Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 79 (2) 241–251 (2014) UDC 532.135:665.33+631.8.022.3:537.872
JSCS–4579 *Original scientific paper*

Rheological behaviour of castor oil mixed with different pyromellitic esters

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(Received 29 January, revised 29 April 2013)

Abstract: The paper presents the rheological behaviour study of castor oil mixed with different pyromellitic esters. The pyromellitic tetra-esters used were obtained through the esterification of pyromellitic anhydride with a special alcohol with a complex alkyl–aryl structure (2-phenoxy-ethanol) in conjunction with linear aliphatic alcohols with variable length (*n*-butanol, *n*-decanol). The influences of the structure and concentration of the pyromellitic esters as well as that of temperature, on the rheological behaviour were determined from the dependence between the shear stress τ and the shear rate $\dot{\gamma}$. An analysis of the dependence between τ and $\dot{\gamma}$ demonstrated that the studied solutions exhibited Newtonian behaviour. The evolution of the viscosity of the samples with temperature was characterized by Arrhenius type equations, the values of activation energy of viscous flow, E_a, were established. This constant can be correlated with the effect of friction reduction in the presence of additives. Characterization of the annulus of fluids flow under the effect of rotational motion was also realized by the calculation of the values of the Taylor–Reynolds number (Ta_{Re}).

Keywords: flow activation energy; Newtonian behaviour; oil additives; viscosity.

INTRODUCTION

The use of lubricants dates back over 3000 years when animal or vegetable fats were used to anoint wood or to facilitate transport processes. The main functions of a lubricant is to reduce friction and wear, to dissipate heat, to disperse deposits and to inhibit corrosion and rusting, while the main properties of a base oil are a relatively constant viscosity, low solidification temperature, low deposit formation, low volatility, good thermal-oxidative and hydrolytic stability, and biodegradablity.[1] The performance and features of lubricants differ from one another. Their only common point is that of composition that includes a main

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doi: 10.2298/JSC130129062B

element called “the basis lubricant” (base oil) in proportion of 75 to 92 mass % and various additives.[2,3] Mineral base oils are a mixture of paraffinic, aromatic and naphthenic hydrocarbons extracted from crude oil. Their physico-chemical characteristics depend on the oil source and quality, as well as on the employed processing method.[1]

Semi-synthetic lubricants are a mixture of mineral and synthetic oils, designed to maintain their viscosity grades. Additives are designed to improve the performance of lubricants and/or give them new properties. Today, practically all types of lubricating oil contain at least one additive, and some oils contain additives of several different types. The amount of additive used varies from a few hundredths of a percent to 30 % or more.[4] They are designed to protect surfaces (decrease friction and implicit wear, increase resistance to high pressure and inhibit corrosion), to meliorate some properties of the base oil (improvement of the pour point and/or viscosity index, de-emulsifier) or to protect it (inhibit oxidetion and foaming).[5,6]

Along with the need to protect the environment, the use of vegetable oil-based lubricants has become an important alternative in tribology. The basic materials suitable for producing ecological lubricants are vegetable oils because of their high biodegradability, regeneration capacity, low toxicity and wide variety of sources.[7] Unlike mineral oil-based lubricants, those based on vegetable oils are rapidly and completely biodegradable, without having a negative effect on the ecosystem. However, their thermal and hydrolytic stability are lower than those of synthetic oils and require improvement through a variety of measures.[8–10]

The vegetable oils used for this purpose can be both edible (sunflower, soybean, coconut, peanut, palm and rapeseed) and inedible (castor oil).[11,12] The lubricating properties of castor oil were studied and were reported to be similar or better than those of the commonly used vegetable oils.[9,13]

Pyromellitic structures are known for their thermal resistance and polyfunctionality. In order to vary the properties of these esters, aliphatic alcohols of variable length in conjunction with a special alcohol of a complex alkyl–aryl structure (2-phenoxyethanol) were used. The special alcohol has an etheric bridge the influence of which can be expressed by the effect of increased flexibility.

