PII S0735-1933(96)00099-1

EMPIRICAL MODELS FOR SHEAR VISCOSITY OF POLYMER SOLUTIONS AND ESTIMATION OF RHEOLOGICAL PARAMETERS

S.A.Bekishev and A.A.Gubaidullin
Tyumen Institute of Mechanics of Multiphase Systems
Siberian Branch of the Russian Academy of Sciences
Taimyrskaya St., 74, Tyumen, 625000, Russia

(Communicated by O.G. Martynenko)

ABSTRACT
The application of the empirical model of Ellis for shear viscosity in order to obtain rheological parameters from extrapolation with non-linear numerical regression of experimental data revealed significant deviation of estimated values from known scaling laws. A new kind of the empirical formulae was proposed. Testing with experimental data shows good advantage of the formulae. *Copyright © 1996 Elsevier Science Ltd*

Introduction

Determination of physical properties of non-Newtonian liquids, in particular of polymer solutions, is necessary when studying bubble systems with non-Newtonian carrier phase. For example, the surface tension is important property in the study of boiling behavior. For aqueous solutions of polyacrylamide and some other polymers it was measured recently by S.Ishiguro and J.P.Hartnett [1]. The knowledge of another properties, namely rheological parameters of those liquids is of great importance too in the study of wave flows in polymeric bubbly systems, because of their significant effect on bubble dynamics.

This work experimentally investigated shear rate dependencies of viscosity $\eta(\dot{\gamma})$ of aqueous solutions of an industrial type of polyacrylamide (PAAm) of different weight concentrations $c = (0.2 \div 1.5) \cdot 10^{-2}$ g/cm^3. The objective was to

obtain the values of zero-shear viscosity η_0 (at $\dot{\gamma} \ll \dot{\gamma}_c$), the critical shear rate $\dot{\gamma}_c$ and power-law exponent $n-1$ (at $\dot{\gamma} \gg \dot{\gamma}_c$). The measurements were carried out with rotational viscometer Rheotest 2.1 and the results are shown in Fig.1. The apparatus range does not cover the region of interest ($\dot{\gamma} < \dot{\gamma}_c$) where η_0 and $\dot{\gamma}_c$ can be obtained just from the experimental data. But the data reveals slight deviation from power law that can be used to estimate the parameters.

Extrapolation Method and Results

The parameters η_0, $\dot{\gamma}_c$, $n-1$ were estimated by non-linear regression numerically with the coordinate descent method on the empirical model of Ellis [2,3]:

$$\frac{\eta}{\eta_0} = \frac{1}{1 + (\tau/\tau_0)^\nu} , \qquad (1)$$

where η_0, τ_0, ν are the parameters, $\tau \equiv \eta \cdot \dot{\gamma}$ is the shear stress, $\nu = (1-n)/n$. The formula can be transformed to the next form for implicit dependencies of stress and viscosity on shear rate :

$$\lambda \cdot \dot{\gamma} = \frac{\tau}{\tau_0} \left[1 + \left(\frac{\tau}{\tau_0} \right)^\nu \right], \qquad (2)$$

$$\lambda \cdot \dot{\gamma} = \frac{\eta_0}{\eta} \left[\frac{\eta_0}{\eta} - 1 \right]^{1/\nu} , \qquad (3)$$

where $\lambda = \eta_0/\tau_0 = 1/\dot{\gamma}_c$ can be approximately regarded as the largest relaxation time of the dissolved molecules [4,5].

The uncertainties of regression parameters were estimated by determination of largest dimensions of the confidence region ($P = 0.95$) defined by Fisher criterion in space of parameters:

$$F(\eta_0,\tau_0,\nu) = \frac{(Q - Q_0)(n - m)}{Q_0 \cdot m} < F_{m,n-m,\ 0.95} , \qquad (4)$$

where $Q = Q(\eta_0,\tau_0,\nu)$ is the sum of squares of data deviations from the curve with defined values of parameters, Q_0 the least sum of squares for regression curve, n the number of experimental points, m the number of parameters. The results of regression are shown in Fig.1 and Tab.1. The average random error of zero-shear viscosity was $\binom{+1.0}{-0.6}$ of decimal orders.

