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ON THE RELATION VISCOSITY VS. SHEAR RATE FOR AGEING EMULSIONS

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Summary: *The aim of this contribution is to present an empirical model taking into account ageing of highly concentrated emulsions. This model enables smooth passage from modelling of viscoelastic fluid (shear-thinning behaviour) corresponding to a 'fresh' material to a description of viscoplastic fluid (viscoplastic behaviour) corresponding to an 'aged' material including yield stress modelling.*

1. Problem Formulation

Analysis of HIPRE (high internal phase ratio emulsion) is more difficult in comparison to the emulsions with concentration $\phi < \phi_c$ where the critical volume fraction ϕ_c of close packed organisation is a value in which the droplets are in contact with each other: this ϕ_c volume fraction is called the 'close-packed' value. In fact, beyond this fraction, the particles become organized in a crowded distribution, which gives them the rheological behaviour of a plastic liquid. For $\phi > \phi_c$ there are not known theoretical equations for relative viscosity similar to those for the case $\phi < \phi_c$. The only possibility is to apply the so-called empirical equations, as e.g. Herschel-Bulkley one

$$\tau = \tau_0 + K_{HB}\dot{\gamma}^n \quad , \tag{1}$$

see the description of plastic and flow regions by Princen and Kiss (1989). This model respects plastic behaviour of HIPRE. More 'operative' model was introduced in Jansen et al. (2001) generalising classical Cross model

$$\eta_r = \eta_{r,\infty}(\phi,K) + \frac{\eta_{r,0}(\phi,K) - \eta_{r,\infty}(\phi,K)}{1+(k\dot{\gamma})^m} + \frac{\tau_0}{\eta_c\dot{\gamma}} \quad . \tag{2}$$

This model, in contrast to the classical Cross one, enables to take into account yield stress. The number of the parameters is five, by two higher than in Herschel-Bulkley model, but this is fully balanced by flexibility and possibility to follow shear thinning of the emulsions studied.

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Water-in-oil concentrated emulsions can be formulated with very high water content (up to 99%) and an emulsifier concentration as low as 0.5% (Pons et al., 1992). Interest in these emulsions has been stimulated by their characteristic properties (rheological, structural, optical), which make them technologically useful, as well as by their economical use of emulsifier.

Ageing of w/o emulsions represents another problem how to properly depict their behaviour. Masalova et al. (2003) studied rheological properties of HIPRE, w/o emulsions, with 94% wt. (90% vol.) concentration of a dispersed phase – aqueous solution of salts in a continuous phase – paraffin. Ageing lead to the changes in rheological behaviour of the emulsion studied: the Newtonian flow domain disappeared, the apparent viscosity increased and yielding was observed. While it was possible to apply Cross equation for description of the 'fresh' emulsion, the flow curve of the 'aged' emulsion was described using Herschel-Bulkley equation, see Fig.3 in Masalova et al. (2003). Their Fig.4 is a sketch only indicating possible gradual behaviour of the flow curves in dependence on the ageing of emulsions.

The aim of this contribution is to propose a new empirical model taking into account process of ageing and enabling smooth passage from modelling viscoelastic fluid (shear-thinning behaviour) to describing viscoplastic behaviour (viscoplastic fluid) including yield stress modelling.

2. Empirical Modelling

The following empirical model is proposed for a description of a 'fan' of the individual rheograms passing from the flow curves with shear-thinning behaviour and tending to a flow curve characterising plastic 'solid-like' behaviour of the material ageing

$$\tau = C\frac{A+(C\dot{\gamma})^{p}}{B(t)+(C\dot{\gamma})^{q(t)}}\dot{\gamma} \quad , \tag{3}$$

$$B(t) = B.\exp\left(-\lambda\frac{t-t_0}{t_1-t}\right) \quad , \quad q(t) = 1+(q-1).\exp\left(-\lambda\frac{t-t_0}{t_1-t}\right) \quad , \quad t\in[t_0,t_1] \quad , \tag{4}$$

where time interval $[t_0,t_1]$ represents time spanning from the initial 'fresh' viscoelastic structure of emulsion up to the final plastic 'solid-like' structure. The parameters A,B,C,p,q,λ are supposed to be non-negative, proper choice of the individual parameters provide for $t=t_0$ various models, a list of the most common ones is given in Table 1.

A number of entry parameters introduced in this model - six - exceeds the number of parameters (2-4) in routinely used models, see Table 1. However, the results having been published recently indicate that a number of the empirical parameters in the commonly used models is not sufficient. These classical models do not exhibit corresponding flexibility in a description of newly developed materials - for details see e.g. Roberts et al. (2001) where the so-called 8-parameter composite Ellis model describing shear-thinning behaviour is introduced. Moreover in the proposed model (3),(4) apart from a necessity to fit a 'fan' of the rheograms characterising shear-thinning behaviour, there is also a necessity to model limiting viscoplastic behaviour, i.e. including a yield stress. The yield stress is also considered in the 5-parameter generalised Cross model (2) presented by Jansen et al. (2001). As the model proposed (3),(4) takes into account - in addition to the preceding factors - ageing of material (resulting in the introduction of a parameter λ), the number of parameters - six - seems to be adequate.

Tab.1 The individual models.

