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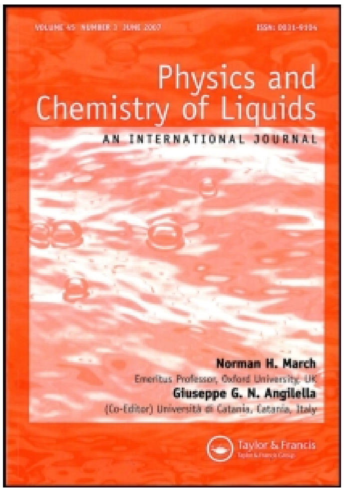

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VISCOSITY OF NEAR-BOILING NONASSOCIATED LIQUIDS: DEPENDENCE ON SURFACE TENSION, MOLECULAR MASS AND INTRAMOLECULAR CONFORMATIONAL TRANSITIONS

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The equation proposed for near-boiling nonassociated liquids describes a new functional dependence of their viscosity on such physico-chemical characteristics as surface tension and molecular mass. It is shown that the viscosity of liquids with conformationally flexible molecules can be calculated adequately by taking into account the influence of intramolecular conformational transitions on the number of bimolecular collisions in the liquid phase.

Keywords: Viscosity; Near-boiling liquids; Conformational transitions

1. INTRODUCTION

One of the most important physico-chemical characteristics of the near-boiling liquid phase of different chemical substances is its viscosity-η. Various methods were proposed in order to calculate this quantity [1,2]. Some of them come from Eq. (1):

$$\eta = A \exp(B/T) \tag{1}$$

which was proposed in the work [3]. In Eq. (1) A and B are some constants, depending on the nature of a liquid. T is its absolute temperature. These methods (see, for instance, [4–6]) have an empirical character because of the use of various empirical structural addenda for the calculation of the constants A and B. The relative calculational errors of Eq. (1) are within 2–3% [7]. Such calculational errors take place in the case, when the above constants are defined on the basis of two experimental values of η, belonging to two different values of T. At the same time the relative calculational errors of the above-mentioned empirical methods may reach as much as 15–20% (see [1]).

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Equation (2) proposed by Batschinski [8] presents another way for the calculation of η:

$$\eta = C/(V - \Omega) \tag{2}$$

In Eq. (2) V is molar volume of a liquid; C and Ω are some constants which depend on its nature. The accuracy of Eq. (2) is also around 2–3%, when its constants C and Ω are obtained by means of two experimental datum points, belonging to different values of T [7].

The above mentioned methods fit for the adequate calculation of η of various liquid chemical substances considered at different temperatures. However, their constants A, B, C, and Ω must be defined over again by passing to new compounds. This circumstance requires new experimental values of η and limits the possibilities of their practical use [9].

It is to be noted that the constant B in Eq. (1) may be considered as a quantity, whose value is proportional to some activation energy of frictional flow (see [1]). Thus, its value is caused by intermolecular interactions. In its turn, the existence of Eq. (2) indicates that the increase in intermolecular distances reduces the above interaction and, therefore, the quantity η. At the same time it has been shown in the work [10] that for different nonassociated liquids, the energy of their intermolecular interaction may be described by means of their surface tension $-\sigma$. In this connection the aim of the present work is to find an equation, which describes the viscosity of such liquids on the basis of σ and some other physico-chemical quantities. As will be shown below this equation can be obtained for near-boiling nonassociated liquids.

2. THEORY

In order to find the above equation let us consider two parallel neighbouring molecular layers of unit area. The velocity gradient of the 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 liquid under consideration. At this moment the second layer is considered as motionless. In other words it is about the involvement of the second layer into this process. On all the above-mentioned conditions the value of η 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).

Further, we shall consider the liquid phase in the temperature range in which it is near its normal boiling point. In this case all molecules may be considered as spherical particles (hard spheres) due to their fast mutual reorientations.

Now we need to take into account some particularities of the molecular motion in both the layers. In order to do it we shall consider in the first place that the near-boiling liquid under investigation does not have any flows therein. Its molecules take part in vibrational and translational motions. Their spatial translations are realized in the form of irregular jumpings. The average energy of its jumping molecules is greater than that of its vibrating ones. It is to be noted that any near-boiling liquid consists of two phases: liquid and gaseous which can coexist in any point of its volume due to their mutual equilibrium. Because of this coexistence the latter phase limited by the above volume may be considered as some quasi-gaseous one which is formed by the irregular jumping molecules [11]. At the same time the vibrating molecules form the liquid phase. The above-mentioned description is applied to the molecular motion in the second layer.

