Thermal Behavior of Water-Electrolyte Mixtures: Structural and Ionic Influences

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ABSTRACT

This study investigates the thermal properties of water-electrolyte mixtures, specifically focusing on binary and ternary electrolyte solutions over a concentration range of 0.01 mol%–23.5 mol% at two constant temperatures (20°C and 40°C). The results indicate that the specific Heat Capacity (C_p) and Thermal Conductivity (λ) exhibit polynomial dependencies on the ionic radius and charge density. As the ionic radius increases from 0.72 Å (Co^{2+}) to 1.65 Å (Cs^{+}), C_p decreases by up to 12%. As the charge density increases from 0.0468 C/Å^2 (Cs^{+}) to 0.4921 C/Å^2 (Co^{2+}), C_p increases by up to 15%, while λ decreases by 8%-20% with an increasing charge density, confirming the influence of hydration. These results provide a quantitative framework for electrolyte-based thermal applications in energy storage, water treatment, and thermodynamic modeling.

Keywords-water-electrolyte mixtures; specific heat capacity; thermal conductivity; hydrated ions; ionic radius

I. INTRODUCTION

Studying solutions is significant in chemistry and chemical technology, as many industrial processes in fields, such as pharmaceuticals, food production, metallurgy, and chemical manufacturing, take place in solutions. Advances in science and technology have expanded the range and complexity of these solution-based processes, especially in emerging chemical sectors, increasing the need for deeper research [1-3]. Despite the interest in the physicochemical properties of solutions, their nature is only partially understood [4]. This is largely due to the diversity of solution types and the absence of a unified theory of the liquid state. Dissolution involves both physical and chemical interactions between the solute and solvent components, making the study of solutions inherently complex. Understanding water-electrolyte systems is crucial for developing new technologies and improving the existing ones. Consequently, the physical chemistry of solutions continues to attract attention from both theoretical and applied researchers across multiple disciplines. Aqueous electrolyte solutions have been extensively studied, with numerous efforts aimed at linking their macroscopic properties to their internal structure and predicting unknown behaviors [5]. Early theories introduced the concept of free ions, anions and cations, providing an understanding of conductivity and electrochemical activity [6]. Subsequent developments have incorporated thermodynamic principles to connect the solution behavior with the molecular properties. However, ideal gas laws proved inadequate for concentrated ionic solutions, leading to more nuanced models that emphasized ion-solvent interactions and ion hydration, which are key factors in influencing dissociation and transport properties [7]. The theories of Arrhenius and Mendeleev, though instrumental, are now recognized as limited to dilute solutions of weak electrolytes. They have failed to describe strong electrolytes even at low concentrations. As a result, research has diverged into two main paths: weak electrolytes, where dissociation equilibrium and minimal ionic interactions dominate, and strong electrolytes, characterized by significant interionic forces. [8, 9] Mendeleev also underscored the importance of studying pure solvents and variations in solution behavior under different temperatures and pressures. The use of differential values to describe concentration-dependent changes laid the groundwork for a more detailed physicochemical theory of solutions.

The complex behavior of solutions has challenged researchers seeking to develop universal theoretical models. D.I. Mendeleev was among the first to recognize that simple models could not fully explain the wide range of dissolution phenomena [10]. That is, a single, quantitative theory applicable to all electrolyte solutions across varying types and concentrations is unattainable due to the diverse nature of ionic interactions, solvation processes, and thermodynamic non-idealities [11]. While Mendeleev did not propose a formal quantitative theory has not been proposed, these limitations have been articulated in his work, and subsequent developments have continued to affirm the relevance of his core ideas [12-15]. The progress in quantitatively describing the physicochemical properties of solutions at practical concentrations remains limited. These properties are influenced by multiple factors, including the nature of the solute and solvent, concentration, temperature, and pressure. Yet, key questions, such as how the structural components of water-electrolyte systems affect thermal properties lack definitive, evidence-based answers [14-16]. Many existing theories remain speculative, offering mostly qualitative interpretations rooted in intermolecular forces, chemical kinetics, hydrostatics, and hydraulics, which often fall short of explaining the phenomena with scientific precision. Considering these gaps, the present study aims to develop new, scientifically grounded principles that clarify how thermal properties, namely the specific heat capacity and thermal conductivity, change with temperature and concentration in aqueous electrolyte solutions. The current research is guided by the contemporary understanding of the water structure and hydration, as well as by the established insights into the behavior of water-electrolyte mixtures [17-19].

II. MATERIALS AND METHODS

A. *Materials*

The methodological foundation of the research was established at the M. Auezov South Kazakhstan University, which houses the "Water Quality Monitoring and Water Technologies" laboratory. The research was conducted using reliable data regarding the ionic radius and charge density of the components in binary and ternary electrolyte solutions of types 1-1, 1-2, 2-1, and 2-2. The experiments covered a wide range of concentrations at constant temperature T = const. Model solutions were prepared using analytically pure electrolytes, including: LiCl, NaCl, KCl, CsCl, LiI, NaI, KI, CsI, Li_2SO_4, Na_2SO_4, K_2SO_4, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Mg(NO_3)_2$, $Mn(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Pb(NO_3)_2$, $CoCl_2$, $NiCl_2$, $MgCl_2$, $MnCl_2$, $FeCl_2$, $ZnCl_2$, $CdCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $CoSO_4$, $NiSO_4$, $MgSO_4$, $MnSO_4$, $FeSO_4$, $ZnSO_4$, $CdSO_4$, $CuSO_4$, and distilled water obtained using an AQUA-Distiller DE-4-2. The details of the ionic radii and surface charge densities of the studied ions are presented in Table I, while Table II provides the parameters for the studied water-electrolyte mixtures.

