HEAT AND MASS TRANSFER
AND PHYSICAL GASDYNAMICS

Study of the Solubility of Gases in Rapeseed Oil as an Insulating Material

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Abstract—The Solubility coefficients of the main diagnostic gases in commodity rapeseed oil have been determined experimentally at various temperatures. The largest differences between the solubility of gases in transformer and rapeseed oils has been detected for ethane and acetylene, ethane being less soluble in rapeseed oil, and acetylene, more soluble. An initial estimation of the application of the liquid as an insulating material in oil-filled electrical equipment has been performed.

INTRODUCTION

Currently, the application of raw plant materials for the production of electrical insulation liquids is of interest. For the time being, this is an experimental design, which has, however, found practical application abroad (Brazil, United States). In our country, there is also experience of the application of plant oil as a technical liquid, but mostly as a fuel (biodiesel). In this case, oil methyl ester used as motor fuel is produced from rapeseed oil. Data on the use of rapeseed oil as an insulating liquid are practically absent in our country. However, there is interest in research in the field of study of the properties of this type of raw materials from plants in terms of its use in high-voltage oil-filled electrical equipment. The good "cold-resistant" properties of rapeseed oil, which are important for the climate of most of the territory of our country, can serve as prerequisites for the studies; the high fat percentage of rapeseed (45–50%) provides a significant amount of starting material. The decision about the use of plant oils in electric power will be very important in terms of environmental, biological, and fire safety. There are also indirect economic benefits: the demand on the international market, for example, for rapeseed oil is growing steadily, increased oilseed crops and the use of the edible part of the plant will promote the development of agriculture [1, 2].

An important condition for operation of insulating liquids in high-voltage equipment is gas stability—the ability to absorb gases. In addition to gases absorbed, for example, by transformer oil because of the contact of its surface in the transformer expander with air or nitrogen, other gases can be contained in the oil, which are products of accelerated aging of the insulation due to its excessive heating as well as decomposi-tion products under the influence of partial discharge and other abnormal processes. By increasing the gas stability of oils, one can reduce the risk of gas breakdown [3]. An important property characterizing gas stability of the insulating liquids is the solubility of gases in them. The results of refinement of solubility coefficients K_s of the investigated gases for various modern brands of transformer oils in the temperature range from 20 to 45°C are presented in [4]. At the same time, the solubility coefficients in rapeseed oil, which can be considered as an alternative, less fire hazardous, and more eco-friendly insulator produced from renewable resources, remain unknown. Investigation of the thermal and physical properties of materials allows us not only to obtain new data, but also to expand the application fields [5].

The aim of this study is to determine the solubility coefficients of gases in rapeseed oil at 20 and 40°C.

STUDY TECHNICS AND RESULTS OBTAINED

Refined, deodorized rapeseed oil of the first grade, *GOST* (State Standard) *53457–2009*, manufactured in Russia, Rostov oblast, was used as the material for the study. The calibration gas mixture (CGM) produced by OOO Monitoring (St. Petersburg, Russia) was used for the experiments. The oil was analyzed on a Kristall 5000M gas chromatographic complex (ZAO SKB Chromatec, Yoshkar-Ola, Russia). ELCHROM Samplers (technical conditions TU 3418-027-11703970-05) were used for oil and gas selection. Various temperature modes were maintained using an HT-3/40-1 air cold thermostat. Several series of experiments to study the gas composition of commodity rapeseed oil and its ability to dissolve some of the gases that are considered

Table 1. Results of the analysis of gases of the initial rapeseed oil dissolved in oil on the Crystal 5000M chromatographic complex

Component name	Hydrogen (H_2)	Carbon oxide (CO)	Carbon dioxide (CO_2)	Ethylene (C_2H_4)	Ethane (C_2H_6)	Methane (CH_4)	Acetylene (C_2H_2)
Component concentration, vol %	0.00142	0.00123	0.01158	0.00027	0.00146	0.00011	0.00000

Table 2. Comparison of the concentration levels of dissolved gases before and after degassing

