NEW METHODS OF CALCULATING PETROLEUM-PRODUCT PARAMETERS

L. P. Filippov

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A unified approach is used in new methods of calculating P—V—T relations, specific heats, and thermal conductivities for petroleum products.

One can devise optimal methods of calculating the parameters of many different oil products if an appropriate methodology is used. There appear to be the following physically sound approaches to describing the properties of these objects.

1. Considering a petroleum fraction as a multicomponent hydrocarbon mixture in the light of chromatographic analysis. This approach is naturally justified in describing any property that is closely an additive sum of the properties of the components. An example is provided by the part of [1] dealing with the specific heats of narrow fractions. An advantage is that the approach has a logical structure, while the disadvantage is the complexity and the large amount of initial data needed.

2. A related approach [2] is one in which the set of components is considered in an essentially different fashion: the mixture is considered as a continuous manifold of components, and the mass distribution is used in characterizing the composition. It is clear that this approach is suitable only for any mixture consisting of related components, such as saturated hydrocarbons. This method has so far not been developed.

3. The third approach is to some extent an alternative. It is based on considering a mixture as a single substance: the single-liquid model in physical chemistry. Effective use of this model involves a knowledge of the fairly general laws describing the properties of the individual liquids. Here one can use regularities established by thermodynamic-similarity methods. In [1, 3-7] we find detailed examples indicating that this is one of the most fruitful approaches.

The approach considered here combines elements from the first and third of the above. It involves schematic incorporation of the composition together with the use of empirical regularities. We restrict ourselves here to minimal information on the composition (two numbers): data on the contents of aromatic hydrocarbons C_A and naphthenic ones C_N, i.e., information providied by standard chemical methods. These data are supplemented with a readily determined characteristic: the effective molar mass M. A large volume of empirical data indicates that these characteristics are quite sufficient to describe a wide range of properties for many different petroleum products. This approach is based on the regularities characteristic of alkanes. Experience has shown that deviations from the properties of alkanes are closely represented by the above elementary composition characteristics. It will become clear from what follows that by establishing composition—property relationships we can eliminate the composition characteristics from the equations for various properties and thereby derive new relationships and working algorithms.

We begin our discussion with a very simple but important characteristic of a petroleum product: the density. We use extensive data given in [1], which include the C_A and C_N for petroleum fractions and refining products with boiling points less than 200°C.

We describe the density at 20°C by considering the ratio ρ_{20}/ρ^A_{20}, where ρ^A_{20} is the density of the normal alkanes at that temperature as interpolated to the corresponding value of M for the oil product. We can use Smittel'berg's formula [8] for the dependence of ρ^A_{20} on M:

$$\rho^A_{20} = 0.8513 - \frac{18.374}{M+9.5}. \quad (1)$$

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The dependence of ρ_{20}/ρ^A_{20} on c_A and c_N is such that it can be represented closely as a function of the variable $c \equiv \frac{2c_A\% + c_N\%}{100}$ and a very weak function of M. The relation can be put as

$$\frac{\rho_{20}}{\rho^*_{20}} = 0.1736c + 0.9933 - \frac{0.0055}{2000c^4+1} + \left(\frac{0.107}{1,4-c}\right)^4, \tag{2}$$

where

$$\rho^*_{20} = \rho^A_{20}\left[1 + 1.8\cdot 10^{-3}\,\frac{5\left(\frac{M}{100}\right)^4 - 9}{3\left(\frac{M}{100}\right)^4 + 1}\right]. \tag{2a}$$

The main term in (2), the linear one, approximates this function in the range of c from 0.3 to 0.7, while the second characterizes the deviation from linearity for relatively small c, and the last for high ones. The term in the brackets in (2a) does not exceed 0.3%.

Figure 1a illustrates the fit of the approximation as a function of c. The standard deviation for the 64 experimental points from the calculated ones is 0.05%, or 0.04% for c in the range from 0.1 to 0.9. The latter quantity is only two times the error in measuring ρ_{20} in [1].

