



СПЕЦИФИЧНА И ЕКВИВАЛЕНТНА ЕЛЕКТРОПРОВОДНОСТ НА РАЗРЕДЕНИ РАЗТВОРИ НА НАТРИЕВ СЕЛЕНИТ В ОБИКНОВЕНА И ТЕЖКА ВОДА

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SPECIFIC AND EQUIVALENT CONDUCTIVITY OF DILUTE SODIUM SELENITE SOLUTIONS IN ORDINARY AND HEAVY WATER

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ABSTRACT: Based on the conductometric measurements of the electrical conductance of dilute sodium selenite solutions in ordinary and heavy water, empirical equations were derived, describing the temperature and concentration dependences of the specific and equivalent conductivity. The activation energies of specific conductivity in both solution series were calculated using the linear form of Arrhenius equation for different solution concentrations. The obtained dependences were correlated to the structure of the solutions. The values of the equivalent conductivity of the ions at infinite dilution in both solvents were determined in the temperature region 12 to 45 °C, using the expressions for asymmetric 1:2 valent electrolytes of the semiempirical Fuoss–Onsager equation. These values were compared with respect to the nature of the solvent.

Key words: Electrical conductivity, Solutions, Sodium selenite, Light and heavy water, Fuoss–Onsager equation, Temperature and concentration dependences, Activation energy of specific conductivity.

Introduction

Electrical conductivity is an intrinsic property to the electrolyte solutions. It depends on the nature of solvent and dissolved substance, the concentration, temperature, pressure, viscosity and dielectric constant of the solvent. By studying the temperature and concentration dependence of the electrical conductivity of electrolyte solutions, inferences could be made about their structure and characteristics (Robinson, Stokes, 1959; Samoylov, 1965; Evans, Matesich, 1973; Blumenthal, Engels, Fitz et al., 1984).

Research of the electrical conductivity of Na_2SeO_3 aqueous solutions is directly related to the preparation of selenites with usefully semi-conducting, optical-electrical and magnetic properties (Peng, Dong, Deng et al., 2002; Mao, Jiang, Kong, 2008; Tian, Ding, Zhang et al., 2011). Na_2SeO_3 is very important for humankind because of its effective antioxidant and antimicrobial activities, positive effect on atopic dermatitis in children, suppressing effect on growth of breast cancer cells, etc. (Ranjbar, Pizzulli, 2001; Azizi, Shoaibi, Ludewige et al., 2003; Baldwin, Wiley, Alayash, 2004; Kumar, Tiwari, Manoj, 2010; Ramoutar, Brumaghim, 2010).

The H/D isotope effect on the electrical conductivity could be determined by substituting the

solvent H_2O with D_2O , which have different bulk properties: density, viscosity and dielectric permittivity (Broadwater, Evans, 1974; Broadwater, Kay, 1975; Vesala, Koskinen, 1975; Erickson, Arcis, Raffa et al., 2011). In going from light to heavy water the viscosity changes by 23%, whereas the dielectric constant changes by only 0.4%. The electrical conductance is greater in light water than in heavy water so the ratio of these values ($\Lambda^{\text{H}}/\Lambda^{\text{D}}$) is noticeable for a variety of salts. Because light and heavy water have similar structures, the analysis and interpretation of the results for isotope effect is not complicated.

The object of the present study was to determine the coefficients in the equations describing the temperature and concentration dependences of both specific and equivalent conductivity of sodium selenite solutions in ordinary and heavy water, respectively, as well as the values of their activation energies of specific conductivity. The obtained results were used for evaluation of the isotopic substitution in the solvent onto the electrical conductance, the structure of the solutions and the properties of the ions.

Experimental

The initial solutions with concentrations less than $0.1 \text{ g-equiv}\cdot\text{dm}^{-3}$ in ordinary or heavy water

were prepared by dissolving a precisely weighed amount of Na_2SeO_3 (Aldrich, 99.999% purity) using a 250 cm^3 volumetric flask at 20 °C. Ordinary water was distilled twice and then passed through a column that contained mixed anion and cation exchange resins. The conductivity of H_2O was measured to be $9.2 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C. Heavy water (Fluka, 99.85% D_2O) with conductivity $\kappa = 3.8 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C was used without any pretreatments. The initial solutions were standardized by iodometric titration with an accuracy of 0.2% (Kotarski, 1965). Two series of eight solutions with concentrations from 0.1000 to 0.0028 g-equiv·dm⁻³ were obtained by diluting aliquots of the initial solutions with appropriate solvent in a 100 cm^3 volumetric flask, placed in a thermostat at 20 °C. The specific conductivities of these solutions were measured using a digital conductivity meter, Inolab Level-1 WTW (Germany), with a cell constant of $k = 0.4752 \text{ cm}^{-1}$. According to the technical specification of the apparatus, the relative error of the electrical conductivity measurements should be $\pm 0.02\%$. The measurements were carried out at 1° increments in the temperature range 5 to 45° C for light water solutions and in the temperature interval 12 to 45° C for heavy water solutions and at atmospheric pressure. The temperature was kept constant with a precision of $\pm 0.05^\circ \text{C}$ using an Ultrathermostat U-1 (Germany). 50 cm^3 of each sample were pipetted into a 70 cm^3 glass container equipped with a water jacket. The measurements were performed under constant pressure and continuous stirring (600 rpm) by an electromagnetic stirrer. To avoid changes in the electrical conductivity of the sample due to dissolution of CO_2 or other gases, present in air, the container was sealed with a rubber cap through which the conductivity cell had been inserted. The relative error of the measurements (temperature, concentration and specific conductivity) was $< 0.1\%$ during the experiments. The experimental data were processed by the method of least squares.

