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Comparative study of the electro-transport characteristics of chalcogenate and chalcogenite ions in aqueous solutions

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A comparative study of the temperature and concentration dependence of the equivalent conductivity has been carried out in aqueous solutions of sulphuric acid, selenic acid, potassium tellurate, sodium selenite and potassium tellurite. A temperature dependence of the equivalent conductivity has been established at infinite dilution of the chalcogenate and chalcogenite ions in aqueous solutions within the temperature interval 15–45°C. The diffusion coefficients, the absolute motion velocities, the Stock's radii and the hydration numbers have been calculated for the following ions: SO_4^{2-} , SeO_4^{2-} , TeO_4^{2-} , SeO_3^{2-} and TeO_3^{2-} . The differences of the electro-transport characteristics between the chalcogenate and chalcogenite ions are contributed to the fact that they are of different sizes, and some linear dependences on the ion radii have been established for the equivalent conductivity at infinite dilution and the diffusion coefficients. The values of the translation energy $\Delta E_{\text{tr}}^\circ$ have been calculated for the water molecules in the hydration shell of the ions within the temperature interval, mentioned above. A tendency of increasing the values of $\Delta E_{\text{tr}}^\circ$ has been observed with the increment of the temperature and the ion radius.

Keywords: electrical conductance; chalcogenate and chalcogenite anions; aqueous solutions; limiting conductance; electro-transport characteristics

1. Introduction

The oxo-anions of the elements from the VIB group of the periodic table in fourth or sixth oxidation state are known as chalcogenites (SO_3^{2-} , SeO_3^{2-} , TeO_3^{2-}) and chalcogenates (SO_4^{2-} , SeO_4^{2-} , TeO_4^{2-}), respectively. The investigation of the electro-transport characteristics of these ions in aqueous solutions is an important stage of the development of new electricity sources, as well as a significant part of the research efforts directed to the processes, which occur during galvanic plating or metal refining through electrophoresis.

The major parameters which provide valuable information about the structure and the behaviour of these ions are the equivalent conductivity at infinite dilution, the diffusion coefficients and the activation energy of translation from one quasi-equilibrium state to another. These quantities depend on both the ion radius and the degree of ionic hydration [1–9]. According to Samoylov's theory [10], the positive/negative hydration of ions is related to the different stabilities of the clusters formed by the ions and their hydration spheres. Following this line of thought, it would be of interest to study and analyse the thermal dependence of the electro-transport characteristics of the hydrated chalcogenate

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and chalcogenite ions in aqueous solutions, since there are no data in the literature describing how the electro-transport parameters of the studied ions depend on their hydrated radii.

The purpose of the present work is to compare the equivalent conductivity of aqueous solutions of sulphuric and selenic acids, potassium tellurate and tellurite and sodium selenite, and to establish a relation between the changes of the electro-transport characteristics of the chalcogenate and chalcogenite ions and their radii.

2. Experimental

The initial solutions were prepared by solving H_2SO_4 and H_2SeO_4 (Merck), K_2TeO_4 , Na_2SeO_3 and K_2TeO_3 (Aldrich) with purity of 99.99% in doubly distilled water ($\kappa = 8.9 \times 10^{-7} \text{ S cm}^{-1}$ at 25°C). Series of 8–12 solutions with concentrations from 0.0800 to 0.0004 equiv. dm^{-3} were obtained by diluting aliquot parts of the initial solutions with doubly distilled water. The specific conductivities of these solutions were measured using a digital conductivity meter, Inolab Level-1 WTW (Germany), with conductivity metric cell constant 0.475 cm^{-1} and having a precision of 0.05%. The measurements were carried out in the temperature range $15\text{--}45^\circ\text{C}$ at 1°C intervals. The temperature was maintained with precision of $\pm 0.02^\circ\text{C}$ using water ultrathermostat U-1 (Germany). The solution studied was placed in a 100 cm^3 glass container with a water jacket. The measurements were performed under constant agitation with an electromagnetic stirrer. To avoid changes of electrical conductivity due to dissolution of CO_2 or other gases present in air, the container was sealed with a rubber cap, through which the conductive metric cell was inserted. The relative error of the measurements (temperature, concentration and specific conductivity) was $<0.1\%$ during to the experiments. The experimental data were processed by the least squares method.

3. Results and discussion

It is well known that the equivalent conductivity is one of the basic parameters which characterise aqueous solutions of electrolytes. On the basis of measured specific conductivities of aqueous solutions of H_2SO_4 , H_2SeO_4 , K_2TeO_4 , Na_2SeO_3 and K_2TeO_3 at different concentrations within the temperature interval $15\text{--}45^\circ\text{C}$ and Equation (1),

$$A = \frac{10^3 \kappa}{c}, \quad (1)$$

the equivalent conductivities of studied electrolytes are calculated. Some of these results are presented in Table 1.

