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# Predicting viscosity of emulsions in the broad range of inner phase concentrations

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#### Abstract

Three new equations for predicting viscosity of emulsions were proposed. For each of these correlations a separate range of applicability dependent on the concentration of emulsions was determined. The viscous properties of emulsions could be calculated using the proposed equations on the basis of the following parameters: volume fraction and droplet size of the inner phase, viscosity and density of the outer phase and also of the shear rate in the case of concentrated dispersions.

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# 1. Introduction

Emulsions consist of droplets of one liquid dispersed in another immiscible liquid usually with an addition of an emulsifying agent to ensure the system stability. Emulsions play an important role as components of many products of several branches of the food, pharmaceutical, cosmetic and paints producing industry. The knowledge of rheological properties of these media is crucial for their proper handling, mixing, storage and transportation and for designing of relevant equipment and apparatus.

From the rheological point of view, emulsions are usually divided into two main groups [1]. Dilute emulsions with low concentration of inner phase and exhibiting almost pure Newtonian viscous behaviour. To the second group belong the concentrated emulsions with high dispersed phase contents and non-Newtonian viscous properties.

In the published literature concerning the properties of emulsions, a number of models for their viscosity prediction have been proposed [2–6]. However, these equations did not take into account the non-Newtonian behaviour of emulsions and first of all the dependence of their viscosity on the shear rate. The influence of this variable and other parameters was included in the model proposed by Pal [7].

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However, this equation was tested for few emulsion systems only.

The aim of the presented paper was to propose correlation equations for prediction of the viscosity of emulsions in a wide range of inner phase concentrations from 10 to 80%. The developed formulae were evaluated on the basis of the idea given in the paper by Pal [7].

#### 2. Pal's model

The model proposed originally by Pal [7] can be used for prediction of the viscosity  $\eta$  of emulsions. According to Pal, the value of this parameter is dependent on several variables listed in Table 1. The parameters listed in Table 1 can be combined into dimensionless groups shown in Table 2, where k is the Boltzmann's constant.

Pal assumed that for typical emulsions in average process conditions the dependence of viscosity on the capillary and Peclet numbers was negligible. Also the relative density which is in most cases close to unity can be eliminated from the modelling considerations.

Pal obtained the following equations for prediction of the viscosity of emulsions. The first one describing the behaviour of emulsions with the inner phase concentration  $\phi$  less than 0.7 is given by

$$\phi_{\rm m}^{0.5}(1 - \eta_{\rm r}^{-1/[\eta]}) = A_0 + A_1 \log Re \tag{1}$$

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Table 1 Parameters affecting viscosity of emulsion

Name of parameter	Symbol	Dimension
Temperature	T	[K]
Shear rate	Ϋ́	[1/s]
Time	t	[s]
Dispersed-phase viscosity	$\eta_{ m d}$	[Pas]
Continuous-phase viscosity	$\eta_{ m c}$	[Pas]
Dispersed-phase density	$ ho_{ m d}$	$[kg/m^3]$
Continuous-phase density	$ ho_{ m c}$	$[kg/m^3]$
Inner phase droplets diameter	d	[m]
Volume fraction	$\phi$	[-] or [%]
Maximum packing fraction of inner phase	$\phi_{ m m}$	[-] or [%]

Table 2 Dimensionless groups

Name of dimensionless group	Definition of dimensionless group
Reduced time	$t_{\rm r} = t/(\eta_{\rm c} d^3/8kT)$
Viscosity ratio	$K = \eta_{\rm d}/\eta_{\rm c}$
Relative density	$ ho_{ m d}/ ho_{ m c}$
Peclet number	$Pe = \eta_{\rm c} \dot{\gamma} d^3 / 8kT$
Capillary number	$Ca = \eta_c \dot{\gamma} d/2\sigma$
Reynolds number	$Re = \rho_{\rm c}\dot{\gamma}d^2/4\eta_{\rm c}$
Relative viscosity	$\eta_{ m r} = \eta/\eta_{ m c}$

The second one applicable according to the author for emulsions at  $\phi \ge 0.7$  is given by

$$\phi_{\rm m}^{0.5}[1 - \eta_{\rm r}^{-1/[\eta]/\phi_{\rm m}}] = A_0 + A_1 \log Re + A_2 (\log Re)^2 \quad (2)$$

where  $A_0$ ,  $A_1$ ,  $A_2$  are constants.

