

Thermoelectrokinetic Effect in Viscous Conductive Media

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Abstract

The article discusses the conditions, in which new thermoelectrokinetic and thermoelectromagnetic phenomena occur. They are cross phenomena emerging in the presence of mass, heat and electric charge transport in the electrically conductive medium. The thermoelectrokinetic and thermoelectromagnetic phenomena in the conditions much different from thermodynamic equilibrium are of particular interest. It is exemplified by the transport of the conductive medium mass, heat and electric charge occurs under the influence of the temperature gradient. As a result, self-organizing dynamic dissipative structures are formed. We provide the results of experimental observation of the new thermoelectrokinetic effect in the electroconductive fluid in an open system in the form of a U-shaped tube, through which the electroconductive fluid flows and in which the thermoelectrokinetic electric motion force arises in the presence of the temperature gradient. The obtained results reliably prove the existence of the new thermoelectrokinetic effect.

Keywords: Cross-Kinetic Phenomena, Non-Equilibrium Thermodynamics, Thermal Diffusion, Thermal Electric Motion Force, ThermoelectrokineticEffect, ThermoelectroMechanical Effect

1. Introduction

In viscous conductive media under conditions much different from thermodynamic equilibrium, the dissipative dynamic vortex structures are formed, for example in the convection zone of the Sun under the influence of the temperature gradient. The simplest model of the study of convective instability and occurrence of vortex motion of a viscous fluid in the transition of the temperature gradient or more precisely, the Rayleigh number, through the critical value is the model of the toroid filled with a viscous medium and located in the gravity field and the vertical temperature gradient. The main objective of this study is to establish the existence in these conditions of vortex electromagnetic structures, in particular the formation of the electric motion forces and the electric currents in the convective vortex flows of the viscous conductive medium, determined by the temperature gradient.

2. Related Data

The science of thermoelectricity gained significant momentum as the science of the cross phenomena of thermodynamics and electricity mainly in solids, metals, and semiconductors¹. The expansion of the range of the applied electrically conductive mediums, as well as thermodynamic conditions, up to the essentially non-equilibrium ones is of scientific and practical interest. In the second half of the 20th century,, new directions in physics at the junction of sciences such as fluid dynamics and thermodynamics, thermodynamics and electrodynamics, especially under conditions much different from equilibrium, in which the processes of self-organization take place with the formation of dissipative dynamic and electrodynamic^{2,3} structures, gain significant momentum.

The condensed matter physics most important research is the study of the transport phenomena,

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including cross phenomena occurring under the influence of two thermodynamic forces. An example can be the thermoelectric effects¹. Unlike traditional materials for thermoelectric energy converters (usually considered by condensed-matter physics), in which solid materials are used, it is proposed to study the thermoelectrokinetic effect in electroconductive liquid with the possibility of not only heat transfer, but also mass transfer. Traditionally in thermoelectricity, the mediums with pre-created static inhomogeneity are used, the nature of which survives the temperature gradient overlay. Typical examples are crystals of semiconductor thermoelectric materials doped with donor or acceptor impurities to give, respectively, n- and p-branches of thermal elements^{1,4}.

Early observations of these phenomena and their phenomenological description date back to the first half of the 19th century (Seebeck, Peltier), but their complete classification and the microscopic theory were built only by the mid-20th century. Yet up to now, the fundamental research on the creation of new theories and approaches to the description of thermoelectric effects is performed and new phenomena of this class are predicted and discovered.

Experimental and theoretical studies in the physics of thermoelectricity and semiconductor physics became the basis for the creation of modern thermoelectric converters that are widely used for cooling household and industrial electronic devices. In the circumstances of the approaching energy and environmental crises, thermoelectric power generators, which are characterized by the direct (machineless) principle of action and also have impressive efficiency, are of particular interest¹.

The majority of classical thermoelectric effects were first discovered and studied in solid, primarily in crystalline semiconductor systems. At the same time, the theories created to describe them are applicable to the condensed matters in general, including plasma⁵ and aqueous solutions of electrolytes⁶. Using the latter as the object of study allowed predicting and discovering a new class of thermoelectric effects. The requirements for a pilot plant to study them are not as stringent as for solid-state electronics (expensive cryogenics, low-pressures, pulsed fields, etc). In the present study, the dynamic heterogeneity in solutions of ionic compounds is created.

Thermoelectrokinetic phenomena⁷ occur in viscous conductive fluid at the transport of mass and electric charge in the presence of the temperature gradient, that

is, under the action of three thermodynamic forces. The cross phenomena will be:

- The mass transport due to the presence of both the transport of internal energy and transport of electric charge;
- The transport of internal energy due to the presence of both the mass transport and the transport of electric charge;
- The transport of electric charge due to the presence of both the mass transport and the transport of internal energy (presence of the temperature gradient).

A new class of these phenomena was first predicted⁷ and the thermoelectrokinetic Electric Motion Force (EMF) was observed in the Laboratory of Semimetals of the Herzen State Pedagogical University of Russia, St. Petersburg. Fundamentally important is the possibility of occurrence of thermoelectrokinetic phenomena, when the inhomogeneity of the medium is formed as a self-organized structure in the strongly non-equilibrium conditions^{2,3,8}, when in the initially homogeneous medium, a self-organizing thermal element is formed. This, of course, is not limited to the solid state of the substance. To date, we can consider the most researched the kinetic phase transitions in essentially non-equilibrium conditions in liquid media⁹. This paper investigates the processes of ion systems separation with electric charges of opposite signs in aqueous solutions of ionic compounds under the action of heat transfer and mass transfer.

