Semiconductors, 2022, Vol. 56, No. 2

Influence of the ionic subsystem on the thermoelectric effect in colloidal solutions

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Received October 20, 2021
Revised October 25, 2021
Accepted October 25, 2021

The thermoelectric effect is investigated in mixtures of colloidal solutions with ionic electrolytes in the initial state, when the formation of concentration gradients under the influence of an inhomogeneous temperature field can be neglected. Based on experimental measurements in mixtures with different concentrations of colloidal particles and ions, the conditions under with the coefficient of thermoelectric EMF is determined by the ion subsystem and under which the main contribution to the value of the thermoelectric force is made by colloidal particles are determined.

Keywords: colloidal solution, thermoelectric effect, ionic subsystem.

DOI: 10.21883/SC.2022.02.53040.32

1. Introduction

The thermoelectric effect in electrolyte solutions was discovered later than in solids, i.e. at the end of the XIX century. It was described in details under the phenomenological theory of irreversible processes only in the middle of the XX century. If in solid-state mediums, when observing and measuring the Seebeck phenomenon, there are only contacts of two different metals or semiconductors [1], on which a drop of electric potential is formed due to the electrons redistribution between conductors, then in liquid solutions of electrolytes, in addition to the contact of two different liquids, there are mandatory solid–liquid phase interfaces [2], through which ions are transported, and where redox chemical reactions occur. Therefore, in electrolyte solutions, the final difference in thermoelectric potentials is the determined by the potential drop at the metal electrode–electrolyte solution interface, and the potential drop inside the liquid in an inhomogeneous temperature field.

Initially, interest in thermoelectric phenomena in electrolyte solutions was theoretical, since measurements of the thermoelectric EMF made it possible to determine such characteristics of ions as heat Q_i and transfer entropy S_i. However, in recent years, practical interest in these phenomena increased in connection with the prospects of creating the thermoelectrochemical cells based on them — ecologically clean, renewable sources of electrical energy [3–5]. The total EMF in such devices, as noted earlier, consists of the potential drop at the interface between solid-state electrodes and liquid solution, and the contribution formed inside the liquid electrolyte, which is subjected to the inhomogeneous temperature field.

In our paper we study the homogeneous contribution due to thermal diffusion processes inside the electrolyte. In this case, the expression for the electric potential gradient can be obtained within the framework of thermodynamics of irreversible processes [6]:

$$\mathrm{grad}(\varphi) = \frac{1}{\mathrm{F}} \frac{\sum\limits_{i,k} z_i a_{ik}}{\sum\limits_{i,k} z_i z_k a_{ik}} \left[-\mathrm{grad}(\mu_k) - \frac{Q_k^*}{T}\,\mathrm{grad}(T) \right]. \quad (1)$$

The following designations are introduced here: φ is electric potential, F is Faraday's constant, z_i is charge of electrolyte ions in units of electron charge, a_{ik} are phenomenological coefficients, μ_k is chemical potential of electrolyte particles, T is absolute temperature, Q_k^* is heat of transfer of particles of the form k. The phenomenological coefficients can be expressed in terms of the so-called reduced numbers of ion transport τ_k:

$$\frac{\sum\limits_{i} z_i a_{ik}}{\sum\limits_{i} z_i z_k a_{ik}} = \tau_k. \quad (2)$$

These values are numerically equal to the relative fraction of the flow of particles of the form k, which they contribute to the total electric current in the electrolyte. The reduced transport numbers can also be expressed in terms of particle concentrations c_k, their mobilities u_k and electric charge:

$$\tau_k = \frac{c_k u_k}{\sum\limits_{k} |z_k| c_k u_k}. \quad (3)$$

Thus, an internal electric field will appear in the electrolyte solution, which at the initial moments of time, when the concentration gradients were not yet formed, will be determined by the following expression:

$$\mathrm{grad}(\varphi_0) = -\frac{1}{\mathrm{F}} \sum_k \tau_k \, Q_k^* \, \frac{\mathrm{grad}(T)}{T}. \qquad (4)$$

This potential φ_0 is called in the literature as the thermal diffusion potential in the narrow sense [6]. After some time, due to the thermal diffusion in the solution the ion concentration gradient will arise, which will cause the diffusion potential occurrence, which together with the thermal diffusion potential in the narrow sense is called the thermal diffusion potential in the broad sense.

