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16. Abstract

The rheological properties of standard fuels and oils are discussed. Temperature relations and relative variation of the Rao constants are determined by ultrasonic measurements for petroleum fractions, fuels, and lubricating and hydraulic oils. The participation of solvation and association processes in the variation of the rheological properties is confirmed.

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ASSOCIATION-SOLVATION CHARACTERISTIC OF FUELS AND LUBRICATING AND HYDRAULIC OILS

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SUMMARY

An attempt is made to give a treatment, more complete from the point of view of the method and interpretation, of phenomena (and their causes) concerning the rheological properties of standard fuels and oils. Temperature relations and relative variation of the Rao constants R and W are determined by ultrasonic measurements for petroleum fractions, fuels, and lubricating and hydraulic oils. The relations R(T) show the occurence of association-solvation processes connected with the structural composition and the physical and chemical properties of the product. They confirmed the participation of solvation and association processes in the variation of its rheological properties.

1. INTRODUCTION

We have shown in the work /1/ that there is a possibility of utilization of results of the ultrasonic studies of naphtha hydrocarbon fractions for studies of standard fuels and lubricating and hydraulic oils. We are concerned here with the Rao constants R and W:

$$R = \sqrt[3]{c}\,\frac{M}{\varrho} \qquad (1)$$

$$R(T) = \frac{R_0}{R_T} \qquad (2)$$

$$W = R^{6/7} M^{1/7} \qquad (3)$$

$$W(T) = W_0/W_T \qquad (4)$$

where: R_o and R_T and W_o and W_T - the Rao constants at reference temperatures and temperatures of studies

M - molecular weight

ϱ - density

c - ultrasonic speed

T - temperature.

It is also necessary to take into account the dependence of the speed of ultrasound on free average distances J between areas of molecules, as given by Jacobson /2, 3/

$$c\varrho^{1/2}J = K \quad \text{or} \quad J = \frac{K}{c\varrho^{1/2}} \qquad (5)$$

where K - a constant dependent on temperature, being 588 for 0°C, 618 for 20°C, 631 for 30°C. According to Jacobson, average intermolecular distances J, verified by the use of other methods, /126 differed only in the limits of several percent /2, 3/.

On the basis of a relationship obtained in the work of Kurtz and Sankin /4/, the length of a molecule of n-parafin hydrocarbon can be calculated from the equation

$$D = 1{,}27n + 2 \qquad (6)$$

where n - number of carbon atoms, assuming that the average distances between molecules are of the order of the dimensions of molecules. This relationship allows to verify the distances obtained from the relationship of Jacobson for n-paraffin fraction. Particularly interesting was found the association-solvation characteristic (AS) determined with the aid of relation (2).

It can be assumed that subtle phase properties of fuels and oils at temperatures near solidification can be responsible partly and sometimes totally for a number of undesirable physico-chemical - rheological changes. The effects of appearance of the mentioned changes are generally known in the exploitation of machines and facilities. Intensification of this type of phenomena, particularly in the systems of automatic regulation, control, fuel supply, etc., may have a catastrophic character. According to data /5/, the reasons for aerial catastrophies in the period 1965-1969 were to 10% interruptions in the inflow of fuel caused by the blockage of filters. The material losses suffered because of the appearance of above discussed phenomena have not been analyzed separately; they are submerged within general summations covering losses arising as a result of application of improper fuels and lubricating-hydraulic oils.

The occurrence of improper functioning of facilities, engines, etc, caused by unsuitable use properties of fuels and lubricating-hydraulic oils, is tried to be prevented by introduction of constructional-technological changes and by requiring that working fluids have suitable physicochemical use properties. Requirements of this type must form a compromise. When demanding a new quality of working fluid and the resultant consequences one should bear in mind that a number of processes and phenomena arising under conditions of use of working fluids are still not fully known. At present, particularly important are becoming the problems of the transport of working fluid through gaps, connected directly with filtration, automatic regulation and the work of servomechanisms.

Problems of the transport of working fluid through gaps are connected with rheological properties of liquid systems: one phase - liquids physically homogeneous, and multiphase - liquids containing suspensions of "foreign" bodies, i.e., solids, liquids or gases of colloidal dimensions, and microsuspensions. In the majority of cases, the applied liquids exhibit properties of non-Newtonian fluids, either by their nature or as a result of their work conditions (lowered temperatures, increased pressures).

Disturbances occurring in functioning of facilities should not be connected only with the presence of a solid phase of the type of mechanical impurities. One should consider also a possibility of the phase or pseudophase changes of the physical state of liquid. In such cases, there can appear, among others, separation of integral components of the liquid in the form of micro- or submicro-suspensions. Probably there will be phases: microcrystalline, colloidal, and the so-called mesophases with undetectable degree of division at microscopic magnifications (of the order of 2000) /7, 7a, 8, 9, 10 and 11/. The colloidal phases and mesophases belong to the systems with developed AS groups /11, 12 and 13/. The formation of AS systems occurs as a result of interactions between particles of liquid, or liquid and solid - electrostatic interactions, ion bonding, Van der Waals forces or hydrogen bonds. The appearance of colloidal, microcrystalline and mesophase systems was established in residual naphtha fractions /14/.

Among naphtha hydrocarbons, n-paraffins are considered /127 to form most easily, under normal conditions, the AS systems of colloidal or crystalline form. As the boiling temperature of naphtha fractions increases, so increases the number of hydrocarbons which are higher melting and have increasing degree of the complexity of their structure. This complexity of structure of hydrocarbon molecules entails the growth of their asymmetry, polarity and ability to form AS systems. The AS systems can be formed also by aromatic and naphthenic hydrocarbons, particularly those that contain long n-paraffin side chains. Naphtha fractions which are components of fuels and oils may contain strongly polar, natural organic heterocompounds, and asphaltenes and resins /15 and 16/. The polarity of these compounds is usually considerably higher than that of hydrocarbons. As the range of boiling fractions and their molecular weight increases, so do the amounts and dipole moments of these compounds.

