Diffusion and Kinetic Characteristics
of Dilute Aqueous Solutions of Manganese(II) Chloride

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Diffusion and Kinetic Characteristics of Dilute Aqueous Solutions of Manganese(II) Chloride: *Conductometric data for dilute aqueous solutions of the strong electrolyte manganese(II) chloride in the temperature range 5-45°C were used for estimation of the molar, cation and anion self-diffusion coefficients at infinite dilution. The values of the limiting ion mobilities, the transport numbers, the Stokes and effective radii, and the hydration numbers of the ions were also calculated, and their temperature dependences were discussed.*
Key words: Manganese(II) Chloride, Aqueous Solutions, Diffusion Coefficients, Limiting Ion Mobilities, Transport Numbers, Ion Hydration Numbers, Temperature Dependences.

INTRODUCTION

The electrical conductivity of the solutions is a property of fundamental importance in connection with the ionic theory [1], as well as for studying the processes of solvation and association, and the transport properties of the ions in the solutions. Using the values at different temperatures of the molecule limiting equivalent conductance Λ° and the ion limiting equivalent conductance $\lambda^\circ_\pm$ determined for certain electrolyte in a given solvent, the kinetics in the solutions can be characterized by calculating the molecule self-diffusion coefficient D°_m and the self-diffusion coefficients of its ions $D^\circ_\pm$, the limiting mobility of the ions $u^\circ_\pm$, the transport numbers of the ions $t^\circ_\pm$, their hydrodynamic (Stokes) radii r_{Stokes}, their effective radii r_{eff}, and the corresponding hydration numbers of the ions n_s [2].

The objective of the present work is to study the diffusion and kinetic characteristics of manganese(II) chloride in aqueous solutions in the temperature interval 5–45°C.

EXPERIMENTAL

Water was distilled twice and then passed through a column, which contained mixed anion and cation exchanger resins. The conductance of this water was measured to be $\kappa = 9.2 \times 10^{-7}$ S/cm at 25°C. The initial solution was prepared by diluting 9.8955 g $MnCl_2 \cdot 4H_2O$ (Fluka) in distilled water using a 1 dm^3 volumetric flask at 20°C. The concentration of Mn(II) in the initial solutions was determined by formaldoxime spectrometric method [3]. A series of seven solutions with concentrations from 0.0530 to 0.0021 g-equiv/dm^3 were prepared by diluting aliquots of the initial solution in 100 cm^3 volumetric flasks at 20°C.

50 cm^3 of each sample was pipetted in a 70 cm^3 glass container sealed with a rubber cap to avoid changes in the electrical conductivity due to dissolution of CO_2 from air (through which the conductivity cell had been inserted), and equipped with a water jacket (to keep temperature constant). The measurements of the specific conductivities were performed using a digital conductivity meter Inolab Level-1 WTW (Germany), and were carried out in the temperature range 5–45°C at 1°C steps. The temperature was kept constant with a precision of ±0.05°C using an Ultrathermostat U-1 (Germany). The experiments were performed at atmospheric pressure and continuous stirring (600 rpm) by an electromagnetic stirrer. The relative error of the measurements (temperature, concentration and specific conductivity) was 0.1% during the experiments.

RESULTS AND DISCUSSION

The concentration and temperature dependence of the specific electrical conductivity κ of manganese(II) chloride aqueous solutions have been studied in our previous work [4]. The values of the equivalent electrical conductivity Λ have been calculated, and using the semi-empirical Fuoss–Onsager equation the values of the limiting equivalent conductance Λ° of $MnCl_2$ in aqueous solutions were found in the temperature interval 5-45°C. An

empirical equation for the temperature dependence of the limiting equivalent conductance of Mn^{2+} ions have been suggested [4]:

$$\lambda^{\circ}_{Mn^{2+}} = 26.5056 + 0.9200\, t + 5.4394 \times 10^{-3} t^2,\qquad(1)$$

where t is the temperature, °C, and $\lambda^{\circ}_{Mn^{2+}}$ is the limiting equivalent conductivity of the manganous ion, $S.cm^2/g\text{-}equiv$.