It can be seen from expression (4) that the value of the thermoelectric potentials difference in the initial state is proportional to the temperature difference, therefore, by analogy with solid mediums, the proportionality coefficient between the differences of electric potential and temperature can be called as coefficient of thermoelectric EMF of the electrolyte in the initial state

$$\alpha_0 = -\frac{1}{\mathrm{F}} \sum_k \frac{\tau_k Q_k^*}{T}. \qquad (5)$$

As follows from expression (5), its value is determined by the ratio between the transport numbers and the transfer heats of the charged particles of the solution. From the study of the thermal diffusion in colloidal solutions it is known that the transfer heat of colloidal particles is by several orders of magnitude higher than the transfer heat of individual ions, which is, in particular, due to their large sizes [7,8], it was also found that the coefficient of thermoelectric EMF of some colloidal solutions has a large value [9]. Therefore, it can be assumed that the presence of colloidal particles in the electrolyte solution can increase its coefficient of thermoelectric EMF and, thereby, the thermoelectric efficiency of thermoelectrochemical cells.

Accordingly, the purpose of our paper is to study the mutual influence of the presence of colloidal particles and ions on the final value of the thermoelectric EMF of colloidal solutions.

2. Description of experimental procedure

The coefficient of thermoelectric EMF in the paper was determined using the following experimental unit (Fig. 1).

The tested solution *2* was poured into a U-shaped tube *1*, one of its elbows was heated by an electric heater *3*. As measuring electrodes *6* the silver chloride electrodes were used, in which a metal wire coated with an insoluble salt of silver chloride was placed into a glass case, into which the saturated solution of potassium chloride was poured.

In the lower part of the case has small holes (electrolytic keys), thanks to which the electrodes are in contact with the tested solution. The temperature in the heated and cold regions of the electrolyte is recorded by a thermistor *4* and a thermometer *5*. When measuring the thermoelectric EMF, the electrolytic keys of the electrodes are located near the upper interface of the solutions, therefore, at the moment when the temperature begins to rise in the heated region of the liquid between the measuring electrodes a difference in thermoelectric potentials $\Delta\varphi_0$ arises, the expression for which was given earlier (4). Only after some time the temperature of the near-electrode solution *6b* and the electrode itself *6a* begin to increase noticeably, and in the recorded signal a component should appear due to the inequality of temperatures of the same type silver chloride electrodes. This is indeed confirmed in experiment [10]. Thus, in this experimental unit specifically the thermoelectric potentials difference corresponding to the initial state is recorded, from it the coefficient of thermoelectric EMF α_0 can be determined.

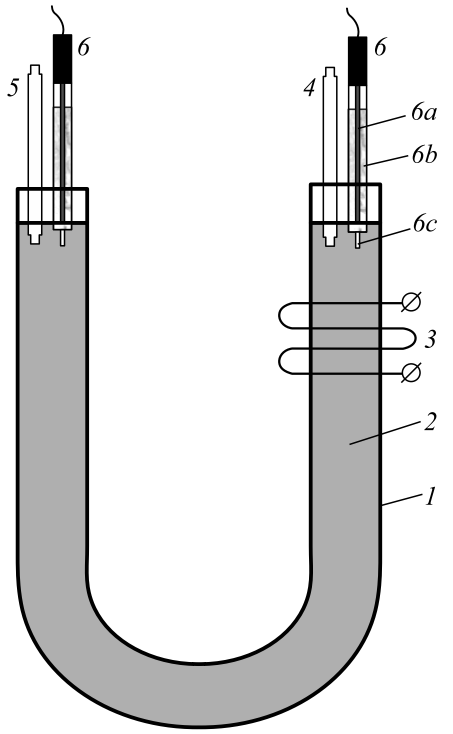

Figure 1. Diagram of experimental unit for measuring the coefficient of thermoelectric EMF in electrolyte solutions.