In standard naphtha products, the contents of high-melting hydrocarbons, heterocompounds, asphaltenes and resins is limited. It does not mean, however, total elimination of these components, both because of technological-economic reasons and because their small amounts are left intentionally (e.g., heterocompounds of sulfur type are natural inhibitors of oxidation, some agents are improving lubricating properties decreasing the possibility of crystallization of n-paraffin). Many synthetic or natural agents are introduced into fuels and lubricating - hydraulic oils to improve their use properties: inhibitors of corrosion and oxidation, additives improving lubricity, agents improving rheological properties, etc. To fulfill their functions, the additives of this type contain various chemical groups: amino, hydroxyl, ester, ether and diether, acid groups neutralized with basic metals, metaloorganic entities and halogens. Some of them form structurally complex molecules of large mass, or are even polymers of average molecular weight reaching 500,000. These additives are characterized by large polarity, and in the case of viscosity additives - a degree of association. After their introduction into a fuel or oil, one should expect the appearance, or increase, of the AS systems, particularly at lowered or moderate temperatures. The presence of the mentioned compounds in mineral oils and fuels may cause the formation of AS systems independently of the composition of hydrocarbon. For these reasons, one should expect difficulties in interpretation of the reasons for the appearance of AS systems.

The studies described below were realized on the basis of measurements of the velocity of ultrasounds as a function of temperature c(T), under normal pressure, at frequency 10 MHz, by means of an ultrasonic interferometer UI-8, by the method developed at the Aviation Institute /17/. The analyzed hydrocarbon fractions were those separated from naphtha fuels and the product 90/300 /1 and 18/, and standard naphtha fuels, mineral oils and synthetic aviation oils. Molecular weights were determined by ebuliometry /19/, the density at 20°C - with pyknometer following PN-66/C-04004, and the group composition by the $n - \varrho - M$ and GL methods /20 and 21/. For some products, values of molecular weights were estimated, but it had no major effect on relative changes of the value of R_o/R_T.

2. RESULTS OF STUDIES, DISCUSSION

2.1. Fractions

The AS effects of analyzed fractions were estimated on the basis of relation (2). Both for fractions extracted from the fuel P-2, and for motor oils A-5 and R, the largest changes $R_o/R_T(T)$ were observed for aromatic fractions VI and VII, containing one- and multi-ring aromatic hydrocarbons (Table 1, /128 Figures 1 and 2). They were characterized by the relatively largest lowering of R_o/R_T - the largest instability of AS forms. Low freezing temperatures of these fractions (less than -50°C) indicated the absence of high-freezing hydrocarbons which could cause a large AS effect. It would appear, therefore, that the AS effects could be caused by the presence of relatively large amounts of strongly polar heterocompounds, particularly of sulfur compounds, or possibly of resin - tar type /22/. The components of resins are polycondensates of oxygen compounds, unsaturated or naphthenic acids or other oxycompounds. These substances are adsorbed on silica gel at least as strongly as aromatic hydrocarbons. In this connection, the use of chromatographic method for partitioning into fractions resulted in grouping of these compounds in aromatic fractions /18/. The presence of these /131 substances was confirmed, among others, by distribution of the contents of sulfur: in fuels - 0.3 to 0.6%, in parafin-naphthene fraction I - 0.01 to 0.09%, and in aromatic fractions VI and VII - from 0.04 to more than 3%. No presence of sulfur in the remaining fractions was established.

In fractions II and III from fuels A-5 and R, the determined values $R_o/R_T > 0$ increased only slightly with the temperature (Table 1, Figures 1 and 2). It indicated the presence or formation of AS systems. In the case of n-paraffinic fraction II, the formation of AS was explained by the presence of high-freezing (11°C) n-paraffin hydrocarbons. In isoparaffin -

TABLE 4. Average intermolecular distances for standard fuels and oils

	PRODUCT	T_k	J_0	J_{20}	J_{30}
I	Paraffin-naphthenes separated from:				
	fuel P-2	-60	0.4715	0.5315	0.5625
	motor oil R (USSR)	- 8			
II	n-paraffins (carbamide extract) separated from:				
	fuel P-3	-32	-	0.5589	-
	fuel P-3 (USSR)	-31	-	0.5592	-
	motor oil R (USSR	11	-	0.5151	-
	motor oil A-5 (USSR)	11	-	0.5083	0.5360
III	isoparaffin-naphthenes (after carbamide extraction) separated from:				
	fuel P-3	-70	-	0.5560	-
	motor oil J	-63	-	0.4919	-
	motor oil A-5 (USSR)	-70	0.4473	0.5000	0.5274
IV	isoparaffin-naphthenes (thiocarbamide extract) separated from:				
	fuel P-2	-70	0.4601	0.5166	0.5462
	motor oil R (USSR)	-70	-	0.5047	-
V	isoparaffin-naphthenes (after thiocarbamide extraction) separated from:				
	fuel P-2	-70	0.4697	0.5304	0.5611
	motor oil J	-60	-	0.4891	-
	motor oil A-5 (USSR)	-60	0.4437	0.4972	0.5238
	motor oil R (USSR)	-70	-	0.4949	-
	motor oil DS	-60	-	0.5224	-
VI	monocyclic aromatics n=1.48-1.53 separated from:				
	fuel P-2	-60	0.4169	0.4653	0.4898
	motor oil J	-35	-	0.4494	-
	motor oil R (USSR)	-65	-	0.4501	-
VII	polycyclic aromatics n>1.53 separated from:				
	motor oil J	-50	-	-	-
	motor oil A-5 (USSR)	-60	0.3825	0.4235	0.4444
	motor oil R (USSR)	-63	-	0.4275	-

