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Effect of Alternating Electric Current Frequency on the Viscosity of Coal Tar

Sh. K. Amerkhanova, M. I. Baikenov, R. M. Shlyapov, and A. S. Uali
Buketov State University, ul. Universitetskaya 28, Karaganda, 100028 Kazakhstan
e-mail: amerkhanova_sh@mail.ru

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Abstract—The results of a study on the effect of alternating electric current on the relative viscosity of coal tar from Shubarkol coal are reported. The optimum conditions of treatment were established. It was found that the entropy of activation is the main characteristic responsible for structure rearrangements in the organic matter of tar. The tar samples were analyzed by chromatography–mass spectrometry before and after treatment with alternating electric current, and an increase in the amount of phenols was detected.

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Upon the catalytic processing of high-boiling hydrocarbon raw materials, heavy residues very rapidly lead to the poisoning and carbonization of the active surface of any catalyst. Rapid catalyst deactivation occurs because of the high concentrations of metals, asphaltenes, sulfur and nitrogen compounds, and other harmful impurities in the raw material; pores become clogged, and the catalyst surface area becomes covered with resinous and coke deposits. As a result this, the selectivity and efficiency of a classical catalytic process decreases to finally increase the prime costs of the processing and the products obtained [1, 2].

However, recently, alternative uncatalyzed processing methods have been proposed more frequently; the efficiency, safety, and ecological compatibility of these methods are very high. This type of processing includes ultrasound treatment [3, 4], electromagnetic irradiation [5, 7], X-ray irradiation [8], cavitation [9, 10], etc.

Alternating electric current can also be used along with these forms of physical action; unlike direct current, the use of alternating current is more economical. The main difference and advantage of the approach and technology proposed is that the raw material, that is, coal tar (coal tar), is subjected to mild noncatalytic cracking.

The aim of this work was to study the effect of alternating electric current on the kinematic viscosity of coal tar from the coal of the Shubarkol deposit (central Kazakhstan).

EXPERIMENTAL

Coal tar from the Shubarkol deposit (central Kazakhstan) was used as a test material. Its density was $d_4^{20} = 0.9341$ g/cm^3, and the elemental composition was as follows (%): C, 91.1; H, 7.5; S, 0.2; N, 0.5; and O, 0.52. A GZ-2 low-frequency generator with two steel electrodes, the surface area of either of them was 11,52 cm^2, was used for generating an ac field.

The treatment by an a field was performed with varied time (30, 60, 90, 120, and 150 min), temperature (288, 298, 308, 318, and 328 K), frequency (50, 250, 500, 2500, and 5000 Hz), and distance between the electrodes (1, 3, 5, 7, and 9 cm). The relative viscosity of coal tar was determined based on the outflow time (in seconds) of 100 mL of liquid through a calibrated nozzle of a VZ-246 viscometer in accordance with a published procedure [11]. Then, the kinematic viscosity was calculated.

Table 1. Equations for the dependence of the kinematic viscosity of coal tar on factors

No.	Equation	Function	R
1	$y = 2 \times 10^{-5}x^2 - 0.14x + 589.82$	$\nu = f(\nu)$	0.95
2	$y = -4.22x^3 + 72.69x^2 - 356.87x + 899.43$	$\nu = f(l)$	0.80
3	$y = 1.11x^2 - 107.87x + 2673.40$	$\nu = f(T)$	0.99
4	$y = -6 \times 10^{-5}x^4 + 0.02x^3 - 2.89x^2 + 145.49x - 1854.40$	$\nu = f(\tau)$	1.00

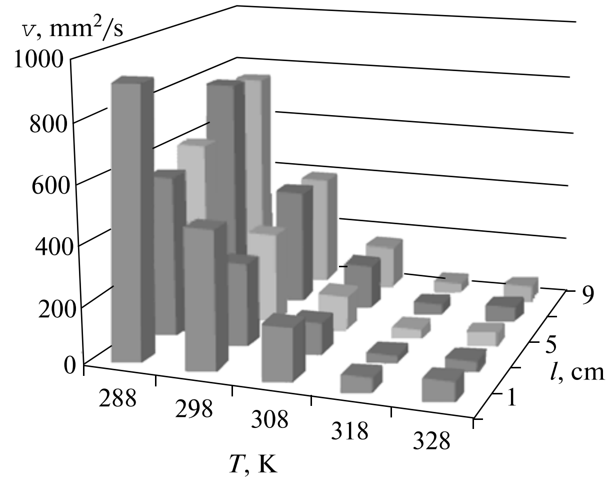

Fig. 1. Changes in the kinematic viscosity depending on temperature and distance between the electrodes at a frequency of 2500 Hz and a treatment time of 90 min.