For the temperature dependence of the limiting equivalent conductance of Cl^- ions in aqueous solutions in the literature is given the following equation [3]:

$$\lambda^{\circ}_{Cl^-} = \exp\left(-7.33 + 3.31 \times 10^{3}/T - 7.69 \times 10^{5}/T^{2}\right),\qquad(2)$$

where T is the absolute temperature, K, and $\lambda^{\circ}_{Cl^-}$ is the limiting equivalent conductivity of the chloride ion, $S.cm^2/g\text{-}equiv$.

Using the mathematical apparatus described in detail earlier [2,6] the diffusion and kinetic parameters of dilute aqueous solutions of $MnCl_2$ were obtained. In Table 1 are summarized the equations used in present study, where D°_m is the molecule self-diffusion coefficient, cm^2/s, $D^{\circ}_{\pm}$ is the self-diffusion coefficients of the ion (cation or anion), cm^2/s, and $u^{\circ}_{\pm}$ is the limiting mobility, $cm^2/(V.s)$, $t^{\circ}_{\pm}$ is the transport number, r_{Stokes} is the hydrodynamic (Stokes) radius, Å, $r_{eff.}$ is the effective radius, Å, and n_s is the hydration number of the ion.

Table 1. Mathematical apparatus.

Characteristic	Mathematical expression	Equation
$D^{\circ}_{\pm}$	$D^{\circ}_{\pm} = \dfrac{RT\,\lambda^{\circ}_{\pm}}{\left\lvert z_{\pm}\right\rvert F^2}$	(3)
D°_m	$D^{\circ}_m = \dfrac{D^{\circ}_{+}D^{\circ}_{-}\left(z_{+} + \left\lvert z_{-}\right\rvert\right)}{z_{+}D^{\circ}_{+} + \left\lvert z_{-}\right\rvert D^{\circ}_{-}}$	(4)
$u^{\circ}_{\pm}$	$u^{\circ}_{\pm} = \dfrac{\lambda^{\circ}_{\pm}}{\left\lvert z_{\pm}\right\rvert F}$	(5)
$t^{\circ}_{\pm}$	$t^{\circ}_{\pm} = \dfrac{u^{\circ}_{\pm}}{u^{\circ}_{+} + u^{\circ}_{-}}$	(6)
r_{Stokes}	$r_{Stokes} = \dfrac{\left\lvert z_{\pm}\right\rvert F^2}{6\pi\, N_A\, \eta\, \lambda^{\circ}_{\pm}}$	(7)
$r_{eff.}$	$r_{eff.} = r_{Stokes} + 0.0103\varepsilon + r_y$	(8)
n_s	$n_s = \dfrac{4\pi}{3V_L}\left(r^3_{eff.} - r^3_{cryst.}\right)$	(9)

The parameters in the equations of Table 1 are as follows: T is the absolute temperature, K, R is the gas constant, $R = 8.314\ J/(mol.K)$, F is the Faraday's constant, $F = 96484.56\ C/mol$, N_A is the Avogadro's number, $N_A = 6.023 \times 10^{23}\ 1/mol$, $z_{\pm}$ is the ion charge, $\lambda^{\circ}_{\pm}$ is the limiting equivalent conductance of the ion, $S.cm^2/g\text{-}equiv$, and the values of the rest parameters: ε – the dielectric constant of H_2O, and η – the viscosity of H_2O, P, are calculated according to the equations given in the literature [7,8]. The values of $r_{cryst.}$ for the Mn^{2+} and Cl^- ions are taken from the literature [9], and r_y is a parameter known to be

1.13 Å for associated solvents having high values of ε (for example, water). V_L is the volume of H_2O molecule at a given temperature, $Å^3$.

In Table 2 are presented the obtained values of the diffusion and kinetic parameters of the ions and molecule in aqueous solutions of $MnCl_2$ at 5, 15, 25, 35 and 45°C.

Table 2. Values for the molecule of D^o_m and for the ions of $D^o_\pm$, $u^o_\pm$, $t^o_\pm$, r_{Stokes}, $r_{eff.}$ and n_s of aqueous solutions of $MnCl_2$ at different temperatures.