In terms of using aliphatic alcohols with a very long chain, the length of alkyl chain enables fluids of high performance in terms of thermal and tribological properties to be obtained, which could be useful in metalworking or as valuable lubricants.

The existence of the pyromellitic structure ensures the maintenance of thermal resistance while the amount of the special alcohol with a mixed aliphatic–aromatic structure can increase this resistance and, respectively, ensures a wide range of viscosity values, a determinant aspect for their use in tribology.

Viscosity is one of the main properties of the employed oil and its value should vary as little as possible in operation, under all engine-operating conditions. It is desirable that any additive added to a base oil to improve its lubricating qualities should not have a negative influence on its rheological properties.

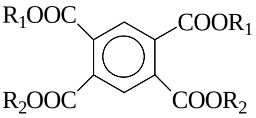
In this study, castor oil was used as the base vegetable oil with as auxiliary materials, paraffin oil and two pyromellitic esters, the synthesis and characterization of which were previously published.[14,15]

The aim of this work was to analyze the rheological behaviour of castor oil mixed with different pyromellitic esters. The influence of the structure and concentration of the pyromellitic esters, as well as that of temperature, on the rheological behaviour were followed. In addition, rheological relations $\tau = f(\dot{\gamma})$ were established and the activation energies, E_a, of flow were determined.[16–18]

EXPERIMENTAL

Materials

The preparation of the mixed esters is realized by reacting pyromellitic anhydride with 2-phenoxyethanol and *n*-butanol or *n*-decanol, using *p*-toluenesulphonic acid as catalyst. The formed water was extracted azeotropically by means of toluene.[6,16] These two esters are illustrated in the following general structure:



where R_1 = 2-phenoxyethyl and R_2 = *n*-butyl or *n*-decyl.

The two esters differ in the number of carbon atoms from the aliphatic alcohol used in the esterification of pyromellitic anhydride: 4 for PE1 ester (coming from *n*-butanol) and 10 for PE2 ester (coming from *n*-decanol). In both cases, the mole ratio between the residues 2-phenoxyethyl and *n*-butyl or *n*-decyl was 2:2.

The thus-prepared esters were analyzed in terms of tribological properties.[19]

The main characteristics of the pyromellitic esters (PE1 and PE2) are given in Table I and those of the castor oil and paraffin oil are given in Table II. Both oils were supplied by Fluka.

TABLE I. The properties of the pyromellitic esters at 20 °C

Ester	Formula	M / g mol^{-1}	ρ / kg m^{-3}	n_D	Saponification index, mg KOH g^{-1}	
					Theoretical	Analytical
PE1	$C_{34}H_{38}O_{10}$	606	1169.6	1.5373	370.36	369.51
PE2	$C_{46}H_{62}O_{10}$	774	1067.6	1.5135	289.97	292.32

Methods

The samples preparation was realized at room temperature (25 °C) by dispersing the pyromellitic ester, under intense stirring, in the oil mixtures. The composition of the samples with the esters content is presented in Table III. Castor oil was used as the standard (sample C0). The samples were analyzed after one day of preparation.

TABLE II. The properties of the castor oil and paraffin oil

Property	Castor oil	Paraffin oil
Composition	Ricinoleic acid, min. 85 mass %; oleic acid, min. 2 mass %; linoleic acid, min. 1 mass %	–
Boiling point, °C	313	–
Pour point (by ASTM D97 method), °C	–33	–
ρ^{20} / kg m^{-3}	960	860
n_D^{20}	1.479	1.473
η^{20} / mPa s	903.3	1000

TABLE III. The composition of the samples

Sample	Composition, wt. %			Sample	Composition, wt. %		
	PE1	Paraffin oil	Castor oil		PE2	Paraffin oil	Castor oil
C1	2	5	93	D1	2	5	93
C2	3.5	3.5		D2	3.5	3.5	
C3	5	2		D3	5	2	
C4	7	0		D4	7	0	

The rheological characterization of the samples was performed under thermostatic conditions (temperature range 50–80 °C), using a Rheotest-2 rotation viscometer with the system vat-drum S/S$_1$ suitable for the viscosity range of these fluids and high sensitivity. The device allows the measurement of the torsion moment appearing thanks to the ring-shaped substance layer placed between a fixed cylinder and one rotating at a known revolution. The torsion moment was correlated with the shear stress. The revolution and the thickness of the ring-shaped layer determine the shear rate.