3. Experimental results and discussion

Using this method, the concentration dependences of the coefficient of thermoelectric EMF for mixtures of colloidal solutions with ionic electrolytes were obtained (Fig. 2 and 3).

In the first case (Fig. 2), we studied the change of coefficient of the thermoelectric emf of a mixture of 2% colloidal solution of rosin with ionic electrolyte NaOH for various concentrations of NaOH. The Figure also shows the concentration dependence for pure NaOH. The results show that at a relatively high content of the ionic electrolyte in the mixture its coefficient of thermoelectric EMF coincides, within the experimental error, with the coefficient of thermoelectric EMF of the pure ionic electrolyte of the same concentration. Upon the relative content of the ionic electrolyte decreasing, the coefficient of thermoelectric EMF of the mixture tends to the value for the pure colloidal solution.

A similar conclusion follows from the analysis of the coefficient of thermoelectric EMF of the mixture of colloidal solution of tannin and tin chloride (Fig. 3). Similar results, but in mixtures of the colloidal solution of starch with different electrolytes, were observed in the paper [11].

Obviously, the obtained result can be explained by decreasing of the ions contribution to the final coefficient of thermoelectric EMF, and by increasing of the contribution of colloidal particles due to decreased transport numbers of ions and increased transport numbers of colloidal particles (5) with their concentrations change in the mixture in accordance with expression (3).

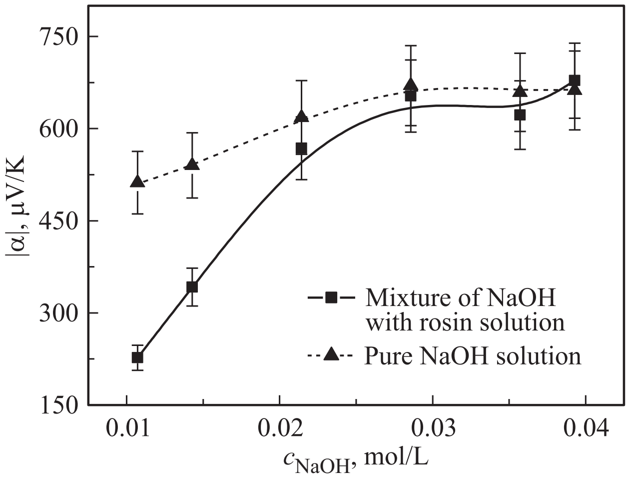

Figure 2. Modulus of the coefficient of thermoelectric EMF of NaOH solutions and its mixture with 2% colloidal solution of rosin vs. NaOH content by volume. The coefficient of thermoelectric EMFof 2% colloidal solution of rosin in distilled water is $\alpha = -53 \pm 8\,\mu$V/K.

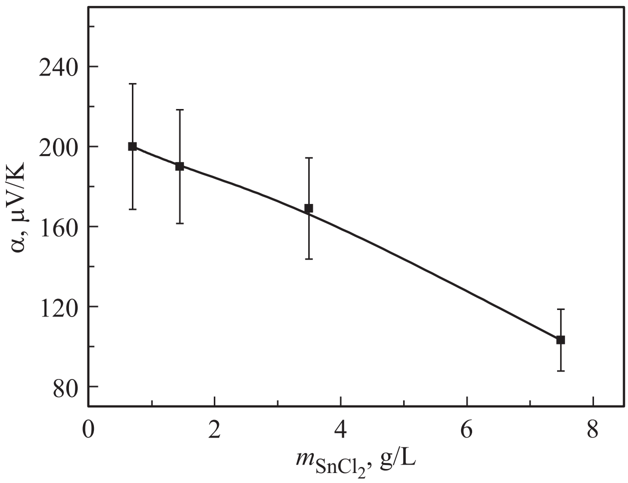

Figure 3. Coefficient of thermoelectric EMF of mixture of $SnCl_2$ and tannin solutions vs. tannin content by weight. The concentration of $SnCl_2$ 0.001 mol/l is fixed. Coefficient of thermoelectric EMF of tin chloride (II) solution of the specified concentration $\alpha = +180 \pm 20\,\mu$V/K.