The  $[\eta]$  in Eqs. (1) and (2) is the intrinsic viscosity calculated using Taylor's dependence [8]:

$$[\eta] = 2.5 \left( \frac{K + 0.4}{K + 1} \right) \tag{3}$$

The parameter  $\phi_m$  is the maximum packing concentration of non deformable uniform spherical droplets of the inner phase. The value of that parameter was taken by Pal equal to 0.74 for monodisperse emulsion. In the case of polydisperse emulsion systems  $\phi_m$  was estimated by the author using Ouchiama and Tanaka expressions [9] given by the following formulae which originates from the theory of solid suspension:

$$\phi_{\rm m} = \frac{\sum d_i^3 f_i}{\sum (d_i \sim \bar{d})^3 f_i + (1/\beta) \sum [(d_i + \bar{d})^3 - (d_i \sim \bar{d})^3] f_i}$$
(4

where

$$\beta = 1 + \frac{4}{13} (8\phi_{\rm m}^0 - 1)\bar{d} \frac{\sum (d_i + \bar{d})^2 [1 - ((3/8)\bar{d}/(d_i + \bar{d}))] f_i}{\sum [d_i^3 - (d_i \sim \bar{d})^3] f_i}$$
(5)

and

$$\bar{d} = \sum d_i f_i \tag{6}$$

In Eq. (5)  $\phi_{\rm m}^0$  is the maximum packing concentration of non-deformable uniform spherical droplets of the inner phase which are packed hexagonally as has been presented in the papers [10,11]. The value of  $\phi_{\rm m}^0$  is 0.74 for such configuration. Moreover it can be noticed that in the case of monodisperse emulsions,  $\phi_{\rm m}$  calculated from Eqs. (4)–(6) equals to  $\phi_{\rm m}^0$  and has also a value 0.74.

In Eqs. (4)–(5)  $f_i$  is the number fraction of droplets of diameter  $d_i$ ,  $d_i$  is the number-average diameter of the droplets in emulsion and the abbreviation  $(d_i \sim d)$  is defined as  $(d_i \sim \bar{d}) = 0$  for  $d_i \leq \bar{d}$  and  $(d_i \sim \bar{d}) = d_i - \bar{d}$  for  $d_i \geq \bar{d}$ .

The values of constants  $A_0$ ,  $A_1$ ,  $A_2$  were estimated by Pal on the basis of viscosity measurements of the following emulsion samples: kerosene-in-water with the inner phase concentration 0.70 and mineral oil-in-water at  $\phi$  equal 0.41, 0.63 and 0.71. At the given concentration samples of different polydispersity and value of  $\phi_m$  were prepared.

The properties of emulsions at  $\phi$  less than 0.7 were used to find values of  $A_0$  and  $A_1$  in Eq. (1). The properties of samples with  $\phi \ge 0.7$  were used to estimate the values of  $A_0$ ,  $A_1$ ,  $A_2$  in Eq. (2). The original values of these parameters as quoted by Pal [7] are summarised in Table 3.

The equations proposed by Pal fit well to experimental data. However, one can see that different values of *A* parameters were found for every investigated concentration and for every system in the same range of concentrations.

## 3. Experimental

To verify the applicability of Pal's model for other emulsions the necessary data were collected from the literature [7,12]. These were the values of temperature of rheological measurements, density and viscosity of both phases, inner phase concentration and droplet diameters. In the case of emulsions with the concentration of the inner phase above 50% the choice was limited to the systems with the maximal droplets size up to  $25\,\mu m$ . Also there were chosen

Table 3 Values of constants in Eqs. (1) and (2) estimated by Pal [7]

$\overline{\phi}$	Equation	$A_0$	$A_1$	$A_2$	Type of emulsion
0.41	(1)	0.41805	-0.018147	_	Mineral oil-in-water
0.63	(1)	0.57716	-0.034562	_	Mineral oil-in-water
0.70	(2)	0.71969	-0.04517	-0.0035424	Kerosene-in-water
0.71	(2)	0.69958	-0.056191	-0.0050269	Mineral oil-in-water

