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THERMOPHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS OF MULTICOMPONENT ELECTROLYTE SYSTEMS AT HIGH TEMPERATURES AND PRESSURES

Speciality: 2003.01 - Mechanics of liquids, gases and plasma

Field of Science: Technical

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ABSTRACT

of the dissertation for the degree of Doctor of Science

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The work was performed at the Department of Energy Efficiency and Green Energy Technologies of the Azerbaijan Technical University

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GENERAL CHARACTERISTICS OF THE WORK

The relevance of the problem is due to the need of modern technologies for accurate empirical thermophysical data for water systems in a wide range of temperature and pressure changes, as well as equations of state based on them, which are used to describe processes in thermodynamics and fluid mechanics.

In thermodynamics and, in particular, hydrodynamics, there are lots of unsolved problems that can be solved using analytical analysis of the thermodynamic characteristics of liquids. The main mechanical properties of a liquid (continuous) medium are viscosity and density, which in turn change depending on temperature and pressure. In this regard, difficulties arise in the question of the nature of heat distribution in the environment of the studied substances, and this is an incentive to study another important thermophysical property of continuous media - thermal conductivity.

The influence of state parameters, temperature distribution, and concentrations of mixture components allows us to determine processes occurring in continuous media and to give their full interpretation. Processes occurring in thermodynamic systems are described by macroscopic quantities such as temperature, pressure, and concentrations of components, which are introduced to describe mechanical systems consisting of a large number of particles and are applicable to individual molecules and atoms, as well as to quantities used in mechanics or electrodynamics.

Accurate data on transport (thermal conductivity), volumetric properties (density, viscosity, excess, apparent and partial molar volume) and acoustic properties of aqueous solutions are extremely important for a deep understanding of many natural and technological processes. For example, the processes of photosynthesis and the main chemical precipitation are formulated with the participation of calcium carbonate, sodium, magnesium, dolomite, gypsum, halides and sulphates. Aqueous solutions at high temperatures and pressures are of fundamental importance in geology and mineralogy (for hydrothermal synthesis), chemistry, oil and gas industry (for example, in the extraction of hydrocarbon raw materials), in geothermal systems and biological processes in living organisms, for some new separation methods. The temperature of surface (rivers, lakes) and ocean waters is close to room temperature, while aqueous solutions with high temperature and hydrostatic pressures from 10 to 60 MPa are found in deep geological formations. Aqueous systems are widely used in steam generators, geothermal power plants, hydrothermal synthesis, seawater desalination processes, and other industrial operations that occur at high temperatures and high pressures. The thermodynamic properties of aqueous electrolyte solutions at high pressures and temperatures are important for understanding the interactions between rock-forming minerals and geothermal fluids in deep geochemical processes. Groundwater found in deep wells, drilled rocks with a crystalline structure, usually represents highly saline solutions.

The properties of the ternary system water + alcohol + electrolyte can also be used to study the kinetics and mechanism of crystallization processes (formation of crystals). Knowledge of the precise values of the thermal properties of geothermal brines is a prerequisite for modelling a geothermal reservoir and a basis for understanding the various physical and chemical processes occurring in the natural environment. The work devotes a large amount of space to the examination of the problems of the influence of temperature and pressure on the volumetric properties of infinitely dilute solutions. An equally important problem is the development of a reliable equation of state for aqueous solutions at high temperatures and pressures. Water, salt, alcohols and their mixtures are complex compounds with a complex nature of intermolecular interactions, and, therefore, complicate experimental and theoretical studies. Analysis of the available literature data in these areas made it possible to substantiate the relevance of the research topic.

The dissertation is devoted to the current problem of studying the thermophysical properties of aqueous solutions of multicomponent electrolyte systems at high temperatures and pressures, which are one of the fundamental for studying the mechanics of continuous media, an important tool for theoretical analysis of processes, interactions between molecules in complex solutions, for analysing the positions of heat transfer in liquids, the processes of formation and destruction of molecular complexes, with their help it is possible to solve the problems of mixability and solubility, to find out the change in the degree of association of components during mixing, etc. The data have practical significance in technology, including being necessary for compiling a reference data bank.

Object and subject of the study.

The object of the study is aqueous solutions of multicomponent electrolyte systems, binary and ternary systems of water + alcohol + electrolyte at high temperatures and pressures, geothermal systems of deposits in the South of Russia.

The subject of the study is the transport (thermal conductivity), volumetric (density, viscosity, expansion and compression coefficients), acoustic (speed of sound) and energy properties of multicomponent aqueous solutions of electrolytes, including natural geothermal fluids from deposits in the South of Russia (Dagestan), as well as the mechanism of structural changes in a liquid multilayer medium. All the studies performed were conducted for the first time in these ranges of changes in state parameters.

The purpose and objectives of the study.

The main objective of the study is to improve existing and develop new scientific foundations for predicting the thermodynamic state of binary and multicomponent mixtures of electrolytes, alcohols in a wide range of state parameters changes, which in turn characterize the mechanical properties of the medium. It is necessary to provide the growing scientific interest and technical needs with reliable data on the thermophysical properties of aqueous solutions of electrolytes. They are also necessary for studying the mechanics of continuous media and thermal physics as a science.

To achieve this goal, the task is set: to experimentally and analytically study the thermodynamic properties of multicomponent solutions, to determine the mechanism of structural changes in aqueous solutions.

One of the important thermophysical properties of fluids is thermal conductivity and density, parameters that are included in the criterial equations of heat exchange and reflect the features of the thermodynamic surface. According to the basic provisions of statistical mechanics, the thermodynamic functions of the system, in particular, the equation of state, can be determined if the structure, internal motions of particles and the law of interaction between them are known. The main source of information on the thermophysical properties of solutions are experimental data. Experimental studies of the transport, volumetric and acoustic properties of the system, in addition to practical value, have exceptionally important scientific significance, since the development and improvement of calculation and theoretical methods for studying the thermodynamic properties of substances are always accompanied by accurate experiments, contribute to the development and improvement of the modern theory of the liquid state. The mechanism of intermolecular interaction in liquids makes it possible to explain a number of physicochemical and thermal phenomena associated with molecular transfer.

To achieve the stated objectives, previously unexplored or minimally studied objects were utilized across a wide range of state parameter variations.

The research conducted in this work aims to **address the following objectives:**

1. Creation of a reliable setup for experimental study of thermal conductivity of fluids
2. Obtaining accurate experimental data on thermal conductivity, viscosity, density, and sound velocity of the studied natural and artificial solutions.
3. Description of the processes and mechanism of intermolecular interactions and models of the structure of solutions, processes of formation and destruction of molecular complexes
4. Based on the statistical method of data analysis and processing, a correlation model has been developed to describe experimental data on volumetric and transport properties as a function of state parameters, including cases where the properties of pure water are known.
5. Presentation of the dynamics of development of processes in the environment from the point of view of continuum mechanics.

Research methods

Empirical methods (experiment, observation and comparative analysis), theoretical methods (analysis and synthesis, deduction and induction), statistical method, correlation and regression analysis, methods of mathematical and computer modeling.

The main points of defense:

1. A large array of experimental data on transport, volumetric, and acoustic properties of multicomponent electrolyte solutions in natural and artificial systems.
2. Wide-range correlation equation for thermal conductivity of binary and multicomponent systems depending on concentration, temperature and pressure (equation of state, criterion equation).
3. Polynomial regression equation of the dependence of the reduced thermal conductivity of aqueous solutions on the solution concentration.
4. A model for describing the influence of combined effect of temperature, pressure and concentration on the reduced thermal conductivity of aqueous solutions.
5. An equation of state describing the dependence of specific volume on the (p, V, T, m) parameters, which can be used to predict and perform scientific and engineering calculations on density, viscosity, partial and apparent molar volumes and other thermodynamic properties of other aqueous solutions in a wide range of changes in state parameters.
6. Polynomial function of the dependence of the molar volume of a ternary mixture on concentration of components for each isobar-isotherm.
7. A regression equation describing experimental data on the density of geothermal systems as a function of temperature.
8. A correlation equation describing the dependence of experimental data on density, viscosity and speed of sound on temperature and concentration, with a known reference value of density, viscosity and speed of sound for pure water at atmospheric pressure.
9. A model that predicts data on the volumetric and acoustic properties of a system at high pressures and temperatures. A correlation model that describes experimental data on geothermal

systems with known density, viscosity, and sound velocity at reference atmospheric pressure.

10. Energy characteristics of the medium that are important for continuum mechanics.

Scientific novelty of the study:

1. A modified reliable experimental setup based on the coaxial cylinder method (stationary method) has been created.
2. A new array of experimental data on thermal conductivity was obtained for binary aqueous solutions of $Sr(NO_3)_2$, $LiNO_3$, Na_2CO_3, $CaCl_2$, K_2CO_3, NaBr, KBr and ternary systems H_2O+NaBr+KBr in previously unexplored ranges of changes in state parameters.
3. A wide-range empirical equation for thermal conductivity of binary and multicomponent systems depending on concentration, temperature and pressure is proposed.
4. A model has been developed to describe the combined effect of temperature, pressure and concentration on the reduced thermal conductivity of the studied aqueous solutions.
5. Polynomial regression equation for the dependence of the reduced thermal conductivity of aqueous solutions on the concentration of solutions.
6. For the first time, a new array (p, V_m, T, x) of experimental data was obtained for binary and multicomponent mixtures $H_2O + C_2H_5OH$; $H_2O + C_2H_5OH + LiNO_3$; $H_2O + C_3H_7OH + Li_2SO_4$; $H_2O + C_3H_7OH + KNO_3$ in a wide range of state parameter changes.
7. The molar volumes of the ternary water-salt-alcohol mixture for each isobar-isotherm are described by polynomial functions of the component concentrations, taking into account the molar volumes of pure water. They can be used to calculate the partial molar volumes of the components of binary systems. Partial, excess and apparent molar volumes of the studied systems were calculated.
8. The influence of temperature and pressure on the volumetric properties of infinitely dilute solutions and the features of their behavior for these systems are revealed.

9. Based on the measured values for (p, V_m, T, m) properties of binary aqueous electrolyte solutions, a polynomial equation of state for the dependence of the specific volume on the state parameters was developed. The equation can be used to calculate the density, viscosity, partial and apparent molar volumes and other thermodynamic properties of other aqueous solutions in a wide range of temperatures (up to 600 K), pressures (up to 40 MPa) and concentrations (up to 5 mol kg^{-1} H_2O).
10. For the first time, a chemical analysis (analysis of cations and anions) was carried out and the volumetric (density), acoustic (sound speed), and transport (viscosity) properties of 8 natural geothermal fluids from deposits in the South of Russia (Dagestan) were experimentally studied at atmospheric pressure.
11. The obtained experimental data on the density of the studied complex systems were described by a regression equation.
12. A correlation model, that describes experimental data on density, viscosity and sound speed for known properties of pure water from state parameters, has been developed, as well as a model that predicts these properties at high pressures. The model describes experimental data on density, viscosity and speed of sound with an accuracy of 0.03%, 2.55% and 0.06%, respectively.
13. The measured values of viscosity, density and sound velocity of geothermal systems were used to calculate properties important for continuum mechanics, such as the coefficient of adiabatic compressibility, the coefficient of isothermal compressibility, the coefficient of thermal expansion, the thermal pressure coefficient, enthalpy, isochoric and isobaric heat capacity, the partial derivative of enthalpy with respect to pressure, and the partial derivative of internal energy. The measured properties at atmospheric pressure can be used as reference values for predicting the properties of geothermal fluids at high pressures.

Theoretical and practical value of the dissertation.

The copyright experimental setup can be successfully used to study the thermal conductivity of other binary and multicomponent aqueous and aqueous-alcohol systems. Tables of recommended data on the thermophysical properties of aqueous solutions of multicomponent electrolyte systems at high temperatures and pressures were developed, which were then used to find the main indicators of fluid mechanics.

The obtained accurate data on the bulk properties (density, excess molar volume, apparent molar volume, and partial molar volume) of aqueous solutions are extremely important for a deep understanding of many technological and natural processes, and they have an applied nature. Aqueous solutions at high temperatures and pressures are of fundamental importance in new separation methods, steam generators, geothermal power plants, hydrothermal synthesis, refrigeration engineering, in seawater desalination processes, in the process of crystal modeling and other industrial operations that occur at high temperatures and high pressures, in biological processes.

Particular attention in this work is paid to the thermodynamic (bulk) and transport (thermal conductivity) properties of aqueous systems (binary and ternary aqueous solutions) at high pressures (up to 60 MPa) and temperatures (up to 600 K). The paper provides several analytical relationships that predict the thermophysical properties of other solutions and thermodynamic systems in a wide range of changes in state parameters.

Approbation and implementation of work results

The main content of the dissertation work has been published in 60 scientific papers, including 21 articles in the Web of Science and Scopus, including 2 works - a collective monograph, as well as in national and international scientific journals (17), presented in the materials of international and national scientific conferences (22). The main provisions of the work have been reported and discussed at conferences and symposia:

- Thermophysical Properties Symposium, Boulder, Colorado, USA, 2005
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- Thermophysical Properties Symposium, Boulder, Colorado, USA, 2009
- 3rd International Conference on Technical and Physical Problems in Power Engineering, 2006, Ankara, Turkey.
- NATO. Security of Industrial Water Supply and Management. 2010. Ankara, Turkey.
- Материалы 3 международной конференции "Возобновляемая энергетика: проблемы и перспективы", 2014. Махачкала. РФ.
- Thermophysical properties for technical thermodynamics”. September 2015, Azerbaijan Technical University. Baku, Azerbaijan.
- 14 Российская конференция по теплофизическим свойствам веществ. 2014. Казань. РФ.
- THERMAM 2015. “Thermophysical properties for technical thermodynamics”. İnternational conference. 2015. AzTU. Baku
- GEOENERGY. Материалы II Международной научно-практической конференции. 2016. Грозный, ГГНТУ.
- Thermam 2017, 6th Rostocker International Conference on Thermophysical Properties for Technical Thermodynamics. 2017. Baku.
- “Azərbaycan və Türkiyə Universitetləri: təhsil, elm, texnologiya” adlı birinci beynəlxalq elmi-praktiki konfrans, III hissə, AzTU. 2019. Bakı, Azərbaycan.
- II Всероссийская научно-практическая конференция с международным участием «Фундаментальные проблемы и прикладные аспекты химической науки и образования», 2022, Махачкала, РФ.
- Beynəlxalq Elm və Texnologiya Konfransı (ISTEC). 2024. AzTU, Bakı, Azərbaycan.

