# THE EQUATION OF STATE FOR A WATER-BASED MAGNETIC FLUID STABILIZED BY LAURIC ACID

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Thermodynamic properties of a water-based magnetic fluid stabilized by a double layer of lauric acid deposited onto magnetite are calculated on the basis of the values of magnetic fluid density measured experimentally at various pressures and temperatures. The pressure and temperature dependences of the density, isobaric coefficient of thermal expansion, and isothermal increment of entropy of the ferrofluid are plotted, analyzed, and compared with the corresponding data for water. The experimental values obtained for the system concerned are described with the use of the semiempirical Tait–Tamman equation of state. The temperature dependences obtained for the parameters of this equation are analyzed and compared with the analogous dependences for water.

## 1. Introduction

Magnetic fluids are unique systems, which simultaneously react to an applied magnetic field and preserve their fluidity property [1–3]. Researches of the thermodynamic properties and the molecular structure of such systems have both fundamental and application importance. According to the statistical theory of fluids and liquid systems, their physical properties depend on the molecular structure, which, in turn, is sensitive to the density of a system. By changing the pressure in the system, it is possible to change its density and its molecular structure [4]. Therefore, researches of the influence of high pressures on the physical properties of magnetic fluid systems allows some details of interrelations between the physical properties of magnetic fluid systems and their molecular structure to be elucidated. It should be noted that the magnetic fluid systems are widely used in the technical facilities and are promising for medical applications. The size of magnetic particles in a liquid system (of about 10 nm) determines their single-domain state and makes such systems sensitive to an external magnetic field. The interaction between particles in a magnetic fluid system can be controlled by varying the physical properties of stabilizing layers covering magnetic particles. The stabilizing surfactant layers in a magnetic fluid system can provide an interface

for functional molecules and complexes [4–6]. For today, there already exist the magnetic fluid systems with a wide spectrum of physical properties, which have been created on the basis of water, hydrocarbons, and liquid metals [7–12].

This work is aimed at the experimental research of the thermodynamic properties of the magnetic fluid system created on the basis of water and magnetite, which is stabilized by a double layer of lauric acid around magnetite particles. Nanoparticles of magnetite $Fe_3O_4$ are used as a magnetic material in the studied magnetic fluid system. The volume fraction of magnetite in the studied ferrofluid was 2.4%.

## 2. Experimental Technique

The $P$–$V$–$T$ studies of the water–magnetite–lauric acid system are executed with the use of the bellows piezometer method [4]. A piezometer was equipped with a differential transformer sensor for measuring the linear displacements. The $P$–$V$–$T$ data for the examined fluid magnetic system are obtained on an installation, which includes a system for the creation and measurement of high pressures, a system for temperature measurement and control, a working chamber, and a registration unit. The block diagram of the installation is depicted in Fig. 1. The installation allowed the $P$–$V$–$T$ data of the fluid system to be obtained in the pressure range 0.1–101.3 MPa and the interval of temperatures 290–330 K.

The data on the density of the system at the vapor-liquid equilibrium curve are obtained with the help of the pycnometric method. The pycnometer-assisted measurement of the density consisted in determining the mass of a substance in the known volume. The error of measurements of the density was ±0.04%.