TABLE I. RADIUS AND SURFACE CHARGE DENSITY OF IONS

Name of ions	Ion radius, Å	Surface charge density of ions, C/Å^2
Co^{+2}	0.72	0.4921
Ni^{+2}	0.736	0.4709
Mg^{+2}	0.74	0.4659
Li^{+}	0.78	0.2096
Mn^{+2}	0.8	0.3986
Fe^{+2}	0.815	0.3841
Zn^{+2}	0.83	0.3703
Na^{+}	0.98	0.1328
Cd^{+2}	0.997	0.2566
Cu^{+2}	1.01	0.2501
Ca^{+2}	1.03	0.2405
Sr^{+2}	1.2	0.1772
Pb^{+2}	1.32	0.1464
K^{+}	1.33	0.0721
Ba^{+2}	1.387	0.1326
Rb^{+}	1.49	0.0574
Cs^{+}	1.65	0.0468

TABLE II. PARAMETERS OF THE STUDIED WATER-ELECTROLYTE MIXTURES

Water-electrolyte solutions	Range of changes in solution concentrations, mol%
H_2O - LiCl	0.05÷14.35
H_2O - NaCl	0.03÷9.87
H_2O - KCl	0.03÷6.48
H_2O - CsCl	0.01÷13.95
H_2O - LiI	0.01÷14.09
H_2O - NaI	0.01÷15.27
H_2O - KI	0.01÷11.66
H_2O – CsI	0.01÷4.31
H_2O – Li_2SO_4	0.02÷3.93
H_2O - Na_2SO_4	0.01÷2.02
H_2O - K_2SO_4	0.01÷2.27
H_2O – $Co(NO_3)_2$	0.01÷7.46
H_2O - $Ni(NO_3)_2$	0.01÷6.17
H_2O - $Mg(NO_3)_2$	0.01÷7.49
H_2O – $Mn(NO_3)_2$	0.01÷6.29
H_2O - $Zn(NO_3)_2$	0.01÷5.96
H_2O - $Cd(NO_3)_2$	0.01÷0.24
H_2O - $Cu(NO_3)_2$	0.01÷8.76
H_2O - $Ca(NO_3)_2$	0.01÷9.89
H_2O - $Sr(NO_3)_2$	0.01÷5.37
H_2O - $Pb(NO_3)_2$	0.01÷2.07
H_2O – $CoCl_2$	0.01÷2.98
H_2O - $NiCl_2$	0.01÷5.58
H_2O - $MgCl_2$	0.02÷8.27
H_2O - $MnCl_2$	0.01÷8.77
H_2O - $FeCl_2$	0.01÷5.81
H_2O - $ZnCl_2$	0.01÷23.5
H_2O - $CdCl_2$	0.01÷7.58
H_2O - $CaCl_2$	0.02÷3.4
H_2O - $SrCl_2$	0.01÷14.61
H_2O - $BaCl_2$	0.01÷2.84
H_2O – $CoSO_4$	0.01÷4.32
H_2O – $NiSO_4$	0.01÷3.93
H_2O – $MgSO_4$	0.02÷3.18
H_2O – $MnSO_4$	0.01÷6.04
H_2O – $FeSO_4$	0.01÷2.88
H_2O – $ZnSO_4$	0.01÷5.67
H_2O – $CdSO_4$	0.01÷4.45
H_2O – $CuSO_4$	0.01÷2.10

B. Methods

The physicochemical properties of the studied water-electrolyte mixtures were analyzed using standard analytical methods and modern control technologies. The obtained results were compared with publicly available reference data. To further analyze and generalize both the literature data and the experimental results, graphical and mathematical methods were employed to study the influence of the ionic radius, charge density, and solution concentration on the changes in specific heat capacity and thermal conductivity. In cases requiring a precise temperature control, experiments were conducted under thermostatic conditions using a liquid laboratory thermostat (SJML-19/2.5-I1). Research data processing, experimental trials, preparation of tables, and construction of graphical dependencies were carried out using average values from multiple parallel experiments.

1) Determination of the Specific Heat Capacity of Solutions Using an Electric Calorimeter

The equipment used in the experiment included two identical calorimeters, two thermometers, two high-resistance heating coils mounted on an insulating plate, and the liquid under investigation. One calorimeter was filled with test solutions, while the other contained water. Both calorimeters were fitted with identical heating coils (denoted as K), which were connected in series using thick copper rods to ensure an equal current flow and, consequently, an equal heat generation in both units. To maintain a uniform temperature distribution within each liquid, both calorimeters were equipped with stirrers.