- VI Beynəlxalq Türk Dünyası Konfransı (TURK-COSE), 2024, AzTU, Bakı, Azərbaycan.
- 6-cı Avrasiya Konfransı "İqlim Dəyişikliklərinin Təbii və Texnoloji Risklərinin minimuma endirilməsi sahəsində yeniliklər: Metodologiya və Təcrübə" 2024. AzTU, Bakı, Azərbaycan.

The results of the work have been implemented:

1. The obtained experimental results on the thermophysical properties of binary systems and ternary systems presented in 12 publications in highly rated journals were included in the Thermo Data Engine standard reference data base (NISTSRD 103b) and SOURCE DATA Archival System of the U.S.A. (National Institute of Standards and Technology).
2. The obtained experimental data on the thermophysical properties of geothermal waters in the South of Russia (Dagestan), detailed data on chemical analysis, as well as correlation equations that allow modeling processes taking into account the mechanics of the environment, were transferred to 'Geoekoprom' LLC (RF) for further use in the design and creation of new production technological processes and the use of known ones (Certificate of Implementation).

Execution of work.

The dissertation was completed at the Department of Energy Efficiency and Green Energy Technologies of the Azerbaijan Technical University. Chemical analysis of geothermal systems, experimental studies on density, viscosity and speed of sound at the Department of Technical Thermodynamics of the University of Rostock (Germany), within the framework of the DAAD academic exchange program.

Volume and structure of the work

The dissertation consists of an introduction, three chapters, a summary and conclusions. The work is presented on 380 pages of computer text, including an appendix and a certificate of data implementation, 330 titles of scientific sources, includes 124 figures and 52 tables. The volume of the dissertation by sections: introduction:

26838 characters; chapter I: 114060 characters; chapter II: 116851 characters; chapter III: 35584 characters; conclusion: 12527 and findings: 14216 characters. Total volume of the dissertation: 320076 characters.

CONTENT OF THE WORK

The introduction substantiates the relevance of the topic of the work, analyzes the issues of definition of the object and subject of the study, formulates the purpose and objectives of the study, shows the research methods and the main provisions submitted for defense, scientific novelty, theoretical and practical value of the study, testing and implementation of the work, as well as a brief summary of the dissertation.

The first chapter provides an analysis of the data on thermal conductivity available in the literature, existing research methods, theories and correlation equations for studying the thermal conductivity of aqueous solutions of multicomponent mixtures. Justification for the choice of the method and objects of study. Experimental studies of the transport (thermal conductivity) properties of aqueous solutions of artificial multicomponent mixtures are presented. Modified experimental setup based on the method of coaxial cylinders (stationary method) has been successfully used previously. The experiments were carried out on isotherms with a step of 20 K in temperature and 10 MPa in pressure. The total measurement error of thermal conductivity, pressure, temperature and concentration with a confidence probability of 95% is 2%, 0.05%, 30 mK, and 0.02%, respectively.

In this method, the heat generated in the inner cylinder is distributed radially through a narrow gap filled with the test solution to the coaxial outer cylinder, which receives the heat.

The thermal conductivity of the studied fluid at a given temperature and pressure was calculated using the ratio (working equation of the method):

$$\lambda = \frac{Q \ln(d_2 / d_1)}{2\pi l \Delta T} \qquad (1)$$

Where $Q=Q_{meas}-Q_{los}$ - the amount of heat passing through the sample layer between the cylinders by heat transfer; Q_{meas} - the amount of heat generated by a calorimetric microheater; Q_{los} - the amount of heat lost through the ends of the measuring cell (due to edge effects);d_1 - outer diameter of the inner cylinder;d_2 - inner diameter of the outer cylinder;l - length of the measuring part of the cylinder; ΔT - temperature difference between the inner and outer cylinders (along the solution layer).

After taking into account all the corrections, the working equation can be written as in equation (2), λ / ($W\cdot m^{-1}\cdot K^{-1}$) :

$$\lambda = A\cdot \frac{Q_{meas}-Q_{los}}{\Delta T_{meas}-\Delta T_{corr}} \qquad (2)$$

where $A=\ln\left(\frac{d_2}{d_1}\right)/2\pi l$ is a geometric constant of the installation, which is determined through the geometric characteristics of the measuring cell. The values of the constant of the measuring cell, determined through its geometric characteristics and by calibration using water at a temperature of 293.15 - 750.15 K, at pressures of 0.101 and 60 MPa.

The characteristics of the measuring cell are as follows: the outer diameter of the inner cylinder d_2= $(10.98 \pm 0.01)\times10^{-3}$ m, the outer diameter of the outer cylinder d_1=$(12.92\pm0.02)\times10^{-3\ m}$, the length of the measuring part (section) of the inner cylinder (emitter) is l=$(150\pm 0.1)\times10^{-3}$, the distance between the cylinders (thickness of the liquid layer) δ =$(0.97\pm0.03)\times10^{-3}$ m. The choice of the optimal distance between the cylinders is determined by the reduction of the degree and probability of convection and the accommodation effect. The acceptable value of the liquid layer thickness δ lies within the range from 0.5 to 1 mm. If δ >1 mm, then natural convection of heat transfer between the cylinder walls appears. The optimal value of the ratio of the length l to the diameter of the inner cylinder d_2 l/d_2 should be from 10 to 15. It is very difficult to achieve uniform temperature distribution along the length of the inner cylinder when the ratio l/d_2>15. If l/d_2<10, then the influence of edge effects becomes significant.

The aqueous solution sample under study was placed vertically in the space between the cylinders of the measuring cell. The measuring cell was filled with the sample using valves 7 (see Figure 1). Before filling, the cell was heated and evacuated. In order to fill the measuring cell (the space between the cylinders) with the solution under study, slits were made on the outer cylinder, 2 mm wide, 3 mm from the ends and 25 mm long. The pressure in the system was created and measured using the MP-600 and MP-60 piston manometers with upper pressure measurement limits of 600 and 60 bar, respectively. Mercury in the U-shaped tube was used as a separating liquid between the oil and the sample under study. All connecting capillary tubes, including filling tubes and high-pressure tubes in the U-shaped separator, were made of stainless steel.

Inside the cell, heat was generated by a microheater-4, which consists of an insulated (coated with high-temperature varnish) constantan wire with a diameter of 0.1 mm. Microheater-4 is placed inside the inner cylinder-emitter and wound on the surface of a ceramic tube with a diameter of 2 mm, and then insulated with high-temperature varnish. The tube is tightly located inside a heater pocket with a diameter of 6 mm on the inner cylinder. The change in cell size due to pressure can be neglected since the volumetric compressibility of stainless steel (1X18H9T) is very small.

Due to the large size of the emitter and the small volume of the solution surrounding it, the influence of the accommodation effect can be completely neglected. Calibration was also carried out at a pressure of 60 MPa to avoid correction for the accommodation effect.

To reduce the Reynolds number *Re* between the cylinders, a small gap between the cylinders $\boldsymbol{\delta} = (0.97 \pm 0.03) \times 10^{-3}$ was taken. Convection develops when the Re number exceeds a certain critical value $Re_к$, which for a vertical coaxial cylinder is 1000. Therefore, the condition *Re* >1000 was considered as a criterion for the onset of convection. Under the conditions of our experiments, the value of the *Re* number was always less than 500, i.e., the Q_{con} value can be neglected. The absence of convection in our experiments can be verified by measuring the thermal conductivity at different temperature differences ΔT in the gap between the cylinders and at different powers Q of heat transfer between the cylinders.

In order to minimize radiative heat transfer, low emissivity 1X18H9T stainless steel was used for the cylinders and the liquid layer between the cylinders was very small (about 0.97 mm). In this way, the heat transfer by radiation can be significantly reduced compared to molecular heat transfer. Due to the lack of optical characteristics of aqueous solutions of salts at high temperatures, it is impossible to theoretically estimate the radiative thermal conductivity λ_r and the radiative heat flux $Q_{rad..}$ The absorption correction for pure water is very small, therefore, for aqueous solutions of salts at temperatures up to 600 K we neglected the contribution of radiation.

The measurement error of thermal conductivity is determined by the measurement errors of the quantities included in the working equation (2). In this method, thermal conductivity, according to the working equation (2), is determined through the measured quantities A, Q, T, ΔT, P и m.

Due to the lack of theoretical foundations for heat transfer phenomena in such complex systems as aqueous solutions of electrolytes (ionic systems), the theoretical analysis of the experimental results is entirely based on empirical and semi-empirical models describing the temperature, baric and concentration dependences of thermal conductivity.

The reliability and validity of the obtained experimental data were confirmed based on measurements of the most well-studied standard liquids, such as pure water, toluene and H_2O+NaCl. Our experimental thermal conductivity data and the formulas calculated based on IAPWS agree within the error limits of AAD = 0.44%.

The agreement between our data on the thermal conductivity of aqueous NaCl solutions and the most reliable data published in the literature ranges from 0.64% to 1.72%.

The thermal conductivity of the system of $H_2O+Sr(NO_3)_2$, $H_2O+LiNO_3$, $H_2O+Na_2CO_3$, $H_2O+K_2CO_3$, $H_2O + CaCl_2$, H_2O+NaBr, H_2O+KBr and tertiary systems of H_2O+NaBr+KBr was experimentally studied in a wide range of changes in state parameters. The experimental setup is shown schematically in Figure. 1.

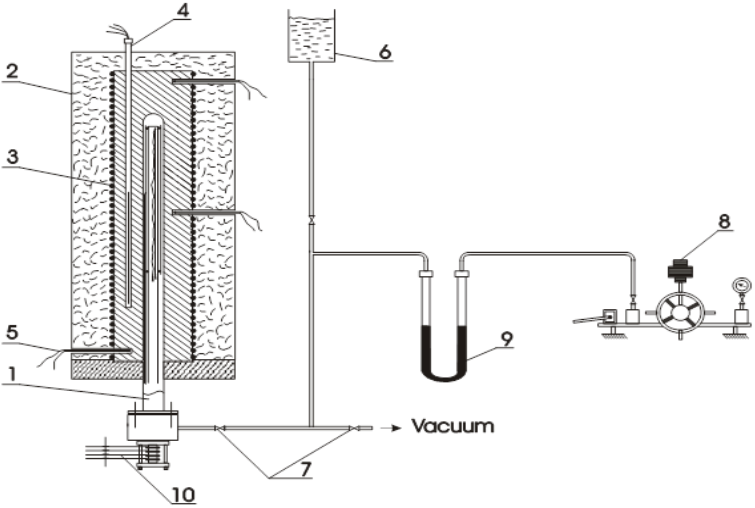

Figure 1. Schematic representation of an experimental setup for measuring the thermal conductivity of aqueous salt solutions at high temperatures and pressures using the coaxial cylinder method.

The experimental setup consists of: high pressure autoclave – 1, thermostat – 2, heater - 3; PTS (Pressure-Temperature Sensor) - 4; thermocouple - 5; filling system - 6; set of valves - 7; piston gauge (MP-600) - 8; U-shaped capillary tube (separator) - 9; electrical wires – 10 (figure 1.)

It is very difficult to achieve uniform temperature distribution along the length of the inner cylinder when the ratio $l/d_2 > 15$. If $l/d_2 < 10$, then the influence of edge effects becomes significant. Graphical analytical processing of data on the thermal conductivity coefficient of solutions revealed patterns of temperature, baric and concentration dependencies that can be represented by equations in the form (λ, P, T, m) for binary aqueous solutions and ternary systems were represented by equation (3):

$$\lambda = \sum_{i=0}^{1} \sum_{j=0}^{1} \sum_{k=0}^{2} a_{ijk} m^i P^j T^k \qquad (3)$$

where λ is the thermal conductivity of the solution, $(\mathrm{W\cdot m^{-1}\cdot K^{-1}})$***;*** T is the temperature in K; P is the pressure in MPa. The average absolute deviation of the experimental and calculated values of thermal conductivity is in the range from 0.5 to 0.7%. The obtained equation (3) is valid for the studied solutions in the temperature range from 290.15 to 595.15 K, for pressures up to 40 MPa, and concentrations up to 4 $\mathrm{mol\cdot kg^{-1}}$.

The temperature, baric and concentration dependences of thermal conductivity were studied in detail (Figures 2-5). Thermal conductivity measurements of aqueous solutions of $Sr(NO_3)_2$ were carried out along 5 isobars (0.1, 10, 20, 30, 40) MPa in the temperature range from 294.11 to 591.06 K, for five concentrations, (0.249, 0.525, 1.181, 2.025, 3.150) $\mathrm{mol\cdot kg^{-}}$.

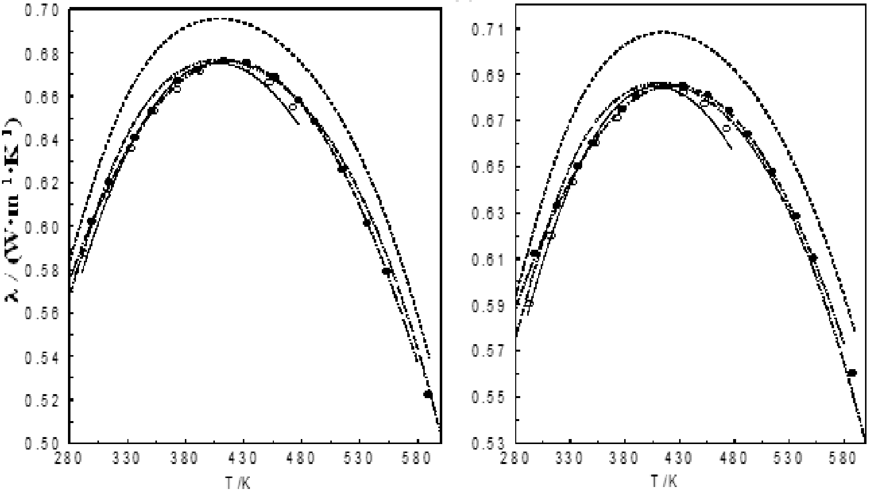

Figure 2. Measured thermal conductivity values of H_2O+ $LiNO_3$ solutions as a function of temperature for different pressures and concentrations together with data for pure water calculated from the IAPWS equation and data from other authors from the literature for pure water.