The diagram of a working chamber for $P$–$V$–$T$ measurements is shown in Fig. 2. The bellows was filled with a liquid under vacuum. An increase of the pressure in the autoclave resulted in changing the bellows length only, whereas the transverse cross-section of the bellows
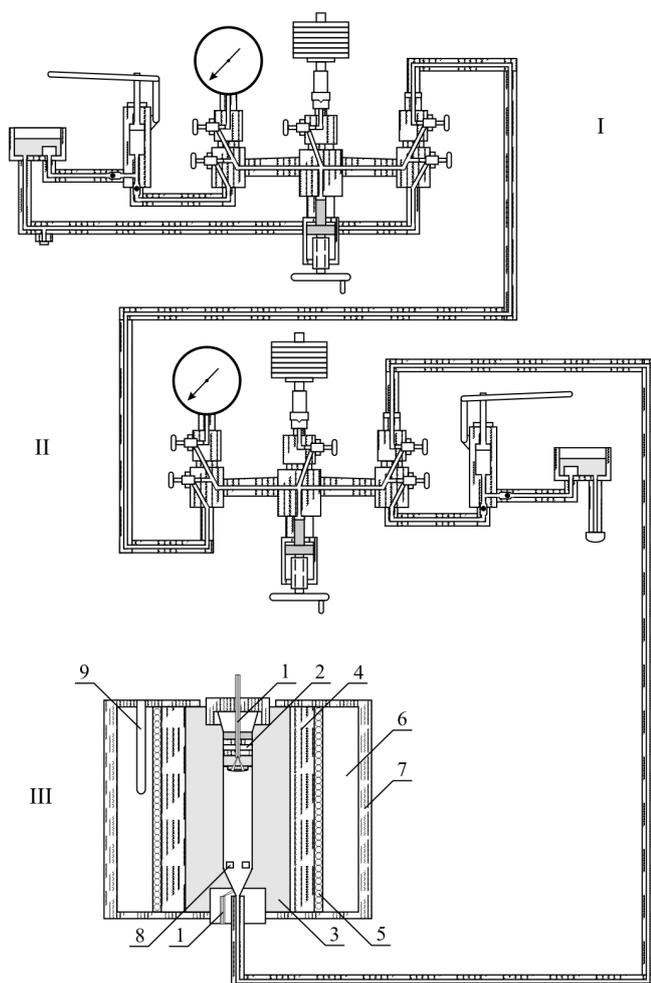
Fig. 1. Block diagram of the installation for $P$–$V$–$T$ researches in liquid systems: (*1*) working chamber core, (*2*) sealing system, (*3*) high-pressure autoclave, (*4*) outer shell of the high-pressure autoclave, (*5*) electroheater winding, (*6*) fiber glass, (*7*) protection cell, (*8*) resistance thermometers, (*9*) cuvette for a thermometer



Fig. 2. Scheme of the working chamber for $P$–$V$–$T$ measurements

remained constant. To register the variations of the bellows length, we used a differential transformer sensor for measuring the linear displacements, which consisted of two combined transformers with a common mobile core. A high sensitivity of the sensor was achieved owing to the application of two secondary windings, which were wound oppositely to each other. The voltage across the secondary winding depended on the position of the core, which was rigidly connected with the working bellows. An advantage of using the transformer sensor for measuring the bellows length was the presence of a substantial (of about 15 mm) linear section in its characteristic, which enabled the rather small displacements of the core (of about 0.001 mm) to be measured, as well as
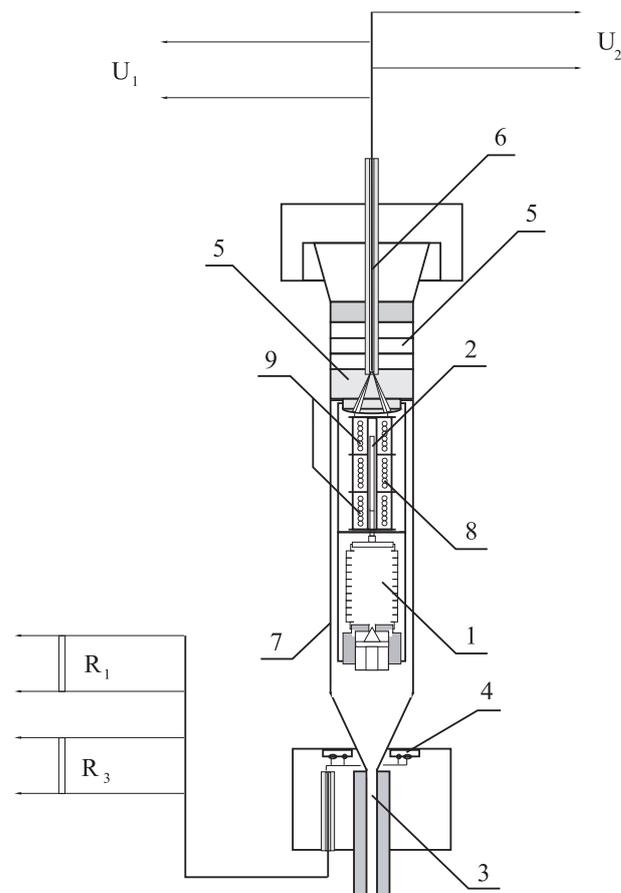
the insignificant corrections for the temperature and the pressure. Such corrections could be made determined by graduating the length sensor. In the framework of this technique, the bellows volume was calculated by the value of induced emf.