The amount of heat received by the first calorimeter is:

$$Q_1 = (cm + w)(\tau - t) \tag{1}$$

The amount of heat received by the second calorimeter is:

$$Q_2 = (c_1 m_1 + w_1)(\tau_1 - t_1) \tag{2}$$

By equating the expressions for Q_1 and Q_2, the value of the specific heat capacity of the solution is obtained from a relationship of the form:

$$c = \frac{1}{m}\left[(c_1 m_1 + w_1)\frac{\tau_1 - t_1}{\tau - t} - w\right] \tag{3}$$

where m is the mass of the solution in the first calorimeter in g, m_1 is the mass of water in the second calorimeter in g, t is the initial temperature of the first calorimeter in °C, t_1 is the initial temperature of the second calorimeter in °C, τ is the final temperature of the first calorimeter in °C, τ_1 is the final temperature of the second calorimeter in °C, c is the specific heat capacity of the solution in the first calorimeter, c_1 is the specific heat capacity of water in the second calorimeter, ω is the water equivalent of the vessel, stirrer, and thermometer in the first calorimeter, and ω_1 is the water equivalent of the vessel, stirrer, and thermometer in the second calorimeter. If water was poured into the second calorimeter, then $c_1 = 1$, and the final equation provides the numerical value of the specific heat capacity of the solution being studied.

To avoid errors caused by potential differences in the resistances of the two calorimeters, the experiment should be repeated, swapping the resistances, and the average value of cc from both trials should be taken. The temperature of the calorimeters should not be allowed to rise more than 2°C–3°C above room temperature. If the liquids into which the coil wires KK are immersed conduct electricity themselves, these wires must be insulated beforehand. This ensures that equal resistances in both calorimeters generate the same amount of heat when current passes through the wires.

2) Calculation of the Specific Heat Capacity of Water-Electrolyte Mixtures

To analyze how specific heat capacity (C_p in J/kg·K) varies with electrolyte concentration (C in mol%), the experimental data were evaluated using polynomial regression. The resulting relationship was expressed as a quadratic equation:

$$C_p = aC^2 + bC + c \tag{4}$$

where C_p is the specific heat capacity of the water-electrolyte a, b, c are the polynomial regression coefficients determined using the least squares method.

3) Calculation of the Thermal Conductivity of Water-Electrolyte Mixtures

To examine the dependence of thermal conductivity (λ in W/m·K) on the electrolyte concentration, the data were also analyzed using polynomial regression. This analysis produced a quadratic equation that describes the observed trend:

$$\lambda = aC^2 + bC + c \tag{5}$$

III. RESULTS AND DISCUSSION

A. The Nature of Processes Influencing the Specific Heat Capacity of Water-Electrolyte Mixtures

The influence of key external factors on the thermal properties of aqueous electrolyte solutions, such as specific heat capacity, is still not fully understood or scientifically substantiated. To address this issue, the objective of this part of the study was to establish new scientific principles that explain how specific heat capacity changes with temperature and concentration in such systems [20]. Using known values for ionic radii [21] and calculated charge densities, as shown in Table I, the study analyzed the specific heat capacity variations in a range of binary and ternary electrolyte solutions, classified as types 1-1, 1-2, 2-1, and 2-2, across various concentrations at constant temperature, as detailed in Table II. The results of the graphical analysis of the changes in the specific heat capacity for representatives of the studied water-electrolyte mixtures are presented as follows: 1-1 (H_2O – LiCl, H_2O – NaCl, H_2O – KCl, H_2O – NaI, H_2O – KI, H_2O – CsI); 1-2 (H_2O – Li_2SO_4, H_2O - Na_2SO_4, H_2O - K_2SO_4); 2-1 (H_2O – $CoCl_2$, H_2O - $NiCl_2$, H_2O - $MnCl_2$, H_2O – $CaCl_2$, H_2O - $MgCl_2$, H_2O - $CdCl_2$, H_2O - $SrCl_2$, H_2O - $BaCl_2$,); 2-2 (H_2O – $CdSO_4$, H_2O – $MnSO_4$, H_2O – $FeSO_4$, H_2O – $ZnSO_4$, H_2O – $CuSO_4$, H_2O – $MgSO_4$) at T=const=20 °C, as depicted in Figures 1-3. Similar dependencies were observed for the studied aqueous salt systems at T=const=40 °C.