As can be seen from the data presented in Table 1, the equivalent conductivity of the aqueous solutions has increased at given temperature and concentration in the following order: $\text{Na}_2\text{SeO}_3 < \text{K}_2\text{TeO}_3 < \text{K}_2\text{TeO}_4 < \text{H}_2\text{SO}_4 < \text{H}_2\text{SeO}_4$. The values of the equivalent conductivity of the aqueous solutions of K_2TeO_3 , Na_2SeO_3 and K_2TeO_4 are much smaller than those of the sulphuric and selenic acid, mainly because of the specific (relay) mechanism of motion of the proton.

To find the value of the limiting equivalent conductance A° at $T = \text{const.}$, the equation of Kohlrausch was first used [1–3,11]:

$$A = A^\circ - A\sqrt{C}, \quad (2)$$

Table 1. Values of equivalent conductance Λ ($\text{Scm}^2\text{equiv}^{-1}$) for some chalcogenates and chalcogenites at different concentrations and temperatures.

Electrolyte	Concentration (equiv. dm^{-3})	Temperature ($^{\circ}\text{C}$)						
		15	20	25	30	35	40	45
H_2SO_4	0.0004	364.88	397.38	428.74	458.95	488.012	515.93	542.70
	0.0020	363.85	396.17	427.34	457.35	486.20	513.90	540.45
	0.0040	362.57	394.66	425.60	455.35	483.94	511.37	537.64
	0.0060	361.29	393.16	423.84	453.35	481.69	508.84	534.82
	0.0099	358.80	390.21	420.43	449.45	477.28	503.91	529.34
	0.0800	313.95	337.33	359.14	379.39	398.08	415.21	430.78
H_2SeO_4	0.0004	359.91	392.38	424.37	455.88	486.90	517.44	547.50
	0.0010	359.64	392.07	424.00	455.45	486.41	516.88	546.87
	0.0029	358.79	391.07	422.84	454.11	484.87	515.13	544.87
	0.0050	357.85	389.97	421.56	452.63	483.17	513.18	542.67
	0.0089	356.11	387.92	419.18	449.87	480.00	509.57	538.58
	0.0789	324.81	351.22	376.42	400.41	423.20	444.78	465.16
K_2TeO_4	0.0004	114.06	128.31	142.90	157.85	173.14	188.79	204.78
	0.0019	113.83	128.05	142.61	157.53	172.79	188.40	204.36
	0.0039	113.51	127.69	142.22	157.10	172.32	187.89	203.80
	0.0060	113.19	127.33	141.81	156.65	171.82	187.35	203.21
	0.0090	112.72	126.80	141.23	156.00	171.11	186.57	202.37
	0.0810	101.45	114.18	127.21	140.52	154.13	168.02	182.20
Na_2SeO_3	0.0004	89.20	94.95	99.72	103.52	106.35	108.21	109.10
	0.0020	88.89	94.59	99.32	103.07	105.84	107.65	108.48
	0.0040	88.50	94.15	98.81	102.50	105.21	106.95	107.70
	0.0060	88.11	93.70	98.31	101.94	104.58	106.25	106.92
	0.0099	87.34	92.83	97.33	100.84	103.35	104.88	105.41
	0.0800	73.58	77.22	79.71	81.06	81.26	80.31	78.22
K_2TeO_3	0.0030	110.25	124.51	139.49	155.18	171.59	188.72	206.56
	0.0089	109.08	123.17	137.97	153.48	169.69	186.61	204.24
	0.0110	108.66	122.69	137.43	152.87	169.01	185.86	203.41
	0.0295	104.96	118.48	132.66	147.52	163.04	179.24	196.10
	0.0494	100.99	113.94	127.53	141.76	156.62	172.12	188.25
	0.0612	98.63	111.26	124.49	138.35	152.81	167.89	183.59

which describes a linear dependence of equivalent conductance of strong electrolytes on the square root of their concentration. The extrapolation to zero concentration gives the limiting equivalent conductance Λ° , and the slope of the straight line is equal to the coefficient A . The latter quantity can be theoretically calculated using the Onsager limiting law [12]:

$$\Lambda = \Lambda^{\circ} - (B_1\Lambda^{\circ} - B_2)\sqrt{C}, \quad (3)$$

where B_1 accounts for the relaxation effects in ions motion in the solution and coefficient B_2 accounts for the electrophoretic effects.