Table 4
Physicochemical and structural parameters for dilute emulsions

System	Symbol used in the figures	Dispersed phase, surfactant and its concentration	φ (-)	$d_{32}$ (×10 <sup>6</sup> m)	$ \eta_{\rm c} $ (×10 <sup>3</sup> Pa s)	$\eta_{\rm d}$ (×10 <sup>3</sup> Pas)	$\rho_{\rm c} \ ({\rm kg/m^3})$	$\rho_{\rm d}$ (kg/m <sup>3</sup> )	$\phi_{\rm m}$ (–)	[η] (-)	T (°C)
S1	۵	Sunflower oil, 2% Rokafenol N8 [*]	0.32	3.8	1	63	998	992	0.74	2.48	21
O1	<b>A</b>	Mineral oil, 2% Triton X-101 [7]	0.41	6.52	1	29.2	998	850	0.74	2.45	22
O2		Mineral oil, 2% Triton X-101 [7]	0.41	19.9	1	29.2	998	850	0.81	2.45	22
O3	lack	Mineral oil, 2% Triton X-101 [7]	0.41	24.8	1	29.2	998	850	0.83	2.45	22
O4	$\triangle$	Mineral oil, 2% Triton X-101 [7]	0.41	14.9	1	29.2	998	850	0.785	2.45	22
E1-1	$\forall$	Mixture of organic oils, 20% Alipal Cd-128 [12]	0.1	26.3	2.65	65.4	1009	1017	0.74	2.44	25
E1-2	$\bowtie$	Mixture of organic oils, 20% Alipal Cd-128 [12]	0.2	26.3	2.65	65.4	1009	1017	0.74	2.44	25
E1-3	$\nabla$	Mixture of organic oils, 20% Alipal Cd-128 [12]	0.3	26.3	2.65	65.4	1009	1017	0.74	2.44	25
E1-4	$\nabla$	Mixture of organic oils, 20% Alipal Cd-128 [12]	0.4	26.3	2.65	65.4	1009	1017	0.74	2.44	25
E1-5	lacktriangledown	Mixture of organic oils, 20% Alipal Cd-128 [12]	0.5	26.3	2.65	65.4	1009	1017	0.74	2.44	25
E2-1	<b>A</b>	Mixture of organic oils, 20% Alipal Cd-128, polyacrylic acid [12]	0.1	8.9	7.99	65.4	1019	1017	0.75	2.34	25
E2-2		Mixture of organic oils, 20% Alipal Cd-128, polyacrylic acid [12]	0.2	8.9	7.99	65.4	1019	1017	0.75	2.34	25
E2-3	☆	Mixture of organic oils, 20% Alipal Cd-128, polyacrylic acid [12]	0.3	8.9	7.99	65.4	1019	1017	0.75	2.34	25
E2-4		Mixture of organic oils, 20% Alipal Cd-128, polyacrylic acid [12]	0.4	8.9	7.99	65.4	1019	1017	0.75	2.34	25
E2-5	$\bigstar$	Mixture of organic oils, 20% Alipal Cd-128, polyacrylic acid [12]	0.5	8.9	7.99	65.4	1019	1017	0.75	2.34	25
E3-1	$\oplus$	Mixture of organic oils, 20% Triton X-100 [12]	0.1	8.1	8.38	72.4	1014	1021	0.74	2.34	25
E3-2	$\otimes$	Mixture of organic oils, 20% Triton X-100 [12]	0.2	8.1	8.38	72.4	1014	1021	0.74	2.34	25
E3-3	$\ominus$	Mixture of organic oils, 20% Triton X-100 [12]	0.3	8.1	8.38	72.4	1014	1021	0.74	2.34	25
E3-4	$\bigoplus$	Mixture of organic oils, 20% Triton X-100 [12]	0.4	8.1	8.38	72.4	1014	1021	0.74	2.34	25
E3-5	ightharpoons	Mixture of organic oils, 20% Triton X-100 [12]	0.5	8.1	8.38	72.4	1014	1021	0.74	2.34	25

Table 5
Physicochemical and structural parameters for medium concentrated emulsions

