

EXPRESSIONS FOR ACTIVITY COEFFICIENTS AND OSMOTIC COEFFICIENTS OF ELECTROLYTE SOLUTIONS BASED ON HYDRATION CLUSTER MODEL. AQUEOUS SOLUTIONS OF HClO_4 , HReO_4 AND HTcO_4 AT 298.15 K

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Abstract

Authors develop a cluster model for electrolyte solutions. In contrast to the Zavitsas model, it is assumed that the composition of clusters formed depends on the composition of the solutions. Clusters are characterized by variable hydration numbers and hydrate distribution parameters by stoichiometric numbers. The report discusses the features of the cluster model, as well as the results of its description by the equations of osmotic coefficients and activity coefficients of HClO_4 , HReO_4 and HTcO_4 solutions at 298.15 K.

Key words: aqueous perchloric, perrhenic and pertechnetic acids, activity coefficient, osmotic coefficient, hydration numbers, cluster model

1. INTRODUCTION

Non-ideal aqueous electrolyte solutions can be due to different factors: Coulomb interactions, ionic association and solvation. Some model solutions, the equations of which describe the dependence of solutions thermodynamic properties (osmotic coefficient, ϕ , water activity, a_w , ion activity coefficient, $\gamma_{\pm}$) are known, taking into account the solvation electrolytes. Robinson-Stokes model [1] takes into account the contribution of electrostatic interactions by Debye-Huckel equation, while the total number of hydration h characterizes electrolyte solvation. It is assumed, that the value of h does not depend on electrolyte concentration. The Robinson-Stokes equation describes the experimental data for ϕ and $\gamma_{\pm}$ in a limited range of concentrations.

Recently the hydration model of Zavitsas [2] attracts considerable interest of researchers. It suggests that the activity of water is defined by the mole fraction of free water, which is calculated taking into account electrolyte hydration numbers with its full electrolytic dissociation. For solutions with negative deviations from Raoult's law nonideality is mainly due to electrolytes hydration. It is typical for concentrated solutions of many electrolytes. That is why the Zavitsas model agrees satisfactorily with the experimental data of water vapor pressure over concentrated solutions [3]. However, the values of $\gamma_{\pm}$ calculated considering the contribution of hydration in non-ideal solutions according to Zavitsas, in all cases, exceed unity [4], that does not agree with the experimental data.

A model, taking into account the dependences of numbers of hydration from solutions composition is more productive. It describes the thermodynamic properties of aqueous solutions of nonelectrolytes such as sucrose and glycerol [5], as well as alkali metal nitrite in changing their concentration from dilute to saturated solutions [6].

In general case, in addition to hydration it is necessary to consider the contribution of other factors to nonideality. The aim of this work is the reasoning of the equations accounting the contribution of hydration and ion association in osmotic coefficients and activity coefficients of electrolyte solutions based on the cluster model. The resulting equations were used to describe literary experimental data of various authors for aqueous solutions of perchloric [7], perrhenic [8] and pertechnetic [9] acids, which with the exception of the dilute solutions exhibit significant negative deviations from Raoult's law.

2. THEORETICAL PART

In this study, it is assumed that the excess thermodynamic properties of aqueous solutions of electrolytes are determined by the independent action of electrostatic interactions, hydration and ion association

2.1 Hydration of ions.

Let the aqueous solution contain a dissolved electrolyte in an amount of n moles. When the particles of a dissolved substance interact with water, a hydrate spectrum is formed with stoichiometric hydration numbers equal to i and equilibrium constants

$$k_i = \frac{a_i}{a_0 a_w^i} \quad (1)$$

where a_i , a_0 , a_w are the activity of stoichiometric hydrate with a hydration number equal to i , solute monomer activity and water activity respectively. According to ideal associated solutions model [10] instead of components activity it is possible to use equilibrium molar fractions y_i , y_0 , y_w hydrate with a stoichiometric hydration number equal to i , molar fraction of solute monomer and water respectively. In this approximation (1) is transformed to

$$k_i = \frac{y_i}{y_0 y_w^i} \quad (2)$$

From Eq. 2 it follows that

$$y_i = y_0 k_i y_w^i \quad (3)$$

After multiplying (3) by i and summing over i , we obtain:

$$\sum_i y_i = y_0 \sum_i k_i y_w^i \quad (4)$$

As $\sum_i y_i = y$, where y is equilibrium molar fraction of solute, associated with equilibrium molar fraction of water by the equation $y = 1 - y_w$, it's clear that

$$1 - y_w = y_0 \sum_i k_i y_w^i \quad (5)$$

Multiplying (3) by i and summing over i , we have

$$\sum_i (i y_i) = y_0 \sum_i (i k_i y_w^i) \quad (6)$$

Dividing (6) by (4) we find that

$$\frac{\sum_i (i y_i)}{\sum_i y_i} = \frac{\sum_i (i k_i y_w^i)}{\sum_i (k_i y_w^i)} \quad (7)$$

The hydrates formation with different stoichiometric hydration numbers i implies the existence of hydrates discrete distribution in solution. The ratio in right-hand side of (7) is the definition of average hydration number h for this distribution. By this means,

$$h = \frac{\sum_i (ik_i y_w^i)}{\sum_i (k_i y_w^i)} \quad (8)$$

This equation can be simplified if instead of equilibrium mole fraction of water y_w to use according to solution preparation procedure the equilibrium molar fraction of water x_w . For limited soluble substances solutions this is true at low concentrations of solute. In this case (8) takes the form:

$$h = \frac{\sum_i (ik_i x_w^i)}{\sum_i (k_i x_w^i)} \quad (9)$$

The main characteristic of hydration is the limit of value $\lim_{x_w \rightarrow 1} h = h^\circ$ in infinite diluted solution as a standard state. It is obvious from (9) that:

$$h^\circ = \frac{\sum_i (ik_i)}{\sum_i k_i}, \quad (10)$$

where h° is an average hydration number in standard state. Consider the derivative $d \ln h / d \ln x_w$. From (10) it follows that:

$$\frac{d \ln h}{d \ln x_w} = \frac{D}{h}, \quad (11)$$

where D is a dispersion of hydrate distribution by stoichiometric hydration numbers. Assume that ratio D/h does not depend on concentration. Then, letting $D/h = D^\circ / h^\circ = r^\circ$ where $D^\circ = D(x_w = 1)$ is a dispersion of hydrate distribution in infinitely dilute solution, from (11) upon integration we have:

$$h = h^\circ x_w^{r^\circ} \quad (12)$$

This equation determines the relationship between the average hydration number with solution concentration and parameters h° and r° , that characterize distribution of hydrates by stoichiometric hydration numbers in a standard state. Obviously, on the one hand r° characterizes the width of the given distribution, and on the other the rate of h quantity decreasing with the increasing of solute concentration.

If aqueous solution contains an electrolyte $M_{v_c} X_{v_a}$ in amount of n moles, then while the infinite dilution there is $(v_c + v_a)n = \nu n$ mole of ions in the solution, where ν is the number of ions to which the electrolyte dissociates. When ions interact with water molecules, a series of stoichiometric hydrates of ions occurs:



Let us consider the hydration effect on thermodynamic properties of solution in terms of cations hydration example. The concentration dependence of average hydration number for cations, h_c is expressed by an equation analogous to equation (12):

$$h_c = h_c^{\circ} x_w^{r_c^{\circ}}, \quad (14)$$

where $r_c^{\circ} = D_c^{\circ} / h_c^{\circ}$, $h_c^{\circ} = h_c(x_w = 1)$ is expectation value, $D_c^{\circ} = D_c(x_w = 1)$ is a dispersion of hydrate distribution of cations at mole fraction of water $x_w = 1$.

