the single-phase states, actually figure in the relationships presented, which removes, at least partially, the question of their jump on the phase equilibrium line). Therefore, it can be considered proved that near the critical point in a two-phase domain, and possibly even on a small section of the gaseous state above the phase equilibrium line, the derivative $(\partial^2 V/\partial p^2)_S$ is negative, and consequently rarefaction shocks can be formed here.

Experiments were recently performed to observe rarefaction shocks. The authors of [7] determined rarefaction shocks in Freon-13. These waves were formed in the critical point domain for initial values of the temperature and pressure equal to the critical values and in complete conformity with those as was assumed in [2].

NOTATION

p, pressure; V, volume; T, temperature; S, entropy; p_c, V_c, T_c, S_c are the p, V, T, S values at the critical point; w, flow velocity; c, speed of sound; c_V, isochoric specific heat; A, a, b, a', b', constants.

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MODELING AND PREDICTION OF THE THERMODYNAMIC PROPERTIES
OF LIQUID PETROLEUM PRODUCTS

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A method for predicting the thermal properties and heat capacity of liquid petroleum fractions and gas condensates is described. The method employs only the data on the density ρ_{20}, the molecular mass, and the average boiling point of the petroleum product as the starting information.

The thermodynamic properties of pure substances are now successfully predicted using methods based on the law of corresponding states with three parameters. According to this law the equation of state of a single-phase substance has the form

$$z = z(\omega, \tau, \beta). \tag{1}$$

The acentricity factor combined with the well-known linear correlation of Pitzer [1] is often employed as the correlation parameter β:

$$z = z^{(0)}(\omega, \tau) + \beta z^{(1)}(\omega, \tau). \tag{2}$$

The expansion (2) is valid, however, for small β, $\beta < 0.4$ [2]. However, a significant number of substances, in particular heavy hydrocarbons, that are widely employed in practice, are characterized by larger values of β. For such substances we proposed [3] a method for predicting the thermal properties from the generalized equation of state (ES) of the liquid.
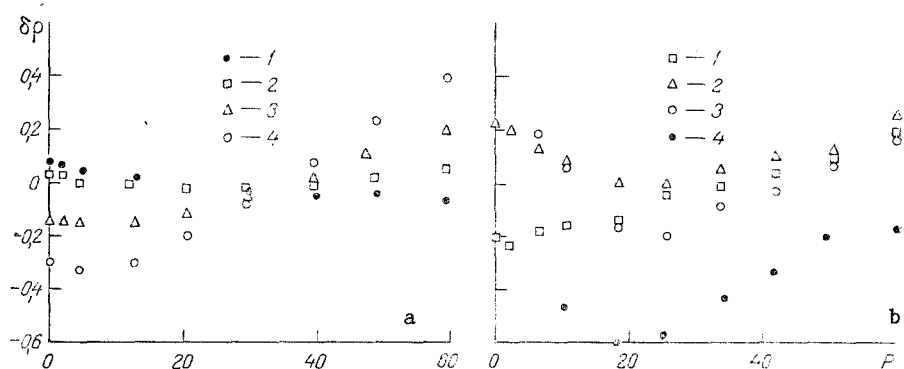
Fig. 1. Deviations of the experimental data from the computed values of the density: a) the 290-300°C fraction of Anastas'ev petroleum [7] (1 — t = 20°C, 2 — 80, 3 — 140, 4 — 200); b) gas condensate from the Vuktyl' deposit [8] (1 — T = 220 K, 2 — 300, 3 — 380, 4 — 460). δρ, %; P, MPa.

The derivation of the general form of the equation of state is based on the ES obtained by modifying the cellular model by introducing the temperature dependence of the structural characteristics of the liquid. The use of the effective (12, 6) potential with temperature-dependent parameters makes it possible to apply successfully the ES to any molecular liquids, including polar liquids. This equation has the following form [4, 5]:

$$z = 1 - 1{,}744 \frac{\varepsilon_{\text{lig}}}{kT} [(b_{0\,\text{lig}} \rho)^2 - 0{,}4654 (b_{0\,\text{lig}} \rho)^4],$$

$$\varepsilon_{\text{lig}}/k = 0{,}795 T_{\text{cr}} \exp[c(1 - T/T_{\text{cr}})], \quad \sigma_{\text{lig}}^{-3} = a - bT, \quad b_{0\,\text{lig}} = 2\pi N \sigma_{\text{lig}}^3/3. \tag{3}$$

The three constants, a, b, and c, which are unique for each substance, are usually determined from experiment.

