$z = \exp(-g\sigma V^{2/3}/T). \quad (15)$$

In Eqs. (14) and (15)  $\varphi$  and  $g$  contain all the constants of Eqs. (7)–(10) and (12), (13). The constant  $g$  which was found in the work [1] (see also Eq. (1)) does not depend on  $T$  and on the nature of the nonassociated liquid phase. In its turn, the quantity  $\varphi$  may depend on  $T$  (because of the coefficient  $\tau$  in Eq. (8)). However,  $\varphi$  remains constant for various nonassociated liquids, when they have the same temperature.

Equation (14) describes the viscosity  $\eta$  of nonassociated liquids with conformationally rigid molecules. If each molecule of the liquid under consideration has a certain number  $N$  of its energetically degenerate (or quasi-degenerate) conformational states, then the intramolecular conformational transitions which occur among these states will lead to the corresponding increase in the number of its bimolecular collisions

with neighbouring molecules. This increase may be described (see [2]) by means of the above function  $G(N)$ , whose analytical form is:

$$G(N) = (1 - \theta \ln N)^{-1}. \quad (16)$$

In Eq. (11) its dimensionless constant does not depend on  $T$  and is equal to 0.05681.

Further, let  $Q_s$  be some physico-chemical quantity of the liquid phase which depends on the number of intermolecular interactions (collisions) therein. In this case the following equation holds for this quantity (see [2]):

$$Q_s = G(N)Q_r. \quad (17)$$

Here  $Q_r$  is its value calculated for the hypothetical case in which there are not any intramolecular conformational transitions among the above conformational states of the molecules under consideration. Thus,  $Q_r$  must be calculated as if all the investigated molecules were conformationally rigid in the liquid phase.

Passing to liquids, whose molecules have such conformational transitions, and bearing in mind the above interpretation of the function  $G(N)$ , we can write Eq. (14) in the form:

$$\eta = \varphi\sigma(m/T)^{1/2}G(N)(V_c^{1/3} - V^{1/3})^{-2}(V/z)^{1/3}(1 - z), \quad (18)$$

where  $z$  is defined by means of Eq. (15).

## RESULTS AND DISCUSSION

The results of the use of Eq. (18) (at  $T = 293.15$  K and  $P = 0.1$  MPa) are given in Table I. The values of  $V_c$ ,  $V$  and  $\sigma$  needed for the calculation of  $\eta$  were taken from [5–13]. All the calculations were performed on the basis of the relative molecular masses  $M$  (see Table I) given in the atomic mass units.

For any investigated molecule its number  $N$  in Eqs. (16) and (18) is supposed (see [14]) to be equal to the total number of local minima on the surface of its full internal potential energy which arise on this surface under all possible internal rotations, changing the conformation of its skeleton. Here it is to be noted that we consider that some atomic groups, entering the molecular structure under investigation and possessing their free rotation (at the considered temperature  $T$ ), do not influence on the above number  $N$ . Thus, the number  $N$  will be only caused by all the hindered (at the given  $T$ ) internal rotations. So the internal rotation of the end methyl groups of different  $n$ -alkanes which have the straight-chain of their carbon atoms do not influence on  $N$ , as it is free near the considered room temperature  $T = 293.15$  K (see [15]). Thus, for the molecules of  $n$ -alkanes taken at 293.15 K their numbers  $N$  will be determined by the conformations of their nonhydrogen skeletons. In this case their carbon atoms are considered hereafter as nonequivalent, so that the conformations similar (for example) to the two conformations of  $n$ -butane with its nonplanar carbon skeleton are different.