For aqueous solutions of $LiNO_3$, measurements were carried out at four isobars (0.1, 10, 20, 30) MPa for four concentrations (1.0, 1.7, 2.8, 3.9) mol·kg^{-1} in the temperature range from 293.15 to 573.15 K. The statistics of deviations between the experimental and calculated values of thermal conductivity from equation (3) for $H_2O+Sr(NO_3)_2$ are shown in Figure 5 for each measured concentration. New experimental data on the thermal conductivity of aqueous solutions of $CaCl_2$ for concentrations of (5, 10, 15, and 20 mass%) in the temperature range from (293 to 573) K and at pressures up to 40 MPa were obtained. The temperature, pressure and concentration dependences of thermal conductivity of aqueous solutions of $CaCl_2$ were investigated. A temperature maximum of thermal conductivity near 423 K was found for each measured isobar-isopleth. Also, a maximum of thermal conductivity of aqueous solutions of CaCl2 was found at low concentrations (dilute solution) near a concentration of 5 mass % for high temperatures.

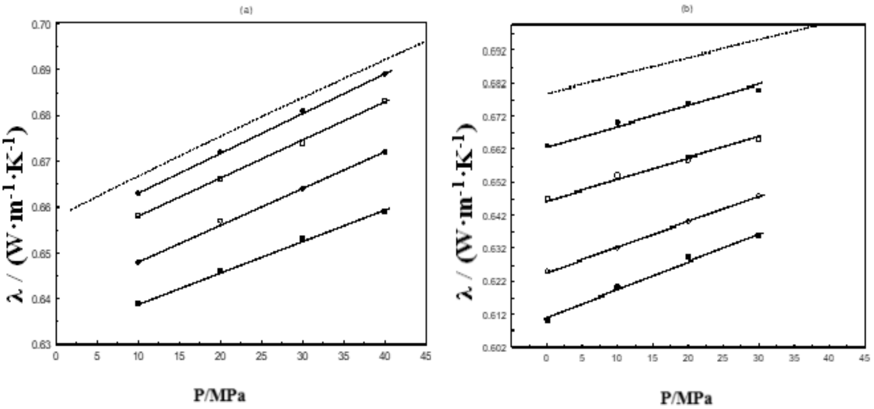

Figure 3. Measured thermal conductivity values. Measured thermal conductivity values of solutions *a*) $H_2O+Sr(NO_3)_2$ and *b*) $H_2O+LiNO_3$ as a function of pressure for various temperatures and concentrations together with data for pure water calculated from the IAPWS equation. (a) H_2O+ $Sr(NO_3)_2$, *T*=479.55 K: ●, 0.249 mol·kg^{-1}; □, 0.525 mol·kg^{-1}; ○, 1.181 mol·kg^{-1}; ■, 2.015 mol·kg^{-1}; (b) H_2O+ $LiNO_3$; T=373.15 K: ●, 1.0 mol·kg^{-1}; □, 1.7 mol·kg^{-1}; ○, 2.8 mol·kg^{-1}; ■, 3.9 mol·kg^{-1}; ——, calculation from equation (2), – – – –, calculation from the IAPWS equation for pure water.

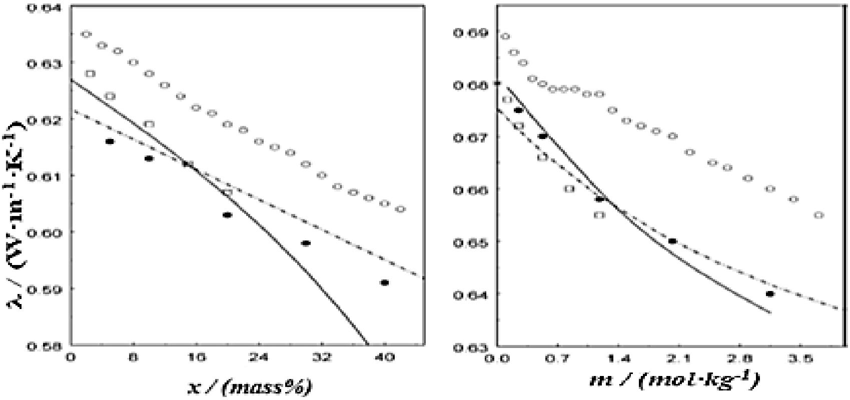

Figure 4. Measured values of thermal conductivity of aqueous solution $H_2O+Sr(NO_3)_2$ as a function of concentration along two selected isotherms 353.15 K (left) and 473.15 (right) for pressures (20 and 40) MPa. ●, this work; □, Abdulagatov and Magomedov, ○,Aseyev ; ——, calculation from equation (3).

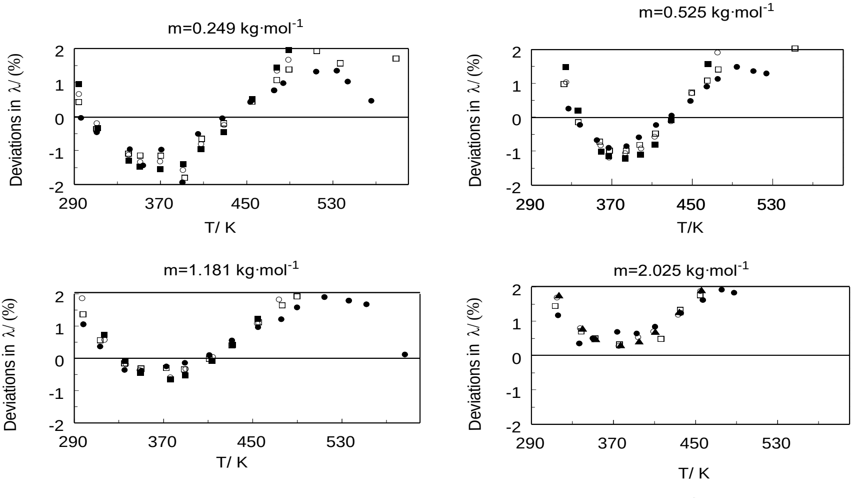

Figure 5. Relative deviation, ,$\delta\lambda=100(\lambda_{eks}-\lambda_{est})/\lambda_{est}$ of the measured and calculated from equation (1) values of thermal conductivity of an aqueous solution of $H_2O+ Sr(NO_3)_2$ as a function of temperature at different pressures. ●, 10 MPa; □, 20 MPa; ○, 30 MPa; ■, 40 MPa.

The concentration dependence of the reduced thermal conductivity of aqueous solutions is presented in the form of equation (4). The behavior of the concentration dependence of the thermal conductivity of aqueous solutions depends significantly on the nature of the ions of the dissolved substances:

$$\lambda_r = 1 + A_\lambda \sqrt{m} + B_\lambda m + B_\lambda m^{3/2}, \tag{4}$$

where $\lambda_r = \lambda_{sol} / \lambda_{H_2O}$ reduced thermal conductivity of aqueous solutions, A_λ and B_λ coefficient values for electrolyte solutions are a very useful tool for studying structural interactions (ion-ion, ion-solvent, and solvent-solvent) in solution. The value of the coefficient parameter depends on the long-range Coulomb interaction forces between ions. The coefficient, at a given concentration, can be interpreted in terms of special interactions of contributions from various effects that affect the transport properties of electrolytes, such as Coulomb interactions, the effects of ion sizes and shapes, or the so-called Einstein effect, the arrangement or orientation of polar molecules in the averaged field of other molecules, and distortion of the solvent structure. These effects control the behavior of the transport properties of aqueous electrolyte solutions.

In this paper, a model is developed to describe the combined effect of temperature, pressure and concentration on the behavior of the reduced thermal conductivity of aqueous solutions of $CaCl_2$ based on the relationship (5):

$$\lambda_r(T,P,x) = 1 + \Phi_0(T,P)x^{1/2} + \Phi_1(T,P)x + \Phi_2(T,P)x^{3/2} \tag{5}$$

where $\lambda_r(T,P,x) = \lambda_{sol}(T,P,x)/\lambda_{H_2O}(T,P)$, x – concentration in mass %, T-temperature in K,P- pressure in MPa, $\Phi_0(T,P)$, $\Phi_1(T,P)$, $\Phi_2(T,P)$, empirical functions of pressure and temperature (*T* и *P*). These functions are responsible for changes in the form of concentration behaviour of the thermal conductivity of the solution, with changes in T and P. The reduced thermal conductivity of an aqueous solution of $CaCl_2$ is an almost linear function of pressure. Consequently, the baric behavior of the thermal conductivity of aqueous solutions of $CaCl_2$ is completely determined by the baric dependence $\lambda_{H_2O}(T,P)$ for pure water. In general, the functional form $\lambda_r(T,P,x)$ must satisfy the final conditions (x=0, $\lambda_r(T,P,x=0)$ =1) of thermal conductivity of pure water (IAPWS), i.e., if $x \to 0$, from equation (5) we automatically obtain the thermal conductivity of pure water $\lambda_{H_2O}(T,P)$. Thus, the structure of the concentration dependence $\lambda_r(T,P,x)$ of equation (5) is chosen correctly. Different functional forms for $\Phi_i(T,P)$ tested in equation (5). Unfortunately, there are no theories that can correctly predict the functional dependence of $\Phi_i(T,P)$ on temperature and pressure in an explicit form. The explicit form of these functions $\Phi_i(T,P)$ in the model equation (5) was determined using the empirical functions reconstructing the program "Eureqa". The best (optimal) description of our experimental data on the thermal conductivity of aqueous solutions of $CaCl_2$ was achieved for the functions:

$$\Phi_0(T,P) = a_1 T_r \tag{6}$$

$$\Phi_1(T,P) = a_2 T_r^2 \tag{7}$$

$$\Phi_2(T,P) = a_3 + a_4 T_r^2 \tag{8}$$

where $T_r = T/1000$, T -в K; x – in mass %; P -in MPa. The obtained values of the parameters of functions (6,7,8) a_i are equal to:

a_1=–0.941773×10^{-2}; a_2=0.113933×10^{-1}; a_3=–0.35569×10^{-3}; a_4=–0.137671×10^{-2}.

The dependence of the reduced thermal conductivity λ_r on pressure is very weak (λ_r changes slightly with pressure P).

Therefore, in the first approximation, the functions $\Phi_i(T,P)$ in the model equation (4) can be considered as functions of temperature only without losing the accuracy of the description of the experimental data themselves (AAD=0.23%).

The developed correlation model for thermal conductivity of the studied aqueous solutions is valid in the temperature range from (293 to 573) K, for pressures up to 40 MPa, and at concentrations from 0 to 20 mass%, although reasonable extrapolation of experimental values of thermal conductivity outside this range of temperatures and pressures is possible. The average absolute deviation between the measured and calculated values of thermal conductivity is 0.21%.

Thermal conductivity measurements of four aqueous solutions of NaBr (10, 20, 30, and 38) mass%, three aqueous solutions of KBr (10, 20, and 30) mass%, and three aqueous solutions of the ternary system H_2O + NaBr + KBr (10% NaBr + 5% KBr, 10% NaBr + 10% KBr, and 10% NaBr + 20% KBr) were carried out at two isobars (10 and 40) mPa and near the saturation line (0.101 - 2 MPa). Selected measurement results are shown in Figure 6 in $\lambda - T$ projections.

The temperature range covers the area from (294 to 577) K. For pure water, this maximum thermal conductivity is achieved at temperatures between 409 - 421 K, when the pressure varies between 20 - 60 MPa. Adding salt slightly shifts the temperature position at which the maximum thermal conductivity is achieved toward higher temperatures. Experimentally, we found the maxima of thermal conductivity of each isobar-isopleth, $\lambda - T$ dependence, at temperatures of 400-427 K for H_2O +NaBr and between 403-410K for H_2O +KBr depending on the pressure and concentration of the solution, similar to the behaviour of thermal conductivity for pure water. A relationship was found between the position of thermal conductivity maxima (temperature values at which the derivative is $(\partial\lambda/\partial T)_{P,\omega} = 0$) with the pressure and concentration of the solution.

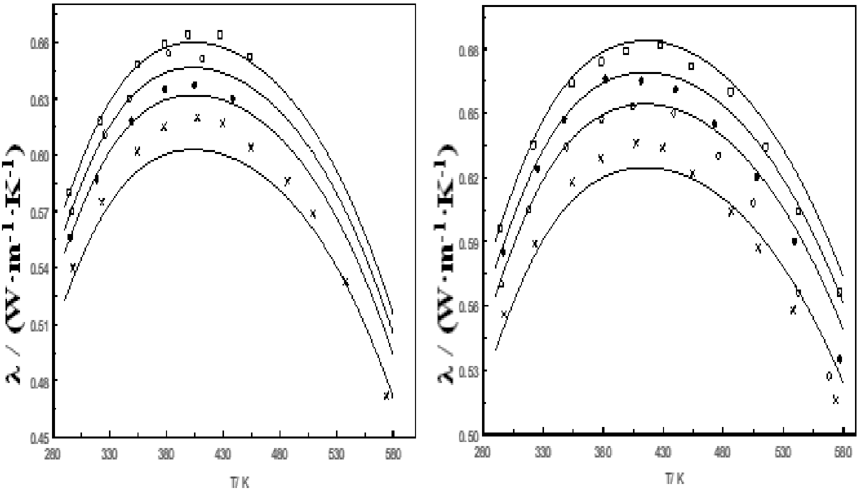

Figure 6. Measured values of thermal conductivity of ternary aqueous solutions H_2O+NaBr+KBr as a function of temperature for different KBr compositions together with data for binary solutions H_2O+NaBr и H_2O+ KBr . (a) P=0.1-2 MPa: □, H_2O+10%NaBr+0%KBr; ●,H_2O+10%NaBr+5%KBr;○,H_2O+10%NaBr+10%KBr;H_2O+10%NaBr+20%KBr. (b) P=40 MPa: □, H_2O+10%NaBr+0%KBr; ●, H_2O+10%NaBr+5%KBr;○,H_2O+10%NaBr+10%KBr;H_2O+10%NaBr+20 %KBr.——, Aseyev.