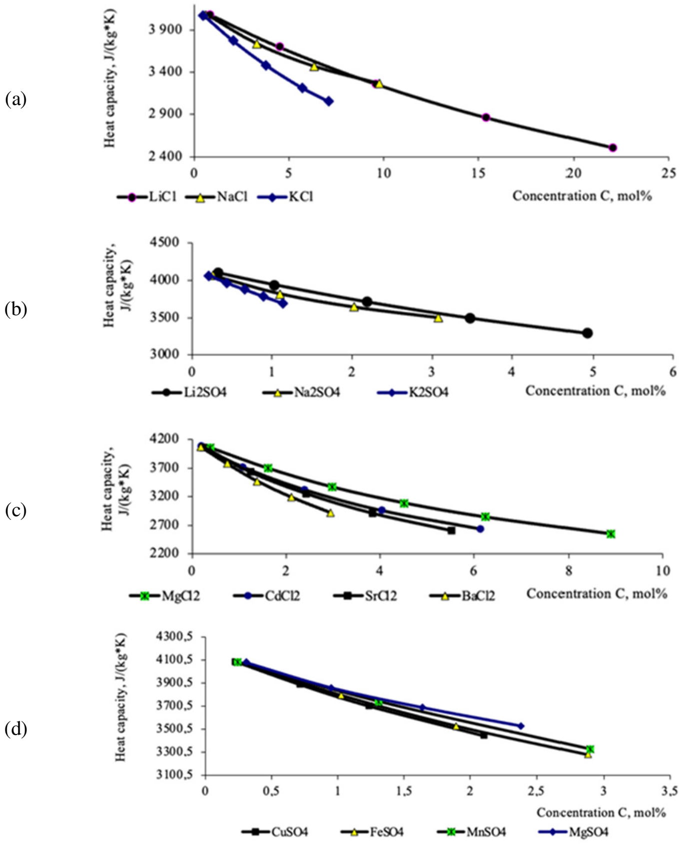
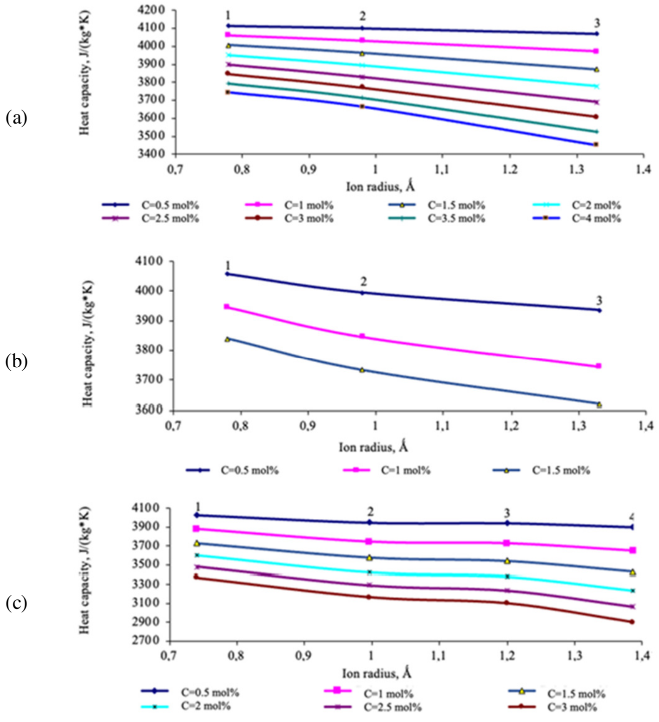


Fig. 1. Dependence of heat capacity of solutions on concentration at T=const= 20 °C.



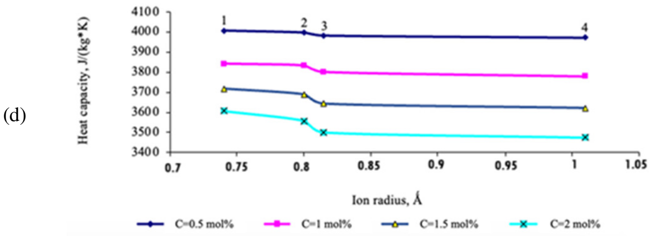


Fig. 2. Dependence of heat capacity of solutions on the ion radius at C=const and T=const 20^0C.

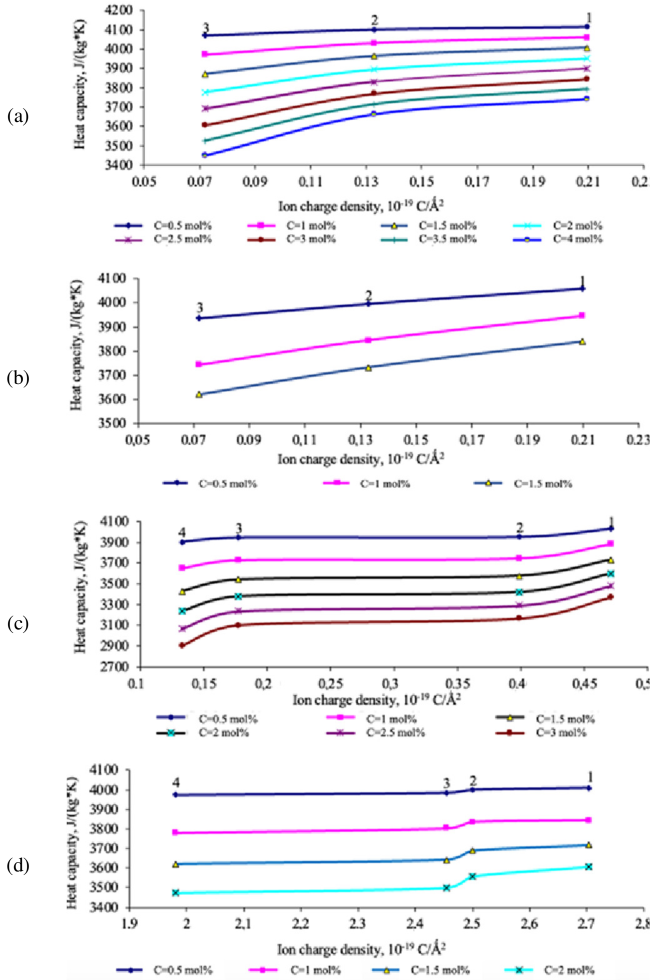


Fig. 3. Dependence of the heat capacity of solutions on the ion charge density at C=const and T=const 20^0C.