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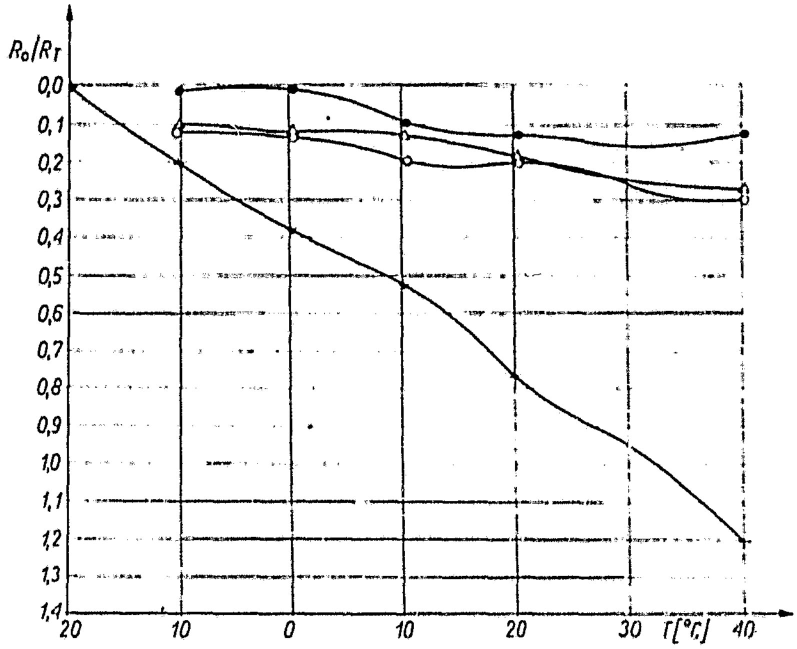

Figure 1. Relation $R_o/R_T(T)$ for hydrocarbon fractions of fuel P-2. Fractions: I – o , IV △, V ●, VI x .

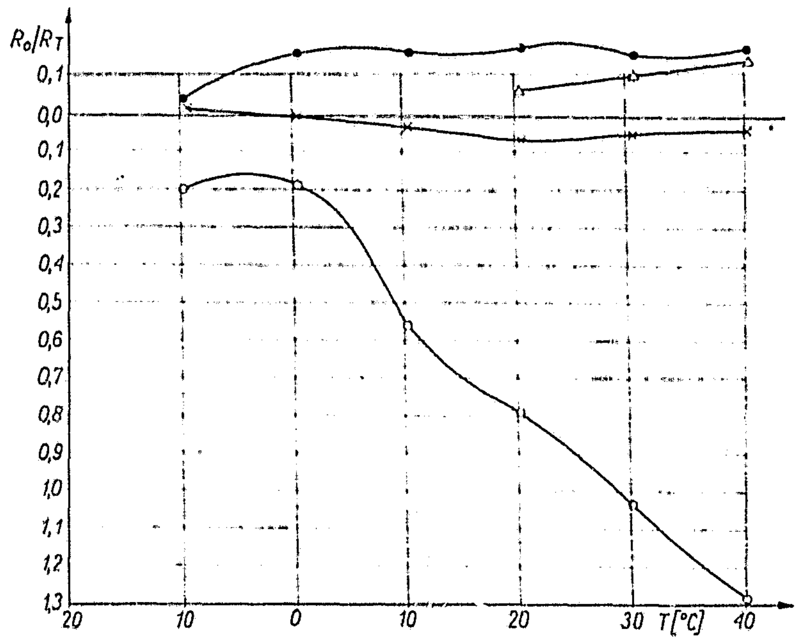

Figure 2. Relation $R_o/R_T(T)$ for hydrocarbon fractions of motor oil A-5. Fractions: II △, III ●, V x, VII o

fraction	J_{20}	fraction	J_{20}	fraction	J_{20}	fraction	J_{20}	fraction	J_{20}	fraction	J_{20}	fraction	J_{20}	fraction	J_{20}
C	0,4903	D	0,4837	E	0,4567	F	0,4411	H	0,4370	I	0,4293	K	0,4182	L	0,4138
C_8	0,4998	D_5	0,4870	E_4	0,4653	F_2	0,4548	H_{11}	0,4446	I_2	0,4199	K_2	0.4260		
C_{12}	0,4920	D_{10}	0.4226	E_8	0.4855	$F_{5,7,9}$	0,4600	H_{17}	0,4465	I_5	0,4236	$K_{7,10}$	0.4259		
C_{20}	0,4859	D_{14}	0,4862	E_{11}	0,4640	$F_{11,14,15,16}$	0,4605	H_{28}	0.4326	I_9	0,4279	K_{21}	0,4268		
C_{22}	0.4903	D_{15}	0,4871	E_{20}	0,4569	F_{29}	0.4490	H_{34}	0,4267						
C_{28}	0.4690	D_{24}	0,4649	E_{21}	0,4523	F_{35}	0,4296								
C_{32}	0,4924			E_{38}	0,4512										
				E_{39}	0,4468										

Table 2. Average intermolecular distances for fractions of aromatic product 90/300

no.	relation	correlation coefficient	coefficients of regression equations *a*	*b*	*c*
	fractions I-IV n-paraffins, isoparaffins, naphthenes				
1	$J(R)$	−0,7929	0,6210	$-0,3867 \cdot 10^{-4}$	–
2	$\lg J(R)$	−0,7947	−0,20061	$-0,3208 \cdot 10^{-4}$	–
3	$\lg J(\lg R)$	−0,7897	0,34370	−0,18426	–
4	$J(\lg R)$	0,7998	0,44870	$1,01808 \cdot 10^{-4}$	$-2,7561 \cdot 10^{-8}$
	fractions VI-XIII mono and polycyclic aromatics				
1	$J(R)$	0,5878	0,54691	$-0,4781 \cdot 10^{-4}$	–
2	$\lg J(R)$	0,5892	−0,25477	$-0,4571 \cdot 10^{-4}$	–
3	$\lg J(\lg R)$	−0,6219	0,43475	−0,23697	–
4	$J(\lg R)$	0,7155	0,954229	$-4,32352 \cdot 10^{-4}$	$8,80867 \cdot 10^{-8}$
	for all fractions paraffin-naphthenic and aromatic				
1	$J(R)$	0,1614	−0,44122	$0,1301 \cdot 10^{-4}$	–
2	$\lg J(\lg R)$	0,1297	−0,4931	0,05058	–

Table 3. Correlation-regression characteristics of fractions I-XII

-naphthene fraction III there were no high-freezing hydrocarbons (freezing temperature less than -70°C) and there were no sulfur compounds.