The comparison was carried out for the set of parameters η_0 obtained from regression and the empirical dependence of

TABLE 1.
The estimations of regression parameters for Ellis model Eq.(1) and aqueous solutions of PAAm of different weight concentrations, see also Fig. 1, $(P = 0.95, m = 3)$.

$c,\%$		min	aver	max	$Q_0, 10^{-3}$	$S_0, 10^{-2}$	n
1.5	η_0, Pa·s	28.3	43.4	160.6	0.549	0.741	13
	τ_0, Pa	5.21	8.89	10.92			
	ν	2.94	3.16	3.38			
	$(n-1)$	-0.746	-0.760	-0.772			
1.0	η_0, Pa·s	6.96	29.9	318	2.52	1.59	13
	τ_0, Pa	1.13	3.70	8.06			
	ν	2.24	2.48	2.86			
	$(n-1)$	-0.691	-0.713	-0.741			
0.75	η_0, Pa·s	3.54	21.6	251	5.92	2.43	13
	τ_0, Pa	0.52	1.81	5.55			
	ν	1.87	2.14	2.61			
	$(n-1)$	-0.652	-0.682	-0.723			
0.5	η_0, Pa·s	1.06	6.03	82.1	1.34	1.64	8
	τ_0, Pa	0.103	0.745	3.10			
	ν	1.33	1.59	2.00			
	$(n-1)$	-0.571	-0.614	-0.667			
0.3	η_0, Pa·s	0.172	1.19	10.5	2.12	2.06	8
	τ_0, Pa	0.0280	0.231	2.34			
	ν	0.856	1.06	1.48			
	$(n-1)$	-0.461	-0.515	-0.597			
0.2	η_0, Pa·s	0.0172	0.0688	1.49	4.89	4.03	6
	τ_0, Pa	0.0196	0.994	18.7			
	ν	0.398	0.739	9.61			
	$(n-1)$	-0.285	-0.425	-0.906			

specific viscosity $\eta_{sp} \equiv (\eta_0 - \eta_s)/\eta_s$ on dimensionless combination $c \cdot [\eta]$, where $[\eta]$ is the intrinsic viscosity of polymer, η_s the viscosity of solvent. It was reported by Kulicke et al. [6] that

$$\eta_{sp} = c \cdot [\eta] + k_H \cdot (c \cdot [\eta])^2 + B_3 \cdot (c \cdot [\eta])^a, \qquad (5)$$

where $k_H \simeq 0.4$, $B_3 = 5.11 \cdot 10^{-4}$, $a = 5.23$ for PAAm in water at $25°C$.

