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Determination of Diffusion Coefficients of Heavy Metal Ions (Ni^{3+}, Zn^{2+}, Ba^{2+}, and Mn^{2+}) at Infinite Dilution through Electrolytic Conductivity Measurements

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Abstract. One important parameter to examine the behavior and mass transfer properties of heavy metal ions is the diffusion coefficient. Due to the costly methods of its determination, a simple process correlating the molar conductivity data to diffusion coefficient was utilized. Molar conductivity data were determined for five (5) different dilute concentrations of the chlorides of the heavy metal ions (Ni^{3+}, Zn^{2+}, Ba^{2+}, and Mn^{2+}) and at temperatures ranging from 303.15 to 323.15 K. The infinite dilution diffusion coefficients of the heavy metals were estimated using the Nernst-Haskell equation and Nernst-Einstein equation. The molar conductivity and the diffusion coefficients values of the ions were in the order of $Ba^{2+} > Mn^{2+} > Zn^{2+} > Ni^{3+}$ with the Ba^{2+} having the highest molar conductivity with a correlated infinite dilution diffusion coefficient of 1.6565×10^{-9} m^2/s at 303.15 K. This study was able to predict the values of the infinite dilution diffusion coefficient of heavy metal ions and could contribute to a better understanding of the mobility of heavy metal ions in a water environment.

Keywords: Diffusion Coefficient, Electrolytic Conductivity, Heavy Metal, Infinite Dilution

INTRODUCTION

Heavy metal contamination is a major global concern today because of rapid industrialization. It occurs naturally on the earth's crust and in minimal amounts and is characterized by having a relatively high density; much higher than the average particle density of soil as well as five times greater than the density of water. Heavy metals are considered essential to human health. However, their excess release in the environment either by production or disposal increases their concentration above the safe threshold. Their ecological toxicity is becoming noticeable especially their effects on the aquatic ecosystem because of their ability to bio-accumulate and bio-magnify (Fu et al. 2014). They also affect human health, especially those people who work in industries such as mining, as they cause various diseases specifically cardiovascular,

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respiratory, reproductive, and endocrine systems (Al Bakheet et al. 2013). Due to the impact of these metals, studies are now conducted in order to further understand the fate and transport of these molecules.

An important transport property is the diffusion coefficient. It is used to further examine the mass transfer phenomena since the diffusion coefficient is required in the solution for notable equations and is a transport parameter that gives fundamental information about this phenomenon in the solution (Ribeiro et al. 2008). However, there are only a few studies published in the literature surrounding the diffusion coefficient of these heavy metals due to different factors such as having costly and time-consuming experiments. The main reason for this is the diffusion of liquids that usually requires experiments to be conducted for several days because of its slow process, therefore obtaining data can be tedious (Alizadeh, 1980).

Nevertheless, methods for determining the diffusion coefficient are available. The common methods for determining the diffusion coefficient include the diaphragm cell method (Robinson et al. 1965), optical method (Ambrosini et al. 2008), NMR spin echo technique (Lutz and Mendenhall, 2000), and Taylor dispersion method (Wang et al. 2009). However, as reported by Harned and French (1945), the conductance method can be applied in the determination of diffusion coefficients of electrolytes in dilute aqueous solutions; a much simpler tool that can yield accurate results. Recent studies have reported successfully correlate infinite dilution diffusion coefficient data from electrolytic conductance measurements (Soriano et al. 2011, and Soriano et al. 2018). These recent works justified the conductance method to evaluate the diffusion coefficient at infinitesimal concentration due to its simplicity along with its ability to provide theoretical information to assess the mobility of its constituent ions.

The present study determined the diffusion coefficient of heavy metal ions (Ni^{3+}, Zn^{2+}, Ba^{2+}, and Mn^{2+}) at infinite dilution using conductivity data. Specifically, it measured and correlated the conductivity as a function of concentration and temperature; calculated the infinite dilution diffusion coefficient based on the measured conductivity; assessed the effect of temperature on the calculated diffusion coefficient, and lastly determined other important parameters associated with the diffusion coefficient such as the infinite dilution self-diffusion coefficient of the ion and the hydrodynamic radii.