For non-associated ionogens, the semi-empiric equation of Fuoss–Onsager was used [5,13–18]:

$$\Lambda = \Lambda^{\circ} - Sc^{1/2} + Ec \ln c + (J'_1 + F\Lambda^{\circ})c + J_2c^{3/2}, \quad (4)$$

where the coefficient S is equal to the expression in parentheses in the Onsager equation (Equation 3) while coefficients E , J'_1 and J_2 account for the relaxation and electrophoretic effects and depend on A° , η , ε and T . The coefficients J'_1 and J_2 also depend on the distance of closest approach between ions: a . The $FA^\circ c$ term describes the change of the solvent viscosity from the addition of the electrolyte, whereas F is the Einstein coefficient. For very diluted solutions $FA^\circ = 0$ and $J'_1 \equiv J_1$, therefore, Equation 4 can be written as:

$$A = A^\circ - Sc^{1/2} + Ec \ln c + J_1 c + J_2 c^{3/2}. \quad (5)$$

The values of the coefficients S , E , J_1 and J_2 for $m - n$ valent electrolytes can be calculated according to [19] and [20]. Since the dielectric constant ε , viscosity of the solution η and limiting equivalent conductance of hydroxonium $\lambda_{\text{H}_3\text{O}^+}^\circ$, sodium $\lambda_{\text{Na}^+}^\circ$ and potassium $\lambda_{\text{K}^+}^\circ$ ions are functions of temperature, the following empirical equations were used [21]:

$$\log \varepsilon = 1.94409 - 1.9910 \times 10^{-3}t, \quad (6)$$

$$\log \eta = \frac{1301}{998.333 + 8.1855(t - 20) + 0.00585(t - 20)^2} - 3.30233, \quad (7)$$

and for the equivalent conductance of the H_3O^+ , K^+ and Na^+ ions at infinite dilution [22]:

$$\lambda_{\text{H}_3\text{O}^+}^\circ = 221.4837 + 5.4370t - 0.0122t^2, \quad (8)$$

$$\lambda_{\text{K}^+}^\circ = 39.9420 + 1.2533t + 0.0037t^2, \quad (9)$$

$$\lambda_{\text{Na}^+}^\circ = 25.8430 + 0.8548t + 0.0047t^2. \quad (10)$$

In these equations, the temperature t is in $^\circ\text{C}$. With the values of ε , η , $\lambda_{\text{H}_3\text{O}^+}^\circ$, $\lambda_{\text{K}^+}^\circ$ and $\lambda_{\text{Na}^+}^\circ$ obtained, the coefficients in Equation (5) for the aqueous solutions of the studied electrolytes were calculated at the selected temperatures.

The approach to the derivation of the equations describing the function $A = f(t, c^{1/2})$, as well as the very empirical equations for aqueous solutions of H_2SO_4 , H_2SeO_4 , K_2TeO_4 , Na_2SeO_3 and K_2TeO_3 are presented in [19,20,23]. The graphic presentation of these dependencies (Figure 1) provides a way of establishing how electrolytes influence the conductivity of solutions, as well as the differences in the behaviour of the chalcogenate and chalcogenite ions in aqueous solutions.

As can be seen from Figure 1, the equivalent conductivity of the aqueous solutions has increased at given temperature and concentration in the same order $\text{Na}_2\text{SeO}_3 < \text{K}_2\text{TeO}_3 < \text{K}_2\text{TeO}_4 < \text{H}_2\text{SO}_4 < \text{H}_2\text{SeO}_4$. The higher location of the surfaces of the two acids in comparison to those of the salts is due to the equivalent conductivity and the transition number of the hydroxonium ion.

The empirical equations presented in [19,20,23], describing the dependence of the equivalent conductivity of the aqueous solutions of H_2SO_4 , H_2SeO_4 , K_2TeO_4 , Na_2SeO_3 and K_2TeO_3 on temperature and concentration, can be used to calculate the equivalent conductivity at infinite dilution A° of the relevant electrolytes by approximating the concentration to zero ($c \rightarrow 0$). On this base, the equations describing the temperature

