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SOME CHARACTERISTICS OF ETHYLENE GLYCOL AS A HEAT-TRANSFER AGENT FOR CLOSED TWO-PHASE SYSTEMS

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The article contains results of studies of thermal properties of ethylene glycol and its corrosive interaction with carbon steel St. 10. The present data can be used for calculation of heat-engineering and operating characteristics of closed two-phase systems and for determination of their optimal range of operating temperatures under long-term functioning.

In development of various kinds of heat-transfer equipment based on heat pipes (HP), two-phase thermosiphons (TTS), and other closed systems that work in a closed evaporation-condensation cycle, it is most important to bear in mind that they should be highly efficient and reliable in long-term operation. These requirements are largely achieved by a reasonable choice of the structural materials of the casing, the capillary-porous structure (CPS), and the heat-transfer agent. This choice should be based on thermal, corrosive, and other characteristics of the material–heat-transfer agent combination.

As a rule, there are numerous reliable data for most of metals, alloys, and other materials that are used for the casing, and CPS and for such widely known heat-transfer agents as water, ammonia, freons, etc. However, for some organic working fluids such as ethylene glycol, which are promising for using at high temperatures ($T \geq 453$ K), their thermal properties are not systematized and some are unknown [1-3]. It particular, we can mention the lack of reliable data on the initial decomposition temperature, pressure, and viscosity of saturated vapor as a function of the saturation temperature, and on the corrosive interaction of ethylene glycol with the material of the casing in a functioning closed system. In view of these, it is impossible to calculate heat-engineering characteristics, to determine the optimal range of working temperatures, or to state that this heat-transfer agent could be used for the systems discussed.

The goal of the present work is to study some of the most important thermal properties of ethylene glycol and its corrosive interaction with carbon steel.

In order to achieve this goal, we made an experimental setup (Fig. 1) whose main component is TTS 1, 843 mm in length, 25 mm in diameter with a wall 2 mm in thickness made of carbon steel St10. Ethylene glycol $C_2H_6O_2$ (GOST 10164-75) was used as the heat-transfer agent. Heat was supplied to the heating zone from a resistance heater 3 mounted on a lateral surface of the TTS. The heat-flux power was varied by an autotransformer 4 connected to single-phase a.c. supply line through a voltage regulator 5 and a power meter 6. Heat was transferred from the condensation region by natural convection. Temperature fields were recorded by chromel-Copel thermocouples 7 that were mounted on the wall in grooves 1 mm in depth. All the thermocouples were connected alternatively through a multipoint switch 8 to a universal digital voltmeter 9. The cold junctions of the thermocouples were placed in a Dewar flask 10 filled with melting ice.

The studies were carried out in the temperature range 453–663 K and in the pressure range $(0.8-53) \cdot 10^5$ Pa. The average saturation temperatures T_{vp} were determined from readings of the thermocouples that were located in the adiabatic region of the TTS, and the ethylene glycol saturated vapor pressures P_{vp}, from readings of a standard pressure gauge 2 connected to the interior of the TTS in its upper part. All measurements

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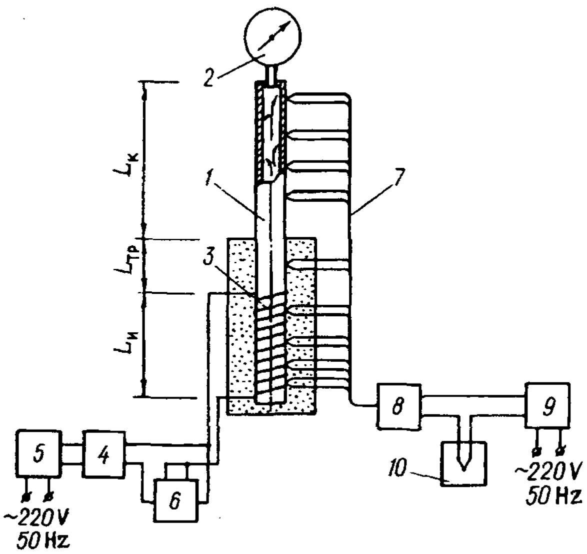


Fig. 1. Scheme of experimental setup.

of temperatures and pressures were conducted after steady-state conditions were attained, which was determined by steady readings of the thermocouples.