TABLE I The values of  $\eta$  calculated by means of Eq. (18)

No.	Compound	$N$	$M$	$V_c \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )	$V \times 10^6$ ( $\text{m}^3 \text{mol}^{-1}$ )	$\sigma \times 10^3$ ( $\text{N m}^{-1}$ )	$\eta \times 10^3$ (Pas)	
							Calc.	Exper.
1	2	3	4	5	6	7	8	9
1	Germanium tetrachloride	1	214.40	330	114.4	24.08	0.641	0.637
2	Silicon tetrachloride	1	169.90	291	114.8	18.79	0.479	0.475
3	Trichlorosilane	1	135.45	268	100.9	17.96	0.337	0.336
4	Dichloromethane	1	84.93	193	64.0	28.12	0.417	0.429
5	1,2-Dichloroethane	3	98.97	220	79.0	32.57	0.812	0.829
6	1-Chloropropane	3	78.54	254	88.1	21.92	0.320	0.322
7	Bromoethane	1	108.97	215	74.9	24.15	0.411	0.400
8	Methyl acetate	2	74.08	228	80.1	24.49	0.376	0.381
9	Diethyl ether	3 <sup>2</sup>	74.12	283	103.9	17.00	0.244	0.245
10	<i>n</i> -Pentane	3 <sup>2</sup>	72.15	311	115.2	16.01	0.225	0.226
11	<i>n</i> -Hexane	3 <sup>3</sup>	86.18	370	130.7	18.40	0.322	0.320
12	<i>n</i> -Heptane	3 <sup>4</sup>	100.21	432	146.6	20.14	0.423	0.418
13	<i>n</i> -Octane	3 <sup>5</sup>	114.23	492	162.7	21.76	0.561	0.546
14	3-Methylpentane	3 <sup>3</sup>	86.18	367	129.8	18.14	0.313	0.323
15	1-Chloro-2-methylpropane	3 <sup>3</sup>	92.57	300	105.3	22.20	0.444	0.443
16	Thiophene	1	84.14	219	79.0	31.34	0.658	0.662
17	Chlorobenzene	1	112.56	308	101.7	33.59	0.778	0.799

Thus, bearing in mind the above-mentioned arguments, one can easily find that, when  $T=293.15$  K,  $N$  is equal to  $3^2$  for *n*-pentane, to  $3^3$  for *n*-hexane and to  $3^{n-3}$  for any *n*-alkane ( $n\text{-C}_n\text{H}_{2n+2}$ ).

In the case of diethyl ether the internal rotation around each of its chemical C–O bonds may be characterized by the presence of the three local minima of its internal potential energy [16]. Thus, the number  $N$  of this compound equals to  $3^2$  at 293.15 K.

The number  $N$  of methyl acetate is equal to 2. This number is caused by the two local minima which are connected with the internal rotation around the chemical C–O bond, belonging to the carboxyl group of the given compounds [16].

Particular attention must be paid to  $N$  of branched alkanes. So, in the molecule of 3-methylpentane one of its methyl groups is connected with its ternary carbon atom. This circumstance causes the corresponding increase in the value of the potential barrier, describing the internal rotation of this methyl group. If for the end methyl groups the potential barrier of their internal rotation is equal to  $14.2$  ( $\text{kJ mol}^{-1}$ ), then, for the given methyl group the value of its barrier equals to  $16.3$  ( $\text{kJ mol}^{-1}$ ) [15]. Thus, the internal rotation of this methyl group will be hindered at  $T=293.15$  K [15]. Owing to this fact the number  $N$  of 3-methylpentane is equal to  $3^3$ .

In its turn, the molecule of 1-chloro-2-methylpropane contains the two methyl groups connected with its ternary carbon atom. The internal rotation of both these groups is hindered [15]; therefore, the number  $N$  of 1-chloro-2-methylpropane equals to  $3^3$ .

The numbers  $N$  presented in Table I were used for the calculation of  $\eta$  (together with the known experimental values of  $V_c$ ,  $V$  and  $\sigma$ ). The comparison of the values of  $\eta$  calculated by means of Eq. (18) and the corresponding experimental ones taken from [5–11,17] shows that, when  $\varphi$  is equal to  $1.772 \times 10^{-4}$  ( $\text{s K}^{1/2} \text{mol}^{-1/3}$ ), Eq. (18) describes the quantity  $\eta$  (at  $T=293.15$ ) adequately. For the liquids presented in Table I the average absolute value (module) of its calculational error equals to 1.3%.