3. Methodology

As the electroconductive viscous medium, we selected aqueous solutions of ionic compounds (acids, bases, salts), which were electrolytes. In the experimental device¹⁰, the design of which is shown in Figure 1, the model toroid was replaced with an open system in the form of a U-shaped tube, through which the fluid flow was supplied at a predetermined rate. Thus, instead of indirect measurements of small electrical currents in a closed toroidal loop, we provided measurements of voltage in an electrically open circuit with significantly higher accuracy.

The U-shaped tube filled with conductive viscous medium can be regarded as a model of the thermal element, in which heterogeneity is of kinetic nature, in contrast to the classical semiconductor thermal element.

The essence of kinetic heterogeneity consists in the fact that in an open system (Figure 2.), just like in the model of a toroidal convection vortex, the direction of the fluid flow in one of the branches coincides with the direction of the temperature gradient and in the other – it is opposite to it.

In the experiment, we used tubes of calcium chloride glass about 1 cm² in the section area and the knee length of up to 30 cm. To create and maintain the desired temperature difference (up to 30 K), we used an electronic temperature regulator and performed its measurements using a thermocouple. To reduce the influence of external factors on the thermodynamic processes, we placed the device in a thermal insulating box.

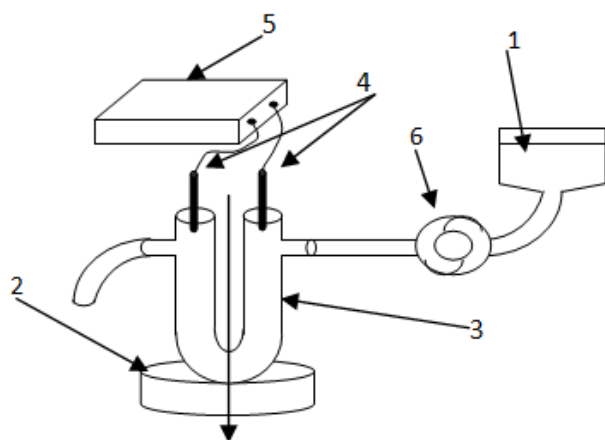


Figure 1. Design of the device for measuring the thermoelectrokinetic EMF.

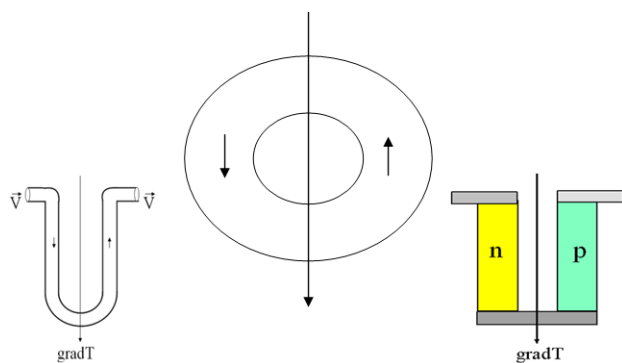


Figure 2. Models of a toroid – an open flow system – a semiconductor thermal element.

Electrical signals corresponding to the EMF under study and the temperature were measured with a multi-channel digital voltmeter.

To establish and maintain a constant flow rate of

the electrolyte, we used external differential pressure or a peristaltic pump⁶. Measurement of the flow rate was carried out by measuring the volume of the fluid flowing through the U-shaped tube for a fixed period.

In the course of preliminary studies, we found that the maximum value of the measured signals was achieved using solutions with the greatest difference between the mobilities of positive and negative ions. One of the examples of such electrolytes is the aqueous solution of potassium hydroxide KOH. This alkali dissociates into K^+ ions with mobility $i = 7.6 \cdot 10^{-8}$, m²·V⁻¹·s⁻¹ and OH^- ions with mobility $i = 20.5 \cdot 10^{-8}$, m²·V⁻¹·s⁻¹ at $T = 300K$ ⁹.

Preliminary studies demonstrated a marked influence on the measured EMF of the associated electrochemical, electrokinetic and thermoelectric effects. To minimize the electrochemical effect contribution, we used silver chloride electrodes containing buffer electrolyte. To minimize the contribution of the electrokinetic effect, we used glass tubes of relatively large diameter of approximately 1 cm. The electrokinetic EMF value was determined in the absence of the temperature gradient and did not exceed 30 μV for typical flow rates. To minimize the contribution of the thermoelectric effect, we were required to maintain the same temperature at the inlet and outlet of the U-shaped tube. The value of the thermoelectric component was measured in the presence of the temperature gradient and in the absence of the fluid flow and did not exceed 100 μV.

Thus, the presence of one thermodynamic force (the temperature gradient or pressure difference) does not cause any significant values of EMF. With the simultaneous presence of temperature difference (about 30K) and pressure difference that provided steady fluid flow at the speed of 1.26 mm/min, the measured EMF reached the value of 0.84 mV. We called this EMF thermoelectrokinetic.

