

*Yuriy Medvedevskikh and Oksana Khavunko*

## FRictional AND ELASTIC COMPONENTS OF THE VISCOSITY OF POLYSTYRENE-TOLUENE DILUTED SOLUTIONS

*Physical Chemistry of Combustible Minerals Department  
L. M. Lytvynenko Institute of Physico-Organic Chemistry & Coal Chemistry  
National Academy of Sciences of Ukraine  
3a, Naukova str., 79053 Lviv, Ukraine; hav.ok@yandex.ru*

Received: February 25, 2011 / Revised: March 01, 2011 / Accepted: June 01, 2011

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**Abstract.** We studied the gradient dependence of the effective viscosity  $\eta$  for the diluted solution of the polystyrene in toluene under three concentrations  $\rho = 0.5 \cdot 10^5$ ,  $1 \cdot 10^5$  and  $2 \cdot 10^5$  g/m<sup>3</sup> and for four polystyrene fractions with average molar weights  $M = 5.2 \cdot 10^4$ ,  $4.4 \cdot 10^4$ ,  $3.3 \cdot 10^4$  and  $1.8 \cdot 10^4$  g/mol, in the temperature range of 293–308 K. The experiments have been carried out with the use of rotary viscometer “Rheotest 2.1” at various cylinder rotation angular rate  $\omega$  (r/s). The analysis of the dependences  $\eta(\omega)$  permitted to mark out the frictional  $\eta_f$  and elastic  $\eta_e$  components of the viscosity and to study their dependences on the concentration  $\rho$  of the polymer into the solution, on the length of the chain  $N$  and on the temperature  $T$ . We have obtained the equation for defining the intrinsic viscosity of the polymer solution. It was shown that the basic contribution into the intrinsic viscosity gives the elastic component of the viscosity with taking into account the gradient dependence of  $\eta_e$ .

**Keywords:** effective viscosity, frictional and elastic components of the viscosity, conformational volume, deformation, segmental motion, activation energy.

### 1. Introduction

The viscosity  $\eta$  of polymer solutions is the object of special attention of numerous experimental and theoretical investigations, generalized for example, in monographs [1-5]. This is connected both by the practical importance of this property of polymeric solutions in series of technological processes and by a variety of factors having an influence on the value  $\eta$ . On the other hand, such interest can be explained by a wide range of its change at the transition from the diluted solutions to the concentrated ones and also to melts. All above-mentioned gives the considerable informative data for testing different theoretical imaginations about equilibrium and dynamical properties of polymeric chains into the solution.

In general, the viscosity of the polymer solution is a function  $h = h(r, M, T)$  of concentration  $\rho$  of the polymer (the density of the solution by polymer, g/m<sup>3</sup>), its molar weight  $M$  and temperature  $T$ . However, even for the diluted polymeric solutions, which are considered only in this paper, the view of the function  $h = h(r, M, T)$  is determined only by the empirical approximate equations such as the Mark-Kuhn-Houwink .

$$[h] = KM^a \quad (1)$$

and Huggins's equation

$$(h - h_s)/h_s = [h]r + k'[h]^2 r^2 + \dots \quad (2)$$

where  $\eta_s$  is the viscosity of the solvent;  $[h] = (h - h_s)/h_s r$  is the intrinsic viscosity at  $\rho \rightarrow 0$ ;  $K$ ,  $\alpha$  and  $\kappa'$  are empirical constants for the homologous series of polymer.

The main attention of numerous theoretical investigations (see [1-5], and also [6]), performed, as a rule, in the middle of the last century, has been paid into physical interpretation of the Mark-Kuhn-Houwink's equation (1).

Only the forces of friction of the polymer chain links, which are considered as the “beads” into “necklace”, against the solvent, are taking into account in the majority of these investigations. An additional assumption about the locality of the bead response on hydrodynamic flow leads to the concept of the hydrodynamically penetrable Gaussian ball. Under this conception the intrinsic viscosity of the diluted polymeric solution is proportional to the square of the hydrodynamic radius  $R_g$  of the polymeric chain:

$$[h] \sim R_g^2 \quad (3)$$

The identification of  $R_g$  with the radius of the Flory ball in  $\theta$ -solvent  $R_g \sim M^{1/2}$  or in a “good” solvent  $R_g \sim M^{3/5}$  leads to the Mark-Kuhn-Houwink equation

(1) with the index  $a \geq 1$ , whereas in accordance with the experimental data, such index is  $0.5 \leq a \leq 1$ .

Taking into account the hydrodynamic interaction, according to which the local hydrodynamic flow around the given bead essentially depends on the position of other beads into necklace, leads to the dependence:

$$[h] \sim R_g^3 / M \quad (4)$$

which gives the values of the index  $a$  in the Mark-Kuhn-Houwink equation (1) under limits 0.5–0.8. This is in good agreement with the experimental data.

The expression (4) is similar to the Einstein equation by the form

$$[h] = 2.5\psi \quad (5)$$

proposed for the diluted solution containing the solid spherical particles of the radius  $R$ . Since the volumetric fraction  $\psi$  of these particles in the solution is proportional to  $R^3/m$  (where  $m$  is the particle's weight), then the conception about the hydrodynamic impenetrability of the polymer ball has appeared from the analogy (4) and (5).

Introduction of the additional factor considering the partial permeability of a polymeric ball does not change the functional dependence (4), although when compared to the experimental data leads to the conclusion, accordingly to which, at the molar weight  $M$  increasing the hydrodynamic permeability of the polymer ball decreases.

This conclusion contradicts to the fact that the volumetric fraction  $\psi$  of the monomer links into conformational volume of the polymer ball is proportional to  $M^{4/5}$ , therefore while molar weight increases the hydrodynamic permeability of the polymeric ball should also increase.

Let us also remark that the consideration only of the friction forces of the monomer links against the solvent, even taking into account their hydrodynamic interaction into conformational volume of the polymer ball, cannot explain the presence of the quadratic term upon  $\rho$  in the Huggins's equation (2).

The "anomalous" character of the viscosity at the gradient rate  $g_s$  of the hydrodynamic flow change is another problem of the polymeric solutions viscosity.

This can be visualized in the decrease of measured viscosity  $\eta$  of polymeric solution at  $g_s$  increasing. It is observed even in the case of the diluted solutions, so the intrinsic viscosity  $[\eta]$  and parameters of the Eqs. (1) and (2) become gradient dependent quantities. As to the solutions containing the asymmetrical macromolecules (accordingly to the models – hard strokes, dumbbells, ellipsoids) the reason of  $[h]$  decrease at  $g_s$  increase is the orientation of asymmetrical macromolecules along the direction of the hydrodynamic flow, that decreases the friction of macromolecules against the solvent under its Brownian rotation movement.

For the solutions of flexible polymeric chains having the spherical conformation, the gradient dependence  $[\eta]$  is explained by the anisotropy of hydrodynamic interaction, which in turn creates the orientation effect.

Finally, it can be noted, that exactly not uniform deformation of polymeric ball causes the change of the hydrodynamic interaction between the beads into necklace, therefore, leads to the oriental effect reinforcement. However, there is the opinion, that with the increase of the hydrodynamic flow gradient rate  $g_s$  the shifted deformation degree of the conformational volume of polymeric chain also increases, and it would seem to lead to the inverse effect, namely  $\eta$  increases at  $g_s$  increasing. Such contradiction can be overcome. If we take into account, that although with the increase of the gradient rate  $g$  of the hydrodynamic flow the external action leading to the shifted deformation of the conformational volume of the polymeric chain increases, but at the same time, the characteristic time  $t_r$  of the external action on the polymeric ball decreases. This fact decreases but not increases the shifted deformation degree on account of the kinetic reasons.

The dependence of the viscosity of polymeric solutions on the elastic properties of the conformational volume of the polymeric chain and its gradient dependence were analyzed in [7, 8].

Here the experimental data on viscosity for diluted solutions of polystyrene in toluene are proposed and also their interpretation is presented on the basis of the above mentioned works.

