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REFRACTOMETRIC DETERMINATION OF THE HYDRATION NUMBER OF IONS IN DILUTED AQUEOUS SOLUTIONS OF MAGNESIUM SULFATE

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The refractive properties of the diluted water solutions of magnesium sulfate have been investigated. The equation Lorenz - Lorentz has been used for explanation of experimental results, which take into account contributions to the total polarization as free water molecules and hydrated ions. The hydration numbers of ions have been determined, as by the refractometric method and by "ion-dipole" model.

Key words: hydration number, polarization, refractive index, solution

The polarization of the medium at optical frequencies, mainly due to moving of the electron oscillating under electric field of the light wave [1,2]. In this case, for a homogeneous medium the Lorentz-Lorenz's law [3] is carried out:

$$\frac{n^2-1}{n^2+2}=\frac{N\alpha}{3} \tag{1}$$

where, n is refractive index, N - number of molecules per unit volume, α - the polarizability of substance's molecules.

For the diluted water solutions of magnesium sulfate $MgSO_4$, assuming additivity of polarizability the formula (1) it is possible to write as follows:

$$\frac{n^2-1}{n^2+2}\approx\frac{N_{H_2O}\alpha_{H_2O}}{3}+\frac{N_{Mg^{2+}}\alpha^*_{Mg^{2+}}}{3}+\frac{N_{SO_4^{2-}}\alpha^*_{SO_4^{2-}}}{3}+\frac{N_{MgSO_4}\alpha_{MgSO_4}}{3} \tag{2}$$

where, n - refractive index of the solution, α_{H_2O} - polarizability of the "free" water molecules, $\alpha^*_{Mg^{2+}}$ and $\alpha^*_{SO_4^{2-}}$ polarizability of hydrated ions Mg^{2+} and SO_4^{2-}, consequently, α_{MgSO_4} - polarizability of the molecule of magnesium sulfate, $N_{Mg^{2+}}$, $N_{SO_4^{2-}}$ and N_{MgSO_4} - the number of ions Mg^{2+}, SO_4^{2-} and molecules of magnesium sulfate in unit volume of solution, respectively, N_{H_2O} - the number of free water molecules per unit volume of diluted water solutions, that in first approximation equals to the number of water molecules $N^0_{H_2O}$ per unit volume of pure solvent $N_{H_2O} \approx N^0_{H_2O}$.

On the right side of the equation (2) the first term describes the contribution to the medium polarization of free water molecules, not involved in hydration, and other members represent the contributions to the polarization of ions Mg^{2+}, SO_4^{2-} and molecules of magnesium sulfate in water solution.

Denoting the degree of dissociation of magnesium sulfate in aqueous solution through β, the number of ions and molecules $MgSO_4$ in unit volume can be expressed through the concentration c of magnesium sulfate in the solution:

$$N_{Mg^{+2}} \approx N_{SO_4^{-2}} = \frac{\beta c \rho N_A}{M_{MgSO_4}} \quad \text{və} \quad N_{MgSO_4} = (1-\beta)\frac{c\rho N_A}{M_{MgSO_4}} \tag{3}$$

where - ρ solution density, N_A - the Avogadro constant, M_{MgSO_4} - the molar mass of magnesium sulfate. For pure water the equation (1) is as follows:

$$\frac{{n_{H_2O}}^2 - 1}{{n_{H_2O}}^2 + 2} = \frac{N^0_{H_2O}\alpha_{H_2O}}{3} \tag{4}$$

Taking into account formulas (3) and (4), in (2) we obtain:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n^2_{H_2O} - 1}{n^2_{H_2O} + 2} + \frac{c\rho N_A}{3M_{MgSO_4}}[\beta\alpha^*_{Mg^{2+}} + \beta\alpha^*_{SO_4^{2-}} + (1-\beta)\alpha_{MgSO_4}] \tag{5}$$

In the case of complete dissociation of magnesium sulfate in water, which is performed for very dilute solutions we can be put $\beta \approx 1$, and the formula (5) gets the following form:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n^2_{H_2O} - 1}{n^2_{H_2O} + 2} + \frac{c\rho N_A \alpha_{H_2O}}{3M_{MgSO_4}}\left(\frac{\alpha^*_{Mg^{2+}}}{\alpha_{H_2O}} + \frac{\alpha^*_{SO_4^{2-}}}{\alpha_{H_2O}}\right) \tag{6}$$