The data from Figures 1-3 show that the specific heat capacity of water-electrolyte systems at T=const decreases with an increasing concentration and can be described by polynomial dependencies as follows:

$$C_p = 1.521C^2 - 108.3C + 4160 \quad \text{(for LiCI)}$$

$$C_p = 5.708C^2 - 147.6C + 4168 \quad \text{(for NaCl)}$$

$$C_p = 7.687C^2 - 212.0C + 4173 \quad \text{(for KCl)}$$

The specific heat capacities of the solutions for other types of salts exhibited similar dependencies. A common characteristic across all studied water-electrolyte mixtures is that for solutions containing the same dissolved anions, at the same concentration, the smaller the cation radius is, the higher is the specific heat capacity of the solution [22].

At T = const, the specific heat capacity of the water-electrolyte systems is influenced by the ionic radius. For solutions, such as LiCl, NaCl, and KCl, a clear mathematical relationship was identified between the specific heat capacity (Cp, in J/kg·K) and ionic radius (r, in Å), which can be described using specific equations.

$$Cp = -33.76r^2 - 10.57r + 4143 \qquad (0.5\%)$$

$$Cp = -33.76r^2 - 90.57\,r + 4151 \qquad (1\%)$$

$$Cp = -81.81r^2 - 71\,r + 4111 \qquad (1.5\%)$$

$$Cp = -89.61r^2 - 127.2\,r + 4106 \qquad (2\%)$$

$$Cp = -100r^2 - 169\,r + 40191 \qquad (2.5\%)$$

$$Cp = -150.6r^2 - 114.8\,r + 4025 \qquad (3\%)$$

$$Cp = -258.4r^2 + 59.85r + 3903 \qquad (3.5\%)$$

$$Cp = -393.5r^2 + 297.5r + 3749 \qquad (4\%)$$

Solutions containing other types of salts show similar trends. A consistent observation across all studied water-electrolyte mixtures is that,when the concentration is constant and the anionic component remains the same, an increase in the cationic radius leads to a decrease in the specific heat capacity, as shown in Figure 2.

Additionally, as illustrated in Figure 3, the specific heat capacity of thye water-electrolyte systems is also affected by the charge density of the cations. When the anion and concentration are held constant, a clear mathematical relationship is observed between the specific heat capacity (and cation charge density (P_e, in C/Å²), as demonstrated for the LiCl, NaCl, and KCl solutions.

$$Cp = -2388Pe^2 + 1000\,Pe + 4009 \qquad (0.5\%)$$

$$Cp = -4228\,Pe^2 + 1838\,Pe + 3861 \qquad (1\%)$$

$$Cp = -6831\,Pe^2 + 2898\,Pe + 3699 \qquad (1.5\%)$$

$$Cp = -8620\,Pe^2 + 3693\,Pe + 3557 \qquad (2\%)$$

$$Cp = -10240\,Pe^2 + 4404\,Pe + 3425 \qquad (2.5\%)$$

$$Cp = -12213\,Pe^2 + 5171\,Pe + 3297 \qquad (3\%)$$

$$Cp = -15044\,Pe^2 + 6179\,Pe + 3158 \qquad (3.5\%)$$

$$Cp = -18159\,Pe^2 + 7246\,Pe + 3021 \qquad (4\%)$$

The specific heat capacities of solutions for other types of salts exhibit similar dependencies. A common characteristic across all studied water-electrolyte mixtures is that as the charge density of cations increases, the specific heat capacity of the solutions also increases.

The data indicate that changes in the specific heat capacity of water-salt systems are mainly influenced by three factors: the concentration of dissolved substances, the ionic radius, and the charge of the ions. At T = const, the specific heat capacity generally decreases with increasing concentration. This is due to the rising number of hydrated ions in the solution, which leads to a higher solution density. However, at a fixed concentration, the specific heat capacity behaves differently depending on the cation's ionic radius and charge density. Smaller cations with higher charge density tend to form more strongly hydrated complexes, increasing the size of the hydrated ions. This results in greater solution viscosity and more free volume between large water-electrolyte clusters, ultimately leading to an increase in the specific heat capacity, as portrayed in Figures 2 and 3. In contrast, larger cations with lower charge density exhibit weaker hydration. Their smaller hydrated size results in lower viscosity and higher solution density due to reduced free volume between the smaller clusters, causing the specific heat capacity to decrease. These findings suggest that the water-electrolyte mixtures function as molecular-kinetic systems, where hydrated ions or water-electrolyte complexes play a key structural role. The behavior and properties of these complexes are strongly influenced by the concentration, ionic radius, and charge density of the solutes, which collectively determine how the specific heat capacity of the solution evolves [23].