The study was limited to four well-known toxic heavy metals: Nickel (Ni^{3+}), Zinc (Zn^{2+}), Barium (Ba^{2+}), and Manganese (Mn^{2+}). The metals were in the form of chloride salts dissolved in water at different concentrations in order to determine the reliability of the experiment. Tests were done from 30°C to 50°C at a 5-degree increment. This research focused on determining the molar conductivity behavior of heavy metals at different concentrations and the molar diffusivities were correlated. The resulting molar conductivity data from the tests were used to determine the diffusion coefficients using the Nernst–Haskell equation. However, the study did not cover the toxicity of heavy metals and the mechanism of the diffusion of ions in solutions.

This research can be an aid in better understanding the behavior and mobility of various heavy metals in the environment. In engineering practice, this will be helpful in assessing the concentration of toxic heavy metals entering the water system, specifically from wastewater released by industrial plants. Moreover, data obtained from this study can be used to monitor the buildup of dissolved ionic species in water in evaporative cooling systems and boilers. Aside from the analysis of the mass transport properties of the ions, the data obtained is beneficial in the analysis of electrolyte systems.

EXPERIMENTAL SECTION

Chemicals

Metal ions of interest came from chloride salts. Five (5) grams of each sample of nickel chloride, zinc chloride, barium chloride, and manganese chloride were bought and used as supplied and without further purification. All of the metal chlorides were from MERCK Chemicals. All solutions were prepared using deionized water as solvent before every run in each experiment.

Preparation of Sample Solutions

The metal chloride solutions were prepared by weighing the amount of solute needed to make a 0.01 M stock solution of each sample using a digital balance. Deionized water was used as the solvent in all of the samples. From the prepared stock solution, it was further diluted to achieve the desired concentrations (0.001, 0.003, 0.005, and 0.008 $kmol/m^3$). A magnetic plate stirrer was used to mix the samples. The specific conductivity measurement procedure was executed five (5) times for each concentration and temperature and the results were recorded.

Conductivity Measurement

A test tube containing 20 ml of the sample was placed in a water bath for its temperature and specific conductivity measurement. A conductivity meter (CON 510 bench meter, Eutech Instruments) was used in such a procedure. A thermocouple (Oakton WD-35627-00 Acorn Temp TC Thermocouple Thermometer) with an accuracy of 0.5°C for temperature was used in the experiment. The specific conductivity was measured for all samples at increasing temperature and concentration. The set-up of the conductivity measurement is shown in Figure 1. This method was adapted as it is proven satisfactory by previous works (Soriano et al. 2011, and Soriano et al. 2018).

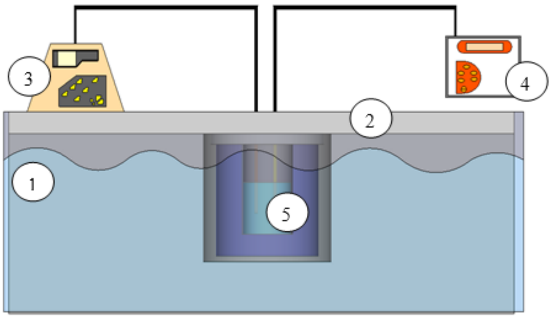


Fig. 1: Conductivity measurement set-up: (1) water bath; (2) polystyrene cover; (3) conductivity meter; (4) thermocouple; and (5) sample cell.