Values of Jacobson indicators J confirmed the AS degree of analyzed samples (Tables 1 and 2). The shortest intermolecular distances were found for aromatic fractions. In the case of fractions of aromatic hydrocarbons, including also those separated from the product 90/300, a correlation was established between J and $R_0/R_T(T)$ (Table 3, Figure 3). Also in this case, an increase of the boiling temperature increased the probability of the appearance of more polarized compounds.

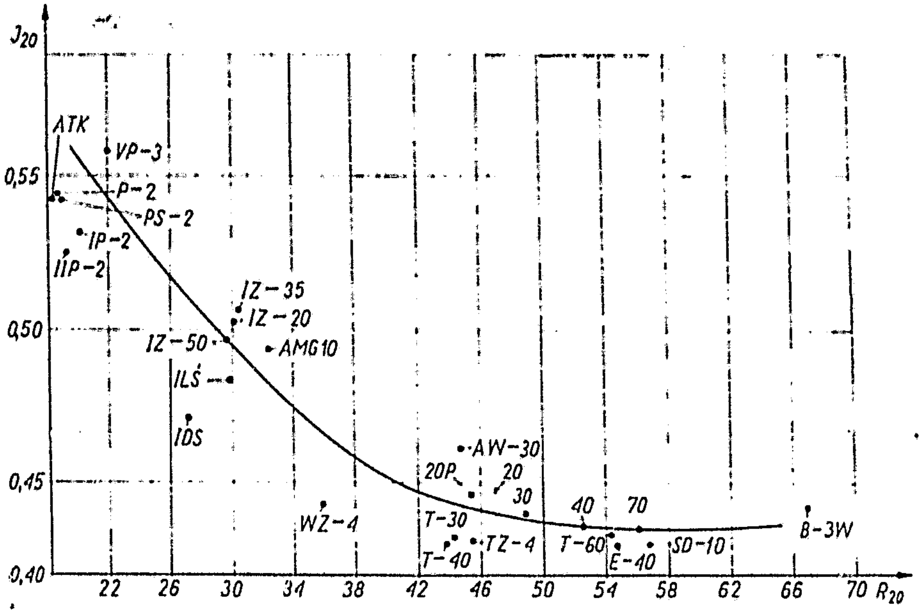

Figure 3. Dependence J(R) for fractions, fuels and lubricating-hydraulic oils

2.2. Fuels

In the group of jet fuels, ATK fuel can be considered as the best refined product - having negligent amount of resins and aromatic hydrocarbons. Besides, it was "the lightest" fuel. It means that it should contain the least amount of componnents responsible for AS effects. The next was P-2 fuel. Although it was "the heaviest" among fuels investigated in the group of jet fuels, it had lower contents of aromatic hydrocarbons and resins than PS2 and P-3 fuels /18, 23 and 24/. Results of estimation of the AS degree (Figure 4) placed jet fuels in the following order of the increasing AS tendency: ATK < P-2 < PS-2 < P-3. The values of constants J did not correlate with values $R_0/R_T(T)$, nor with other physico-chemical properties of jet fuels.

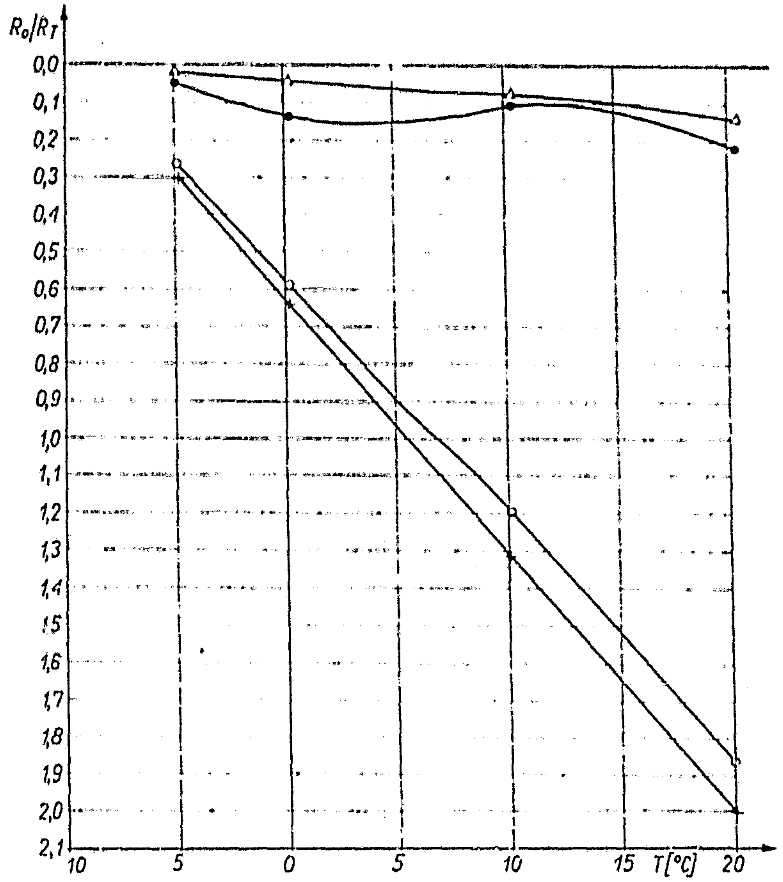

Figure 4. Dependence $R_o/R_T(T)$ for aviation jet fuels.
Legend: P-2° - ●, PS-2 - o, P-3 - x, ATK - Δ

