GENERALIZATION OF DATA ON THE THERMOPHYSICAL PROPERTIES OF PETROLEUM PRODUCTS. VISCOSITY

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We describe the investigation and generalization of data on the viscosity of fractions of Romashkin petroleum. We develop a method for calculating the viscosity of petroleum products in the liquid phase.

In the design and calculation of various types of engineering equipment for the petroleum-processing and chemical industry, it is necessary to have reliable information on the thermophysical properties of petroleum products and, in particular, on the dynamic viscosity (η). Accordingly, we experimentally investigated the viscosities of 12 fractions of one of the most representative types of petroleum, namely, Romashkin petroleum, in the temperature range 240-600°K and at pressures of up to 10 MPa. The measurements were carried out by the method of capillary viscometry designed by Golubev (variant 5) on an apparatus previously used by one of the authors in investigating the viscosity of Freons [1]. Some of the experiments in the low-temperature range were carried out on an apparatus with an external capillary [2].

Viscosity was investigated on viscometers with different measuring capillaries, whose characteristics are shown in Table 1. The temperature of the experiments was measured by means of standard platinum resistance thermometers of the PTS-10 and TSPN-2A types, manufactured and graduated at the VNIIFTRI, and the pressure was measured by means of load-piston manometers, class 0.05, of the MP-60 and MP-600 types. The time required for the substances investigated to flow out through the working segment of the capillary was determined by means of an F-599 frequency meter—chronometer equipped with an automatic adapter.

The dynamic viscosity of the fractions of Romashkin petroleum, which had previously been subjected to special purification to remove the sulfur and sulfur compounds, was found from isotherms plotted at temperature intervals of 20°K at pressures of 0.1, 1.0, 5.0, and 10 MPa. In the viscosity measurements, at each experimental point we made no fewer than 3-5 parallel measurements of the outflow time. After completing the experiments at maximum temperature, we carried out control measurements on the initial isotherm; the good agreement between the results was evidence that the composition and properties of the petroleum products had not changed during the measurement process. An analysis of the errors in the measurements of η, carried out in accordance with the recommendations of [3], showed that the maximum error in the evaluation, for a confidence probability of $\alpha = 0.95$, was no more than 1.5%.

The results of the viscosity measurements for the fractions of Romashkin petroleum at atmospheric pressure are shown in Table 2.

TABLE 1. Characteristics of the Measuring Capillaries and Ranges of Their Application

Geometric dimensions of the capillaries, mm		Range of investigated parameters		Efflux time, sec	Re
diameter	length	T, K	p, MPa		
0,07341	53,30	240—573	0,1÷10	150—320	500÷1070
0,11086	51,79	240—573	0,1÷10	180—360	450—900
0,20355	54,60	303—600	0,1÷10	120—350	260÷760

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TABLE 2. Values of the Dynamic Viscosities of Fractions of Romashkin Petroleum at Atmospheric Pressure, μPa·sec

t, °C	η
BO-120°C	
—30	825
—20	705
0	541
20	430
40	347
120—180° C	
—20	1469
0	998
20	741
40	583
60	475
80	394
100	329
140—240° C	
—20	2605
0	1625
20	1116
40	830
60	654
80	535
100	447
120	378
180—240° C	
0	1365
20	1164
40	970
60	777
80	599
100	482
120	403
140	342
160	291
195—270° C	
20	1775
40	1235
60	934
80	730
100	599
120	504
140	430
160	368
180	317
240—280° C	
40	2104
60	1398
80	1089
100	847
120	705
140	581
160	467
180	400
200	346
240—350° C	
20	3857
60	1707
100	974
140	690
180	487
220	370
280—350° C	
40	4860
80	2007
120	1135
160	713
200	481
240	335
350—420° C	
60	10460
100	3880
140	1975
180	1165
220	750
260	470
300	320
>300° C	
40	27310
80	11030
120	5074
160	2710
200	1631
240	1177
280	834
>420° C	
40	127500
80	52090
120	23140
160	11220
200	6000
240	3581
280	2378
320	1730
>500° C	
60	221100
100	96270
140	44840
180	22290
220	11900
260	6820
300	3480