The equation of state (3) can be justified theoretically for a wide range of values of the state parameters $T_{\text{tr}} \le T \le T_{\text{cr}}$; $p \ge 1.8 \, \rho_{\text{cr}}$. This equation reproduces with high accuracy the experimental data on the density ($\delta\rho = 0.01$-0.2%), correctly describes all the characteristics of the thermodynamic behavior of a liquid, and gives reliable results when extrapolated to high pressures [6].

The equation of state (3) was tested on a series of petroleum fractions and fractions of gas condensates. The maximum deviation of the computed values of the density, calculated using the ES (3), from the experimental values is $\delta\rho_{\max} = 0.8\%$ with an average error of $\delta\rho = 0.2\%$. This is illustrated in Fig. 1, which shows the quality of the description of the experimental PVT data for the 290-300°C fractions of Anastas'ev petroleum and gaseous condensate from the Vuktyl' deposit. We note that out of 238 experimental points of both petroleum products the error $\delta\rho > 0.5\%$ at only six points. The results obtained give grounds for using the ES (3) to calculate and predict the thermodynamic properties of petroleum fractions and fractions of gas condensates, regarded here as a pure substance.

With the help of the parameters presented

$$\pi = P/P_{\text{cr}}, \quad \tau = T/T_{\text{cr}}, \quad \omega = \rho R T_{\text{cr}}/P_{\text{cr}} \tag{4}$$

the equation of state (3) can easily be put into the dimensionless form

$$z = 1 - 1{,}744 \frac{\overline{\varepsilon}}{\tau} [(\overline{b}_0\omega)^2 - 0{,}4654 (\overline{b}_0\omega)^4] \tag{5}$$

or

$$\pi = \omega\tau - 1{,}744\overline{\varepsilon} [\overline{b}_0^2\omega^3 - 0{,}4654\overline{b}_0^4\omega^5], \tag{6}$$

where

$$\overline{b}_0 = b_{\text{lig}} P_{\text{cr}}/RT_{\text{cr}}; \quad \overline{\varepsilon} = 0{,}795 \exp[c(1 - \tau)]; \quad \overline{b}_0^{-1} = \overline{a} - \overline{b}\tau;$$

$$\overline{a} = \frac{3}{2\pi N} \frac{RT_{\text{cr}}}{P_{\text{cr}}} a; \quad \overline{b} = \frac{3}{2\pi N} \frac{RT_{\text{cr}}^2}{P_{\text{cr}}} b.$$

TABLE 1. Parameters of the Basic Equations of State

Constants in ES (5)	z_0	z_1	z_2	z_3
$\bar{a}$	8,111002	9,282139	11,250289	13,491271
$\bar{b}$	2,948202	3,791172	5,217069	6,647563
c	2,17	3,04	4,00	4,32

In view of the nonlinearity of the function $z(\beta)$ for larger values of the Pitzer parameter terms of higher orders are retained in the expansion of the compressibility factor [3] and the corresponding correlation acquires the form

$$z = z^{(0)} + \beta z^{(1)} + \beta^2 z^{(2)} + \beta^3 z^{(3)}. \qquad (7)$$

To determine $z^{(i)}$ ($i = 0$, 1, 2, 3) four reference substances from the interval $0 \leq \beta <$ 1 were chosen: $Ar\text{--}z_0$, $n\text{--}C_4H_{10}\text{--}z_1$, $C_{11}\text{--}H_{24}\text{--}z_2$, and $C_{20}H_{42}\text{--}z_3$; for these substances the corresponding values of the acentricity factor were taken to be $\beta = 0$, 0.197, 0.539, and 0.894. For each of the substances chosen the exact ESs in the form (5) [5, 9], constructed from the experimental data, were employed. The coefficients $\bar{a}$, $\bar{b}$, and c in this equation for four reference substances are presented in Table 1.

In applying (7) to each reference substance a closed system of equations, from which $z^{(i)}$ can be found as a function of z_0, z_1, z_2, and z_3, is obtained. Substituting them into (7) and carrying out simple transformations we obtain the equation

$$z = A_0(\beta) z_0 + A_1(\beta) z_1 + A_2(\beta) z_2 + A_3(\beta) z_3, \qquad (8)$$

which is the generalized equation of state of a liquid (GES).