In a first approximation, assuming that the polarizability of hydrated ion is proportional to the cube of the radius of this ion, which can be determined from volume of hydrated ion we obtain:

$$V_h \approx V_i + hV_{H_2O},\ \alpha^*_{Mg^{2+}} \sim r^3_{hMg^{2+}} \approx r^3_{Mg^{2+}} + h_1 r^3_{H_2O},$$

$$\alpha^*_{SO_4^{2-}} \sim r^3_{hSO_4^{2-}} \approx r^3_{SO_4^{2-}} + h_2 r^3_{H_2O},\ \alpha_{H_2O} \sim r^3_{H_2O} \tag{7}$$

where, V_h, V_i, V_{H_2O} are the volumes of hydrated ion, nonhydrated ion and water molecule, respectively, h_1 and h_2 - are the numbers of hydration of ions Mg^{2+} and SO_4^{2-}, $r_{Mg^{2+}}$, $r_{SO_4^{2-}}$, r_{H_2O} - the radii of ions Mg^{2+}, SO_4^{2-} and water molecule. Taking into account formula (7) in (6) we obtain:

$$\frac{n^2-1}{n^2+2}=\frac{n_{H_2O}^2-1}{n_{H_2O}^2+2}+\frac{c\rho N_A\alpha_{H_2O}}{3M_{MgSO_4}}((\frac{r^*_{Mg^{2+}}}{r_{H_2O}})^3+(\frac{r^*_{SO_4^{2-}}}{r_{H_2O}})^3+h_1+h_2) \qquad (8)$$

Plotting the ratio $(n^2-1)/(n^2+2)$ - c from (8), by angular coefficient $tg\phi$ of this dependence, we can determined the sum of hydration numbers of ions Mg^{2+}, SO_4^{2-}:

$$h_1+h_2=\frac{3M_{MgSO_4}tg\phi}{\rho N_A\alpha_{H_2O}}-(\frac{r_{Mg^{2+}}}{r_{H_2O}})^3-(\frac{r_{SO_4^{2-}}}{r_{H_2O}})^3 \qquad (9)$$

We measured the concentration dependence of the refractive index of dilute aqueous solutions of magnesium sulfate. The obtained data in the coordinates $(n^2-1)/(n^2+2)$ - c are represented in Fig. 1. As can be seen from the figure up to a certain concentration of magnesium sulfate ($\approx 1.5\%$), this dependence is linear, while above this concentration, the slope of the curve decreases. This can be explained by the fact that at low concentrations magnesium sulfate dissociated completely into ions and these ions did not interact with each other to the concentration $\approx 1.5\%$. Therefore, the thickness of hydration shells and the polarizability of hydrated ions up to this concentration remain constant and thus as it follows from (8) in this region the slope $tg\phi$ does not depend on concentration. And at the indicated concentrations due to the strong diluted solution the density variation can be neglected. With further increase of the concentration the radii of the hydration ions $r_{hMg^{2+}}, r_{hSO_4^{2-}}$ and, respectively, the polarizability of hydrated ions $\alpha^*_{Mg^{2+}}$ and $\alpha^*_{SO_4^{2-}}$ (the formula (7)), as well as the density ρ of the the solution become dependent on c.

When it begins the interaction of ions with each other, the hydration shells of the ions begin to break down, the numbers of hydration of ions Mg^{2+} and SO_4^{2-}, the polarizability of hydrated ions ($\alpha^*_{Mg^{2+}}, \alpha^*_{SO_4^{2-}}$) decreases, which is appeared in the decrease of the slope in the formula (8) (Fig. 1).

The appearing of the interaction, starting with a certain concentration and changes in the structure of an aqueous solution have been confirmed by our researches examined aqueous solutions of magnesium sulfate by the low-frequency dielectric spectroscopy method [4,5].

Substituting of the values of the parameters taken from the literature [6-9] in formula (9), by the angular coefficient of the linear section of the graph presented

$$r_{Mg^{2+}}=65pm, r_{SO_4^{2-}}=150pm, r_{H_2O}=140pm, \alpha_{H_2O}=1.45\cdot 10^{-30}m^3, p_{H_2O}=6.13\cdot 10^{-30}Klm$$

in Figure 1, we determined the sum of hydration numbers of ions Mg^{2+} and

SO_4^{2-} in an aqueous solution of magnesium sulfate for the following cases: $h_{Mg^{2+}} + h_{SO_4^{2-}} \approx 21{,}71$ at the concentrations $c < 1.5\%, tg\phi = 0.0559$ and $h_{Mg^{2+}} + h_{SO_4^{2-}} \approx 7{,}46$ at the concentrations $1.5\% < c < 2\%, tg\phi = 0.0224$.

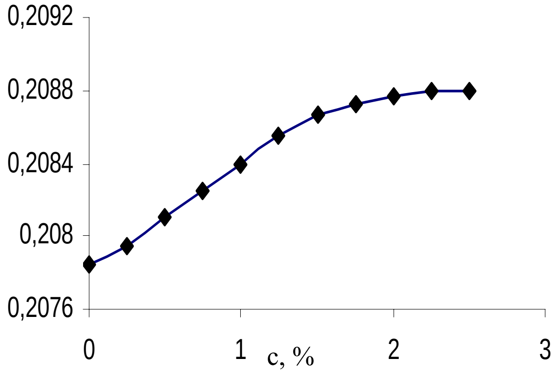

Fig. 1. Concentration dependence of the relation $\frac{n^2-1}{n^2+2}$ for a water solution of magnesium sulphate

In order to estimate the number of hydration of each ion we present a new "ion-dipole" model below. Ion with the hydrated shell is shown in Fig. 2.

