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

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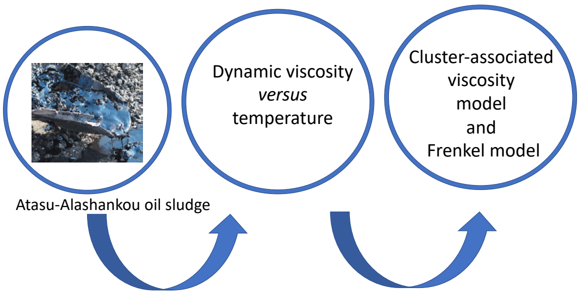
The temperature dependence of dynamic viscosity was calculated on the basis of a new cluster-association equation, which was derived within the framework of the concept of chaotic particles. It was shown that the degree of cluster association naturally decreases with an increase in temperature, on average corresponding to the arrangement of three to four cluster particles in the association. For the first time, the values of the activation energy per monomer were obtained when assigning the activation energy to the average number of clusters.



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In an effort for sustainable energy solutions and the effective use of resources, oil sludge processing has become a promising area.[1,2] One of the most important aspects of this processing is the determination of the viscosity of the obtained liquid fractions, since this directly affects the fluidity, circulation and processing of these materials.[3–5] To this end, the development of a complex viscosity model capable of working in the entire temperature range from the beginning to the end of the boiling of fractions becomes critical. This article discusses the method of creating a cluster-associated model of viscosity (CAMV) for fractions obtained as a result of hydrogenation of oil sludge.

CAMV of a liquid in the entire temperature range of the existence of this aggregate state was previously developed by the authors of this article based on the concept of chaotic particles.[6] In this regard, a detailed development of a hierarchical cluster-associated mathematical model of viscosity was carried out. The model is based on the Boltzmann equilibrium distribution and, therefore, is considered as a chaos-sensitive property of a liquid inherent in it not only in motion, but also at rest. In this model, the key features are thermal chaotization barriers at melting and boiling points, whereby the fluid behavior is determined by the effects of three energy classes of particles moving as in a crystal, liquid and vapor. The only important indicator in the new model depends on the temperature and it makes sense of the degree of association of clusters of particles moving as in a crystal. The ratio of the energy of activation of the flow of a viscous melt, determined by the Frenkel equation, to the magnitude of the degree of association of clusters gives a constant value, commensurate with the particles binding energy due to the van der Waals attraction forces. On this basis, the authors hypothesized that viscous flow occurs due to the destruction of cluster associations with the preservation of the clusters themselves. To adapt the cluster-associated model to experimental data, certain data processing techniques have been developed to identify unknown parameters of the model.[6] CAMV is a semi-empirical approach that considers the overall structure of a liquid as consisting of molecules, clusters and associations to predict its viscosity. The model takes into account the formation of clusters from molecules and associations from clusters that influence the behavior of liquid flow. CAMV has shown promising results in various industries in terms of accurately predicting viscosity in complex systems such as heavy oil residues, heavy oils and oil sludge.

In this work, we investigated the effect of a microsilicate-supported nickel–cobalt nanocatalyst on the viscosity of the middle fraction obtained in the process of hydrogenation of oil sludge (Atasu-Alashankou).

The behavior of fractions resulting from the hydrogenation of oil sludge, understanding and modeling viscosity are critical to optimizing processing conditions, predicting flow properties and designing efficient processing and transportation systems.

The development of CAMV for liquid fractions resulting from the hydrogenation of oil sludge has great potential for optimizing their processing, transportation and overall use. By considering the molecular interactions within these fractions, CAMV offers a comprehensive approach to predicting viscosity over a wide range of temperatures, thereby expanding the field of sustainable energy solutions and resource management.

The purpose of this work was to substantiate the CAMV for fractions with a boiling point up to 350 °C, isolated from oil sludge and its hydrogenate obtained in the process of destructive hydrogenation of oil sludge in the presence of various amounts of nanocatalyst (microsilicate containing nickel and cobalt).

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Table 1 Initial viscosity data for samples 1–3.

Entry	T/K	η(exp)/mPa s		
		Sample 1	Sample 2	Sample 3
1	293	2.56	1.59	1.50
2	298	2.41	1.52	1.41
3	303	2.26	1.46	1.31
4	308	2.12	1.39	1.22
5	313	1.97	1.33	1.12
6	323	1.68	1.20	0.93

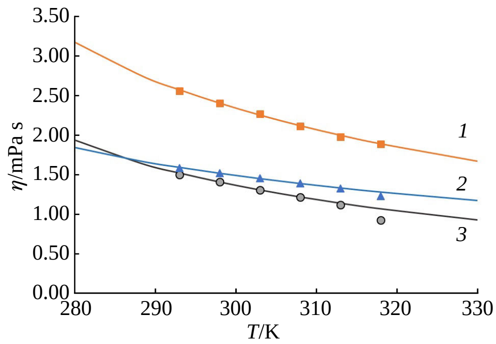

Figure 1 Dynamic viscosity of (*1*) sample 1, (*2*) sample 2 and (*3*) sample 3 as a function of temperature, with dots representing experimental data and lines calculated using equations (S7)–(S9) in Table S1 (see Online Supplementary Materials), respectively.