Since the values of the acentricity factor are known for the reference substances the coefficients $A_i(\beta)$ have the specific form:

$$A_0(\beta) = 1 - 8,044255\beta + 17,151808\beta^2 - 10,519355\beta^3,$$
$$A_1(\beta) = 10,258059\beta - 30,499893\beta^2 + 21,279490\beta^3, \qquad (9)$$
$$A_2(\beta) = -2,694154\beta + 16,674962\beta^2 - 15,278506\beta^3,$$
$$A_3(\beta) = 0,480350\beta - 3,326877\beta^2 + 4,518371\beta^3.$$

The region of applicability of the GES (8) is bounded by the maximum reduced pressure $\pi = 50$ at temperatures $\tau = 0.3\text{-}1.0$.

In applying the GES (8) to all substances studied, including the reference substances, the values of the correlating parameter β were calculated from the Lee–Kessler formula [2]

$$\beta = \frac{-\ln P_{cr}(\text{MPa}) - 8,216562 + 6,096480\Theta^{-1} + 1,28862 \ln \Theta - 0,169347\Theta^6}{15,2518 - 15,6875\Theta^{-1} - 13,4721 \ln \Theta + 0,43577\Theta^6}. \qquad (10)$$

Thus, for any substance it is sufficient to have the values of the critical parameters P_{cr} and T_{cr} and the normal boiling point T_b as starting data in order to predict with the help of the GES (8) the thermal properties of the liquid over a wide range of temperatures and pressures with accuracy acceptable for engineering calculations. For petroleum fractions and gas condensates the critical parameters are usually determined computationally. This can affect the error in the determination of the density with the help of the GES. If at least one experimental point is available (for the petroleum fractions, fractions of gas condensates, and many hydrocarbons the point ρ_{20} is such a point) the values of the constants a and b can be corrected for a fixed value of c and a set of the parameters in the ES (3), giving reliable values of the PVT properties [3], can be obtained.

The generalized ES (8) was used to predict the density of a large number of liquids over a wide range of values of β, including also for 44 fractions of eight oils and 41 fractions of seven gaseous condensates, for which experimental PVT data are available. The results of the investigation are given in Table 2. The relative error in the description of the density (prediction) with the correction made based on the value of ρ_{20} is $\delta\bar{\rho} = 0.4\text{-}0.6\%$.

TABLE 2. Quality of the Description (prediction) of the Density of Liquid Petroleum Products

Petroleum product	T, K	P, MPa	$\bar{\delta\rho}$, %	$\delta\rho_{max}$, %
Anastas'ev oil [7]				
130—140°C	293—473	0,094—58,89	0,34	—1,06
160—170	293—473	0,095—59,54	0,20	—0,66
240—250	293—473	0,093—59,56	0,35	—0,80
290—300	293—473	0,094—59,67	0,29	—0,62
330—340	293—473	0,093—60,29	0,39	—1,24
Mangyshlak [20, 12]				
120—130	293—473	0,094—59,14	0,16	0,54
160—170	293—473	0,095—58,77	0,23	—0,53
240—250	293—473	0,096—59,15	0,25	—0,54
290—300	293—473	0,095—59,13	0,12	0,53
330—340	293—473	0,094—59,08	0,43	—1,15
62—140	293—473	0,095—59,58	0,20	0,83
140—180	293—473	0,095—59,77	0,15	0,49
180—240	293—473	0,093—59,71	0,15	0,53
Samotlor [12]				
62—140	293—473	0,094—59,30	0,28	1,39
140—180	293—473	0,094—60,10	0,17	—0,50
180—240	293—473	0,094—59,39	0,17	0,46
240—350	303—473	0,094—59,54	0,53	—0,64
350—420	303—473	0,094—59,64	0,54	—1,45
Gas condensates				
Gazli [21]				
95—122	290—473	0,098—39,22	0,27	1,09
122—150	289—473	0,098—39,22	0,15	0,63
150—175	294—473	0,098—39,22	0,22	0,57
175—200	290—473	0,098—39,22	0,19	0,82
Shatlyk [21]				
150—175	291—473	0,098—39,20	0,47	1,60
175—200	293—473	0,098—39,22	0,34	1,08
200—225	290—473	0,098—39,22	0,36	1,40
225—250	291—473	0,098—39,22	0,27	—1,00
Oposhnskii [22]				
122—150	293—443	0,098—39,20	0,16	0,62
150—175	293—443	0,098—39,20	0,38	—1,67
175—200	293—443	0,098—39,20	0,39	—1,49
200—225	293—443	0,098—39,20	0,59	—1,61
250—275	293—443	0,098—39,20	0,26	0,55
Solokhovaskii [22]				
95—122	293—443	0,098—39,20	0,31	—1,43
150—175	293—443	0,098—39,20	0,45	—1,61
175—200	293—443	0,098—39,20	0,34	—0,84
200—225	293—443	0,098—39,20	0,39	—1,05
225—250	293—443	0,098—39,20	0,33	—0,97