System	Symbol used in the figures	Dispersed phase, surfactant and its concentration	φ (-)	$d_{32}$ (×10 <sup>6</sup> m)	$ \eta_{\rm c} $ (×10 <sup>3</sup> Pa s)	$\eta_{\rm d}$ (×10 <sup>3</sup> Pa s)	$\rho_{\rm c}$ (kg/m <sup>3</sup> )	$\rho_{\rm d}$ (kg/m <sup>3</sup> )	$\phi_{\rm m}$ (–)	[η] (-)	T (°C)
S2		Sunflower oil, 7% Rokafenol N8 [*]	0.52	4	1	63	998	992	0.74	2.48	21
E1-6	$oldsymbol{ abla}$	Mixture of organic oils, 20% Alipal Cd-128 [12]	0.6	26.3	2.65	65.4	1009	1170	0.74	2.44	25
O5	Δ	Mineral oil, 2% Triton X-101 [7]	0.63	6.52	1	29.2	998	850	0.74	2.45	22
O6	$\triangleright$	Mineral oil, 2% Triton X-101 [7]	0.63	15.3	1	29.2	998	850	0.788	2.45	22
O7	₽	Mineral oil, 2% Triton X-101 [7]	0.63	21.5	1	29.2	998	850	0.816	2.45	22
O8	<b>•</b>	Mineral oil, 2% Triton X-101 [7]	0.63	18.2	1	29.2	998	850	0.80	2.45	22

Table 6 Physicochemical and structural parameters for highly concentrated emulsions

System	Symbol used in the figures	Dispersed phase, surfactant and its concentration	φ (-)	$d_{32}$ (×10 <sup>6</sup> m)	$ \eta_{\rm c} $ (×10 <sup>3</sup> Pa s)	$\eta_{\rm d}$ (×10 <sup>3</sup> Pa s)	$\rho_{\rm c}$ (kg/m <sup>3</sup> )	$ ho_{ m d}$ (kg/m <sup>3</sup> )	φ <sub>m</sub> (–)	$[\eta]$ (–)	T (°C)
S3	$\oplus$	Sunflower oil, 7% Rokafenol N8 [*]	0.672	4	1	63	998	992	0.74	2.48	21
S4	$\otimes$	Sunflower oil, 7% Rokafenol N8 [*]	0.72	4.1	1	63	998	992	0.74	2.48	21
S5	$\ominus$	Sunflower oil, 7% Rokafenol N8 [*]	0.777	4.4	1	63	998	992	0.74	2.48	21
S6	$\bigcirc$	Sunflower oil, 2% Rokafenol N8 [*]	0.72	2.9	1	63	998	992	0.74	2.48	21
S7	lacktriangle	Sunflower oil, 2% Rokafenol N8 [*]	0.777	3.3	1	63	998	992	0.74	2.48	21
09	<b>A</b>	Mineral oil, 2% Triton X-101 [7]	0.71	9.0	1	29.2	998	850	0.74	2.45	22
N1	$\Leftrightarrow$	Kerosene, 2% Triton X-101 [7]	0.7	7.4	1	2.2	998	790	0.74	2.03	22
N2	$\Leftrightarrow$	Kerosene, 2% Triton X-101 [7]	0.7	22	1	2.2	998	790	0.74	2.03	22
N3	$\Leftrightarrow$	Kerosene, 2% Triton X-101 [7]	0.7	11.6	1	2.2	998	790	0.764	2.03	22
N4	$\Diamond$	Kerosene, 2% Triton X-101 [7]	0.7	20.5	1	2.2	998	790	0.783	2.03	22
N5	$\diamondsuit$	Kerosene, 2% Triton X-101 [7]	0.7	19.1	1	2.2	998	790	0.789	2.03	21
p1	$\otimes$	Liquid paraffin, 7% Rokacet 0.7 [*]	0.696	7.2	1	115	998	850	0.74	2.49	21
p2	$\Theta$	Liquid paraffin, 7% Rokacet 0.7 [*]	0.796	7.4	1	115	998	850	0.74	2.49	21
p3	Φ	Liquid paraffin, 2% Rokacet 0.7 [*]	0.696	7.7	1	115	998	850	0.74	2.49	21
p4	lue	Liquid paraffin, 2% Rokacet 0.7 [*]	0.796	8.3	1	115	998	850	0.74	2.49	21
n1	$\boxplus$	Kerosene, 7% Rokafenol N22/30 [*]	0.65	4.6	1	2.2	998	790	0.74	2.03	21
n2		Kerosene, 7% Rokafenol N22/30 [*]	0.70	5	1	2.2	998	790	0.74	2.03	21
n3		Kerosene, 7% Rokafenol N22/30 [*]	0.75	5.3	1	2.2	998	790	0.74	2.03	21

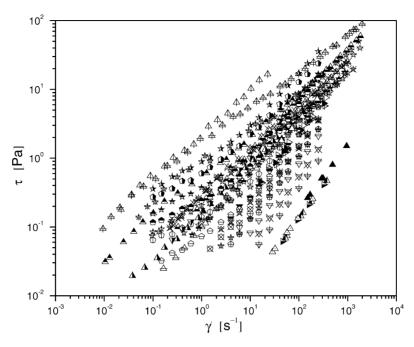


Fig. 1. Flow curves of emulsions obtained from the literature [7,12].

the emulsions with no modified structure of the continuous phase which was in the paper [12] the result of an addition of polymeric liquids or high emulsifier concentration.