Model	Relation	Choice of corresponding parameters in the empirical model (3,4)					
		A	B	C	p	q	λ
Bingham	$\tau = \left(\eta_B + \frac{\tau_0}{\lvert\dot{\gamma}\rvert} \right) \dot{\gamma}$	τ_0 / η_B	0	η_B	1	1	0
power law	$\tau = K \lvert\dot{\gamma}\rvert^{n-1} \cdot \dot{\gamma}$	0	0	$K^{1/n}$	n	1	0
Herschel-Bulkley	$\tau = \left(K \lvert\dot{\gamma}\rvert^{n-1} + \frac{\tau_0}{\lvert\dot{\gamma}\rvert} \right) \dot{\gamma}$	τ_0	0	$K^{1/n}$	n	1	0
Sisko	$\tau = \left(K \lvert\dot{\gamma}\rvert^{n-1} + \eta_\infty \right) \dot{\gamma}$	$K^{-1/n}\eta_\infty$	0	$K^{1/n}$	n-1	0	0
Williamson	$\tau = \left(\frac{A}{B + \lvert\dot{\gamma}\rvert} + \eta_\infty \right) \dot{\gamma}$	$A + \eta_\infty B$	$\eta_\infty B$	η_∞	1	1	0
Cross	$\tau = \left[\frac{\eta_0 - \eta_\infty}{1 + \left(K \lvert\dot{\gamma}\rvert \right)^n} + \eta_\infty \right] \dot{\gamma}$	$\eta_0 \eta_\infty^{-\frac{n+1}{n}}$	$\eta_\infty^{-\frac{n+1}{n}}$	$K \eta_\infty^{\frac{1+n}{n^3}}$	n	n	0

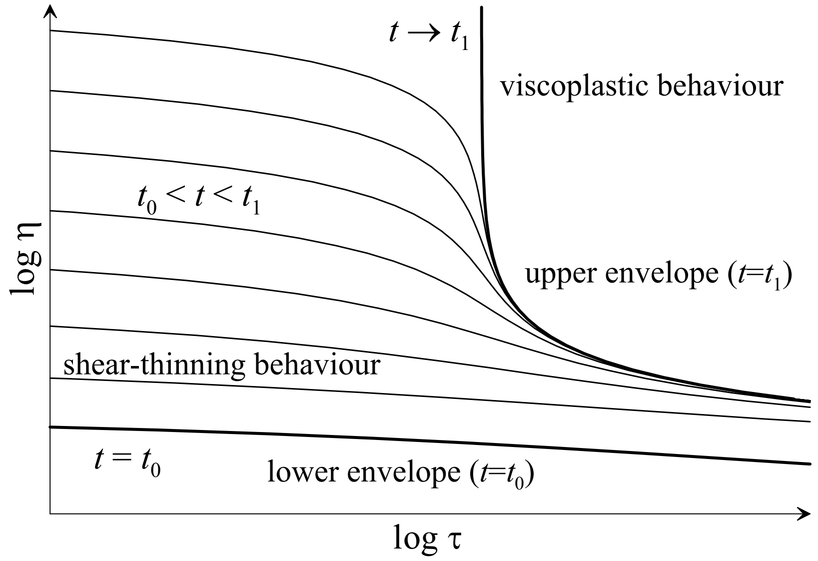

Fig.1 Continuous passage from shear-thinning to viscoplastic behaviour given by the model (3),(4); lower envelope represents initial structure of 'fresh' emulsion (t=t_0), upper envelope represents resulting structure of 'aged' emulsion (t=t_1).

The possibility of the above introduced model to provide continuous passage from shear-thinning to viscoplastic behaviour is depicted in Fig.1. This Figure corresponds to a sketch outlined in Fig.4 in Masalova et al. (2003).

The model was tested with the data taken from Fig.3 (Masalova et al., 2003), and also represented as in (Masalova et al., 2003) by solid curves, the comparison is presented in Fig.2. A solid line for $t=t_0$ corresponds to the measurements of fresh w/o emulsion, a solid line for $t=t_1$ to the measurements of this emulsion after storage at rest for 2-4 weeks. The empirical (dashed) curves given by the model, Eqs.(3,4), are two in fact, one of them is identical with a solid (experimental) line for $t=t_1$. The agreement between the modelling curves and experimental data is very good.

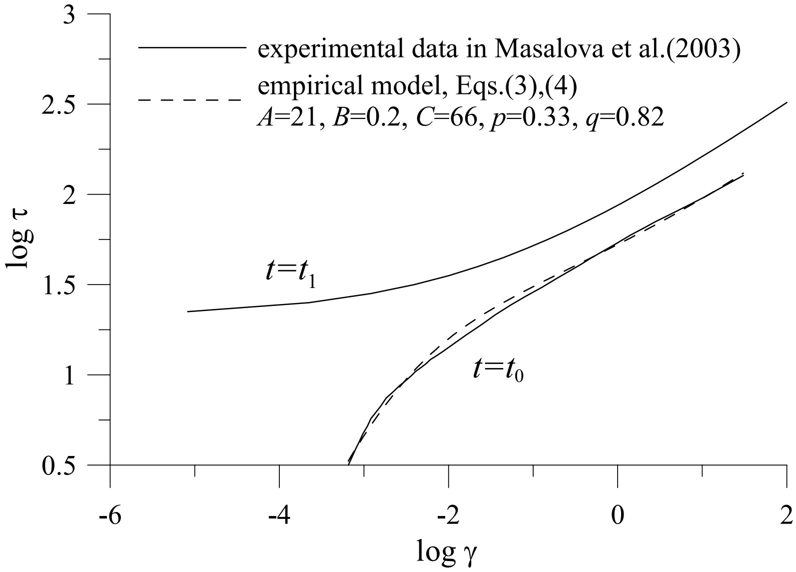

Fig.2 Application of the proposed model, Eqs.(3),(4), to the experimental data in Masalova et al. (2003); for $t=t_1$ the solid (experimental data) and dashed (empirical model) lines coincide.

3. Conclusion

The new empirical model taking into account ageing of highly concentrated emulsions is proposed and experimentally tested for water-in-oil emulsions where experimental data viscosity vs. shear stress were taken from Masalova et al. (2003).

4. Acknowledgement

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