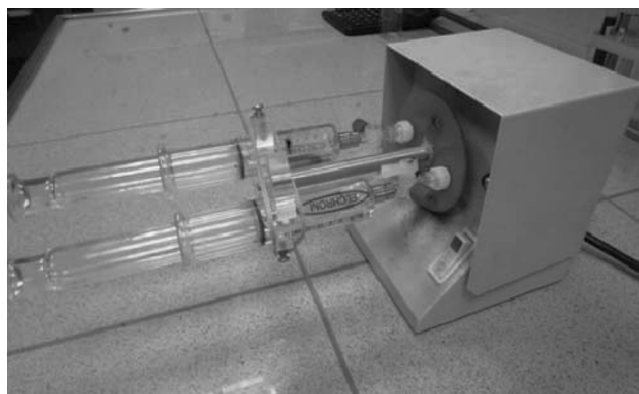| Component name	Concentration of gases in the initial commodity oil (from Table 1)	Concentration of gases after degassing, vol %			
		sampler 1	sampler 2	sampler 3	sampler 4
H_2	0.00142	0	0	0.00009	0.00005
CO	0.00123	0.0001	0.00031	0.00049	0.00012
CO_2	0.01158	0.00441	0.00544	0.0072	0.00347
CH_4	0.00011	0	0	0.00001	0
C_2H_4	0.00027	0.00001	0.00001	0.00001	0.00001
C_2H_6	0.00146	0.00005	0.00011	0.0003	0.00016
C_2H_2	0.00000	0	0	0	0
O_2	2.30468	0.07022	0.46714	0.70218	0.0693
N_2	14.74366	0.14073	1.80944	2.47859	0.27707

to be diagnostic in high-voltage power engineering were carried out. The main stages of the work were the following: (1) obtaining of the initial information about the gas composition of rapeseed oil; (2) verification of the time needed to reach equilibrium between the gas and the liquid phase (or determination of the time of gas extraction from the oil), study of the sufficiency of the time of gas extraction from the oil; (3) determination of the solubility coefficients of gases in rapeseed oil at room temperature and at +40°C; (4) determination of the solubility of gases in the insulating liquid Midel 7131.

According to the method of equilibrium extraction of gases in the atmosphere isolated from the gas space

Fig. 1. Appearance of DRE with established samplers.

described in [6], a sample was prepared and dissolved gases of the starting rapeseed oil were analyzed to obtain initial information about the gas composition (Table 1).

In the absence of precise information on the viscosity of rapeseed oil, it can be assumed that the conventional mixing time of the liquid in the device to reach equilibrium (DRE in Fig. 1) with the gas mixture is insufficient to establish equilibrium according to the procedure mentioned above. In this regard, it was planned to carry out an experiment to determine the time required to establish equilibrium between the gas and oil phases.

The minimum concentrations of the diagnosed gases in the sampler oil (close to the detection limit of the gas chromatograph) were reached by degassing. Degassing of the initial oil was carried out by the method mentioned above of equilibrium extraction of gases in the atmosphere isolated from the gas space [2]: 10 mL of inert gas—argon—were added to a sampler with 10 mL of oil; after stirring the mixture in DRE, the obtained gas phase was analyzed by passing it through the chromatograph column. This was accompanied by release of the dissolved gases from oil because of diffusion. The procedure was repeated with the same sampler several times to obtain acceptable results (minimum values of gas concentrations). The degassing level of rapeseed oil can be estimated by comparing the data for column 2 in Table 2 (the gas concentration in the starting oil) with the data for col-
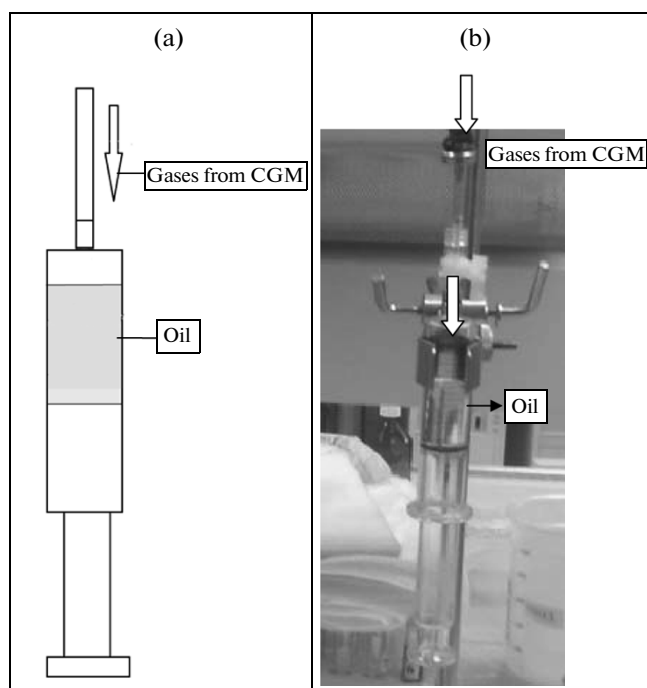
Fig. 2. The process of adding gases from CGM to rapeseed oil: (a) scheme; (b) view of the installation.

Fig. 3. The concentrations of gases in the samplers at room temperature (for H_2, CO, CH_4, C_2H_4, C_2H_6, and C_2H_2): *1*, concentration of gases in the balloon; *2*, after stirring for 10 min; *3*, 20 min; *4*, 30 min; *5*, 40 min.

umns 3−6 (the gas concentration in samplers after degassing).