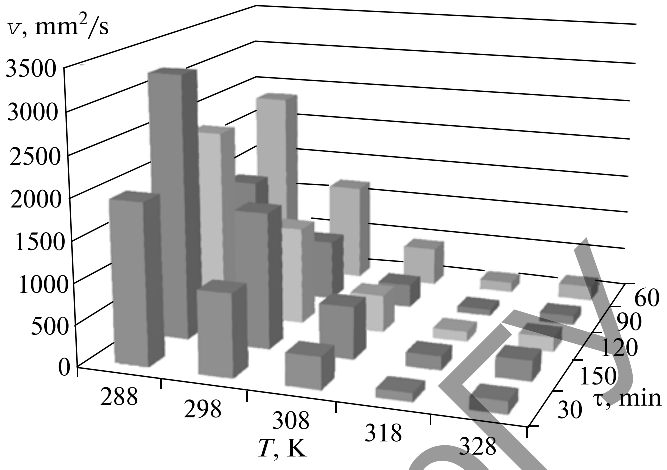

Fig. 2. Dependence of the kinematic viscosity on temperature and treatment time at a frequency of 2500 Hz and a distance of 3 cm between the electrodes.

RESULTS AND DISCUSSION

In this work, we studied changes in the kinematic viscosity of heavy coal tar under the influence of different factors: temperature, current frequency, time of action, and distance between electrodes. An experimental design method was used to optimize the number of experiments. On this basis, equations were derived to express the dependence of the kinematic viscosity on each of the individual factors given above, which are summarized in Table 1.

Based on the generalized Protod'yakonov equation, we calculated the theoretical values of the kinematic viscosity of tar samples under the action of the following factors: distance between electrodes, temperature, ac frequency, and treatment time. In this case, two of the above factors had constant values of variables (Fig. 1).

Figure 1 indicates that the temperature dependence of relative viscosity adequately describes the occurring processes because a decrease in the relative viscosity with temperature is explained by the occurrence of different structural changes and changes in the mobility of molecules. An optimum distance between the electrodes was 3 cm; it is likely that irreversible polarization processes manifested themselves to a larger degree at this distance. Therefore, a decrease in the viscosity of coal tar upon treatment with alternating current (Fig. 2) in a range of 30–90 min was caused by an increase in the mobility of the individual fragments of macromolecules as a result of the occurrence of polar-

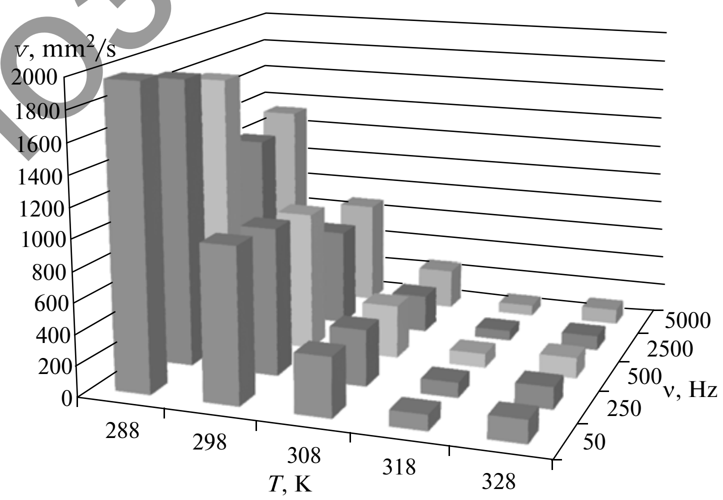

Fig. 3. Effects of temperature and ac frequency on the kinematic viscosity at a constant treatment time of 90 min and a distance of 3 cm between the electrodes.