## 2. Experimental

In order to obtain the statistically important experimental data we studied the gradient dependence of the viscosity for the diluted solution of the polystyrene in toluene under three concentrations  $\rho = 0.5 \cdot 10^5$ ,  $1 \cdot 10^5$  and  $2 \cdot 10^5$  g/m<sup>3</sup> and for four polystyrene fractions with average molar weights  $M = 5.2 \cdot 10^4$ ,  $4.4 \cdot 10^4$ ,  $3.3 \cdot 10^4$  and  $1.8 \cdot 10^4$  g/mol.

Molar weights  $M$  of the polystyrene were determined by the viscosimetric method with the use of the Ostwald viscometer having the capillary diameter  $d_c = 0.62 \cdot 10^{-3}$  m. The gradient dependence of the viscosity for four temperatures 293, 298, 303 and 308 K were studied for every pair of the values  $M$ - $\rho$ .

The experiments have been carried out with the use of rotary viscometer "Rheotest 2.1" by VEB MLW production with the working cylinder containing two rotation surfaces with the diameters  $d_1 = 3.4 \cdot 10^{-2}$  m and  $d_2 = 3.9 \cdot 10^{-2}$  m.

The typical viscosity dependences  $\eta$  on the used cylinder rotation angular rate  $\omega$  (r/s) represented in Fig. 1. We have obtained 48 curves  $\eta(\omega)$ .

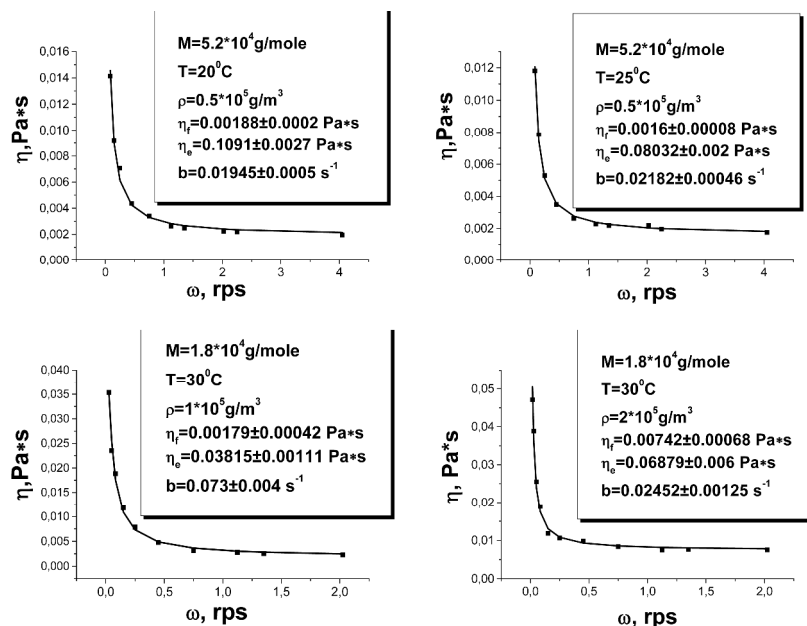


Fig. 1. The typical experimental (points) and calculated according to the Eq. (10) (full line graph) dependences of the effective viscosity  $\eta$  on the rotation rate of the working cylinder  $\omega$

Table 1

Optimization parameters  $\eta_f$ ,  $\eta_e$  and  $b$  according to the Eq. (10)

$\rho \cdot 10^{-5}, \text{g/m}^3$		0.5				1.0				2.0			
T, K	$M \cdot 10^4, \text{g/mol}$	5.2	4.4	3.3	1.8	5.2	4.4	3.3	1.8	5.2	4.4	3.3	1.8
293	$\eta_f \cdot 10^3, \text{Pa}\cdot\text{s}$	1.88	1.79	1.66	1.49	5.39	4.91	4.40	2.50	16.3	15.32	11.70	7.55
	$\eta_e \cdot 10, \text{Pa}\cdot\text{s}$	1.09	0.90	0.72	0.47	2.20	1.95	1.45	0.94	4.40	3.68	2.80	1.81
	$b \cdot 10^2, \text{s}^{-1}$	1.95	1.73	2.40	3.80	1.45	1.49	1.70	2.73	0.72	0.71	0.83	1.24
298	$\eta_f \cdot 10^3, \text{Pa}\cdot\text{s}$	1.72	1.65	1.58	1.28	5.30	4.52	3.70	1.96	16.00	14.22	10.50	6.90
	$\eta_e \cdot 10, \text{Pa}\cdot\text{s}$	0.80	0.58	0.42	0.35	1.64	1.33	0.89	0.56	3.43	2.60	1.86	0.99
	$b \cdot 10^2, \text{s}^{-1}$	2.14	2.27	3.22	4.75	1.79	1.84	2.90	5.39	0.83	0.88	1.06	1.94
303	$\eta_f \cdot 10^3, \text{Pa}\cdot\text{s}$	1.62	1.57	1.43	1.24	4.80	3.77	3.10	1.79	15.30	13.21	9.60	6.66
	$\eta_e \cdot 10, \text{Pa}\cdot\text{s}$	0.48	0.33	0.31	0.24	1.15	0.74	0.64	0.38	2.20	1.49	1.19	0.69
	$b \cdot 10^2, \text{s}^{-1}$	2.85	3.00	3.82	5.37	2.37	3.24	4.28	7.30	1.15	1.35	1.44	2.45
308	$\eta_f \cdot 10^3, \text{Pa}\cdot\text{s}$	1.57	1.37	1.29	1.22	3.97	3.42	2.77	1.44	14.8	11.97	9.20	6.00
	$\eta_e \cdot 10, \text{Pa}\cdot\text{s}$	0.29	0.25	0.20	0.12	0.72	0.49	0.39	0.24	1.56	0.95	0.69	0.45
	$b \cdot 10^2, \text{s}^{-1}$	3.33	3.72	4.99	7.85	3.74	4.57	6.12	10.12	1.30	1.83	1.98	4.15

These dependences were analyzed with the use of the following equation [8]:

$$h = h_f + h_e (1 - \exp\{-t_v/t_0\}) / (1 + \exp\{-t_v/t_0\}) \quad (6)$$

where  $\eta$  is the measurable viscosity of the solution at given value  $\omega$ ,  $\eta_f$  is frictional, and  $\eta_e$  is elastic component of the viscosity  $\eta$ ;  $t_0$  is the characteristic time of the shifted deformation of the macromolecule conformational

volume and  $t_v$  is the characteristic time of the external action of the gradient rate  $g_s$  of the hydrodynamic flow on the conformational volume of the polymeric chain, leading to its deformation and rotation.

Since the shifted deformation of the conformational volume is realized in accordance with the reptation mechanism, *i.e.* via the segmental movement of the

polymeric chain,  $t_0$  is also by the characteristic time of its own rotation polymeric chain, *i.e.* without the action of  $g_s$  [7].

The expression (6) leads to these two asymptotes:

$$\mathbf{h} = \mathbf{h}_f + \mathbf{h}_e \text{ at } t_v \gg t_0 \quad (7)$$

$$\mathbf{h} = \mathbf{h}_f \text{ at } t_v \ll t_0 \quad (8)$$

Thus, if the characteristic time  $t_v$  of the external action of the gradient rate  $g_s$  of the hydrodynamic flow on the macromolecule chain conformational volume is more than the characteristic time  $t_0$  of its shifted deformation, the experimental measured viscosity  $\eta$  is equal to the sum of the frictional and elastic components; on the contrary, at  $t_v \ll t_0$  the shifted deformation of the macromolecule conformational volume due to the kinetic reasons is not discovered in time and the measured viscosity  $\eta$  is equal to the frictional component  $\eta_f$ .

The characteristic time  $t_v$  is the function of the gradient rate  $g_s$  of the hydrodynamic flow which is caused by the working cylinder rotation in the rotary viscometer. Therefore, we can introduce the following ratio:

$$t_v / t_0 = b / \omega \quad (9)$$

where  $\omega$  is the rate of the working cylinder rotation, rps.