As a rule, in their operation, HP, TTS, and other similar devices that are manufactured with all specifications met are characterized by a low heat resistance, which can be explained by a high temperature uniformity and, accordingly, by constantcy of saturated vapor pressure in the interior of a closed system. Therefore, the appearance of some uncondensed gas that has thermal properties different from those of heat-transfer agent vapors can have an important effect on the behavior of the functions $P_{\mathrm{pv}} = f(T_{\mathrm{vp}})$ and $\eta = f(T_{\mathrm{vp}})$, change the relationships of heat and mass transfer in the condensation region, and, eventually, lead to an increase in the thermal resistance of the closed system [4, 5]. Consequently, feasibility studies of ethylene glycol as a heat-transfer agent require reliable data on its decomposition temperature, thermal, and corrosion properties, which allows the researchers to determine the optimal operating temperature range and to calculate heat-engineering and operating characteristics of closed two-phase systems for their long-term functioning.

As the known data on $P_{\mathrm{vp}} = f(T_{\mathrm{vp}})$ are inconsistent and not systematic, before the experiments we analyzed the existing methods used for calculation of this function. As follows from [6], in most cases for polar liquids: a) Antoine's correlation

$$\ln P_{\mathrm{vp}} = A - \frac{B}{T_{\mathrm{vp}} + C} \quad \text{at} \quad 0.0013\ \mathrm{MPa} \le P_{\mathrm{vp}} \le 0.2\ \mathrm{MPa}\,, \tag{1}$$

and b) Teck–Steel's method

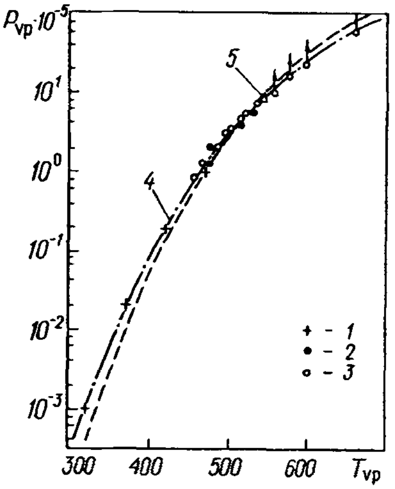
$$\ln P_{\mathrm{vp_r}} = A' \left(1.14893 - \frac{1}{T_{\mathrm{vp_r}}} - 0.11719\, T_{\mathrm{vp_r}} - 0.03174\, T^2_{\mathrm{vp_r}} - 0.375 \ln T_{\mathrm{vp_r}}\right) +$$

$$+ (1.042\alpha_{\mathrm{c}} - 0.46284A') \times$$

$$\times \left[\frac{T_{\mathrm{vp_r}}^{5.2691+2.0753A'-3.1738h} - 1}{5.2691+2.0753A'-3.1738h} + 0.040 \left(\frac{1}{T_{\mathrm{vp_r}}} - 1\right)\right], \tag{2}$$

for

$$P_{\mathrm{vp}} > 0.0013\ \mathrm{MPa}\,,$$



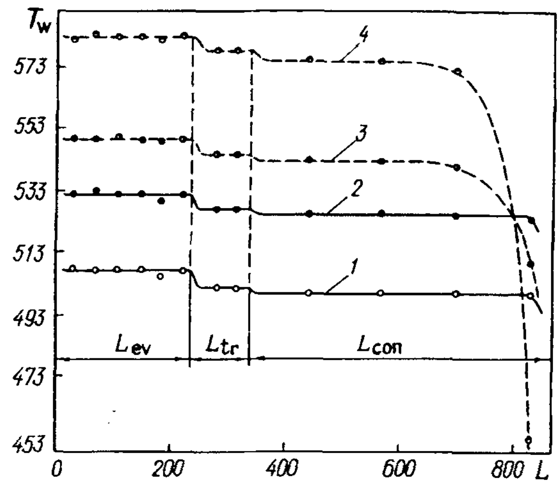


Fig. 2. Plot of saturated vapor pressure of ethylene glycol versus saturation temperature: 1) data from [1], 2) from [7], 3) present authors' data, 4) calculated with Antoine's correlation, 4) calculated from Teck–Steel's equation. P_{vp}, Pa; T_{vp}, K.

Fig. 3. Temperature distribution along TTS as a function of heat flux: 1) $Q = 200$ W, 2) 300, 3) 320, 4) 370. T_w, K; L, mm.

where

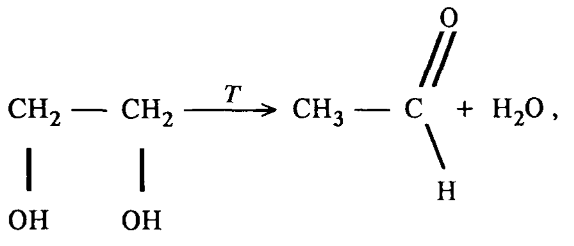
$$A' = \frac{\Delta H_v}{RT_c\,(1 - T_{b_r})^{0.375}}; \quad \alpha_c = \frac{0.315\psi_b + \ln P_c}{0.0838\psi_b - \ln T_{b_r}};$$

$$h = T_{b_r}\frac{\ln P_c}{1 - T_{b_r}}; \quad \psi_b = -35 + \frac{36}{T_{b_r}} + 42\ln T_{b_r} - T_{b_r}^6 .$$

provide the most reliable results.