In ideal associated solution approximation [10], water activity will be equal to mole fraction of free water. In the absence of all other interactions on conversion to a kilogram of water for a_w , the following relation encounters:

$$a_w = \frac{n_w^{\circ} - v_c h_c^{\circ} x_w^{r_c^{\circ}} m}{n_w^{\circ} - v_c h_c^{\circ} x_w^{r_c^{\circ}} m + v m}. \quad (15)$$

Here n_w° is an amount of substance in one kilogram of water; m is a molality of electrolyte. Taking into account the determination of water activity coefficient, from (15) we find:

$$\ln f_w = \ln \left(\frac{1 - (v_c / v) h_c^{\circ} x_w^{r_c^{\circ} - 1} x}{1 - (v_c / v) h_c^{\circ} x_w^{r_c^{\circ}} x} \right). \quad (16)$$

Here x is a molar fraction of electrolyte. After simple transformations (16) takes the form:

$$\ln f_w = \ln \left(1 - \frac{(v_c / v) h_c^{\circ} x_w^{r_c^{\circ} - 1} x^2}{1 - (v_c / v) h_c^{\circ} x_w^{r_c^{\circ}} x} \right). \quad (17)$$

In equation (17), the subtrahend under the logarithm is much less than unity. Therefore, this relation can be simplified by expanding the right-hand side in a series in powers of this small parameter. Restricting to the first term of the expansion, we obtain:

$$\ln f_w = - \frac{(v_c / v) h_c^{\circ} x_w^{r_c^{\circ} - 1} x^2}{1 - (v_c / v) h_c^{\circ} x_w^{r_c^{\circ}} x}. \quad (18)$$

Carrying out similar arguments for anions and using the assumption of cations and anions hydration independence, we obtain the following equation for water activity coefficient:

$$\ln f_{w,h} = -x^2 \left(\frac{v_c h_c^{\circ} x_w^{r_c^{\circ} - 1}}{v - v_c h_c^{\circ} x_w^{r_c^{\circ}} x} + \frac{v_a h_a^{\circ} x_w^{r_a^{\circ} - 1}}{v - v_a h_a^{\circ} x_w^{r_a^{\circ}} x} \right). \quad (19)$$

Subscript «h» in $\ln f_{w,h}$ in equation (19) indicates that here in addition to ion hydration, no other interactions are included.

2.2 Ion association.

In increasing of electrolytes concentration in solutions, ion-associates may be formed. Generally, the associate consists of several cations and anions. Let us consider this process as association in a solution containing $N = v n$ single-type particles of solute B according to reaction equation



We determine the number of bound particles or stoichiometric association number by the equation:

$$A_i = i - 1. \quad (21)$$

The presence of ionic associates with different numbers of association i , as in the case of hydration, is equivalent to the assertion of the existence of a distribution of associates to the order of association numbers. For solutions of electrolytes, as for systems with limited solubility of components, the condition $x \ll 1$ is satisfied. It is noted in the literature that the presence of associates with large association numbers in solutions is quite a rare phenomenon. This allows using the concentration dependence of an average number of associations in the form

$$A = A^\circ x. \quad (22)$$

A° is an average association number in hypothetical solution with a molar fraction of electrolyte equal to unity. Considering this dependence, let us write the equation for water activity in the following form:

$$a_w = \frac{n_w^0}{n_w^0 + \nu m / (1 + A^\circ x)}. \quad (23)$$

For the coefficient of water activity we find:

$$\ln f_w = \ln \left(1 + \frac{A^\circ x^2}{1 + A^\circ x \cdot x_w} \right). \quad (24)$$

Since the systems under consideration always satisfy inequalities $A^\circ x^2 \ll 1$ and $A^\circ x_w x \ll 1$, Eq. (24) can be simplified:

$$\ln f_{w,as} = A^\circ x^2. \quad (25)$$

Subscript «as» in $\ln f_{w,as}$ in eq. (25) indicates that here in addition to ionic association no other interactions are included.