This relationship is quite satisfactory for practical purposes and also for calculating c, which is shown below to appear in other correlations; the error in determining c is then 0.2-0.3% absolute. It is clear that a relation of the type of (2) can be established also for the density at other temperatures; 20°C is in no way exceptional. We will not consider the corresponding equations here however, on the basis that the temperature coefficient of the density $\alpha = -\frac{1}{\rho_{20}}\frac{d\rho}{dT}$ can be determined from the same initial data (ρ_{20} and M) by means of an equation we have derived previously [4]:

$$\alpha\cdot 10^3 = x(1 + 5{,}38e^{-5x}), \tag{3}$$

where

$$x = \frac{8.8}{\rho_{20}M^{1/2}}. \tag{4}$$

Therefore, the density of a petroleum product as a function of temperature can also be determined from the initial data on c and M. To determine the pressure dependence of the density, we use a general relation between the isothermal compressibility of a liquid $\beta_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ and the reduced density:

$$\frac{\beta_T RT\rho}{M} = 120\left(\frac{\rho_c}{\rho}\right)^8. \tag{5}$$

Here ρ_c is the pseudocritical density for a mixture [6]. It has been shown [9] that (5) describes the compressibility of mixtures. Integration of (5) gives

$$\rho^9 = \rho_0^9 + \frac{P-P_0}{T}B, \tag{6}$$

where

$$B = \frac{1080M}{R}\rho_c^8, \tag{7}$$

and P_0 and ρ_0 relate to some selected state (to 1 atm, to P = 0, or to the saturation line). The scope for using (6) to describe the density on isotherms is related to that for finding ρ_c. We naturally consider ρ_c/ρ^A_c in order to reveal the regularities in ρ_c for oil products, as in the case of ρ_{20}. The following formula is recommended for the critical densities of the alkanes:

$$\rho^A_c = \frac{1 - 1{,}9\left(\frac{M}{100}\right) - 0.00942\left(\frac{M}{100}\right)^2}{3{,}878 - 7{,}4025\left(\frac{M}{100}\right) - 0.3342\left(\frac{M}{100}\right)^2}. \tag{8}$$