Thermal conductivity measurements for an aqueous solution of Na_2CO_3 were carried out at three isobars (0.1, 10 and 30) MPa between (294.11 and 627.06) K and molarity (0.4966, 1.0483 and 1.6650) $mol \cdot kg^{-1}$. Thermal conductivity of $H_2O+Na_2CO_3$ solutions was measured as a function of temperature at constant pressure for different concentrations. The maximum thermal conductivity is at (406 and 440) K depending on pressure and concentration. Thermal conductivity increases almost linearly with increasing pressure in the temperature range up to 627.15 K and at pressures up to 30 MPa. Thermal conductivity of the solution decreases monotonically with increasing concentration.

New data on thermal conductivity were obtained for 5 aqueous solutions of $H_2O + K_2CO_3$ (5, 10, 15, 20, 25) mass% at a pressure near the saturation line of 0-1 MPa. These data were linearly extrapolated to the saturation pressure. Measurements were carried out in the temperature range of 293-573 K. Present studies significantly expand the existing database NIST USA on the thermal conductivity of these above-mentioned systems. The existing theoretical results describing the concentration dependence of transport properties, such as viscosity and electrical conductivity of ionic solutions, given in the works of FalkenhagenOnsager-Fuoss [1], Onsager and Fuoss[2], Debye-Hückel-Onsager[3], Debye – Hückel[4] can determine the concentration dependence of relative properties in infinite dissolution (c→0). These theories correctly explain the concentration dependences of transport properties in the limit of very low concentrations (dilute solutions c<0.05 мol·кg^{-1}), but not very practical due to their limited concentration range. These theories are not very practical because of their limited concentration range. The data for various values of the reduced thermal conductivity A_λ and B_λ , calculated by equation (4) for each measurement, depending on the temperature, are presented in Figure 7, where it is evident that at low temperatures (below 340 K), the value of the parameter is always negative. The behavior of the concentration dependence of thermal conductivity of viscous solutions depends on the ions of the solution. Figure 7 demonstrates the effect of various anions on the data and temperature dependence of the thermal conductivities of aqueous solutions of salts. The values of the coefficients are used as a tool for describing and constructing the ion-ion, ion-solution, solution-solution structure.

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[4] P. Debye,H. Hückel. Bemerkungen zu einem satze über die kataphoretische wanderungsg eschwindigkeit suspendierter teilchen //- Berlin: Z. Phys., - 1924. № 25, -p. 49-52.

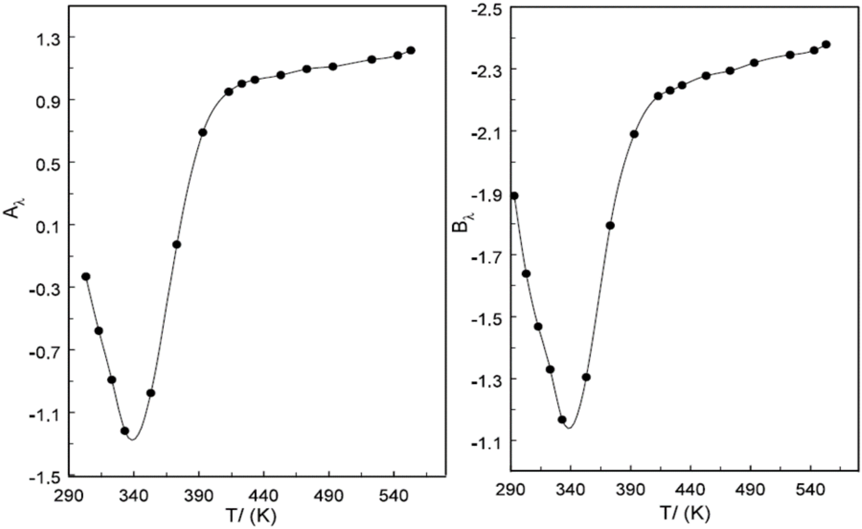

Figure 7. Values of the coefficients A_λ (left) and B_λ (right) for $H_2O+K_2CO_3$ depending on temperature.

The second chapter provides a review of the literature on the study of volumetric properties (PVT data) of aqueous solutions of artificial multicomponent mixtures, conducted on the basis of the TRC/NIST Database (USA). The number of publications providing measurements of density (PVT data) and other volumetric properties of aqueous solutions of alcohols under pressure and at high temperatures is very limited. Water, salt and alcohols are complex compounds with a complex nature of intermolecular interactions, and, therefore, complicate the task of their experimental and theoretical study. Another equally important problem is the development of a reliable equation of state for multicomponent water-alcohol mixtures at high temperatures and pressures. Alcohol is a standard representative of associated liquids. Alcohol molecules greatly affect the structure of water, which leads to anomalies in many thermodynamic and transport properties of aqueous solutions of alcohols. Alcohol molecules rearrange the structure of water in the mixture. The study of excess, apparent and partial molar volumes of aqueous solutions is important for testing and studying the nature of intermolecular (structural) interactions solvent - solute, solvent - solvent, solute - solute. - a soluble substance, whose molecules have different shapes, sizes, and chemical nature. As noted earlier, the bulk properties of aqueous solutions play a key role in many industrial and natural processes, many of which occur at high temperatures and pressures. Thus, for a deep understanding at the microscopic level of the physicochemical nature and mechanism that determines the anomalous properties of aqueous solutions, precise experimental data on their volumetric properties are necessary. The partial derivative of density from pressure, temperature and concentration is an important value that is used to calculate caloric properties such as enthalpy, entropy, internal energy, Gibbs free energy, etc. The total (second) derivative determines the behaviour of molar heat capacity at constant pressure and constant volume.

The measurement error of density in this method depends on the measurement errors of mass (δM) and volume of the piezometer (δV_{pT}) at a given temperature *T* and pressure *P*.

Experimental (PVmTx) data for water-alcohol solutions of binary and ternary systems $H_2O+C_2H_5OH$, $H_2O+C_2H_5OH+LiNO_3$, $H_2O+C_3H_7OH+KNO_3$, $H_2O+C_3H_7OH+Li_2SO_4$ were obtained using a constant-volume piezometer placed in a liquid thermostat. The thermostat controls the constancy of temperature with high accuracy (±0.02 K). The measurement errors of density, pressure, temperature, and concentration at a 95% confidentiality level and k = 2 are 0.06%, 0.05%, 15 mK, and 0.015%, respectively. A full description and operating principle of the experimental setup are given in the paper.

The density, (PVTx) properties and other volumetric properties (excess, apparent and partial molar volumes) obtained from PVTx measurements for binary $H_2O+C_2H_5OH$ and ternary $H_2O+C_2H_5OH+LiNO_3$ mixtures were investigated experimentally and theoretically for four compositions of 0.0168, 0.0368, 0.0855, and 0.1166 molar fractions of ethanol in the temperature range from 298

K to 448 K and pressures up to 40 MPa using a constant volume piezometer. For the ternary $H_2O+C_2H_5OH+LiNO_3$ system, measurements were carried out in the same temperature and pressure range for 12 concentrations.

The experimental values of the density of the binary system water+ethanol obtained in this work, together with the most accurate (internationally recognized) data for pure water (IAPWS standard), were used to calculate the apparent partial molar volumes of each component. Calculations of the values of apparent and partial molar volumes were carried out on the basis of our data on the density ρ_{mix} of solutions and pure water ρ_w using well-known thermodynamic relationships.

The apparent molar volumes of the water+ethanol system that we obtained were used to calculate the values of the apparent molar volume at infinite dilution V_Φ^0 (infinitely diluted partial molar volume, $V_\Phi^0 = \bar{V}_2^\infty$) at various temperatures and pressures. For the calculation of V_Φ^0 we used the standard procedure of extrapolation of V_Φ to zero concentration ($m \to 0$).

The thermodynamics of dilute binary mixtures is a subject of wide scientific interest, since during dilution the dominant role in determining their properties is played by the interaction between the molecules of the solvent and the solute, while the interaction between the molecules of the solute and the solute can be neglected due to the low concentration of the solute. Dilute solutions have not only scientific significance, but also important practical (technological) application, such as the effect of small impurities on the thermodynamic behaviour of the system. For dilute solutions, the effect of impurities (here we consider the solute as an impurity, and not as an impurity in the solute) is proportional to the compressibility of the pure solvent.

The concentration dependences of the ternary mixture water+ethanol+ LiNO$_3$ are shown in Figures 8, 9 together with the values for the binary mixture water+ethanol.

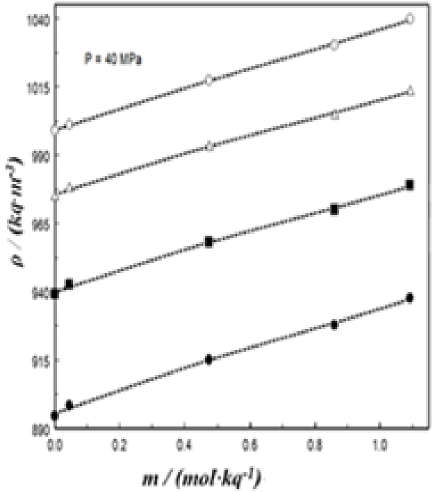

Figure 8. Measured values of the density of the ternary system water+ethanol+LiNO$_3$ depending on the concentration (molarity of LiNO$_3$) for the selected isobar of 40 MPa and various isotherms and at a fixed concentration of ethanol (9.32 mass%). ● - 448.15 K; ■ - 398.15 K; △ - 348.15 K; ○ - 298.15 K;

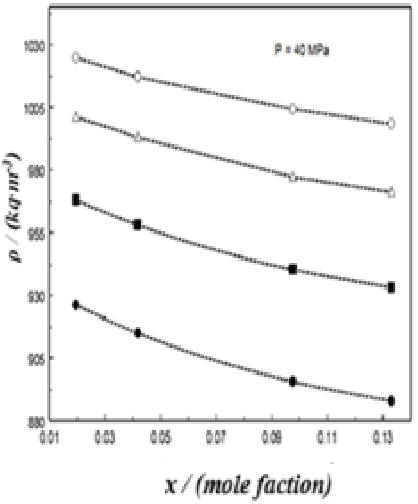

Figure 9. Measured values of density of the ternary system water+ethanol+LiNO$_3$ as a function of concentration (molar fractions of ethanol) for the selected isobar of 40 MPa and various isotherms and at a fixed concentration of LiNO$_3$(0.4387 mol·kg^{-1}). ●, 448.15 K; ■, 398.15 K; △, 348.15 K; ○, 298.15 K;

These figures demonstrate how the addition of the electrolyte LiNO$_3$ affects the behavior of the density of the binary system of the mixture water+ethanol. The addition of ethanol decreases the density of the ternary system, while the addition of LiNO$_3$ increases it. Excess (V_m^E), apparent (V_Φ), and partial ($\overline{V}_2^\infty$) molar volumes were calculated based on the measured density values for the binary water+ethanol mixture and the pure components (water and ethanol). The concentration dependence of the apparent (V_{Φ}) molar volume was extrapolated to zero ($x \rightarrow 0$) to calculate the partial molar volumes of ethanol at infinite dilution ($\bar{V}_2^{\infty}$).

The temperature, pressure, and concentration dependences of the density were investigated and the volumetric properties (V_m^E, V_{Φ} $\bar{V}_2^{\infty}$) of the studied solutions were calculated on this basis. All measured and calculated (V_m^E, V_{Φ}, $\bar{V}_2^{\infty}$) properties were compared in detail with the literature data for the water + ethanol binary system in order to demonstrate the accuracy of the measured and calculated data and to assess the reliability of our and published data. It was found that the excess molar volume of the water + ethanol binary system is very small and negative for all studied concentration, temperature and pressure ranges. We also found that the excess molar volume of the water + ethanol binary system has a minimum at a concentration of 0.4 molar fractions of ethanol. The minimum of the apparent molar volume V_{Φ} was found near a concentration of 2 mol·kg^{-1} (dilute mixture).

New data on the density of the ternary system water+1-propanol+KNO3 were obtained experimentally at temperatures from (298 to 448) K and pressures up to 40 MPa for six concentrations, namely: KNO_3 (0.261 mol· kg $^{-1}$ H_2O)- C_3H_7OH (5 mass%); KNO_3 (0.261 mol·kg^{-1} H_2O) – C_3H_7OH (20 mass %); KNO3 (0.261 mol·kg^{-1} H_2O) – C_3H_7OH (15 mass %); KNO3 (0.435 mol·kg^{-1} H_2O) – C_3H_7OH (15 mass %); KNO3 (1.130 mol·kg^{-1} H_2O)- C_3H_7OH (15 mass %); KNO3 (0.261 mol·kg^{-1} H_2O) – C_3H_7OH (25 mass %). The measured values of density of the ternary system water+1-propanol + KNO_3 were used to calculate the partial molar volumes of the electrolyte (KNO_3) and alcohol (1-propanol) at infinite dilution as a function of temperature, pressure and component concentration. The maximum partial molar volume was found at a temperature of about 323 K at low (dilute) electrolyte concentrations and shifted significantly towards high temperatures (up to 373 K) at high electrolyte concentrations of 1.13 mol·kg^{-1}. The influence of pressure on the partial molar volume of the electrolyte $\overline{V}_2^0$ is very weak at low temperatures of 350 K, and at high temperatures the slope $\overline{V}_2^0 - p$ of the isotherms changes sharply.

In the presence of alcohol in the binary system water + KNO_3 under the same *T* and *P* conditions, the partial molar volume of the electrolyte (KNO_3) increases compared to the value in the water + KNO_3 mixture free of alcohol (in the absence of alcohol). Addition of 15 mass% alcohol (1-propanol) to the binary mixture water + KNO_3 increases the partial molar volume of the electrolyte (KNO_3) by 7.5%. The thermal expansion coefficients $\left(\partial\overline{V}_2 / \partial T\right)_{PTx}$ of the partial molar volume of the electrolyte (KNO_3) were calculated based on measurements of the molar volume of the ternary mixture.

New data on the bulk properties (viscosity, PVT properties) for complex ternary fluid mixtures of water + 1-propanol + Li_2SO_4 were obtained for nine compositions (four compositions of 0.0155, 0.0254, 0.0322 and 0.0502 mole fraction of 1-propanol and four compositions of salt 0.0062, 0.0124, 0.0199 and 0.0274), in the temperature range from (303 to 448) K and at pressures up to 40 MPa, using the constant volume piezometer method. Partial molar volumes of salt (Li_2SO_4) $\overline{V}_2$ and alcohol (1-propanol) $\overline{V}_1$ were calculated based on the measured values of the density of the ternary mixture of water + 1-propanol + Li_2SO_4 as a function of temperature, pressure and concentrations of both solutes. The maximum partial molar volume of the salt $\overline{V}_2$ was found in the low temperature range (around room temperature). The influence of pressure on the position of the temperature maximum of the salt $\overline{V}_2$ is insignificant. We also found that the dependence $\overline{V}_1$- x_2 for all measured isotherms exhibits a minimum at concentrations of about x_2 =0.017 molar fraction of salt.