Using a balloon filled with a mixture of certified diagnostic gases with a known concentration (CGM), it was assembled in an installation for saturation of degassed rapeseed oil by diagnosable gases (Fig. 2). The ratio of the oil and gas phases was 1: 1 by volume. The mixture of gases from CGM under pressure pushed the ground-glass piston of the sampler to the desired volume (10 mL).

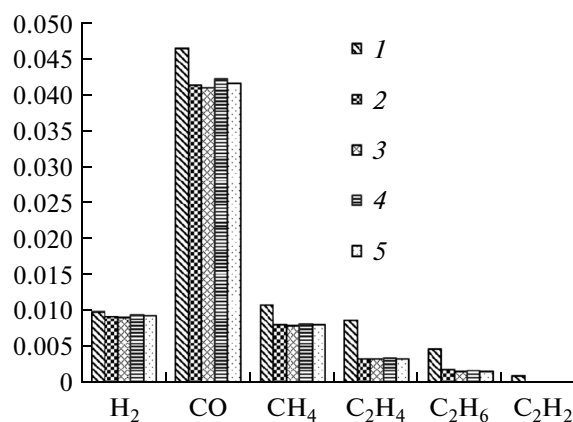After filling the oil sampler with the mixture of gases, the samples were subjected to mixing in the DRE device during different periods: 10, 20, 30, and 40 min. Then the resulting mixtures were analyzed. The results showed that the conventional time for stirring (for the transformer oil, it was a 10-min period to reach equilibrium) with the gas phase is sufficient to establish equilibrium between the liquid phase and the gas phase, because the level of concentrations is not reduced at 20, 30, and 40 min of treatment of the mixture in DRE (Table 3; Figs. 3, 4).

The procedure to determine K_s was the following. After addition of the gas mixture to the sampler, the process of gas dissolution in oil begins, whereas the gas concentration in the gas part of the sampler decreases, and in the oil part, it increases. It is believed that equilibrium for each gas is established independently. Moreover, we can use the fact that at the equilibrium state the amount of gas in the oil simply needs to be equal to the difference in the amounts of gas in the starting mixture and in the above-oil area, rather than determine experimentally the gas content in the oil. It

Table 3. Concentration of gases in samplers at room temperature

| Component name	Concentration of gases in the calibration mixture	Mixing time, min			
		10	20	30	40
H_2	0.00991	0.00927	0.00918	0.00953	0.00945
CO	0.04677	0.04167	0.04117	0.04247	0.04193
CH_4	0.01083	0.00815	0.008	0.0082	0.00809
C_2H_4	0.00879	0.00344	0.00334	0.00346	0.0034
C_2H_6	0.0047	0.00177	0.00159	0.00168	0.00158
C_2H_2	0.00094	0.00023	0.00026	0.00025	0.00023
CO_2	0.40094	0.17129	0.16735	0.1712	0.16987
O_2	0.99648	1.18373	1.33159	0.8912	0.8584
N_2	2.94263	3.76035	4.44444	2.79578	2.71031
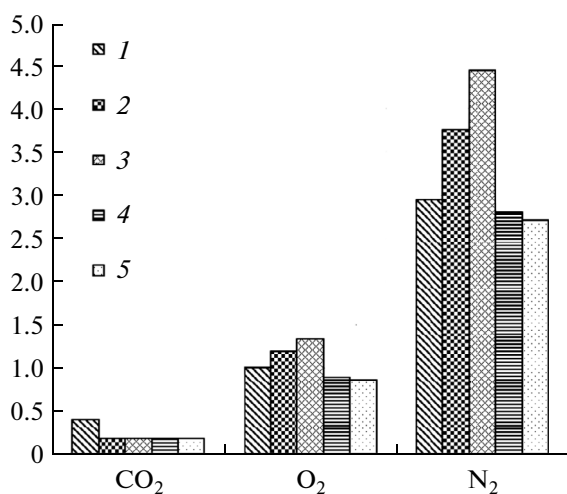
Fig. 4. Gas concentrations in samplers at room temperature (for CO_2, O_2, and N_2): *1–5*, as in Fig. 3.

can be shown that neglecting the gas content in the degassed oil K_s is defined as

$$K_{si} = (A_i - B_i)/B_i, \qquad (1)$$

where A_i is the concentration of i gas in CGM and B_i is the concentration of i gas in the above-oil space.

Accounting for the gases remaining in the oil after degassing with the concentration C_i can be performed by modifying the Eq. (1)

$$K_{si} = (A_i - B_i)/B_i + C_i/B_i. \qquad (2)$$

RESULTS AND DISCUSSION

The data needed to determine the desired values were obtained directly using the gas chromatograph, and the comparison of the results allowed us to estimate the importance of these values for the liquids tested.