Figure 2 shows the authors' experimental results as well as the curves $P_{vp} = f(T_{vp})$ calculated by the method of [6] and results of [1, 7]. It can be seen that in the ranges of pressures of $(0.001-2)\cdot 10^5$ Pa and temperatures of 323–493 K, the experimental results and calculations (Antoine's correlation) fairly agree. Tech–Steel's equation gives acceptable results in narrow ranges of temperatures of 500–550 K and pressures of $(2-8)\cdot 10^5$ Pa, which can probably be explained by the error of the critical parameters and ΔH_v in this equation, which can only be determined by calculating methods, because of the thermal decomposition of ethylene glycol.

The present authors' curves of saturated vapor pressure versus temperature show that thermal decomposition of ethylene glycol starts at temperature $T_{vp} \approx 530$ K (Fig. 2). These results fairly agree with [7] and are confirmed indirectly by the experimental distribution of temperature fields along the TTS. In Fig. 3 it can be clearly seen that the temperature drop gradually increases in the terminal part of the condensation region (curves 3, 4) because of thermal decomposition of ethylene glycol in the reactions [3, 8, 9]:



$$\underset{\displaystyle OH}{\underset{|}{CH_2}} - \underset{\displaystyle OH}{\underset{|}{CH_2}} \xrightarrow{T} CH_3 - \overset{\displaystyle O}{\overset{/\!/}{\underset{\displaystyle H}{\underset{\backslash}{C}}}} + H_2O, \qquad (3)$$

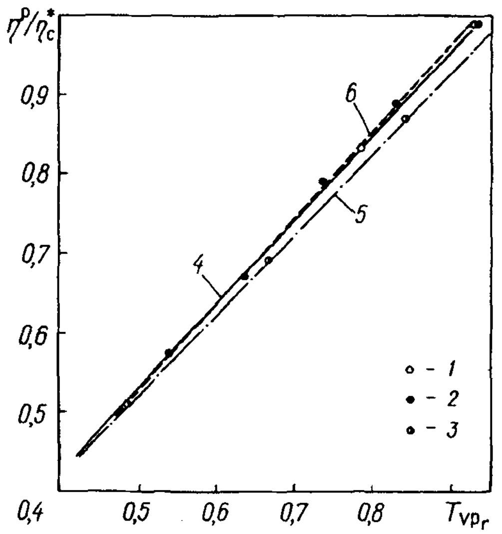
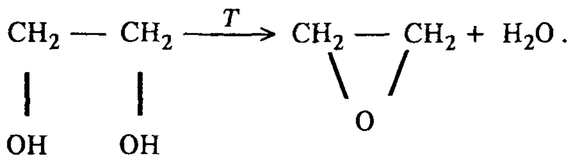


Fig. 4. Plot of dynamic viscosity of ethylene glycol, propanol, and *n*-butanol vapors versus saturation temperature: 1) propanol [6]; propanol [10]; 3) *n*-butanol [10]; 4, 5, 6) calculated with Reichenberg's method [6] for propanol, *n*-butanol, and ethylene glycol, respectively.



$$\underset{\mathrm{OH}}{\mathrm{CH_2}} - \underset{\mathrm{OH}}{\mathrm{CH_2}} \xrightarrow{T} \underbrace{\mathrm{CH_2} - \mathrm{CH_2}}_{\mathrm{O}} + \mathrm{H_2O}. \tag{4}$$

Water vapor that is released in the decomposition is accumulated in the terminal part of the TTS and forms a plug that prevents heat and mass transfer in the condensation region, which results in an increase in the thermal resistance and deterioration of the heat-engineering characteristics of the TTS. It should be noted that as the heat flux and the temperature of the TTS increase, decomposition of ethylene glycol becomes more and more intense and is accompanied by production of large amounts of water vapor, which results in an increase in the pressure in the interior of the thermosiphon (see Fig. 2, dots with arrows).

Thus, the present results indicate that the optimal range of operating temperatures of ethylene glycol used as a heat-transfer agent for HP and TTS is $453 \le T \le 530$ K. It should be noted that the highest temperature is limited by initiation of thermal decomposition of ethylene glycol, and the lowest temperature, by the fact that at operating temperatures lower than 453 K, other liquids are more effective, as they have more acceptable thermal properties that are necessary for heat-transfer agents used in HP and TTS.