In the group of motor oils, an increase of the AS effects - that is lowering of $R_o/R_T(T)$ - and the course of J values (their decrease) correlated with an increase of freezing temperatures and ranges of boiling of these fuels (Tables 4 and 5, Figure 5). In the case of IDS fuel, the lack of correlation between AS features and freezing temperature can be explained by the presence of lighter fractions in this fuel. Similar results were obtained for heating oils. /132

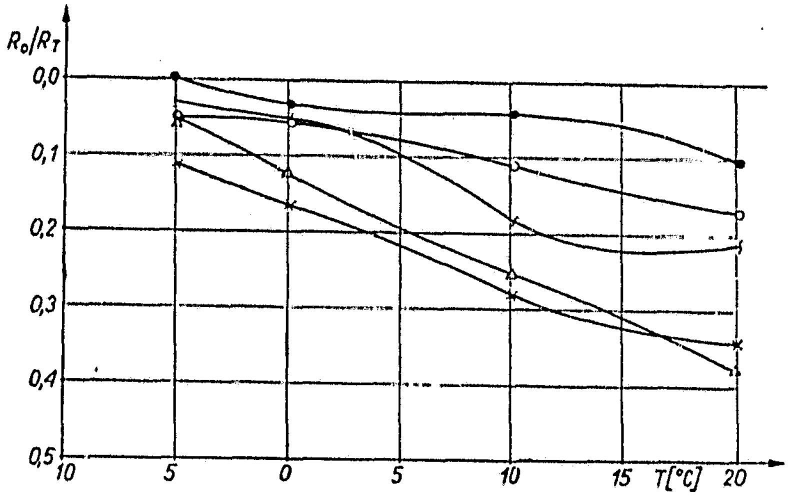

Figure 5. Dependence $R_o/R_T(T)$ for motor (propulsion) oils.
Legend: ILS — x, IZ-20 — o, , IZ-35 — Δ, , IZ-50 --- s, IDS — ●

2.3. Oils

For mineral oils not containing additives the degree of AS was found to be larger than for fuels (Table 8, Figure 6). The lowering of R_o/R_T with the rise of temperature was taking place faster, and correlated with the rise of freezing temperature and viscosity of oils. The near linearity of the course of relation $R_o/R_T(T)$ for this group of oils appears interesting. The values of constants J correlated with AS characteristics. In order to confirm the effect of structural composition, and in particular of the effect of high-freezing n-paraffin hydrocarbons, the previously analyzed turbine oil T-60 was supplemented with 10% of n-paraffin fraction II /1/. Fraction II was separated from motor (propulsion) oil R. Its freezing temperature was about 18°C. An increase of the AS degree, in comparison with pure oil, was established (Table 6, Figure 7). This confirmation explained some suggestions regarding irregularities of the courses of $c(T)$ and $K_s(T)$ for this type of products /7, 7a and 17/.

product	$J_0 \cdot 10^{-2}$ Å	$J_{20} \cdot 10^{-2}$ Å	$J_{30} \cdot 10^{-2}$ Å
1	2	3	4
fuel P-2	0,4656	0,5253	–
PS-2	0,4851	0,5446	–
P-3	0,4856	0,5466	–
ATK	0,4808	0,5442	–
motor oil ILS	0,4327	0,4840	–
IZ-20	0,4432	0,4964	–
IZ-35	0,4470	0,5062	–
IZ-50	0,4494	0,5048	–
IDS	0,4346	0,4718	–
heating oil I	0,3752	0,4213	–
II	0,3536	0,4164	–
turbine oil T-30	0,3903	0,4328	0,4547
T-40	0,3867	0,4318	0,4536
T-60	0,3898	0,4361	0,4583
compressor oil WZ-4	0,3914	0,4440	0,4664
TZ-2	0,3989	0,4430	0,4650
TZ-3	0,3933	0,4361	0,4582
TZ-4	0,3896	0,4321	0,4527
SD10	0,3779	0,4302	0,4540
hydraulic oil AMG10	0,4397	0,4941	0,5208
20P	0,4019	0,4487	0,4715
20	0,4015	0,4474	0,4714
30	0,3969	0,4408	0,4630
40	0,3941	0,4388	0,4617
70	0,3920	0,4384	0,4860
Shell Tellus 11	0,4348	0,4857	0,5135
27	0,4238	0,4535	0,4776
29	0,4173	0,4521	0,4754
33	0,4213	0,4498	0,4710
69	0,3925	0,4383	0,4606
72	0,4073	0,4383	0,4604
Transol 40	0,3891	0,4363	0,4575
190	0,3811	0,4444	0,4525
Hipol 10	0,3963	0,4409	0,4638
30	0,3787	0,4277	0,4501
synthetic oils			
Aeroshell 750	0,4107	0,4570	0,4803
AW-30	0,4163	0,4618	0,4851
E-40	0,3893	0,4319	0,4540
B-3W	0,3987	0,4427	0,4653
turbine oil + 10% n-paraffin fraction (II) of motor oil R	–	0,4472	0,4714

Table 4. Average intermolecular distances for standard fuels and oils

aviation fuels	density ϱ_4^{20}	boiling range					temperature, °C	
		start	10%	50%	90%	98%	freezing	blockage filter
ATK	—	161	167	178	199	233	less than −50	—
P-3	—	60	145	195	230	250		—
PS-2	—	150	165	195	230	250		—
P-2	—	150	175	195	225	270		—
propulsion (motor) oils	—	50%	90%	95%	96%		—	—
IZ-35	0,8240	280	—	350	—		−35	−20
IZ-50	0,8260	280	—	350	—		−50	−30
IZ-70	0,8331	280	350	—	—		−20	−12
ILS	0,8523	290	350	—	—		− 5	—
LDS	0,8740	280	—	—	340		−15	—