Taking into account the expression (9) the Eq. (6) can be represented as follows:

$$\mathbf{h} = \mathbf{h}_f + \mathbf{h}_e (1 - \exp\{-b/\omega\}) / (1 + \exp\{-b/\omega\}) \quad (10)$$

The conditions (7) and (8) in (10) correspond to  $b/\omega \gg 1$  and  $b/\omega \ll 1$  conditions respectively. Since, the parameter  $b$  under determination of (9) does not depend on  $\omega$ , but depends on the properties of the polymeric solution and temperature, then the measured dependence  $\eta(\omega)$  is the function of three parameters  $\eta_f$ ,  $\eta_e$  and  $b$ .

Thus, measuring experimentally the effective viscosity of polymeric solution as the function of the angular rate  $\omega$  (rps) of the working cylinder, we have found all three parameters  $\eta_f$ ,  $\eta_e$  and  $b$  applying the optimization method with the use of the Origin 5.0 program.

The dependence of obtained parameters on the concentration  $\rho$  ( $\text{g}/\text{m}^3$ ) of the polymer in the solution, on the molar weight  $M$  of the polymer and on the length of the polymeric chain  $N = M/M_0$ , where  $M_0$  is the molar weight of the monomer, and also on temperature has been investigated.

As the analysis showed, the numerical values of the frictional viscosity  $\eta_f$  can be easily determined on a plateau of the experimental curve  $\eta(\omega)$  under the condition  $\omega \rightarrow \infty$ . However, the optimization method used by us did not always give the adequate values of the parameters  $\eta_e$  and  $b$ , denoting their relationship. There are two reasons for this. Firstly, in a range  $\omega \rightarrow 0$  the measurement error sharply increases, since the measurement moment of the force is small. Secondly, in a

very important range of the transfer of the curve  $\mathbf{h} = \mathbf{h}(\omega)$  from the strong dependence  $\eta$  on  $\omega$  to the weak one, the parameters  $\eta_e$  and  $b$  are merged into a product  $\eta_e b$ , *i.e.* they are as a single parameter.

Indeed, under the condition  $b/\omega < 1$ , decomposing the exponentials in (10), and limiting by two terms of the range,  $\exp\{-b/\omega\} \approx 1 - b/\omega$ , from (10) we obtain  $\mathbf{h} = \mathbf{h}_f + \mathbf{h}_e b / 2$ . Thereby, the optimization method gives the values  $\eta_e$  and  $b$ , depending on each other, but not giving the global minimum of the functional errors. Therefore, at the estimation of  $\eta_e$  and  $b$  it was necessary to complete the optimization method by the "manual" method of the functional errors global minimum search, varying mostly by the numerical estimation  $\eta_e$ .

The results of such estimations of the numerical values  $\eta_e$ ,  $\eta_f$  and  $b$ , for all 48 experimental curves  $\eta(\omega)$  are represented in Table 1.

A review of these data shows, that all three parameters are the functions of the polymeric solution concentration, the chain length and temperature. But at the same time,  $\eta_e$  and  $\eta_f$  increase at the  $\rho$  and  $N$  increasing but they decrease at the  $T$  increasing, whereas the  $b$  parameter is varied in the opposite way.

The analysis of these dependences will be given in Section 3. Here, let us put in the additional parameters which are necessary for this analysis:  $\psi$  is the volumetric fraction of the conformational volume of polymeric chains in the solution;  $\varphi$  is the volumetric fraction of the monomer links in the conformational volume of a polymeric chain.

In accordance with the definition,

$$\mathbf{y} = c N_A R_f^3 \quad (11)$$

where  $c$  is the molar-volumetric concentration of the polymer in the solution ( $\text{mol}/\text{m}^3$ ),  $R_f$  is the most probable radius of the conformational volume of the non deformed polymeric ball, *i.e.* radius Flory:

$$R_f = a N^{3/5} \quad (12)$$

where  $a$  is the statistical length of the chain's link.

Since  $\rho = M \cdot c$ , we have

$$\mathbf{y} = N_A R_f^3 r / M \quad (13)$$

At the critical concentration  $c^*$ , corresponding to the beginning of the macromolecules conformation volumes overlapping,  $\Psi=1$ .

This value corresponds to the critical concentration  $\rho^* = M \cdot c^*$ :

$$\mathbf{r}^* = M / N_A R_f^3 = M_0 N / N_A R_f^3 \quad (14)$$

For diluted solutions the convenient form for the  $\Psi$  definition is obtained from the Eqs. (13) and (14) *via* the concentration of the polymer:

$$\mathbf{y} = r / \mathbf{r}^*, \quad r \leq \mathbf{r}^* \quad (15)$$

At all  $r \geq r^*$ ,  $\Psi = 1$ .

The critical concentration  $r^*$  is a function of the chain length according to the expression:

$$r^* = r_0 N^{-4/5} \quad (16)$$

in which

$$r_0 = M_0 / a^3 N_A \quad (17)$$

can be named as the density in the volume of the monomer link.

The volumetric fraction  $\varphi$  of the monomer links in the conformational volume of polymeric chain is defined by the expression:

$$j = V_m N / N_A R_f^3 \quad (18)$$

where  $V_m$  is the partially molar volume of links of a chain in the solution. Comparing (18) and (14) we have:

$$j = V_m r^* / M_0. \quad (19)$$

The relation  $M_0/V_m$  should be similar to the density  $\rho_m$  of the liquid monomer by the implication. Assuming this approximation  $M_0/V_m \approx \rho_m$ , we obtain:

$$j = r^* / r_m \quad (20)$$

### 3. Results and Discussion

#### 3.1. The Frictional Component of the Effective Viscosity

The whole range of the dependence  $h_f$  on  $\rho$ ,  $N$  and  $T$  we consider as the superposition of three movement forms giving the endowment into the impulses flow [9], where the notion of the viscosity coefficient is legibly determined.

For a solvent such movement form is the Brownian motion of the macromolecules, *i.e.* their translational degree of freedom. We associated this form of movement with the viscosity coefficient of the solvent  $\eta_s$ . An analogue of the Brownian motion of the solvent molecules is the transition of polymer chain links from one state into another one, which we call the segmental motion. It is associated with the viscosity coefficient  $h_{sm}$ . Under the action of the gradient rate of the hydrodynamic flow the polymer ball is in a rotational motion, which also makes a contribution into  $h_f$ . In accordance with the principle of superposition, the internal segmental motion and the external rotational motion of the polymeric ball should be considered as the independent ones. In this case, the external rotational motion of the polymeric ball (without taking into account the segmental motion) is the same as the rotation of hard wire in the Kuhn's model; but here the segmental motion is not disregarded. The rotational

motion of polymeric ball is associated with the viscosity coefficient  $h_{pp}$ .

The contribution of the above-mentioned motion forms, respectively, the viscosity coefficients  $h_s$ ,  $h_{sm}$  and  $h_{pp}$ , into  $\eta_c$  in the range of the conformational volume of polymeric chain is determined by the equation:

$$h_c = h_s(1-j) + (h_{sm} + h_{pp})j \quad (21)$$

For the whole volume of the solution we have:

$$h_f = h_s(1-y) + h_c y \quad (22)$$

Comparing (21) and (22), we obtain:

$$h_f - h_s = (h_{sm} + h_{pp} - h_s)j y \quad (23)$$

Since  $\varphi\psi = \rho/\rho_m$ , the Eq. (23) gives a linear dependence of  $h_f$  on  $\rho$ . However, in accordance with the data represented in Table 1, a frictional component of the viscosity  $h_f$  depends stronger on  $\rho$ , and this dependence is similar to the quadratic one.