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. These regular jumpings occur in the direction of the frictional flow. At the same time some part of the molecules of the first layer will belong to the above quasi-gaseous phase. Based on the fact that the viscosity of the liquid phase is many times larger than that of the quasi-gaseous one (in any case near the normal boiling point [1]), we may neglect the influence of the molecules, forming the quasi-gaseous phase, on the quantity η.

Thus, bearing in mind all the above reasons, we shall suppose that the process of the momentum transfer between both the layers takes place, when the regular jumping molecules of the first layer interact with the vibrating molecules of the second one. In its turn, this interaction is being realized by means of their bimolecular collisions.

For further considerations let us apply the law of conservation of energy to the process of the intermolecular interaction between the layers under investigation. This law applied to the above bimolecular collisions leads to the following equality:

$$Pv/2 = \eta v/2 = \chi nu \tag{3}$$

In (3) v is some average value of the velocity of the regular jumping 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, χ is some coefficient of proportionality which is supposed to be constant for various near-boiling liquids. χ describes the relative share of the vibrating molecules which can be displaced from their equilibrium positions per unit time, when the temperature gradient is unit. Thus, χn is the number of the above vibrating molecules which are being involved (on these conditions) in the process of the frictional flow due to their bimolecular collisions with the regular jumping molecules of the first layer. This process is being accompanied by the transfer of the kinetic energy – $\eta v/2$. It is to be noted that the quantity $\eta v/2$ is the total kinetic energy taken over all the regular jumping molecules of the first layer which participate (per unit time) in the above collisions.

For the molecules, taking part in their translational motion realized in the form of molecular jumpings, their one-particle energy is greater than or equal to some critical value – E [11]. Thus, the energy of any vibrating molecule is lower than E. Then the number n may be easily found by means of Boltzmann statistics. In the two-dimensional case considered this gives (see [11]) the following equation:

$$n = N_s[1 - \exp(-E/kT)], \tag{4}$$

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

It has been shown in the work [10] that the quantity E may be expressed in the form:

$$E = j\pi r^2\sigma, \tag{5}$$

where σ 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 liquids. As the number N_s is equal to $1/\pi \mathrm{r}^2$, so we have for n:

$$n = (\pi r^2)^{-1}[1 - \exp(-j\pi r^2 \sigma/kT)]. \tag{6}$$

Further, using the principle of corresponding states and taking into account the above-mentioned spherical symmetry of molecules, we may consider that for different near-boiling nonassociated liquids their average one-particle energy barrier $-u$ is some constant share of their critical energy $-E$. Bearing in mind this circumstance, we shall have for the quantity u:

$$u = \alpha E, \tag{7}$$

where α is some coefficient of proportionality which is constant for various near-boiling nonassociated liquids.

The velocity ν in Eq. (3) may be defined on the basis of the above coexistence of both the equilibrium phases: liquid and quasi-gaseous. Using this phenomenon, we shall suppose that the quantity ν, describing the regular jumping molecules is proportional to the average velocity – ν_i of the molecules, belonging to the quasi-gaseous phase. In its turn, ν_i may be defined by means of the perfect gas law. In this case we shall have the following equation for ν (see [11]):

$$\nu = \mu \nu_i = \mu(8kT/\pi m)^{1/2}, \tag{8}$$

where m is molecular mass of a liquid and μ is some coefficient of proportionality which is supposed to be constant for different near-boiling nonassociated liquids.

Using Eqs. (5)–(8) in Eq. (3), we can write for the quantity η:

$$\eta = \alpha j \chi \mu^{-1} (\pi/2k)^{1/2} \sigma (m/T)^{1/2} [1 - \exp(-j\pi r^2 \sigma/kT)]. \tag{9}$$

The quantity r is proportional to $V^{1/3}$, where V is molar volume of a liquid. Bearing in mind this circumstance and combining all the constants of Eq. (9), we obtain for η:

$$\eta = \xi \sigma (m/T)^{1/2} [1 - \exp(-g\sigma V^{2/3}/T)], \tag{10}$$

where ξ and g are constant for various near-boiling nonassociated liquids.

Here it is to be noted that Eq. (10) describes the viscosity η of different near-boiling nonassociated liquids with conformationally rigid molecules. If each molecule of the liquid under investigation 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. It has been shown in [12,13] that this increase may be described by means of the function $G(N)$ given below:

$$G(N) = (1 - \theta \ln N)^{-1}, \tag{11}$$

where the dimensionless constant does not depend on temperature 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 [12,13]):

$$Q_s = G(N)Q_r, \tag{12}$$

where 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, the quantity Q_r must be calculated as if all the investigated molecules were conformationally rigid in the liquid phase.