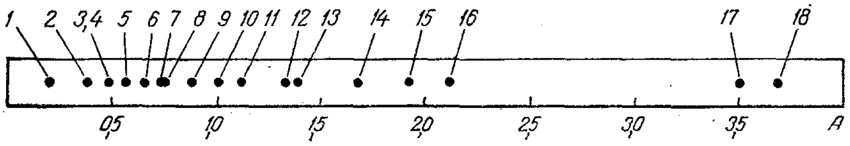

Fig. 1. Scale of the determining parameter: 1) eicosane; 2) pentadecane; 3) tridecane; 4, 7, 8, 11, 12) fractions of Romashkin petroleum which boil in the temperature ranges 240-350, 195-270, 140-240, 120-180, and boiling onset (BO) to 120°C; 5) dodecane; 6) undecane; 9) nonane; 10, 13) fractions of Samotlor petroleum which boil in the temperature ranges BO-180°C and BO-120°C; 14) pentachlorofluoroethane; 15) difluorochloromethane; 16) trichlorofluoromethane; 17) nitrogen; 18) oxygen.

The experimental material obtained was processed on the basis of the single-parameter law of corresponding states (SPLCS), developed at Filippov's seminar [4, 5] and successfully used by him in describing the thermal properties of a large group of normal (nonassociated) liquids. We based our generalizations on experimental data concerning the viscosity of petroleum products from petroleums with various hydrocarbon compositions, obtained recently at the Grozny Petroleum Institute and the Odessa Technological Institute, as well as data [6-9] on the viscosity of aromatic and saturated hydrocarbons and their halogen derivatives.

According to [5], the SPLCS for the viscosity can be represented in the form

$$\varphi(\pi, \tau, \eta, A) = 0, \tag{1}$$

where φ is a universal function; $\pi = p/p_{cr}$; $\tau = T/T_{cr}$; $A = 100\pi$ when $\tau = 0.625$ on the curve showing the saturated vapor pressure versus a dimensionless determining parameter.

In order to find the parameter A determining what group of similar substance to which a specific substance belongs, we must have data relating to the elasticity curves. For petroleum products, which are highly complex mixtures with a large number of components, no such information is available. However, for most liquid petroleum products we can find data

TABLE 3. Coefficients of Eq. (2)

j	i = 0	1	2	3
0	7,1060	—26,2547	14,2964	—2,2968
1	—76,0349	116,0592	—57,3253	9,0503
2	54,0543	—76,2222	32,9154	—4,1633
3	—2,7132	—1,3478	4,6404	—1,6319

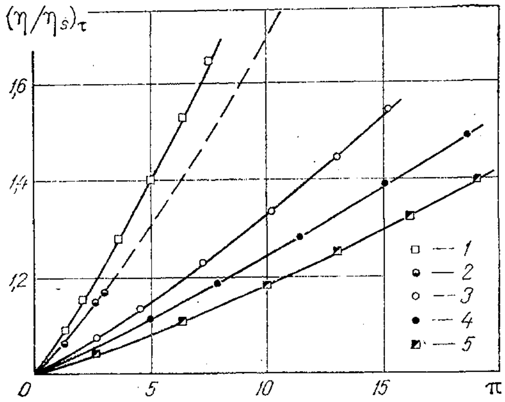

Fig. 2

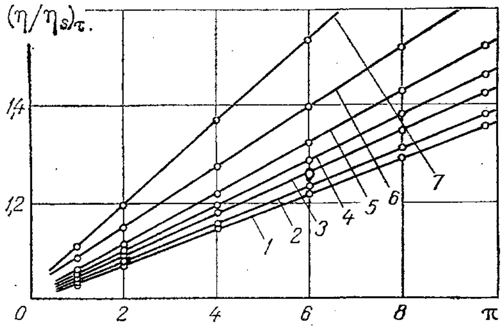

Fig. 3

Fig. 2. Graphs of $(\eta/\eta_s)_\tau = f(\pi)$ for the reduced temperature $\tau = 0.514$: 1) oxygen; 2) nitrogen; 3) trichlorofluoromethane; 4) undecane; 5) pentadecane.