B. The Nature of Processes Influencing the Thermal Conductivity of Water-Electrolyte Mixtures

A substantial amount of experimental data has been collected to date, illustrating how various physicochemical, thermal, and thermodynamic properties of solutions change under different external conditions—particularly temperature and concentration [24]. However, the underlying cause-and-effect mechanisms driving the changes in the thermal conductivity of aqueous electrolyte solutions remain poorly understood and not fully substantiated. The aim of this part of the study was to establish new scientific principles that explain how thermal conductivity varies with temperature, concentration, ionic radius, and charge. To achieve this, the thermal conductivity of several binary and ternary electrolyte solutions, classified as types 1-1, 1-2, 2-1, and 2-2, was examined at T = const across a broad range of concentrations. The analysis incorporated known ionic radii [14] and calculated charge density values, as detailed in Tables I and II. The results of the graphical analysis of the thermal conductivity changes for certain representatives of the studied water-electrolyte mixtures of types 1-1 (H_2O – LiI, H_2O – NaI); 1-2 (H_2O - Na_2SO_4, H_2O - K_2SO_4); 2-1 (H_2O – $CoCl_2$, H_2O - $NiCl_2$, H_2O - $MnCl_2$, H_2O – $CaCl_2$, H_2O –$Mg(NO_3)_2$, H_2O - $Co(NO_3)_2$, H_2O - $Ca(NO_3)_2$, H_2O - $Sr(NO_3)_2$, H_2O – $Mn(NO_3)_2$) at T=const=20 °C are presented in Figures 4-6. The studied water-salt systems at T=const=40 °C exhibit similar dependencies.

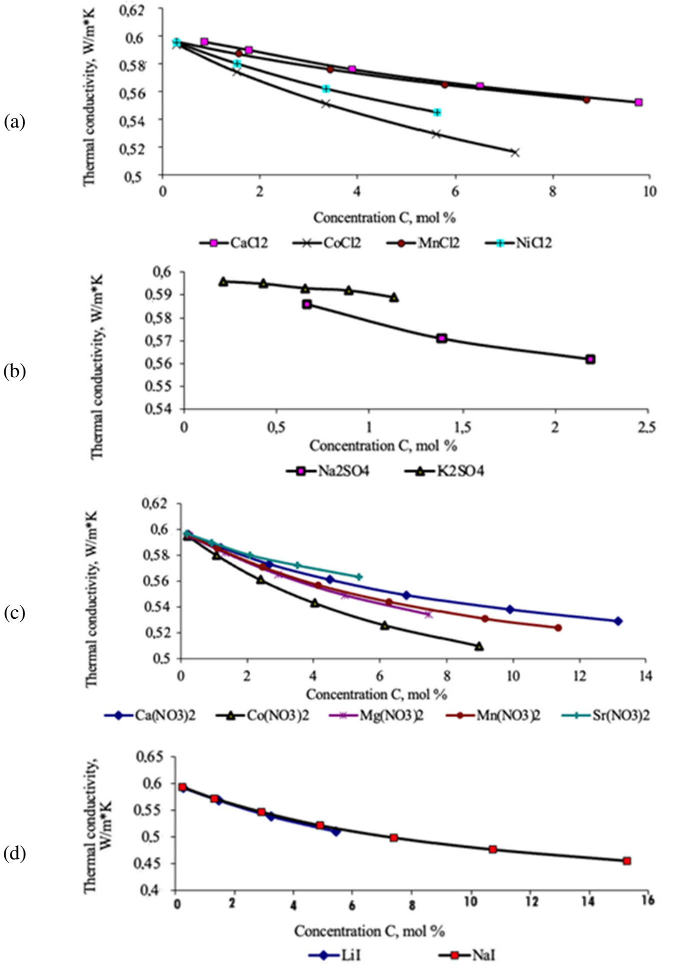
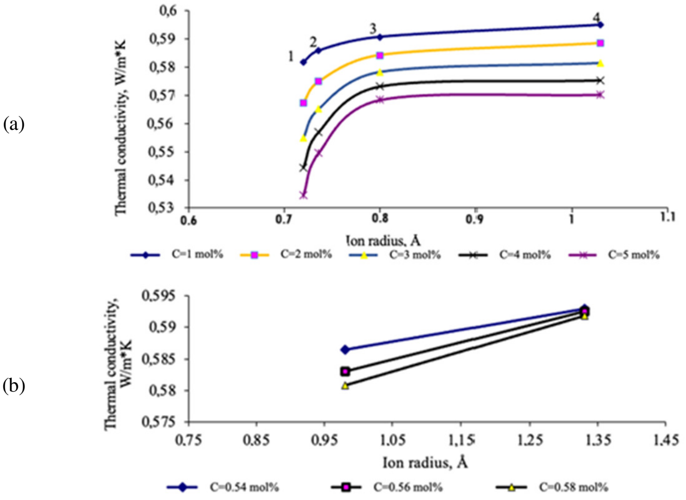


Fig. 4. Dependence of thermal conductivity of solutions on concentration at T=const 20 °C.