Shear rate values were changed in the range 9–1312 s^{-1}.

RESULTS AND DISCUSSION

The influence of ester type used as an additive on the rheological behaviour of castor oil was studied for different concentrations of additive, at three temperature values. In Fig. 1, the $\tau = f(\dot{\gamma})$ dependence is shown for an ester concentration of 5 % by weight.

The rheological equations corresponding to these dependencies are given in Table IV.

It was registered that for these pyromellitic esters, increasing the number of carbon atoms of the aliphatic alcohol used for the esterification did not change the viscosity of the oil significantly and did not modify its Newtonian behaviour. Increasing the temperature led to a decrease in the viscosity of the samples but without change of the Newtonian behaviour.

In addition, the influence of the additive concentration on the rheological behaviour of castor oil was studied. Thus, the $\tau = f(\dot{\gamma})$ dependence at a temperature of 50 °C when using the pyromellitic ester PE1 as an additive is shown in Fig. 2.

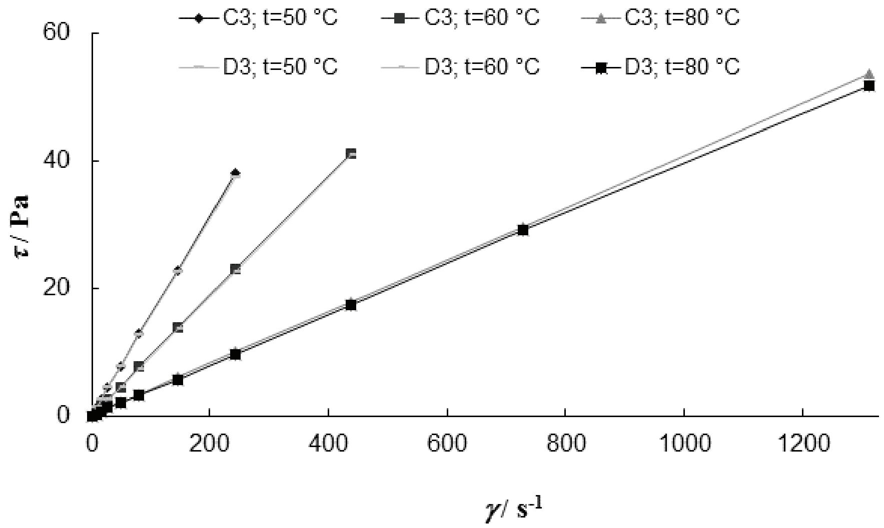


Fig. 1. Shear stress *vs.* shear rate for samples C3 and D3 at different temperatures.

TABLE IV. Rheological equations for samples C3 and D3

t / °C	Eq. ($\tau = \eta\dot{\gamma}$)		Viscosity decreasing[a], %
	C3	D3	
50	$\tau = 0.1565\dot{\gamma}$	$\tau = 0.1538\dot{\gamma}$	1.725
60	$\tau = 0.0939\dot{\gamma}$	$\tau = 0.0937\dot{\gamma}$	0.213
80	$\tau = 0.0407\dot{\gamma}$	$\tau = 0.0405\dot{\gamma}$	0.490

[a] Sample D3 compared with sample C3

From the slopes of the obtained straight lines, it was observed that the addition of a pyromellitic ester leads to a decrease of in the viscosity of the samples in comparison with the viscosity of oil without additives. The viscosity decrease is relatively small (about 15 %), the most pronounced decrease corresponds to an additive content of 2 mass %, followed by its increase with increasing the ester content, but without reaching the corresponding value of the pure oil. A similar situation occurs when PE2 pyromellitic ester was added to the oil. The obtained viscosity values are presented in Table V.