The larger magnitude of the error refers to fractions with widely differing boiling points, which is natural, since in the proposed model the petroleum product is regarded as a pure substance.

We note that for petroleum fractions the critical parameters P_{cr} and T_{cr} are determined, as a rule, based on ρ_{20} and T_b (we employed the formulas from [10]). In addition, in order to transfer the molar values of the density calculated based on the GES into the SI system it is necessary to know the molecular mass. Thus, to predict the thermal properties based on the GES (8) it is sufficient to have ρ_{20}, M, and T_b as the starting data; for petroleum products these parameters are usually known. The error in the computed (predicted) values of the density depends on the accuracy of the data indicated, but the deciding factor is the accuracy of ρ_{20}, since the constants a and b in the equation of state are corrected based on this quantity. For this reason the arithmetic-mean value of the temperatures at the start and end of distillation of the product were used for T_b.
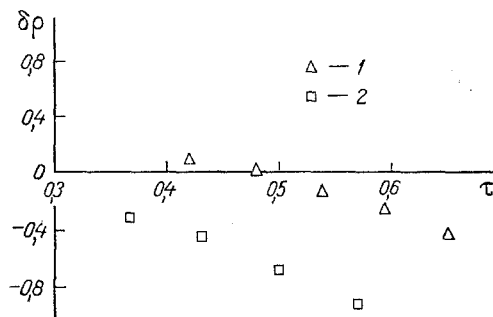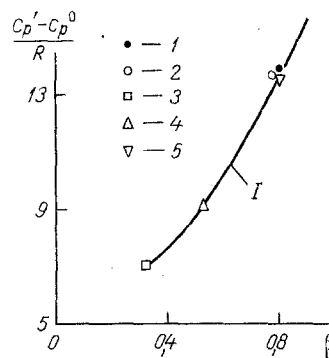
Fig. 2. Deviation of the experimental data from the computed values of the density (prediction): 1) $C_{36}H_{74}$ [11], P = 0.1013 MPa, $\beta = 1.418$; 2) 350-420°C fraction of Samotlor petroleum [12], P = 59.5 MPa, $\beta = 1.122$.

Fig. 3. Change in the configurational heat capacity $\Delta c_p'/R$ as a function of the correlation parameter β for $\tau = 0.5$: 1) $C_{18}H_{38}$, 2) $C_{17}H_{36}$; mangyshlak oil; fractions: 3) 120-130°C, 4) 240-250, 5) 350-420°C; I) calculation.

It should be kept in mind that the function (1) can be expanded in a series in the parameter β only for $\beta < 1$, so that the generalized ES (8) is valid for the interval $0 \le \beta < 1$. For some hydrocarbons and heavy petroleum fractions, however, the values of the correlating parameter β can be greater than 1 (see Fig. 2). The thermal properties of such substances, including also heavy petroleum fractions, can be described by interpolation into the interval bounded by the values of β_1 and β_2 for which the ES are known ($\beta_1 < \beta < \beta_2$). When the interval ($\beta_1$, β_2) is sufficiently narrow it is convenient to employ linear interpolation. In this case the coefficient of compressibility of the substance studied is determined by an expression of the form

$$z = \frac{\beta_2 - \beta}{\beta_2 - \beta_1} z_1 + \frac{\beta - \beta_1}{\beta_2 - \beta_1} z_2, \tag{11}$$

where (z_1, β_1), (z_2, β_2), and (z, β) are the coefficients of compressibility and the value of the correlating parameter of the first and second reference substances and of the substance under study, respectively.