Results and Discussion

The dependence of the specific conductivity of sodium selenite solutions in ordinary and heavy water of the concentration and temperature were described by empirical equations with a common type $\kappa = f(t, c)$. Using the mathematical procedure described in detail earlier (Vlaev, Tavliva, Barthel, 2007), the coefficients in these empirical equations were found to be:

$$\begin{aligned} \kappa_{\text{H}_2\text{O}} = & 3.6100 \times 10^{-5} + 1.0728 \times 10^{-6} t \\ & + 2.1599 \times 10^{-8} t^2 + (4.7415 \times 10^{-2} \\ & + 1.6620 \times 10^{-3} t + 7.3143 \times 10^{-6} t^2) c \\ & - (7.0922 \times 10^{-2} + 2.6205 \times 10^{-3} t \\ & + 7.5377 \times 10^{-6} t^2) c^2 \end{aligned} \quad (1)$$

$$\begin{aligned} \kappa_{\text{D}_2\text{O}} = & 2.0948 \times 10^{-5} + 1.0532 \times 10^{-7} t \\ & + 1.1467 \times 10^{-8} t^2 + (3.7145 \times 10^{-2} \\ & + 1.6623 \times 10^{-3} t + 5.5495 \times 10^{-6} t^2) c \\ & - (4.8845 \times 10^{-2} + 3.9788 \times 10^{-3} t \\ & - 3.0884 \times 10^{-6} t^2) c^2 \end{aligned} \quad (2)$$

where t is the temperature in centigrade and c is the analytical concentration of the solutions in g-equiv·dm⁻³. These empirical equations describe surfaces (Vlaev et al., 2007) and can be used to calculate the analytical concentration of sodium selenite in light or heavy water with a relative error not greater than 0.8% if there are available data of specific conductivity at a given temperature in the temperature range 5 to 45 °C for solutions in ordinary water, and 12 to 45 °C for solutions in heavy water, respectively.

In Table 1 are presented values of specific conductivity of Na_2SeO_3 solutions in light and heavy water, calculated by equations (1) and (2) as well as the relative error in percentage.

As can be seen from the table, the specific conductivity of Na_2SeO_3 solutions in H_2O was higher than that in D_2O at any concentration and temperature. The reason for this is the higher density and viscosity of D_2O compared to H_2O .

To obtain information on solution structure and its change with the increase of temperature and electrolyte concentration, the linear form of Arrheniu equation is usually used where the specific conductivity of the solution κ at certain temperature is treated as a rate constant (Valyashko, Ivanov, 1979; Ivanov, 2008):

$$\ln \kappa = \ln A - \frac{E_A^\kappa}{RT} \quad (3)$$

Based on measured values of specific conductivity of each one of the solutions for each one of the studied concentrations at different temperatures are calculated the values of $\ln \kappa$. Then are drawn linear dependencies of $\ln \kappa = f(1/T)$ at a

constant concentration. From the tangents of these lines are calculated the values of activation energy of specific conductivity at the given concentration. These calculations were made for

both electrolyte systems. It turns out that the values of activation energy are a function of concentration. Fig. 1 shows the dependences $E_A^k = f(c)$ for Na_2SeO_3 solutions in H_2O and D_2O .

Table 1 Values of specific conductivity $\kappa \cdot 10^3$, $\text{S} \cdot \text{cm}^{-1}$, of Na_2SeO_3 solutions in H_2O and D_2O at different temperatures and concentrations, calculated by equation (1) and (2)