The exponential decrease of the samples viscosity with temperature is described by an Arrhenius-type equation:

$$\eta = A\exp\left(\frac{E_a}{RT}\right) \tag{1}$$

where E_a is the activation energy of flow, J mol^{-1}, R is the universal gas constant, J mol^{-1} K^{-1}, T is the absolute temperature and A represents a material constant, Pa s.

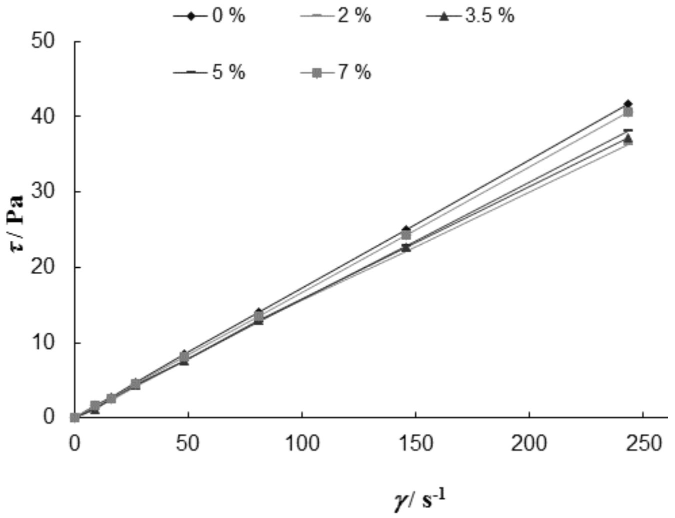


Fig. 2. Shear stress *vs.* shear rate for samples C0–C4 at 50 °C.

TABLE V. Dynamic viscosities of the samples

Sample	η / mPa s			Sample	η / mPa s		
	50 °C	60 °C	80 °C		50 °C	60 °C	80 °C
C0	171.4	103.6	43.5	D1	149.4	87.2	36.0
C1	149.7	88.2	37.6	D2	150.5	92.5	39.5
C2	153.4	90.4	39.2	D3	153.8	93.7	40.5
C3	156.5	93.9	40.7	D4	167.2	101.2	42.8
C4	167.1	98.3	42.3				

Through the measurements at different temperatures, it was possible to establish the dependence ln $\eta = f(1/T)$ and to calculate the E_a values. Particular expressions of Eq. (1) for the castor oil with the two types of pyromellitic esters additives are given in Table VI.

It was found that for the same type of ester, the variation of the activation energy of flow with the concentration of additive was insignificant. Moreover, this finding was valid even when the type of additive was changed, although they were of very different molecular weights.

Using particular expressions of the ln $\eta = f(1/T)$ dependence, the values of the dynamic viscosity of the samples was determined in the temperature range 20–100 °C. Thus, for pure castor oil (C0) and samples C3 and C4, the evolution of the viscosity is shown in Fig. 3.

TABLE VI. Arrhenius-type equations for samples C0–C4 and D1–D4

Sample	Eq. ($\eta = A\times10^5\exp(E_a/RT)$)	E_a / kJ mol^{-1}
C0	$\eta = 1.70\exp(5212/T)$	43.3
C1	$\eta = 1.35\exp(5237/T)$	43.5
C2	$\eta = 1.70\exp(5167/T)$	42.9
C3	$\eta = 2.10\exp(5108/T)$	42.5
C4	$\eta = 1.65\exp(5204/T)$	43.2
D1	$\eta = 0.80\exp(5398/T)$	44.9
D2	$\eta = 1.75\exp(5160/T)$	42.9
D3	$\eta = 2.10\exp(5096/T)$	42.3
D4	$\eta = 1.80\exp(5178/T)$	43.0