2.3 Osmotic coefficient of solution and average ionic coefficient of electrolyte activity.

The assumption of the independence of the actions of electrostatic interactions, the hydration of cations and anions, as well as ionic association, allows us to write down the equations for the average ionic activity coefficient of the electrolyte and the osmotic coefficient in the form of the sum of individual contributions. Consequently, for the osmotic coefficient

$$\varphi = \varphi_D - \frac{n_w^0}{\nu m} (\ln f_{w,h} + \ln f_{w,as} + \ln x_w), \quad (26)$$

where, according to the Debye-Hückel theory, φ_D is defined by the equation

$$\varphi_D = - \frac{A_D |z_1 z_2| \sqrt{I}}{(B_D \sqrt{I})^3} \left(\frac{(1 + B_D \sqrt{I})^2 - 2 \ln(1 + B_D \sqrt{I}) - 1}{1 + B_D \sqrt{I}} \right),$$

and for an average ionic electrolyte activity coefficient

$$\ln \gamma_{\pm} = \ln \gamma_{\pm,D} + \ln f_{\pm,h} + \ln f_{\pm,as} + \ln(x_w), \quad (27)$$

where $\ln \gamma_{\pm,D}$, $\ln f_{\pm,h}$ and $\ln f_{\pm,a}$ are defined by equations

$$\ln \gamma_{\pm,D} = -\frac{A_D |z_1 z_2| \sqrt{I}}{1 + B_D \sqrt{I}}$$

$$\ln f_{\pm,h} = -\int_0^x \left(\frac{1-x}{x} \frac{d(\ln f_{w,h})}{dx} \right) dx$$

$$\ln f_{\pm,a} = -A^\circ x(1 + x_w)$$

Here A_D , B_D are parameters of Debye-Hückel theory, I is the ionic strength of solution, z_1 , z_2 are ion charges.

3. EXPERIMENTAL DATA SIMULATION AND RESULTS DISCUSSION

In literature, the criterion of electrolytes solutions thermodynamic models adequacy to experimental data, as a rule, is the quality of concentration dependences $\gamma_{\pm}$ description. It is known that $\gamma_{\pm}$ are calculated from ϕ data based on a number of assumptions. In turn, the calculation of ϕ quantities is based only on the assumption of electrolyte complete dissociation. It seems that it is more appropriate to obtain descriptions of concentration dependence ϕ firstly, and then use the obtained model parameters estimates to calculate $\gamma_{\pm}$ values and compare them with the literature data.

The parameters of equations obtained in describing the concentration dependences and calculations for aqueous solutions of the acids are shown in Table. 1.

Table 1. Results of concentration dependences of osmotic coefficient and average ionic activity coefficient in aqueous solutions HClO_4 , HReO_4 and HTcO_4 at 298.15 K

Electrolyte	HClO_4	HReO_4	HTcO_4
m, mol/kg	16	8	5.44
B_D	1.69	1.48	0.89
h_1	7.42	9.49	4.71
r_1	1.82	3.15	36.0
h_2	6.49	7.82	8.81
r_2	0.97	1.41	1.42
A_1	3.41	7.76	2.11
$A_{\max}$	1.2	1.7	0.4
$\sigma_\phi * 10^3$	1.5	0.3	0.3
Δ_ϕ , %	0.05	0.02	0.02
$\sigma_{\gamma_{\pm}} * 10^2$	17.4	0.2	0.2
$\Delta_{\gamma_{\pm}}$, %	0.17	0.12	0.15
source	[7]	[8]	[9]

The values of σ_ϕ and Δ_ϕ are within the error of measurement, which indicates a mathematically adequate description of experimental data on osmotic coefficients. It can be seen (Fig. 1-3) that equations of model adequately reproduce the concentration dependences of the average ionic activity coefficients.

4. CONCLUSION

The equations for the contribution of hydration and ionic association to the osmotic coefficients and activity coefficients of electrolyte solutions based on the cluster model are substantiated. It is established that these equations mathematically adequately describe both the dependence the osmotic coefficient and average ionic activity coefficients on the concentration aqueous solutions of HClO_4 , HReO_4 and HTcO_4 at 298.15 K.

It is shown that the equations of the cluster model adequately describe mathematically the data for osmotic coefficients and activity coefficients of the acids under consideration in a wide range of changes in their concentration. Therefore, the proposed version of the cluster model is more universal than the Zavitsas model.