Concentration, g-equiv·dm ⁻³	Temperature, °C							
	12	15	20	25	30	35	40	45
$\text{Na}_2\text{SeO}_3 - \text{H}_2\text{O}$								
0.0999	5.85	6.33	7.15	8.01	8.90	9.82	10.78	11.78
	-0.04*	0.08	0.10	0.26	0.11	0.21	0.06	-0.04
0.0499	3.21	3.47	3.92	4.39	4.88	5.39	5.92	6.46
	-0.57	-0.33	-0.33	-0.41	-0.44	-0.35	-0.56	-0.72
0.0399	2.62	2.83	3.20	3.59	3.99	4.40	4.83	5.27
	-0.36	-0.13	-0.09	-0.20	-0.16	-0.25	-0.22	-0.38
0.0300	2.01	2.17	2.46	2.75	3.06	3.38	3.71	4.05
	0.37	0.51	0.62	0.55	0.67	0.63	0.57	0.49
0.0200	1.38	1.49	1.68	1.89	2.10	2.32	2.55	2.78
	0.38	0.42	0.54	0.58	0.62	0.66	0.72	0.57
0.0100	0.73	0.79	0.89	1.00	1.11	1.23	1.35	1.48
	0.47	0.48	0.53	0.53	0.57	0.58	0.64	0.59
0.0060	0.46	0.50	0.56	0.63	0.70	0.78	0.86	0.94
	-0.47	-0.49	-0.43	-0.52	-0.54	-0.53	-0.60	-0.71
0.0040	0.32	0.35	0.40	0.45	0.50	0.55	0.61	0.67
	-0.50	-0.54	-0.55	-0.57	-0.61	-0.63	-0.68	-0.73
$\text{Na}_2\text{SeO}_3 - \text{D}_2\text{O}$								
0.0715	3.67	4.00	4.57	5.16	5.77	6.40	7.05	7.72
	-0.02	-0.02	0.15	0.07	-0.02	-0.03	0.09	0.04
0.0357	1.97	2.15	2.46	2.78	3.11	3.45	3.81	4.17
	-0.11	-0.27	-0.42	-0.56	-0.37	-0.38	-0.41	-0.57
0.0286	1.60	1.75	2.00	2.26	2.53	2.81	3.09	3.39
	0.04	-0.14	-0.13	-0.02	0.01	0.08	0.02	-0.14
0.0214	1.22	1.33	1.53	1.73	1.93	2.14	2.36	2.59
	0.42	0.35	0.26	0.28	0.51	0.30	0.53	0.46
0.0143	0.83	0.91	1.04	1.18	1.32	1.46	1.61	1.76
	0.76	0.57	0.52	0.50	0.60	0.69	0.74	0.74
0.0072	0.43	0.47	0.54	0.61	0.68	0.76	0.84	0.92
	0.70	0.64	0.51	0.46	0.55	0.48	0.58	0.48
0.0043	0.27	0.29	0.34	0.38	0.43	0.47	0.52	0.57
	-0.40	-0.53	-0.38	-0.53	-0.54	-0.58	-0.59	-0.72
0.0029	0.19	0.21	0.23	0.26	0.30	0.33	0.36	0.40
	-0.67	-0.65	-0.59	-0.59	-0.61	-0.64	-0.66	-0.72

*relative error of specific conductivity in percentage.

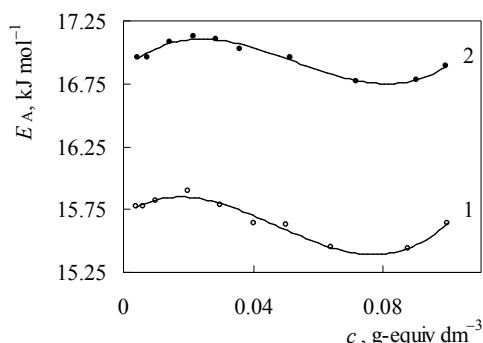


Fig. 1. Dependence of E_A^k on the concentration of Na_2SeO_3 in H_2O (1) and in D_2O (2)

Similar dependencies for aqueous solutions of various inorganic salts are presented in (Valyashko et al., 1979; Ivanov, 2006) but they have only a local minimum. The reason for this is that the studied solutions were with higher concentrations. The higher values of E_A^k for the ions motion in heavy water can be explained with the higher density and viscosity compared to ordinary water, as well as with the better structuredness of heavy water and the higher energy of O–D bonds compared to O–H bonds. At solution concentration $c \rightarrow 0$, the values of E_A^k decreased towards the values corresponding to E_A^k for the ion motion due to autoprotolysis of

H₂O and D₂O, respectively. With the increase of electrolyte concentration in the solution, the values of E_A^k increased since its ions disturb the migration of H⁺ and OH⁻ (respectively, D⁺ and OD⁻) ions by the so-called Grotthuss mechanism, or the “relay” mechanism, which is related to the hydrogen-bonded structure of the solvent. The special conductance mechanism, i.e. proton jump, is considered to be composed of two steps: (a) a water molecule adjacent to an oxonium ion H₃O⁺ reorients so that it may accept a proton from the H₃O⁺ ion, followed by (b) the proton in the resulting H₃O⁺ ion jumps to the adjacent hydrogen-bonded water molecule. Above certain concentration, the values of E_A^k decreased since it is determined mainly by the activation energy of Na⁺ and SeO₃²⁻ ions motion in the solution. The values of E_A^k reached a minimum at certain electrolyte concentration in the solution and then increased again. The existence of this minimum in the curves was attributed to some significant changes in solvent structure induced by the ions of the solved substance. The increase of E_A^k above this concentration is due to the increase of the number of ions in the solution and the corresponding increase of inter-ion interactions (Valyashko et al., 1979; Ivanov, 2006). The curves shown in Fig. 1 can be quite well described by third-order polynomials:

$$E_{A(H_2O)}^k = 15.7079 + 17.4695 c - 614.0284 c^2 + 4333.2743 c^3 \quad (4)$$

$$E_{A(D_2O)}^k = 16.8609 + 22.5969 c - 609.1145 c^2 + 3866.9750 c^3 \quad (5)$$

which were further used to calculate solutions concentrations at the extreme points. For sodium selenite solutions in H₂O, the extreme points of the curve were found to be at concentrations of 0.0175 and 0.0770 g-equiv·dm⁻³, respectively, while for sodium selenite solutions in D₂O – at 0.0164 and 0.0886 g-equiv·dm⁻³. The higher concentration of Na₂SeO₃ in D₂O, at which the minimum value of E_A^k was observed, can be explained with the better “structuredness” of heavy water compared to light water.

Using the values of the specific conductivity κ of the solutions at corresponding temperatures and concentrations and the relationship between the specific and equivalent conductivity Λ of the solutions (Evans, Matesich, 1973):

$$\Lambda = \frac{\kappa 1000}{c} \quad (6)$$

the values of the equivalent conductivity Λ of Na₂SeO₃ solutions in H₂O and D₂O were calculated. The results are presented in Table 2.

Table 2. Values of equivalent conductance Λ , S·cm²·g-equiv⁻¹, of Na₂SeO₃ in H₂O and D₂O at different concentrations and temperatures

Concentration, g-equiv·dm ⁻³	Temperature, °C							
	12	15	20	25	30	35	40	45
Na ₂ SeO ₃ – H ₂ O								
0,0999	58.58	63.44	71.70	80.41	89.22	98.59	108.05	117.87
0.0499	63.89	69.30	78.31	87.62	97.34	107.55	117.76	128.38
0.0399	65.35	70.86	80.12	89.63	99.65	109.91	120.68	131.57
0.0300	67.42	73.10	82.78	92.62	103.14	113.82	124.83	136.18
0.0200	69.55	75.34	85.43	95.82	106.66	117.93	129.69	141.21
0.0100	73.32	79.38	89.94	100.90	112.41	124.37	136.94	149.65
0.0060	75.71	81.97	92.99	104.26	116.19	128.71	141.57	154.76
0.0040	77.94	84.21	95.49	107.27	119.42	132.33	145.36	159.02
Na ₂ SeO ₃ – D ₂ O								
0.0715	51.34	55.96	64.00	72.19	80.65	89.47	98.70	108.07
0.0357	55.06	60.02	68.55	77.36	86.74	96.25	106.04	115.98
0.0286	56.00	61.04	69.85	79.05	88.49	98.29	108.25	118.40
0.0214	57.18	62.41	71.36	80.69	90.53	100.28	110.77	121.27
0.0143	58.78	64.03	73.23	82.79	92.79	103.15	113.79	124.67
0.0072	61.19	66.71	76.15	86.01	96.43	106.99	118.18	129.37
0.0043	62.59	68.07	77.97	87.88	98.37	109.21	120.51	131.93
0.0029	63.81	69.55	79.55	89.86	100.52	111.54	123.08	134.79

The values of the limiting equivalent conductance Λ^0 of sodium selenite solutions in light and heavy water at the corresponding temperatures can be determined according to the Kohlrausch equation:

$$\Lambda = \Lambda^0 - A\sqrt{c} \quad (7)$$

That describes a linear dependence of the equivalent conductivity of strong electrolytes on the square root of solution concentration.

The following empirical equations describing the temperature and concentration dependences of Λ for Na_2SeO_3 solutions in H_2O and in D_2O are obtained:

$$\Lambda_{\text{H}_2\text{O}} = 64.1382 + 2.2515t + 1.3591 \times 10^{-2}t^2 - (124.2792 + 4.4402t + 3.4266 \times 10^{-2}t^2)\sqrt{c} \quad (8)$$

$$\Lambda_{\text{D}_2\text{O}} = 48.4395 + 1.9982t + 1.0071 \times 10^{-2}t^2 - (93.6289 + 3.8716t + 2.9550 \times 10^{-2}t^2)\sqrt{c} \quad (9)$$

At solution concentration $c \rightarrow 0$, the values of the limiting equivalent conductivity Λ^0 can be determined.

