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Viscosity model for the middle fraction of Atasu-Alashankou oil sludge

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Methods

Object of study for experimental works on determination of wide fraction viscosity with boiling point up to 350°C. Oil sludge was formed during the transportation of oil through the pipeline of the Kazstransoil enterprise of the West Kazakhstan oils of the Republic of Kazakhstan. Physical and chemical characteristics of oil sludge (Atasu-Alashankou): density - 0.87 g/cm^3, viscosity - 30 cSt, ash content - A - 0.36%, C - 72.3%, H - 11.1%, N - 0.1%, O - 16.1%. The atomic ratio of hydrogen to carbon in oil sludge is 1.8. The used microsilicate acts as a carrier and catalyst - product of Karaganda silicon plant "Tau-Ken.temir" LLP. Component chemical composition of initial microsilicate was determined by X-ray spectral and gravimetric methods. The content of components, %: SiO_2 - 95.5; TiO_2 - 0.02; Al_2O_3 - <0.95; Fe_2O_3 - <1.0; CaO - 0.5; MgO – 0.4; MnO – 0.04; P_2O_5 – 0.06; K_2O - <0.1; Na_2O - 0.3. The initial microsilicate was pre-crushed, then samples with a particle size of 0.1 mm were taken using sieve analysis. Leaching of the initial microsilicate was carried out using 20% hydrochloric acid solution to remove alkali and alkaline earth metals. The catalyst was prepared by wet impregnation of the leached microsilicate with a 1.5% solution of $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$. Microsilicate nitrate impregnated with solutions (20 g) was kept in a drying oven for 2 hours, at 80-90 °C temperature, and then dried at 105 °C temperature also for 2 hours. Further, the obtained catalyst samples were calcined in a muffle furnace at 650 °C temperature for 2 hours (supported catalyst), the conditions for conducting catalytic hydrogenation experiments of oil sludge and the synthesis of nanocatalysts are presented in [S1,S2].

The individual and group chemical composition of the fraction with boiling point up to 350 °C was determined by chromato-mass spectrometry using HP 5890/5972 MSD from Aguilent (USA).

Identification of substances was carried out using the mass spectral database of NIST98.

Chromatographic conditions:

Column: DB-5, 30 m × 0.25 mm × 0.5 μm

Gas: helium, 0.8 mL/min

Thermostat: 50 °C - 4 min

50–150 °C - °C/min

150–300 °C - 20 °C /min

300 °C - 4 min

Evaporator: 250 °C

Evaporator: 200 °C

Dynamic viscosity determination of oil sluge wide fraction with a temperature of the end of boiling to 350 °C was carried out at a temperature of 25 °C, 30 °C, 35 °C by means of SYD-265B-1 automatic viscometer (production of the People's Republic of China) where as samples the fractions received from initial oil slime and a hydrogenate were chosen. Sample 1 - initial fraction with boiling point up to 350°C obtained from oil sludge, Sample 2 - fraction with boiling point up to 350°C fractionated from hydrogenate (the hydrogenate is obtained by hydrogenation of oil sludge in the presence of a nanocatalyst containing cobalt and nickel-supported microsilicate), Sample 3 - fraction with boiling point up to 350°C fractionated from hydrogenate (hydrogenate obtained during hydrogenation of oil sludge in the presence of nanocatalyst containing cobalt-supported microsilicate).[S1]

It should be noted that the samples taken for the study are not individual substances. It is a mixture of different substances with their individual boiling points. In this case, in fact, boiling does not refer to one temperature, but to the temperature range, starting with low-boiling substances. Therefore, one can see some similarity to the liquid state of behavior of this mixture of substances in three samples. The reference consideration of the individual substance under heating from melting point to boiling point in our samples, the ranges of the heating process from lower to upper boiling points in some approximation simulate the behavior of pure substances.

To describe the dependence of viscosity on temperature in this range, it is determined by the existence of unstable structures of different levels of organization - clusters, associations and aggregation of associations.

Taking into account the existing real existence of these structures, the most suitable model and the display of the behavior of a mixture of substances can be used a cluster-associated model in which there are structures for any liquids (including melts). It is displayed as a two-level and three-parameter viscosity model (S1).

According to the concept of chaotic particles,[S3] according to the fundamental Boltzmann distribution, viscous flow is considered as destruction of associations of clusters consisting of crystal-movable particles. Destruction occurs by overcoming the forces of van der Waal attraction between clusters, which in principle does not contradict the existing ideas about viscous flow and is subject to a new dependence:[S4]

$$\eta = \eta_1 (T_1/T)^{a_2 (T_2/T)^b}, \quad \text{(S1)}$$

where η_1 – reference experimental point of dynamic viscosity at temperature T_1 (K), mPa·s; a – dimensionless degree of association of clusters (in approximation of its constancy). To express the temperature dependence of a parameter, you must have a second reference point η_2, T_2:

$$a = a_2 (T_2/T)^b, \quad \text{(S2)}$$

where b – takes on the meaning of the degree of decrease in aggregation from associates with an increase in temperature. Third reference point η_3, T_3 is used to identify b.

