Viscosity and density of vacuum oils for diffusion pumps

D I Sagdeev¹, I R Gabitov¹, M G Fomina¹, V A Alyaev¹, V S Minkin¹, I M Abdulagatov²

¹ Kazan National Research Technological University, Karl Marx street 68, Kazan, 420015, Russia
² Dagestan State University, Gadzhiyev street 43a, Makhachkala, 367000, Russia
E-mail: sagdeev@mail.ru

Abstract. Current paper represents the results of viscosity and density measurements of vacuum oils for diffusion vacuum pumps. Vacuum oil samples are represented by the following brands: VM-1S, LEYBONOL LVO 500 and Alcarin-D24. All the measurements have been carried out at atmospheric pressure: viscosity has been measured by the capillary method in the temperature range from 293 K to 373 K, and density has been measured by the pycnometer and hydrostatic weighing methods in the temperature range from 293 K to 473 K.

1. Introduction
Viscosity and density, along with other transport phenomena coefficients (diffusion and thermal conductivity), are the most important structural and mechanical characteristics of materials that determine their technological, operational and consumer properties. Viscosity is an important physical-chemical property that determines fluidity of liquids. Density is considered to be the main thermophysical characteristic of a substance. Viscosity and density are widely applied in computational practice for various vacuum-technological processes and pumping equipment, as well as in oil production, petrochemistry, biochemistry, food, cosmetic, paintwork and other industries.

Viscosity and density data are necessary for theoretical calculations, including the near-critical region [1, 2].

The purpose of this research is the measurement of viscosity and density of the vacuum oils at atmospheric pressure in the temperature range from 293 K to 473 K.

2. Brief description of the vacuum oil samples investigated
The experimental measurements of viscosity and density have been carried out for the following brands of vacuum oil: sample 1 (VM-1S by OJSC “Moscovskiy neftemaslozavod”, TR 38.1011187–88); sample 2 (VM-1S by “Volganeftekhim”, TR 38.1011187—88); sample 3 (LEYBONOL LVO 500 by “Oerlikon Leybold Vacuum”); sample 4 (Alkaren – D24 by OJSC “Khimprom”). All the measurements have been carried out at temperatures from 293 K to 473 K at atmospheric pressure. Some basic characteristics of the samples investigated including density, dynamic viscosity and refraction index are presented in table 1.
Table 1. Characteristics of the vacuum oil samples at $T = 293.15 \text{ K}$ at atmospheric pressure.

| Sample No. | Density (kg$\cdot$m$^{-3}$) | Viscosity (mPa$\cdot$s) | Refraction index |
|------------|----------------------------|-------------------------|-----------------|
| 1          | 866.38                     | 192.292                 | 1.47584         |
| 2          | 856.67                     | 161.610                 | 1.47215         |
| 3          | 867.48                     | 267.581                 | 1.47624         |
| 4          | 902.91                     | 290.609                 | 1.51831         |

Figure 1. High-resolution NMR$^{-1}$ – spectra of the oil samples investigated: a) – sample 1 (VM-1S, Moscow); b) – sample 2 (VM-1S, Nizhny Novgorod); c) – sample 3 (LVO 500, Germany); d) – sample 4 (Alkaren (synthetic), Kemerovo).

The composition of the vacuum oil samples has been identified by nuclear magnetic resonance method (NMR$^{-1}$H) [3] with use of BS-567A “Tesla” NMR-high-resolution spectrometer at the proton resonant frequency of 100 MHz. The obtained NMR spectra for the samples investigated are presented in figure 1.

The signal with a chemical shift of 0.95 ppm (parts per million) belongs to methyl protons of CH$_3$–group and is observed for all the investigated oil samples (CH$_3$–C–). It is a part of the main structure of hydrocarbons and, apparently, of various isomers presented in oil composition.
Sample 4 (synthetic oil) comparing to other samples has a slightly larger (∼ 8%) number of proton groups with this chemical shift.

A signal with chemical shift of 1.3 ppm is observed for all the samples 1–4. This is the most intense signal of the spectra and relates to proton-containing groups of a close structure. The contribution to this signal are made by CH₂–groups close to branched fragments of the saturated hydrocarbons of oil chains, as well as CH₃–groups of the main chain and various isomers that make up the oils. It should be noted that this particular signal in synthetic oil is 5%–8% higher.

Synthetic oil (sample 4) is also described by the presence of the signal with a chemical shift of 1.65 ppm. This signal refers to the proton-containing groups of low-molecular cyclic structures due to the polydispersity of the synthetic oil sample.

There is a weak signal with 2.05 ppm observed for samples 1 and 2. This signal, apparently, belong to CH₃S groups and CH₃C=O– chains fragments of saturated hydrocarbons. It should be noted that there is a signal with 4.75 ppm observed in sample 2 (Nizhny Novgorod).

NMR spectrum of the sample 4 (synthetic oil) is the most dissimilar among all the samples’ spectra. In addition to the previously indicated signals, the spectrum of sample 4 presents a low-intensity multiplet in the 7.5 ppm region. This multiplet may refer to the imposition of signals from several groups due to the presence of impurities (C₆H₅NO₂–; C₆H₅Cl–; C₆H₅CH₃– and C₆H₅OH– groups). Overlaying of signals from several groups requires an individual analysis. This signal cannot be resolved due to the high viscosity of the oil (dynamic viscosity of 290.7 mPa·s). This also applies to other industrial oils.