The position of the concentration minimum $\overline{V}_1$ shifts slightly toward the region of high concentrations with increasing temperature. The apparent molar volume of the salt $\overline{V}_2$ is a linear function of x_2 with nearly identical slopes for all measured isotherms.

The concentration dependences of the obtained partial molar volumes of salt and alcohol were extrapolated to zero concentration (x_1 = 0 and x_2 = 0) to obtain the partial molar volumes at infinite dilution of the salt ($\overline{V}_1^0$ and $\overline{V}_2^0$). The dependences of the density and the obtained partial molar volumes of the ternary mixture on temperature, pressure and concentration are studied in detail. The partial molar volumes of the salt at infinite dilution $\overline{V}_2^0$ depend little on temperature in the low-temperature region (below 350 K) and decrease rapidly at high temperatures (above 350 K). The dependence $\overline{V}_2^0$ on pressure is very weak at low temperatures of 350 K, while at high temperatures the angular coefficient of the isotherms $\overline{V}_2^0 - P$ changes significantly. In the presence of alcohol in a binary solution of water + Li_2SO_4 under the same conditions of T and P, the partial molar volume of the salt (Li_2SO_4) increases compared to the values for anhydrous binary solutions of water + Li_2SO_4. In the presence of alcohol in a binary solution of water + Li_2SO_4 under the same conditions of T and P, the partial molar volume of salt (Li_2SO_4) increases compared to the values for anhydrous binary solutions of water + Li_2SO_4. The values of the partial molar volumes of alcohol $\overline{V}_1^0$ and salt $\overline{V}_2^0$ in a ternary mixture are calculated at infinite dilution ($x_1 = x_2$ = 0) of both solutes (salt and alcohol simultaneously). A very pronounced temperature maximum $\overline{V}_2^0$ (especially at high pressures) is found to be near 325 K, while $\overline{V}_1^0$ increases monotonically with temperature.

The obtained values $\overline{V}_1^0$ and $\overline{V}_2^0$ are presented in Table 1 at P=5 MPa.

Table 1.

Calculated values of partial molar volumes ($cm^3 \cdot mol^{-1}$) of 1-propanol ($\bar{V}_1^0$) and Li_2SO_4 ($\bar{V}_2^0$), at infinite dilution $x_1 \to 0$, for different salt concentrations in the ternary system water + 1-propanol + Li_2SO_4 depending on temperature and pressure.

P=5 MPa, x_2=0.00623 m.f.			P=5 MPa, x_2=0.0124	P=5 MPa, x_2=0.0274	P=5 MPa, x_2=0.0199
T, K	$\bar{V}_1^0$	$\bar{V}_2^0$	$\bar{V}_1^0$	$\bar{V}_1^0$	$\bar{V}_1^0$
303.15	67.29	22.77	65.29	68.51	65.48
323.15	69.09	22.49	66.87	69.40	66.73
348.15	71.22	20.70	68.85	70.84	68.47
373.15	73.49	17.95	70.99	72.57	70.42
398.15	75.98	14.70	73.32	74.40	72.52
423.15	78.85	11.09	75.86	76.33	74.71
448.15	82.10	6.760	78.69	78.43	77.13

$u(p)$ =0.025%; $u(\rho)$=0.03%; $u(T)$ =0.02 K; $u(x)=5\times10^{-5}$;
$u(\bar{V}_2^0)$ =0.2%

The partial molar volumes of 1-propanol ($\bar{V}_1^0$) and Li_2SO_4 ($\bar{V}_2^0$) were calculated at infinite dilution with both dissolved substances (alcohol and salt) ($x_1 \to 0$ and $x_2 \to 0$, simultaneously) depending on the temperature for three selected isobars of 5, 20 and 40 MPa in Figure 10.

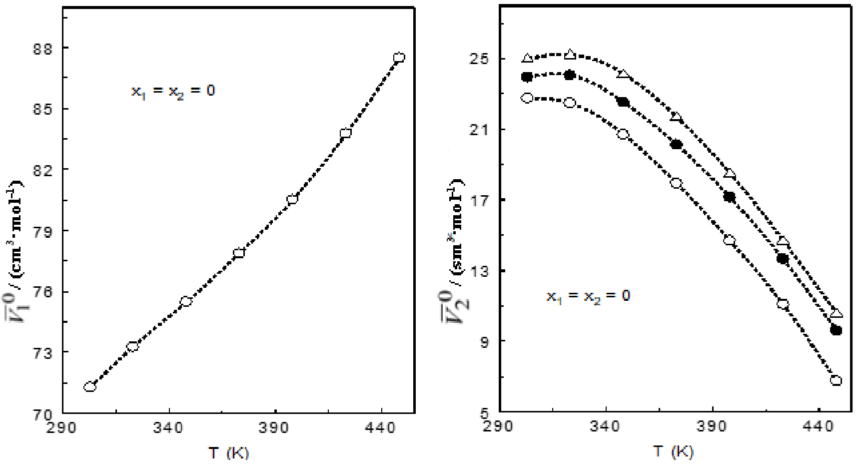

Figure 10. Values of partial molar volumes of alcohol (1-propanol,) $\overline{V}_1^0$ and salt (Li_2SO_4, $\overline{V}_2^0$) at infinite dilution of both solutes (alcohol $x_1 \to 0$ and salt $x_2 \to 0$), calculated from experimental values of molar volumes of the ternary system water + 1-propanol + Li_2SO_4 depending on temperature for fixed isobars. Left: ○, 5 MPa; Right: ○, 5 MPa; ●, 20 MPa; and □△, 40 MPa.

The influence of pressure on the $\overline{V}_1^0$ values obtained from the measured data for the ternary mixture is shown in Figure 10. The $\overline{V}_2^0$ values decrease nonlinearly with increasing temperature, while $\overline{V}_1^0$ monotonically increase with increasing temperature and are almost independent of the alcohol concentration.

The temperature dependence of partial molar volumes at infinite dilution of alcohol, when the alcohol concentration is small, $x_1 \to 0$, for individual salt concentrations along the 5 MPa isobar shows the state in an alcohol-free solution. This allows us to say that adding alcohol to a water + Li2SO4 solution increases the $\overline{V}_2^0$ values and slightly smooths out the very clearly expressed temperature maximum $\overline{V}_2^0$ in the alcohol-free binary solution water + Li2SO4 in the low-temperature region. Partial molar volumes of alcohol (1-propanol, $\overline{V}_1^0$

) and salt (Li_2SO_4, $\overline{V}_2^0$) at infinite dilution of the salt ($x_2 \to 0$) in ternary mixtures of water+1-propanol+ Li_2SO_4 depending on temperature for the selected isobar of 5 MPa for four fixed concentrations of alcohol (0.01553, 0.02541, 0.03224, 0.05024) are shown in Figure 11.

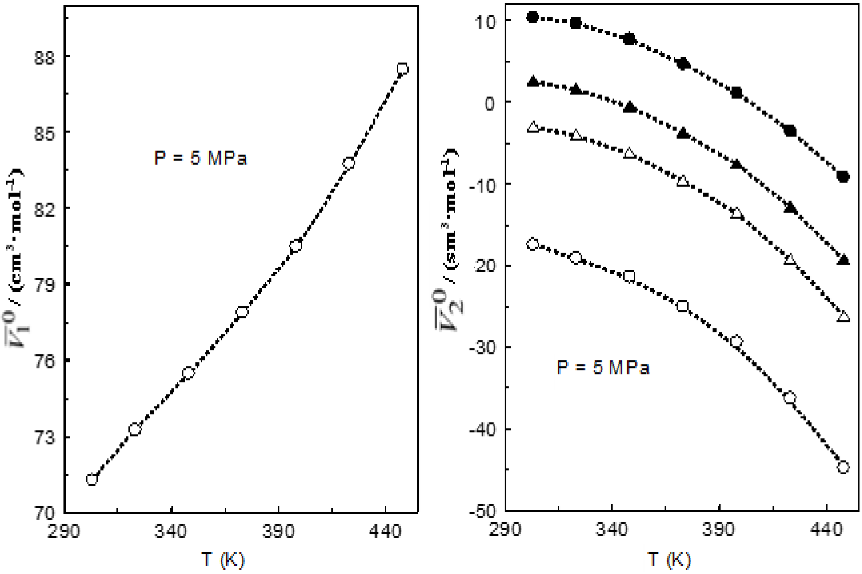

Figure 11. Values of partial molar volumes of alcohol (1-propanol) ($\overline{V}_1^0$) and salt ($\overline{V}_2^0$) at infinite dilution of salt ($x_2 \to 0$), calculated from experimental values of molar volumes of the ternary system water + 1-propanol + Li_2SO_4 depending on temperature for a constant concentration of alcohol 1-propanol at a fixed isobar of 5 MPa. ●, x_1 =0.0155; ○, x_1=0.0502; ▲, x_1 =0.0254; □△, x_1 =0.0322.

The values of partial molar volumes of salt (Li2SO4) ($\overline{V}_2^0$) at infinite dilution of both dissolved components (alcohol $x_1 \to 0$ and salt $x_2 \to 0$), calculated from experimental data on the molar volumes of the ternary system water + 1-propanol + Li2SO4 depending on the pressure for isotherms are shown in Figure 12.

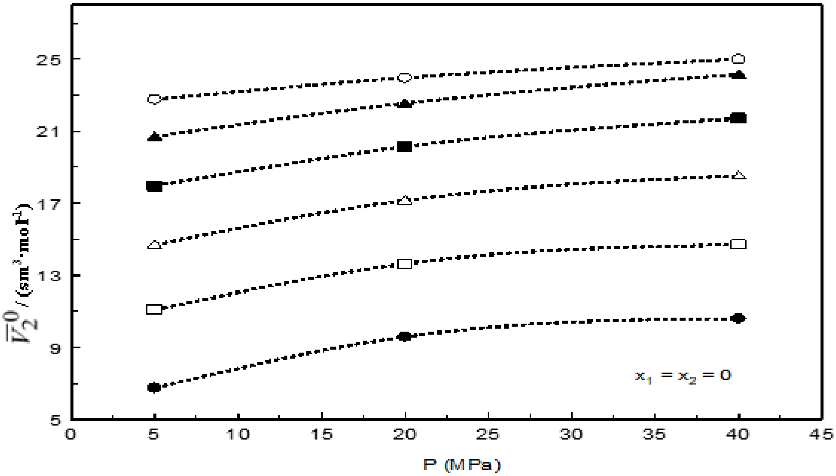

Figure 12. Values of partial molar volumes of salt (Li_2SO_4) ($\overline{V}_2^{o}$) at infinite dilution of both dissolved components (alcohol $x_1 \to 0$ and salt $x_2 \to 0$), calculated from experimental values of molar volumes of the ternary system water + 1-propanol + Li_2SO_4 depending on pressure for experimental isotherms.○, 303 K; ▲, 348 K; ■ 373 K; △, 398 K; □, 423 K; ●, 448 K.

The coefficient of thermal expansion (molar partial expansibility) is related to thermodynamic relationships with entropy and heat capacity, they contain information about structural changes in the system during thermal expansion. The calculated values of the thermal expansion coefficient of the partial molar volumes of the salt Li2SO4 (left) and 1-propanol (right) at infinite dilution (x_2 =0 on the left and x_1 =0 on the right) in the ternary system water + 1-propanol + Li2SO4 depending on the temperature along the 5 MPa isobar and constant concentrations of the salt and alcohol are shown in Figure 13.

As shown in Figure 13, the partial molar expansion of salt $\left(\partial \overline{V}_2^0 / \partial T\right)_{Px} < 0$ is negative and decreases with increasing temperature, while alcohol $\left(\partial \overline{V}_1^0 / \partial T\right)_{Px} > 0$ is positive and increases with increasing temperature, i.e. the partial molar expansions of both solutes have opposite signs and opposite temperature behavior. The same results were found for the ternary solution water + 1-propanol + KNO_3. The second derivatives of the partial molar volumes of the salt and alcohol with respect to temperature (i.e., curvature) are $(\partial^2 \overline{V}_2^0 / \partial T^2)_{Px} <0$, negative values and the solute destroys the structure of the solution, and $(\partial^2 \overline{V}_1^0 / \partial T^2)_{Px} >0$ is positive and the solute creates the structure of the solution. The molar expansibility of pure water $\left(\partial V_W / \partial T\right)_P$ and pure 1-propanol $\left(\partial V_m / \partial T\right)_P$ at the same T and P are positive and lie almost on a straight line. The second temperature derivative of the dependence of the molar volumes of pure water $\left(\partial^2 V_W / \partial T^2\right)_P$, and 1-propanol $\left(\partial^2 V_m / \partial T^2\right)_P$, are positive values. Thus, the salt (Li_2SO_4) destroys (tends to reduce the structure of water) the structure of the adjacent water molecules, while the alcohol molecules (1-propanol), unlike the salt, structure the water (surround it with a layer of increased structure). Thus, two opposite competing effects determine the volumetric properties of a complex mixture such as water + 1-propanol + Li_2SO_4.

Partial molar volumes at infinite dilution and its derivatives with respect to temperature $\left(\partial \overline{V}_i^0 / \partial T\right)_{Px}$ and $\left(\partial^2 \overline{V}_i^0 / \partial T^2\right)_{Px}$ are a measure of the change in the structure of the mixture, curvature $\left(\partial^2 \overline{V}_i^0 / \partial T^2\right)_{Px} > 0$ is positive for hydrophobic solutes (forming the structure) and negative $\left(\partial^2 \overline{V}_i^0 / \partial T^2\right)_{Px} <0$ for a hydrophilic solute (breaking the structure). Note that the values of $\left(\partial \overline{V_2^0} / \partial T\right)_{Px}$ and $\left(\partial^2 \overline{V_2^0} / \partial T^2\right)_{Px}$ are also negative and decrease with increasing temperature. The limiting values of the coefficient of thermal expansion of the partial molar volume of salt (Li_2SO_4) $\left(\partial \overline{V}_2 / \partial T\right)_{Px}$ and the coefficient of volumetric expansion of pure water (solvent) $\left(\partial V_w / \partial T\right)_P$ have opposite signs and opposite temperature behaviour.