For serial measurements, we used electrolyte solutions of three types: acetic acid (CH₃COOH), sodium sulfate (Na₂SO₄) and potassium hydroxide (KOH).

We used the following procedure of experimental determination of the thermoelectrokinetic EMF (Figure 3). First of all, we measure the voltage between the electrodes in the case of thermodynamic equilibrium to estimate the value of the electrochemical EMF. This is followed by determining the steady-state temperature gradient between the area of the bend and the ends of the U-shaped tube in the absence of electrolyte leak.

The value of voltage U_1 measured in these conditions corresponds to the contribution of the thermoelectric and electrochemical EMF. The noises are caused by fluctuations of the parameters defining the conditions of the experiment.

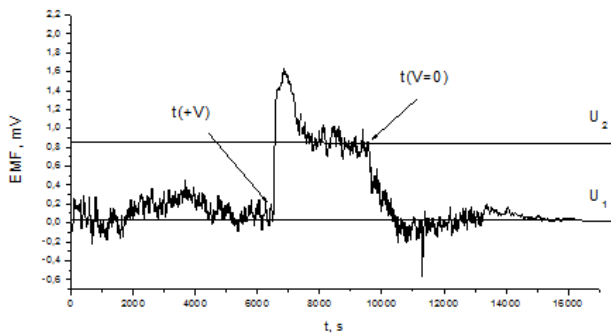


Figure 3. The thermoelectrokinetic effect in a diluted aqueous solution of potassium hydroxide in the concentration of 0.09 mole/liter at the temperature difference of 10K, $V=2$ ml/min.

The next step is to establish a constant rate of flow of electrolyte in the presence of the temperature gradient. The voltage difference between the electrodes, in the circumstances of the steady-state flow rate and the temperature gradient is the contribution of the thermoelectrokinetic and thermoelectric effects. The next step is to minimize the temperature difference at the inlet and outlet of the U-shaped tube with an additional heater, which minimizes the contribution of the thermoelectric effect to the measured EMF and determine the steady-state value of signal U_2 . As a result, the difference between values U_1 and U_2 gives the value of the thermoelectrokinetic EMF (Figure 3.) (points $t(+V)$ and $t(V=0)$ correspond to the start and stop of the fluid flow). The emission at the flow activation is associated with the processes of establishing steady-state values of the rate of flow and temperature distribution.

For reliable measurement of the thermoelectrokinetic EMF, it is necessary to ensure reproducibility of the results by creating identical conditions of the experiment. Errors due to the presence of concomitant effects are mostly systematic, while errors in the series of measurements are statistical.

Systematic errors (11%) exceed the statistical ones (2.25%). This ensures good reproducibility, since systematic errors in the series are similar and do not lead to a difference in the results of the series.

The presence of additional heaters at the inlet and

outlet of the U-shaped tube also provides the possibility of maintaining a steady temperature difference between the electrolyte zones in the vicinity of the inlet and outlet and subsequent measurement of the voltage between the electrodes, which is a joint display of the thermoelectrokinetic and thermoelectric effects. At the same time, depending on the sign of the temperature difference at the fixed direction of the electrolyte flow rate and the temperature gradient in the knees, the measured voltage will be a sum or difference of both the thermoelectrokinetic and thermoelectric EMFs. In case of the difference of the specified EMFs, adjustment of the electrolyte flow rate or temperature difference can provide for achievement of their compensation when the measured voltage between the electrodes is close to zero. The chart of voltage measurement depending on the time at the observance of the co-existence of the thermoelectric and thermoelectrokinetic effects is provided in Figure 4. The temperature difference in the solution between the inlet and outlet of the U-shaped tube is provided by additional heaters (Figure 5 b,c) in the presence of the vertical temperature gradient.

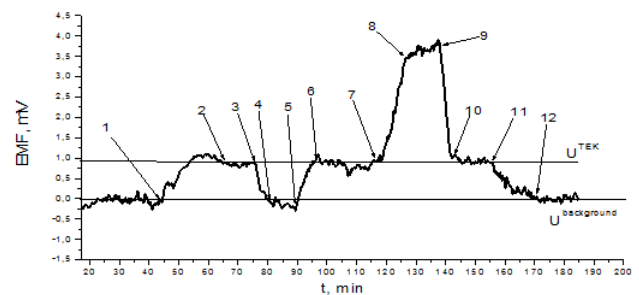


Figure 4. Co-occurrence of the thermoelectric and thermoelectrokinetic effects, section 4-5 – the EMFs cancel each other out, section 8-9 – the EMFs are summed.

Section 0-1: A vertical temperature gradient was set; there is no fluid flow, $U_{background}$.

Point 1: Setting a constant rate of the fluid flow.

Section 1-2: The process of establishing the stationary value of the thermoelectrokinetic EMF associated with the transient processes at activation of the fluid flow and the need to minimize the interfering thermoelectric EMF.

Section 2-3: Corresponds to the thermoelectrokinetic effect, U^{TEK} .

Point 3: Activation of the heater forming additional temperature difference ΔT^{add} , creating the thermoelectric EMF opposite in sign to the thermoelectrokinetic EMF.