The compounds presented in Table II were investigated in order to establish the dependence of  $\varphi$  on  $T$  (at  $P=0.1$  MPa). The values of  $T$ ,  $V_c$ ,  $V$  and  $\sigma$  needed for the



TABLE II The use of Eqs. (18) and (19) for the calculation of  $\eta$  at adifferent temperatures

No.	Compound	T (K)	N	M	$V_c \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	$V \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	$\sigma \times 10^3$ (N m <sup>-1</sup> )	$\eta \times 10^3$ (Pa s)	
								Calc.	Exper.
1	2	3	4	5	6	7	8	9	10
1	Hydrogen	15	1	2.02	63.8	24.25	2.83	0.0214	0.0211
		17	1			25.81	2.49	0.0168	0.0168
2	Oxygen	75.15	1	32.00	74.4	26.07	16.99	0.308	0.304
3	Fluorine	69.2	1	38.00	66.2	23.56	17.9	0.410	0.414
4	Chlorine	220.05	1	70.91	124	44.0	29.82	0.563	0.569
5	Methane	103.15	1	16.04	99.0	36.9	14.72	0.149	0.151
6	Ethylene	134.10	1	28.05	129	45.2	23.02	0.333	0.333
		118.15	3	30.07	148	47.6	27.21	0.502	0.516
7	Ethane	123.15	3			48.1	26.34	0.459	0.456
		133.15	1			49.1	24.62	0.362	0.367
		150.3	1			50.9	21.71	0.272	0.271
		166.8	1			52.8	18.97	0.209	0.207
		193.15	3 <sup>2</sup>	44.10	196	70.5	20.6	0.329	0.327
9	<i>n</i> -Butane	203.15	3 <sup>3</sup>	58.12	255	86.6	23.31	0.463	0.461
10	<i>n</i> -Pentane	193.15	3 <sup>4</sup>	72.15	311	100.5	27.22	0.767	0.768
11	<i>n</i> -Hexane	223.15	3 <sup>5</sup>	86.18	370	119.7	25.55	0.741	0.742
		253.15	3 <sup>3</sup>			124.1	22.68	0.479	0.479
		273.15	3 <sup>3</sup>			127.3	20.44	0.390	0.381
		333.15	3 <sup>3</sup>			138.6	14.31	0.210	0.216
12	<i>n</i> -Heptane	353.15	3 <sup>4</sup>	100.21	432	158.8	14.35	0.235	0.239
13	<i>n</i> -Octane	373.15	3 <sup>5</sup>	114.23	492	179.9	14.01	0.256	0.256
14	Isopentyl acetate	298.15	2 × 3 <sup>5</sup>	130.19	447	150.1	24.28	0.784	0.790
		300.15	2 × 3 <sup>5</sup>			150.5	24.08	0.772	0.766
		323.15	2 × 3 <sup>3</sup>			154.4	21.81	0.535	0.550
		328.15	2 × 3 <sup>3</sup>			155.3	21.31	0.513	0.515
		415.65*	2 × 3 <sup>3</sup>			172.7	12.66	0.210	0.211
15	Toluene	323.15	1	92.14	316	109.8	25.04	0.417	0.425
		333.15	1			111.1	23.94	0.385	0.387
		348.15	1			113.1	22.35	0.341	0.339
		363.15	1			115.2	20.70	0.299	0.300
		383.78*	1			118.1	18.40	0.245	0.248
16	Chlorobenzene	333.15	1	112.56	308	105.8	28.28	0.55	0.53
17	Bromobenzene	333.15	1	157.03	324	109.0	30.09	0.71	0.72
18	Iodobenzene	333.15	1	204.01	351	115.5	34.78	1.04	1.04
19	Tin (IV) chloride	323.15	1	260.50	351	121.2	24.25	0.668	0.668
20	Tin (IV) bromide	373.15	1	438.31	425	139.8	29.14	1.04	1.01
21	Arsenic tribromide	373.15	1	314.63	298	98.0	43.48	1.75	1.69