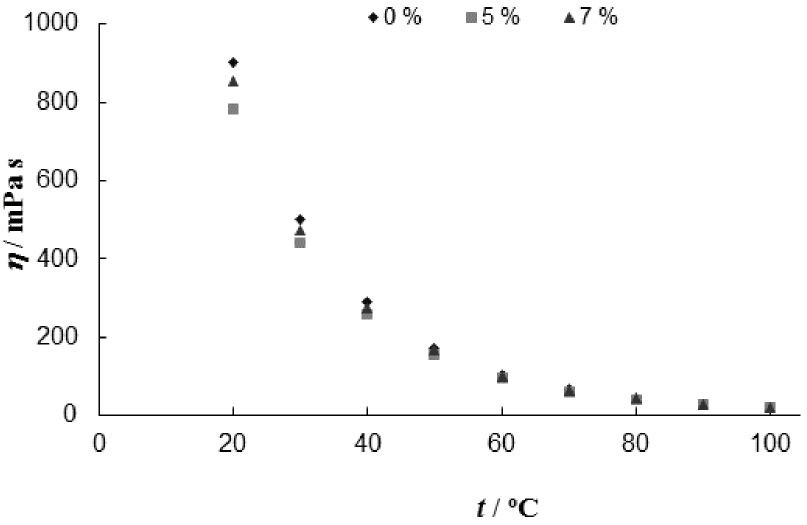


Fig. 3. Dynamic viscosity *vs.* temperature for samples C0, C3 and C4.

It is found that with increasing temperature, the values of the dynamic viscosity of the samples became more similar, regardless of the percentage of additive used.

Rotation in the annulus bounded by the concentric cylinders consisted of the relative flow of successive fluid layers. Changes in the additive process could be quantified by measuring the shear stress of the fluid layers when they were subjected to a controlled rotational motion. This change is reflected on the viscosity of the liquid.[20,21]

Since lubrication is usually used in rotating systems (bearings, gears, *etc*.), the dynamic characteristics (speed, dynamic pressure and shear stress) are expressed in terms of Taylor–Reynolds number (Ta_{Re}) specific to this type of motion. This criterion is also used to characterize fluids flow in the annulus under the effect of rotational motion and allows all the changes that appear in the flow layers through the gradual increase in revolution to be highlighted.

The values of Ta_{Re} number were calculated using relation (2), taking into account the radii of the inner and outer cylinder (r_i and r_o), the inner cylinder revolution number, n, and the fluid properties (viscosity η and density ρ):[18]

$$Ta_{Re} = \frac{2\pi n r_i (r_o - r_i)\rho}{\eta} \tag{2}$$

Increasing the hydrodynamic regime (characterized by the Ta_{Re} number) leads to a pronounced decrease of the ratio between shear stress τ (experimentally determined) and dynamic pressure P_{dyn} calculated with the maximum speed.

By analogy with fluids flow through straight pipes, the dynamic pressure of the fluid in motion in ring-shaped spaces is calculated by:

$$P_{dyn} = \frac{\rho w_{max}^2}{2} \tag{3}$$

$$w_{max} = \pi d_i n \tag{4}$$

where w_{max} is the speed of fluid laminar layer placed next to the moving wall (inner cylinder) and d_i is the inner diameter of the ring-shaped space.

The variation of the τ/P_{dyn} ratio *vs.* Ta_{Re} for the samples C0, D2 and D4 at a constant temperature (50 °C) is shown in Fig. 4. The variation of the same ratio for sample D2 as a function of temperature is shown in Fig. 5.