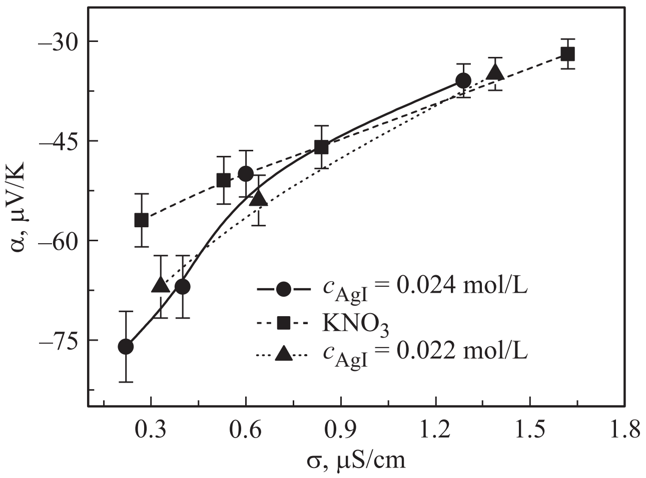

Figure 4. Coefficient of thermoelectric EMF vs. electrical conductivity coefficient for AgI colloidal solutions and KNO_3 pure solution. Dependences for colloidal solutions were obtained during their dialysis purification.

You can also change the ratio between the concentrations of free ions and colloidal particles in a mixture by removing ions from the solution using the dialysis purification method [12]. The method is based on the property of semipermeable membranes to pass small ions and retain large colloidal particles. A cellulose shell was used as such membrane, into which the tested solution was poured. The shell was placed into a vessel with distilled water. The dialysis process was controlled by measuring the electrical conductivity of the purified solution and water in the vessel. When their electrical conductivities became equal, the colloidal solution was poured into the new shell, which was placed in the next portion of distilled water.

Thus, we studied the change of the coefficient of thermoelectric EMF of the colloidal solution of silver iodide during its dialysis purification. The colloidal solution was obtained as a result of the double exchange reaction $AgNO_3 + KI = AgI + KNO_3$. Therefore, it was a mixture of colloidal particles — silver iodide, and ionic component — potassium nitrate. The reaction was carried out with an excess of potassium iodide, as a result of which the particles of silver iodide were negatively charged due to adsorption of I^- ions from the solution, so a small amount of unreacted potassium iodide also present in the solution.

Fig, 4 shows coefficient of thermoelectric EMF of AgI colloidal solutions vs. their electrical conductivity coefficient. Type of this dependence was chosen due to the fact that the electrical conductivity of the colloidal solution decreases during dialysis purification, and, obviously, is a function of the concentration of the ionic electrolyte, which also decreases during purification.

Fig. 4 also shows the dependence for the pure ionic electrolyte KNO_3, in which upon the concentration decreasing the electrical conductivity coefficient decreases accordingly. As can be seen from the graphs, in the initial colloidal solution, the coefficient of thermoelectric EMF coincides, within the experimental error, with the coefficient of thermoelectric EMF of the potassium nitrate solution of the concentration that presents in the colloidal solution.