In between measurements, the conductivity cell was washed with de-ionized water to remove any adhering solution, and then dried. Measurements were done using the desired temperatures (at increments of 5°C from 30-50°C) and concentrations in five independent replicate runs for each metal chloride. The molar conductivity, Λ, is evaluated from the measured electrolytic conductivity, κ, and molar concentration, C, using the following relationship:

$$\Lambda = \frac{\kappa}{C} \quad (1)$$

Conductivity Measurement

The infinite dilution diffusion coefficients of the heavy metal chloride (A) in water (B) are computed using the Nernst–Haskell equation shown in Eq. (2).

$$D_{AB}^{0} = \frac{RT}{F^{2}} \frac{|z_{+}| + |z_{-}|}{|z,z|} \frac{\Lambda_{+}^{0}\Lambda_{-}^{0}}{\Lambda_{+}^{0} + \Lambda_{-}^{0}} \qquad (2)$$

Where D_{AB}^{0} is the diffusion coefficient of the solute (in this case the heavy metal chloride, A, in water, B) at infinite dilution in m^2/s, R the universal gas constant in J/mol-K, T the temperature in K and F the Faraday's constant. Other parameters in the equation are z_+ and z_- which designate the charge numbers of the cation and anion, respectively, and Λ_{+}^{0} and Λ_{-}^{0} are the molar conductivities of the cation and anion in S-m^2/mol, respectively, at infinite dilution. The self-diffusion coefficients of the heavy metal ions at infinite dilution are correlated using the Nernst–Einstein equation as presented in Eq. (3).

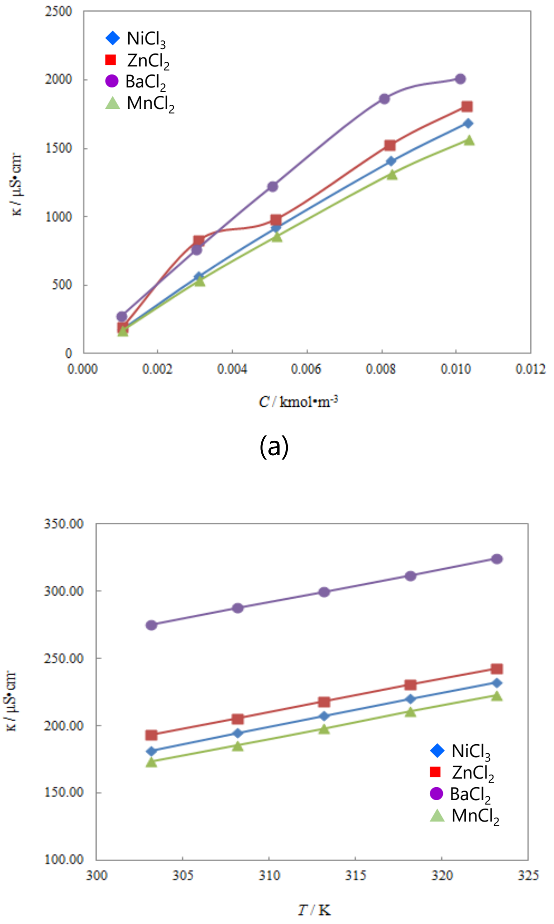
$$D_{ion}^{0} = \frac{RT\,\Lambda_{ion}^{0}}{|z_{ion}|F^{2}} \qquad (3)$$

Where D_{ion}^{0} is the self-diffusion coefficient of the ion at infinite dilution in m^2/s, Λ_{ion}^{0} the infinite dilution molar conductivity of the ion, and z_{ion} is the charge number of the ion.

RESULTS AND DISCUSSION

Conductivity Data

The measured electrolytic conductivities were presented in Table 2. The obtained results show that the specific conductivity of the metal chloride samples increases with an increase in temperature and an increase in concentration which are also representatively shown in Figures 2a and 2b, respectively. The electrical conductivity is temperature-dependent and an increase in the solution's temperature will cause a decrease in its viscosity and an increase in the mobility of the ions in the solution (Vanýsek, 2002). An increase in the temperature may also increase the number of ions in the solution due to the dissociation of molecules. As the conductivity of a solution is dependent on these factors then an increase in the solution's temperature will lead to an increase in its conductivity (Wagner, 2012).



(a)

(b)

Fig. 2: Plot of the molar conductivity of heavy metal chloride aqueous solutions as functions of (a) concentration at 303.15 K and (b) temperature at 0.001 M.