Table 5. Physicochemical properties of fuels

Mineral oils with additives were characterized by higher values of R_o/R_T and J than those found for oils without additives (Figures 8 and 9). The curves of dependence $R_o/R_T(T)$ of some oils were clearly irregular, indicating an increase of AS. Similarly as in the case of products discussed earlier, a lowering of the value of R_o/R_T with the rise of temperature suggested thermal decomposition of AS structures and decrease of their amount. /136 In general, these structures were more stable than similar ones in oils without additives. The effect of strongly polar additives was difficult to establish. In spite of their various amounts, the correlation between the lowering of the values R_o/R_T with the rise of freezing temperature was preserved, which appears very significant. For this group of oils there was also taking place the same type of irregularities of relations c(T) and $K_s(T)$ with the course of relation $R_o/R_T(T)$, established in the works /7, 7a and 17/. This could be observed particularly clearly

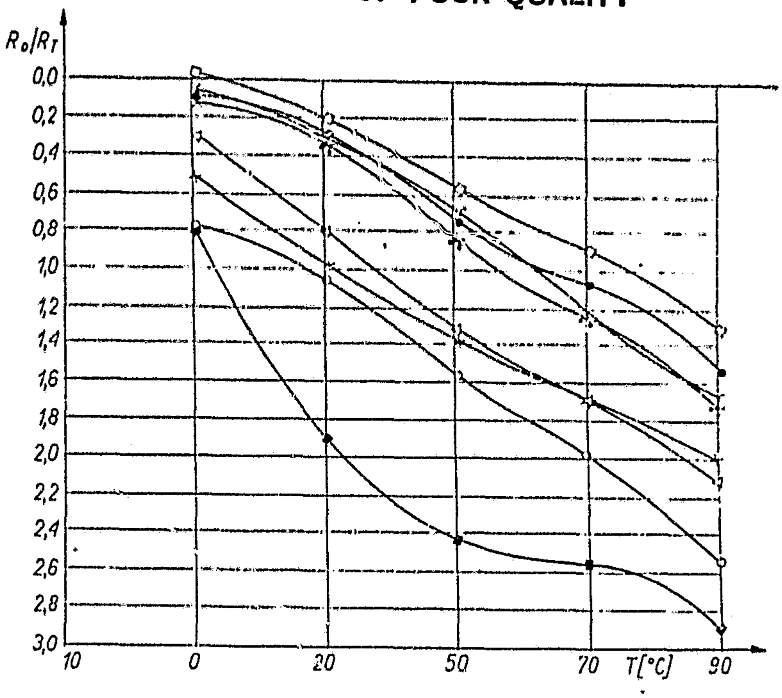

Figure 6. Dependence $R_o/R_T(T)$ for mineral oils not containing additives.
Legend: turbine oil T-30 —— o, T-40 — — Δ, T-60 —·— x, compressor oil WZ4 —— s, TZ-2 —— □, TZ-3 —— x, TZ-4 —— o, SD-10 —— ■

for oils of the group Shell Tellus. Irregularities c(T) were the most pronounced in the temperature range 20-50°C. In this range, one could see the extreme values R_o/R_T for particular oils of the discussed group. In the case of the majority of analyzed mineral oils without additives, irregularities of the curves c(T) were less distinct, which was confirmed by the course $R_o/R_T(T)$. In this case, changes of $R_o/R_T(T)$ values were nearly regular, and most of all unidirectional ones.

For synthetic oils, whose properties are listed in Table 7, an increase of R_o/R_T was observed as the temperature rose, reaching a maximum at about 20°C. Further rise of temperature caused a lowering of the R_o/R_T value (Table 7, Figure 10). The highest values of R_o/R_T were found for AW-30 oil. Changes of the dependence R_o/R_T, showing well developed broad extremes, /138

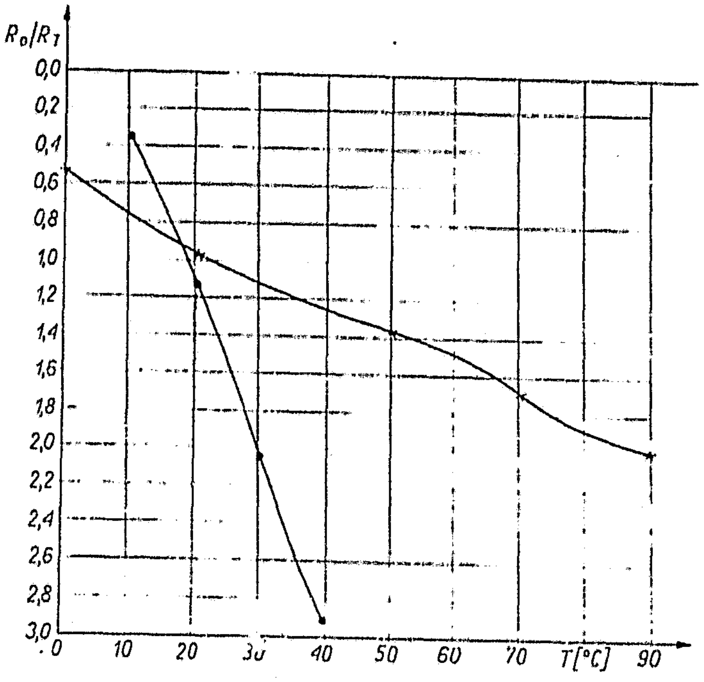

Figure 7. Dependence $R_0/R_T(T)$.
Legend: turbine oil T-60 - x,
T-60 oil + 10% n-paraffin fraction - ● .