The n-alkanes were chosen as the reference substances, since the parameter β for them varies over a wide range right up to $\beta = 2.6$ for C_{100}. On the other hand, and this is decisive, the thermal properties of n-alkanes are described with high accuracy by the ES (3) with the coefficients a, b, and c calculated from the generalized dependences for C_4-C_{100} [9]:

$$a = \frac{0,87374}{M + 11,31}, \quad b = a\frac{M + 44,741}{1799,8\,(M + 1)},$$
$$c = 1,8\lg(M - 2,016) - 6,454 \cdot 10^{-2}. \tag{12}$$

The density of the substance studied in accordance with (11) is calculated in the following order: for fixed P and T the vlaues of π and τ are determined and the values of the reduced density ω_1 and ω_2 are calculated for the chosen reference substances based on Eq. (6) with the help of the constants a, b, and c, found from (12), and correspondingly z_1 and z_2 are calculated using the formula

$$z = \frac{\pi\tau}{\omega}, \tag{13}$$

which follows from (4). Next the coefficient of compressibility z for the substance under study is calculated with the help of Eq. (11), and ω and then the density ρ are found from z based on (13). The PTρ properties found are represented in the form of the equation of state (3) with its own constants a, b, and c, determined according to the corresponding program and corrected based on the value of ρ_{20}.

TABLE 3. Coefficients in Equation (15) for the Reference Substances

Reference material	i	α	γ	δ
Ar	0	1,60865	3,20001	0,47223
n-C_4H_{10}	1	4,26020	12,93625	0,35212
$C_{11}H_{24}$	2	3,63894	57,98017	0,91739
$C_{20}H_{42}$	3	4,62888	112,62686	2,06010

TABLE 4. Quality of the Description (prediction) of the Isobaric Heat Capacity of Liquid Petroleum Products

Petroleum product	T, K	δc_p, %	$\delta c_{p_{max}}$, %
Malgobek petroleum [12]			
60—70 °C	293,57—318,57	0,49	—0,92
80—90	300,00—334,07	1,59	2,03
130—140	297,52—378,42	0,63	0,88
150—160	301,65—378,52	0,46	0,76
190—200	296,92—389,50	0,68	1,12
Troitsk-anastas'ev [12]			
130—140	313,83—353,94	2,27	2,74
160—170	299,98—353,74	0,67	1,18
Mangyshlak [19]			
120—130	293,15—473,15	0,68	—0,92
240—250	293,15—473,15	3,60	—5,35
330—340	303,15—473,15	3,65	6,65
Gas condensates			
Shatlyk [23]	270,54—371,02	2,49	—4,52
Shakhpakhty [23]	242,33—371,55	3,05	—5,14
Gugurtli	239,98—372,88	2,51	—6,00
Naip [23]	248,89—370,59	3,29	6,20
Gazli [23]	237,86—367,94	2,29	—3,85
Uchkyr [23]	244,42—369,67	2,08	5,12

Thus, it is now possible to predict the thermal properties of the liquid for which $\beta \geq 1$ over a wide range of parameters of state, determined by the range of applicability of Eq. (3).

This method was tested on a series of hydrocarbons and heavy petroleum fractions for which experimental PVT data are available. As an example we present Fig. 2. The average deviation of the computed values of the density from the experimental values [11] with the uncorrected values of the coefficients a, b, and c for $C_{36}H_{74}$ is $\bar{\delta\rho} = 0.8\%$. By correcting the parameters the average computational error can be reduced to 0.4%.

Figure 2 and Table 2 show that the predicted and experimental data on the density agree for the 350-420°C fraction of Samotlor oil.

Comparison of the results of the prediction of n-alkanes, petroleum fractions, and a number of other substances whose correlation parameter $\beta > 1$ shows that the error in describing the density is somewhat higher for petroleum fractions than for pure substances, and in predicting the properties based on Eqs. (3) and (11) for them $\bar{\delta\rho} = 0.5$-0.8% with $\delta\rho_{max} = 1.6$-1.8%.