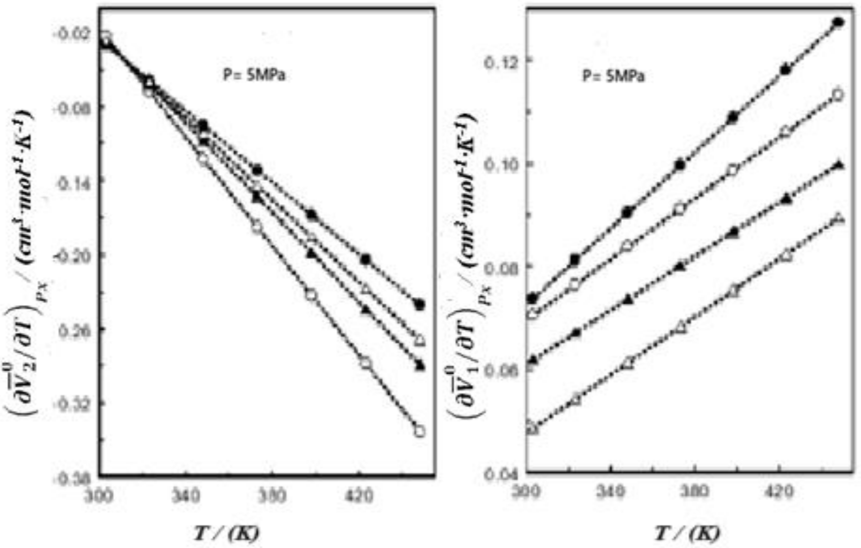

Figure 13. Calculated values of the thermal expansion coefficient of partial molar volumes $\left(\partial \overline{V}_2^0 / \partial T\right)_{Px}$ of Li_2SO_4 salt and $\left(\partial \overline{V}_1^0 / \partial T\right)_{Px}$ 1-propanol (on the right) at infinite dilution (x_2 =0 on the left and x_1 =0 on the right) in the ternary system water + 1-propanol + Li_2SO_4 depending on the temperature along the 5 MPa isobar and constant concentrations of salt and alcohol. Left (x_2 =0): ○, x_1 =0.0155; ▲, x_1 =0.0502; ●, x_1 =0.0254; △, x_1 =0.0322. Right (x_1 =0):○, x_2 =0.00623; ▲, x_2 =0.0124; ●, x_2 =0.0274; △, x_2 =0.0199.

Figure 14 shows comparisons of the thermal expansion coefficients of partial molar volumes $(\partial \overline{V}_2^0 / \partial T)_{Px}$ and $(\partial \overline{V}_1^0 / \partial T)_{Px}$ at infinite dilution x_2 = 0 of salt (Li2SO4) and x_1 = 0 of alcohol, 1-propanol) in a ternary solution of water + 1-propanol + Li_2SO_4 depending on the temperature along the selected isobar (5 MPa) and at constant concentrations of alcohol and salt. The thermal expansion coefficients of partial molar volumes of both dissolved substances have different signs and opposite temperature dependences.

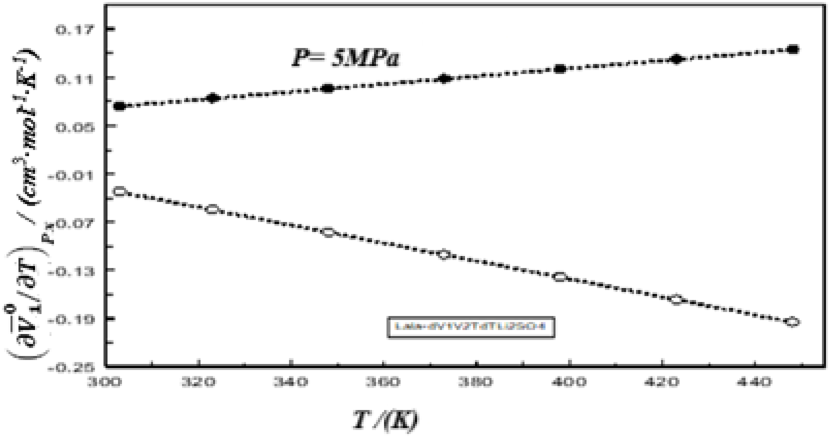

Figure 14. Calculated values of the thermal expansion coefficient of the partial molar volumes of Li_2SO_4 salt and $\left(\partial\overline{V}_1^0/\partial T\right)_{Px}$ 1-propanol at infinite dilution (x_2 =0 and x_1 +0) in the ternary system water + 1-propanol + Li_2SO_4 depending on the temperature along the 5 MPa isobar and constant concentrations of salt and alcohol. ○, x_1 =0.0155 and x_2 =0; ●, x_2 =0.00623 and x_1 =0.

The values of the molar volumes of the ternary mixture for each isobar-isotherm (constant P and T) were separately described by polynomial functions of the concentrations x_1 and x_2 :

$$V_m(P,T,x_1,x_2) = V_{m0}(P,T,x_1 = x_2 = 0) + A_1x_1 + A_2x_2 + A_3x_1x_2 + A_4x_1x_2^2 \quad (9)$$

where $V_{m0}(P,T,x_1 = x_2 = 0)$ is the molar volume of pure water; x_1 are the molar fractions of 1-propanol; x_2 are the molar fractions of

KNO3; A_i (i=1;4) are the fitting parameters, which are a function of temperature and pressure.

Liquids occupy an intermediate position between solids and gases in their molecular structure and thermal motion. The current concept of the model of molecular structure and thermal motion is that around a certain molecule, which assumes the role of a central molecule, neighbouring molecules are grouped, performing small oscillations with a frequency close to that indicated earlier for the oscillations of molecules of a solid in a lattice, and an amplitude of the order of the average distance between molecules. The central molecule either (at rest of the liquid) remains motionless or migrates with a velocity, the magnitude and direction of which coincides with the local average velocity of the macroscopic motion of the liquid. In the molecular structure of a liquid, the potential energy of interaction of molecules is comparable in order with the kinetic energy of their thermal motion; in this case, short-range order is found, but long-range order is absent. The difference in the molecular structure and thermal motions of solids, liquids and gases is clearly revealed in the phenomenon of diffusion, which consists in the spread of one substance (inclusion) into another (carrier). When alcohol molecules are introduced into the mixture, the hydrogen bond network is restructured, i.e. alcohol molecules can no longer fit into the cavities of the spatial hydrogen network, typical for hydrogen bonds. Then the polar OH groups of ethanol replace the water molecules, and the more extended hydrophobic groups of ethanol enter the cavity formed by the water molecules. New compounds are formed - hydrates of the first type. At concentrations above 25 wt. %, with an increase in temperature, hydrates of the second type are formed - water molecules form two or three hydrogen bonds. In hydrates of the second type, there is a weakening of hydrogen bonds compared to pure water. Also, with an increase in temperature, a weakening of hydrogen bonds is observed. This is true for all studied concentrations of water-alcohol solutions. Weak or broken hydrogen bonds are observed and, consequently, a decrease in the average energy of a hydrogen bond, with a decrease in temperature, the proportion of OH groups with strong hydrogen bonds increases. Liquid compressibility reflects the balance of intermolecular attraction and repulsion energies. This property of liquid largely determines the change in the partial molar volume of compounds in different environments, the change in viscosity at elevated pressure, and also allows us to clarify the causes of changes in the activation volume, reaction volume, and the effect of reaction acceleration under pressure. To assess the compressibility of substances in a wide range of pressures, equations of state are used that express the relationship between P, V, and T.

In engineering and thermodynamic calculations, specific volume is most often used to predict the behavior of liquids under changing conditions. Based on measured values for (p, Vm, T, m) properties of binary electrolyte solutions, a polynomial-type equation of state (10) was developed that describes the specific volume of a solution as a function of temperature, pressure, and concentration:

$$\upsilon_{sol} = A + Bt + Ct^2 + Dt^7 \qquad (10)$$

where υ_{sol} is the specific volume of the solution in $cm^3 \cdot g^{-1}$ (the density of the solution is determined as $\rho_{sol} = 1/\upsilon_{sol}$), and **t** is the temperature in °C. The dependence of the specific volume υ_{sol} on the pressure p and concentration m is determined through the coefficients *A*, *B*, *C*, and *D* (11), which have the form of a quadratic function of P (MPa) and concentration m ($mol \cdot kg^{-1}$ H_2O).

$$A = \sum_{i=0}^{2}\sum_{j=0}^{2} a_{ij} P^i m^j \ , \quad B = \sum_{i=0}^{2}\sum_{j=0}^{2} b_{ij} P^i m^j \ ,$$

$$C = \sum_{i=0}^{2}\sum_{j=0}^{2} c_{ij} P^i m^j \ , \quad D = \sum_{i=0}^{2}\sum_{j=0}^{2} d_{ij} P^i m^j \qquad (11)$$

Values of fitting parameters (11) of the equation of state (10) a_{ij}, b_{ij}, $c_{i,j}$ и d_{ij} calculated from our (p, V_m, T, m) measurements. The equation of state (10) describes our experimental values of the specific volume υ_{sol} (p, T, m) within 0.02%, which is much lower than the experimental error. The statistics of the deviations for 195 experimental points are: AAD=0.02%, Bias=0.011%, St.Dev=0.028%, St.Error=0.002%, and MaxDev.=0.105%. This equation was used to calculate the thermodynamic properties of a solution of other aqueous electrolyte solutions in a wide range of temperatures (up to 600 K), pressures (up to 40 MPa) and concentrations (up to 5 mol·kg^{-1}H_2O), including partial and apparent molar volumes.

The third chapter presents the results of studies of volumetric (density), acoustic (sound velocity) and transport (viscosity) properties of 8 natural geothermal fluids from the fields of the South of Russia in the temperature range from 278 to 353 K at atmospheric pressure Izberbash (No. 68 and No. 129), Ternair (No. 27T and No. 38T), Kayakent No. 4, No. 5, Kizlyar No. 4, No. 17T. The optical emission spectrometer IRIS Intrepid II and ion chromatograph were used for quantitative determination of the elemental composition (cations and anions) in geothermal brines. The accuracy of chemical composition measurements was from 0.2% to 1.0%. The chemical composition and percentage content of the main ions in the geothermal samples are presented in detail in the work in the form of tables.

One of the key factors in planning the exploitation of geothermal resources is the availability of reliable data on the thermodynamic properties of geothermal brines. Accurate knowledge of the thermal properties of geothermal waters with relatively high mineralization and brackish waters is a prerequisite for modelling geothermal waters and the basis for understanding the various physical and chemical processes occurring in the natural environment. Geothermal waters are a source of hydrocarbon-containing gases and valuable minerals.

In order to understand and control the processes occurring in geothermal waters, it is necessary to know their thermophysical and physicochemical, energy properties. The available data on the thermodynamic parameters of complex solutions similar to geothermal fluids, is insufficient for the needs of geothermal production.

Viscosity is more sensitive to salt concentration than other thermodynamic properties (density and speed of sound). However, this effect depends not only on the concentration of ions, but also on their chemical nature, i.e. the chemical type of ions. For example, samples from different geothermal fields may have the same mineralization and different ion concentrations, but they exhibit different properties. This demonstrates how the chemical nature of the ions in a geothermal brine affects their properties. Assessing the contribution of a single ion species in multi-component geothermal solutions to their properties is difficult because the properties are determined not only by the interactions between water molecules and individual ions, but also by ion-ion interactions, which complicates the problem. The presence of different ion types in a solution significantly changes the effect of a particular ion type on its properties.

When the composition, temperature and pressure of the geothermal brine in a geological fluid formation changes (during reservoir evolution, production, energy extraction or injection processes), the original reservoir conditions change to new P, T, x conditions. As a result, some solid minerals may precipitate, dissolved gases are present, and heat is lost. Almost all geothermal energy operations experience these phenomena. The presence of different types of ions in solution significantly alters the effect of the specific type of ion on its properties. The presence of dissolved gases in geothermal fluids has a significant impact on the thermodynamic properties and therefore on the energy extraction processes. Due to the pressure difference at different depths (near the surface the pressure is 0.101 MPa), degassing occurs during the production process.

The work reveals the mechanism of interaction of molecules in a static environment, and also studies the process of intermolecular interaction in the solvent-solute system, and determines important mechanical properties of continuous systems.

The density, sound velocity and viscosity of natural solutions were measured using an Anton Paar DMA 4500 and DSA 5000 densimeter and a Stabinger SVM 3000 viscometer. The combined measurement error of density, viscosity and sound velocity at a confidence level of 95% with a coverage factor of k=2 was 0.0005%

(DMA4500), 0.02% or 0.5 kg·m^{-3} (for SVM3000) and 0.01% (for the DSA5000 M sound velocity analyzer) for density; 0.35% (for SVM 3000) for viscosity and 0.1% (DSA 5000 M) for sound velocity.

The experimental setup and the course of the experiments are presented in detail in the author's articles. The speed of sound and the density of the medium in geothermal brines at atmospheric pressure were measured using the DSA 5000 M device from Anton Paar . The device simultaneously determines the density of the sample. The measurement ranges of density and speed of sound are 0-3000 kg/m^3 and 1000-2000 m/s, respectively. The measurement errors of density and speed of sound are 0.001 kg/m^3 and 0.1 m/s, respectively. The device is equipped with measuring cells for density and speed of sound, thus combining the oscillating U-tube method with high-precision measurement of the speed of sound. The temperature of both cells is controlled by a built-in Peltier thermostat. The sample is introduced into the measuring cell, which is bounded on one side by an ultrasound source and on the other side by a receiver. The transmitter sends sound waves with a certain period through the sample.

Samples of the geothermal mixture were collected at a temperature of about 59 °C and filtered to remove suspended solids.

The principle of operation of the oscillatory densimeter, in which the U-shaped tube is completely filled with the sample under study and exposed to electromagnetic forces, is based on the law of harmonic oscillation. Measuring the frequency and duration of vibration of the tube filled with the sample allows us to determine its density. The measuring cell consists of an oscillator formed by an empty U-shaped glass or metal tube. This type of vibration tube densimeter was successfully used in our previous works for accurate measurement of the density of various liquids (ionic liquids, hydrocarbonates and their alcohol solutions.