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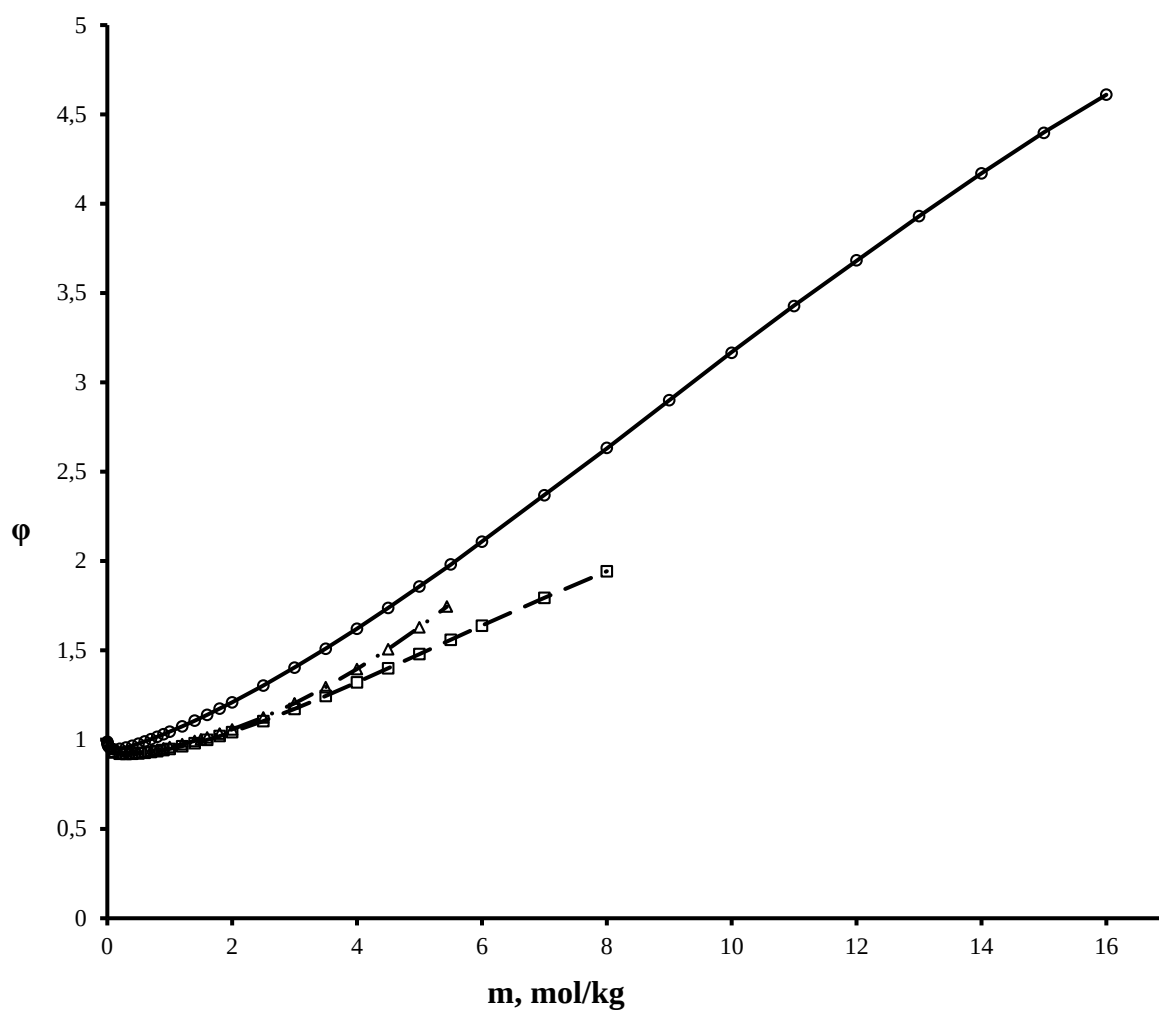


Fig. 1. Concentration dependence description of the osmotic coefficient in aqueous solutions HClO_4 ($\circ$ – experimental data, solid line - calculated values), HReO_4 ($\square$ – experimental data, dash line - calculated values) and HTcO_4 (Δ - experimental data, dot-and-dash line - calculated values) at 298.15 K.