Besides, the dependence of  $h_f$  on the chain length  $N$  is also determined by the concentration of the polymer in the solution: the greater is  $\rho$ , the stronger is dependence  $h_f$  on  $N$ . Since,  $h_{sm}$  and  $h_s$  per definition should not depend on  $\rho$ , (at least the diluted solution), the rotational movement of the polymeric ball, *i.e.*  $h_{pp}$ , is responsible for these peculiarities of  $\rho$  influence on  $\eta_f$  and the dependence of latter on  $N$ .

In order to explain these experimental facts, we employ the concept of the hydrodynamic interaction between the polymeric balls which rotate under the action of the gradient rate  $g_s$  of the hydrodynamic flow.

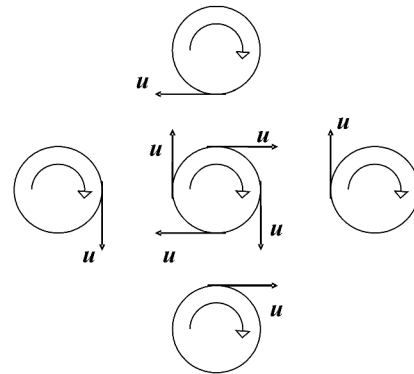


Fig. 2. The effect of the hydrodynamic interaction between the rotating polymeric balls ( $u$  is a linear rate of their rotation)

In accordance with the scheme, represented in Fig. 2, at the rotation of polymeric balls under the action of  $g_s$ , the linear rates of their rotation are directed into the opposite ways between them in a perigee field (see Fig.

2). This creates the local additional gradient rate  $g_{sL}$  of the hydrodynamic flow. The total action of all local  $g_{sL}$  for the presented polymeric ball creates the effect of its rotation in the external medium, rotating into the opposite direction.

Tangential tension  $G$ , which is created by frictional forces under the action of gradients  $g_s$  and  $g_{sL}$  on the rotational motion of polymeric ball, will be equal to:

$$G = h_s (g_s + g_{sL}) \quad (24)$$

However, the measured tangential tension is correlated with the given external gradient  $g_s$ , but not with the total gradient  $g_s + g_{sL}$ , which gives another viscosity coefficient:

$$G = h_{pp} \cdot g_s \quad (25)$$

Comparing (24) and (25), we have

$$h_{pp} - h_s = h_s g_{sL} / g_s \quad (26)$$

The effect of hydrodynamic interaction between the rotating polymeric balls, respectively  $g_{sL}$ , depends on the volumetric fraction  $\psi$  of the conformational volumes of macromolecules in the solution. At the first approximation we can assume the linear dependence of  $g_{sL}$  on  $\psi$ :  $g_{sL} \sim \psi$ . Under the critical concentration  $r^*$ , corresponding to the beginning of polymeric chains conformation volumes overlapping,  $g_{sL}$  achieves maximum possible value  $g_{sL}^*$  for diluted solutions. This value  $g_{sL}^*$  at  $\psi = 1$  is chosen as the frame for the evaluation of  $g_{sL}$ :

$$g_{sL} = g_{sL}^* \psi \quad (27)$$

If to note

$$h_{pp}^* = h_s g_{sL}^* / g_s \quad (28)$$

then taking into account the Eq. (27) we can rewrite (26) in the following view:

$$h_{pp} - h_s = h_{pp}^* \psi \quad (29)$$

Substituting (29) in (23), we obtain:

$$h_f - h_s = (h_{sm} + h_{pp}^* \psi) \cdot j \psi \quad (30)$$

Taking into account the definitions of  $\varphi$  and  $\psi$  according to (20) and (15) respectively, we have:

$$(h_f - h_s) = h_{sm} r / r_m + h_{pp}^* r^2 / r_m r^* \quad (31)$$

In order to testify graphically the above-said it is necessary to transform the Eq. (31) as:

$$(h_f - h_s) r_m / r = h_{sm} + h_{pp}^* r / r^* \quad (32)$$

During the calculations of the left part of the Eq. (32), the experimental data were taken from Table 1, the values of  $h_s$  – from the Ref. [10], ( $h_s = 0.584, 0.552, 0.517, 0.493$  Pa·s at the temperatures of 293, 298, 303 and 308 K, respectively), a density of liquid styrene  $\rho_m$  was equal to  $0.907 \cdot 10^6$  g/m<sup>3</sup> at 293 K, but the temperature dependence of  $\rho_m$  was neglected. During the calculations of  $r^*$  according to (16) and (17) we used the values of  $M_0 = 104.15$  g/mol;  $a = 1.86 \cdot 10^{-10}$  m.

The results of calculations are represented in Fig. 3.

As we can see, the experimental data, at every temperature for all values of  $N$ , are linearized in the coordinates of the expression (32) satisfactorily. This permits to obtain the numerical values of  $h_{sm}$  and  $h_{pp}^*$  according to the regression equations, shown in Fig. 3. According to these data, we have  $h_{pp}^* > h_{sm} > h_s$ , i.e. the values of  $h_{pp}^*$  and  $h_{sm}$  are more than  $h_s$ , in one order moreover.

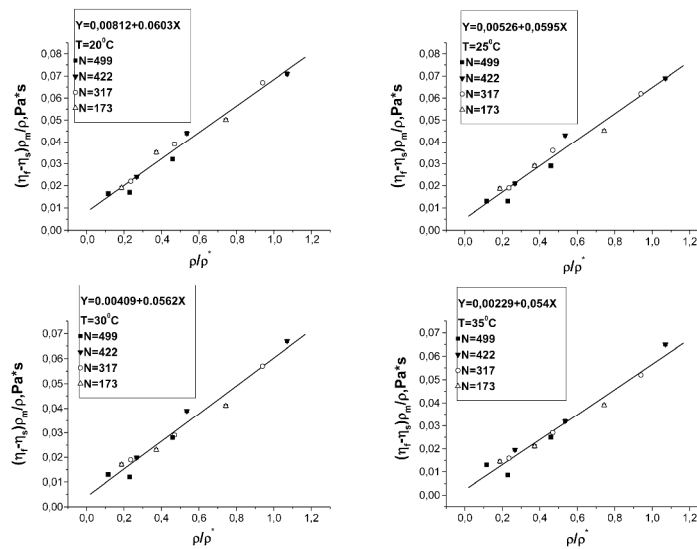


Fig. 3. Interpretation of the experimental values of friction viscosity  $\eta_f$  in coordinates of the Eq. (32)

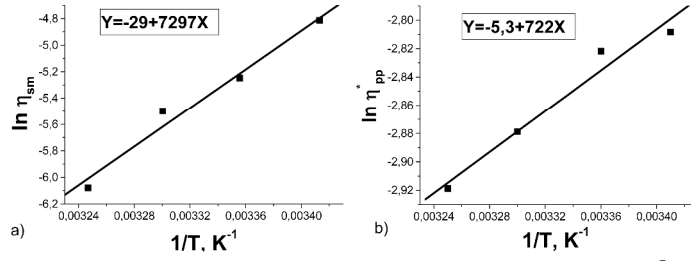


Fig. 4. Temperature dependences of the coefficients of viscosity  $h_{sm}$  (a) and  $h_{pp}^*$  (b) in the Arrhenius equation plots

Since  $h_{sm}$  and  $h_{pp}^*$  do not depend on  $N$ , the dependence of  $h_f$  on the chain length is determined by the second term in (32) via  $r^* = r_0 N^{-4/5}$ . This explains the experimentally found regularity, in accordance to which at the concentration of the polymer in the solution increasing, the influence of  $N$  on  $\eta_f$  increases too.