The values of the A coefficients can be determined graphically from the slope of the straight lines or can be theoretically calculated using the limiting Onsager law (Robinson et al., 1959):

$$\begin{aligned} \Lambda &= \Lambda^0 - S\sqrt{c} \quad \Lambda^0 - (B_1\Lambda^0 + B_2)\sqrt{c} \\ &= \Lambda^0 - \left(\frac{8.2041 \times 10^5}{(\varepsilon T)^{3/2}} \Lambda^0 + \frac{82.4837}{\eta(\varepsilon T)^{1/2}} \right) \sqrt{c} \end{aligned} \quad (10)$$

where the coefficients B_1 and B_2 take into account relaxation and electrophoretic effects, respectively. These coefficients depend on the absolute temperature T , viscosity η , and dielectric constant ε of the solvent. Shedlovsky (Robinson et al., 1959) transformed Eq. (10) to obtain the following equation:

$$\Lambda^0 = \frac{\Lambda + B_2\sqrt{c}}{1 - B_1\sqrt{c}}, \quad (11)$$

where Λ^0 for $m:n$ valent electrolytes is not independent on c , but depends linearly on it up to a concentration of $\approx 0,1 \text{ g-equiv}\cdot\text{dm}^{-3}$. Robinson and Stokes took into account the size of the ions

and suggested the following formula (Robinson et al., 1959):

$$\Lambda^0 = \Lambda + \frac{(B_1\Lambda + B_2)\sqrt{c}}{1 + (B_1\Lambda + B_2)\sqrt{c}}, \quad (12)$$

where a is the distance of closest approach between cation and anion. According to Eqs. (7, 10–12), the dependences of Λ on $\sqrt{c}$ at 25 °C were drawn (Fig. 2) for the solutions of Na_2SeO_3 in H_2O and D_2O .

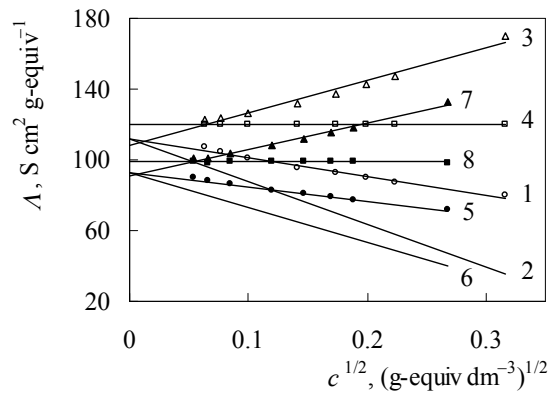


Fig. 2. Dependence of Λ on $c^{1/2}$ for solutions of Na_2SeO_3 in H_2O (1–4) and in D_2O (5–8) according to the equations of Kohlrausch: lines 1 and 5; limiting Onsager law: lines 2 and 6; Shedlovsky: lines 3 and 7; and Robinson and Stokes: lines 4 and 8, respectively.

As can be seen from Fig. 2, the experimental data were described quite well by the corresponding linear equations. Using the ratio of the constants A and S from Eqs. (7) and (10):

$$R = \frac{A - S}{A} \quad (13)$$

conclusions can be made for the presence or absence of ion associations in the solution (Maiofis, Filanovskii, Grilikhes, 1979). As can be seen from Fig. 2 the slopes of the straight lines corresponding to the limiting Onsager law (Eq. 10) are higher than these of the straight lines corresponding to the Kohlrausch equation (Eq. 7) which, according to Eq. (13), gives the values of $R < 0$ and indicates the lack of ion association in the solution. The value R is equal to $-1,28$ for the solutions of Na_2SeO_3 in H_2O and is $-1,43$ for the solutions in D_2O . The equation of Shedlovsky (Eq. 11) gives straight lines which are not parallel to the abscissa. Such lines were

obtained, however, with the equation of Robinson and Stokes (Eq. 12) which takes into account $\bar{a}$ – the distances of closest approach between cation and anion centers.

The values of Λ^0 obtained from Eq. (7) at different temperatures were used in the semi-empirical Fuoss–Onsager equation (Kunze, Fuoss, 1963; Fuoss, Onsager, Skinner, 1965; Chiu, Fuoss, 1968; Vlaev, Tavlieva, 2002.) to calculate more precisely the values of Λ^0 :

$$\Lambda = \Lambda^0 - S\sqrt{c} + Ec \ln c + J_1 c + J_2 c^{3/2} \quad (14)$$

This equation is applicable for non-associated ionophores, where S is the limiting slope of Onsager Eq. (10) and the E , J_1 and J_2 values describe the relaxation and electrophoretic effects and depend on Λ^0 , η , ε and T . Moreover, the coefficients J_1 and J_2 depend on $\bar{a}$. The coefficients of Eq. (14) for 1:2 valent electrolytes are described in detail earlier (Vlaev et al., 2007):