To calculate the caloric properties of liquid substances in the single-phase region of states it is necessary to have data on the isobaric heat capacity on the bounding curve or some isoline (isobar, isochore). For petroleum fractions there exist a number of formulas that permit calculating the heat capacity c_p at one atmosphere based on data on ρ_{20}, M, and the average boiling point [2, 13, 14]. However, they describe a narrow temperature interval (below the boiling point) and are obtained based on generalization of the experimental data for a limited range of petroleum fractions, which limits the possibility of extending these formulas to a wide range of petroleum products (for example, for gaseous condensates and their fractions).

In this work we employ the theory of thermodynamic similarity, which permits predicting in the most general form (without using experimental data) the values of the isobaric heat capacity c_p' on the line of boiling of little-studied liquids.

TABLE 5. Constants in the Equation of State (3) and Eq. (17) of Ozeksuat Oil

Frac., °C	T_{cr}, K	$a \cdot 10^2$	$b \cdot 10^4$	c	A	m
60—70	518,82	0,945438	0,075566	3,17	1,582	0,314
80—90	541,95	0,866880	0,067038	3,26	1,605	0,314
110—120	573,62	0,752851	0,056107	3,43	1,618	0,325
140—150	604,35	0,655657	0,047301	3,58	1,663	0,310
170—180	634,44	0,573546	0,040144	3,72	1,673	0,321
190—200	654,20	0,527054	0,036208	3,81	1,688	0,319
210—220	672,32	0,481192	0,032603	3,90	1,708	0,324
240—250	702,47	0,429935	0,028322	3,99	1,714	0,331
270—280	729,43	0,381489	0,024646	4,07	1,755	0,327
300—310	750,66	0,329378	0,021087	4,14	1,823	0,320
340—350	783,84	0,285109	0,017816	4,23	1,899	0,314

Since for substances with the same value of β (β = idem) the law of corresponding states in the form (1) is satisfied, together with (8) the following should hold:

$$\frac{c_p' - c_p^0}{R} = A_0(\beta)\left(\frac{c_{p_0}' - c_{p_0}^0}{R}\right) + A_1(\beta)\left(\frac{c_{p_1}' - c_{p_1}^0}{R}\right) +$$
$$+ A_2(\beta)\left(\frac{c_{p_2}' - c_{p_2}^0}{R}\right) + A_3(\beta)\left(\frac{c_{p_3}' - c_{p_3}^0}{R}\right), \tag{14}$$

where the functions $A_0(\beta)$, $A_1(\beta)$, $A_2(\beta)$, and $A_3(\beta)$ are calculated based on the relations (9). The isobaric heat capacities c_p' and c_p^0 of the reference substances are taken at the same reduced temperatures τ.

The values of the configurational heat capacity of the basic substances were approximated by an equation of the form

$$\frac{c_p' - c_p^0}{R} = \alpha + \gamma(1 - \tau)^4 + \delta(1 - \tau)^{-1}, \tag{15}$$

which is valid for $\tau = 0.4$-0.9. The numerical values of the coefficients are presented in Table 3.

Equation (15) describes the data on c_p' of the reference substances [15, 16] with an error $\overline{\delta c_p'} = 1\%$ and not exceeding $\delta c_{pmax}' = 3\%$.

The value of c_p^0 for the substance studied was calculated using the formula [17]

$$\frac{c_p^0}{c_{pT=298,15}^0} = 1,1917 T_{red} - 0,190889 T_{red}^2 + 0,0118889 T_{red}^3 - \frac{0,0118236}{T_{red}},$$

$$\frac{c_{pT=298,15}^0}{R} = \frac{21,2016}{\rho_{red}} - 45,81936 + 146,74225\rho_{red} -$$
$$- 246,352\rho_{red}^2 + 195,8219\rho_{red}^3 - 59,466\rho_{red}^4. \tag{16}$$

To determine the accuracy of the calculation the relation (14) was used to predict the isobaric heat capacity c_p (at atmospheric pressure) of 44 petroleum fractions from eight deposits and 30 fractions of gaseous condensates from ten deposits, for which experimental data are available. The results of the prediction are presented in Table 4. As one can see from the table, the average error in describing c_p' is $\delta c_p' = 1.9\%$, and the maximum error is $\delta c_{pmax}' = 6\%$. The values obtained for c_p' for petroleum products were approximated by a dependence of the form

$$c_p' = A(1 - \tau)^{-m} \ [\text{kJ/(kg·K)}], \tag{17}$$

which is valid for $\tau = 0.4$-0.9.