In view of the satisfactory agreement of experimental and theoretical functions $P_{vp} = f(T_{vp})$ and of the lack of data on the dynamic viscosity of ethylene glycol vapors as a function of the saturation temperature, we analyzed the methods used to calculate this function for subsequent comparison with known results for compounds of the same class to which ethylene glycol belongs that have properties similar to those of ethylene glycol.

The calculation was carried out with Reichenberg's correlation [6], which has a minimal error for determination of dynamic viscosities of alcohol vapors:

$$\eta = \frac{a^* T_{vp_r}}{[1 + 0.36 T_{vp_r} (T_{vp_r} - 1)]^{1/6}}, \tag{5}$$

where $a^* = M^{0.5} T_c / \sum\limits_i n_i C_i$.

TABLE 1. Chemical Analysis of Waste Ethylene Glycol

T_{vp}, K	Concentration of iron, mg/mliter	
	solution	sediment
327	0.26	$1.4 \cdot 10^{-3}$
389	0.28	$4.0 \cdot 10^{-3}$

In Fig. 4 one can see calculated dynamic viscosities of ethylene glycol (curve 3) as well as experimental data and calculations for propanol and *n*-butanol (curve 1, 2). Analysis of these data shows that in this case calculations and experimental data also agree well.

Consequently, in view of the present results and of the fact that changes in the shape of the curve $\eta^{p}/\eta_c^* = f(T_{vp_r})$ are similar for the just enumerated compounds, it seems possible to suggest that Reichenberg's correlation can be used for determination of dynamic viscosities of ethylene glycol vapors in the ranges of temperatures of 323–530 K and pressures of $(0.001-6) \cdot 10^5$ Pa.

After the thermophysical studies, we studied the corrosive interaction of ethylene glycol with the steel on the basis of results of qualitative and quantitative analyses of the waste heat-transfer agent and corrosion products contained in it. Visualization of the heat-transfer agent revealed the presence of an oily film on its surface and changes in its color from colorless to dark brown. This can probably be explained by a polymerization reaction between the products of processes (3) and (4) [9].

It is also found that the heat-transfer agent contains dark suspended particles, which were filtered out, washed, and dissolved in nitric acid. Results of analysis of the solution of the heat-transfer-agent and the solid phase following [11] that are presented in Table 1 show that they contain substantial amounts of iron, which can be explained by the reaction between ethylene glycol and steel [8, 9]:

$$2\,C_2H_6O_2 + Fe \longrightarrow Fe\,(C_2H_5O_2)_2 + H_2\uparrow . \qquad (6)$$

As can be seen from Table 1, the content of iron in the solution of the heat-transfer agent exceeds substantially its content in the sediment. A general trend is found that its content increases in both the liquid and solid phases as the temperature increases as a result of intensification of corrosion under these conditions.

It should also be noted that release of the oxygen that is produced in reaction (6) did not cause a temperature drop in the terminal part of the condensation region (Fig. 3) in view of the short time of operation of the TTS. However, in design and calculation of closed two-phase systems with the use of the above mentioned materials for their casings and heat-transfer agents that are intended for long-term operation, this factor should be taken into consideration.

The present studies provided new data on the thermal properties of ethylene glycol and allowed us to determine its optimal operating temperature range. The present data on the corrosive interaction of ethylene glycol with carbon steel in a closed system can also be useful in design and manufacture of both HP and TTS and various kinds of heat-transfer systems that operate at high temperatures for a long time.

For the calculation we used the values of initial T_b, T_c and ΔH_v from [6].

NOTATION

T_{vp}, P_{vp}, temperature and pressure of saturated vapor; T_b, normal boiling point; T_c, P_c, critical temperature and pressure; ΔH_v, vaporization heat at T_b; A, B, C, parameters of Antoine's correlation; R, universal gas constant; T, temperature of TTS; η, dynamic viscosity; a^*, parameter in Reichenberg's correlation; n_i, number of atomic groups of i-th type; C_i, group components; M, molecular mass; L, length; L_{ev}, L_{tr}, L_{con}, evaporation, transport, and condensation regions, respectively; Q, heat flux; $T_{vp_r} = T_{vp}/T_c$, $T_{b_r} = T_b/T_c$; $P_{vp_r} = T_{vp}/P_c$, dimensionless temperature and pressure; $\eta_c^* = (3.5M^{1/2}P_c^{2/3})/T_c^{1/6}$, dynamic viscosity at critical temperature and pressure of 1 atm. Subscripts: w, wall; cal, calculated.

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