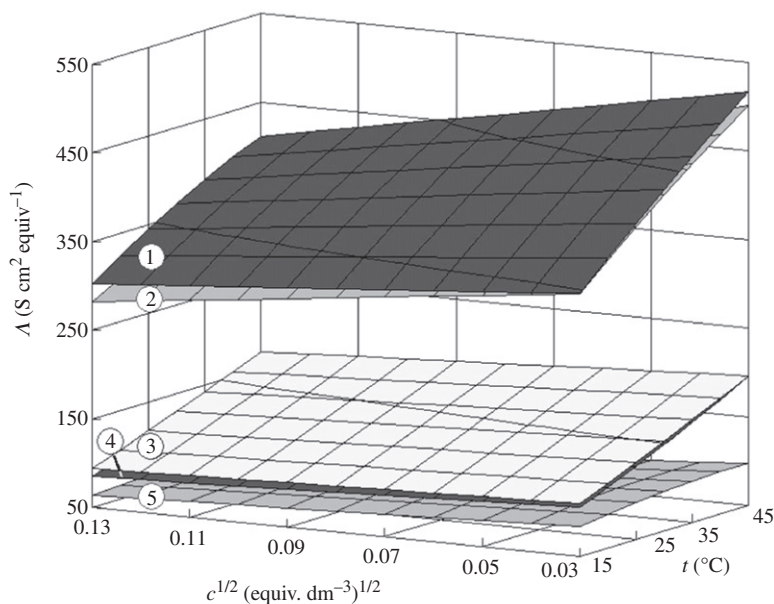


Figure 1. Dependence of the equivalent conductivity of aqueous solutions of: 1 – H_2SeO_4 , 2 – H_2SO_4 , 3 – K_2TeO_4 , 4 – K_2TeO_3 and 5 – Na_2SeO_3 on the temperature and square root of concentration.

dependence of Λ^0 for the studied electrolytes are derived and presented in the following order:

$$\Lambda_{\text{H}_2\text{SO}_4}^0 = 260.610 + 7.3116t - 0.0229t^2, \quad (11)$$

$$\Lambda_{\text{H}_2\text{SeO}_4}^0 = 259.690 + 6.8370t - 0.0096t^2, \quad (12)$$

$$\Lambda_{\text{K}_2\text{TeO}_4}^0 = 73.464 + 2.6057t + 0.0070t^2, \quad (13)$$

$$\Lambda_{\text{Na}_2\text{SeO}_3}^0 = 66.204 + 1.8296t - 0.0194t^2, \quad (14)$$

$$\Lambda_{\text{K}_2\text{TeO}_3}^0 = 72.155 + 2.3632t + 0.0144t^2. \quad (15)$$

In order to calculate the coefficients of the empirical equations, describing the temperature dependence of the equivalent conductivity at infinite dilution for the relevant anions, Equations (8)–(10) are subtracted from Equations (11)–(15). The obtained equations have the following coefficients:

$$\lambda_{\text{SO}_4^{2-}}^0 = 39.13 + 1.8746t - 0.0107t^2, \quad (16)$$

$$\lambda_{\text{SeO}_4^{2-}}^0 = 38.206 + 1.400t + 0.0026t^2, \quad (17)$$

$$\lambda_{\text{TeO}_4^{2-}}^0 = 33.522 + 1.352t + 0.0033t^2, \quad (18)$$

$$\lambda_{\text{SeO}_3^{2-}}^{\circ} = 40.361 + 0.9748t + 0.0147t^2, \tag{19}$$

$$\lambda_{\text{TeO}_3^{2-}}^{\circ} = 31.654 + 1.144t + 0.0103t^2. \tag{20}$$

Figure 2 represents the temperature dependence of the equivalent conductivity at infinite dilution for the anions λ_{-}° in the aqueous solutions of H_2SO_4 , H_2SeO_4 , K_2TeO_4 , Na_2SeO_3 and K_2TeO_3 .

As can be seen from Figure 2, the values of the equivalent conductivity at infinite dilution for the studied anions have regularly increased with the temperature in the order: $\text{TeO}_3^{2-} < \text{TeO}_4^{2-} < \text{SeO}_3^{2-} < \text{SeO}_4^{2-} < \text{SO}_4^{2-}$, the curves being with different slopes. The different angles of the slopes ($d\lambda_{-}^{\circ}/dt$) can be contributed to the different size, hydration number and positive/negative hydration of the ions according to Samoylov's theory [10]. The shape and degree of curvature depend on the values and mathematical sign of the third terms in the polynomials. For example, in Equation (16) the third term is negative and the corresponding curve 1 is bent to the abscise axis. In the other Equations, (17)–(20), the third term is positive and the corresponding curves 2–5 are bent to the ordinate axis. The diffusion kinetics of the ions have been studied within the temperature interval 15–45°C using the data from the measured conductivity of the aqueous solutions of H_2SO_4 , H_2SeO_4 , K_2TeO_4 , Na_2SeO_3 and K_2TeO_3 , as well as the calculated values of the equivalent conductivity at different temperatures and concentrations. Using the appropriate mathematical apparatus [1–3,24–30], calculations can be performed in order to find the values of the self diffusion coefficients of the ions at infinite dilution D_{\pm}° , the change in the translation energy $\Delta E_{\text{tr}}^{\circ}$ of water molecules from the ion hydration shell, as well as the ion radii and their hydration numbers.