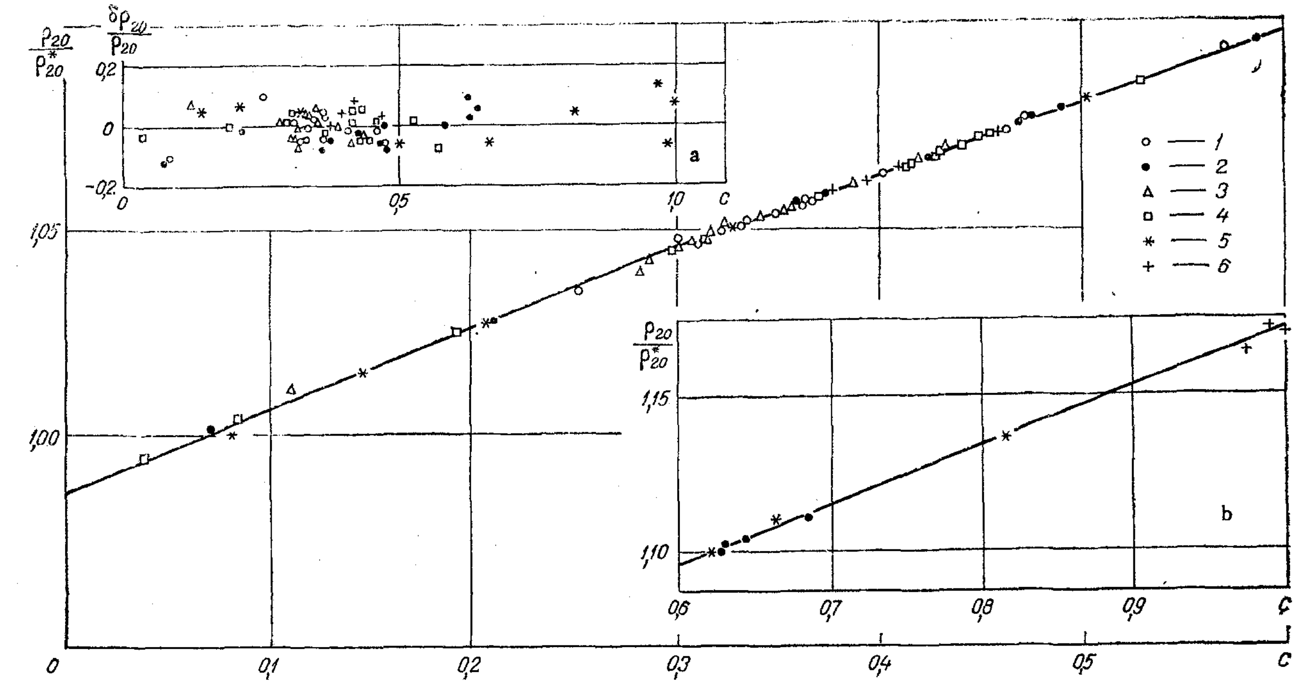

Fig. 1. Dependence of ρ_{20}/ρ^*_{20} on the variable $c = \frac{2c_A\% + c_N\%}{100}$: 1) Ozeksuat oil fractions; 2) Troitsk-Anastas'evo; 3) Uzen'; 4) Malgobek; 5) catalytic-cracking gasoline; 6) thermal cracking kerosene.

The dependence of ρ_c/ρ^A_c on c_A and c_N is such that the function is closely controlled by the same argument $c = \frac{2c_A\% + c_N\%}{100}$ and takes the form

$$\frac{\rho_c}{\rho^A_c} = 0{,}978 + 0{,}189c. \tag{9}$$

This resembles (2) in being less than one for $c < 0.1$, which is due to branched-chain alkane isomers.

It follows from (9) that the pressure dependence of the density is also defined by c and M alone, while eliminating c from (2) and (9) one can determine ρ_c from ρ_{20} and M. This means that specifying the density at 20°C and M in fact determines the entire P–V–T field, and it enables one to calculate the density as a function of temperature and pressure. This algorithm can be extended to high-boiling fractions not appearing in the initial correlations because of the lack of chemical-analysis data. This method is illustrated for a high-temperature fraction (290-300°C) for Uzen' oil. The initial data were $M = 236$, $\rho_{20} = 0.8137$ g/cm³ [1]. The results in Table 1 show that the calculations are effective for a wide temperature and pressure range. This method undoubtedly can substantially reduce the volume of measurements and expand the ranges of materials and states accessible to quantitative a priori calculation.

This composition dependence of the density can be used as an element in determining c_A and c_N if the relationship is combined with one we have derived from data on the refractive index n.

We introduce the quantity

$$^n\rho \equiv 0{,}0813\rho\,\frac{n^2+2}{n^2-1} \tag{10}$$

where ρ and n in (10) may be conveniently referred to 20°C. The values of $^n\rho$ for the normal alkanes C_5 to C_9 scarcely differ from ρ_c, while for the higher members of the series they represent an effective characteristic. The following formula can be used to approximate $^n\rho^A$:

$$^n\rho_A = \frac{1 - 6.712\cdot 10^{-2}M + 2.773\cdot 10^{-4}M^2}{3{,}2525 - 0{,}27047M + 1{,}1327\cdot 10^{-3}M^2} \tag{11}$$

TABLE 1. Comparison of Calculated Isotherms for the 290-300°C Fraction of Uzen' Petroleum with the Experimental Data ($\delta V/V$ is the standard deviation)