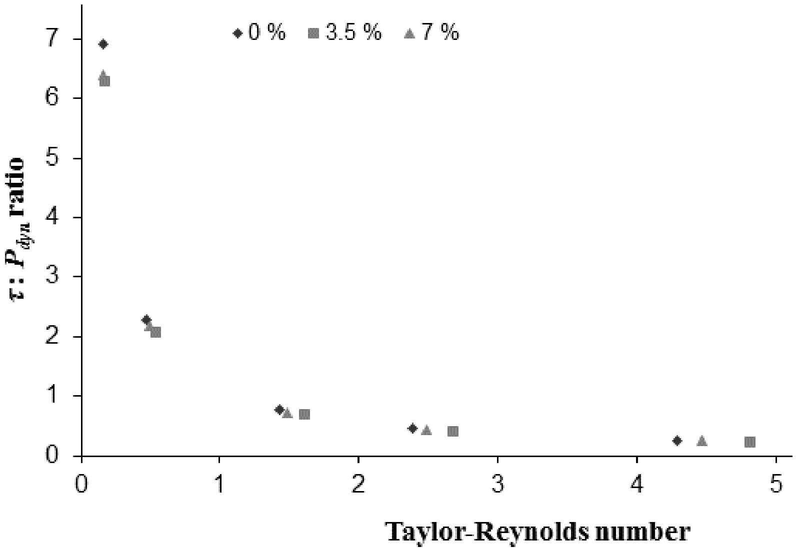


Fig. 4. Ratio τ:P_{dyn} *vs.* Ta_{Re} at 50 °C for samples C0, D2 and D4.

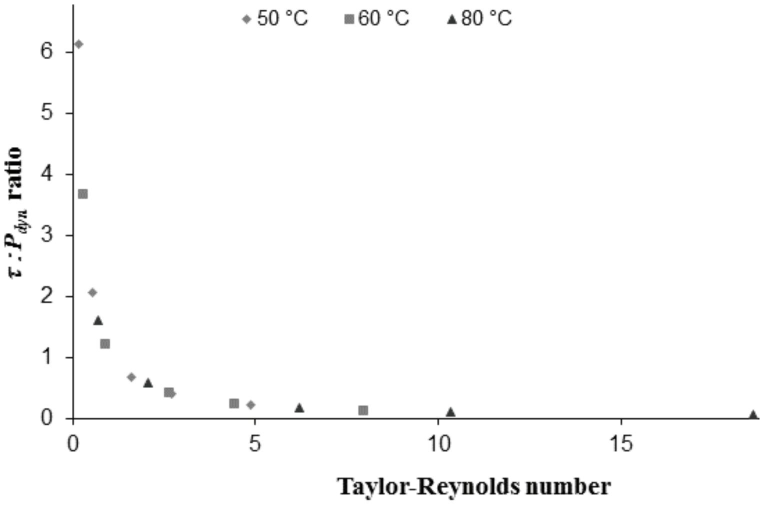


Fig. 5. The influence of temperature on the dependence of the τ:P_{dyn} ratio on Ta_{Re} for sample D2.

It can be seen from Figs. 4 and 5 that that neither the additive concentration nor the temperature have a significant effect on the dependence of the τ/P_{dyn} ratio on the Ta_{Re} number. The profile of both dependencies shows an accentuated decrease with increasing hydrodynamic flow regime.

By analogy, for circular motion of the fluid in stirring processes,[22] the ratio τ/P_{dyn} is correlated with Ta_{Re} number by a relationship of the type:

$$\tau / P_{\mathrm{dyn}} = C Ta_{Re}^{m} \tag{5}$$

or in the linear logarithmic form:

$$\ln(\tau / P_{\mathrm{dyn}}) = \ln C + m \ln\left(Ta_{Re}\right) \tag{5a}$$

The linear forms of the relationship, Eq. (5a), determined for sample D2 at different temperatures and for C0, D2 and D4 at 50 °C are given in Tables VII and VIII, respectively.

TABLE VII. Linear forms of Eq. (5a) for sample D2

t / °C	Eq. ($\ln(\tau/P_{\mathrm{dyn}}) = \ln C + m \ln Ta_{Re}$)	C
50	$\ln(\tau/P_{\mathrm{dyn}}) = 0.1004 - 1.0102 \ln Ta_{Re}$	1.105
60	$\ln(\tau/P_{\mathrm{dyn}}) = 0.0824 - 1.002 \ln Ta_{Re}$	1.086
80	$\ln(\tau/P_{\mathrm{dyn}}) = 0.1256 - 1.013 \ln Ta_{Re}$	1.134

Considering that the shear stress τ is equivalent to the friction pressure drop, it could be assumed that the ratio of the two quantities is equal to the friction coefficient, λ, which in the laminar flow regime has a value of $64Re^{-1}$.