Temperature dependence of  $h_{sm}$  and  $h_{pp}^*$  in the Arrhenius equation plots (see Fig. 4), leads to the following activation energy values:  $E_{sp} = 60.6$  kJ/mol,

$E_{pp}^* = 6.0$  kJ/mol. The distinction in one order between  $E_{sm}$  and  $E_{pp}^*$  indicates the essentially different forms of the motion, which determine these values. The activation energy  $E_s$ , calculated on the basis of reference data of  $\eta_s$  for toluene gives the value of 8.6 kJ/mol. Taking into account the determination error of  $E_{pp}^*$  (see Fig. 4),

$E_{pp}^* \approx E_s$  can be accepted thoroughly. This means that the rotational motion of the polymer ball under the action of gradient rate of the hydrodynamic flow is realized via the Brownian motion of the solvent molecules. It justifies the insertion into (24) the viscosity coefficient  $\eta_s$  of the solvent. Therefore, using the experimental value  $h_{pp}^*$  in the Eq. (28) (see Fig. 3) and the reference data  $\eta_s$ , we have calculated the ratio  $g_{sL}^*/g_s$  for every temperature. They were equal to: 102.7, 106.9, 108.3 and 109.5 at 293, 298, 303 and 308 K, respectively. Taking into account the error of their estimation, the temperature dependence of the relation  $g_{sL}^*/g_s$  can be neglected. According to experimental conditions let us assume the average value  $\langle g_{sL}^*/g_s \rangle = 107$ , which we will use in Subsection 3.4 for the analysis of the parameter  $b$ . Also in Subsection 3.4 the explanation of sufficiently great values of the  $g_{sL}^*/g_s$  ratio determining the efficiency of the hydrodynamic interaction of the rotating polymer balls will be given.

### 3.2. The Elastic Component $\eta_e$ of the Effective Viscosity

It follows from the data presented in Table 1, that the elastic component of the viscosity  $\eta_e$  for the diluted solution of the polystyrene in toluene is determined as a function of the polymeric concentration  $\rho$ , the chain length  $N$  and temperature  $T$ . At the same time, the dependence of  $\eta_e$  on  $\rho$  is linear, and the dependence of  $\eta_e$  on  $N$  is near to the linear one.

The elastic properties of the polymer chain conformation state are displayed in the form of the conformational volume deformation resistance under the action of the external force. Therefore, the contribution of the elastic properties of the polymer chains conformation into the elastic component of the solution viscosity can be determined by the equation:

$$h_e = h_e^0 y = h_e^0 r/r^* \quad (33)$$

in which  $h_e^0$  is the elastic component of the viscosity in the conformational volume of the polymeric chain.

The value  $h_e^0$  was determined earlier [7]:

$$h_e^0 = \mu_0 L \quad (34)$$

where  $\mu$  is the shift module of the macromolecular conformation volume,  $t_0$  is the characteristic time of a shift,  $L$  is a factor of the form for the deformed Flory ball.

At that [7]:

$$m = 1.36 \frac{RT}{N_A a^3} N^{-8/5} \quad (35)$$

$$t_0 = \frac{4}{7} N^{7/5} \tau \quad (36)$$

where  $\tau$  is the characteristic time of the segmental motion.

At the deformation of the Flory ball with the radius  $R_f$  into the ellipsoid of rotation, elongated or pressed, for example, along  $z$  axis, the factor of the form  $L$  is determined by the equation [7]:

$$L = 3 \sqrt{I_v^2 \left( \frac{1}{I_x} + \frac{4}{(I_x + I_z)} \right)} \quad (37)$$

where  $I_x = I_y$  and  $I_z$  are repetition factors of the linear deformations of the Flory ball along the corresponding axes:  $I_i = R_i/R_f$ , where  $R_i$  is the semi-axis of the ellipsoid, and  $I_v$  is the repetition factor of the volumetric deformation:

$$I_v = I_x I_y I_z = I_x^2 I_z \quad (38)$$

At any deformations of the Flory ball  $I_v \leq 1$ .

Substituting (35) and (36) in (34), we obtain:

$$h_e^0 = \frac{RT}{N_A a^3} N^{-1/5} L t \quad (39)$$

Using (39) in (33) and exposing the dependence of  $\rho^*$  on  $N$  in the form of the Eqs. (16) and (17), we find the expression defining the solution viscosity elastic component:

$$h_e = \frac{RT}{M_0} N^{3/5} L t r \quad (40)$$



Thus, according to the experimental data,  $\eta_e$  is the linear function of  $\rho$  and decreases at the temperature increasing in accordance with the characteristic time  $\tau$  of the segmental motion decreasing.

The dependence of  $\eta_e$  on  $N$  is similar to the linear one. This fact indicates that the factor of the form  $L$  is also a growth function on  $N$ . This is agreed with the theoretical analysis of the macromolecules conformation state in the

real solution, according to which the work of the conformational volume deformation at the transition of the Flory ball with radius  $R_f$  from the ideal solution into the real one, is numerically equal (in the system of the mechanics symbols) to the change of the conformation free energy  $\Delta F_{def} = F_{real} - F_{id}$ :

$$\Delta F_{def} = \Delta F_V^0 N (a - a_{id}) = \frac{5}{2} RT N^{1/5} \left( \frac{1}{I_v} - 1 \right) \quad (41)$$

where  $\Delta F_V^0 = \Delta F_{V2}^0 - \Delta F_{V1}^0$  is a difference of the normal free energies of two adjacent link's states of the polymeric

chain:  $S_1$   and  $S_2$  ;  $\alpha$  and  $\alpha_{id}$  are fractions of the states  $S_1$  and  $S_2$  in real and ideal solutions respectively. At this:

$$a = g \exp \left\{ \frac{\Delta F_V^0}{RT} \right\} / \left( 1 + g \exp \left\{ \frac{\Delta F_V^0}{RT} \right\} \right) \quad (42)$$

The  $S_1$  and  $S_2$  states are the energy-wise equivalent, and then  $\Delta F_V^0 = 0$ , therefore

$$a_{id} = g / (1 + g) \quad (43)$$

where  $g = g_1 / g_2$  is the ratio of the statistical weights of the states  $S_1$  and  $S_2$ :  $g_1 = 4$ ,  $g_2 = 1$ .

Table 2

Calculated values  $L\tau$ ,  $\tau/L$ ,  $\tau$  and  $L$  based on the experimental values of  $\eta_e$  and  $b$

$\rho \cdot 10^{-5}, \text{g/m}^3$		0.5				1.0				2.0				$\bar{\tau}, 10^{-10}, \text{s}$
$T, \text{K}$	$M \cdot 10^4, \text{g/mol}$	5.2	4.4	3.3	1.8	5.2	4.4	3.3	1.8	5.2	4.4	3.3	1.8	
293	$(L\tau)_{\eta_e} \cdot 10^{10}, \text{s}$	22.4	20.5	19.4	18.2	22.6	22.0	19.6	18.0	22.6	20.9	18.9	17.4	5.31
	$(\tau/L)_b \cdot 10^{10}, \text{s}$	1.46	1.88	1.71	1.72	1.06	1.17	1.30	1.29	1.14	1.28	1.39	1.48	
	$\tau \cdot 10^{10}, \text{s}$	5.70	6.20	5.80	5.60	4.90	5.10	5.10	4.80	5.10	5.20	5.10	5.10	
	$L$	3.90	3.30	3.40	3.30	4.60	4.30	3.90	3.70	4.50	4.00	3.70	3.40	
298	$(L\tau)_{\eta_e} \cdot 10^{10}, \text{s}$	16.2	12.9	11.2	13.1	16.6	14.8	11.7	10.5	16.2	14.5	12.4	9.40	3.76
	$(\tau/L)_b \cdot 10^{10}, \text{s}$	1.31	1.44	1.59	1.38	0.86	0.96	0.75	0.65	1.01	1.05	1.09	0.97	
	$\tau \cdot 10^{10}, \text{s}$	4.60	4.30	4.20	4.30	3.80	3.80	2.90	2.60	4.00	3.90	3.70	3.00	
	$L$	3.50	2.90	2.60	3.10	4.40	3.90	3.90	4.00	4.00	3.70	3.40	3.10	
303	$(L\tau)_{\eta_e} \cdot 10^{10}, \text{s}$	9.59	7.21	8.20	8.75	11.4	8.00	8.20	7.08	10.4	8.20	7.80	6.40	2.57
	$(\tau/L)_b \cdot 10^{10}, \text{s}$	1.00	1.09	1.08	1.22	0.65	0.54	0.52	0.48	0.75	0.68	0.79	0.76	
	$\tau \cdot 10^{10}, \text{s}$	3.10	2.80	2.90	3.30	2.70	2.10	2.10	1.90	2.80	2.40	2.50	2.20	
	$L$	3.10	2.60	2.70	2.70	4.20	3.80	3.90	3.80	3.70	3.50	3.10	2.90	
308	$(L\tau)_{\eta_e} \cdot 10^{10}, \text{s}$	5.80	5.78	5.70	4.38	7.00	5.30	5.00	4.33	7.70	5.10	4.50	4.10	1.74
	$(\tau/L)_b \cdot 10^{10}, \text{s}$	0.86	0.93	0.91	0.84	0.41	0.38	0.36	0.35	0.55	0.51	0.59	0.44	
	$\tau \cdot 10^{10}, \text{s}$	2.20	2.30	2.20	1.90	1.70	1.40	1.40	1.20	2.10	1.60	1.60	1.30	
	$L$	2.60	2.50	2.50	2.30	4.10	3.70	3.70	3.50	3.70	3.20	2.80	3.10	