t, °C	P, MPa	V, cm^3/g (calc.)	V, cm^3/g [1]	t, °C	P, MPa	V, cm^3/g (calc.)	V, cm^3/g [1]
20	2,290	1,227	1,226	80	2,304	1,289	1,290
	5,373	1,224	1,223		5,490	1,285	1,286
	11,696	1,218	1,217		11,352	1,278	1,278
	21,273	1,210	1,209		19,729	1,268	1,268
	31,194	1,202	1,202		29,340	1,258	1,258
	39,879	1,195	1,196		38,687	1,249	1,249
	49,505	1,189	1,189		47,858	1,240	1,240
	58,769	1,182	1,183		56,210	1,233	1,233
		$\delta V/V$=0,06 %				$\delta V/V$=0,04 %	
140	2,446	1,358	1,362	200	2,272	1,434	1,447
	5,304	1,353	1,356		5,624	1,425	1,436
	11,283	1,342	1,345		11,029	1,411	1,420
	20,700	1,328	1,329		20,867	1,390	1,395
	29,601	1,315	1,315		30,360	1,371	1,376
	39,318	1,302	1,302		39,908	1,355	1,358
	48,973	1,291	1,291		48,808	1,342	1,344
	59,129	1,280	1,279		58,812	1,328	1,330
		$\delta V/V$=0,15 %				$\delta V/V$=0,52 %	

(ρ in g/cm³). The main effect on n_ρ/n_ρ^A comes from c_N:

$$\frac{n_\rho}{n_\rho^A} = 0.998 + 0.0705\,\frac{c_N}{100} - 1.0555\cdot10^{-2}\left(\frac{c_N}{100}\right)^2. \tag{12}$$

The standard deviation along the ordinate is 0.04% for $c_N > 10\%$, which corresponds to an inaccuracy in c_N of 0.6%.

On combining (12) and (2) we can determine c_A and c_N separately from data on ρ_{20}, n_{20}, and M. Therefore, the n-ρ-M method can be used to determine group compositions. This effective method of determining c_A and c_N makes it possible to use these values to describe other properties for products for which direct data on c_A and c_N are lacking. In particular, it is possible to extrapolate (2) and (12) to M > 170, for which we do not have composition data. Then one can compare the c_A and c_N with calculations on the C_A and C_N characteristics derived from the same information [8] (C_A and C_N characterize the relative numbers of carbon atoms in the aromatic and naphthenic rings correspondingly; essentially $C_A < c_A$, $C_N < c_N$). Calculations on c_N for the high-boiling fractions of the oils quoted in the caption to Fig. 1 indicate that C_N is lower than c_N by about 1% on average in concentration (for up to $c_N <$ 40%; for fractions of the Troitsk-Anastas'evo oil, for which $c_N > 40\%$, this difference is much larger). The calculated c_A for high-boiling products are close to the C_A but somewhat larger than them, on average by about 1% by concentration. As errors of about 1% are characteristic of the method of determining C_A and C_N [8], we can say that almost identical results are obtained in calculating the group and structure-group compositions within these limits. This method of composition determination is applicable up to M ~ 250.

The following regularities occur in the isobaric specific heat at atmospheric pressure on applying this method to the caloric properties (data taken from [1]). We consider the ratio c_p/c_p^A for 20°C. The specific heats of the normal alkanes are represented by the formula

$$c_p^A = 2.165 + \left(\frac{46}{M}\right)^4 \tag{13}$$

in J/g·K. The dependence of c_p/c_p^A on c_A and c_N is fairly weak and can be represented satisfactorily as a function of $c = \frac{2c_A\% + c_N\%}{100}$. We do not give the form of this function here, but instead consider the result from eliminating c from this function and (2), i.e., the dependence

$$\frac{c_p}{c_p^A} = f\left(\frac{\rho_{20}}{\rho_{20}^*}\right). \tag{14}$$

TABLE 2. Calculations on Specific Heat and Thermal Conductivity for Wide Fractions of Samotler Oil at 20°C.

Fraction	c_p, J/g·K		λ, W/m·K	
	[1]	calc.	[1]	calc.
LB –62	2,14	2,13	0,107	0,111
85—105	2,02	2,03	0,114	0,107
105—140	2,01	2,00	0,115	0,111
140—180	1,97	1,96	0,117	0,115
180—240	1,94	1,93	0,120	0,119
240—280	1,92	1,90	0,124	0,124
280—350	1,89	1,86	0,127	0,125
LB –120	2,05	2,06	0,112	0,109
120—180	1,98	2,04	0,116	0,114
LB –180	2,02	2,02	0,114	0,113
62—140	2,02	2,02	0,113	0,110
LB –195	2,00	2,02	0,115	0,115
195—270	1,93	1,91	0,121	0,121
270—420	1,87	1,85	0,128	0,131
140—240	1,95	1,92	0,118	0,116
240—350	1,89	1,87	0,126	0,126