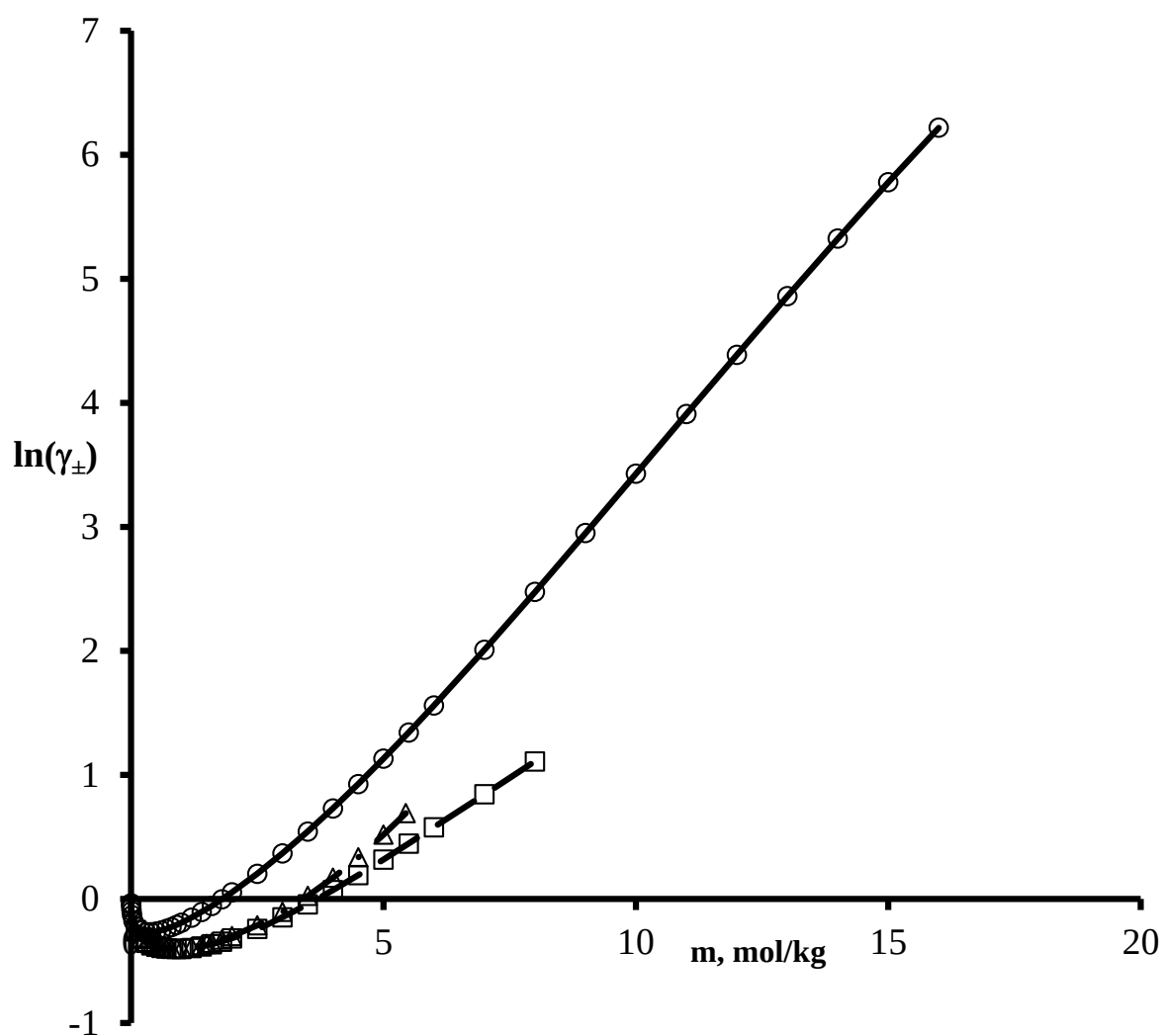


Fig. 2. Concentration dependence description of average ionic activity coefficient logarithm HClO₄ (○ – experimental data, solid line – calculated values), HReO₄ (□ – experimental data, dash line – calculated values) and HTcO₄ (Δ – experimental data, dot-and-dash line – calculated values) in aqueous solutions at 298.15 K