From the specific conductivity values obtained, the molar conductivity was calculated using Eq. (2). The molar conductivity is a characteristic quantity for every ion type. It is not only dependent on the ion type, but also the concentration and the temperature. The computed molar conductivity data for aqueous metal chloride solutions at different temperatures (303.15 to 323.15 K) and concentrations (0.001 to 0.01 kmol/m^3) are presented in Table 2.

Table 1. Electrolytic conductivities of the investigated binary systems at different concentrations and temperatures

Electrolytic Conductivity, κ [µS/cm]					
$NiCl_3$ (A) + Water (B): *C* [kmol/m^3]					
***T* (K)**	**0.00103**	**0.00309**	**0.00515**	**0.00824**	**0.01030**
303.15	181.52 ± 4.87*	570.08 ± 7.50	921.68 ± 6.16	1408.08 ± 11.28	1690.28 ± 4.77
308.15	194.73 ± 4.87	585.95 ± 3.54	935.95 ± 8.37	1423.35 ± 7.83	1702.95 ± 4.47
313.15	207.53 ± 5.27	600.21 ± 4.24	952.61 ± 7.89	1437.21 ± 5.83	1716.41 ± 5.89
318.15	220.29 ± 5.49	614.67 ± 3.90	968.07 ± 7.63	1453.07 ± 5.59	1730.87 ± 5.59
323.15	232.56 ± 5.77	628.73 ± 4.24	981.53 ± 6.61	1466.93 ± 5.54	1744.83 ± 5.32
$ZnCl_2$ (A) + Water (B): *C* [kmol/m^3]					
***T* (K)**	**0.00103**	**0.00308**	**0.00514**	**0.00822**	**0.01027**
303.15	193.06 ± 2.30	828.68 ± 5.10	981.48 ± 2.39	1527.08 ± 2.19	1809.88 ± 2.39
308.15	205.41 ± 3.04	844.95 ± 6.86	999.15 ± 7.79	1542.75 ± 4.09	1836.95 ± 1.41
313.15	218.09 ± 3.01	857.81 ± 6.58	1012.01 ± 10.16	1558.61 ± 5.32	1854.01 ± 0.84
318.15	230.69 ± 3.16	869.87 ± 6.19	1023.67 ± 11.08	1572.87 ± 6.27	1870.07 ± 3.58
323.15	242.61 ± 3.58	884.13 ± 6.88	1035.73 ± 11.98	1587.73 ± 4.53	1882.53 ± 3.11
$BaCl_2$ (A) + Water (B): *C* [kmol/m^3]					
***T* (K)**	**0.00101**	**0.00303**	**0.00505**	**0.00807**	**0.01009**
303.15	275.28 ± 1.52	762.28 ± 5.86	1224.48 ± 8.67	1867.48 ± 3.90	2013.68 ± 0.00
308.15	287.75 ± 1.79	775.35 ± 5.22	1239.35 ± 9.13	1882.75 ± 5.89	2032.95 ± 4.47
313.15	299.61 ± 2.07	789.81 ± 4.62	1253.01 ± 9.83	1898.21 ± 6.00	2048.21 ± 4.47
318.15	311.87 ± 2.07	803.27 ± 5.76	1266.47 ± 9.67	1912.07 ± 8.62	2065.47 ± 4.47
323.15	324.53 ± 1.79	817.73 ± 6.04	1281.73 ± 11.00	1926.53 ± 9.26	2078.73 ± 0.00
$MnCl_2$ (A) + Water (B): *C* [kmol/m^3]					
***T* (K)**	**0.00103**	**0.00310**	**0.00517**	**0.00826**	**0.01033**
303.15	173.40 ± 2.07	537.68 ± 2.45	859.28 ± 9.34	1316.68 ± 6.44	1565.28 ± 8.20
308.15	185.59 ± 2.55	553.15 ± 3.77	873.57 ± 8.02	1331.55 ± 9.63	1580.95 ± 7.04
313.15	197.91 ± 2.69	567.21 ± 4.24	888.81 ± 9.18	1346.21 ± 9.49	1598.41 ± 4.97
318.15	210.91 ± 2.00	580.27 ± 3.70	903.87 ± 8.53	1361.07 ± 8.65	1612.07 ± 3.85
323.15	222.85 ± 2.00	594.33 ± 2.79	917.73 ± 8.09	1374.93 ± 8.61	1626.53 ± 4.09

*mean value ± standard deviation.