It follows from the analysis of Eqs. (41) and (42), that the work of the conformational volume deformation has the positive value at every sign of  $\Delta F_V^0$  (if  $\Delta F_V^0 < 0$ , then  $a < a_{id}$ ; if  $\Delta F_V^0 > 0$ , then  $a > a_{id}$ ). It leads to the compression of the conformation volume, *i.e.* to the decreasing of  $\lambda_v$ . Thus, the factor of the form  $L$  increases.

Since the work of the deformation is proportional to  $N$ , then at the length of the chain increasing the factor of the form increases. The dependence of  $L$  on  $N$  should be numerically estimated for known values  $\Delta F_V^0$ . These calculations show a rather complicated and strong dependence of  $L$  on  $N$ . In this work we obtain the numerical values of  $L$  *via* the experimental values of  $\eta_e$  and parameter  $b$ .

As it can be seen from the Eq. (40), the parameters  $L$  and  $\tau$  are inseparable, and we can calculate only their product *via* the values  $\eta_e$ :

$$(Lt)_h = h_e \frac{M_0}{RT} N^{-3/5} r^{-1} \quad (44)$$

The results of the calculation  $(Lt)_h$  are present in Table 2. We make sure, that the values of  $(Lt)_h$  depend on the length of the chain and temperature only. It thoroughly corresponds to the physical sense of the parameters  $L$  and  $\tau$ .

### 3.3. Parameter $b$

Accordingly to the ratio (9) the parameter  $b$  is a measure of the influence of the gradient rate of the hydrodynamic flow (caused by the rotation of the working cylinder) on the characteristic time  $t_v$ , on the action  $g_s$ , on the deformation of shift of the polymeric ball and its rotation movement. The own characteristic time  $t_0$  of the shift deformation and rotation of the polymer chain accordingly to (36) depends on  $N$  and  $\tau$ .

Thus, as it follows from the experimental estimations (see Table 1), the parameter  $b$  is the function on all three arguments  $\rho$ ,  $N$  and  $T$ , but at this it is increased at the temperature increasing and it is decreased at  $\rho$  and  $N$  increasing. In order to describe these dependencies let us determine previously the angular rate  $w_f^0$  ( $c^{-1}$ ) of the rotation of the deformed polymeric ball with the effective radius  $R_f L$ , contacting with the surface of the working cylinder with the diameter  $d$ .

$$w_f^0 = pdw/R_f L \quad (45)$$

Here  $\pi$  appears due to the distinction of the dimensionalities  $w_f^0$  ( $s^{-1}$ ) and  $w$  ( $r/s$ ).

Then  $t_v^0$  can be determined as the inverse value of  $w_f^0$ :

$$t_v^0 = R_f L / pdw \quad (46)$$

According to the definition (46),  $t_v^0$  is the time during which the polymeric ball with the effective radius  $R_f L$  under the action of the rotating working cylinder with the diameter  $d$  rotates on the unit angle equal to one radian. Let us note that own characteristic time of the shift and rotation  $t_0$  of the polymeric ball at the expense of the segmental motion was determined [7], in calculation on the same unit angle. Thus, the ratio  $t_v^0/t_0$  should not depend on the choice of the standard in defining the notion "characteristic time".

Since in our experiments the working cylinder had two rotating surfaces with the diameters  $d_1$  and  $d_2$ , then the value of  $w_f^0$  in (45) was averaged in accordance with the condition  $d = (d_1 + d_2)/2$ . The expression for  $t_v^0$  is changed respectively:

$$t_v^0 = 2R_f L / p(d_1 + d_2)w \quad (47)$$

Thus,  $t_v^0$  is inversely proportional to  $w$ ; therefore, it is inversely proportional to  $g_s$  *via* the constant of the instrument:

$$t_v^0 \sim g_s^{-1} \quad (48)$$

As we have suggested in Section 3, the hydrodynamic interaction takes place between the rotating polymeric balls, which leads to the appearance of the additional to  $g_s$  local gradient rate  $g_{sL}$  of the hydrodynamic flow. This local gradient  $g_{sL}$  does not act on the conformational volume of the polymeric chain, but it has an influence on its monomer frame (Kuhn's model of the hard wire). Therefore the contribution of the local gradient rate into characteristic time  $t_v$  depends on the volumetric fraction  $\varphi$  of the polymeric chain links in its conformational volume.

Thus, the characteristic time  $t_v$  depends on the total effect of  $g_s$  and  $g_{sL}\varphi$ , therefore, we can write:

$$t_v \sim (g_s + g_{sL}j)^{-1} \quad (49)$$

Taking into account the ratio  $g_{sL} = g_{sL}^* Y$  and combining (48) and (49), we obtain:

$$t_v/t_v^0 = g_s / (g_s + g_{sL}^* j Y) \quad (50)$$

Finally, we have:

$$t_v = t_v^0 / \left( 1 + \frac{g_{sL}^*}{g_s} \frac{r}{r_m} \right) \quad (51)$$

Accordingly to (47), (51) and definition (9), we obtain a general expression for the parameter  $b$ :

$$b = \frac{7R_f L}{2p(d_1 + d_2)} / N^{7/5} t \left( 1 + \frac{g_{sL}^*}{g_s} \frac{r}{r_m} \right) \quad (52)$$

As it was stated earlier (see Section 3), the ratio  $g_{sL}^*/g_s$  almost does not depend on temperature, and so at the calculations we use its average value:  $g_{sL}^*/g_s = 107$ . Assuming the known values  $a = 1.86 \cdot 10^{-10}$  m,  $d_1 = 3.4 \cdot 10^{-2}$  m and  $d_2 = 3.9 \cdot 10^{-2}$  m and combining the constants, we obtain:

$$b = 2.84 \cdot 10^{-9} \frac{L}{t} / N^{4/5} \left(1 + 107 \frac{r}{r_m}\right) \quad (53)$$

Thus, accordingly to the experimental data (see Table 1), the parameter  $b$  is a decreasing function on  $N$  and  $\rho$  and the increasing function of temperature.

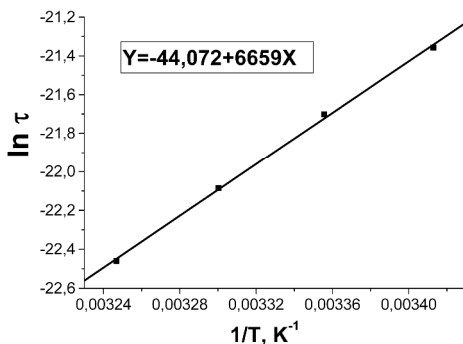
Since  $\tau$  and  $L$  are unknown, the Eq. (53) can be used for the calculation of the ratio  $\tau/L$  at the experimental values of  $b$ :

$$\left(\frac{t}{L}\right)_b = 2.84 \cdot 10^{-9} / N^{4/5} \left(1 + 107 \frac{r}{r_m}\right) b \quad (54)$$

The results of the calculations are represented in Table 2.