The experimental results on density, viscosity and sound velocity depending on temperature for four wells are presented in Table 2 and Figure 15.

Table 2.

Experimental data on density, sound velocity and viscosity of geothermal solutions at atmospheric pressure

(№ 68) Izberbash (Dagestan)							
T, K	ρ^a ,kg·m^{-3}	T, K	ρ^b , кг·m^{-3}	η^b, MPa·s	T, K	ρ^c ,kg·m^{-3}	W^c, m·s^{-1}
277.16	1000.97	277.15	1000.78	1.588	278.15	1000.72	1429.79
283.16	1000.65	283.15	1000.55	1.328	283.15	1000.51	1450.32
293.17	999.00	293.15	999.01	1.032	293.15	998.91	1484.84
303.13	996.42	303.15	996.40	0.835	303.15	996.43	1511.31
313.13	992.94	313.15	992.92	0.700	313.15	992.91	1530.94
323.13	988.73	323.15	988.70	0.603	323.15	988.72	1544.64
		333.15	983.69	0.536	333.15	983.72	1553.12
(№ 129) Izberbash (Dagestan)							
T, K	ρ , kg·m^{-3}	T, K	ρ , kg·m^{-3}	η, MPa·s	T, K	ρ , kg·m^{-3}	W, m·s^{-1}
277.17	1002.02	277.15	1002.04	1.576	278.13	1002.01	1430.42
283.15	1001.71	283.15	1001.69	1.339	283.15	1001.74	1451.31
293.16	1000.13	293.15	1000.17	1.048	293.15	1000.10	1486.27
303.13	997.56	303.15	997.55	0.816	303.15	997.79	1512.68
313.13	994.10	313.15	994.05	0.676	313.15	994.02	1532.20
323.13	989.83	323.15	989.80	0.568	318.15	992.07	1539.74
		333.15	984.60	0.488	323.15	989.76	1545.85
		343.15	979.17	0.421	333.15	984.64	1553.97
		353.15	973.39	0.372			
(№ 27T) Ternair (Dagestan)							
T, K	ρ , kg·m^{-3}	T, K	ρ , kg·m^{-3}	η, MPa·s	T, K	ρ , kg·m^{-3}	W, m·s^{-1}
277.17	1016.60	277.15	1016.4	1.660	278.14	1016.50	1456.68
283.17	1015.82	283.15	1015.87	1.420	283.15	1015.89	1476.34
293.17	1013.75	293.15	1013.73	1.119	293.14	1013.70	1508.65
303.13	1010.80	303.15	1010.78	0.917	303.15	1010.76	1533.06
313.13	1007.06	313.15	1007.03	0.785	313.15	1007.01	1551.46
323.13	1002.84	323.15	1002.81	0.679	323.10	1002.70	1564.20
					333.15	997.98	1571.92
(№ 38T) Ternair (Dagestan)							
T, K	ρ , kg·m^{-3}	T, K	ρ , kg·m^{-3}	η, MPa·s	T, K	ρ , kg·m^{-3}	W, m·s^{-1}
277.16	1017.00	277.15	1017.08	1.618	278.14	1016.82	1455.79
283.17	1016.03	283.15	1016.05	1.373	283.15	1016.03	1475.53
293.16	1014.34	293.14	1014.38	1.089	293.15	1014.36	1507.58
303.13	1011.45	303.15	1011.43	0.885	303.15	1011.47	1532.40
313.13	1007.77	313.15	1007.73	0.756	313.15	1007.80	1550.72
		323.15	1003.45	0.648	318.15	1005.85	1558.02
		333.15	998.65	0.570	323.15	1003.50	1563.40
		343.15	993.47	0.516			

aDMA4500. bSVM3000. cDSA 5000M.

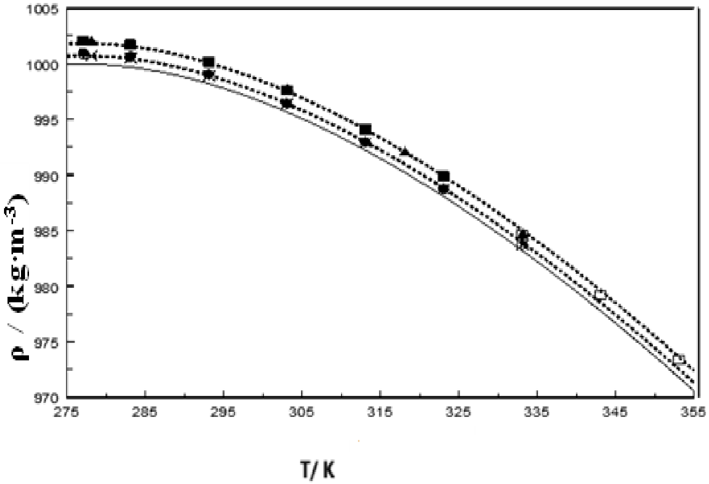

Figure 15. Measured values of geothermal fluid density together with values for pure water calculated using IAPWS formulas. Solid line – for pure water, calculated using the IAPWS fundamental equation of state. Dashed lines are calculated using the correlation equation (12) for samples No.68 and No.129. □×- No.68 (DSA); ○- No.68 (SVM); ●- No.68 (DMA); ■- No.129 (DMA); □- No.129 (DSA); ▲- No.129 (DSA).

The presence of dissolved gases in geothermal fluids has a significant impact on the thermodynamic properties and therefore on the energy extraction processes. Due to the pressure difference at different depths (near the surface the pressure is 0.101 MPa), degassing occurs during the production process. Average dissolved gas ratio in geothermal samples (near surface, upper part of boreholes): 2.5 m^3 (gas)/m^3 (brine) for No. 27T and 4.2 m^3 (gas)/m^3 (brine) for No. 38 T. Approximately 90-92% of the total gas volume is hydrocarbon gases in samples No. 27T and No. 38 T, while in samples from wells No. 68 and No. 129 their content is from 95% to 98%. The carbon dioxide content in samples (No. 68 and No. 129) is from 4% to 5%, while in samples (No. 27T and No. 38T) it is about 4.6% - 6.8%. The content of nitrogen and other inert gases is within the range of 2.6% to 3.3%. When the composition, temperature, and pressure of the geothermal brine in a geological fluid formation changes (during reservoir evolution, production, energy recovery, or injection processes), the original reservoir conditions change to new P, T, x conditions. As a result, some solid minerals may precipitate, dissolved gases are present, and heat is lost. Almost all geothermal energy operations experience these phenomena. Viscosity is more sensitive to salt concentration than other thermodynamic properties (density and sound velocity). It is evident that the measured properties of geothermal fluids, for example, No. 27T and No. 38T, deviate significantly (up to 1.77% for density, 21% for viscosity and 2.04% for sound velocity) from the values for pure water than for other geothermal samples (No. 68 and No. 129). This is a result of the large difference in composition between samples No. 27T and No. 38T (salinity is about 15.5 g/l) and the other samples No. 68 and No. 129 (salinity 1.8 g/l). However, this effect depends not only on the concentration of ions but also on their chemical nature, i.e. the chemical type of ions. For example, samples from different geothermal fields may have the same salinity but different ion concentrations. At the same time, they exhibit different properties. This demonstrates how the chemical nature of ions in a geothermal brine affects their properties. Estimating the contribution of a single ion type in multicomponent geothermal solutions to their properties is difficult because the properties are determined not only by the interaction between water molecules and individual ions but also by ion-ion interactions, which complicates the problem. The presence of different ion types in a solution significantly changes the effect of a particular ion type on their properties.

The obtained experimental data on the density of the studied solutions depending on the temperature were described by the regression equation (12):

$$\rho_b(T) = a_0 + a_1 / T_r + a_2 / T_r^2 \qquad (12)$$

Here =T/1000; =296.621299; =393.834401; = -55.042651 for sample No.4 and =410.721591; =327.278915; = -45.315956 for sample No.5. This equation describes the obtained data for geothermal solutions with a relative error of 0.015 - 0.0009%.

The obtained experimental values of density (Table 2), sound speed, and viscosity of multicomponent systems based on samples of geothermal fluids from Izberbash, Ternair, Kizlyar, and Kayakent were presented by correlation equations that describe the experimental data depending on temperature and concentration, with a known value of density, viscosity, and sound speed of water:

$$\rho(T, x_i) = \rho_{H_2O}(t)\left(1 + \sum_{i=1}^{n} a_i x_i\right) \tag{13}$$

$$W(T, x_i) = W_{H_2O}(t)\left(1 + \sum_{i=1}^{n} c_i x_i\right) \tag{14}$$

$$\eta(T, x_i) = \eta_{H_2O}(t)\left(1 + \sum_{i=1}^{n} b_i x_i\right) \tag{15}$$

where $\rho_{H_2O}(T)$, $W_{H_2O}(T)$ and $\eta_{H_2O}(T)$ are the density, speed of sound, and viscosity (IAPWS) of pure water, respectively, at temperature T and at atmospheric pressure; x_i is the ion concentration (g/l); n is the number of components; a_i, b_i, c_i is the characteristic ion constant (density, speed of sound, viscosity) for each type of ion. These relationships (13-15) give good agreement with experimental data for many aqueous salt solutions. Many authors have tested the accuracy and prediction capabilities of the Riedel[5] model.

The correlation equations reproduce the measured values of density, sound velocity and viscosity for geothermal brines within the error limits of AAD=0.03%, 0.06%, and 2.55%, respectively. If the density, viscosity, and sound speed of a salt solution (or geothermal fluids) are known at a reference pressure (for example, P_0 = 0.101 MPa), then it is possible to predict the properties of the system at any pressure (with known properties of pure water):

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[5] Riedel, L. The heat conductivity of aqueous solutions of strong electrolytes// Chem. İng. Tech. Wiley, -1951. N23, -p.59-64.

$$\rho(P,T,x_i)=\rho(P_0,T,x_i)\left(\frac{\rho_{H_2O}(P,T)}{\rho_{H_2O}(P_0,T)}\right)_{H_2O} \tag{16}$$

$$\eta(P,T,x_i)=\eta(P_0,T,x_i)\left(\frac{\eta_{H_2O}(P,T)}{\eta_{H_2O}(P_0,T)}\right)_{H_2O} \tag{17}$$

$$W(P,T,x_i)=W(P_0,T,x_i)\left(\frac{W_{H_2O}(P,T)}{W_{H_2O}(P_0,T)}\right)_{H_2O} \tag{18 }$$

Where $\rho(P_0,T,x_i)$, $\eta(P_0,T,x_i)$, and $W(P_0,T,x_i)$ can be calculated using formulas (16-18) at P_0=0.101 MPa.

Since the compressibility of a fluid reflects the balance of attractive and repulsive energies, it is useful to compare the values calculated by different approaches. Knowing the density, viscosity, speed of sound in the system, and also calculating the coefficient of adiabatic compressibility, thermal (thermal) expansion, thermal pressure coefficient, it is possible to determine the mechanism of intermolecular bonds in the studied system, find the energy properties of the medium - activation enthalpy, isochoric heat capacity, isobaric heat capacity, enthalpy difference, partial derivative of enthalpy with respect to pressure and partial derivatives of internal energy with respect to volume. Table 3 presents the thermodynamic properties of geothermal fluids calculated on the basis of measurements of density and speed of sound values.

Derived thermodynamic properties for all studied natural geothermal mixtures (β_S), (β_T), (α_P), (γ_V), (ΔH), (C_V), (C_P), $\left(\frac{\partial H}{\partial P}\right)_T$ are given in the work in detailed tables.

All these thermodynamic properties were calculated using well-known thermodynamic relations (functions of state). The measured properties at atmospheric pressure can be used as reference values for predicting the properties of geothermal fluids at high pressures.

Table 3.

Adiabatic compressibility coefficient (β_S), isothermal compressibility coefficient (β_T), thermal expansion coefficient (α_P) thermal pressure coefficient (γ_V), enthalpy (ΔH), isochoric heat capacity (C_V), isobaric heat capacity (C_P), calculated from measurements of density and sound speed.

T, K	β_S×10^3, MPa^{-1}	$\alpha_P \times 10^3$ α_p×10^3, K^{-1}	$\left(\frac{\partial H}{\partial P}\right)_T$ cm^3·г$^{-1}$	$\left(\frac{\partial U}{\partial V}\right)_T$ MPa	β_T×10^3, MPa^{-1}	γ_V MPa·K^{-1}	C_V, $\frac{\text{кJ}}{\text{кg}\cdot\text{K}}$	C_P, $\frac{\text{кJ}}{\text{кg}\cdot\text{K}}$
(№ 68) Izberbash (Dagestan)								
278.15	0.4888	0.0637	0.9816	36.12	0.4891	0.1302	4.259	4.262
283.15	0.4752	0.1089	0.9687	64.68	0.4760	0.2287	4.217	4.224
293.15	0.4541	0.1996	0.9425	127.95	0.4569	0.4368	4.163	4.188
303.15	0.4394	0.2908	0.9151	197.73	0.4455	0.6525	4.121	4.179
313.15	0.4297	0.3828	0.8864	271.85	0.4408	0.8684	4.080	4.185
323.15	0.4239	0.4758	0.8559	348.14	0.4415	1.0776	4.031	4.198
333.15	0.4214	0.5702	0.8235	424.47	0.4474	1.2744	3.990	4.236
(№ 129) Izberbash (Dagestan)								
278.13	0.4878	0.0964	0.9712	54.82	0.4884	0.1974	4.282	4.288
283.15	0.4739	0.1356	0.9600	80.73	0.4752	0.2854	4.257	4.268
293.15	0.4526	0.2140	0.9372	137.52	0.4558	0.4694	4.209	4.238
303.15	0.4380	0.2929	0.9132	199.77	0.4442	0.6593	4.163	4.222
313.15	0.4285	0.3724	0.8887	265.60	0.4389	0.8484	4.110	4.209
318.15	0.4252	0.4125	0.8757	299.44	0.4381	0.9415	4.092	4.217
323.15	0.4228	0.4528	0.8625	333.50	0.4387	1.0323	4.070	4.223
333.15	0.4206	0.5344	0.8348	401.43	0.4434	1.2052	4.020	4.238

Standard errors of the obtained data: $u(T)$ =0.01K; $u(\beta_S)$=0.008%; $u(\alpha_P)$=(0.05-0.10)%; $u(\beta_T)$=(0.2-0.4)%; $u(C_V)$ =(2-3)%; $u(C_P)$ =(3-4)%.