$$S = \left(6.4671 \times 10^6 \Lambda^0 \right) / \left\{ (\varepsilon T)^{3/2} \left[1 + \lambda_+^0 / \Lambda^0 + 0.8165 \left(1 + \lambda_+^0 / \Lambda^0 \right)^{1/2} \right] \right\} + \frac{214.3533}{\eta (\varepsilon T)^{1/2}} \quad (15)$$

$$E = \frac{3.5289 \times 10^{13} \Lambda^0}{(\varepsilon T)^3} - \frac{7.7959 \times 10^8}{\eta (\varepsilon T)^2} \quad (16)$$

$$J_1 = \left\{ \frac{7.0579 \times 10^{13}}{(\varepsilon T)^3} \left[-2.68 \times 10^7 (\bar{a} \varepsilon T)^3 + 1.7911 \times 10^5 (\bar{a} \varepsilon T)^2 + 5.985 \times 10^2 \bar{a} \varepsilon T + 0.9074 + \ln \frac{8.7091 \times 10^9 \bar{a}}{(\varepsilon T)^{1/2}} \right] \right\} \Lambda^0 + \frac{214.3533}{\eta (\varepsilon T)^{1/2}} \left[\left(6.4671 \times 10^6 \Lambda^0 \right) / \left\{ (\varepsilon T)^{3/2} \left[1 + \lambda_+^0 / \Lambda^0 + 0.8165 \left(1 + \lambda_+^0 / \Lambda^0 \right)^{1/2} \right] \right\} \right. \\ \left. + \frac{7.9832 \times 10^9 \bar{a}}{(\varepsilon T)^{1/2}} - \frac{3.6377 \times 10^6}{(\varepsilon T)^{3/2}} \left(1.017 + \ln \frac{8.7091 \times 10^9 \bar{a}}{(\varepsilon T)^{1/2}} \right) \right] \quad (17)$$

$$J_2 = \left\{ \frac{1.4524 \times 10^{21}}{(\varepsilon T)^{9/2}} \left[2.68 \times 10^7 (\bar{a} \varepsilon T)^3 + 1.7912 \times 10^5 (\bar{a} \varepsilon T)^2 - 3.225 \times 10^2 \right. \right. \\ \left. \left. \times \bar{a} \varepsilon T \right] \right\} \Lambda^0 + \frac{1.6258 \times 10^{22} \bar{a}^2}{\eta (\varepsilon T)^{3/2}} \quad (18)$$

As the permittivity ε and viscosity η of the solvent and the limiting equivalent conductivity of Na^+ ions $\lambda_{\text{Na}^+}^0$ used in the equations are functions of temperature, some empirical equations are used in the present paper. For the temperature dependence of the dielectric constant ε and the viscosity η of ordinary water, the following empirical equations were used (Vidulich, Evans, Kay, 1967; Kay, Vidulich, Priyadi, 1969; Korson, Drost-Hansen, Millero, 1969):

$$\log \varepsilon_{\text{H}_2\text{O}} = 1.94409 - 1.991 \times 10^{-3} t \quad (19)$$

$$\log \frac{\eta_t}{\eta_{20}} = \left[1.1709 (20 - t) - 0.001827 (t - 20)^2 \right] / (t + 89.93) \quad (20)$$

For heavy water, the equations suggested in the literature (Vidulich et al., 1967; Millero, Dexter, Hoff, 1971) were used:

$$\log \varepsilon_{\text{D}_2\text{O}} = 1.94275 - 2.013 \times 10^{-3} t \quad (21)$$

$$\log \frac{\eta_t}{\eta_{20}} = \left[1.3580 (20 - t) - 0.00067 (t - 20)^2 \right] / (t + 96.71) \quad (22)$$

The equation used for the temperature dependence of limiting equivalent conductivity of Na^+ ions in ordinary water was (Smolyakov, Veselova, 1974):

$$\lambda_{\text{Na}^+(\text{H}_2\text{O})}^0 = 25.8783 + 0.8552 t + 4.6019 \times 10^{-3} t^2 \quad (23)$$

and in heavy water, respectively (Gierer, 1950):

$$\lambda_{\text{Na}^+(\text{D}_2\text{O})}^{\circ} = 19.7509 + 0.7825 t + 3.6161 \times 10^{-3} t^2 \quad (24)$$

where t is the temperature in degree centigrade.

Substituting the values of ε , η , $\Lambda_{\text{Na}_2\text{SeO}_3}^{\circ}$, and $\lambda_{\text{Na}^+}^{\circ}$ for the corresponding temperature and solvent into the Eq. (14), the coefficients S , E , J_1

and J_2 were calculated, which allowed the temperature and concentration dependences of the equivalent conductivity of Na_2SeO_3 in ordinary and heavy water, respectively, to be studied. These values are presented in Table 3.

The “goodness” of the fit of the determined equivalent conductance is expressed by the mean-square deviation. The highest error was equal to 0.15 when the solvent was heavy water and the temperature was with highest values.