According to the independent estimates of  $(tL)_h$  and  $(t/L)_b$ , we found the values of  $\tau$  and  $L$ , which are also presented in Table 2. As follows from these data, taking into account the experimental error, the characteristic time  $\tau$  of the segmental motion into the diluted polymeric solution does not depend on  $\rho$  and  $N$ , but it is the function of temperature.

The temperature dependence of  $\bar{t}$ , obtained by averaging of  $\tau$  at the given temperature for all values of  $\rho$  and  $N$ , in the Arrhenius equation plots presented in Fig. 5. This dependence allows to estimate the activation energy of the polymeric chain segmental motion:  $E_\tau = 55.34$  kJ/mol.



**Fig. 5.** Temperature dependence of the average values of characteristic time  $\bar{t}$  of the segmental movement of polymeric chain in the Arrhenius equation plots

Comparing  $E_{sm} = 60.64$  kJ/mol with  $E_\tau = 55.34$  kJ/mol, we can conclude, that within the limits of errors of their estimations, they are equal:  $E_{sm} = E_\tau$ . This gives the evidence that the frictional coefficient of the

viscosity  $\eta_{sm}$  is defined by the segmental motion of the polymeric chain.

The analysis of the factor of the form values (see Table 2) indicates, that  $L$  does not depend on  $\rho$ , but increases with the  $N$  increasing and decreases with the  $T$  increasing. The dependence of  $L$  on  $N$  was discussed earlier (see Section 3). Here we indicate, that the experimentally determined decreasing of  $L$  with  $T$  increasing is also agreed with the theoretical analysis of the temperature influence on the conformational state of the macromolecules in the real solution. Thus, let us use the Eq. (41) and find its derivative:

$$\frac{\partial \Delta F_{def}}{\partial T} = -\frac{(\Delta F_v^0)^2}{kT^2} \cdot \frac{g \exp\{\Delta F_v^0/kT\}}{1 + g \exp\{\Delta F_v^0/kT\}} \quad (55)$$

Hence, the differential coefficient  $\frac{\partial \Delta F_{def}}{\partial T} < 0$  at

any sign of  $\Delta F_v^0$ . Consequently, the work of the conformational volume deformation decreases with the temperature increasing and the factor of the form  $L$  decreases correspondingly.

### 3.4. The Intrinsic Viscosity of the Polymeric Solution

The effective viscosity of the polymeric solution, taking into account its gradient dependence, is determined by the Eq. (6). By substituting in this equation of the determined expressions (31) for  $\eta_f$  and (40) for  $\eta_e$ , we obtain:

$$h - h_s = h_{sm} r/r_m + h_{pp}^* r^2/r_m r^* + \frac{RT}{M_0} L t N^{3/5} \cdot r (1 - \exp\{-t_v/t_0\}) / (1 + \exp\{-t_v/t_0\}) \quad (56)$$

Let us transform this expression into a form of the relative viscosity:

$$\frac{h - h_s}{r h_s} = \frac{h_{sm}}{r_m h_s} + \frac{h_{pp}^*}{h_s} \cdot \frac{r}{r_m r^*} + \frac{RT}{M_0} L \frac{t}{h_s} N^{3/5} \frac{1 - \exp\{-t_v/t_0\}}{1 + \exp\{-t_v/t_0\}} \quad (57)$$

Accordingly to the condition  $r \rightarrow 0$  it is easy to obtain an analytical expression for the intrinsic viscosity of the polymeric solution:

$$[h] = h_{sm}/r_m h_s + \frac{RT}{M_0} L \frac{t}{h_s} N^{3/5} \cdot (1 - \exp\{-t_v/t_0\}) / (1 + \exp\{-t_v/t_0\}) \quad (58)$$

Thus, the intrinsic viscosity  $[\eta]$  of the polymeric solution is also represented by the frictional  $[\eta]_f$  and elastic  $[\eta]_e$  components:

$$[h] = [h]_f + [h]_e \quad (59)$$

Here

$$[h]_f = h_{sm}/h_s r_m \quad (60)$$

depends on the segmental motion of the polymeric chain only, and the Eq. (61) is a function of the elastic properties of the polymeric chain conformational volume and is a gradient dependent quantity.

$$[h]_e = \frac{RT}{M_0} L \frac{t}{h_s} N^{3/5} (1 - \exp\{-t_v/t_0\}) / (1 + \exp\{-t_v/t_0\}) \quad (61)$$

As it was determined,  $\eta_{sm}$  does not depend on the length of the polymeric chain. The frictional component  $[\eta]_f$  of the intrinsic viscosity does not depend on  $N$  either. Therefore, the empirical Mark-Kuhn-Houwink equation represents only the elastic  $[\eta]_e$  component. Probably, that is why, all the attempts to obtain the theoretical form of the Mark-Kuhn-Houwink's equation from the analysis of the forces of friction in a model of the beads did not lead to the positive results. Besides, due to the presence of the frictional  $[\eta]_f$  component of the intrinsic viscosity not depending on  $N$ , the linear dependence of  $\ln[\eta]$  on  $\ln M$  (in Mark-Kuhn-Houwink's equation) is an approximate and will be disfigured in a field of lesser values of  $M$ ; this fact is observed experimentally.

In connection with this fact, let us estimate the contributions of frictional and elastic components to the intrinsic viscosity of the solution of polystyrene in toluene at  $N = 500$ ,  $T = 298$  K, using the experimental values  $\eta_{sm}$ ,  $\tau$  and  $L$  obtained by us. We will compare the results of the calculation of  $[\eta]$  with the experimental value  $[\eta]_{\text{exp}}$ , presented in the form of the Mark-Kuhn-Houwink's equation:

$$[\eta]_{\text{exp}} = 1.18 \cdot 10^{-8} (M)^{0.72} \quad (62)$$

For  $M = 500 \cdot 104.15$  we obtain  $[\eta]_{\text{exp}} = 2.94 \cdot 10^{-4} \text{ m}^3/\text{g}$ .

The frictional component  $[\eta]_f$  is calculated according to the Eq. (60), assuming  $\eta_{sp} = 5.26 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$  (see Fig. 3);  $\eta_s = 0.55 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$ ;  $\rho_m = 0.906 \cdot 10^6 \text{ g/m}^3$ ;  $[\eta]_f = 1.06 \cdot 10^{-5} \text{ m}^3/\text{g}$ .

For convenience of the analysis the elastic component of the intrinsic viscosity is present according to the Eq. (61) in the form of two co-factors:

$$[h]_e = [h]_e^0 \cdot g(t_v, t_0) \quad (63)$$

Here

$$[h]_e^0 = \frac{RT}{M_0} L \frac{t}{h_s} N^{3/5} \quad (64)$$

represents the maximum possible contribution of the elastic properties of the polymeric chain into intrinsic viscosity under condition  $t_v \gg t_0$  in the function

$$g(t_v, t_0) = (1 - \exp\{-t_v/t_0\}) / (1 + \exp\{-t_v/t_0\}) \quad (65)$$

which reflects the gradient dependence  $[\eta]_e$ .

Calculation of  $[h]_e^0$  according to the Eq. (64) at the average values  $\bar{\tau} = 3.76 \cdot 10^{-10} \text{ s}$ ,  $L = 4.0$  (see Table 2)

gives the value  $[h]_e^0 = 2.71 \cdot 10^{-3} \text{ m}^3/\text{g}$ . As we can see,  $[h]_e^0$  is greater than  $[\eta]_{\text{exp}}$  in two orders. This fact indicates the considerable effect of the gradient dependence  $[\eta]_e$ , which is displayed as the low value of the function  $g(t_v, t_0)$ , under condition  $t_v \ll t_0$ .

The characteristic time of the shift  $t_0$  of the polymeric ball is calculated according to the Eq. (36): at  $N = 500$  and  $\bar{\tau} = 3.76 \cdot 10^{-10} \text{ s}$  we have  $t_0 = 1.29 \cdot 10^{-6} \text{ s}$ .