TABLE 3. Calculations on Specific Heat and Thermal Conductivity for the 110-120°C Fraction from Ozeksuat Oil

t, °C	c_p, J/g·K		λ, W/m·K	
	calc.	[1]	calc.	[1]
19,82	2,01	2,01	0,114	0,113
29,89	2,06	2,05	0,112	0,111
38,01	2,09	2,08	0,110	0,109
55,51	2,17	2,15	0,106	0,105
70,22	2,24	2,21	0,103	0,102
73,38	2,26	2,22	0,102	0,102
87,82	2,32	2,28	0,099	0,099
96,38	2,36	2,32	0,097	0,097

The function of (14) can be approximated by the following for $\rho_{20}/\rho^*_{20} < 1.15$:

$$\frac{c_p}{c_p^A} = \frac{0.933085 - 1.59927\left(\frac{\rho_{20}}{\rho^*_{20}}\right) + 0.69105\left(\frac{\rho_{20}}{\rho^*_{20}}\right)^2}{1 - 1.72305\left(\frac{\rho_{20}}{\rho^*_{20}}\right) + 0.74947\left(\frac{\rho_{20}}{\rho^*_{20}}\right)^2}. \tag{15}$$

For $\rho_{20}/\rho^*_{20} < 1.1$ one can use the very simple formula

$$\frac{c_p}{c_p^A}\,\frac{\rho_{20}}{\rho^*_{20}} = 0{,}965. \tag{16}$$

The standard deviation of the data from values given by (15) is about 1% for oil fractions. From (15) one can calculate the specific heat simply from data on ρ_{20} and M. This method gives good results not only for narrow fractions but also for wide ones, as can be seen from Table 2, which gives calculations on broad (technological) fractions from Samotlor oil. There is a standard deviation of 1% between the calculations and the experimental data. Good results are obtained also for the specific heats of wide fractions of oil-product mixtures. For example, for oil mixtures from the Uzen' and Zhetebai deposits, the above standard deviation of the calculations from the experimental data of [1] is 0.7%. The method is also applicable for petroleum oils; the calculation error is also about 1%. Therefore, this method is uniquely applicable to a wide variety of oil products while being based on the minimal empirical information, while its accuracy is not inferior to that of the best methods represented by different formulas for different materials [10].

The above applies to the specific heats at 20°C, but it is clear that this temperature is not exceptional and similar calculations can be performed for other temperatures. In addition to the direct approach there is a possible simpler approach to the temperature dependence of the specific heat. This is based on the decisive role of volume in the description of liquid properties [11]. Accordingly, the change in any property along the saturation line is determined primarily by the volume change, so we assume that more general regularities are

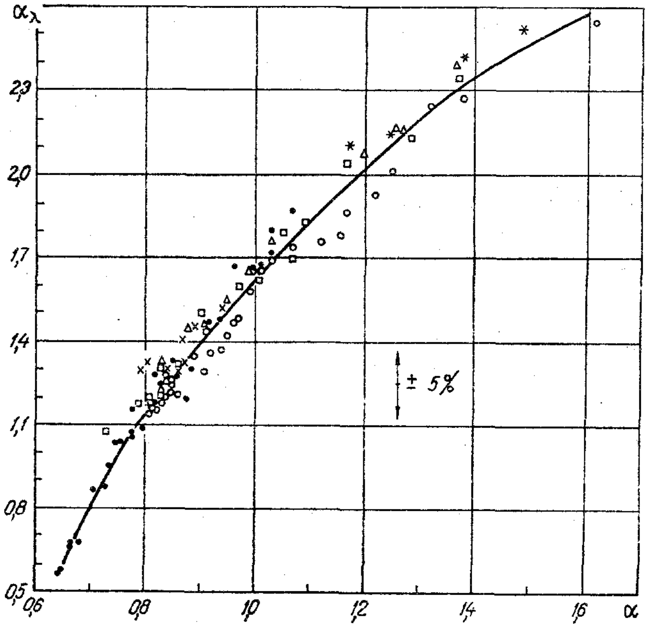

Fig. 2. Relation between the temperature coefficients of thermal conductivity and density. Symbols as in Fig. 1.