The temperature difference was about 7 °C.

Section 4-5: Both effects have been offset, the signal is approximately equal to the background value, $U^{background}$.

Point 5: Removal of the additional temperature difference ΔT^{add} .

Section 5-6: The signal returns to the original value of the thermoelectrokinetic EMF – section 6-7, U^{TEK} .

Point 7: Activation of the heater forming additional temperature difference ΔT^{add} , creating the thermoelectric EMF coinciding in sign to the thermoelectrokinetic EMF.

Section 8-9: The sum of two effects.

Point 9: Removal of the extra difference ΔT^{add} .

Section 9-10: The signal returns to the original value of the thermoelectrokinetic EMF – section 10-11, U^{TEK} .

Point 11: Cutoff of the fluid flow.

Section 11-12: Return of the signal to background values, $U^{background}$.

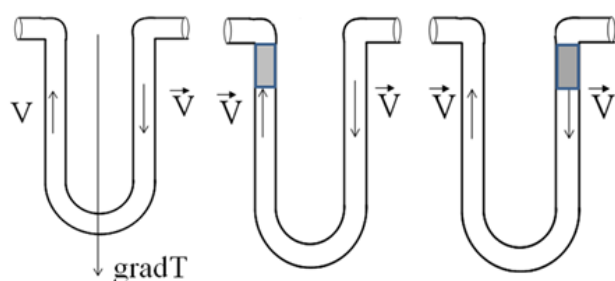


Figure 5. When we heat only one of the knees b, c (the heated area is colored gray), one of the branches of the U-shaped tube a is modeled.

Now, we consider the system in the “other” configuration: ΔT^{add} and the fluid flow are present, the vertical temperature gradient is absent (Figure 5b,c). In this case, the whole U-shaped tube will be one of the knees of the system for measuring the thermoelectrokinetic effect (Figure 5 a). In one case (Figure 5b), the fluid flow coincides with direction ΔT^{add} , in the other case they are opposite (Figure 5c). As mentioned above, the formed EMF should be different in the knees, as evidenced by the performed experiment. At section 4-5, wherein the directions of the fluid flow and ΔT^{add} are opposite, the thermal EMF is less than in section 8-9, wherein the directions of the fluid flow and ΔT^{add} coincide.

Based on these results, we can formulate the following relationship:

$$U = U^{background} + \begin{cases} U^{TEK}, \bar{\nabla} T^{add} = 0 \\ U^{TEK} - U^{TE}, \bar{\nabla} T^{add} \uparrow \uparrow \bar{V} \\ U^{TEK} + U^{TE}, \bar{\nabla} T^{add} \uparrow \downarrow \bar{V} \end{cases}$$

The developed experimental device allows measuring the thermoelectric EMF in the absence of the flow of the electrolyte solution, with turned-off heater and turned-on one of the additional heaters on the right or left knee of the U-shaped tube. This is how the coefficients of the thermal EMFs of the aqueous solutions of ionic compounds (electrolytes) under study were measured.

These results confirm the conclusions about the nature of the new thermoelectrokinetic effect. The possibility of compensation of the thermoelectrokinetic and thermoelectric EMFs represents new opportunities for a quantitative analysis of the thermoelectrokinetic effect and the obtaining of a cumulative effect of the thermoelectric and thermoelectrokinetic EMFs may be promising for practical use.

Thus, the proposed technique of the experiment allows obtaining independent estimates of the contributions of the thermoelectrokinetic EMF and other related kinetic effects.

Based on the general theory of cross-kinetic phenomena, we can conclude that a new class of thermoelectrokinetic phenomena should be described with the Onsager reciprocal relations². One would expect that for the formation of the thermoelectrokinetic EMF, the determining factor is the relative motion of the electrolyte: the movement of the solution or the heater with respect to it in the laboratory system. It was therefore decided to construct a new experimental device, in which the temperature gradient was moved relative to the electrolyte solution stationary in the laboratory system. The basis of this device is the horizontal straight glass tube 1 (10 mm in diameter, 1.5 m in length), filled with electrolyte 4 (Figure 6). Heating element 2 fastened in support 3 can perform linear movement in the forward and backward directions along the axis of the glass tube. With silver-chloride electrodes 5 of the measuring device and computer, we read the values of the thermoelectrokinetic EMF.

When voltage is applied to the heating element, local heating of the electrolyte in the tube was created (the input power ~10 W). With the start of movement of the heater along the tube by arrow a) (this direction is conventionally denoted “forward” and the one by arrow b) – “reversed”), the process of separating ions in the electrolyte takes place, whereby more mobile ions accumulate in front of the moving heater that leads to

occurrence of the thermoelectrokinetic effect.

In the experiment, electrolyte was represented by the aqueous solution of acetic acid (concentration – $n=10$ g/l); the speed of the heater motion along the tube was $V = 0.5$ mm/s.

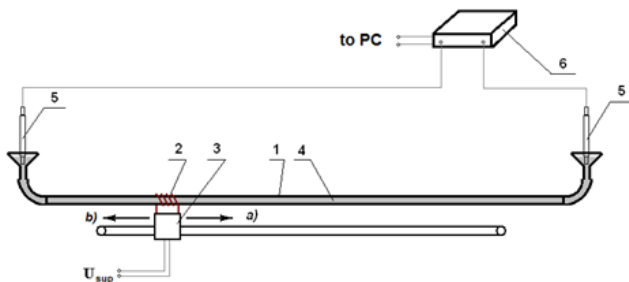


Figure 6. The design of the experimental device.