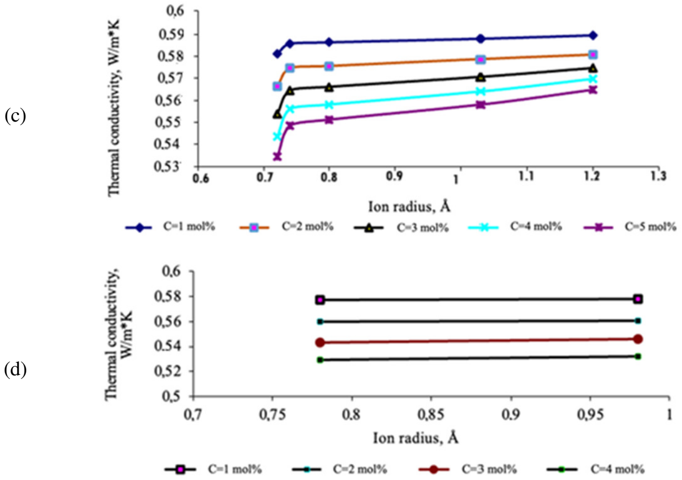


Fig. 5. Dependence of thermal conductivity of solutions on the ion radius at C=const and T=const 20 °C.

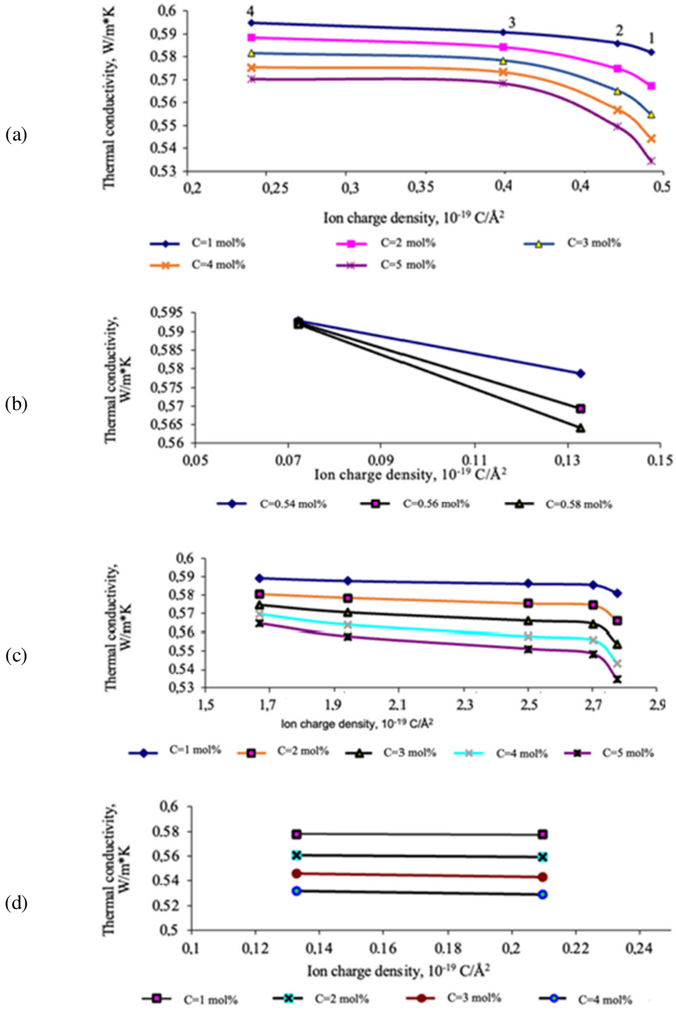


Fig. 6. Dependence of thermal conductivity of solutions on the ion charge density at C=const and T=const 20 °C.

Figures 4-6 show that the thermal conductivity (λ in W/m·K) of the water-electrolyte systems decreases with increasing concentration (C in mol%) at constant temperature (T = const). This behavior can be accurately described using polynomial equations.

$$\lambda = 0.0003C^2 - 0.0077C + 0.6025 \qquad \text{(for CaCl}_2\text{)}$$

$$\lambda = 0.0002C^2 - 0.0071C + 0.5978 \qquad \text{(for MnCl}_2\text{)}$$

$$\lambda = 0.0006C^2 - 0.0130C + 0.5985 \qquad \text{(for NiCl}_2\text{)}$$

$$\lambda = 0.0007C^2 - 0.0164\mathrm{C} + 0.5981 \qquad \text{(for CoCl}_2\text{)}$$

Similar trends are observed across other types of salt solutions. A consistent pattern among all studied water-electrolyte mixtures is that, at the same concentration and with identical anions, solutions containing cations with larger ionic radii exhibit higher thermal conductivity (Figures 4(a) and 4(b)). At T = const, the thermal conductivity of the water-electrolyte systems is influenced by the ionic radius. For solutions, such as $CaCl_2$, $MnCl_2$, $NiCl_2$, and $CoCl_2$, a clear mathematical relationship has been established between the thermal conductivity (λ in W/m·K) and the ionic radius (r in Å), demonstrating how changes in the ion size affect the heat transfer in these systems.