TABLE 4. Calculations on Specific Heat and Thermal Conductivity for the 310-320°C Fraction of Troitsk-Anastas'evo Oil

t, °C	c_p, J/g·K		λ, W/m·K	
	calc.	[1]	calc.	[1]
25,96	1,78	1,78	0,116	0,115
32,59	1,80	1,83	0,115	0,114
49,51	1,85	1,86	0,113	0,112
53,72	1,86	1,87	0,113	0,112
63,48	1,89	1,90	0,111	0,110
80,1	1,93	1,95	0,109	0,108

provided by $c_p(\rho)$ rather than $c_p(T)$, so there should be a correlation between the temperature coefficient of the specific heat α_c and that for the density α. The data [1] show that the correlation for oil-product fraction is

$$\alpha_c \approx 2\alpha. \tag{17}$$

The spread of the data around (17) is approximately 10% and is mainly random. If we assume that the correlation of (17) applies with a probable error of the same order, then the inaccuracy in calculating c_p from (17) is about 2% per 100°K of extrapolation. This is quite acceptable as a simple approximate method of deriving the temperature dependence of the specific heat for oil fraction. We give examples of calculations of $c_p(T)$. Table 3 gives calculations for the 110°-120°C fraction from Ozeksuat oil (the widest temperature range has been examined for this). The initial data are $M = 110.3$ and $\rho_{20} = 0.7372$ [1]. We used (3) to determine α. The mean calculation error is 1.4%, maximal 2%. Table 4 gives analogous calculations for a high-boiling fraction (310-320°C) from Troitsk-Anastas'evo oil ($M = 256$, $\rho_{20} = 0.8980$); mean error 1%, maximal 1.8%.

We first take the thermal conductivity λ in examining the scope for applying this method to the kinetic characteristics. We use the following formula for λ/λ^A at 20°C in considering the ratio:

$$10^3\lambda^A = 112.6 + 14.4\,\frac{M}{100} - \frac{3.5}{\left(\frac{M}{100}\right)^4 + 0.09}, \tag{18}$$

which is based on the data of [1]. The dependence of λ/λ^A on c_A and c_N is not very pronounced, so it is difficult to give preference to either of the forms of the relationship: $\lambda/\lambda^A = f(c_N)$ or $\lambda/\lambda^A = f(1.5c_A + c_N)$. In the first case, eliminating c_N gives the simple formula

$$\frac{\lambda}{\lambda^{A}} = 0.95 - 3.83\left(\frac{{}^{n}\rho_{20}}{{}^{n}\rho_{20}^{A}} - 1\right), \tag{19}$$

while in the second we get the more complicated

$$\frac{\lambda}{\lambda^{A}} = 1 - 3.83\left(\frac{{}^{n}\rho_{20}}{{}^{n}\rho_{20}^{A}} - 1\right) - 0.7\left(\frac{\rho_{20}}{\rho_{20}^{*}} - 1\right). \tag{19a}$$

For the 100 products for which data are given in [1], (19) gives the standard deviation of 2.6%, while (19a) gives 2.5%. For (19) in that case we eliminated two fractions of the Troitsk-Anastas'evo oil, and for (19a) three cracking gasoline fractions. Formula (19a) gives somewhat better results in describing the conductivities of petroleum oils [4.6% by comparison with 6% for (19)]. Both expressions reproduce the thermal conductivities of gas-condensates with about the same precision (2.5%). They are also suitable for wide-fraction products. As an example, Table 2 gives calculations for technological fractions from Samotlor oil; calculations from (19) deviate from the data of [1] by 2.5%.