The values of  $\phi_m$  were also taken from original sources [7] or in the case of data from paper [12] estimated using a graphical method [7]. The values of  $[\eta]$  were calculated using Taylor's formula given by Eq. (3). All these data necessary for modelling work are presented in Tables 4–6. Also the flow curves of investigated emulsions were read out from the appropriate graphs in the papers [7,12] and are presented in Fig. 1.

Also our own experiments were performed. Oil-in-water emulsions were prepared using kerosene, sunflower oil and liquid paraffin as the inner phase. The outer phase was the solution of appropriate emulsifier in distilled water. The following emulsifying agents produced by Rokita SA, Brzeg Dolny, Poland were added: Rokafenol N22/30 for kerosene-in-water system, Rokafenol N8 for sunflower-in-water emulsion and Rokacet 07 to prepare liquid paraffin-in-water dispersion.

The emulsions were prepared at ambient temperature by shearing together the known volumes of the aqueous sur-

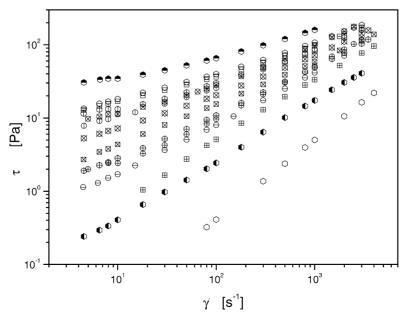


Fig. 2. Flow curves of our own emulsions.

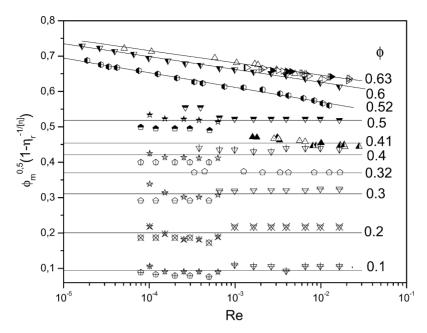


Fig. 3. Correlation of viscosity data for dilute and medium concentrated emulsions.

factant solution and oil phase in high-speed homogenizer (12 000 rpm). Formation of emulsions lasted for 3 min in the case of systems: S1, S2, S3, S4, S5, n1, n2, n3, p1, p2, p3, p4 and for 5 min in the case of S6, S7 dispersions. An increase of emulsification time allowed us to prepare the systems with smaller droplet size. The flow curves were obtained using RC-20 rheometer produced by Rheo-Thec, Germany. Two different coaxial cylinder systems with gaps 0.5 and 1.9 mm were used to investigate if slippage effects were present. Since in both cases the flow curves were almost the same it was assumed that wall slip was negligible. All rheological data concerning our emulsions were collected at 21 °C.

The average droplet size and droplet size distributions of the dispersed phase were determined using a Nikon Alphaphat-2 optical microscope equipped with a video Panasonic camera connected to the computer. The captured images of the samples were analysed using appropriate software. Using these data the average droplet diameter was calculated according to the following formula:

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{7}$$

where  $n_i$  is the number of the droplets of diameter  $d_i$ .

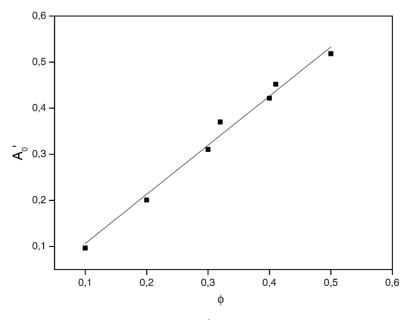


Fig. 4. The dependence of  $A'_0$  on the volume fraction  $\phi$ .