To determine the dynamic viscosity, a cluster-associated model was used, for which viscosity values determined experimentally for fractions of oil sludge and its hydrogenate were used as initial data. The viscosity values of samples 1–3 were measured by the dynamic viscosity method in the temperature range from 293 to 323 K using an automatic viscometer (see Online Supplementary Materials). Sample 1 is the initial fraction with a boiling point of up to 350 °C, obtained from oil sludge. Samples 2 and 3 are fractions of hydrogenates with a boiling point of up to 350 °C, obtained by hydrogenation of oil sludge in the presence of Co–Ni and Co nanocatalysts on a microsilicate support, respectively.[7,8] The experimental viscosity values of the samples are presented in Table 1.

Based on the available data, viscosity was calculated using the CAMV equation (1):

$$\eta = \eta_1 (T_1/T)^a, \qquad (1)$$

in which the indicator a is determined by the formula $a = a_2(T_2/T)^b$, with $b = 1$.

From the above set of experimental data (see Table 1), the following values of viscosity (η_i) and temperature (T_i) were selected as representative (reference) points: η_1 = 2.41 mPa s at T_1 = 298 K and η_2 = 2.12 mPa s at T_2 = 308 K. At these points, the a_2 values were calculated using the formula $a_2 = \ln(\eta_2/\eta_1)/\ln(T_1/T_2)$, and the viscosity data were calculated using equation (1).

The change in viscosity for the test samples is shown in Figure 1.

As can be seen from Table 2, the degree of association of clusters a naturally decreases with increasing temperature for all substances, which corresponds to the dynamics of cluster destruction.[9] It should be noted that in this case, for organic substances, which are samples 1–3, the concepts of cluster and association will differ from those for molten metal alloys.[9] In this case, it is necessary to take a monomer as a cluster unit, and a polymer consisting of the corresponding monomers as an associate. The higher the temperature, the shorter the chain length or polymer length. Therefore, the degradation of a substance occurs with an improvement of its fluidity.

The cluster-associated model allows one to display the actual curvature of the viscosity–temperature relationship, and due to its hierarchical structure, such a model displays this curvature as decreasing with slowdown.

The high accuracy of the obtained viscosity models allows, as is customary for semi-empirical models, to extrapolate in both directions from the studied arguments by ±30%, which in this case is 225–420 K, taking into account the non-exceeding phase transitions during heating and cooling.

To compare CAMV with the Frenkel model, as well as for mutual agreement of these models, the obtained thermodynamic characteristics, such as the temperature (K) interval of applicability, the correlation coefficient with its significance and the values of η (mPa s) according to the CAMV equation (1), were presented in logarithmic coordinates (Figure 2).

In these coordinates in the studied temperature range of points for all samples, a close to rectilinear arrangement of data is observed. The least squares treatment of this data for each line equation was highly significant. Meaningful rectilinear arrangement of data allows us to determine the activation energy of viscous flow using the Frenkel equation (2):

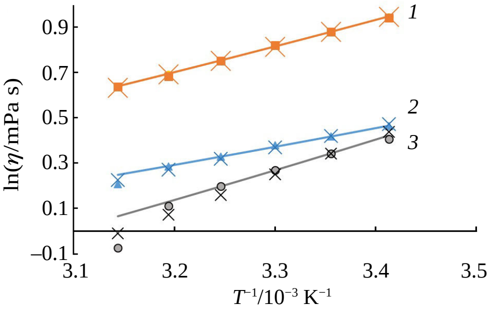

Figure 2 Logarithmic dependence of the viscosity of (*1*) sample 1, (*2*) sample 2 and (*3*) sample 3 on the inverse temperature. The dots represent experimental data, the lines are drawn according to the cluster-associated model, and the values for the crosses are calculated using the Frenkel equation (2).

Table 2 Viscosity values of samples 1–3 calculated using the CAMV equation (1).

Entry	T/K	η(exp)/mPa s			η(calc)/mPa s			a		
		Sample 1	Sample 2	Sample 3	Sample 1^a	Sample 2^b	Sample 3^c	Sample 1	Sample 2	Sample 3
1	293	2.56	1.59	1.50	2.58	1.60	1.52	4.02	2.85	4.61
2	298	2.41	1.52	1.41	2.41	1.52	1.41	3.95	2.80	4.53
3	303	2.27	1.46	1.31	2.26	1.45	1.31	3.88	2.75	4.46
4	308	2.12	1.39	1.22	2.12	1.39	1.22	3.82	2.71	4.39
5	313	1.98	1.33	1.12	2.00	1.33	1.14	3.76	2.67	4.32
6	323	1.89	1.23	0.93	1.89	1.28	1.07	3.70	2.62	4.25

^{a} Equation (S7) in Table S1. ^{b} Equation (S8) in Table S1. ^{c} Equation (S9) in Table S1.