## 3. Results and Their Discussion

In Table 1, the experimental results obtained for the density of the water–magnetite–lauric acid system are quoted together with the corresponding data for water obtained on the same installation. One can see that, in the given temperature interval, the density of the water-based magnetic fluid system increases much more rapidly with the pressure than the water density. This fact testifies that the repulsion forces between molecules in this magnetic fluid system are smaller than those in water.

Using the obtained $P$–$V$–$T$ data, we calculated the isobaric coefficient of thermal expansion for water and the studied magnetic fluid system according to the for-
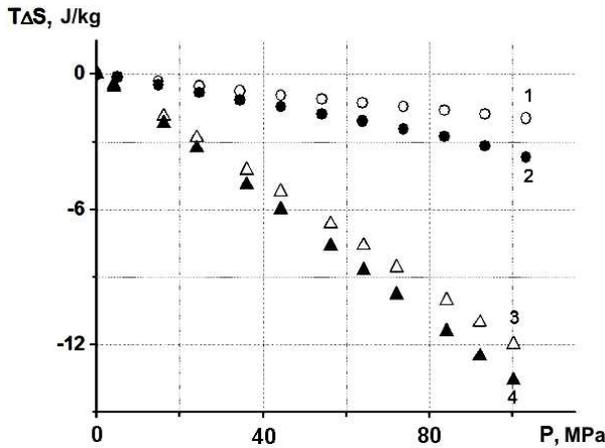
Fig. 3. Baric dependences of the isothermal entropy increment for the water–magnetite–lauric acid system and water at temperatures 308.8 (*1* and *3*) and 317.4 K (*2* and *4*)

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$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P. \qquad (1)$$

The calculated values for the thermal expansion coefficient $\alpha_P$ for water and the studied magnetic fluid system are presented in Table 2.

The analysis of the data in Table 1 shows that the isobaric coefficient of thermal expansion in the water–magnetite–lauric acid system is several times lower than that for water. Such a reduction of this quantity in the analyzed temperature interval is associated with the increase of the energy of intermolecular interaction in the system, when magnetite particles covered with lauric acid molecules are inserted into water. This effect takes place owing to the action of attraction forces between the inserted magnetic particles.

The obtained experimental data allowed us to calculate the isothermal increment of the entropy using the

formula

$$T\Delta S = -T\int_{P_0}^{P}\left(\frac{\partial V}{\partial T}\right)_P dP. \qquad (2)$$

The numerical integration was carried out, by using the Simpson method. The isothermal increments of the entropy calculated for water and the water–magnetite–lauric acid system are depicted in Fig. 3.

The comparison of the baric dependences obtained for isothermal entropy increments in the water–magnetite–lauric acid system and pure water shows that the pressure growth affects this parameter in the magnetic fluid system to a much less extent than in water. Therefore, proceeding from the obtained relations between the entropy increments and the coefficients of thermal expansion, the conclusion can be drawn that the substantial change of the latter, when water is added to magnetite surrounded with lauric acid, is associated with the action of two factors, namely, an increase of the particle-to-particle interaction forces and a modification of the molecular structure of the fluid system under study in comparison with the water structure.

