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TRANSVERSE HALL EFFECT IN DILUTED BINARY SOLUTIONS OF ELECTROLYTES

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Analytical dependences of Hall's constant, Hall's angle and Hall's transverse potential difference on magnetic induction for diluted binary solutions of electrolytes are obtained. The nonlinear character of these dependences known from experimental data is confirmed.

The extreme values of magnetic induction at which Hall's transverse potential difference and Hall's angle obtain their maximum values, are estimated and juxtaposed with experimental data for various ions. The extreme values of magnetic induction are optimal ones, since at these values Hall's effect in the given solution is manifested stronger.

***Keywords*:** Hall's constant, Hall's angle, Hall's transverse potential difference (Hall's EMF).

Introduction Investigation of longitudinal and transverse effects in electrolyte solutions at simultaneous superposition of electric and magnetic fields accompanied with mass, charge and heat transfer is a fundamental problem of contemporary physical chemistry. Hall's effect is the most important one among other transverse effects, since it can be used in development of new methods for extraction of useful components from diluted solutions in hydrometallurgy of non-ferrous metals, in design of various chemotronic devices controlled by magnetic field, and development of new methods for waste water treatment [1, 2]. The essence of this effect is as follows: if an electric current of $\vec{j}$ density flows along the sample (a metal or semiconductor plate) in the absence of magnetic field, then in the points A and K, located on the equipotential surface, the difference of potentials is equal to zero (Fig. 1).

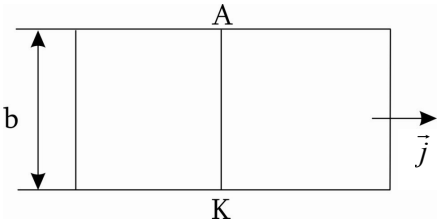

Fig. 1. $(\varphi_A - \varphi_K = 0)$.

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Upon superposition of an external magnetic field $\vec{B}$ perpendicular to $\vec{j}$, a certain potential difference emerges between the points A and K (Fig. 2).

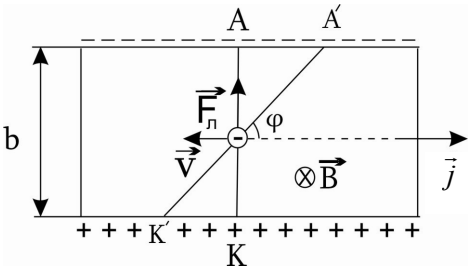

Fig. 2. $(\varphi_A - \varphi_K \neq 0)$.

This effect was discovered by an American physicist E. Hall in 1879 and is called Hall's or galvanomagnetic effect. From the viewpoint of classical concepts, the origin of potential difference in points A and K may be explained as follows. The electric charge e, moving in mutually perpendicular electric and magnetic fields, is affected by a force

$$\vec{F} = e\vec{E} + \frac{e}{c}[\vec{v} \cdot \vec{B}]. \tag{1}$$

Two components of this force $\vec{F}$, namely the electric force $\vec{F}_{el} = e\vec{E}$ and the magnetic force (Lorentz force) $\frac{e}{c}[\vec{v} \cdot \vec{B}]$ act in different ways, here e is the elementary charge . The electric force transfers the charge and does work, while the Lorentz force bends the trajectory of the moving particle and does no work, since it always is perpendicular to the velocity vector. However, under the action of this force the equipotential lines are being shifted on a certain angle φ, and the point of equal potential shifts towards the points A' and K'. As a result, a transverse potential difference appears between the points A and K (Fig. 2). This transverse difference of potentials is frequently called Hall's electromotive force (Hall EMF), and the angle φ is called Hall's angle. Most commonly, the electron theory is used to obtain the value of the transverse difference of potentials [3]. Upon imposing the magnetic field, each charge carrier (electron) becomes subject to the action of a magnetic force directed along the side *b* of the plate and equals by absolute value to

$$\vec{F_L} = ev_{\perp}\vec{B}, \tag{2}$$

where e is the elementary charge, $v_{\perp}$ is the rate of ordered motion of charge carriers in a direction perpendicular to the magnetic induction $\vec{B}$. As a result, at a given direction of $\vec{j}$, the electrons obtain a velocity component directed towards the upper face of the plate. At this face, excess of negative charges is being formed, and excess of positive charges arises at the inferior face (Fig. 2). Hence, a transverse electric field $\vec{E}_H$ arises between the edges of the plate. When the