It should be noted here that the formulas presented in [2] for calculating the configurational of heat capacity c_p' show that $\Delta c_p'/R$ is a linear function of β. This is qualitatively incorrect for heavy petroleum fractions and hydrocarbons for which the values of β are large. This is confirmed by the graph (Fig. 3) constructed based on the experimental data; the character of the dependence under study is obviously nonlinear for large values of β.

Analysis of the results obtained shows that the proposed generalized equation of state (8) and the linear interpolation (11), together with Eq. (5), can be used to calculate and predict the thermal properties, while the formula (14) together with the equation of state and the corresponding differential relations of thermodynamics can be used to predict the caloric properties of little-studied liquid hydrocarbons, in particular, petroleum fractions and gaseous condensates. The simplicity of the equations, combined with their theoretical proof, can be employed in computer-aided design systems for rapid and high-quality engineering calculations.

Table 5 gives the constants of the ES (3) and the equation for c_p' (17) for fractions of ozeksuat oil. The constants were obtained by the method of prediction and are adequate for calculating a complex of thermodynamic properties of the indicated petroleum fractions over a wide range of temperatures and pressures ($\tau = 0.4\text{-}0.9$, $P = 0.1\text{-}60$ MPa). Information on all fractions of domestic petroleum and gas-condensate deposits can be given rapidly in this form, if the density ρ_{20}, the molecular mass M, and the average boiling point for them are known.

NOTATION

Here $z = P/RT\rho$; P, T, and ρ, pressure, temperature, and density; k, Boltzmann's constant; N, Avogadro's number; M, molecular mass; T_{tr}, temperature at the triple point; c_p', c_p^0, isobaric heat capacity on the line of boiling in an ideal gas state; $z^{(0)}$, coefficient of compressibility of "simple" substances; $z^{(i)}$, correction functions; $\theta = T_b/T_{cr}$; ρ_{20}, density of the liquid at T = 293.15 K and P = 1 atm; $\rho_{pr} = 100\ \rho_{20}/M$; $T_{pr} = T/298.15$.

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RELAXATION TIME OF ELASTIC STRESSES IN LIQUIDS WITH SMALL
ADDITIONS OF SOLUBLE POLYMERS OF HIGH MOLECULAR WEIGHTS

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Measurements have been made of the characteristic times of dilute solutions of polyethylene oxide in water and of polyisobutylene in kerosene. Considerable deviations are observed between the experimental data and the predictions of the theories assuming complete distribution of the macromolecules in the solution.

Solutions of polymers of high molecular weights possess distinct viscoelastic properties even at extremely small concentrations of the dissolved material. These properties lead to a number of dramatic hydrodynamic effects, many of which are of practical value. In this connection, the reduction of the hydrodynamic resistance and heat transfer during flow in tubes and in external flows around solids and the increase in the filtrational resistance in porous media are quite well known.

Investigators of this area of hydromechanics have found considerable difficulties in the way of obtaining generalizations of the behavior which arise from the absence of quantitative methods of measuring the elasticities of polymer solutions of low concentrations. The known methods for the experimental determination of the elastic characteristics based on the linear response of the medium are not sufficiently sensitive. The minimum concentration of solutions whose elasticities can be investigated by these methods is 0.1%.

The difficulties can be surmounted to a certain extent if nonlinear effects are used. Among these methods there has been developed [1, 2] a relative method for determining characteristic times (the times of relaxation of the elastic stresses at small perturbation frequencies) which is applicable to solutions with polymer concentrations starting at a few parts per million. It is based on the transition from the laminar flow regime to the regime of elastic turbulence in channels of varying cross section.

In the present work measurements have been carried out by this method of the characteristic times of aqueous solutions of polyethylene oxide (PEO) and of solutions of polyisobutylene (PIB) in kerosene. The investigation of the elastic properties of the PEO solutions has been carried out in particular detail. In this case, the concentration and temperature of the solution and the molecular weight of the polymer have been varied. Industrial samples of PEO of domestic manufacture have been used, as well as samples manufactured by the firms Union Carbide (USA) and Meisei (Japan). Dissolution was carried out in distilled water. The molecular weight of the polymer was not varied in the investigations of the PIB solutions. The domestic industrial polymer P-200 was used, with technical-grade kerosene as the solvent.

The characteristic time was measured by using a collection of geometrically similar channels previously investigated in [1] which had square cross sections which varied peri-