Fig.2 and Tab.2 show the results of regression with Eq.(5) on parameter $[\eta]$ for the set of η_0 from Tab.1.
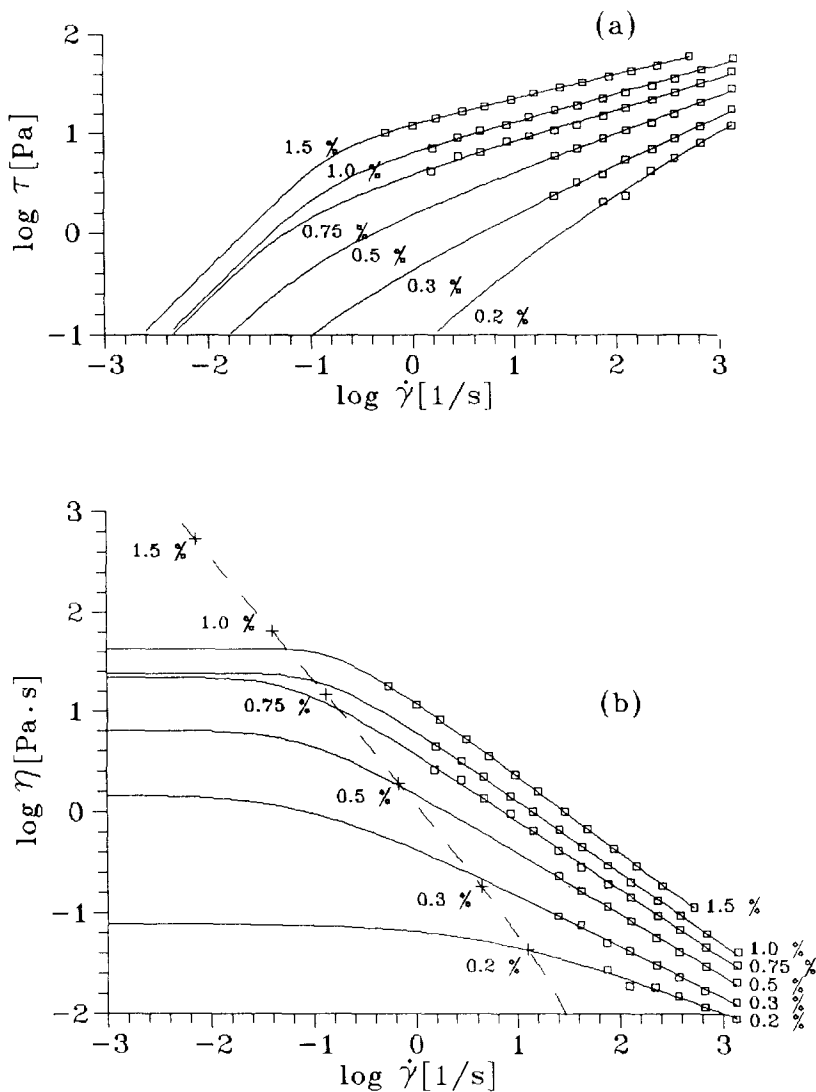
The dashed line in Fig.1 shows the parametric dependence of

FIG.1.

The shear tension (a) and viscosity (b) curves for aqueous
PAAm solutions of different concentrations; (□) the experimental
data. Solid line (———) is the extrapolation by Ellis model,
Eq.(1). Dashed line (- - -) the parametric dependence of η_0 and
$\dot{\gamma}_c$ on c according to Kulicke et al., Eq.(5), and Rouse et al.,
Eq.(6), corresponding c values marked by crosses (+).

TABLE 2.

The parameters of Eq.(5) with intrinsic viscosity [η] estimated from the data of this work, see Tab.1 and Fig.1

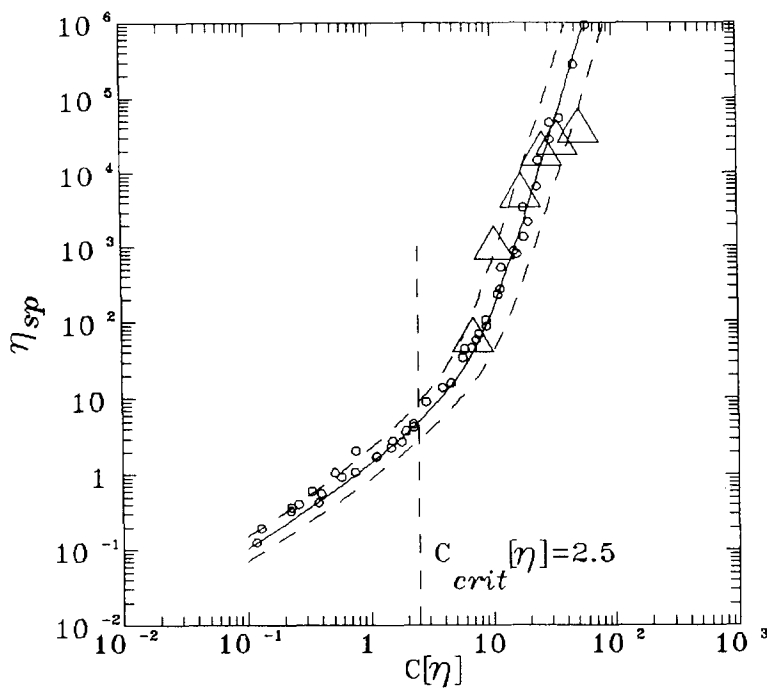|	min	aver	max	Q_0	S_0
[η],cm^3/g	2 420	3 530	5 000	2.31	0.679
k_H	–	0.4	–		n = 6
B_3	–	$5.11 \cdot 10^{-4}$	–		m = 1
a	–	5.23	–		
M_{Sh},g/mol	$9.5 \cdot 10^6$	$15.3 \cdot 10^6$	$23.7 \cdot 10^6$	Eq.(7),	[9]
M_{Ku},g/mol	$13.5 \cdot 10^6$	$22.3 \cdot 10^6$	$35.4 \cdot 10^6$	Eq.(7′),	[6]