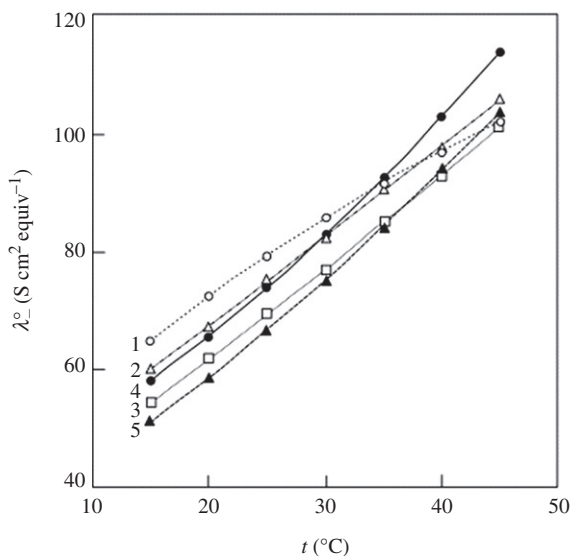


Figure 2. Temperature dependence of λ_{-}° for: 1 – SO_4^{2-} , 2 – SeO_4^{2-} , 3 – TeO_4^{2-} , 4 – SeO_3^{2-} and 5 – TeO_3^{2-} ions.

The following equation was used to calculate the diffusion coefficient values at infinite dilution (D_{\pm}°) [1–3]:

$$D_{\pm}^{\circ} = \frac{RT \lambda_{\pm}^{\circ}}{|z_{\pm}|F^2}, \quad (21)$$

where z_{\pm} – ion charge, F – Faraday number, T – absolute temperature and R – universal gas constant. The limiting mobility of ions, u_{\pm}° , at different temperatures can be calculated using the following Equation [24]:

$$u_{\pm}^{\circ} = \frac{\lambda_{\pm}^{\circ}}{|z_{\pm}|F}. \quad (22)$$

The migration of difference in nature hydrated ions in a solution at each temperature is accompanied by a corresponding number of water molecules surrounding them and the moving of water molecules from their hydrate coating needs from different energies. Because of this, the activation energy for migration of hydrated ions from one quasi-equilibrium state to another is different. At first approximation, the apparent activation energy of the ions' electric conductance in water, E_{λ}° , can be described as a sum of the activation energy determined by water viscosity, E_{η}° , and an additional member, ΔE_{tr}° , accounting for the differences between water molecules in the hydrate coating and pure water. It is related to a breaking of the bonds in ion coating and formation of appropriate 'holes' for their translation [10]. The change of the activation energy of ion translation is the difference between the values of the activation energies of the 'jumps' of water molecules from the hydrate coating in the solution E_{λ}° and in pure water E_{η}° [24,25]:

$$\Delta E_{tr}^{\circ} = E_{\lambda}^{\circ} - E_{\eta}^{\circ}. \quad (23)$$

According to Samoylov's theory [10], ΔE_{tr}° can be either positive or negative. A characteristic of the positively charged ions is that the mobility of the water molecules near the ion decreases compared to that in pure water [26–28]. Since the limiting mobility of ions, u_{\pm}° , is directly proportional to the limiting equivalent conductance λ_{\pm}° (Equation 18), ΔE_{tr}° of certain ions can be calculated using the temperature dependence of Walden's product ($u_{\pm}^{\circ} \eta$) according to the expression [7,24,25]:

$$\Delta E_{tr}^{\circ} = -R \frac{d \ln(u_{\pm}^{\circ} \eta)}{d(1/T)} = RT^2 \frac{d \ln(u_{\pm}^{\circ} \eta)}{dT}. \quad (24)$$

In order to calculate ΔE_{tr}° for the investigated ions at different temperatures, a graphic should be built, which represents the temperature dependence of $\ln(u_{\pm}^{\circ} \eta)$. The latter can be described by polynomials of the second degree, such as follows:

$$\ln(u_{\pm}^{\circ} \eta^{\circ}) = a + \frac{b}{T} + \frac{c}{T^2}. \quad (25)$$

The differentiation of Equation (25) against temperature has produced an equation which can be used to calculate ΔE_{tr}° :

$$\Delta E_{tr}^{\circ} = -R \frac{d \ln(u_{\pm}^{\circ} \eta)}{d(1/T)} = -R \left(b + \frac{2c}{T} \right). \quad (26)$$

The variation of the electro-transport characteristics of the ions can be explained with the variation of the ion radius and hydration number. From Stokes' equation [29,30]:

$$r_S = \frac{|z_{\pm}|F^2}{6\pi N_A \eta \lambda_{\pm}^{\circ}}, \quad (27)$$

the Stokes' radii of the moving solvated ions can be calculated, as for their effective radii we can use the equation proposed by Gill [31,32]:

$$r_{\text{eff.}} = r_S + 0.0103\varepsilon + r_Y, \quad (28)$$

where ε – dielectric permeability of water [2], r_Y – parameter, which equals 0.85 Å for non-associated solvents and 1.13 Å for associated solvents, which have high values of ε (water). Combining the calculated values of the effective ion radii and Equation (29):

$$n_s = \frac{4\pi}{3V_L}(r_{\text{eff.}}^3 - r_{\text{cryst}}^3), \quad (29)$$

provides a way to calculate the hydration numbers of the ions n_s [22,23]. Here V_L is the volume, occupied by a single water molecule, which is equal to 12.2 Å³, and r_{cryst} is the crystallographic radius of each ion [33–35].