The proof was achieved through a series of experiments performed on the device. The experiments took place in two stages—with the forward and reverse movement of the heater. When changing the direction of movement, we expected a change in sign of the signal of the thermoelectrokinetic EMF. One of the experimental results is shown in Figure 7.

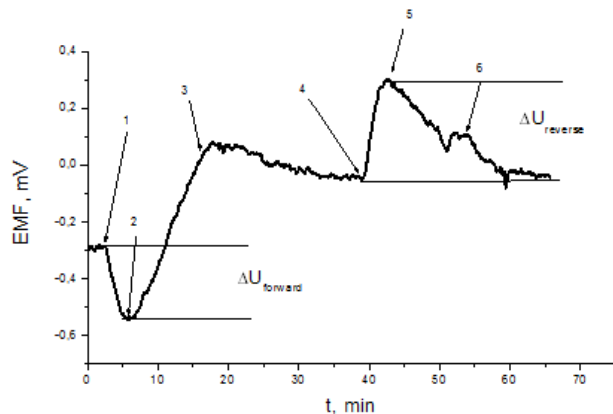


Figure 7. Thermoelectrokinetic EMF in the dilute solution of acetic acid at a concentration of 10 g/l, with the heater speed 0.5 mm/s (at forward and reverse motion) and the fluid temperature difference between the tube edges and near the heater about 20 K..

Section 0-1: It corresponds to the thermodynamic equilibrium in the absence of disturbing factors.

Point 1: Activation of the heater, setting the constant speed of the heated area.

Section 1-2: The process of the thermoelectrokinetic EMF establishment.

Section 2-3: It corresponds to “smearing” of the

temperature gradient (the heat transfer leads to warming the fluid and consequently, reduces the temperature gradient) and thus the decreasing effect.

Point 3: Switching off and stopping the heater forming the temperature gradient.

Section 3-4: The signal returns to background values.

Point 4: Activation of the heater, setting the constant speed of the heated area. The heater moves in the opposite direction.

Section 4-5: The process of the thermoelectrokinetic EMF establishment.

Section 5-6: It corresponds to the “blurring” of the temperature gradient and thus a decrease in the effect.

Point 6: Switching off and stopping the heater forming the temperature gradient.

$\Delta U_{\text{forward}}$ and $\Delta U_{\text{reverse}}$ correspond to the thermoelectrokinetic EMF under the given conditions of the experiment for both forward and reverse movement of the heater. As seen from graph $\Delta U_{\text{forward}} \approx -\Delta U_{\text{reverse}}$, which corresponds to changes in the direction of the heater. The presented result was obtained at the speed of the heater equal to 0.5 mm/s. The thermoelectrokinetic EMF previously obtained at a similar mass transport rate is close in value to that obtained in this experiment (about 0.3 V). In¹⁰ it was argued that the thermoelectrokinetic EMF passes through a maximum depending on the rate of mass transfer. In these experimental conditions, it is assumed that the transition through a maximum will occur at similar rates of the heater.

The experimental results obtained using the given installation confirm the reliable detection of the thermoelectrokinetic EMF and change in its sign when the direction of movement of the heater changes. When the heater moves, the temperature field in the tube becomes asymmetric, leading to the formation of the thermoelectrokinetic EMF. This variant of the experiment showed that for the formation of the thermoelectrokinetic EMF, the determining factor is the relative motion of the electrolyte and the temperature difference. For obtaining more accurate quantitative results, this version of the device should be improved, above all, to achieve the same values of temperature of the electrolyte at the ends of the horizontal tube by their thermostating.

4. Results

Experimental dependences of the thermoelectrokinetic EMF on the magnitude of the temperature difference,

concentration and flow rate of the electrolyte are represented in Figures 8-10¹⁰.

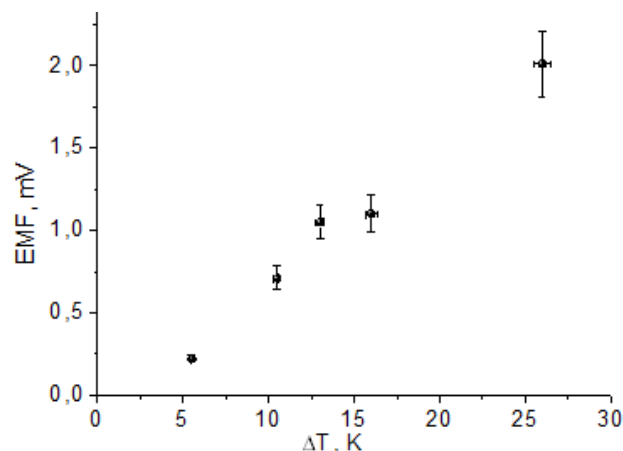


Figure 8. The dependence of the thermoelectrokinetic EMF in the solution of potassium hydroxide at a concentration of 0.089 mole/liter of the temperature difference at a fixed flow rate of solution $V = 1.26$ mm/s.