FIG.2.

Specific viscosity η_{sp} vs. $c \cdot [\eta]$ for aqueous PAAm solutions, (o) – data of Kulicke et al. [6], $T = 25$ °C, $M_w = (12.3 \cdot 10^3 \div 6.9 \cdot 10^6)$ g/mol, $c = (0.1 \div 5) \cdot 10^{-2}$ g/cm^3; (Δ) – data of this work.

η_0 and $\dot{\gamma}_c$ on concentration c drawn according to Eq.(5) and Rouse and Zimm theory [4,7] (another literature gives different names - Kargin, Slonimski and Rouse [2,8]):

$$1/\dot{\gamma}_c \simeq \lambda = \frac{6}{\pi^2} \frac{(\eta_0 - \eta_s) \cdot M}{c \cdot R \cdot T} , \qquad (6)$$

where R is the gas constant, T the temperature, M the molecular weight of polymer calculated from Mark-Houwink relations

$$[\eta] = 6.31 \cdot 10^{-3} \cdot M_w^{0.80} , \qquad (7)$$

$$[\eta] = 1.00 \cdot 10^{-2} \cdot M_w^{0.755} , \qquad (7')$$

with the coefficients for PAAm in water determined by Scholtan [9] in Eq.(7) and Kulicke et al. [6] in Eq.(7'), with M_w to be the weight average molecular weight in g/mol and $[\eta]$ in cm^3/g.

Discussion

One can see from Fig.2 that estimated values of η_0 quite reasonably correspond to the curve lying in the concentration region above the critical value $c_{crit} = 2.5/[\eta]$. But there are systematic underestimating at higher concentration (1 % ÷ 1.5 %) and overestimating at lower concentration (0.2 % ÷ 0.3 %), see also Fig.1.

This deviations are caused by incorrect description of transitional zone of $\eta(\dot{\gamma})$ dependencies near $\dot{\gamma}_c$ with the Ellis model Eq.(1). The transitional zone is more narrow if the asymptotic negative slope $n-1 = -\nu/(\nu+1)$ becomes greater tending to -1, whereas the real data [5,6,10] shows an opposite tendency.

One can draw another form of generalized power law:

$$\frac{\eta}{\eta_0} = \frac{1}{\left(1 + \frac{\tau}{\nu \cdot \tau_0}\right)^\nu} , \qquad (8)$$

which, *firstly*, fits naturally into conventional extrapolation methods described in [2] for determination of zero shear viscosity, with exponential function (this used in [3])

$$\log \eta = \log \eta_0 - \tau/\tau_0 , \quad \text{i.e.} \quad \eta/\eta_0 = \exp(-\tau/\tau_0) , \qquad (9)$$

and with formula

$$1/\eta = 1/\eta_0 \cdot (1 + \tau/\tau_0) , \qquad (10)$$

since at $\nu \to \infty$ Eq.(8) transforms to Eq.(9), and at $\tau \ll \tau_0$ both Eqs. (8) and (9) approximately give Eq.(10).