T °C	ϱ gcm³	c ms⁻¹	$\beta_S 10^6$ cm²kg⁻¹	$K_S 10^{-3}$ kgcm⁻²	R	W	R_0/R_T %
5	0,91458	1522,5	47,169	21,200	4453,4	3449,7	–
10	0,90708	1501,6	48,892	20,453	4971,4	3460,5	−0,36
20	0,89208	1463,2	52,358	19,099	5011,5	3484,4	−1,16
30	0,87708	1429,4	55,803	17,920	5057,7	3511,9	−2,06
40	0,86208	1393,8	59,712	16,747	5102,6	3538,6	−2,92

Table 6. The AS characteristics and the Rao constants for mineral oil T-60 with addition of 10% n-paraffin fraction.

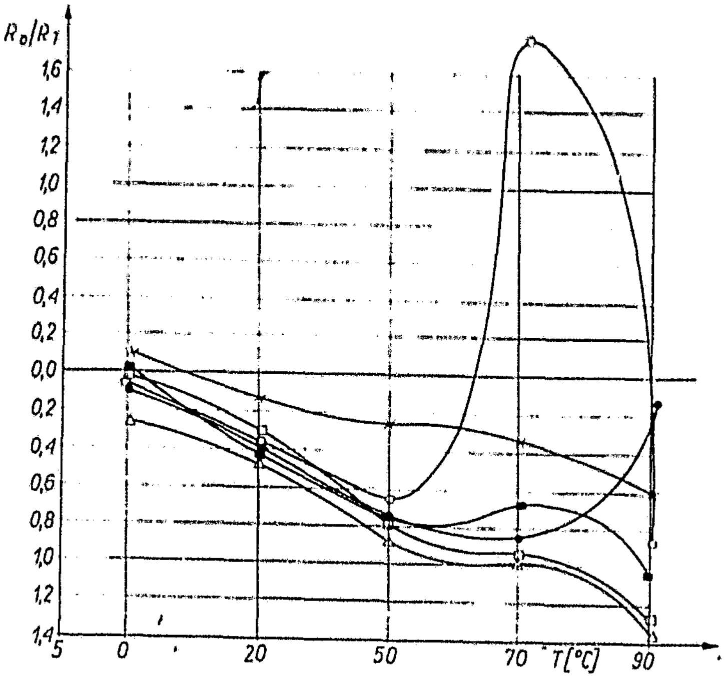

Figure 8. Dependence $R_o/R_T(T)$ for hydraulic oils with additives. Legend:
AMG 10 - - x, Hydrol 20 ●, 20P o, 30 △, 40 - - - +, 70 ■

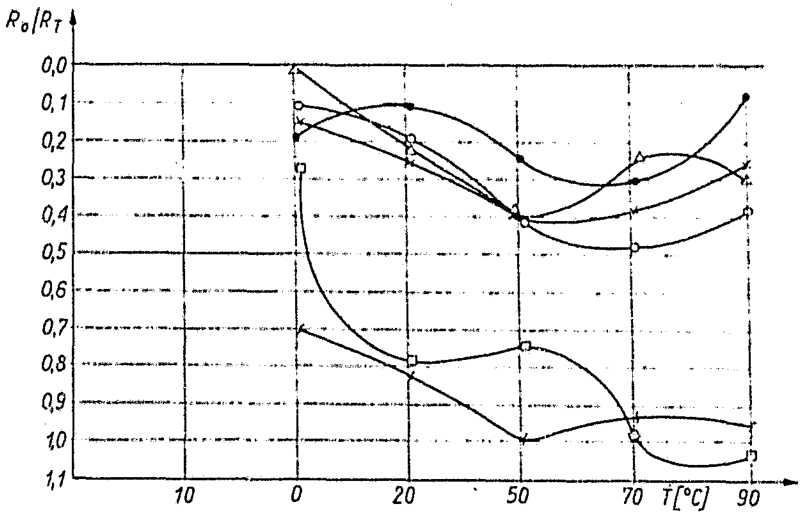

Figure 9. Dependence $R_o/R_T(T)$ for hydraulic oils Shell Tellus with additives. Legend: 11 - - - o,
27 —— ●, 29 —— x, 33 ---- △, 69 - - s, 72 · — □