MAIN CONCLUSIONS AND RESULTS OF THE WORK

The dissertation is devoted to the study of thermophysical properties of aqueous solutions of multicomponent electrolyte systems at high temperatures and pressures. For a deep understanding at the microscopic level of the nature and physicochemical mechanism of the anomaly of the properties of aqueous solutions of electrolytes, accurate experimental data on thermophysical properties are extremely necessary. Mathematical models of continuous media, widely used to solve various problems of physics, chemistry and technology, usually contain simplifying hypotheses and empirical parameters. Based on the general equations of conservation of heterogeneous multicomponent mixtures, a mathematical model of an equilibrium mixture can be constructed. The system of conservation laws in the equilibrium mathematical model of a multicomponent mixture can be reduced to a system of conservation laws for a mixture, when the closing equations are the equations of state for the specific internal energy and pressure of the phases, as well as the usual relationships for heterogeneous mixtures.

In this work the thermodynamic properties of multicomponent solutions were experimentally and analytically investigated, which in turn characterize the mechanical properties of the medium.

In solving this problem, the following results were obtained:

1. A modification of the experimental setup for studying the thermal conductivity of aqueous electrolyte solutions at high pressures and temperatures using the coaxial cylinder method has been created, which makes it possible to minimize the influence of convection and radiation.
2. New reliable experimental data on the thermal conductivity of aqueous solutions of H_2O+ $Sr(NO_3)_2$, H_2O+$LiNO_3$, H_2O+$CaCl_2$, H_2O+Na_2CO_3, H_2O+K_2CO_3 H_2O+NaBr, H_2O+KBr and ternary systems H_2O+NaBr+KBr, in a wide range of changes in state parameters, using the method of coaxial cylinders (stationary method) have been obtained:

a) $H_2O + Sr(NO_3)_2$ along 5 isobars (0.1, 10, 20, 30, 40 MPa), for five concentrations (0.249, 0.525, 1.181, 2.025, 3.150 mol·kg^{-1}), in the temperature range from 294.11 to 591.06 K.

b) $H_2O+LiNO_3$ of four isobars (0.1, 10, 20, and 30) MPa, concentrations (1.0, 1.7, 2.8, and 3.9) mol·kg^{-1}, temperatures 293.13 to 591.06 K.

c) $H_2O + K_2CO_3$ for different isotherms between 293-573 K along the saturation line (0-1 MPa) for five concentrations (5, 10, 15, 20 and 25) mass%.

d) $H_2O + Na_2CO_3$ at three isobars of 0.1, 10 and 30 MPa with molality (0.4966, 1.0483 and 1.6650) mol kg-1, in the temperature range of 293.15 - 627.06 K.

e) $H_2O + CaCl_2$ at pressures up to 40 MPa, for concentrations of (5, 10, 15, and 20 mass%) in the temperature range from (293 -573) K.

f) H_2O+NaBr, H_2O+KBr, H_2O + NaBr + KBr. The measurements were carried out for NaBr (10, 20, 30, and 38 mass%), and KBr 10,20,30 mass% for concentrations and ternary aqueous solutions of H_2O+ NaBr+KBr (10NaBr+5KBr, 10NaBr+10KBr, and 10NaBr+20KBr) mass% near the saturation line of 0.1 - 2 MPa and along two isobars (10 and 40) MPa at temperatures between (294 and 577) K, at high temperatures (from room temperature to 593 K) and pressures up to 40 MPa.

3. A wide-range empirical equation of state for the thermal conductivity of binary and multicomponent systems depending on concentration, temperature and pressure has been obtained. The regularity of the behaviour of the concentration dependence of the thermal conductivity of aqueous solutions on the nature of the ions of dissolved substances has been confirmed.
4. An equation for the reduced thermal conductivity of the studied aqueous binary solutions depending on the concentration was developed. This equation is universal and valid for other aqueous systems in the mentioned range of changes in the state parameters. Thermal conductivity measurements were used to find the A_λ and B_λ coefficients, with the help of which it is possible to study changes occurring in the structure of the solution.

5. Baric, concentration, and temperature dependences of binary multicomponent systems have been studied in detail. The thermal conductivity maxima in aqueous solutions as a function of temperature have been determined. For pure water, this thermal conductivity maximum is achieved at temperatures between (409 and 421) K, when the pressure changes between (20 and 60) MPa. The position of the thermal conductivity maximum strongly depends on pressure and concentration. Consequently, adding salt slightly shifts the position of the temperature maximum for solutions toward higher temperatures. Thermal conductivity for solutions as a function of pressure increases almost linearly with increasing pressure in the temperature range up to 627.15 K and at pressures up to 30 MPa. The dependences of the measured thermal conductivities for all isotherms and isobars show that the thermal conductivity of the solution decreases monotonically with concentration. The concentration dependence of the thermal conductivity is expressed by a small curvature at high concentrations ($m>1 \mathrm{mol \cdot kg^{-1}}$) The value of the increase in thermal conductivity at a pressure of 40 MPa and a temperature of 373 K for dilute solutions is from 2 to 2.5%. The slopes of the isotherms for pure water are higher than the corresponding slopes of the isotherms for the solution, especially at high concentrations, i.e. this means that the thermal conductivity of pure water increases faster with pressure than that of the solution. At high pressures of 40 MPa and high concentrations (20 mass%), the absolute value of the thermal conductivity of pure water is higher than that of the solution by approximately 8-12%. At low pressures (10 MPa) and low concentrations (10 mass%), the difference between the thermal conductivity of pure water and the solution is in the range from 5 to 8%.
6. New experimental (P, V, T, x) data were obtained for water-alcohol solutions of binary and ternary systems $H_2O+C_2H_5OH$, $H_2O+C_2H_5OH+LiNO_3$, $H_2O+C_3H_7OH+KNO_3$, $H_2O+C_3H_7OH+Li_2SO_4$ using a constant volume piezometer placed in a liquid thermostat:

a. Measurements of PVT properties for the water+ethanol system were carried out for four compositions of 0.0168, 0.0368, 0.0855, and 0.1166 molar fractions of ethanol in the temperature range of 298 K - 448 K and pressures up to 40 MPa.

b. Data on PVT properties of water+ethanol+ $LiNO_3$ were obtained. PVT properties were measured in the temperature range (298.15-448.15) and pressure (5,10,20,30,40 MPa) for 12 concentrations, namely: $LiNO_3$ (0.520 mol·кg^{-1} H_2O)-C_2H_5OH (4.67 mass%); $LiNO_3$ (0.940 moll·кg^{-1} H_2O) –C_2H_5OH (4.67 mass%); $LiNO_3$ (0.0457 mol·кg^{-1}H_2O) – C_2H_5OH (9.32 масс%); $LiNO_3$ (0.4757 moll·кg^{-1} H_2O) – C_2H_5OH (9.32 mass%); $LiNO_3$ (0.8599 mol·кg^{-1} H_2O)- C_2H_5OH (9.32 mass%); $LiNO_3$ (1.0931 mol·кg^{-1} H_2O) – C_2H_5OH (9.32 mass%); $LiNO_3$ (0.0422 moll·кg^{-1} H_2O)- C_2H_5OH (18.53 mass%); $LiNO_3$(0.4387 mol·кg^{-1} H_2O)- C_2H_5OH (18.53 mass%); $LiNO_3$ (0.7930 моl·кg^{-1} H_2O)- C_2H_5OH (18.53 mass%); $LiNO_3$ (1.1870 mol·кg^{-1} H_2O)- C_2H_5OH (23.09 mass%).

c. The data on PVT properties were obtained for the H_2O+C_3H_7OH+KNO_3 system in the temperature range of 303.15 to 448.15 K, pressures up to (5-35) MPa, at the concentrations of KNO_3 (0.261 mol·кg^{-1} H_2O)-C_3H_7OH (5 mass %); KNO_3 (0.261 mol·кg^{-1} H_2O) – C_3H_7OH (20 mass%); KNO_3 (0.261 mol·кg$^{-1\ -1}$ H_2O) – C_3H_7OH (15 mass%); KNO_3 (0.435 mol·кg^{-1} H_2O) – C_3H_7OH (15 mass%); KNO_3 (1.130 mol·кg^{-1} H_2O)- C_3H_7OH (15 mass %); и KNO_3 (0.261 mol·кg^{-1} H_2O) – C_3H_7OH (20 mass %).

d. Data on PVT properties were obtained for the H_2O+C_3H_7OH+ Li_2SO_4 system at pressures of 5-40 MPa, temperatures of 303.15 - 448.15 K, for nine compositions (four compositions of 0.0155, 0.0254, 0.0322 and 0.0502 molar fraction of 1-propanol and four compositions of salt of 0.0062, 0.0124, 0.0199 and 0.0274).

7. A polynomial equation of state has been developed as a function of specific volume on temperature, pressure and concentration. This equation can be used to calculate density, viscosity, partial and apparent molar volumes and other thermodynamic properties of other aqueous solutions in a wide range of temperatures (up to 600 K), pressures (up to 40 MPa) and concentrations (up to 5 mol kg^{-1} H_2O).

8. The obtained values of molar volumes of the ternary water-salt-alcohol mixture for each isobar-isotherm are described by polynomial functions of component concentrations taking into account the molar volumes of pure water. They can be used to calculate partial molar volumes of components of binary systems.
9. Based on experimental data, excess, apparent and partial molar volumes of multicomponent mixtures were calculated, as well as at infinite dilution, as a function of temperature, pressure and concentration, and their behavioural features were revealed. The processes occurring during mixing of solutions into a single multicomponent system were studied at the molecular level. The influence of state parameters on the thermodynamic properties of combined systems was revealed. The values of the thermal expansion coefficient of partial molar volumes for ternary water-salt-alcohol systems at infinite expansion were calculated. Molar expansibility and thermal expansion coefficient are associated with thermodynamic relationships with entropy and heat capacity and contain information on structural changes in the system during thermal expansion. Salt (Li_2SO_4) destroys (tends to reduce the structure of water) the structure of adjacent water molecules, while alcohol molecules (1-propanol), unlike salt, structure water (surround it with a layer of increased structure). Two opposite competing effects determine the volumetric properties of a complex mixture such as water + 1-propanol + Li_2SO_4. The temperature coefficient of partial molar volumes (partial molar expansibility) $\left(\partial\overline{V}_i / \partial T\right)_{Px_j}$ is a sensitive measure of the structural interaction of dissolved substances with water and can be a good tool for fundamental studies of the structural and thermodynamic properties of complex solutions. For the first time, the chemical composition (analysis of cations and anions) was determined, and experimental data were obtained on the volumetric (density), acoustic (sound speed), and transport (viscosity) properties of 8 natural geothermal fluids from deposits in the South of Russia, taken from wells in Izberbash, Ternair, Kizlyar, and Kayakent (Russia).

10. For the first time, the chemical composition (analysis of cations and anions) was determined, and experimental data were obtained on the volumetric (density), acoustic (sound speed), and transport (viscosity) properties of 8 natural geothermal fluids from deposits in the South of Russia, taken from wells in Izberbash, Ternair, Kizlyar, and Kayakent (Russia).
11. A regression equation has been developed that relates the density of the studied solutions to temperature. This equation describes the obtained data for geothermal solutions with a relative error of 0.015 - 0.0009%.
12. A correlation model has been developed that describes experimental data on density, viscosity, and sound velocity as a function of temperature and solution concentration with known properties of pure water. The model reproduces measured values of density, viscosity, and sound velocity within 0.03%, 2.55%, and 0.06%, respectively. The contribution of the main ions (Riedel's characteristic constants) of the studied geothermal fluids is determined. When the composition, temperature and pressure of the geothermal brine in the geological formation of the fluid changes (during the evolution of the reservoir, production, energy extraction or injection processes), the conditions of the state that were initially in the reservoir conditions change to new P, T, x conditions. As a result, some solid minerals may precipitate, dissolved gases are present, and heat is lost. Almost all geothermal energy operations experience these phenomena. The presence of different types of ions in solution significantly alters the effect of the specific type of ion on its properties. The presence of dissolved gases in geothermal fluids has a significant impact on the thermodynamic properties and therefore on the energy extraction processes. Due to the pressure difference at different depths (near the surface the pressure is 0.101 MPa), degassing occurs during the production process.
13. An equation has been developed for finding the viscosity, density, and sound velocity of salt solutions, geothermal fluids at high pressures with a known reference pressure (P_0 = 0.101 MPa), and the properties of pure water. The measured values of density and

sound velocity were used to calculate other thermodynamic properties of geothermal fluids that are important for geothermal energy: adiabatic compressibility coefficient, isothermal compressibility coefficient, thermal expansion coefficient, thermal pressure coefficient, enthalpy, isochoric heat capacity, isobaric heat capacity, partial derivative of enthalpy with respect to pressure, and partial derivative of internal energy.

14. In this work, for the first time for the studied static medium, the mechanism of the process of intermolecular interaction in the “solute- solvent” system was revealed and important energy properties of the entire system were determined.

For analytical processing of the obtained experimental data, methods of mathematical and computer modeling were used. The following methods of numerical data processing were used: approximation, interpolation, data extrapolation (data approximation methods), the Laplace method, smoothing using curves, the least squares method, uniform and root mean square approximation, etc. Thermophysical properties of aqueous solutions of multicomponent systems are presented in the form of different combinations of polynomials, power functions of temperature, pressure and concentration. The definition of the type and model of dependence of empirical values on state parameters was carried out using the intelligent program “Eureqa”. “Tait type equation” – equations for describing the thermal conductivity of aqueous solutions from pressure and temperature – were successfully used.

THE MAIN PROVISIONS OF THE DISSERTATION ARE REFLECTED IN THE FOLLOWING WORKS:

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Personal contribution of the author

The works [9,10,13,18,19,30,35,37,42,44,48,49,50,58] listed in the list of scientific works were written by the author personally. In the remaining works, written in co-authorship, the formulation of the scientific problem, the ways and methods of its solution, a large array of experimental data, their processing, and the equations of state belong to the author. The works [45,46,50,53] were completed with the active participation of the author.

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