Passing to liquids whose molecules are capable of such conformational transitions, and bearing in mind the above interpretation of the function $G(N)$, we can write Eq. (10) in the form:

$$\eta = \xi\sigma(m/T)^{1/2}G(N)[1 - \exp(-g\sigma V^{2/3}/T)]. \tag{13}$$

3. RESULTS AND DISCUSSION

The results of the use of Eq. (10) (at the pressure $P = 0.1\,\mathrm{MPa}$) are presented in Table I. The values of T, V, and σ needed for the calculation of η were taken from [1,7,14–22]. The comparison of the values of η calculated by means of Eq. (10) and the corresponding experimental ones (see [1,7,14–22]) shows that, when the constants ξ and g are equal to $4.352 \times 10^{-2}(\mathrm{s\,K^{1/2}m^{-1}})$ and $9.35 \times 10^{6}(\mathrm{J^{-1}K\,mol^{2/3}})$ respectively, Eq. (10) describes the quantity η adequately. All the above calculations were performed on the basis of the relative molecular masses – M (see Table I) given in the atomic mass units. For the liquids presented in Table I the average absolute value (module) of the relative calculational error of Eq. (10) is equal to 2.1%.

It should be noted that the numerical value of the constant g is essentially higher than that of the constant δ which was found in the work [23], describing the thermal conductivity of nonassociated liquids ($\delta = 7.03 \times 10^{5}(\mathrm{J^{-1}K\,mol^{2/3}})$, see Eq. (12) in [23]). This difference is caused by the fact that in the case of the thermal conductivity the vibrating molecules of the liquid phase do not abandon their equilibrium positions therein. Thus, their critical energy needed for this process is essentially less than that required for the frictional flow under investigation.

In order to verify the calculational possibilities of Eq. (13) let us consider the viscosity η of some organic liquids with conformationally flexible molecules (see Table II). For any molecule of the compounds given in Table II its number N in Eqs. (11) and (13) is supposed (see [13]) 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 nonhydrogen skeleton. Its nonhydrogen atoms are considered hereafter as nonequivalent; so that the conformations similar (for instance) to the two conformations of *n*-butane with its nonplanar carbon skeleton are different.

Internal rotation of the end groups (such as methyl ones) does not cause an increase in N. Bearing in mind the above-mentioned arguments one can easily find that N is equal to 3 for *n*-butane, 2-methylbutane and also for the chloroderivatives: 1-chloropropane and 1, 2-dicholoroethane; to 3^2 for *n*-pentane and 2-methylpentane.

TABLE I The values of η calculated by means of Eq. (10)

No.	*Compound*	*M*	*T* (K)	$V \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$)	$\sigma \times 10^3$ ($\mathrm{Nm^{-1}}$)	$\eta \times 10^3$ (Pa s)	
						Calc.	*Exper.*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
1	Hydrogen	2.02	20.40	28.47	1.90	0.0145	0.0140
2	Deuterium	4.03	23.67	24.87	2.77	0.0302	0.0302
3	Neon	20.18	27.09	16.75	4.99	0.127	0.124
4	Nitrogen	28.02	77.35	34.68	8.84	0.157	0.156
5	Carbon monoxide	28.01	81.65	35.4	9.5	0.167	0.166
6	Argon	39.95	87.29	28.66	12.6	0.266	0.270
7	Hydrogen sulfide	34.08	212.80	35.9	29.6	0.390	0.403
8	Propane	44.10	231.08	75.8	15.43	0.197	0.205
9	Ammonia	17.03	239.82	24.97	34.0	0.267	0.261
10	Chloromethane	50.49	249.41	50.9	23.42	0.321	0.313
11	Methylamine	31.06	266.80	44.7	23.81	0.230	0.236
12	Ethylene oxide	44.05	283.88	49.8	26.39	0.313	0.320
13	Chloroethane	64.51	285.42	71.2	20.31	0.286	0.285
14	Acetaldehyde	44.05	293.15	56.3	21.2	0.225	0.220
15	Trichlorosilane	135.45	305.20	102.8	16.5	0.321	0.307
16	Acetone	58.08	329.39	77.5	19.96	0.235	0.226
17	Chloroform	119.38	334.30	83.3	22.0	0.395	0.395
18	Sulfuryl chloride	134.97	342.65	86.3	24.0	0.473	0.480
19	Benzene	78.12	353.25	96.0	21.20	0.300	0.314
20	Thiophene	84.14	357.27	85.3	22.83	0.331	0.340
21	Fluorobenzene	96.10	358.50	101.9	19.39	0.292	0.302
22	Toluene	92.14	383.78	118.1	17.75	0.245	0.248
23	Pyridine	79.11	388.45	89.4	24.76	0.339	0.341
24	2-Methylpyridine	93.14	402.59	111.5	20.0	0.276	0.286
25	Pyrrole	67.09	403.20	77.9	25.50	0.299	0.302
26	Chlorobenzene	112.56	405.15	114.7	20.25	0.310	0.301
27	*p*-Xylene	106.17	411.50	140.7	15.83	0.218	0.215
28	Bromobenzene	157.03	429.15	120.4	20.04	0.346	0.337
29	Iodobenzene	204.01	461.75	130.7	20.34	0.385	0.383
30	Mercury (II) bromide	360.40	529.15	74.2	50.3	1.288	1.292