To examine the temperature dependence of the conductivity, we use the arguments above for the temperature dependence of the specific heat, i.e., that the temperature dependence of the specific heat, i.e., that the temperature coefficient α_λ is correlated with that for the density α. Figure 2 shows that there is a close correlation between these quantities. For practical purposes we can combine this relationship with the dependence of α on $\rho_{20}M^{1/2}$. We then get the simple formula

$$10^{3}\alpha_{\lambda} = \frac{16}{\rho_{20}M^{1/2}} - 0.1. \tag{20}$$

Tables 3 and 4 give calculations on the temperature dependence of the conductivity from (19a) and (20) (the same examples as for the specific heat). On the whole, these methods of calculating the conductivity are comparable with the best recommended in [12].

We have previously considered [5] the viscosities of oil products by the same method. We found that ν_{20}/ν^{A}_{20} (where ν is kinematic viscosity) is close to one for products having $M < 160$ (the values of ν for them differ by a factor three). The mean-square deviation was about 8%. No substantial correlation between this ratio and c_A or c_N has been established. The existence of the simple regularity $\nu_{20}/\nu_{2V}^{0} \simeq 1$ enables one to estimate the viscosity in a simple fashion. In [5] it was found that similarity arguments imply a correlation between ν and the combination x in (4), which is convenient in calculating the viscosity from simple information. It has been shown [7] that analogous relations are applicable in calculating the viscosities of gas condensates.

We have thus considered the regularities in the thermodynamic and transport parameters of oil products as deviating from the parameters of alkanes and as correlated with the composition characteristics, with the subsequent eleminiation of these characteristics in expressions for the correlations between different properties. This has given a method of calculating P—V—T relations for oil products from data on the density at 20°C and the molar mass, and methods have been proposed for calculating the specific heat, thermal conductivity, and viscosity. There is every reason to assume that this approach is not yet exhausted and that it will probe capable of providing more methods of calculating various properties for a wide class of oil products.

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TIME-DEPENDENT VISCOELASTIC CHARACTERISTICS OF MIXTURES OF POLYBUTADIENES DIFFERING IN MICROSTRUCTURE*

Yu. G. Yanovskii, G. V. Vinogradov, and L. I. Ivanova

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A dynamic method has been used to examine the rheological behavior of binary mixtures of polybutadienes (PB) differing in microstructure.

One can use the viscoeleastic behavior of a polymer in small-amplitude periodic deformation (dynamic testing) to describe features of the transition from one physical state to another on the basis of nondestructive tests (for fluid, rubber-type, leathery, and vitreous states), and in that way one can determine changes in characteristics such as the accumulation modulus G' and the loss modulus G''. From the practical viewpoint, there are two experimental approaches: with varying temperature and constant frequency or with varying frequency at a fixed temperature. In both cases, one obtains a rheological evaluation of the state and defines the limits to it from measurements on the moduli.

Fundamental parameters such as the maximum Newtonian viscosity η_0, the elasticity A°_G, and the quasiequilibrium reversible shear compliance J°_e are very important to the viscoelastic behavior of a polymer system. The linear theory indicates that these quantities are usually derived from the dependence on frequency ω of the above moduli in the region of the flowing state, i.e., where G' is proportional to ω^2 and $G'' \sim \omega$. According to [1], this corresponds to deforming the polymer with the structure unchanged. Then

$$\eta_0 = \lim_{\omega \to 0} G''/\omega;\ A_G^0 = \lim_{\omega \to 0} G'/\omega^2;\ J_e^0 = A_G^0/\eta_0^2.$$

However, a wide-ranging rheological technique is required to attain the flow state for a macromolecular system, particularly at low frequencies, which involves considerable difficulties. New scope for estimating the initial parameters is opened up by the temperature dependence of the moduli recorded at relatively low frequencies to determine with high accuracy not only the absolute values of η_0, A°_G in a single experiment in the flow state but also the temperature dependence of these. Therefore, the simpler experiment (temperature scanning at constant frequency) provides a large volume of very important information.

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Topchiev Petrochemical Synthesis Institute, Academy of Sciences of the USSR, Moscow.
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