The most pure product is oil sample 3 (LVO 500, Germany). The spectrum of this product does not contain signals with a chemical shift of 2.1 ppm and 7.5 ppm.

Thus, all the oil samples investigated contain a mixture of branched hydrocarbon chains and various mobile isomers. Each of them contributes to the observed NMR spectra. There is a fairly good correlation of the structure of the oils with their viscosity and density.

3. Density measurements

The density measurements have been carried out at temperatures from 293 K to 473 K at atmospheric pressure with the use of the experimental plant for measuring density of liquids by the hydrostatic weighing method [4].

The following quadratic function has been applied for an accurate representation of the measured density values:

$$\rho(T) = a_0 + a_1 \cdot T + a_2 \cdot T^2. \tag{1}$$

The experimental results of density measurements are presented in figure 2, as well as the approximation coefficients are presented in table 2. Average deviation does not exceed ± 0.5%, being less than the total measurement error.

| Sample No. | $a_0$   | $a_1$   | $a_2$   | Coefficient of determination $R^2$ |
|------------|---------|---------|---------|-----------------------------------|
| 1          | 0.087839| -0.602422| 0.000100| 0.999854                          |
| 2          | 0.086949| -0.650203| 0.000473| 0.998990                          |
| 3          | 0.088029| -0.650525| 0.000504| 0.999793                          |
| 4          | 0.091691| -0.711770| 0.000590| 0.999828                          |
4. Viscosity measurements

Kinematic viscosity of vacuum oils has been measured with the use of standard glass capillary viscometers VPG-2M by LABTEX (GOST 10028-81) with capillary diameters of 0.73 mm, 0.99 mm, 1.31 mm and 1.77 mm and viscometer constants of 0.032147 mm$^2$/s$^2$, 0.10065 mm$^2$/s$^2$, 0.34271 mm$^2$/s$^2$ and 0.088675 mm$^2$/s$^2$, respectively. This particular set of viscometers guarantees the requirement for time interval to be between 200 s and 600 s as it is written in GOST 22524-77.

The uncertainty estimation for the dynamic viscosity measurements for sample 1 has been carried out in accordance with GOST R 54500.3-2012 [5]. The results are presented in table 3.

Table 3. The results of uncertainty estimation for the dynamic viscosity measurements of VM-1S vacuum oil (Moscow) at atmospheric pressure and temperature $t = 92.0^\circ$C.

| No. | Parameter | Dimension | Value   | Standard uncertainty | Expanded uncertainty at 95% confidence limit |
|-----|-----------|-----------|---------|----------------------|--------------------------------------------|
| 1   | $\tau$   | sec       | 339.367 | 0.207                | –                                          |
| 2   | $t$       | $^\circ$C | 92.0    | 0.05                 | –                                          |
| 3   | $\rho$   | kg·m$^{-3}$ | 823.81  | 0.21                 | –                                          |
| 4   | $\eta$   | mPa·s     | 8.995   | 0.003                | 0.007 (0.08%)                              |

The temperature dependence of the viscosity can be represented by the well-known Arrhenius–Andrade type equation, which is modified to extend the temperature range [6–9]

$$\eta(T) = b_0 \cdot \exp \left( \frac{b_1}{T_r} \right) \quad \text{or} \quad \ln(\eta(T)) = \ln(b_0) + \frac{b_1}{T_r}$$  \hspace{1cm} (2)

where $T_r = T/100$, $b_0$ – viscosity at a high-temperature limit, $b_1 = \epsilon_a/R$ and $\epsilon_a$ – flow activation energy (activation enthalpy), where $T$ is temperature in K. Expression (2) is theoretically confirmed by the Eyring’s absolute velocities theory [8]. This equation has been successfully applied earlier to present experimental viscosity data for aqueous solutions [9–13] and ionic
liquids [6]. As it can be seen from equation (2), the activation enthalpy can be directly calculated using experimental viscosity data from the slope of the straight line.

Such an experimental viscosity curves for some liquids and liquid mixtures at high temperatures appear to be not a straight line. This effect has been well shown in [10–16]. Thus the Arrhenius-Andrade equation (2) can be slightly changed to extend the temperature range:

\[
\eta(T) = b_0 \cdot \exp\left(\frac{b_1}{T_r} + \frac{b_2}{T_r^2}\right) \quad \text{or} \quad \ln(\eta(T)) = \ln(b_0) + \frac{b_1}{T_r} + \frac{b_2}{T_r^2}.
\] (3)

The results of dynamic viscosity measurements are presented in figure 3. The obtained values have been approximated by a second-degree polynomials with coefficients presented in table 4. Average deviation does not exceed ±3%, being less than the total measurement error.

\[\text{Figure 3. Logarithm of the oil samples dynamic viscosity as a function of the reduced temperature.}\]

\[\text{Table 4. Approximation results of vacuum oils dynamic viscosity measurement}\]

| Sample No. | \(b_0\)   | \(b_1\)  | \(b_2\)  | Coefficient of determination \(R^2\) |
|------------|-----------|-----------|-----------|-------------------------------------|
| 1          | 0.428193  | -0.196799 | 2.34326   | 0.999454                            |
| 2          | 0.394854  | -0.179383 | 2.11330   | 0.999268                            |
| 3          | 0.448824  | -0.206956 | 2.48505   | 0.998800                            |
| 4          | 0.468764  | -0.217300 | 2.61436   | 0.999137                            |

5. Conclusion
The viscosity and density of four samples of vacuum oils for diffusion vacuum pumps has been measured. The obtained values of the properties have been approximated by the basic quadratic function.
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