## **MARINE CHEMISTRY** =

## Activity Coefficient of Nitrate Ions in Seawater

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Abstract—The coefficients of selectivity of a nitrate-selective electrode to Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> ions were experimentally determined: 0.006, 0.0002, and 0.0003, respectively. The value of the activity coefficient of NO<sub>3</sub><sup>-</sup> ions in seawater with 35% salinity was ascertained:  $0.533 \pm 0.011$  at 25°C.

*Keywords:* nitrates, seawater, activity coefficient, experimental determination, nitrate-selective electrode **DOI:** 10.1134/S0001437020010208

The development of new types of ion-selective electrodes with crystalline and liquid-film membranes [1, 2, 4] has contributed to the widespread adoption of ionometry methods in hydrochemical studies, including methods for determining the physicochemical state of ions in seawater [6]. The applicability criterion for ion-selective electrodes in both physical and analytical chemistry is their selectivity to the measured ions. The correct use of a particular ion-selective electrode in natural waters, which are multicomponent electrolyte solutions where the absolute and relative ion concentrations vary over a wide range of values, depends on its selectivity under specific conditions.

The aim of this work was to obtain the selectivity characteristics of a nitrate ion-selective electrode and to experimentally determine the activity coefficient of  $NO_3^-$  in seawater.

The ELIT-021 nitrate-selective electrode manufactured by Niko Analit LLC (Russia), which is competitive in selectivity with the best foreign counterparts and has a significantly longer operational lifetime, was used for this work. The potential of the nitrate electrode was measured with respect to a silver chloride reference electrode in a saturated potassium chloride solution at a temperature of 25°C. The accuracy of the measured electromotive force (*E*) of the electrochemical circuit was ±0.1 mV. Calibration was carried out with 0.001– 0.1 M KNO<sub>3</sub> solutions, where the NO<sub>3</sub> activity coefficients were assumed equal, according to [3]. The relationship between *E* (mV) and the activity of nitrate ions ( $a_{NO_2}$ , M) corresponded to the Nernst equation:

$$E = 231.3 - 56.85 \log a_{\rm NO_3^-} \tag{1}$$

with a correlation coefficient of  $r^2 = 0.9998$ .

In general, the electromotive force of the electrochemical circuit with charge transfer, which includes an electrode selective to ions A, in the presence of other ions in the solution i, ..., j is [2, 4]

$$E = E_0 + \frac{\vartheta}{z_A} \log \left( a_A + \sum_i^j \lambda_{B/A} a_B^{z_A/z_B} \right) + \varphi_d, \qquad (2)$$

where  $a_A$  and  $a_B$  are the activities of A and B ions in the solution;  $z_A$  and  $z_B$  are the A and B charges;  $\lambda_{B/A}$  is the selectivity coefficient of B with respect to A;  $E_0$  is the electromotive force of the circuit for  $a_A = 1$  in the absence of competing ions;  $\vartheta$  is the ideal temperature factor, equal to  $2.303RT/Fz_A$  (*R* is the gas constant; *T* is temperature, K; *F* is the Faraday number);  $\varphi_d$  is the diffusion potential at the interface between two solutions with different compositions. It is impossible to determine the exact value of the diffusion potential; however, estimates show that it would be small, provided the mobility of the cations and anions present in solutions are similar. The diffusion potential of the silver chloride reference electrode and the saturated KCl solution at the contact with KNO3 solutions and seawater, calculated by the approximate Henderson equation, was small [6]. Therefore, the contribution of the diffusion potential was presumed negligible.

If one of the two solutions contains either ion A or ion B, then

$$E_1 = E_0 + \frac{\vartheta}{z_A} \log a_A, \tag{3}$$

$$E_2 = E_0 + \frac{\vartheta}{z_A} \log \left( \lambda_{B/A} a_B^{z_A/z_B} \right)$$
(4)

Salt	E, mV	Anion activity coefficient*	Anion activity, M	$\lambda_{B/NO_3^-}$
KNO <sub>3</sub>	293.6	0.771	0.0771	
KCl	416.0	0.771	0.0771	0.006
NaHCO <sub>3</sub>	477.4	0.771	0.0771	0.00025
MgSO <sub>4</sub>	496.1	0.233	0.0233	0.00032

Table 1. Nitrate-selective electrode selectivity coefficients determined by bi-ionic potential method in 0.1 M salt solutions

\* Calculated using semiempirical Davies equation [7].

and

$$E_2 - E_1 = \Delta E = \frac{\vartheta}{z_A} \log \frac{\lambda_{B/A} a_B^{z_A/z_B}}{a_A}.$$
 (5)