Parameter	Temperature									
	5°C		15°C		25°C		35°C		45°C	
	$MnCl_2$		$MnCl_2$		$MnCl_2$		$MnCl_2$		$MnCl_2$	
	Mn^{2+}	Cl^-	Mn^{2+}	Cl^-	Mn^{2+}	Cl^-	Mn^{2+}	Cl^-	Mn^{2+}	Cl^-
$D^o_m \times 10^5$, cm^2/s	0.70		0.95		1.25		1.58		1.95	
$D^o_\pm \times 10^5$, cm^2/s	0.39	1.16	0.53	1.56	0.71	2.02	0.90	2.54	1.12	3.08
$u^o_\pm \times 10^4$, $cm^2/(V.s)$	1.62	4.83	2.15	6.29	2.74	7.88	3.38	9.55	4.09	11.25
$t^o_\pm$	0.251	0.749	0.255	0.745	0.258	0.742	0.262	0.738	0.267	0.733
r_{Stokes}, Å	3.457	1.159	3.469	1.187	3.478	1.211	3.492	1.237	3.482	1.267
$r_{eff.}$, Å	5.472	3.174	5.444	3.162	5.416	3.149	5.393	3.318	5.348	3.134
n_s	22.89	3.65	22.53	3.60	22.13	3.53	21.78	3.48	21.15	3.45

The diffusion and kinetic parameters of the ions depend on other parameters which are temperature-dependent parameters. The limiting equivalent conductance of chloride ions in aqueous solutions $\lambda^o_{Cl^-}$ grows exponentially as the average increase is by 7.74 $S.cm^2/g$-equiv for each 5 degrees, and the limiting equivalent conductance of manganous ions in aqueous solutions $\lambda^o_{Mn^{2+}}$ is described by polynomial temperature dependence as the average increase is by 5.97 $S.cm^2/g$-equiv for each 5 degrees (see Eqs. (1) and (2)). The dielectric constant of water decreases with the increase in temperature (average decrease – 0.12 cP for each 5 degrees), and the viscosity of water η decreases with the increase in temperature (average decrease – 1.80 for each 5 degrees), but the decrease for ε in percentages is about 60%, and for η is only about 17%.

As can be seen in Table 2 the self-diffusion coefficients of the molecule and ions increase symbatically with temperature. The dependences that were obtained are second order polymomials with determination coefficients R^2 unities. The limiting mobility of the ions $u^o_\pm$ increases with the increase of temperature for both ions. This is due to the directly proportional dependence of $u^o_\pm$ on $\lambda^o_\pm$. The value of the transport number $t^o_\pm$ represents that part of the total quantity of electricity, which is transported by cations or anions, respectively. With the increase of temperature the ion transport number $t^o_\pm$ for Cl^- ions increases and that for Mn^{2+} ions decreases, and $t^o_\pm$ tend to become equal [6].

While the hydrodynamic radius r_{Stokes} of chloride ions increase with temperature almost linearly from 1.159 to 1.267 Å (see Table 2), the temperature dependence of r_{Stokes} of manganous ions pass through a maximum at around 38°C, as the change in the values is slight for the temperature interval 5-45°C, and the average r_{Stokes} of Mn^{2+} is 3.447 Å. This behavior can be explained mathematically if the temperature dependence of the product of $\lambda^o_\pm$ and η is taken into account. The relationship between the two radii, namely the Stokes and effective radius is simple (see Eq. (8) in Table1), but the obtained temperature dependences of $r_{eff.}$ for Mn^{2+} and Cl^- ions do not follow the same trends as those of r_{Stokes}.

The effective radii of the both ions decrease with increase in temperature, which is due to significantly reduction in viscosity of H_2O with temperature increase.

As can be seen from Table 2 the hydration numbers of the ions n_s decrease with the increase of temperature, because the parameter n_s follows the decreasing trend of the parameter $r_{eff.}$ for both Mn^{2+} and Cl^- ions. Moreover the increase of temperature leads to increase of the H_2O molecule volume V_L, and because of the inversely proportional dependence of n_s on V_L, the number of H_2O molecules in the hydration shells of the ions reduces by 1.74 for Mn^{2+} and by 0.20 for Cl^- ions in the studied temperature interval.

CONCLUSION

Using one relatively simple method, namely conductometric measurements on the series of electrolyte solutions, and by using appropriate mathematical apparatus, valuable parameters for the theory and practice of Mn^{2+} and Cl^- ions in aqueous solutions of manganese(II) chloride were derived. The temperature dependences of the diffusion and kinetic characteristics of Mn^{2+} and Cl^- ions were studied and the relationship with the properties of the solvent H_2O was evaluated.

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