Secondly, model (8) shows correct tendency to the extension of transition region with growth of the curve slope and index ν. This can be easily shown graphically using normalized co-ordinates $\log(\eta/\eta_0)$ vs. $(1-n)\cdot\log(\dot{\gamma}/\dot{\gamma}_c')$ proposed by Schurz [5], where $\dot{\gamma}_c'$ is the intersection of the power-law line $\eta \sim \dot{\gamma}^{n-1}$ with the line $\eta = \eta_0$. At $\nu \to 0$ the shear rate dependence of viscosity given by Eq.(8) becomes broken line. At $\nu \to \infty$ (whereas $n-1 \to -1$) the transition region infinitely extends, since the model transforms to exponential one, Eq.(9), that have no asymptote in logarithmic axes $\log \eta$ vs. $\log \dot{\gamma}$ excluding $\eta = \eta_0$.

Thirdly, it is of knowledge that the slope index n shows a dependence on concentration c according to $1/n = 1 + k\cdot c$ [5], which corresponds to simple proportion for index $\nu = k\cdot c$. It holds well also for the data discussed in this paper. Therefore, $\tau/\nu \sim \tau/c$ in Eq.(8) and it is possibly proportional to the share of stress falling on one molecule. The relation $1 + \tau/(\nu\cdot\tau_0)$ in this way can be treated as the stretch ratio of a macromolecule with the elastic modulus proportional to τ_0. Consequently, Eq.(8) supposes the power-law dependence of viscosity on stretch ratio of molecules with exponent $\nu \sim c$.

Testing and Improvement of Model

To test this model, a non-linear regression had been undertaken with the data carrying total information about transitional region and zero-shear viscosity available from literature [6,10]. The results are exhibited in Figures 3, 4 and listed in Tables 3, 4. They show more adequate description for "elastic" model Eq.(8) at less remainder variance compared with Ellis model for the polymer solution of high concentrations and with different molecular weights (Fig.3 and Tab.3). At less concentrations (Fig.4 and Tab.4) the grade of description goes downward. The transitional region of experimental dependencies with less index ν shrinks faster than in model Eq.(8).

This can be explained if one follows "elastic" hypotheses. In polymer physics the macromolecules are believed to be linear-elastic (at least at small deformation) in concentrated solutions and melts of polymers ($\nu \gg 1$) where the macromolecule is ideal and Gaussian due to mutual screening the effect of

TABLE 3.

The sample variances S_0^2 of the models Eqs. (1) and (8) for aqueous solutions of PAAm with concentration c = 5 % and different molecular weights [6, Fig.26] (m = 3).