Table 2. Molar conductivities of the investigated binary systems at different concentrations and temperatures

	Molar Conductivity, Λ [Sm^2/mol]				
	$NiCl_3$ (A) + Water (B): *C* [kmol/m^3]				
***T* (K)**	**0.00103**	**0.00309**	**0.00515**	**0.00824**	**0.01030**
303.15	0.01762	0.01845	0.01790	0.01709	0.01641
308.15	0.01891	0.01896	0.01817	0.01727	0.01653
313.15	0.02015	0.01942	0.01850	0.01744	0.01666
318.15	0.02139	0.01989	0.01880	0.01763	0.01680
323.15	0.02259	0.02035	0.01906	0.01780	0.01694
	$ZnCl_2$ (A) + Water (B): *C* [kmol/m^3]				
***T* (K)**	**0.00103**	**0.00308**	**0.00514**	**0.00822**	**0.01027**
303.15	0.01874	0.02691	0.01910	0.01858	0.01762
308.15	0.01994	0.02743	0.01944	0.01877	0.01789
313.15	0.02117	0.02785	0.01969	0.01896	0.01805
318.15	0.02240	0.02824	0.01992	0.01913	0.01821
323.15	0.02355	0.02871	0.02015	0.01932	0.01833
	$BaCl_2$ (A) + Water (B): *C* [kmol/m^3]				
***T* (K)**	**0.00101**	**0.00303**	**0.00505**	**0.00807**	**0.01009**
303.15	0.02726	0.02516	0.02425	0.02314	0.01996
308.15	0.02849	0.02559	0.02454	0.02333	0.02015
313.15	0.02966	0.02607	0.02481	0.02352	0.02030
318.15	0.03088	0.02651	0.02508	0.02369	0.02047
323.15	0.03213	0.02699	0.02538	0.02387	0.02060
	$MnCl_2$ (A) + Water (B): *C* [kmol/m^3]				
***T* (K)**	**0.00103**	**0.00310**	**0.00517**	**0.00826**	**0.01033**
303.15	0.01684	0.01734	0.01662	0.01594	0.01515
308.15	0.01802	0.01784	0.01690	0.01612	0.01530
313.15	0.01921	0.01830	0.01719	0.01630	0.01547
318.15	0.02048	0.01872	0.01748	0.01648	0.01561
323.15	0.02164	0.01917	0.01775	0.01665	0.01575

As presented in Table 2, the results of the present calculations of molar conductivities are found to be similar to the previous study conducted by Soriano et al. (2014) that reported molar conductivities of other heavy metal ions (Pb^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, and Hg^{2+}) behavior as a function of temperature and concentration. The experiment showed that the calculated molar conductivities of the heavy metal samples increase with the increase in temperature and decrease with the increase in concentration. The relationship between the molar conductivity and concentration can be associated with the interionic attractions which reduce the ability of the ions in an electrolyte solution to conduct the electric current between the electrodes. At more dilute solutions, ions would be so far that no interionic attractions are exerted, and the dissociation of the ions is increased. Therefore, this increases the molar conductivity. The behavior of these ions is in accordance with Kohlrausch's principle that at very low concentrations, ions are unaffected by each other's motion and therefore they migrate independently.

The samples used in the experiment are chloride salts and they are considered strong electrolytes in which the ions completely dissociate but the value of the molar conductivity would remain the same regardless of the concentration at which κ was measured. However, it was found that an increase in the concentration would result in a decrease in the molar conductivity, thus, at low concentrations, the molar conductivity is a linear function of C but tends to a limiting value, $\Lambda°$, the molar conductivity at infinite dilution. This often is applied to strong electrolytes and follows the empirical relation as shown in Eq. (4) where the κ depends primarily on the type of the electrolyte.

$$\Lambda = \Lambda^0 - \kappa C^{1/2} \tag{4}$$

Eq. (4) is the general formula that can be modified based on observed behavior as a function of concentration. In this present work the following equation was used:

$$\Lambda = \Lambda^0 + \alpha_1 C^{1/2} + \alpha_2 C \tag{5}$$

Where α_1 and α_2 are empirical parameters. Table 3 shows the calculations using Eq. (5). With an overall average absolute deviation (AAD) of 3.09 %, Eq. (5) satisfactorily correlated the concentration dependency of the molar conductivity.