Table 2 contains all the kinetic parameters of the chalcogenate and chalcogenite ions at different temperatures.

As can be seen from Table 2, the values of the corresponding parameters of each chalcogenate ion are greater than those of the relevant chalcogenite ion. In order to explain the differences between the chalcogenate and chalcogenite ions, an analysis should be conducted of all quantities that influence the kinetic parameters, bearing in mind the connections and the relations among them.

A basic quantity, characterising the behaviour of an ion in a solution, is the equivalent conductivity at infinite dilution. The other parameters, which add to the information about ion behaviour, recognise the relation between the equivalent conductivity at infinite dilution and the quantities, characterising an ion as a material particle – these are the ion size and charge, as well as the parameters characterising a solvent.

The diffusion coefficient D_{-}° and the absolute motion velocity u_{-}° are quantities which are proportional to λ_{-}° and inversely proportional to the charge of the relevant chalcogenate and chalcogenite ions. Since all investigated anions are divalent, the differences in the values of D_{-}° and u_{-}° are due to λ_{-}° . These anions, with respect to nature, can be ordered in the same sequence of increase of D_{-}° and u_{-}° , as has been observed with λ_{-}° .

The change of the translation energy of the water molecules from ion hydration shell $\Delta E_{\text{tr}}^{\circ}$ is a basic parameter in Samoylov's theory, on the basis of which a judgement can be made of the type of ion hydration and the influence of an ion over the structure of the solvent. As an indicator for the action (positive or negative hydration) of the ions on its hydration shell, the values of the parameter B'^{-} [36] may be used, which is connected with proton relaxation rates in aqueous solution. As a criterion for the positive/negative hydration of ions, the parameter B'^{-} can be used [36]. It is known from other reports [36] that the values of the parameter B'^{-} for SO_4^{2-} , SeO_4^{2-} , TeO_4^{2-} , and SO_3^{2-} , SeO_3^{2-} and TeO_3^{2-} ions are positive (0.12, 0.16, 0.20, 0.22, 0.26, 0.31, respectively) and have had structure breaker effects on hydration shells. For example, the calculated values of $\Delta E_{\text{tr}}^{\circ}$.

Table 2. Kinetic parameters of SO_4^{2-} , SeO_4^{2-} , TeO_4^{2-} , SeO_3^{2-} and TeO_3^{2-} ions.