Fig. 3. Graphs of $(\eta/\eta_s)_\tau = f(\pi, \tau)$ for difluorochloromethane: 1) for $\tau = 0.487$; 2) 0.541; 3) 0.595; 4) 0.649; 5) 0.758; 6) 0.812; 7) 0.866.

on the density at atmospheric pressure in the literature (or obtain them without great difficulty). Using such data, by the method in [5], we calculated the values of the determining parameter and the "critical" parameters for the petroleum products. The values of A for other substances included in our processing were calculated on the basis of the literature data concerning the functional relation between p_s and T_s on the saturation curves. The range of variation of the determining parameter for the substances used in our processing is shown in Fig. 1.

The processing of the data on the viscosity of liquid petroleum products at atmospheric pressure was carried out in the form of $\eta = f(\tau, A)$ on the basis of the data of [10] concerning the viscosity of Samotlor petroleum, the data of [6, 7] for paraffin and aromatic hydrocarbons, and the results of the present study. The calculation equation for the viscosity was obtained in the form

$$\ln\eta = \sum_{i=0}^{3}\sum_{j=0}^{3} a_{ij}\tau^{-i}A^{j}. \tag{2}$$

The coefficients of Eq. (2) are shown in Table 3. It describes the viscosity of 23 substances included in our processing, with a maximum error of 8.6% and a mean-square error of 3.7%. Thus, the existence of a generalized {η, τ, A} relation shows that the introduction of only one determining parameter is sufficient to give us positive results.

To generalize the variation of viscosity with pressure, we used extensive information on η for a large number of substances, for which the value of the determining parameter A varied from 0.2 to 3.7 (see Fig. 1). An analysis of the various cross sections of the {η, π, τ, A} surface, which are illustrated in Figs. 2 and 3, enabled us to obtain the generalized equation in the form

$$(\eta/\eta_s)_\tau = \sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{k=0}^{3} a_{ijk}\tau^{i}\pi^{j}A^{2k}, \tag{3}$$

TABLE 4. Coefficients of Eq. (3)

i, j, k	$a_{ijk}\cdot 10^2$	i, j, k	$a_{ijk}\cdot 10^2$
0, 0, 0	99,86466	1, 0, 0	5,17348
0, 0, 1	11,42817	1, 0, 1	—27,69476
0, 0, 2	—5,05444	1, 0, 2	10,77975
0, 0, 3	0,32810	1, 0, 3	—0,68014
0, 1, 0	—0,85060	1, 1, 0	4,98845
0, 1, 1	5,80750	1, 1, 1	—7,33936
0, 1, 2	—1,98461	1, 1, 2	2,91109
0, 1, 3	0,11871	1, 1, 3	—0,17668

where η_s is the viscosity near the saturation curve.

The coefficients of Eq. (3) are shown in Table 4. The maximum error in the description of the data on the viscosity of 18 substances of various types does not exceed 9.3%, and the mean-square error 2.1%.

Thus, the proposed method enables us to calculate both the temperature and pressure dependence of the viscosity of liquid petroleum products at temperatures of up to $0.9T_{cr}$ and pressures of up to 50-60 MPa on the basis of minimal initial information.

Example of a Calculation

1. Problem. Determine the viscosity of a fraction of Romashkin petroleum which boils in the temperature range 240-350°C, with T = 313°K and p = 10 MPa.