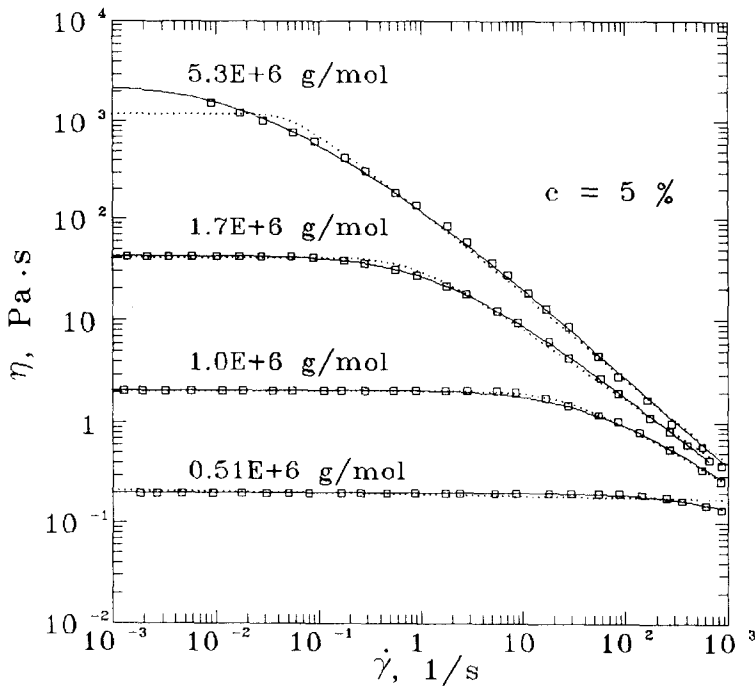| M_w, g/mol	S_0^2 (1)	S_0^2 (8)	$S_0^2(8)/S_0^2(1)$	n	$F_{n-m, n-m}$
$5.3 \cdot 10^6$	$34.7 \cdot 10^{-4}$	$8.62 \cdot 10^{-4}$	1/ 4.0	22	2.2
$1.7 \cdot 10^6$	$9.94 \cdot 10^{-4}$	$0.698 \cdot 10^{-4}$	1/ 14.2	25	2.1
$1.0 \cdot 10^6$	$0.650 \cdot 10^{-4}$	$2.77 \cdot 10^{-4}$	4.3 /1	25	2.1
$0.51 \cdot 10^6$	$12.3 \cdot 10^{-4}$	$0.477 \cdot 10^{-4}$	1/ 26	25	2.1

FIG.3.

Viscosity as a function of shear rate for aqueous PAAm solutions of different molecular weights at a given concentration c = 5 %, T = 25 °C [6, Fig.26]. Dotted line (·····) shows the regression by Ellis model, Eq.(1), solid line (———) that of "elastic" model, Eq.(8).

TABLE 4.

The sample variances S_0^2 of the models Eqs.(1), (8) and (11) for aqueous solutions of PAAm ($M_w = 5.3 \cdot 10^6$ g/mol) with different weight concentrations [6, Fig.27] (m = 3).

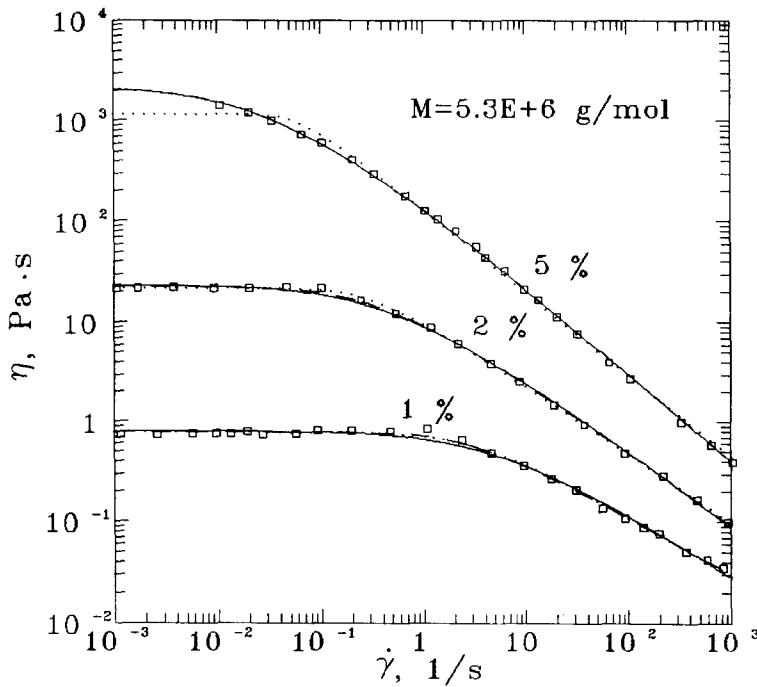| $c,\%$	$S_0^2(1)$	$S_0^2(8)$	$\dfrac{S_0^2(8)}{S_0^2(1)}$	$S_0^2(11)$	$\dfrac{S_0^2(11)}{S_0^2(1)}$	n	$F_{n-m,\,n-m}$
$5^{+)}$	$24 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	1/ 4.5	$5.3 \cdot 10^{-4}$	1/ 4.6	23	2.1
5	$13 \cdot 10^{-4}$	$9.4 \cdot 10^{-4}$	1/ 1.4	$9.2 \cdot 10^{-4}$	1/ 1.5	17	2.5
2	$2.0 \cdot 10^{-4}$	$9.2 \cdot 10^{-4}$	4.5 /1	$3.3 \cdot 10^{-4}$	1.6 /1	19	2.4
1	$8.4 \cdot 10^{-4}$	$16. \cdot 10^{-4}$	1.9 /1	$6.4 \cdot 10^{-4}$	1/ 1.3	24	2.1