Ion	Parameter	Temperature (°C)						
		15	20	25	30	35	40	45
SO_4^{2-}	$D_-^\circ \times 10^5 (\text{cm}^2 \text{s}^{-1})$	0.83	0.95	1.05	1.16	1.26	1.36	1.45
	$u_-^\circ \times 10^4 (\text{S C}^{-1} \text{cm}^2)$	3.36	3.75	4.11	4.44	4.75	5.03	5.28
	$\Delta E_{\text{tr},(-)}^\circ (\text{kJ mol}^{-1})$	-12.19	-10.43	-8.72	-7.08	-5.49	-3.95	2.45
	$r_S (\text{Å})$	2.15	2.26	2.32	2.40	2.49	2.59	2.70
	n_S	15.76	17.40	18.25	19.25	20.65	22.34	24.34
SeO_4^{2-}	$D_-^\circ \times 10^5 (\text{cm}^2 \text{s}^{-1})$	0.77	0.88	1.00	1.11	1.25	1.37	1.50
	$u_-^\circ \times 10^4 (\text{S C}^{-1} \text{cm}^2)$	3.12	3.47	3.90	4.26	4.69	5.06	5.48
	$\Delta E_{\text{tr},(-)}^\circ (\text{kJ mol}^{-1})$	-11.47	-8.90	-6.42	-4.01	-1.69	0.56	2.74
	$r_S (\text{Å})$	2.40	2.44	2.45	2.50	2.52	2.57	2.60
	n_S	18.94	19.24	19.30	19.85	20.15	20.46	20.80
TeO_4^{2-}	$D_-^\circ \times 10^5 (\text{cm}^2 \text{s}^{-1})$	0.70	0.81	0.92	1.04	1.17	1.30	1.43
	$u_-^\circ \times 10^4 (\text{S C}^{-1} \text{cm}^2)$	2.83	3.21	3.60	3.99	4.40	4.81	5.24
	$\Delta E_{\text{tr},(-)}^\circ (\text{kJ mol}^{-1})$	-10.09	-7.57	-5.13	-2.77	-0.48	1.73	3.87
	$r_S (\text{Å})$	2.63	2.64	2.65	2.67	2.69	2.70	2.72
	n_S	21.80	21.82	21.85	21.88	21.91	21.93	21.96
SeO_3^{2-}	$D_-^\circ \times 10^5 (\text{cm}^2 \text{s}^{-1})$	0.75	0.86	0.98	1.12	1.27	1.44	1.61
	$u_-^\circ \times 10^4 (\text{S C}^{-1} \text{cm}^2)$	3.02	3.41	3.83	4.29	4.79	5.33	5.91
	$\Delta E_{\text{tr},(-)}^\circ (\text{kJ mol}^{-1})$	-10.98	-7.61	-4.36	-1.21	1.83	4.77	7.63
	$r_S (\text{Å})$	2.52	2.50	2.49	2.47	2.46	2.44	2.41
	n_S	22.99	21.99	21.66	21.10	20.40	19.60	18.73
TeO_3^{2-}	$D_-^\circ \times 10^5 (\text{cm}^2 \text{s}^{-1})$	0.66	0.77	0.89	1.02	1.16	1.31	1.48
	$u_-^\circ \times 10^4 (\text{S C}^{-1} \text{cm}^2)$	2.66	3.04	3.45	3.90	4.36	4.86	5.38
	$\Delta E_{\text{tr},(-)}^\circ (\text{kJ mol}^{-1})$	-8.81	-5.92	-3.11	-0.41	2.22	4.75	7.21
	$r_S (\text{Å})$	2.82	2.79	2.76	2.73	2.71	2.67	2.65
	n_S	29.85	28.70	27.69	26.67	25.64	24.61	23.61

at 288 K are negative (Table 2) and give rise with the temperature in the same order as the values of the parameter B'^- . Whether the changes of $\Delta E_{\text{tr}}^\circ$ are negative or positive, as well as their values for chalcogenate and chalcogenite ions, can be related to ion radius and the structure breaker effects on the ion hydration shells.

The hydrodynamic (Stokes') radii r_S of the moving and solvated SO_4^{2-} , SeO_4^{2-} , TeO_4^{2-} , SeO_3^{2-} and TeO_3^{2-} ions are inversely proportional to the equivalent conductivity at infinite dilution λ_-° and proportional to the charge z_- , though this is not the same for their absolute motion velocities and diffusion coefficients. That is why the Stokes' radius of the investigated ions increase in the reverse order with respect to the increase of D_-° and u_-° , and in the same order of increase as $\Delta E_{\text{tr}}^\circ$.

When calculating the hydration number n_S of the chalcogenate and chalcogenite ions at given temperature there are some factors which affect the ion radii and should be taken into consideration – the equivalent conductivity at infinite dilution of an anion, the anion charge and the solvent viscosity. The parameters which characterise any solvent – dielectric permeability and volume of solvent molecule – should also be taken into consideration. Since the same solvent has been used for all investigated electrolytes, the latter are

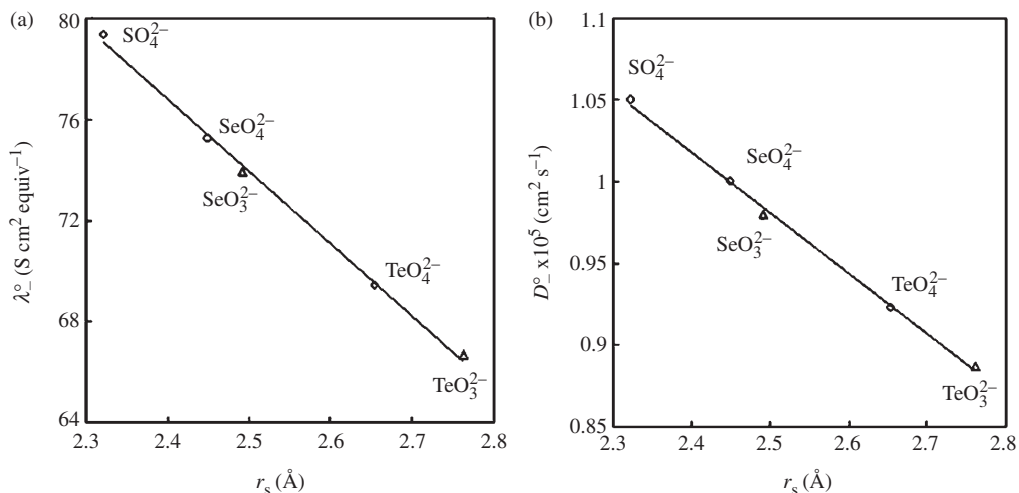


Figure 3. Dependence of λ_-^0 (a) and D_-^0 (b) on the Stokes' radii of SO_4^{2-} , SeO_4^{2-} , SeO_3^{2-} , TeO_4^{2-} and TeO_3^{2-} ions at 25°C.