In the process of dialysis purification the coefficient of thermoelectric EMF of the colloidal solution increases in absolute value, while its electrical conductivity decreases. A similar regularity in the behavior of the coefficient of thermoelectric EMF is also observed for pure solution of potassium nitrate when its concentration decreases. However, in the colloidal solution a more significant increasing of the modulus of the coefficient of thermoelectric EMF is observed than in the ionic electrolyte. Therefore, the increasing of the coefficient of thermoelectric EMF of the colloidal solution cannot be explained only by the effect of increasing of the coefficient of thermoelectric EMF of the ionic electrolyte with its concentration decreasing. Obviously, in addition to this contribution, the increasing of the thermoelectric force of the colloidal solution can also be due to the increased partial contribution to the thermoelectric EMF from colloidal particles of silver iodide.

Thus, the results obtained confirm the previously stated assumptions about the contribution of free ions and colloidal particles to the final value of the thermoelectric EMF of colloidal solutions, which follow from the analysis of the experimental results for mixtures of colloidal solutions and ionic electrolytes.

As further experiments showed, the increasing of the coefficient of thermoelectric EMF of the colloidal solution as a result of its dialysis purification can be significant, as, for example, it was observed in $La(OH)_3$ colloidal solution obtained as a result of the double exchange reaction $LaCl_3 + NaOH = La(OH)_3 + 3NaCl$. This reaction was carried out with a significant excess of lanthanum chloride. The result was $La(OH)_3$ colloidal solution with concentration of $c = 1.2 \cdot 10^{-4}\,\text{mol/l}$ in the presence of a mixture of $LaCl_3$ salts with concentration of $c = 11.5 \cdot 10^{-4}\,\text{mol/l}$ and NaCl with concentration of $c = 3.5 \cdot 10^{-4}\,\text{mol/l}$. The coefficient of thermoelectric EMF of the initial colloidal solution coincided with the thermoelectric EMF of the pure ionic solution $LaCl_3$, which was present there in the prevailing amount and was equal to $\alpha_0 = -17 \pm 5\,\text{mkv/K}$. The electrical conductivity coefficient was equal to $\sigma = 2.02\,\mu\text{S/cm}$. Next, a multi-stage dialysis purification procedure was carried out, at the end of which the electrical conductivity of the purified solution decreased to $\sigma = 0.07\,\mu\text{S/cm}$, and the coefficient of thermoelectric EMF increased to $\alpha_0 = -182\,\mu\text{V/K}$, while the coefficient of thermoelectric EMF of the pure aqueous solution of lanthanum chloride, which has the same electrical conductivity as the colloidal solution, was $\alpha_0 = -55\,\mu\text{V/K}$.

4. Conclusion

Thus, based on the above stated, the following conclusions can be made.

1. The homogeneous part of the thermoelectric potentials difference in solutions of ionic electrolytes is determined by the charged particles of the solution, which have the highest absolute value of the factor $\alpha_{0k}\frac{\tau_k Q_k^*}{T}$, which depends on the transfer heat Q_k^*, the contribution to the electrical conductivity of the whole solution τ_k (transport number), and can be called as the partial thermoelectric EMF of the corresponding particles.

2. In colloidal solutions, where large colloidal particles that carry a charge due to the ions adsorbed by them, are found together with free ions, the coefficient of thermoelectric EMF of solutions with significant electrical conductivity is determined by the ionic subsystem in view of the excess of the partial thermoelectric EMF α_{0k} for ions compared to colloidal particles. This is due to the prevailing contribution of small, mobile ions to the electrical conductivity of the colloidal solution in comparison with colloidal particles [13] and their high transport numbers.

3. As the relative contribution of ions to the electrical conductivity of colloidal solutions decreases in comparison with colloidal particles (for example, due to dialysis purification), the partial thermoelectric EMF of colloidal particles begin to exceed similar values for ions. Herein, the coefficient of thermoelectric EMF of colloidal solutions begins to be determined by colloidal particles, but not by free ions.

Funding

The study was financially supported by the Russian Foundation for Basic Research and the Administration of the Lipetsk Region under the scientific project 19-42-480001 and the state task of the Ministry of Education of Russia (project FSZN-2020-0026).

Conflict of interest

The authors declare that they have no conflict of interest.

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