The density of the water–magnetite–lauric acid system obtained experimentally was described with the use of the semiempirical Tait–Tamman equation of state

$$\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{A}{B+P}, \qquad (3)$$

where $A$ and $B$ are the corresponding constants, $V$ is the system volume, $V_0$ is the system volume at the atmospheric pressure, and $P$ is the pressure. By analyzing the experimental data for water and the water–magnetite–lauric acid system, we determined the constants in this equation and compared them. From the

**T a b l e 1. Baric dependence of the densities (kg/m³) of the water–magnetite–lauric acid system and water at temperatures of 308.8 and 330.2 K**

| T, K | 0.1 MPa | 10.0 MPa | 50.0 MPa | 103.2 MPa |
|---|---|---|---|---|
| water–magnetite–lauric acid | | | | |
| 308.8 K | 2481 | 2511 | 2633 | 2799 |
| 330.2 K | 2467 | 2498 | 2618 | 2784 |
| water | | | | |
| 308.8 K | 993 | 998 | 1014 | 1034 |
| 330.2 K | 984 | 989 | 1005 | 1025 |

**T a b l e 2. Isobaric coefficient of thermal expansion $\alpha_P \times 10^3$, (1/K) of the water-based magnetic fluid system and water**

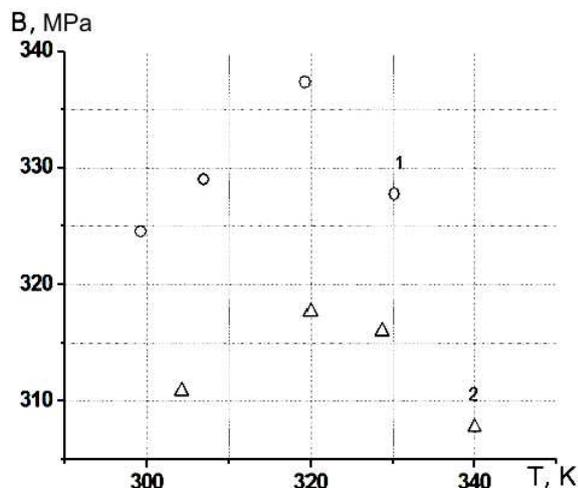| P, MPa | 307.0 K | 308.8 K | 317.4 K | 319.3 K |
|---|---|---|---|---|
| water–magnetite–lauric acid | | | | |
| 0.1 MPa | 0.21 | 0.22 | 0.24 | 0.25 |
| 44.3 MPa | 0.19 | 0.20 | 0.27 | 0.29 |
| 63.9 MPa | 0.18 | 0.19 | 0.28 | 0.30 |
| 103.2 MPa | 0.12 | 0.16 | 0.32 | 0.35 |
| water | | | | |
| 0.1 MPa | 0.26 | 0.36 | 0.41 | 0.49 |
| 44.3 MPa | 0.32 | 0.39 | 0.43 | 0.48 |
| 63.9 MPa | 0.33 | 0.39 | 0.43 | 0.47 |
| 103.2 MPa | 0.35 | 0.40 | 0.43 | 0.47 |

Fig. 4. Values of the constant $B$ in the Tait–Tamman equation of state for the water–magnetite–lauric acid system (1) and water (2) in the temperature interval under study
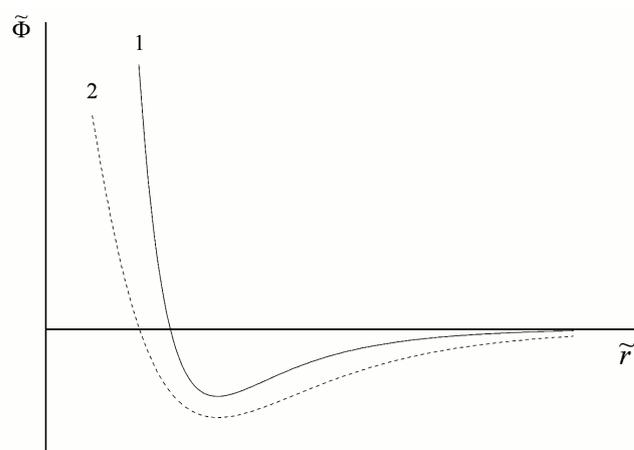