\*The normal boiling point of the given compound.

calculation of  $\eta$  were taken from [5–11,13,17–20]. The comparison of the values of  $\eta$  calculated by means of Eq. (18) and the corresponding experimental ones (see [5–8,10,20,21]) shows that this equation describes the quantity  $\eta$  adequately, when the following linear equation holds for the temperature dependence of the quantity  $\varphi$ :

$$\varphi = \beta T + \gamma, \quad (19)$$

where  $\beta$  and  $\gamma$  are constant quantities for different nonassociated liquids. Their numerical values are equal to  $3.916 \times 10^{-7}$  (s K<sup>-1/2</sup> mol<sup>-1/3</sup>) and  $6.240 \times 10^{-5}$  (s K<sup>1/2</sup> mol<sup>-1/3</sup>), respectively. For the compounds presented in Table II the average absolute value (module) of the calculational error of Eqs. (18) and (19) equals to 1.4%.

Here it is to be noted that, in the case of ethane and *n*-hexane, the internal rotation of their methyl groups becomes free, when *T* is around 128 and 238 K, respectively (see the numbers *N* for compounds 7 and 11 in Table II). The values of the corresponding potential barriers, describing the internal rotation of these methyl groups, are equal to 12.1 and 14.2 (kJ mol<sup>-1</sup>), respectively [15].

The internal rotation of the methyl groups of propane, *n*-butane and *n*-pentane remains hindered at *T* within 193.15–203.15 K (see Table II).

In its turn, in the case of isopentyl acetate, the internal rotation of the two methyl groups connected with the ternary carbon atom of this compound becomes free, when *T* changes from 300.15 to 323.15 K (see *N* of compound 14 in Table II). The multiplier 2 and the one multiplier 3, entering the number *N* of isopentyl acetate, are caused by the internal rotation around the two ordinary chemical C–O bonds of the given molecular structure [16].

It should be mentioned that for any nonassociated liquid there is a lower temperature limit of the use of Eq. (18). It follows from the fact that the above-mentioned supposition about the spherical symmetry of the investigated molecules does not fit for the liquid phase considered at low temperatures, when effective molecular form must differ from spherical.

So, for instance, toluene, whose molecules are nearly plane, has the above temperature limit near *T* = 333.15 K (see Table II). The internal rotation of their methyl groups is free for all the liquid range of toluene (due to its negligible potential barrier: 0.12 (kJ mol<sup>-1</sup>) [15]); and, therefore, it cannot influence on *N*.

The second cause, restricting the temperature range of the use of Eq. (18), may be formation of molecular associates, when *T* of the investigated liquid phase is near its normal freezing point.

Let us consider an example. Argon has its normal freezing point at *T* = 83.78 K [8]. Its liquid phase considered at *T* = 85.0 K possesses the following experimental values of *V<sub>c</sub>*, *V* and *σ*: 74.5 × 10<sup>-6</sup> (m<sup>3</sup> mol<sup>-1</sup>), 28.4 × 10<sup>-6</sup> (m<sup>3</sup> mol<sup>-1</sup>) and 13.20 × 10<sup>-3</sup> (N m<sup>-1</sup>), respectively (see [8,10]). The value of its viscosity calculated by means of Eqs. (18) and (19) is equal to 2.30 × 10<sup>-4</sup> (Pa s). The corresponding experimental one equals to 2.80 × 10<sup>-4</sup> (Pa s) [8].

## CONCLUSION

The following conclusions may be drawn. Both the rate of the straight-line formation of holes' total volume caused by irregular jumpings of excited molecules and intramolecular conformational transitions, occurring among degenerate (or quasi-degenerate) molecular conformational states, influence on the viscosity of the nonassociated liquid phase. In its turn, the action of these transitions may be properly described on the basis of the function *G(N)* (see Eq. (16)). For different nonassociated liquids Eqs. (18) and (19) allow one to perform the adequate calculation of this transport property at different temperatures which are high enough in order to consider the investigated molecules as spherical particles.

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