Table 2. Changes in the kinetic characteristics of coal tar upon treatment with alternating electric current

l, cm	E_a, kJ/mol	$-\ln A$	$-\Delta G^{\neq}$, kJ/mol				
			288	298	308	318	328
1	59.0	−17.84	58.96	63.14	67.32	71.51	75.70
3		−18.35	60.17	64.39	68.61	72.84	77.07
5		−18.26	59.95	64.16	68.38	72.60	76.82
7		−18.01	59.37	63.56	67.76	71.96	76.16
9		−18.05	59.45	63.65	67.85	72.05	76.26

ization processes. However, an increase in the exposure time to 150 min facilitated an increase in the viscosity, which is explained by the predominance of association processes in the system.

Figure 3 shows that, as the frequency was increased from 500 to 2500 Hz, a sharp decrease in the viscosity was observed due to the destruction of hydrogen bonds and, consequently, the structure degradation of the component with a maximum concentration and a minimum viscosity, which played the role of a solvent. A further increase in the frequency to 5000 Hz did not lead to substantial changes in the viscosity because the relaxation time decreased so that macromolecules and individual units became inert to the external action. Under the action of current with a frequency of 500 Hz, the viscosity change had a medium value.

As a result of the experiments, we found that optimum conditions for treating the coal tar by alternating current are the following: temperature, 318 K; distance between the electrodes, 3 cm; and a treatment time of 90 min at a frequency of 2500 Hz. Under these treatment conditions, the viscosity of the tar decreased several times from 268 to 36.66 mm^2/s, that is, by a factor of 7.3. At the same time, the viscosity changed from 268 to 178 mm^2/s, that is, by a factor of 1.5, as a result of cavitation action for 5 min at 318 K and a rotational velocity of $3 \cdot 10^5$ rpm.

The mathematical model obtained makes it possible to forecast the viscosity of materials under changes of ac frequency, temperature, and contact time, which influence the process of destruction. We also calculated the energy parameters of intermolecular interaction, the apparent activation energy, the enthalpy and entropy of activation, and the Gibbs energy of activation (Table 2, Fig. 4).

With the use of equations analogous to those in the activated complex theory and taking into account the fact that the displacement of macromolecules in a liquid occurs by the jumps of individual molecular segments, we calculated the entropy of activation and the free activation energy of viscosity (Table 2, Fig. 4). It is well known that the activation energy of viscous flow is the energy required for the detachment of a structural unit from its neighbors as a result of thermal motion. The same values of the activation energies make it possible to conclude that the free energy of viscosity rather than the heat of process predominantly affects the dynamic viscosity of the system.

All of the test samples of the initial coal tar and the tar after ac treatment were characterized by the positive values of the entropy of viscous flow; consequently, the environment of macromolecular segments possesses a loose structure. However, a large difference between the values is indicative of the more compact structure of macromolecular fragments, which form the initial coal tar, as compared with the samples treated with alternating current. In this case, a maximum was reached at a distance of 3 cm between the electrodes; at the same time, an increase in the interelectrode space from 5 to 9 cm led a decrease in the entropy of activation of viscous flow; that is, the sample structure was strengthened due to an insufficient polarizing effect of alternating current. Thus, for

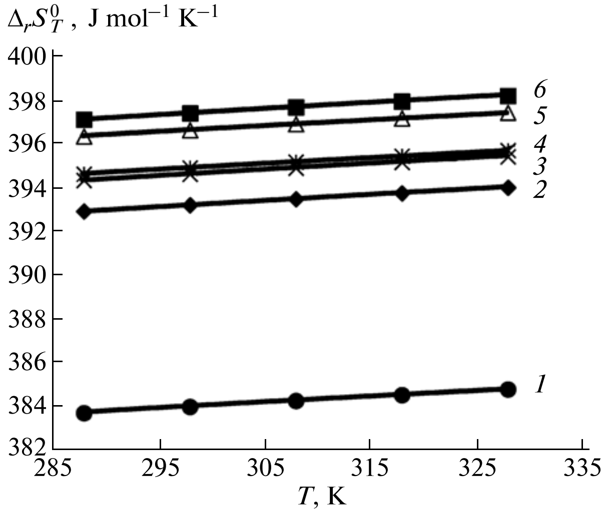

Fig. 4. Changes in the entropy of activation of viscous flow with temperature under optimum conditions: ν = 2500 Hz, τ = 90 min: (*1*) initial coal tar, (*2*) 1 cm, (*3*) 7 cm, (*4*) 9 cm, (*5*) 5 cm, and (*6*) 3 cm.