The infinite dilution molar conductivities of each ion can be predicted by the relationship as in Eq. (5). This equation further demonstrates the behavior of the cations and anions to migrate without or negligible interionic forces at low concentrations. Therefore, these ions can be considered as migrating independently from each other, thus values for total molar conductivity can be expressed as the sum of contributions from its cation and anion:

$$\Lambda^0 = z_+ \Lambda_+^0 + z_- \Lambda_-^0 \tag{6}$$

The calculated values for the infinite dilution conductivities are presented in Table 4. From the calculated data, it was observed that for all temperatures, Ba^{2+} has the highest molar conductivity while Ni^{3+} has the lowest. The infinite dilution molar conductivities for the ions are of the order $Ba^{2+} > Mn^{2+} > Zn^{2+} > Ni^{3+}$.

Table 3. Calculated parameters of the investigated systems using Eq. (5)

T **(K)**	**$\Lambda°$ [Sm^2/mol]**	**α_1 [$m^3/kmol]^{1/2}$**	**α_2 [$(m^3/kmol)^{1/2}$ (Sm^2/mol)]**	**AAD* (%)**
		$NiCl_3$ (A) + Water (B)		
303.15	0.01572	0.10878	-0.95824	0.59
308.15	0.01800	0.05006	-0.63939	0.40
313.15	0.02066	-0.00408	-0.34778	0.19
318.15	0.02335	-0.05988	-0.04248	0.16
323.15	0.02602	-0.11597	0.26787	0.27
		$ZnCl_2$ (A) + Water (B)		
303.15	0.00908	0.45982	-3.82044	9.92
308.15	0.01171	0.40536	-3.51315	9.66
313.15	0.01453	0.34360	-3.15915	9.28
318.15	0.01743	0.27890	-2.78313	8.92
323.15	0.01996	0.22616	-2.49397	8.64
		$BaCl_2$ (A) + Water (B)		
303.15	0.02743	0.13162	-0.80608	2.20
308.15	0.03021	-0.04746	0.45631	2.27
313.15	0.03276	-0.10049	-0.16302	2.35
318.15	0.03552	-0.16044	0.17966	2.45
323.15	0.03823	-0.21673	0.48794	2.58
		$MnCl_2$ (A) + Water (B)		
303.15	0.01513	0.08002	-0.78710	0.60
308.15	0.01767	0.02844	-0.50872	0.54
313.15	0.02028	-0.02610	-0.20626	0.45
318.15	0.02313	-0.08700	0.13537	0.39
323.15	0.02567	-0.13971	0.42452	0.03

* AAD (%) = $(\frac{100}{n}) \times \sum_{i=1}^{n} |\frac{Calc-Expt}{Expt}|$ where *n* is the number of data points.

Table 4. Infinite dilution conductivities of the individual ions, $\Lambda°_{ions}$ at different temperatures

	10^2 $\Lambda°_{ions}$ [S-m^2/mol]				
T / K	**Ni^{3+}**	**Zn^{2+}**	**Ba^{2+}**	**Mn^{2+}**	**Cl^{-*}**
303.15	0.7140	0.7390	1.6565	1.0415	0.5700
308.15	0.8107	0.9015	1.8265	1.1995	0.6320
313.15	0.9147	1.0655	1.9770	1.3530	0.6780
318.15	1.0303	1.2495	2.1540	1.5345	0.7560
323.15	1.1410	1.4085	2.3220	1.6940	0.8210

*Taken from Soriano et al. (2011).