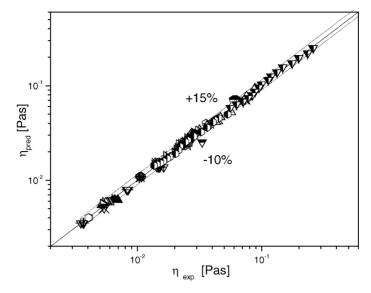


Fig. 5. Comparison of the predicted and experimental values of viscosity for dilute and medium concentrated emulsions.

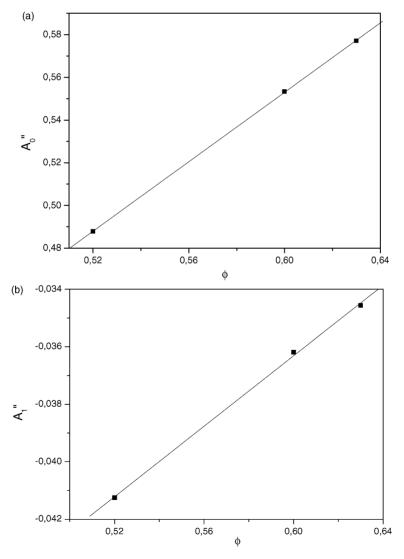


Fig. 6. (a) The dependence of  $A_0''$  on the concentration  $\phi$ . (b) The dependence of  $A_1''$  on the concentration  $\phi$ .

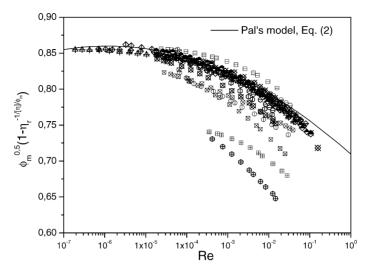


Fig. 7. Correlation of relative viscosity  $(\eta_r)$  data of emulsion systems described in Table 6 with Reynolds number (Re).

The values of  $\phi_{\rm m}$  were calculated using Eq. (4) with  $\phi_{\rm m}^0 = 0.74$  and values of  $[\eta]$  were obtained using Eq. (3). The parameters characterising our emulsions have been gathered also in Tables 4–6 and are denoted by asterisk.

The flow curves of our own emulsions are presented in Fig. 2. One can observe that rheological behaviours of these dispersions are dependent on the inner phase concentration and the droplet diameters—see data in Tables 4–6.

For emulsion S1 the measured points can be approximated by the straight line of the slope close to the unity. It means that this system can be considered as the pure Newtonian liquid. Also the data points for emulsion S2 can be described by the straight line of the slope equals 0.81. It means that this emulsion is the shear-thinning liquid. The

flow curves for other investigated systems are not straight lines in the log-log scale. From the shape of these curves it can be concluded that some of the concentrated emulsions, most noticeable the sample S7, can exhibit the yield stress phenomena. The same profile of the flow curves can be observed for the emulsions of the high volume fraction investigated by other authors [7,12]—see Fig. 1.

## 4. Modelling work

All the presented emulsion systems from the point of view of the concentration of the inner phase have been divided into three groups.

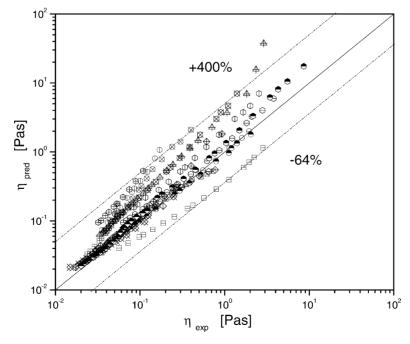


Fig. 8. Comparison of calculated and experimental values of viscosity.

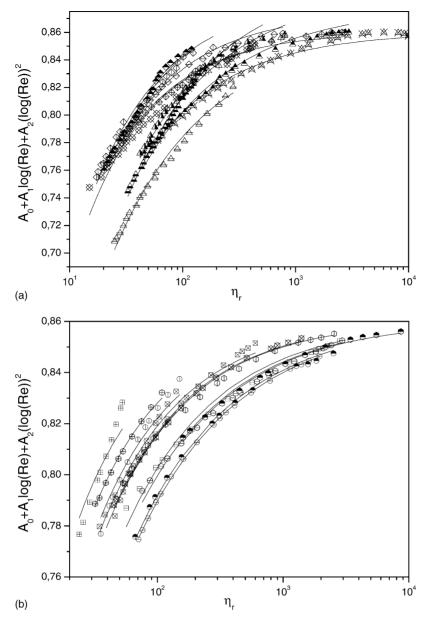


Fig. 9. (a) The dependence of right side of Eq. (14) on relative viscosity for literature data [7]. (b) The dependence of right side of Eq. (14) on relative viscosity for our own data.