$$\lambda = -0.279r^2 + 0.528r + 0.347 \qquad (1\%)$$

$$\lambda = -0.587r^2 + 1.091r + 0.088 \qquad (2\%)$$

$$\lambda = -0.855r^2 + 1.576r - 0.134 \qquad (3\%)$$

$$\lambda = -1.080r^2 + 1.983\mathrm{r} - 0.320 \qquad (4\%)$$

$$\lambda = -1.268r^2 + 2.324r - 0.478 \qquad (5\%)$$

Solutions containing other types of salts exhibit a similar behavior. A consistent trend observed across all studied water-electrolyte mixtures is that when the concentration is constant and the anionic component remains the same, an increase in the cationic radius leads to a higher thermal conductivity (Figures 5(a) and 5(b)). Additionally, as illustrated in Figures 6(a) and 6(b), the thermal conductivity is also affected by the charge density of cations. For solutions, such as $CaCl_2$, $MnCl_2$, $NiCl_2$, and $CoCl_2$ with identical anions and constant concentrations, a clear mathematical relationship has been established between the thermal conductivity and cation charge density.

$$\lambda = -0.265P_e^2 + 0.145\, P_e + 0.575 \qquad (1\%)$$

$$\lambda = -0.601\, P_e^2 + 0.361\, P_e + 0.536 \qquad (2\%)$$

$$\lambda = -0.903\, P_e^2 + 0.562\, P_e + 0.498 \qquad (3\%)$$

$$\lambda = -1.159\, P_e^2 + 0.733\, P_e + 0.466 \qquad (4\%)$$

$$\lambda = -1.367\, P_e^2 + 0.869\, P_e + 0.440 \qquad (5\%)$$

The solutions containing other types of salt follow similar patterns. A key finding across all studied water-electrolyte mixtures is that, as the charge density of cations increases, the thermal conductivity of the solutions decreases. Overall, the thermal conductivity of the water-salt systems is primarily influenced by three factors: the concentration of dissolved substances, the ionic radius, and the ionic charge. At constant temperature (T = const), an increase in the electrolyte concentration generally leads to reduced thermal conductivity. This is due to a higher number of hydrated ions in the solution, which raises viscosity, hindering efficient heat transfer.

However, at a fixed concentration, the thermal conductivity varies depending on the cation's ionic radius and charge density. Smaller cations with higher charge densities tend to coordinate more strongly with water molecules, forming larger hydrated ion complexes. These larger structures increase the amount of free space between clusters, reducing the solution's density and, consequently, its thermal conductivity, as portrayed in Figures 5 and 6. In contrast, cations with larger radii and lower charge densities form smaller hydrated complexes result in lower viscosity and higher solution density due to the reduced spacing between complexes. This leads to an increased thermal conductivity. These findings support the view that water-electrolyte systems function as molecular-kinetic environments, where hydrated ions organized as water-electrolyte complexes define the thermal behavior of the solution [25]. The concentration, ionic radius, and charge density of the solutes directly shape the structure and properties of these complexes, thereby influencing the thermal conductivity. Compared to earlier studies, which often focused on a limited number of systems or emphasized temperature effects [1, 2], this research adopts a broader and more quantitative approach. By analyzing 40 different binary and ternary electrolyte mixtures across a wide concentration range (0.01 mol%–23.5 mol%), the current study establishes robust mathematical models that clearly relate the thermal properties to the ionic radius and charge density. Authors in [5] focused on theoretical sorption models in aqueous environments, but did not quantify macroscopic thermal properties. This experimental-calorimetric approach adds a direct, empirical dataset supported by regression modeling. Authors in [7] used molecular simulations to explore hydration-mediated forces, while the present study bridges/connects molecular hydration characteristics with measurable thermal behavior, such as C_p and λ. Unlike authors in [11, 12], who addressed viscosity and density in specific salt systems, this study provides quantitative expressions for both heat capacity and thermal conductivity across different electrolyte types (1-1, 1-2, 2-1, 2-2), with explicit dependence on ionic radii (0.72–1.65 Å) and charge density (0.0468–0.4921 C/Å^2). Therefore, the key contribution of this work is a generalized, experimentally validated framework that quantitatively relates fundamental ionic properties to the thermal behavior of electrolyte solutions. These results may be directly useful for improving the heat transfer modeling, solution design in energy systems, and advancing the theoretical understanding of ion hydration thermodynamics.

IV. CONCLUSIONS

The present study offers a detailed quantitative analysis of how ionic radius, charge density, and concentration affect the thermal properties of water-electrolyte mixtures, namely the specific heat capacity (C_p) and thermal conductivity (λ). While earlier research has focused on qualitative insights into ion–solvent interactions, this work introduces new empirical models based on polynomial regression. These models describe C_p and λ as functions of both ionic size and charge density, using data from 40 different electrolyte systems. The key innovations of this study include:

- Establishing explicit mathematical correlations between C_p and λ with ionic radii (r) and charge densities (P_e) for different classes of electrolytes (types 1-1, 1-2, 2-1, 2-2) at fixed temperatures.
- Demonstrating that, at constant conditions, C_p decreases by up to 12% with an increasing cationic radius, while λ increases by up to 20%, a behavior not quantitatively reported in prior literature.
- Showing for the first time that the charge density (not just the ionic size) plays a decisive, inversely proportional role in λ, while directly increasing C_p, was confirmed across multiple salt types.

Furthermore, this study introduces the concept of the water-electrolyte system as a coordinated molecular-kinetic structure, where hydrated ions act as medium-defining units. These findings extend the current understanding of electrolyte thermophysics and offer predictive tools for applications in energy storage, chemical engineering, and solution thermodynamics.

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