In the equilibrium state (the location of the dipole in the picture drawn by a dotted line) the potential energy $W = -p_d E(r)$ of the dipole in the field of the ion and the other dipoles is balanced with its kinetic energy $\approx \frac{5}{2}kT$:

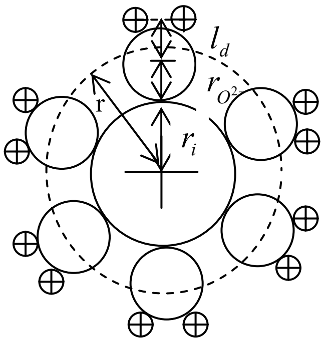

Fig.2 Ion with hydrated shell

$$-\frac{p_d}{\varepsilon}\left(\frac{q_i}{4\pi\varepsilon_0 r^2}-\frac{h_i q_d}{4\pi\varepsilon_0 r^2}\right)=\frac{5kT}{2} \qquad (10)$$

where, h_i - the number of ion hydration, $r = r_i + r_{O^{2-}} + l_d/2$ - the distance between the centers of the ion and water molecule of hydration shell in the equilibrium position, r_i the radius of the considered ion, $r_{O^{2-}}$ - ion radius O^{2-}, $l_d = p_d/q_d$ - the length of the dipole of water, p_d - the water molecule dipole moment, $q_d = 2e$ - the charge of the dipole of water, q_i - charge of the ion, e - the elementary charge, ε_0 - dielectric constant, ε - the permittivity of the solution, k - Boltzmann constant, T - the absolute temperature.

The number of ion hydration can be determined from equation (10):

$$h_i=\frac{q_i}{q_d}+\frac{10\pi\varepsilon\varepsilon_0 kT\left(r_i + r_{O^{2-}} + {p_d}/{2q_d}\right)^2}{p_d q_d} \qquad (11)$$

The calculation of the number of hydration of ions Mg^{2+} and SO_4^{2-} in aqueous solution by obtained formula (11) ($r_{Mg^{2+}} = 65pm, r_{SO_4^{2-}} = 150pm, r_{O^{2-}} = 140pm$) gave the following values: $h_{Mg^{2+}} = 3.4, h_{SO_4^{2-}} = 5.3, h_{Mg^{2+}} + h_{SO_4^{2-}} = 8.7$. This values of the sum are comparable with the values of $h_{Mg^{2+}} + h_{SO_4^{2-}} \approx 7{,}46$ at the concentrations $1.5\% < c < 2\%, tg\phi = 0.0224$ obtained by the above-presented refractometric method. This means that at the indicated concentrations the hydration shell of ions Mg^{2+} and SO_4^{2-} are single-layer as the above-mentioned "ion-dipole" model.

Calculated by formula (11) values of hydration numbers for ions K^+ and Na^+ agrees well with the values of hydration numbers of these ions determined by the rate of diffusion through the membrane by Brintsmiger [10, 11]: $h_{K^+} = 4.56, h_{Na^+} = 3.57$.

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MAQNEZİUM SULFATIN DURU SULU MƏHLULLARINDA İONLARIN HİDRATASİYA ƏDƏDİNİN TƏYİNİ

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XÜLASƏ

Maqnezium sulfatın duru sulu məhlullarının refraksiya xassələri tədqiq edilmişdir. Eksperimental nəticələri izah etmək üçün həm sərbəst su molekullarının, həm də hidratlaşmış ionların ümumi polyarizasiyaya verdiyi paylar nəzərə alınmaqla Lorens-Lorens tənliyindən istifadə edilmişdir. İonların hidratlaşma ədədləri həm refraktometrik metodla, həm də yeni təklif etdiyimiz "ion-dipol" modeli əsasında hesablanmışdır.

Açar sözlər: hidratasiya ədədi, polyarizasiya, sındırma əmsalı, məhlul.

РЕФРАКТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЧИСЛА ГИДРАТАЦИИ ИОНОВ В РАЗБАВЛЕННЫХ ВОДНЫХ РАСТВОРАХ СУЛЬФАТА МАГНИЯ

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РЕЗЮМЕ

Были исследованы рефракционные свойства разбавленных водных растворов сульфата магния. Для объяснения экспериментальных результатов было использовано уравнение Лоренц – Лоренца, в котором учитывали вклады в общую поляризацию как свободных молекул воды, так и гидратированных ионов. Были определены числа гидратации ионов как рефрактометрическим методом, так и предложенной нами «ион-дипольной» моделью.

Ключевые слова: число гидратации, поляризация, показатель преломления, раствор.

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