From Eq. (5), it follows that the expression for calculating the selectivity coefficients is

$$\log \lambda_{B/A} = \frac{\Delta E z_A}{\vartheta} + \log \frac{C_A f_A}{C_B^{z_A z_B} f_B^{z_A z_B}},\tag{6}$$

where  $C_A$  and  $C_B$  are the concentrations of A and B ions;  $f_A$  and  $f_B$  are the activity coefficients of A and B ions, and by definition  $a_i = C_i f_i$ . The activity coefficients of ions in diluted solutions can be calculated with satisfactory accuracy using the semi-empirical equation of the second or third approximation of Debye–Hückel theory, which taking into account the known concentrations of A and B, makes it possible to determine the  $\lambda_{B/A}$  value from the measured  $\Delta E$ .

**Table 2.** Activity coefficient of  $NO_3^-$  ion in seawater with 35% salinity

Concentration, M		М	E	£
$NO_3^-$	Cl	$a_{\text{Cl}^-}$ , M	E, mv	$J_{\rm NO_3^-}$
0	0.548	0.343	386.3	—
0.00005	0.548	0.343	386.0	—
0.00011	0.548	0.343	385.7	—
0.00055	0.547	0.342	383.0	—
0.0011	0.547	0.342	380.3	—
0.0055	0.543	0.339	364.2	—
0.011	0.537	0.336	352.1	—
0.055	0.493	0.308	317.3	0.525
0.110	0.438	0.274	300.5	0.536
0.219	0.329	0.206	283.6	0.543
0.329	0.219	0.137	274.0	0.537
0.438	0.110	0.069	267.2	0.532
0.548	0	0	262.2	0.522
	$0.533\pm0.011$			

Table 1 presents the measured *E* values in 0.1 M solutions of KNO<sub>3</sub>, KCl, NaHCO<sub>3</sub>, and MgSO<sub>4</sub> and the coefficients of selectivity of the nitrate-selective electrode to Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. As it follows from the results obtained, in seawater, only chloride ions have a more or less significant effect on the readings of the nitrate-selective electrode.

The NO<sub>3</sub><sup>-</sup> activity coefficients were measured at 25°C in artificial seawater with 35% salinity and variable nitrate and chloride concentrations, in total equal to the chloride content in natural seawater. The water was prepared according to the data on the composition of natural seawater [5] and contained the following, mM: NaCl, 419.35; KCl, 10.46; MgCl<sub>2</sub>· 6H<sub>2</sub>O, 54.67; CaCl<sub>2</sub>, 10.62; Na<sub>2</sub>SO<sub>4</sub>, 28.94; NaHCO<sub>3</sub>, 2.00; Na<sub>2</sub>CO<sub>3</sub>, 0.20. Calculations were carried out by Eq. (2) taking into account the contribution of Cl<sup>-</sup> ions:

$$E = E_0 + \vartheta \log(C_{NO_3^-} f_{NO_3^-} + \lambda_{Cl^-/NO_3^-} C_{Cl^-} f_{Cl^-})$$
(7)

and

$$f_{\rm NO_3^-} = \frac{10^{\frac{E-E_0}{\vartheta}} - \lambda_{\rm CI^-/NO_3^-} C_{\rm CI^-} f_{\rm CI^-}}{C_{\rm NO_3^-}},$$
(8)

where  $E_0 = 231.3$  mV,  $\vartheta = 56.85$ ,  $\lambda_{CI^-/NO_3^-} = 0.006$ ,  $f_{CI^-} = 0.625$  [6]. The measured *E* and calculated  $f_{NO_3^-}$ values are presented in Table 2 (to ensure the reliability of  $f_{NO_3^-}$  determination, only the experiments where  $C_{NO_3^-} > 0.1C_{CI^-}$  were counted). The average value  $f_{NO_3^-} = 0.533 \pm 0.011$  is appreciably lower than the activity coefficient of chloride ions  $f_{CI^-} = 0.626$  [6]. This is due to the higher stability of nitrate complexes with the main cations of seawater compared to that of chloride complexes [8], which leads to a higher degree of complexation of nitrate ions and, accordingly, to a decrease in the overall activity coefficient.

## CONCLUSIONS

The coefficients of selectivity of a nitrate ion-selective electrode with to  $Cl^-$ ,  $HCO_3^-$ , and  $SO_4^{2-}$  were

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determined experimentally: 0.006, 0.0002, and 0.0003, respectively.

The experimental value of the NO<sub>3</sub><sup>-</sup> activity coefficient in seawater with 35% salinity, obtained using the corrections for the selectivity of the nitrate electrode to chloride ions, is  $0.533 \pm 0.011$  at 25°C.

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Translated by M. Hannibal