The results of calculations of the solubility coefficients of the diagnosed gases at room temperature (close to +20°C) are presented in Table 4 for four samplers. The average solubility coefficients accurate to two significant figures obtained in accordance with Eqs. (1) and (2) are listed in the sixth column.

Likewise, the solubility coefficients were determined for the same gas at a temperature of +40°C. Table 5 shows only the average value of the coefficients.

For comparison, these indicators were also identified for a dielectric fluid—the synthetic ester Midel 7131 widely used in Europe for more than 30 years. This fluid is used in switchgear and power transformers and other electrical equipment, primarily due to its fire safety, nontoxicity, and complete biodegradability [7].

Analysis of the data obtained shows that the solubility of gases in rapeseed oil depending on the temperature is similar to the solubility of gases in mineral transformer oil. Moreover, the values of the solubility coefficients of the main so-called "diagnostic" gases [8] are close to the corresponding coefficients for transformer oil. Exceptions are the reduced solubility of ethane as well as the increased solubility of acetylene and carbon dioxide. As regards the solubility of gases in Midel 7131, their values are close to the corresponding values for rapeseed oil. The closeness of the values of the coefficients allows us to hope that the diagnostics of high-voltage electrical equipment filled with both rapeseed oil and Midel 7131 will not fundamentally differ from the diagnostics of conventional oil-filled electrical equipment.

However, the question arises whether the same gases, namely hydrogen, methane, ethane, ethylene, and acetylene are diagnostic for electrical equipment filled with rapeseed oil. To answer this question, we should refer to a comparison of the compositions of rapeseed oil and mineral oil. The main components of mineral oil are saturated cycloparaffins C_nH_{2n} and saturated paraffins C_nH_{2n+2} with an average molecular weight of 220−340 a.u. [7]. The main components of rapeseed oil are erucic $CH_3–(CH_2)_7–CH=CH–(CH_2)_{11}–COOH$, oleic

Table 4. Solubility coefficients of gases in rapeseed oil at +20°C

Component name	Solubility coefficient				Average value of K_s
	sampler 1	sampler 2	sampler 3	sampler 4	
H_2	0.048677	0.079521	0.06904	0.039874	0.06
CO	0.11543	0.136021	0.12239	0.101248	0.12
CH_4	0.33869	0.35375	0.328834	0.320732	0.34
C_2H_4	1.585294	1.631737	1.555233	1.540462	1.58
C_2H_6	1.974684	1.955975	1.655367	1.797619	1.85
C_2H_2	3.086957	2.615385	3.086957	2.76	2.89
CO_2	1.360276	1.395817	1.340709	1.341939	1.36
O_2	0.160857	—	—	0.118133	0.14
N_2	0.085717	—	—	0.052526	0.07

Table 5. Comparison of solubility coefficients of gases in various types of dielectric liquids

Component name	Solubility coefficient			
	transformer oil at $T = +20°C$ (data from [5])	rapeseed oil at $T = +20°C$	rapeseed oil at $T = +40°C$	Midel 7131 liquid at $T = +20°C$
H_2	0.05	0.06	0.04	0.08
CO	0.12	0.12	0.10	0.10
CH_4	0.40	0.34	0.30	0.33
C_2H_4	1.75	1.58	1.34	1.61
C_2H_6	2.78	1.85	1.07	1.96
C_2H_2	1.20	2.89	2.00	3.27
CO_2	1.08	1.36	1.10	1.67
O_2	0.15	0.14	0.16	0.15
N_2	0.09	0.07	0.05	0.08

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, and linoleic $CH_3(CH_2)_3-(CH_2CH=CH)_2(CH_2)_7COOH$ acids. Based on their composition, it is evident that both oils have similar gross elemental composition; therefore, all the gases mentioned are formed during the decomposition of rapeseed oil and their appearance indicates some unfavorable processes in the oil-filled electrical equipment.

The great difference of rapeseed oil from mineral oil is the presence of double bonds in molecules of the main substances of rapeseed oil. This leads to low thermal oxidative stability of the oil, which requires additional research on the selection and introduction of oxidation inhibitors.

The difference in the composition leads to some differences in the solubility. The largest difference is observed for acetylene; as compared with mineral oil, acetylene is more soluble in both rapeseed oil and Midel 7131. We believe that this is due to the presence of double bonds and acid groups in the main components of rapeseed oil as well as the presence of oxygen bridges in the pentaerythritol ester, which is the basis of Midel 7131.

CONCLUSIONS

Measurements of the solubility coefficients of the main diagnostic gases in rapeseed oil have been carried out. It has been shown that the solubility of gases in rapeseed oil depending on the temperature behaves similarly to the solubility of gases in mineral transformer oil. Furthermore, the solubility coefficients of the main diagnostic gases is close to the corresponding coefficients of transformer oil. Exceptions are the poor solubility of ethane and the increased solubility of carbon dioxide and, in particular, that of acetylene.

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