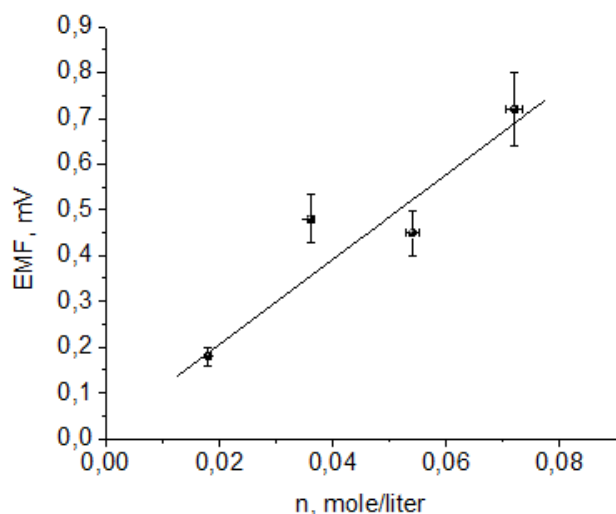


Figure 9. The dependence of the thermoelectrokinetic EMF in the solution of potassium hydroxide on the electrolyte concentration at fixed temperature differences $\Delta T = 30$ K and the flow rate of solution $V = 0.84$ mm/s.

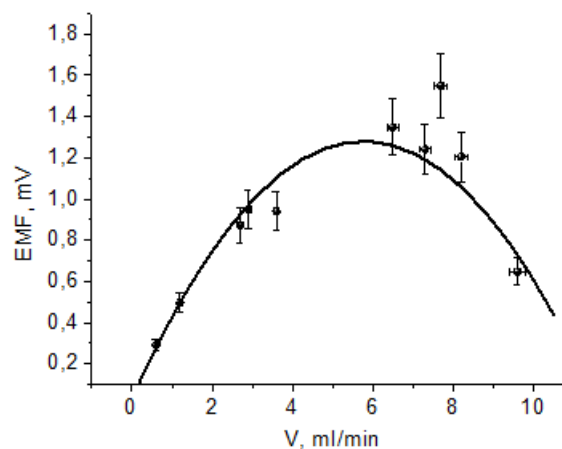


Figure 10. The dependence of the thermoelectrokinetic EMF in the potassium hydroxide solution at a concentration of 0.072.

Diagrams like the one shown in Figure 10 helped determine the value of the thermoelectrokinetic EMF for the given concentration of the solution at different flow rates. Serial experiments were conducted to study the dependence of the thermoelectrokinetic EMF on the flow rate of the electrolyte. As seen, the thermoelectrokinetic EMF depending on the flow rate of the electrolyte passes through a maximum. Qualitatively, this behavior seems obvious. When electrolyte is static, i.e. the flow rate is zero, the thermoelectrokinetic EMF is equal to zero. At a high flow rate, the effective temperature difference decreases and the ions of both signs practically equally are carried by the flow, so that the thermoelectrokinetic EMF again approaches zero. For the given temperature difference, there is a certain rate of flow of the electrolyte, at which the thermoelectrokinetic EMF has a maximum as observed experimentally. The directly proportional dependence (Figures 8, 9) indicates that the investigated range of concentrations of the aqueous solution of KOH is within the validity of the condition of the diluted solution, wherein the ions are surrounded by solvent molecules and therefore, have the characteristics such as the structure of the environment, the diffusion and mobility coefficients, independent of the concentration of the solution.

Figure 11 shows the experimental graphs on the study of the thermoelectrokinetic effect. The plots of the curves corresponding to the set steady-state value of the thermoelectrokinetic EMF (beginning of the plot) and the stopping time of the fluid flow (point $t(V=0)$) are provided. The comparison shows that when the fluid flow stops (point $t(V=0)$), the measured signal behaves the same way at various directions of the temperature gradient. This is determined by the dynamic nature of non-uniformity in the experiment. As is evident from Figure 12, in this case when the direction of the temperature gradient is changed, the branches of the dynamic thermal element are also swapped, in which the gradient is directed along the direction of the flow or against the direction of flow of the electrolyte. This is another significant difference of the thermoelectrokinetic effect of the known thermoelectric effect.

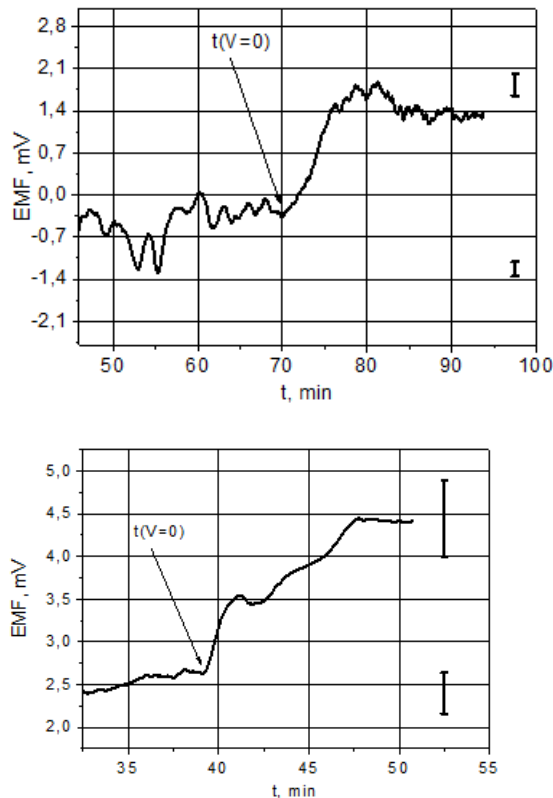


Figure 11. Thermoelectrokinetic EMF in the dilute solution of acetic acid at a concentration of 0.17 g/l at “forward” – a) and “reverse” – b) temperature gradient direction. Moment $t(V=0)$ corresponds to cutoff of the fluid flow.