+) [10, Abb.4].

FIG.4.

Viscosity as a function of shear rate for aqueous PAAm solutions of different concentrations $c = 1\ \%$, $2\ \%$ [6, Fig.27]; $5\ \%$ [10, Abb.4]; $M_w = 5.3 \cdot 10^6$ g/mol, $T = 25°C$. Dotted line ($\cdots\cdots$) shows the regression by Ellis model, Eq.(1), solid line (———) that of "elastic" model, Eq.(8), dashed line (- - -) that of "nonlinear-elastic" model, Eq.(11).

excluded volume in compact system of molecular chains [11]. In dilute and medium concentrated solutions nonideality of macromolecule can result in nonlinear dependence of stretch ratio on applied stress.

We propose two probable variants of "nonlinear-elastic" generalization of model (8):

$$\frac{\eta}{\eta_0} = \left[1 + \left(\frac{\tau}{\nu \cdot \tau_0}\right)^{1+1/\nu}\right]^{-\frac{\nu}{1+1/\nu}} \quad , \qquad (11)$$

$$\frac{\eta}{\eta_0} = \left[1 + \left(\frac{\tau}{\nu \cdot \tau_0}\right)^{\nu/(\nu-1)}\right]^{-(\nu-1)} \quad . \qquad (12)$$

All mentioned above special features of the "elastic" model are proper to these models also.
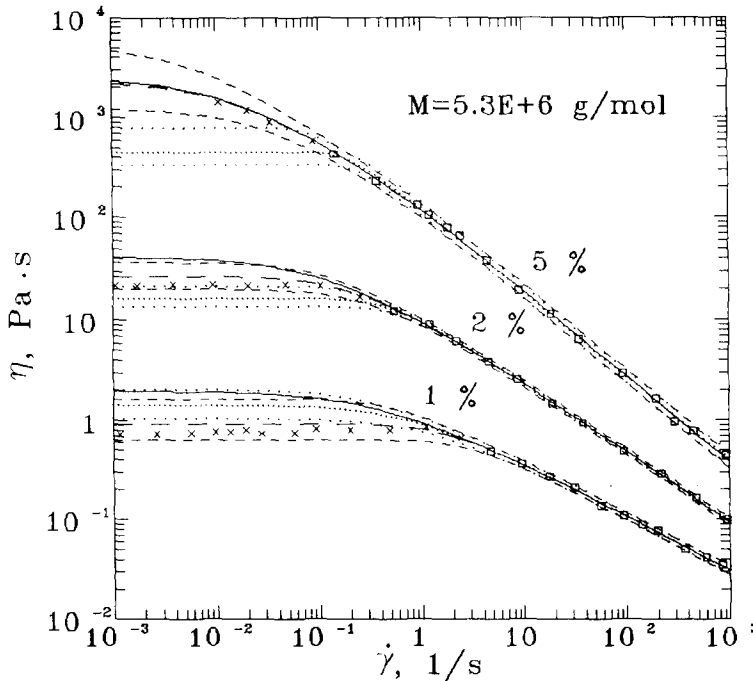

FIG.5.