Table 3. Values of the limiting equivalent conductance Λ° , $\text{S}\cdot\text{cm}^2\cdot\text{g}\cdot\text{equiv}^{-1}$, and the coefficients S , E , J_1 , J_2 and $\bar{a}$ in Eq. (14) for Na_2SeO_3 solutions in H_2O and in D_2O at different temperatures

$t, ^{\circ}\text{C}$	Parameter					
	Λ°	S	E	J_1	J_2	$\bar{a}, \text{\AA}$
$\text{Na}_2\text{SeO}_3 - \text{H}_2\text{O}$						
5	75.87	147.43	106.24	496.42	– 134.31	4.670
10	88.00	172.09	125.45	584.00	– 159.80	4.669
12	93.07	182.47	133.71	620.73	– 170.86	4.667
15	100.88	198.53	146.66	680.81	– 188.23	4.671
20	114.63	226.83	170.38	784.39	– 220.36	4.667
25	128.86	256.65	195.77	896.49	– 255.27	4.666
30	143.91	288.30	224.02	1016.22	– 294.42	4.661
35	159.66	321.70	254.99	1147.21	– 337.77	4.659
40	176.03	356.78	288.73	1286.48	– 385.50	4.655
45	192.82	393.38	324.89	1437.11	– 437.38	4.654
$\text{Na}_2\text{SeO}_3 - \text{D}_2\text{O}$						
12	73.94	144.45	108.55	572.86	– 133.70	4.931
15	80.65	158.33	119.69	631.92	– 148.32	4.934
20	92.41	182.84	139.91	736.91	– 175.39	4.935
25	104.61	208.80	161.58	848.94	– 205.08	4.934
30	117.48	236.41	185.54	970.38	– 238.54	4.932
35	130.69	265.33	211.13	1100.81	– 274.92	4.932
40	144.56	295.86	239.45	1241.24	– 315.95	4.930
45	158.66	327.57	269.49	1391.10	– 360.25	4.930

It can be seen from Table 3 that the values of Λ° increase with temperature, besides those for Na_2SeO_3 in H_2O remain higher due to the lower density and viscosity of H_2O compared to D_2O . The values of the limiting equivalent conductivity Λ° of Na_2SeO_3 in H_2O and in D_2O in the temperature range 5 to 45 $^{\circ}\text{C}$ and 12 to 45 $^{\circ}\text{C}$, respectively, can be calculated by the following empirical equations:

$$\Lambda_{\text{Na}_2\text{SeO}_3(\text{H}_2\text{O})}^{\circ} = 64.1846 + 2.2481 t + 1.3631 \times 10^{-2} t^2 \quad (25)$$

$$\Lambda_{\text{Na}_2\text{SeO}_3(\text{D}_2\text{O})}^{\circ} = 48.4964 + 1.9945 t + 1.0116 \times 10^{-2} t^2 \quad (26)$$

Knowing the temperature dependence of the limiting equivalent conductivity of Na^+ cations in both solvents, the values of the limiting equivalent conductivity of SeO_3^{2-} anions in H_2O and in D_2O , respectively, are calculated and pre-

sented in Table 4, as well as the corresponding empirical equations describing the temperature dependences of limiting equivalent conductivity of SeO_3^{2-} ions in H_2O and D_2O are determined:

$$\lambda_{\text{SeO}_3^{2-}(\text{H}_2\text{O})}^{\circ} = 38.3063 + 1.3929 t + 9.0292 \times 10^{-3} t^2 \quad (27)$$

$$\lambda_{\text{SeO}_3^{2-}(\text{D}_2\text{O})}^{\circ} = 28.7455 + 1.2120 t + 6.4995 \times 10^{-3} t^2 \quad (28)$$

Table 4 shows that the values of $\Lambda_{\text{Na}_2\text{SeO}_3}^{\circ}$, $\lambda_{\text{Na}^+}^{\circ}$ and $\lambda_{\text{SeO}_3^{2-}}^{\circ}$ in H_2O are higher than the same values in D_2O . This can be attributed to the lower values of the density and viscosity of H_2O compared to D_2O . It can be also seen that, at a given temperature, the values of $\lambda_{\text{Na}^+}^{\circ}$ were significantly lower than these of $\lambda_{\text{SeO}_3^{2-}}^{\circ}$ despite the nature of the solvent and the values of the

Walden's product for both solvents were practically the same and slightly decreased with the increase of temperature. The changes of the isotope ratios for the molecule, Na^+ and SeO_3^{2-}

ions $\Lambda_{\text{Na}_2\text{SeO}_3(\text{H}_2\text{O})}^0 / \Lambda_{\text{Na}_2\text{SeO}_3(\text{D}_2\text{O})}^0$, $\lambda_{\text{Na}^+(\text{H}_2\text{O})}^0 / \lambda_{\text{Na}^+(\text{D}_2\text{O})}^0$ and $\lambda_{\text{SeO}_3^{2-}(\text{H}_2\text{O})}^0 / \lambda_{\text{SeO}_3^{2-}(\text{D}_2\text{O})}^0$ with the increase of temperature can be assessed using Fig. 3.