- Dilute emulsions with the dispersed phase volume fraction φ up to 0.5.
- Medium concentrated systems at  $\phi$  between 0.5 and 0.63.
- Highly concentrated emulsions at  $\phi$  above 0.63 till 0.8

For every group a separate correlation equation has been proposed.

## 4.1. Dilute emulsions

The data for emulsions at volume fraction from 0.1 up to 0.5 plotted as a function of the left side of Eq. (1) versus Reynolds number are presented in Fig. 3. As can be seen,

the dependence of  $\phi_{\rm m}^{0.5}(1-\eta_{\rm r}^{-1/[\eta]})$  on the Reynolds number in the range of values of Re from  $1\times 10^{-4}$  to  $3\times 10^{-2}$  is almost negligible.

Thus it can be concluded that for dilute emulsions the droplet size and shear rate do not affect their viscosity. Therefore it can be proposed to simplify Eq. (1) to the following form:

$$\phi_{\rm m}^{0.5}(1 - \eta_{\rm r}^{-1/[\eta]}) = A_0' \tag{8}$$

However, for all emulsions of the given concentration the data points can be approximated by a separate line. Therefore one can notice that the values of  $A_0'$  are dependent on volume fraction. The values of  $A_0'$  for every concentration were calculated as an average value of the left side of

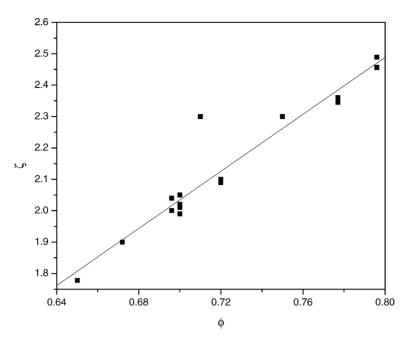


Fig. 10. The dependence of  $\zeta$  on the concentration  $\phi$ .

expression (8) on the basis of experimental data. The plot of  $A'_0$  as a function of  $\phi$  is shown in Fig. 4.

The data points in Fig. 4 were approximated by the straight line given by the following equation with the correlation coefficient equal to 0.988:

$$A_0' = 1.07\phi \tag{9}$$

Substituting now Eq. (9) into Eq. (8) one gets the following formula:

$$\phi_{\rm m}^{0.5}(1 - \eta_{\rm r}^{-1/[\eta]}) = 1.07\phi \tag{10}$$

It allows to predict the viscosity of dilute emulsions as the function of the volume fraction  $\phi$ , the maximum packing concentration  $\phi_{\rm m}$ , intrinsic viscosity [ $\eta$ ] and the viscosity of the continuous phase  $\eta_{\rm c}$ .

The comparison between the viscosity values calculated using Eq. (10) and the experimental values are shown in Fig. 5. The differences are within the range from -10 to +15% which is acceptable from the engineering point of view.

### 4.2. Medium concentrated emulsions

During analysis of the experimental data it was found that from the point of view of the modelling work, the range of medium concentration of emulsions at  $\phi$  from 0.5 to 0.63 can be indicated—see appropriate data in Table 5 and points in Fig. 3. For these emulsions the dependence on the Reynolds number can be observed. However, the points can be still approximated by a linear function. Thus, Eq. (1) is here directly applicable in the form:

$$\phi_{\rm m}^{0.5}(1 - \eta_{\rm r}^{-1/[\eta]}) = A_0'' + A_1'' \log Re \tag{11}$$

where  $A_0''$ ,  $A_1''$  are constants.

The dependences of  $A_0''$  and  $A_1''$  on the concentration  $\phi$  are shown, respectively, in Fig. 6a and b.

The approximating equations have the following form:

$$A_0'' = 0.064 + 0.814\phi \tag{12}$$

$$A_1'' = -0.073 + 0.061\phi \tag{13}$$

with the correlation coefficients equal to 0.999.

Using now Eq. (11) and dependences (12) and (13) one can calculate the viscosity of emulsions in the medium range of inner phase concentration. The comparison between the predicted and experimental values of viscosity is also presented in Fig. 5. The differences are in the same range as in the case of dilute emulsions.