Testing of the extrapolation by power-law models of Ellis (·····), Eq.(1), "elastic" (———), Eq.(8), and "nonlinear-elastic" (- - -), Eq.(11), with data of Kulicke et al. [6,10]. (□) data taken into account, (×) data not taken into account. The confidence regions, excluding "elastic" model, are limited by related lines.

The results of testing one of this model, Eq.(11), are also shown in Fig.4 and Tab.4. It reveals in much the same remainder variance compared with Ellis model at lower concentrations and significant advantage at higher concentration.

To test the validity of zero-shear viscosity estimations obtained by extrapolation on generalized power-law models Eqs. (1), (8) and (11), the nonlinear regression had been made with the same data as in Fig.4 but without taking into account the experimental points lying below critical shear rate $\dot{\gamma} < \dot{\gamma}_c$ and in the transitional region. The results illustrated in Fig.5 show that only "nonlinear-elastic" model Eq.(11) correctly predicts true values of viscosity for all concentrations. The experimental data fall into the confidence interval, although the estimations are somewhat higher them. The Ellis model Eq.(1) underestimates zero-shear viscosity at higher concentration and overestimates it at lower that. Formula (8) predicts proper viscosity values at higher concentration coinciding with Eq.(11) and overestimates the viscosity at lower concentration.

Conclusion

This work established that empirical model of Ellis for shear viscosity of polymer solutions does not correctly describe the transitional region of viscosity dependencies on shear rate and since it should not be applied in the aim to determine rheological parameters of the liquids through extrapolation. Another empirical formulae based on some physical reasons including elasticity of polymer solutions were proposed, with the description of the transitional region being more adequate. That was confirmed by preliminary testing the formulae on the experimental data from literature.

References

1. S.Ishiguro, J.P.Hartnett, Surface tension of aqueous polymer solutions, *Int. Comm. Heat Mass Transfer*, Vol.19, No.2, pp.285 - 295 (1992).

2. G.V.Vinogradov, A.Ya.Malkin, *Rheology of Polymers*, Springer-Verlag, Berlin, 1980.

3. N.A.Park, T.F.Irvine,Jr., Measurements of rheological fluid properties with the falling needle viscometer, *Rev. Sci. Instrum.*, Vol.59, No.9, pp.2051-2058 (1988).

4. J.D.Ferry, *Viscoelastic Properties of Polymers*, John Wiley & Sons, N.Y., 1980.

5. J.Schurz, Empirical scaling laws in polymer solution rheology, *J.Polym.Sci.C.*, Vol.28, No.4, pp.141-145 (1990).

6. W.-M.Kulicke, R.Kniewske, J.Klein, Propagation, characterization, solution properties and rheological behavior of polyacrylamide, *Prog.Polym.Sci.*, Vol.8, pp.373-468 (1982).

7. R.B.Bird, C.F.Curtiss, R.C.Armstrong, O.Hassager, *Dynamics of Polymeric Liquids*, John Wiley & Sons, N.Y., 1987, Vol.1,2.

8. С.П.Левицкий, З.П.Шульман. Динамика и тепломассоообмен пузырьков в полимерных жидкостях.- Минск: Навука i тэхнiка, 1990.
    That is:
    S.P.Levitski, Z.P.Schulman, *Dynamics and Heat and Mass Transfer of Bubbles in Polymeric Liquids*, Navuka i tekhnika, Minsk, 1990, in Russian.

9. W.Scholtan, *Makromol.Chem.*, Vol.14, p.169 (1954); cited from W.-M.Kulicke et al. [6].

10. J.Klein, W.-M.Kulicke, Rheologische Untersuchungen zur Struktur hochmolekularer Polyacrylamide in wäßrigen und nicht-wäßrigen Lösungen, *Rheol. Acta*, Vol.15, pp. 558-576 (1976), in German.

11. P.G.De Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca & London, 1979.