2. Initial data. For T_1 = 293°K we have ρ_1 = 852.7 kg/m^3; for T_2 = 353°K we have ρ_2 = 811.2 kg/m^3; M = 233; T_{boil} = 560°K; ρ_{boil} = 668.1 kg/m^3.

3. Method of calculation.

3.1. We determine the "critical" parameters and the determining parameter A:

$$T_{cr} = 0{,}493\left(T - \rho\frac{T_1 - T_2}{\rho_1 - \rho_2}\right), \tag{4}$$

$$\rho_{cr} = 0{,}253\left(\rho - T\frac{\rho_1 - \rho_2}{T_1 - T_2}\right), \tag{5}$$

$$p_{cr}\left[6.62 + 1{,}075\frac{T_{boil}}{T_{cr} - T_{boil}}\lg(9.87p_{cr})\right] = \frac{R\rho_{boil}T_{cr}}{M\cdot 10^6}, \tag{6}$$

$$\frac{p_{cr}M\cdot 10^6}{RT_{cr}\rho_{cr}} = (3.92 - 0{,}85\lg A)^{-1}. \tag{7}$$

The results of the calculation on the basis of Eqs. (4)-(7) are: T_{cr} = 752.2°K; ρ_{cr} = 267.0 kg/m^3; p_{cr} = 1.71 MPa; A = 0.50

3.2. We find the reduced temperature and pressure, $\tau = T/T_{cr} = 0.416$; $\pi = p/p_{cr} = 5.847$.

3.3. By Eq. (2), we calculate the viscosity for T = 313°K on the saturation curve $\eta = 2422\cdot 10^{-6}$ Pa·sec.

3.4. By Eq. (3), we find the viscosity for T = 313°K and p = 10 MPa to be $\eta = 2667\cdot 10^{-6}$ Pa·sec. The deviation from the experimental value ($\eta_{exp} = 2792\cdot 10^{-6}$ Pa·sec) is 4.4%.

NOTATION

η, dynamic viscosity; π, reduced pressure; τ, reduced temperature; p, pressure; p_{cr}, critical pressure; T, temperature; T_{cr}, critical temperature; η_s, viscosity near the saturation curve; *a*, coefficients; Re, Reynolds number.

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VISCOSITY AND DENSITY OF APROTONIC SOLVENTS AND ELECTROLYTES BASED ON THEM

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The results of an experimental determination of the viscosity and density of organic solvents and electrolytes based on them are given.

Organic solvents are widely used in applied chemistry. Interest has recently been shown in them in electrochemical power engineering, where these nonaqueous solvents are used to produce an electrolyte for current sources in which alkali metals, primarily lithium, are used as the anodic material [1].

Research on the design of such current sources has led to a fairly precise specification of the indices that determine the suitability of these solvents [2]. It is difficult, however, to find substances that directly satisfy the whole set of requirements and this has led to the use of electrolytes that employ not individual substances, but mixtures, in which the drawbacks of some solvents are compensated by the advantages of others.

An index of particular importance is the viscosity, since it has an appreciable effect on the electrical conductivity of the electrolyte and diffusion transfer in it, which ultimately affects the output parameters of the current source.

Unfortunately, the reference literature usually provides no data for solvents of practical interest, while data found in periodicals is of a specific and fragmentary nature, and in most cases relate to individual solvents [3, 4] – data for mixtures have only recently begun to appear [5]. These circumstances stimulated the present investigation.

For the considered class of current sources interest is now confined to a relatively small group of substances, which includes such solvents as propylene carbonate (PC), γ-butyrolactone (γ-BL), tetrahydrofuran (THF), and mixtures of these. As regards the electrolyte, lithium perchlorate ($LiClO_4$) is one of the compounds used for its preparation. The results of an investigation of their properties are given below.

The purity of the samples used for the investigation was ensured by the high purity of the initial substances (these were usually "pure" grade, in which the total impurity content

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