5. Discussion

As can be seen from the results of the experiment (Figures 8-10), the thermoelectrokinetic EMF demonstrates the dependence close to linear on the magnitude of the temperature difference (Figure 8.) and on the rate of flow of the electrolyte in the initial section (Figure 10). The passage of the maximum and the subsequent decrease in the EMF is determined not by the violation of the linear dependence on the rate, but by the decrease in the effective temperature difference, because at high speeds of the flow, the electrolyte does not have time to heat up.

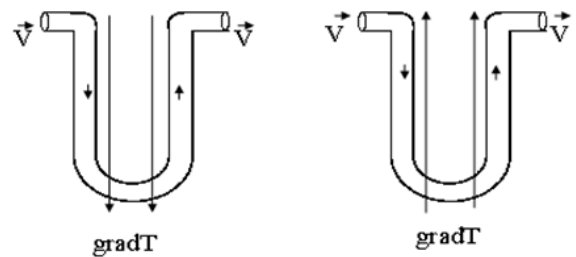


Figure 12. Independence of the sign of the thermoelectrokinetic EMF on the sign of the temperature gradient. When the direction of the temperature gradient changes, the branches of the dynamic thermal element swap places.

Thus, under the impact of three thermodynamic forces, when there is a transfer of mass (particles), heat (presence of the temperature gradient) and electric charge, the electric current density is determined by the value of the intensity of electric field E , thermoelectric field E_T and thermoelectrokinetic field E_{TEK} . In accordance with the experimentally determined regularities, the thermoelectric field intensity is equal to $E_T = \alpha \text{grad}T$ and the intensity of the thermoelectrokinetic field is proportional to the value of the thermoelectric field and the particle flux density^{7,10}.

$$E_{TEK} = \beta (\alpha \text{grad}T) (nv) \quad (1)$$

The sign of coefficient β is reversed at the transition from the parallel gradient of the fluid flow to antiparallel. Hereinafter, we consider the projections of vectors on the specified direction, corresponding to the axes of the tube. Thus, the electric current density in these conditions is equal to:

$$J_q = \sigma E + \sigma (\alpha \text{grad} T) + \sigma \beta (\alpha \text{grad} T) (nv) \quad (2)$$

Under these conditions the thermoelectric EMF $\int (\alpha \text{grad} T) dl = 0$, but the thermoelectrokinetic EMF $\int \beta (\alpha \text{grad} T \cdot nv) dl \neq 0$, as coefficients β in the knees of the U-shaped tube have opposite signs, dependent on the parallelism or anti-parallelism of the vectors of the particle flux density and temperature gradient. Then, in accordance with the conditions set above:

$0 = \sigma E + \sigma \beta (\alpha \text{grad} T) (nv)$ or $E = -\beta (\alpha \text{grad} T) (nv)$ and the magnitude of the measured voltage is equal to the thermoelectrokinetic EMF:

$$E_{TEK} = \int (\alpha \text{grad} T \cdot nv) dl \quad (3)$$

Since the density of the mass (particles) flow is proportional to the pressure gradient, the intensity of the thermoelectrokinetic field and the thermoelectrokinetic EMF will be proportional to the product of two thermodynamic forces determined by the gradients of temperature and pressure:

$$E_{TEK} = \chi (\alpha \text{grad} T) (\text{grad} P) \quad (4)$$

Thus, the thermoelectrokinetic EMF demonstrates quadratic dependence with respect to the thermodynamic forces. Such ratios are characteristic of nonlinear thermodynamics and physical kinetics. In the quadratic approximation by the field strength, the expression for the electric current density of type 2 with account of the strength of the field E_{EK} determined by the electrokinetic effect can be represented as:

$$j_q = \sigma (E + E_T + E_{EK}) + \sigma_1 (E + E_T + E_{EK})^2 = \sigma (E + E_T + E_{EK}) + \sigma_1 (E^2 + E_T^2 + E_{EK}^2 + 2EE_T + 2EE_{EK} + 2E_T E_{EK})^2 \quad (5)$$

In expression 5, the fundamentally new summand is $\sigma_1 \cdot 2E_T E_{EK}$ describing the thermoelectrokinetic effect. The remaining summands can be described as the non-linear contribution to the known regularities of non-linear electrical conductivity and non-linear thermoelectric and electrokinetic effects.