From the results of calculation using Eq. (6), the infinite dilution conductivities of the individual ions were correlated as a function of temperature using a simple exponential equation such as the Arrhenius-type equation given:

$$\Lambda_{ion}^{0} = A \times e^{\left(\frac{-E_a}{RT}\right)} \qquad (7)$$

Where A is the pre-exponential factor and E_a is the activation energy of ionic migration. The activation energy is attributed to causing configurational changes that occur during the migration of ions. Table 5 presents the calculation results using Eq. (7). With an overall AAD value of 0.70%, Eq. (7) satisfactorily correlated the temperature dependency of the infinite dilution conductivities of the considered heavy metal ions. As presented in Table 5, in terms of activation energy E_a for each ion, Zn^{2+} has the highest value and Ba^{2+} has the lowest value. The low value of activation energy of Ba^{2+} indicates the high mobility of the ions in the sample and can be associated with the high conductivity value as previously found. As such, the high AAD value for the Zn+2 ion can be attributed to its high activation energy which is an indication that the ion has low mobility resulting in a significant difference between the calculated and observed value.

Table 5. Parameters for Eq. (7) for the heavy metal ions considered in this study

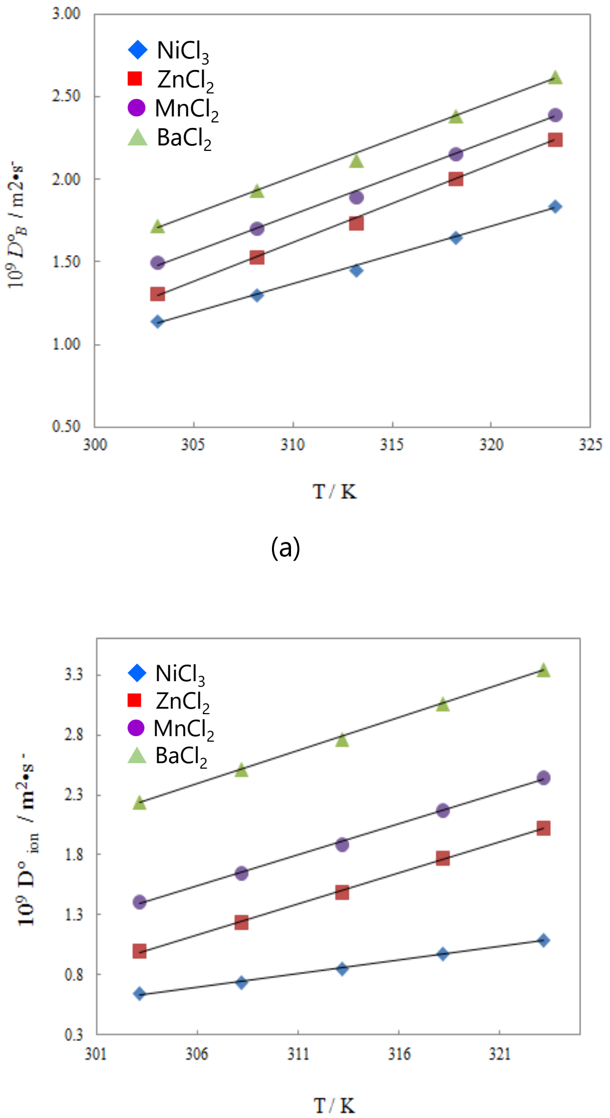
Ions	**A [Sm^2/mol]**	**10^{-4} E_a [J/mol]**	**AAD**
Ni^{3+}	13.93	1.9084	0.31
Zn^{2+}	202.23	2.5680	1.53
Ba^{2+}	3.73	1.3643	0.31
Mn^{2+}	25.76	1.9667	0.66