## 4.3. Highly concentrated emulsions

Emulsions at the inner phase concentration above 0.63 have randomly close pack droplets [13] and are strongly non-Newtonian liquids. According to our concept they can be called the highly concentrated emulsions.

Fig. 7 illustrates an attempt to predict viscosity of the systems listed in Table 6 using original Pal's model and his values of constants. One can see that only for few emulsions the proposed correlation is satisfactory. A comparison of predicted values of viscosity calculated using Eq. (2) and experimental values of this parameter is presented in Fig. 8. Deviations are in the range from -64 to +400%. The smallest differences can be observed for data from the paper [7].

It resulted from the modelling work that the range of the applicability of Eq. (2) can be extended by replacing  $[\eta]$  by the new parameter  $\zeta$  which is dependent on the volume fraction of emulsions.

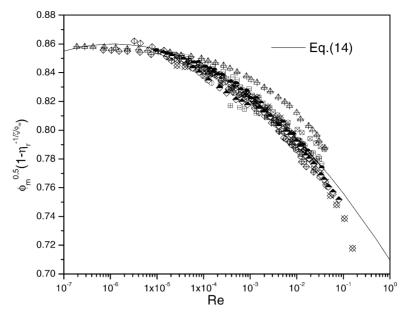


Fig. 11. Correlation of viscosity data using Eq. (14).

To find the values of  $\zeta$  for each dispersion, the experimental points for all emulsion have been presented as a function of  $A_0 + A_1 \log Re + A_2 (\log Re)^2$  versus relative viscosity  $\eta_r$ . These dependences are shown in Fig. 9a for the data from literature [7] and in Fig. 9b for our data. The points for every emulsion were approximated using the following equation with  $\zeta$  as the parameter which has to be evaluated—continuous lines in Fig. 9a and b:

$$\phi_{\rm m}^{0.5}[1 - \eta_{\rm r}^{-1/\zeta/\phi_{\rm m}}] = A_0 + A_1 \log Re + A_2 (\log Re)^2$$
 (14)

It was found that for investigated emulsions the parameter  $\zeta$  increased linearly with the inner phase concentration as presented in Fig. 10. One can see also that the  $\zeta$  parameter is not strongly dependent on the droplet diameter in the case of concentrated emulsions.

The points in Fig. 10 could be approximated by the following equation:

$$\zeta = -1.145 + 4.542\phi \tag{15}$$

Fig. 11 shows the function of  $\phi_{\rm m}^{0.5}(1-\eta_{\rm r}^{-1/\zeta/\phi_{\rm m}})$  versus Reynolds number. As can been seen, a much better fit for

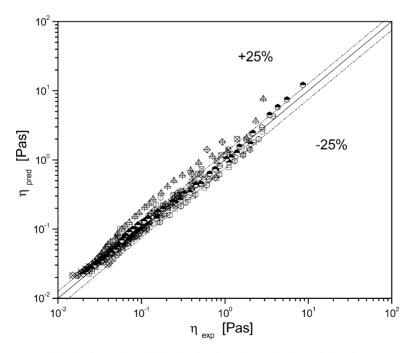


Fig. 12. Comparison of calculated and experimental values of viscosity.

investigated emulsion systems was obtained using expression (14) as well as for media with and without the exhibition of the yield stress. The differences between the values of emulsions viscosity predicted using Eq. (14) and experimental ones are shown in Fig. 12. The errors for most emulsions are in the range  $\pm 25\%$  and not more than +40%.

#### 5. Conclusions

- 1. Emulsions can be divided into three groups from the point of view of the inner phase concentration: dilute, medium and highly concentrated systems.
- 2. The viscosity of dilute emulsions is not dependent on the Reynolds number in the range of this variable changing from  $10^{-4}$  to  $3 \times 10^{-2}$  but is a function of the inner phase concentration, maximal packing  $\phi_{\rm m}$  and the intrinsic viscosity  $[\eta]$ . It can be predicted using Eq. (8).
- 3. For medium concentrated emulsions the viscosity is a function of the Reynolds number in the range of this variable changing from  $2 \times 10^{-5}$  to  $3 \times 10^{-2}$  and the same parameters as in the case of dilute emulsions. Viscosity of these systems can be calculated using Eqs. (11)–(13).

4. Viscosity of highly concentrated emulsions can be predicted using Eq. (14) where  $\zeta$  is the parameter calculated on the basis of Eq. (15).

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