TABLE VIII. Particular forms of Eq. (5a) for samples C0, D2 and D4, at 50 °C

Sample	Eq. ($\ln(\tau/P_{\text{dyn}}) = \ln C + m \ln Ta_{Re}$)	C
C0	$\ln(\tau/P_{\text{dyn}}) = 0.0850 - 1.0055 \ln Ta_{Re}$	1.089
D2	$\ln(\tau/P_{\text{dyn}}) = 0.1004 - 1.0102 \ln Ta_{Re}$	1.105
D4	$\ln(\tau/P_{\text{dyn}}) = 0.1735 - 1.0247 \ln Ta_{Re}$	1.189

This assumption was confirmed from two directions: on the one hand, the Ta_{Re} values lower than 60, which is the critical value that separates the laminar from the turbulent regime, for fluids flow in annulus.[21,23,24] On the other hand, from the equations presented in Tables VII and VIII, it could be seen that the values of the m coefficient are very close to the value –1, similar to the Reynolds exponent from the expression of the friction coefficient, and the values of the C coefficient increase slightly with increasing additive content.

CONCLUSIONS

The rheological behaviour of castor oil mixed with was studied, whereby the influence of the type and concentration of the pyromellitic ester and of temperature were monitored.

For each analyzed sample, a linear dependence between shear stress and the shear rate, without a yield point, was found, which shows Newtonian behaviour.

The addition of castor oil led to a slight decrease in viscosity, the most pronounced decrease corresponding to an additive content of 2 mass %. This finding was independent of the nature of the additive used and the temperature. Moreover, increasing the number of carbon atoms of the aliphatic alcohol had an insignificant influence on the viscosity of the castor oil and did not change its Newtonian behaviour.

The viscosity of the samples decreased exponentially with temperature in an Arrhenius-type manner, which enabled the calculation of the activation energy of flow. It is found that these values are insignificantly influenced by changing the type and concentration of the additive.

For the studied system, the dependence between the rheological parameters and the Taylor–Reynolds number (Ta_{Re}) was established. From graphical representations of this dependence, it could be concluded that circular motion of the fluid occurred in the laminar regime.

ИЗВОД

РЕОЛОШКО ПОНАШАЊЕ РИЦИНУСОВОГ УЉА ПОМЕШАНОГ СА РАЗЛИЧИТИМ ПИРОМЕЛИТИЧКИМ ЕСТРИМА

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Овај рад представља испитивање реолошког понашања рицинусовог уља помешаног са различитим пиромелитичким естрима. Коришћени пиромелитички тетраестри су добијени естирификацијом пиромелитичког анхидрида специјалним алкохолом сложене алкил–арил структуре (2-фенилетанол), заједно са линеарним алифатичким алкохолом променљиве дужине (n-бутанол и n-деканол). Утврђен је утицај струцтуре и концентрације пиромелитичких естара, као и температуре, на реолошко понашање, постављањем зависности између напона смицања, τ, и брзине смицања, $\dot{\gamma}$. Анализа зависности између τ и $\dot{\gamma}$ показује да испитивани раствори имају Њутновско понашање. Промена вискозности узорака са температуром је карактерисана једначином Аренијусовог типа, уз успостављање вредности активационе енергије вискозног тока, E_a. Ова константа може да се доведе у корелацију са ефектом смањења трења у присуству адитива. Такође је извршена карактеризација ануларног тока флуида при ефектима ротационог кретања, уз израчунавање вредности Таулор–Реунолдсовог броја (Ta_{Re}).

(Примљено 29. јануара, ревидирано 29. априла 2013)

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