$$a_2 = \frac{\ln (\eta_2/\eta_1)}{\ln (T_1/T_2)}, \quad \text{(S3)}$$

$$a_3 = \frac{\ln (\eta_3/\eta_1)}{\ln (T_1/T_3)}, \quad \text{(S4)}$$

$$b = \frac{\ln (a_3/a_2)}{\ln (T_2/T_3)}. \quad \text{(S5)}$$

The authors in [S4] showed that for metals the b-indicator is not more than one and is taken constant. The cluster-associated model was tested for simple substances and complex inorganic compounds in the melt state. Data from the new model adequately described the range of fluid state and corresponded to experimental data. Organic compounds are characterized by a preferentially directed bond between atoms in the molecule than inorganic substances, which differ in negligible or small manifestation of homeopolar bonds. Therefore, the b – indicator for organic substances (in this study - oil sludge and two fractions from hydrogenate) is poorly expressed and can be neglected in the new model, then the model will be expressed as

$$\eta = \eta_1 (T_1/T)^{a=a_2 (T_2/T)}, \quad \text{(S6)}$$

in which the exponent a is determined by (S2) with $b = 1$

As is well known, the theoretical model of the liquid is still absent. Therefore, the authors found a form of such a mathematical model that maps the real structure of the liquid and the real curvature of the temperature dependence as decreasing with slowdown both at the cluster and association levels.

In this case, CAMV (S6) can be defined as generalized semi-empirical, since, while maintaining involvement in the fundamental Boltzmann distribution, it uses reference values (at T_1 and T_2).

For each sample, Table S1 shows the design equations and the temperature range of their application.

Table S1 Calculation equations of temperature dependence of viscosity, applicability range and correlation coefficient for samples 1, 2, 3.

Sample	Applicability interval, K	Correlation coefficient and its significance	η by CAMV (S6), mPa·s
1	225-420	R = 0.998, t_R = 956 >>2	$\eta = 2.41 \left(\frac{298}{T}\right)^{3.88\,(308/T)}$, (S7)
2	225-420	R = 0.979, t_R = 96 >2	$\eta = 1.52 \left(\frac{298}{T}\right)^{2.71\,(308/T)}$, (S8)
3	225-420	R = 0.937, t_R = 31 >2	$\eta = 1.41 \left(\frac{298}{T}\right)^{4.39\,(308/T)}$, (S9)

Equilibrium characteristics of the test substances when matching the cluster-associated model with the Frenkel equation

To compare the cluster-associated viscosity model with the Frenkel model, as well as the mutual agreement of these models and obtain thermodynamic characteristics, the data from Table S1 were presented in logarithmic coordinates (Table S2).

Table S2 Calculated values by viscosity of samples 1, 2, 3 in logarithmic coordinates.

T, K	$10^3/T$	Sample 1		Sample 2		Sample 3	
		$\ln\eta_1$ (e)	ln η(7)	$\ln\eta_2$ (e)	ln η(8)	$\ln\eta_3$ (e)	ln η(9)
293	3.41	0.94	0.95	0.46	0.47	0.41	0.42
298	3.36	0.88	0.88	0.42	0.42	0.34	0.34
303	3.30	0.82	0.81	0.38	0.37	0.27	0.27
308	3.25	0.75	0.75	0.33	0.33	0.20	0.20
313	3.19	0.68	0.69	0.29	0.29	0.11	0.13
323	3.14	0.64	0.64	0.21	0.25	-0.07	0.07

In these coordinates, close to straight-line data placement is observed in the studied temperature range of points for all samples. The least squares processing of this data per equation of the line was quite significant.

Meaningful straight-line data placement entitles the determination of viscous flow activation energy by the Frenkel equation

$$\eta = \eta_0 e^{\frac{E_a}{RT}}, \tag{S10}$$

where η_0 and E_a – constant (η_0 is sometimes seen as a function of temperature); *e* - base of natural logarithms; *T* - absolute temperature; *R* - gas constant.

Processing of viscosity data in logarithmic coordinates according to this equation

$$\ln\eta = \ln\eta_0 + \frac{E_a}{R}\cdot\frac{1}{T} \tag{S11}$$

should be carried out by the least squares method using the calculated viscosity data from the model (S6), since linearization is based on the Frenkel equation, and not on the CAMV (S6), which ensures the correspondence of the cluster-associative dependence of viscosity on temperature

Moreover, in the equation of the line $y = ax + b$:

$$y = \ln\eta,\ a = \frac{E_a}{R},\ x = \frac{1}{T},\ b = \ln\eta_0.$$

As a result, we will get

$$E_a = aR,\ \text{J/mol},\ \eta_0 = e^b,\ \text{mPa·s}.$$

All necessary parameters for the Frenkel equation and the equation itself for the test substances are given in Table 3 of the article.

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