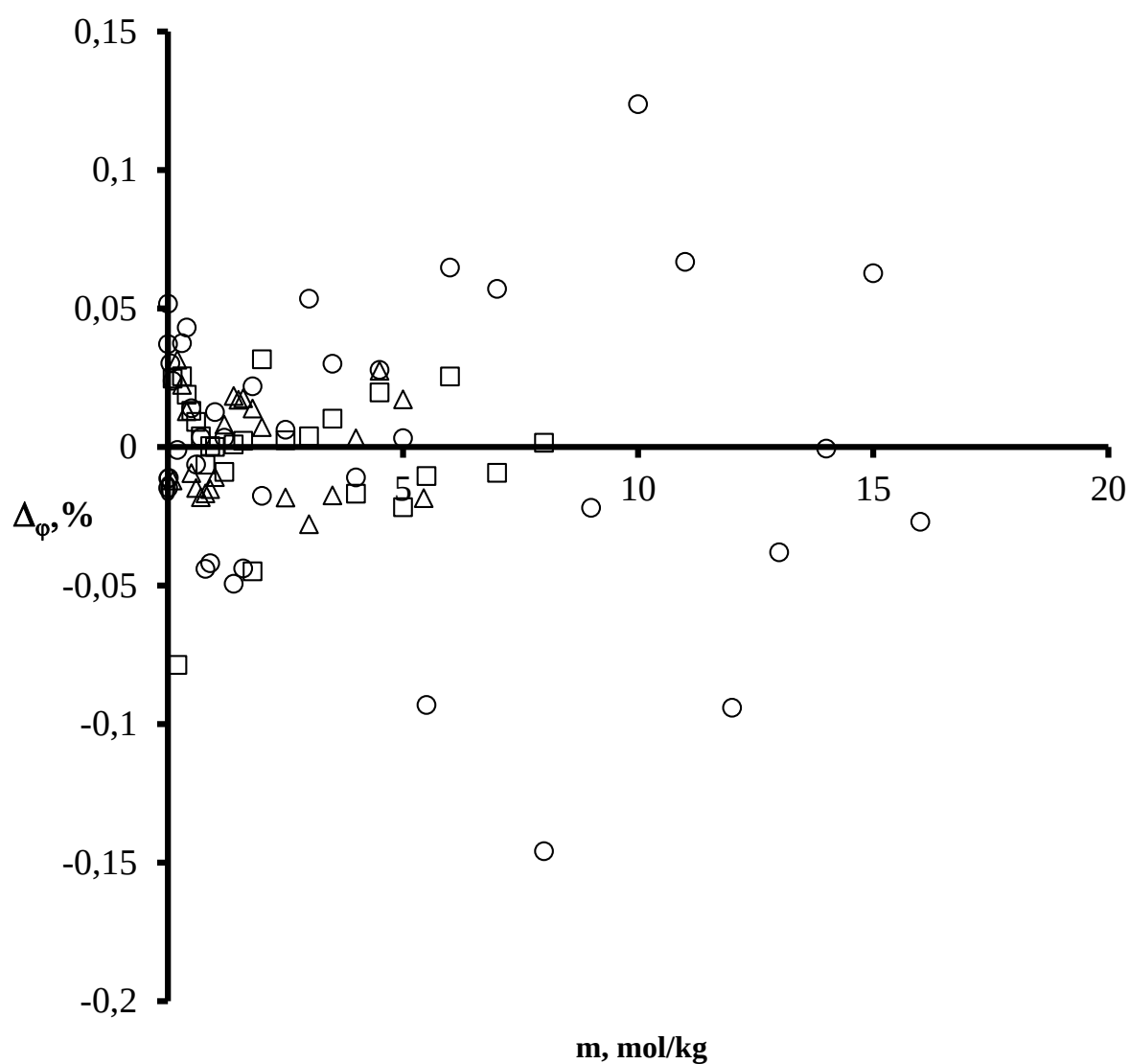


Fig. 3. Relative errors in description of concentration dependence of osmotic coefficient in HClO_4 ($\circ$), HReO_4 ($\square$) and HTcO_4 (Δ) aqueous solutions at 298.15 K