of no great significance. The values of r_s and n_s have been found to be the highest for TeO_3^{2-} ions, which means that these ions are the largest among the investigated ones and are the most positively hydrated.

In order to explain the differences in the electro-transport characteristics of the chalcogenate and chalcogenite ions, an investigation has been conducted over the dependence of these characteristics on the ion radii. Figure 3 represents the relation between the equivalent conductivity at infinite dilution λ_-^0 , the diffusion coefficient D_-^0 of the investigated ions and their radii.

As can be seen from Figure 3 λ_-^0 and D_-^0 are linearly proportional to the Stokes' radii and maintain similar trends. The values of the two parameters decrease with the increase of the Stokes' radius in the following sequence $\text{SO}_4^{2-} > \text{SeO}_4^{2-} > \text{SeO}_3^{2-} > \text{TeO}_4^{2-} > \text{TeO}_3^{2-}$. The chalcogenate ions possess higher values of λ_-^0 than the corresponding chalcogenite ions, since the latter are greater in size and have higher values of n_s . The smaller in size an ion is, the higher its equivalent conductivity becomes, since its hydration number decrease (see the values of n_s in Table 2). For this reason, in Figure 3(a), the limiting conductivity of anions λ_-^0 linearly decreases with increasing of its radius r_s . The similar situation, which has been observed for D_-^0 (Figure 3(b)), is due to the fact that the diffusion coefficient of ions is proportional to λ_-^0 .

The change of the translation energy of the water molecules from the hydration shell of the chalcogenate and chalcogenite ions has also been monitored and their relation is displayed on Figure 4.

Figure 4 clearly shows that the increase of the ion radius has led to the increase of ΔE_{tr}^0 , which is more pronounced for the chalcogenite ions. With the accordance to Samoylov's theory, it is obvious that the chalcogenite ions are more positively hydrated. The larger the size of an ion, the more positively hydrated it is. This leads to a better organisation of the water molecules in the hydration shell of the ion, which impedes the ion mobility in the water solution.

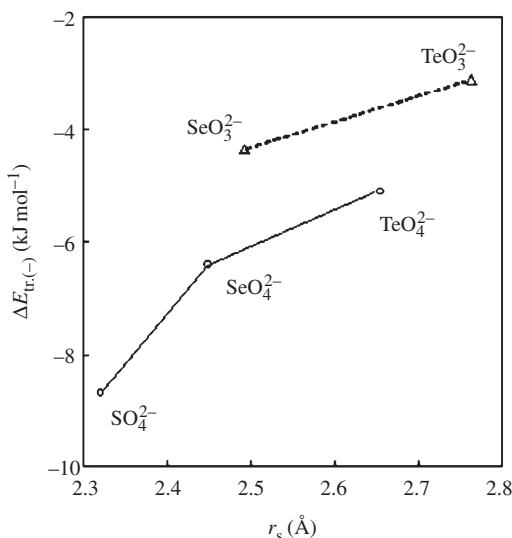


Figure 4. Dependence of $\Delta E_{\text{tr}}^{\circ}$ on the Stokes' radii of SO_4^{2-} , SeO_4^{2-} , SeO_3^{2-} , TeO_4^{2-} and TeO_3^{2-} ions at 25°C.

4. Conclusion

The comparison that has been carried out between the temperature dependences of the electro-transport characteristics of H_2SO_4 , H_2SeO_4 , K_2TeO_4 , Na_2SeO_3 and K_2TeO_3 gives us a common idea about the behaviour of the hydrated chalcogenate and chalcogenite ions in the aqueous solution of each electrolyte. The calculated values of λ_-° , D_-° and u_-° are higher for the chalcogenate ions than those for the chalcogenite ions, and vice versa, the values of r_s and n_s are lower for the chalcogenate ions than those for the corresponding chalcogenite ions. The differences in the electro-transport characteristics of SO_4^{2-} , SeO_4^{2-} , SeO_3^{2-} , TeO_3^{2-} and TeO_4^{2-} ions have been contributed to the differences of the ion radii. A linear dependence has been established between the equivalent conductivity at infinite dilution of the chalcogenate and chalcogenite ions and their ion radii.

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