Let us estimate the characteristic time of the external action  $t_v$  of the hydrodynamic flow on the polymeric ball for Ostwald's capillary viscometer used by us, since, as a rule, exactly these viscometers are applied for the experimental estimation of  $[\eta]$ .

We calculate  $t_v$  without taking into account the hydrodynamic interaction between the polymeric balls accordingly to the condition  $\mathbf{r} = \mathbf{0}$ .

The same as it was shown earlier (see Eqs. (45) and (46)),  $t_v$  was defined as a quantity inversed to the rate of rotation of the polymeric ball, touching the wall of the capillary with the radius  $R$ . For this, we use the rate of the shift  $\omega_R$ , which is determined by the expression [5]:

$$w_R = 4Q/pR^3 \quad (66)$$

where  $Q$  is the volumetric liquid consumption,  $\text{m}^3/\text{s}$ .

The shift tension on the capillary wall is determined exactly *via*  $\omega_R$ . However, by implication,  $\omega_R$  is also the rate of the rotational motion of a particle with radius  $R$  under the action of the gradient rate of the hydrodynamic flow in the capillary. That is why, the angular rate of the rotation  $w_f$  of the polymeric ball near the capillary wall can be found according to the equation:

$$w_f = w_R \frac{R}{R_f L} \quad (67)$$

where  $R_f L$  is an average radius of the polymeric ball.

Hence, by definition  $t_v = w_f^{-1}$  we have:

$$t_v = pR^2 R_f L / 4Q \quad (68)$$

The radius of our viscometer  $R = 0.31 \cdot 10^{-3} \text{ m}$ , the volume of the flowing fluid  $V = 4 \cdot 10^{-6} \text{ m}^3$ , time of the solvent outflow 65 s, and so  $Q = 6.15 \cdot 10^{-8} \text{ m}^3/\text{s}$  and  $t_v = 3.85 \cdot 10^{-8} \text{ s}$ . Substituting the obtained values of  $t_v$  and  $t_0$  into (65), we find  $g(t_v, t_0) = 0.0149$ . Thus, only 1.5 % of the maximum possible contribution of the elastic properties of the polymeric ball  $[h]_e^0$  is displayed in the elastic component of the intrinsic viscosity  $[h]_e$ :  $[h]_e = 2.71 \cdot 10^{-3} \cdot 0.0149 = 4.04 \cdot 10^{-5} \text{ m}^3/\text{g}$ . Total calculated value of the intrinsic viscosity of the polystyrene in toluene solution at  $N = 500$  and  $T = 298$  K is equal to:

$$[h] = 1.06 \cdot 10^{-5} + 4.04 \cdot 10^{-5} = 5.1 \cdot 10^{-5} \text{ m}^3/\text{g}$$

We consider, that the value of  $[\eta]$  is sufficiently agreed with  $[\eta]_{\text{exp}} = 2.94 \cdot 10^{-5} \text{ m}^3/\text{g}$ .

Based on the above-mentioned estimation of  $t_v = 3.85 \cdot 10^{-8}$  s, we can answer the question: why the effect of the hydrodynamic interaction of rotating polymeric balls (*i.e.* square term per  $\rho$  in the Eq. (31)) has an essential endowment into the frictional component of the viscosity.

Since the angular rate of rotation  $W_f$  of the polymeric ball is inversely proportional to  $t_v$ , we have  $W_f = 2.6 \cdot 10^7$  s<sup>-1</sup>. Exactly a great angular rate of the polymeric balls rotation creates a significant effect of the hydrodynamic interaction between them and makes the greatest contribution into the frictional component of the viscosity. However, despite the Kuhn's model, the contribution of the polymeric balls segmental motion can not be neglected, at least, in theoretical aspect, especially at the determination of  $[\eta]$ .

## 4. Conclusions

The investigation of the gradient dependence of the effective viscosity of diluted solution of polystyrene in toluene permitted to mark out the frictional  $\eta_f$  and elastic  $\eta_e$  components of the viscosity and to study their dependences on the concentration  $\rho$  of the polymer into solution, on the length of the chain  $N$  and on the temperature  $T$ . The frictional component of the viscosity  $\eta_f$  is determined by three coefficients of the viscosity  $\eta_s$ ,  $\eta_{sm}$  and  $\eta_{pp}$ , representing three forms of motion: Brownian motion of the solvent molecules, the segmental motion of polymeric chain and the rotational motion of its frame, respectively. High angular rate of the rotation of the polymeric balls creates a hydrodynamic interaction between them and leads to the appearance of the quadratic term of the dependence of  $\eta_f$  on  $\rho$ , exactly the hydrodynamic interaction makes a basic contribution into  $\eta_f$ .

The elastic component of the viscosity  $\eta_e$  is determined by the elastic properties of the polymeric ball conformational volume under its shifted deformation. Due to the kinetic reasons, *i.e.* due to the distinction between the characteristic time of the external action  $t_v$  and own characteristic time of the shifted deformation  $t_0$  of the polymeric chain the endowment of the elastic component into effective viscosity of the solution depends on the gradient rate of the hydrodynamic flow, and respectively, on the angular rate  $\omega$  of the rotary viscometer working cylinder rotation. A measure of this dependence is the parameter  $b$ , described by the equation  $b = t_v / t_0 W$ . It was determined, that  $\eta$  and  $b$  have the opposite functional dependence on  $\rho$ ,  $N$  and  $T$ . The numerical estimates of the factor of the form  $L$  for the deformed polymeric ball and the characteristic time of the segmental motion  $\tau$  were obtained based on the experimental values of  $\eta_e$  and  $b$ . These estimations showed that  $\tau$  does not depend on  $\rho$  and  $N$ , but depends only on  $T$ . Moreover, the activation energy

of the segmental motion is equal to the activation energy, defined from the temperature dependence of the coefficient viscosity  $\eta_{sm}$ .

The factor of the form  $L$  does not depend on  $\rho$  in a diluted solution. It increases with the  $N$  increasing and slightly decreases with the  $T$  increasing. These regularities agree with the theoretical analysis of the work of the polymer chain conformational volume deformation at its transforming from the ideal solution into the real one.

We have obtained the equation for defining the intrinsic viscosity of the polymeric solution. It was shown that the basic contribution into the intrinsic viscosity gives the elastic component of the viscosity taking into account the gradient dependence of  $\eta_e$ .

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### ФРИКЦІЙНА ТА ПРУЖНА КОМПОНЕНТИ В'ЯЗКОСТІ РОЗВЕДЕНИХ РОЗЧИНІВ ПОЛІСТИРОЛ-ТОЛУОЛ

**Анотація.** Вивчена градієнтна залежність ефективної в'язкості  $\eta$  розведеного розчину полістиролу в толуолі для трьох концентрацій  $\rho = 0.5 \cdot 10^5, 1 \cdot 10^5, 2 \cdot 10^5$  г/м<sup>3</sup>, чотирьох фракцій полістиролу з середніми молярними масами  $M = 5.2 \cdot 10^4, 4.4 \cdot 10^4, 3.3 \cdot 10^4, 1.8 \cdot 10^4$  г/моль, при чотирьох температурах в інтервалі 293–308 К. Досліди проводили на ротаційному віскозиметрі Rheotest 2.1 за різних кутових швидкостей  $\omega$  (об/с) обертання робочого циліндра. Аналіз залежностей  $\eta(\omega)$  дав можливість виділити фрикційну  $\eta_f$  та пружну  $\eta_e$  компоненти в'язкості та вивчити їх залежність від температури  $T$ , концентрації  $\rho$  та довжини ланцюга  $N$ . Одержано математичний вираз для характеристичної в'язкості полімерного розчину та показано, що основну роль в ній відіграє пружна компонента в'язкості  $\eta_e$  з врахуванням її градієнтної залежності.

**Ключові слова:** ефективна в'язкість, фракційна та пружна компоненти в'язкості, конформаційний об'єм, деформація, сегментальний рух, енергія активації.