Fig. 5. Effective potential of the molecule-to-molecule interaction $\tilde{\Phi}(\tilde{r})$ in water (1) and the water–magnetite–lauric acid system (2), where $\tilde{\Phi} = \Phi/(k_B T_m)$, $\tilde{r} = r/\sigma_{H_2O}$, $k_B T_m$ is the energy scale for the thermal motion of molecules in a vicinity of the ice melting point, and $\sigma_{H_2O}$ is the effective diameter of water molecules

statistical substantiation of the Tait–Tamman equation of state, it follows that the value of constant $B$ in this equation is proportional to the potential well depth in the effective potential of the particle-to-particle interaction, and the value of constant $A$ is reciprocal to the steepness of the repulsive branch of this potential [4]. As our experiment showed, the value of constant $A$ does not depend on the temperature, being equal to 0.137 for water and 0.420 for the water–magnetite–lauric acid system. Contrary to the constant $A$, the quantity $B$ in this equation does depend on the temperature. In Fig. 4, the temperature dependences of the coefficient $B$ in the Tait–Tamman equation of state are compared for the water–magnetite–lauric acid system and water. As follows from the obtained values for the magnetic fluid system, the latter is characterized by a smaller value of the derivative in the repulsive branch of the potential and by a deeper effective potential of the particle-to-particle interaction in comparison with the corresponding parameters of the interaction potential between molecules in water (Fig. 5).

## 4. Conclusions

To summarize, on the basis of the experimental $P$–$V$–$T$ data obtained for the magnetic fluid system (water–magnetite–lauric acid) and water and their analysis with the use of the Tait–Tamman equation of state, we took the statistical substantiation of this equation into account and drew conclusion that, for the stud-

ied magnetic fluid system, a reduction in the steepness of the repulsive branch of the effective intermolecular interaction potential is observed. At the same time, the observed growth of the parameter $B$ in the Tait–Tamman equation of state for the water–magnetite–lauric acid system in comparison with that for water testifies to an increase of the potential well depth in the effective potential of the interparticle interaction by approximately 10%, which, in its turn, brings about a reduction of the isobaric coefficient of thermal expansion and a modification of the molecular structure of the system concerned in comparison with those for water. Hence, the examined magnetic fluid system (water–magnetite–lauric acid) has a considerably lower coefficient of thermal expansion in comparison with that of water, which can be explained by a variation of the interparticle interaction energy and by the reconstruction of a water structure, when the magnetic particles covered with lauric acid are added.

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РІВНЯННЯ СТАНУ МАГНІТНОЇ РІДИННОЇ СИСТЕМИ НА ОСНОВІ ВОДИ ТА МАГНЕТИТУ, СТАБІЛІЗОВАНОЇ ЛАУРИНОВОЮ КИСЛОТОЮ

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Р е з ю м е

Представлено результати дослідження термодинамічних властивостей магнітної рідинної системи на основі води та магнетиту, стабілізованої подвійним шаром лауринової кислоти, що нанесений на магнетит. Значення термодинамічних властивостей досліджуваної системи розраховано на основі експериментально виміряних для різних тисків і температур значень густини магнітної рідинної системи. Побудовано, проаналізовано та зіставлено з аналогічними даними для води баричні та температурні залежності густини, ізобаричного коефіцієнта теплового розширення, та ізотермічного приросту ентропії досліджуваного ферофлюїду. Отримані експериментальні $P$–$V$–$T$ дані для магнітної рідинної системи описано за допомогою напівемпіричного рівняння стану Тейта–Таммана. Проаналізовано та зіставлено з аналогічними даними для води температурні залежності параметрів побудованого рівняння стану.