intensity of this field reaches a value when its action on electrons balances the Lorentz force, a steady distribution of charges is being reached in the transverse direction. The relevant value of $\vec{E}_H$ is given by the condition

$$eE_H = \frac{e}{c} v_\perp B, \tag{3}$$

hence,

$$E_H = \frac{v_\perp}{c} B. \tag{4}$$

Multiplying of the intensity E_H by the plate width b, we obtain the voltage between the points A and K, i.e. Hall's transverse difference of potentials:

$$U_H = bE_H = b v_\perp B. \tag{5}$$

From the expression $j = env_\perp$ it follows that $v_\perp = \frac{j}{ne}$, where n is the concentration of current carriers (number of current carriers in 1 cm^3). Substituting the value of $v_\perp$ in (5), we obtain

$$U_H = \frac{1}{nec} jbB = RbjB. \tag{6}$$

Here $R = \frac{1}{nec}$ is called Hall's constant, which depends on the substance.

Taking into account that the current strength in the plate is equal to $I = jbd$, we obtain:

$$U_H = R\frac{IB}{d}, \tag{7}$$

where d is the thickness of the plate. So Hall's transverse potential difference is proportional to magnetic induction B, current strength I.

Galvanomagnetic effects in metals and semiconductors, and Hall's effect in particular, are well investigated both theoretically and practically. However, similar effects in electrolyte solutions are investigated to an incomparably lesser degree. The attempts to detect Hall's effect in electrolyte solutions have been initiated long time ago. The first research stage started immediately upon discovery of Hall's effect in metals and continued almost up to 1939. Within the period 1939–1962, Hall's effect in solutions of electrolytes actually has not been investigated. The most fruitful period in Hall's effect investigations started in 1962 with the work of A.M. Evseev [4]. He observed Hall's effect in 0.2 normal water solution of copper sulphate $CuSO_4$. Hall's EMF was about 20÷30 *mV* at current strength 0.03–0.04 *A* and magnetic field strength ~1000 *Oersted*, with a distance of 1 *cm* between the measuring electrodes. According to A.M. Evseev's experimental data, Hall's EMF depends nonlinearly on the magnetic induction. In the range of small fields, Hall's EMF does not increase with the increase of magnetic induction, i.e. the curve "Hall's EMF vs. magnetic induction" is characterized with saturation. Later on, the nonlinearity of "Hall's EMF vs. magnetic induction" curves also was experimen-

tally proved in [5]. Theoretical publications appeared as well. In [6], a system of equations describing the motion of ions' of a fluid placed in the electromagnetic field is given. The solution of the system of equations is found for a finite volume of electrolyte in crossed stationary fields (Hall's effect in a finite volume cell).

Results and Discussion. The goal of the present work was to obtain the analytical dependence of Hall's EMF and Hall's angle on the value of magnetic induction for diluted binary solutions of electrolytes, thus creating an opportunity to explain the experimental data.

In solutions of electrolytes the current is transferred by cations and anions. Under the impact of magnetic field electrolyte becomes anisotropic. The electromagnetic properties of an anisotropic binary electrolyte are completely characterized by the dielectric constant tensor and the electric conductivity tensor [7, 8]. According to these works, the current density in a diluted binary solution of electrolyte is as follows:

$$\vec{j}_{\text{cond}} = \sigma_E \vec{E} + \sigma_H \left[\vec{B} \cdot \vec{E} \right], \tag{8}$$

where $\sigma_E = \sigma_{xx}$ and $\sigma_H = \sigma_{yy}$ are the components of the specific electric conductivity tensor of electrolyte.

In order to calculate Hall's EMF, one has to solve the aforementioned vector equation. From this equation it follows that the expressions for conductivity current's density along the x axis (E) and the y axis (Hall direction) are respectively

$$j_E = \sigma_E E_x + \sigma_H E_y, \tag{9}$$

$$j_H = \sigma_E E_y + \sigma_H E_x, \tag{10}$$

Now let us suppose that the conductivity current in Hall's direction is completely compensated, i.e. $j_H = 0$.