Table 3. Results of the chromatographic–mass spectroscopic analysis of the samples of the initial coal tar and the coal tar treated with alternating electric current

Groups of substances	Relative concentration, wt %	
	initial coal tar	tar after treatment with an ac field (under optimum conditions)
Benzene derivatives	4.81	7.20
Naphthalene derivatives	15.71	30.05
Anthracene derivatives	0.83	–
Phenols	3.13	32.00
Other compounds (cyclic compounds, alcohols, carboxylic acids, and ketones)	75.10	28.62
Compounds*	0.42	2.13
Total	100.00	100.00

* Compounds whose concentrations are lower than 0.1 %.

a distance of 1 cm, the steric factor was smaller due to the association processes of polarized molecules. On the other hand, the positive values of the entropy of activation were caused by the presence of phenols and their derivatives.

It follows from the transition state theory that the free energy of activation is the quantity responsible for the rate of reaction, whereas this parameter characterizes the possibility of a jump of a molecular segment to a vacant place in the case of viscosity. The enthalpy of activation determines the strength of a bond between the sections of a segment of the macromolecule, and it depends on temperature. It was found that the maximum and minimum values of Gibbs free energy were observed for distances between the electrodes of 3 and 1 cm, respectively, and the temperature dependence of the enthalpy of activation had a negative slope. This suggests a decrease in the stability of intermolecular bonds. To confirm the theoretical findings, we studied the composition of coal tar with the use of chromatography–mass spectroscopy (Table 3).

Table 4. Isokinetic temperature of the ac treatment of coal tar at an ac frequency of 2500 Hz for 90 min

l, cm	T_{iso}, K				
	288	298	308	318	328
0	141.27	140.74	140.20	139.67	139.15
1	137.96	137.44	136.92	136.41	135.90
3	136.51	135.99	135.48	134.97	134.47
5	136.77	136.25	135.74	135.23	134.73
7	137.47	136.95	136.43	135.92	135.41
9	137.37	136.85	136.33	135.82	135.31

We found that the amounts of phenols, naphthalene derivatives, and benzene derivatives increased by factors of 10, 2, and 1.5, respectively. Consequently, phenol, benzene, and their derivatives served as a solvent, and naphthalene derivatives were a macromolecular segment. The increase in the amount of phenols and benzene and naphthalene derivatives was related to the destruction of cyclic compounds and anthracene derivatives.

In this case, the medium acquired a looser structure, thus increasing the possibility of displacing the macromolecular segments. At the same time, it is very important to determine the factor that makes a maximum contribution to the Gibbs energy of activation. In connection with this, we calculated the values of isokinetic temperature (Table 4).

According to published data, the isokinetic temperature or compensation temperature corresponds to the inversion point of relative activity within the limits of a series of reactions. Thus, in the temperature range $T < T_{iso}$, the kinetic behavior of particles is determined by the enthalpy of activation or by the entropy of activation at $T > T_{iso}$ [12]. In our case, the temperature T is higher than the isokinetic temperature; therefore, the degradation of the organic matter of coal tar is determined by the entropy of activation; moreover, the higher the difference between the experiment temperature and T_{iso}, the greater the influence of the entropy of activation. The minimum influence of the entropy of activation is characteristic of the initial coal tar, whereas the maximum influence is characteristic of a sample treated in an ac field at a distance of 3 cm between the steel electrodes.

CONCLUSIONS

Based on the data of viscometric measurements, we obtained mathematical models to describe the process of the viscous flow of samples under the influence of several factors. We found that the factors are arranged in the following sequence according to their effects on the sample: $T > \tau_f > \nu > l$. Optimum conditions were chosen, under which a minimum viscosity was attained: $T = 318$ K, $\tau_f = 90$ min, $\nu = 2500$ Hz, and $l = 3$ cm. The following kinetic parameters of the viscous flow were calculated: activation energy, enthalpy of activation, entropy of activation, and free energy of activation. The samples of coal tar were analyzed by chromatography–mass spectroscopy; a change in the composition toward a decrease in the amount of complex polyaromatic compounds due to the destruction of aromatic substances upon the polarization of both individual segments and the macromolecules was determined. Based on the isokinetic temperature, it was found that the destruction process is characterized by a change in the entropy of activation of viscous flow.

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