Table 4. Values of $\Lambda_{\text{Na}_2\text{SeO}_3}^0$, $\lambda_{\text{Na}^+}^0$, $\lambda_{\text{SeO}_3^{2-}}^0$ and Walden's product $\Lambda^0\eta$ for Na_2SeO_3 solutions in H_2O and in D_2O at different temperatures

t , °C	$\text{Na}_2\text{SeO}_3 - \text{H}_2\text{O}$				$\text{Na}_2\text{SeO}_3 - \text{D}_2\text{O}$			
	Λ^0	$\Lambda^0\eta$	$\lambda_{\text{Na}^+}^0$	$\lambda_{\text{SeO}_3^{2-}}^0$	Λ^0	$\Lambda^0\eta$	$\lambda_{\text{Na}^+}^0$	$\lambda_{\text{SeO}_3^{2-}}^0$
12	93.07	1.16	36.80	56.27	73.94	1.16	29.66	44.28
15	100.88	1.15	39.74	61.14	80.65	1.16	32.30	48.35
20	114.63	1.15	44.82	69.81	92.41	1.15	36.85	55.57
25	128.86	1.15	50.13	78.72	104.61	1.15	41.57	63.04
30	143.91	1.14	55.68	88.23	117.48	1.14	46.48	71.00
35	159.66	1.14	61.45	98.21	130.69	1.14	51.57	79.12
40	176.03	1.14	67.45	108.58	144.56	1.14	56.84	87.73
45	192.82	1.14	73.68	119.14	158.66	1.13	62.29	96.37

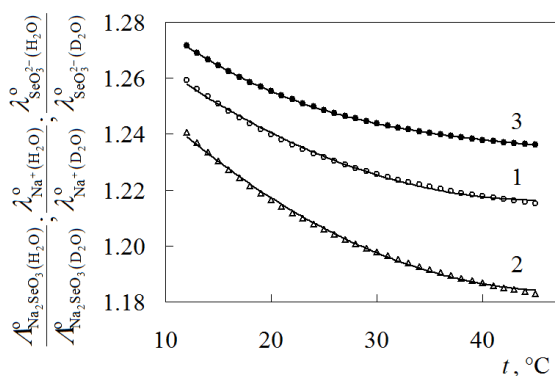


Fig. 3. Temperature dependence of isotope ratios: $\Lambda_{\text{Na}_2\text{SeO}_3(\text{H}_2\text{O})}^0 / \Lambda_{\text{Na}_2\text{SeO}_3(\text{D}_2\text{O})}^0 - 1$, $\lambda_{\text{Na}^+(\text{H}_2\text{O})}^0 / \lambda_{\text{Na}^+(\text{D}_2\text{O})}^0 - 2$, $\lambda_{\text{SeO}_3^{2-}(\text{H}_2\text{O})}^0 / \lambda_{\text{SeO}_3^{2-}(\text{D}_2\text{O})}^0 - 3$.

Fig. 3 shows that the values of the isotope ratios slightly decrease with the increase of temperature. Similar tendency was observed for solutions of other salts in light and heavy water (Broadwater et al., 1975; Tada, Ueno, Tsuchihashi et al., 1992; Tavlieva, Vlaev, 2007) which can be explained by the decrease of the viscosities of ordinary and heavy water with the increase of temperature.

Conclusions

The temperature and concentration dependence of the specific and equivalent conductivity of Na_2SeO_3 was studied in light and heavy water solutions. The coefficients of the corresponding empirical equations were calculated. The derived empirical equations for the specific conductivity

of Na_2SeO_3 in H_2O and D_2O allow calculation of the solution concentration at a given temperature and specific conductivity with an error not greater than 0.8%. The activation energies of specific conductivity of Na_2SeO_3 solutions in light and heavy water were calculated and empirical equations describing the concentration dependence of activation energy and also the values E_A^k at the extreme points were obtained. The values of the limiting equivalent conductance of SeO_3^{2-} ions were determined in the temperature region 5 to 45 °C for the solutions in light water and 12 to 45 °C for the solutions in heavy water. The temperature dependences for the isotopic ratios of the limiting equivalent conductance of Na_2SeO_3 molecules, Na^+ cations and SeO_3^{2-} anions were determined. The results in present paper confirm that the conductometric method could give useful information about the solution structure, the state of the ions, and the influence of the solvent isotopic effect on their properties. Based on that, the role of the solvent for the dissociation of the dissolving substance, the ion solvation, and the kinetics of ionic reactions in solutions could be estimated.

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