From (10) we obtain:

$$E_x = -\frac{\sigma_E}{\sigma_H} E_y. \tag{11}$$

Substituting this result into (9), we get:

$$j_E = j_x = -\frac{\left(\sigma_E^2 + \sigma_H^2\right)}{\sigma_H} E_y. \tag{12}$$

According to formula (6), Hall's constant is equal to

$$R_H = \frac{U_H}{j_x \cdot B \cdot b} = \frac{E_y}{j_x \cdot B} = -\frac{\sigma_H}{B\left(\sigma_E^2 + \sigma_H^2\right)} \tag{13}$$

and the tangent of Hall's angle is

$$\operatorname{tg}\theta = \frac{E_y}{E_x} = -\frac{\sigma_H}{\sigma_E}. \tag{14}$$

Multiplying the transverse component of electric intensity E_y by cell width b, we obtain Hall's EMF:

$$U_H = E_y \cdot b = E_x \cdot b \cdot \mathrm{tg}\theta. \tag{15}$$

We suppose that the cation and the anion have the same electrochemical valence Z and concentration n. Then, according to [7], in stationary fields $\left(E_x = E = \mathrm{const},\ B_z = B = \mathrm{const}\right)$, σ_E and σ_H will have the following form:

$$\sigma_E = n|Ze|^2\left[\frac{\beta_+}{m_+\left(\beta_+^2+\omega_+^2\right)}+\frac{\beta_-}{m_-\left(\beta_-^2+\omega_-^2\right)}\right], \tag{16}$$

$$\sigma_H = n|Ze|^2\left[\frac{\omega_-}{m_-\left(\beta_-^2+\omega_-^2\right)}-\frac{\omega_+}{m_+\left(\beta_+^2+\omega_+^2\right)}\right], \tag{17}$$

where $\beta_+ = \dfrac{6\pi\eta r_+}{m_+}$, $\beta_- = \dfrac{6\pi\eta r_-}{m_-}$, $\omega_+ = \dfrac{|Ze|\cdot B}{m_+\cdot c}$, $\omega_+ = \gamma\dfrac{|Ze|\cdot B}{m_-\cdot c}$, η is the solution's viscosity, r_+, r_-, m_+, m_- are electrochemical radii and masses of ions respectively, γ is a dimensionless correlation factor, which takes into account (as first approximation) the multiparticle processes in the solution [9]. Having the expressions σ_E and σ_H from (13–15), one can see that theoretical results on dependences of Hall's constant, Hall's angle's tangent and Hall's EMF on the induction of external magnetic field are of nonlinear character, similar to experimental results. In particular, by substituting the values of σ_E and σ_H into (15) and performing some elementary transformations, for Hall's EMF we obtain:

$$U_H = \frac{E\cdot b\left(\dfrac{1}{r_+}-\dfrac{1}{r_-}\right)\gamma\ \dfrac{|Ze|B}{6\pi\eta c}}{1+\dfrac{1}{r_+r_-}\left(\dfrac{|Ze|B}{6\pi\eta c}\right)^2}. \tag{18}$$

From (18) one can see that Hall's EMF depends nonlinearly both on magnetic induction B and medium viscosity η. Let obtain the extremal value of magnetic induction, at which Hall's EMF reaches its maximum, for the case of a fixed viscosity. For practical applications of Hall's effect, the extremal value of magnetic induction is actually its optimal value. We denote it as B_{opt}. From necessary condition of function's maximum $\dfrac{dU_H}{dB}=0$ we obtain the optimal value of magnetic induction equals to

$$B_{\mathrm{opt}} = \frac{6\pi\eta c\sqrt{r_+r_-}}{\gamma|Ze|}. \tag{19}$$

Provided that electromagnetic radii differ slightly ($r = r_+ \approx r_-$), one can write

$$B_{\text{opt}} = \frac{6\pi\eta rc}{\gamma |Ze|}. \tag{20}$$

From (20) it follows that each binary electrolytic solution has a corresponding value of B_{opt} depending on medium viscosity and radius of ions. For such fields, Hall's effect in the given solution is manifested stronger.

In the Table below the calculated optimal values of magnetic induction for various ions are presented.