Table 3 Activation energy E_a and parameter η_0 in the Frenkel equation for the test substances (samples 1–3).

Entry	Sample	E_a/kJ mol^{-1}	η_0/mPa s	$\bar{a}$	$(E_a/\bar{a})$/kJ mol^{-1}
1	1	9.630	0.049	3.85	2.499
2	2	7.654	0.069	2.73	2.803
3	3	13.887	0.005	4.42	3.141

$$\eta = \eta_0\, e^{\frac{E_a}{RT}}. \tag{2}$$

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

The results obtained using the cluster association model and the Frenkel equation, as well as experimental viscosity data and correlation coefficients for samples 1–3 are presented in Table 4.

The correlation coefficient of experimental data in comparison with the cluster-associated model and the Frenkel equation is high in all cases. This indicates the proximity of the viscosity calculation results for both models, which consider this characteristic from various points of view, molecular-kinetic and probabilistic.

It is also possible to determine how much activation energy is per monomer. To do this, it is necessary to calculate the weighted average of the degree of association of clusters. This value $\bar{a}$ can be determined analytically using a known formula of the form

$$\bar{a} = \frac{\sum_1^n a_i T_i}{\sum_1^n T_i}. \tag{3}$$

Since the value $\bar{a}$ characterizes the average number of clusters in an association (or, in our case for an organic matter, the number of monomers in a polymer), then from the ratio $E_a/\bar{a}$ one can determine the activation energy, which falls on one cluster or one monomer and means the energy of bond breaking in association, that is, the beginning of the destruction of the association or polymer.

The weighted average values of the degree of cluster association according to equation (3) and the $E_a/\bar{a}$ ratio in the test range for samples 1–3 are given in Table 3.

As was shown earlier on other objects,[9–12] in all cases the specific activation energy of the viscous flow, $E_a/\bar{a}$, did not exceed the energy of van der Waals attraction (2–20 kJ mol^{-1}), as indicated in the published work.[13] All activation energy values for fractions of samples 1–3, given in Table 3, are in the lower range of energies of van der Waals attraction of molecules, that is, they can be compared with polymer materials,[13] where the formation of molecular chains is based on very weak bonds caused by the physical attraction of monomers to each other without forming fixed bonds. Being the weakest and unsaturated intermolecular bonds, they are overcome first, which gives grounds to assert the nature of viscous flow in which the destruction of associates occurs without the destruction of clusters, which retain the binding energy of atoms in the solid state even during their virtual existence. For organic substances, the analogy with inorganic substances regarding viscous flow is heating to destroy polymers without destroying monomers. Thus, the values of activation energy per monomer were obtained for the first time when the activation energy was assigned to the average number of clusters.

As a result of this work, dynamic viscosity was experimentally measured at six temperatures for oil sludge and two fractions. Based on these data, the temperature dependences of dynamic viscosity were constructed using a new cluster-associated model. For test samples, this model was able to display the actual curvature of the viscosity–temperature curve as decreasing with deceleration.

The lack of knowledge about the nature of the viscous state and fluid flow, with incommensurable temperature dependences of viscosity, with the fragmented and narrow experimental determination of this characteristic and the impossibility of displaying it over the entire temperature range of the liquid state, especially for heavy oil residues, heavy oils and oil sludge,[14–23] makes this research relevant. The scientific novelty of the work lies in displaying the temperature dependence of viscosity using a cluster-associated probabilistic mathematical model, the hierarchical structure of which is adequate to the physical nature of particle aggregation, without taking into account their specific structure, but taking into account the change in the degree of their association with increasing temperature.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.04.043.

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Table 4 Comparison of the calculated viscosity values of samples 1–3 with experimental data and correlation coefficients.

Entry	T/K	Viscosity/mPa s								
		Experiment			CAMV equation (1)			Frenkel equation (2)		
		Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
1	293	2.56	1.59	1.50	2.58	1.60	1.52	2.57	1.61	1.55
2	298	2.41	1.52	1.41	2.41	1.52	1.41	2.41	1.52	1.41
3	303	2.27	1.46	1.31	2.26	1.45	1.31	2.26	1.45	1.28
4	308	2.12	1.39	1.22	2.12	1.39	1.22	2.12	1.38	1.17
5	313	1.98	1.33	1.12	2.00	1.33	1.14	2.00	1.31	1.08
6	323	1.89	1.23	0.93	1.89	1.28	1.07	1.88	1.25	0.99
Correlation coefficients										
7	R				0.998	0.979	0.937	0.999	0.990	0.968
8	t_R				996	96	31	1647	192	61

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