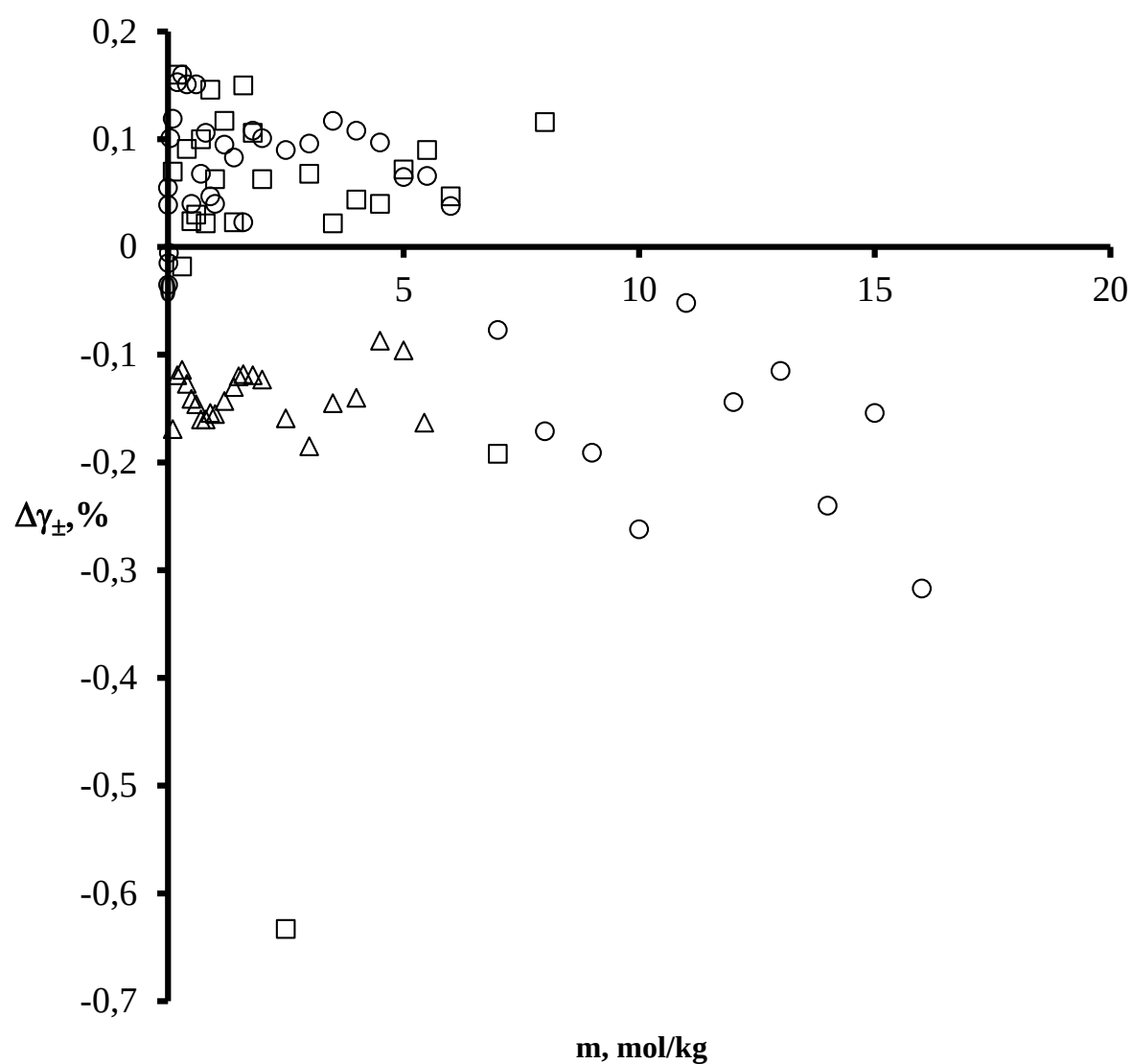


Fig. 4. Relative error of description of concentration dependence of average ionic activity coefficient HClO_4 ($\circ$), HReO_4 ($\square$) and HTcO_4 (Δ) in aqueous solutions at 298.15 K.