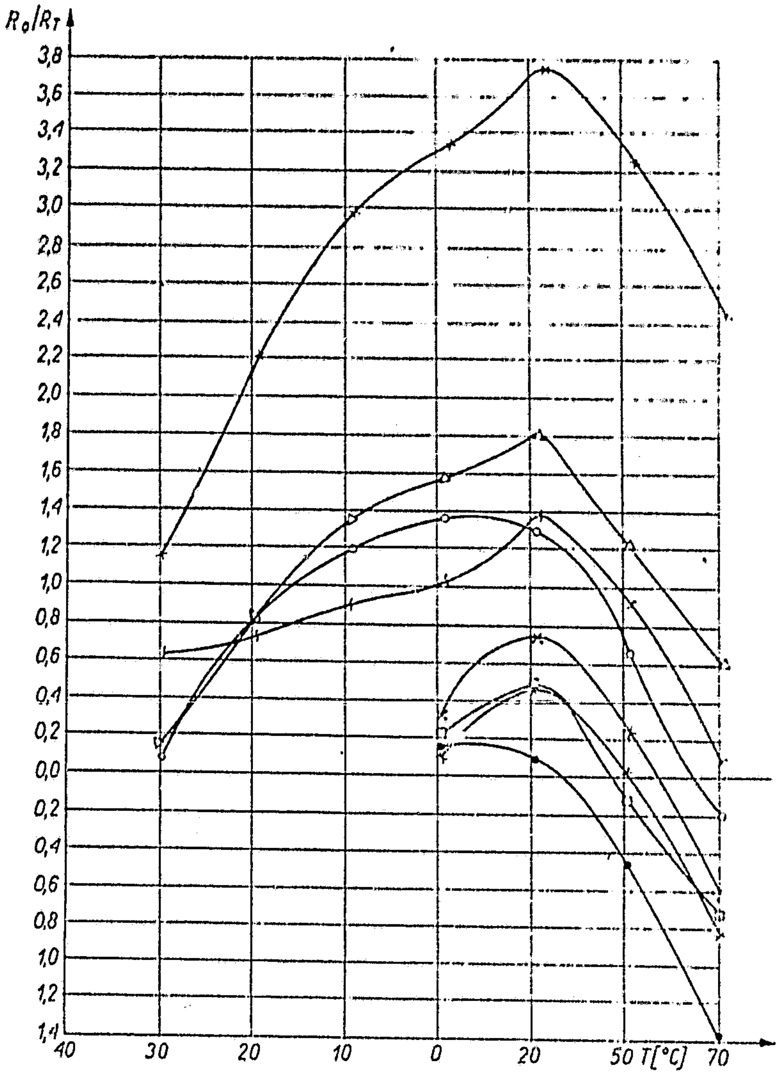

Figure 10. Dependence $R_o/R_T(T)$ for synthetic oils.
Legend: AW-38 - x, ,x, ; B-3W - △, □;
E-40 - s, ,x, ; Aero Shell 750 - ○, ● .

suggested the occurrence of consecutive states of building and rebuilding of AS systems. A characteristic feature was was that maxima R_o/R_T were larger for oils with lower viscosity (at 100°C). The same relation, but to a smaller degree, applied to viscosity coefficients and to freezing temperatures. These oils could be placed, from the aspects of correlating values of viscosity and AS degree, in the following order:

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Table 7
Properties of standard aviation oils

Oil	Viscosity cSt		Visc. coeff. WL	Freezing temp. °C	Main components
	50°C	100°C			
Aeroshell 750	7.5	23.8	209	-53	Di-2-ethylhexyl sebacate
E-40	5.2	15.7	189	-62	Di-2-ethylhexyl adipate plus ester of adipic acid with ethylene glycol
B-3W	5.0	17.5	135	-59	Ester of pentaerythritol with $C_6 - C_9$ acid
AW-30	3.3	8.5	193	-60	Di-2-ethylhexyl adipate

AW-30 > B-3W > E-40 > Aeroshell 750.

Studies of this group of oils have confirmed most convincingly that it is the AS systems forming in the oils that are responsible for advantageous rheological properties, in the broader sense.

3. SUMMATION

The results of studies of various fuels and standard oils provide general confirmation of various suggestions and reports /8, 9, 10, 22, 25, 26, 27 and 28/ concerning the role of the processes of solvation and association and mechanisms of stabilization of viscosity in oils and fuels, occurring at changes of temperature, gelation, cooling down and freezing, and also about non-Newtonian effects. According to the authors, there are also reasons for additional suggestions. It would appear that other aspects could be included as co-decisive factors about the use of rheological properties of working fluids: relatively high temperatures of the formation of associates-solvates, increase of the number of associates-solvates with the rise of temperature, relatively high thermal stability of associates-solvates at elevated temperatures, relatively large mechanical stability of associates-solvates (to the action of shearing forces), etc.

By advantageous rheological properties of working fluid we understand in this case:

- high coefficient of viscosity
- low freezing temperature /139
- absence or limited tendency to separate out microsuspensions of solid phase in liquid, at lowered temperatures
- absence or limited tendency to form mesophase systems as the temperature of liquid decreases. It applies also to the behavior of liquid at increased pressures.

On the basis of AS degree, preliminary determination was made of critical values R_0/R_T, by which particular groups of standard fuel and oil products should be characterized (Table 8).

In the light of considerations connected with thermal stability of associates-solvates, attention should be directed to another aspect which may have connection with thermooxidative stability of oils. To simplify the matter, the problem was considered on an example of solutions of polymer additives in mineral oils. In this case we neglected the effect of other /140 factors on processes of building or rebuilding of associates-solvates, i.e., action of other physicochemical processes such as catalysis or synergistic effects. Thus, we evaluated energetic effects of the formation of associative-solvative structures. The energy required for building-rebuilding associations of polymers in the medium of mineral oil, joined by hydrogen bonding, is about 10-14 Kcal/mole /21 and 29/. For comparison, activation energies for thermal depolymerization of polymers are of the order of 10-30 Kcal/mole /30 and 31/, while activation energies of mechanical disintegration of polymers are below 10 Kcal/mole /32/. Hence, the energy required for breaking of associates-solvates may be relatively large. It would follow

Table 8

Critical values R_o/R_T for standard fuels
and lubricating-hydraulic oils

Products	Critical values R_o/R_T	
	Temp. °C	Temp. °C
Jet fuels and motor oils low-freezing	-0.05 at -5°C	-0.20 at 20°C
Low-freezing mineral oils (without additives) WL 80	-0.80 at 0°C	-1.60 at 50°C
Mineral oils (without additives) freezing at ab. 0°C, WL 80	-1.00 at 0°C	-2.50 at 50°C
Mineral oils (with additives) low-freezing, WL ab. 100	0.10 at 0°C	-0.50 at 50°C
Synthetic oils very low-freezing WL more than 100	0.05 at -30°C	0.60 at 50°C

that, from energetic point of view, the associative-solvative forms present in the liquid may absorb a relatively large amount of thermal energy, which will be "lost" in their rebuilding. In this way, the associates-solvates may act as a kind of thermal buffer. Before thermooxidative or thermal decomposition processes are initiated, part of supplied thermal energy will be absorbed for rebuilding of associates-solvates. Also, a part of energy will be absorbed - will undergo viscous dissipation, connected with movement of large aggregates.

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