Experience has shown^{7,10} that the thermoelectrokinetic EMF is linearly dependent on the value of one of the thermodynamic forces at a fixed value of the second thermodynamic force and is not small in the observed area of the specified linear relationship (Figures 8-10). Such an approximation can be defined as quasi-linear. In

this approximation, small quadratic corrections in⁵ may be omitted and with the experimental achievement of the smallness of the electrokinetic effect¹⁰, the electric current density can be described as:

$$j_q = \sigma E + \sigma E_T + 2\sigma_1 (E_T E_{EK}) \quad (6)$$

Which corresponds to expression 2 at the value of the thermoelectrokinetic EMF determined by expression 3.

In general, the action of the three thermodynamic forces in quasi-linear approximation for the flows of electric charge, heat and mass (particles) can be written in the following system of Equations 7:

$$\begin{cases} J_q = a_1 \Delta \phi + a_2 \Delta T + a_3 \Delta P + a_4 (\Delta T \Delta P) \\ J_q = b_1 \Delta T + b_2 \Delta \phi + b_3 \Delta P + b_4 (\Delta \phi \Delta P) \\ J_q = c_1 \Delta P + c_2 \Delta \phi + c_3 \Delta T + c_4 (\Delta \phi \Delta T) \end{cases} \quad (7)$$

In expressions 7, for ease, the thermodynamic forces are presented with the differences of the electric potential $\Delta \phi$, temperature ΔT and pressure ΔP . To date, we have studied the thermoelectrokinetic effect $a_4 (\Delta T \Delta P)$ – the transport of electric charge in the presence of temperature difference and particle transport (flow of the electrolyte). The effect of heat transfer determined by the passage of the medium and the electric current, $b_4 (\Delta \phi \Delta P)$, as well as the effect of the transport of particles determined by the presence of the temperature difference and the flow of the medium $C_4 (\Delta \phi \Delta T)$ – have not yet been studied. In addition, there may be scalar $(\text{grad } \phi \text{ grad} T)$ and vector $[\text{grad } \phi, \text{grad} T]$ products of thermodynamic forces, which increases the potential number of new possible effects.

At a fixed rate of the electrolyte flow, the thermoelectrokinetic field strength is proportional to the temperature gradient 5 with the coefficient $\gamma \approx 0.1 \mu\text{V/K}$ 5, 6.

$$E = -\beta (\alpha \text{grad} T) (nv) = -\gamma \text{grad} T \quad (8)$$

If we apply to a convective vortex flow of plasma in the solar convection zone a toroid model (Figure 2.) with the value of the outer diameter of the order of 10^4 km, and the diameter of the cross section of the toroid of about $3 \cdot 10^3$ km, take the value of the electrical conductivity of the plasma $\sigma = 3 \cdot 10^3 \text{ Ohm}^{-1}\text{m}^{-1}$, take the temperature gradient average value $\text{grad} T = 10^{-2} \text{ K/m}$ and take for the coefficient of the thermoelectric field strength the value obtained in the experiment with electrolytes $\gamma \approx 0.1 \text{ mV/K}$ 8, then for the value of the magnetic induction vector in

the center of the toroid (Figure 2.), we will obtain the value $B \approx 0.1$ T, which by the order of magnitude is close to the experimentally observed sunspots in the area¹¹. This magnetic field can be regarded as primary in the plasma, as a dissipative medium, which is transformed in magnetohydrodynamic processes and is a large range of the observed values of the magnetic field in the solar convection zone.

6. Conclusion

In natural conditions, in viscous conductive media, with the presence of difference in temperature, pressure and electrical potential, there is a new class of phenomena that can be called the class of thermoelectrokinetic phenomena.

The phenomenon of formation of the thermoelectrokinetic EMF as a cross-kinetic phenomenon of electric charge transport (formation of the EMF) in the presence of the transport of mass (particles) and internal energy (heat) has been experimentally detected and studied in detail.

Within the framework of physical kinetics, the cross kinetic phenomena under the influence of three thermodynamic forces can be described in quadratic approximation, which actually becomes quasi-linear at a fixed value of one of the thermodynamic forces in the field of correctness of the linear approximation to describe the coupled transport phenomena.

The thermoelectrokinetic EMF and closed electric currents are formed in the convection cells of plasma in the solar convection zone, which create the experimentally observed magnetic fields.

Based on the results of the study of the thermoelectrokinetic phenomena, we can conclude that a significant increase in the thermoelectric EMF can be achieved by the application of non-thermodynamic methods for creation of non-equilibrium of the systems of charge carriers, for example, by injection of non-equilibrium charge carriers, irradiation of semiconductors with the electromagnetic or corpuscular radiation, which can be very effective in the nanoscale region.

The aim of further research is the measurement of EMF for the thermoelectrokinetic and thermo electromechanical effect in dilute solutions of electrolytes with multiply charged ions. It is planned to continue the research of the solutions of electrolytes, characterized by

multiply charged ions with the largest values of mobility: Ba^{2+} , Mg^{2+} , Cd^{2+} , Al^{3+} , La^{3+} , $(\text{SO}_4)^{2-}$, $(\text{S}_2\text{O}_6)^{2-}$, $(\text{CO}_3)^{2-}$ etc. Electrolyte solutions, which are composed of the above ions and which are strong solutions (with high conductivity), appear most promising for further studies. Serial measurements will allow obtaining a set of data on the kinetics of multiply charged ions in condensed media.

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