TABLE II The use of Eq. (13) for the calculation of η of some organic liquids with conformationally flexible molecules

No.	*Compound*	*N*	*M*	*T* (K)	$V \times 10^6$ ($\mathrm{m^3\,mol^{-1}}$)	$\sigma \times 10^3$ ($\mathrm{Nm^{-1}}$)	$\eta \times 10^3$(Pa s)	
							Calc.	*Exper.*
1	*n*-Butane	3	58.12	272.65	96.7	14.93	0.211	0.210
2	*n*-Pentane	3^2	72.15	309.22	118.2	14.21	0.220	0.215
3	2-Methylbutane	3	72.15	301.0	117.8	14.13	0.209	0.209
4	*n*-Hexane	3^3	86.18	341.89	140.3	13.41	0.227	0.227
5	2-Methylpentane	3^2	86.18	333.4	140.0	13.36	0.215	0.217
6	1-Chloropropane	3	78.54	319.75	91.6	18.20	0.277	0.272
7	1,2-Dichloroethane	3	98.96	356.6	86.1	23.51	0.402	0.403
8	Diethyl ether	3^2	74.12	308.75	106.5	15.13	0.237	0.239
9	Methyl formate	2	60.05	304.9	62.7	23.30	0.317	0.312
10	Ethyl formate	2×3	74.08	327.4	84.3	19.34	0.292	0.286
11	Nitrobenzene	4	123.12	484.05	122.2	20.51	0.304	0.291

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 molecular potential energy [24]. Thus, the number N of this compound is equal to 3^2.

TABLE III The use of Eq. (10) for the calculation of η of toluene at different temperatures

T (K)	$V \times 10^6$ ($m^3\,mol^{-1}$)	$\sigma \times 10^3$ (Nm^{-1})	$\eta \times 10^3$ (Pa s)	
			Calc.	*Exper.*
383.78	118.1	17.75	0.245	0.248
382.15	117.9	17.94	0.250	0.251
381.15	117.8	18.06	0.253	0.253
380.15	117.6	18.18	0.256	0.255
379.15	117.5	18.30	0.260	0.258
378.15	117.4	18.42	0.263	0.260
377.15	117.2	18.53	0.266	0.262
376.15	117.1	18.65	0.269	0.264
375.15	116.9	18.77	0.273	0.266
374.15	116.8	18.89	0.276	0.269
373.15	116.6	19.01	0.279	0.271
363.15	115.2	20.20	0.314	0.296

The numbers N of methyl formate and ethyl formate contain the multiplier 2. This multiplier is caused by the presence of the two local minima which are connected with the internal rotation around the chemical C–O bonds, belonging to the carboxyl groups of these compounds [24].

For nitrobenzene the number of the minima which characterize the internal rotation of its plane group: $-NO_2$ is equal to four [24]. Therefore, the number N of nitrobenzene is also equal to four.

The values of T, V, and σ needed for the use of Eq. (13) were taken from [1,14,16,18,21,22]. The comparison of the values of η calculated by means of Eq. (13) and the corresponding experimental ones (see [1,14,16,19]) shows that Eq. (13) describes the quantity η of the near-boiling nonassociated liquids with conformationally flexible molecules adequately. For the data set given in Table II the average absolute value of the relative calculational error of Eq. (13) is equal to 1.3%.

The results presented in Table III were calculated by means of Eq. (10) in order to define the temperature range of its use. The experimental values of V, σ and η (at the values of T which are near the normal boiling point of toluene) were taken from [14,19]. The comparison of the values of η calculated on the basis of Eq. (10) and the corresponding experimental ones shows that within the temperature range 363.15–383.78 K the module of the relative calculational error of Eq. (10) is less than 3.0%.

4. CONCLUSION

The following conclusions may be drawn. The viscosity of the near-boiling liquid phase of different chemical compounds, whose molecules do not possess their molecular association due to strong intermolecular hydrogen bonds (such as in water, glycerol etc.), may be properly described by means of Eqs. (10) and (13). The function $G(N)$ in Eq. (11) allows one to take into account the influence of intramolecular conformational transitions on the viscosity η.

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