Optimal values of magnetic induction for various ions

Ion	$r \cdot 10^{-8}\, cm$	Optimal values of magnetic induction at viscosities $\eta \cdot 10^{-2}$ poise, *Gauss*					
		1.79	1.31	1.0	0.8	0.65	0.55
H^+	0.253	533	390	298	238	194	164
K^+	1.21	2550	1866	1425	1140	926	784
Cu^{2+}	1.7	1792	1311	1001	801	650	551
Li^+	2.36	4974	3640	2774	2223	1805	1529
NH_4^+	1.99	4194	3070	2343	1875	1522	1290
OH^-	0.443	933	683	521	417	339	287
H_3O^-	1.35	2845	2314	1590	1272	1033	875
Cl^-	1.2	2529	1851	1411	1130	918	778
F^-	1.68	3541	2591	1978	1583	1285	1089
SO_4^{2-}	2.3	2424	1774	1354	1084	880	745

From this Table it can be seen that the order of magnitude for optimal values of magnetic induction is within the range of 100÷5000 *Gauss*. Our estimates permit to explain some contradictive experimental results described in [10]. Thus, the researchers who worked with magnetic fields significantly exceeding the upper limit, should not observe any transverse effect, while those working within the range of magnetic fields between the upper and lower limits, could observe such an effect. Now it is obvious that very strong magnetic fields are of low efficiency, hence fields within certain values of magnetic induction should be applied for each object.

The obtained formulae (18) and (19) permit us to juxtapose the theoretical results with the known experimental data. In [5], Hall's effect was experimentally investigated in water solution of potassium fero–ferricyanide in the concentration range 0.04÷0.024 *M*, and the nonlinearity of EMF and Hall's angle have been confirmed at magnetic induction values within the range 100÷4000 *Gauss*. It can be seen that these values have the same order of magnitude as the theoretically obtained data presented in the Table.

As to the values of $\mathrm{tg}\,\theta$, U_H the experimental measurements showed that at the intensity of longitudinal electric field $2\cdot10^2 \div 10^3$ *V/m* and cell width $b = 10^{-3}$ *m*, within the magnetic induction range up to 4000 *Gauss*, Hall's EMF is of 10^{-3} *V* order of magnitude, while $\mathrm{tg}\,\theta = 10^{-3}$.

Let us calculate the order of magnitude for these quantitites by means of (18) for a diluted binary solution of KCl. The parameters of such a solution are well known: $r_+ = 1.21\cdot10^{-8}$ *cm*; $r_- = 1.2\cdot10^{-8}$ *cm*; $\eta = 1.79\cdot10^{-2}$ *poise*; $\gamma = 10^8$; $z = 1$; $B_{\mathrm{opt}} = 2530$ *Gauss*. Substituting these values into (18), we obtain

$$U_H \cong 10^{-3}\ V,\ \ \mathrm{tg}\,\theta \cong 10^{-3}.$$

The juxtaposition of theoretical and experimental data permits one to conclude that the selected theoretical approach and assumptions made in [7] and [8] are correct, and the obtained theoretical results can be used for simple models of electrolytes' solutions.

Conclusion. It is shown that for solutions placed in an electromagnetic field Hall's constant, Hall's angle and Hall's EMF generally have a nonlinear dependence on magnetic induction and possess extreme properties. The order of value for optimal magnetic induction when the transverse Hall's effect is being observed in diluted binary electrolyte solutions is 100–500 *Gauss* (see the Table). Now it is clear that very strong magnetic fields are of less effective, hence certain ranges of magnetic induction values should be applied for every single sample. The obtained results are extremely important for the optimal magnetohydrodynamic (MHD) deminarelization of fluids – a method that recently got a wide recognition due to its universalism, high efficiency and the possibility to be used in corrosive medium, relatively small size of the MHD apparatuses, and comparative cheapness. Finally, let us note that the investigations of transversal and longitudinal effects in electrolyte solutions at a supersposition of an electromagnetic field are structurally sensitive. Basing on experimental and theoretical investigations of these effects, one can derive the quantitative relationships between the measured quantities and the parameters of the dispersion law, which is important, e.g. for the theory of fluid state. These investigations also have deep routs ranging to biology and medicine.

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