Infinite Dilution Diffusion Coefficient

The diffusion of aqueous salts at low concentrations has already been studied and is a well-established subject. In this study, the Nernst-Haskell equation given in Eq. (2) was used to estimate the diffusion coefficient for dilute solutions of a single salt. This correlation was applied because for metal chloride solutions when the salt dissociates in the solution, ions rather than molecules are formed. The Nernst-Haskell equation can be an accurate estimation of the diffusion coefficient by correlating the diffusion coefficient with the ion conductivity. The data for molar conductivity shown in Table 2 was used to estimate the infinite dilution diffusion coefficient of the investigated metal chloride systems. This method was already found accurate and reliable in correlating measured values of conductivity to predict the diffusion coefficient (Soriano et al. 2011, and Soriano et al. 2018). The resulting diffusion coefficient data using the Nernst-Haskell equation (Eq. 2) was presented in Table 6 and illustratively shown in Figure 3a. For all the studied metal chloride systems, it was found that higher temperatures cause an increase in the value of the diffusion coefficient indicating that mobility is greater at higher temperatures.

Table 6. Calculation results using Eq. (2), (3), and (8).

***T* / K**	**10^9 *D*°$_B$ [m^2/s] (Nernst-Haskell equation)**	**10^9 *D*°$_{[Cation]}$ [m^2/s] (Nernst-Einstein equation)**	**10^{10} r_s [m] (Stokes-Einstein equation)**	**10^9 *D*°$_{[Anion]}$ [m^2/s] (Nernst-Einstein equation)**	**10^{10} r_s [m] (Stokes-Einstein equation)**
			$NiCl_3$ (A) + Water (B)		
303.15	1.1441	0.64433	4.3185	1.5431	1.8032
308.15	1.3031	0.74366	4.2213	1.7392	1.8050
313.15	1.4519	0.85267	4.1195	1.8961	1.8525
318.15	1.6519	0.97577	4.0071	2.1480	1.8203
323.15	1.8372	1.0976	3.9424	2.3693	1.8263
			$ZnCl_2$ (A) + Water (B)		
303.15	1.3068	1.0003	2.7816	1.5431	1.8032
308.15	1.5336	1.2404	2.5308	1.7392	1.8050
313.15	1.7381	1.4899	2.3576	1.8961	1.8525
318.15	2.0074	1.7751	2.2027	2.1480	1.8203
323.15	2.2452	2.0324	2.1291	2.3693	1.8263
			$BaCl_2$ (A) + Water (B)		
303.15	1.7221	2.2423	1.2409	1.5431	1.8032
308.15	1.9382	2.5132	1.2491	1.7392	1.8050
313.15	2.1178	2.7644	1.2706	1.8961	1.8525
318.15	2.3849	3.0600	1.2778	2.1480	1.8203
323.15	2.6256	3.3505	1.2915	2.3693	1.8263
			$MnCl_2$ (A) + Water (B)		
303.15	1.4960	1.4098	1.9737	1.5431	1.8032
308.15	1.7086	1.6505	1.9020	1.7392	1.8050
313.15	1.8947	1.8919	1.8567	1.8961	1.8525
318.15	2.1585	2.1799	1.7936	2.1480	1.8203
323.15	2.3938	2.4443	1.7703	2.3693	1.8263



(a)

(b)

Fig. 3: Plot of the (a) infinite dilution diffusion coefficients (D°_B) and (b) infinite dilution self-diffusion coefficients (D°_{ion}) of the metal chloride systems as a function of temperature based on conductivity data, lines, and correlated values using (a) Eq. (2) and (b) Eq. (3), respectively.

The self-diffusion coefficients of the heavy metal ions at infinite dilution are correlated using the Nernst–Einstein equation as in Eq. (3). This equation specifically relates the molar conductivity of the electrolyte to the diffusion coefficients of its constituent ions. Table 6 presented the results of the calculations as well using Eq. (3) and is graphically shown in Figure 3b. The results showed that the self-diffusion coefficient also increase with an increase in the temperature. This may indicate that at higher temperatures, ions move faster as vibrational energy increases, therefore ionic migration is higher. From the results, it shows that among the heavy metal ions, Ba^{2+} has the highest mobility in water based on the diffusion coefficient, while Ni^{3+} is the least. The order of the values of diffusion coefficient are in order of $Ba^{2+} > Mn^{2+} > Zn^{2+} > Ni^{3+}$. This trend was observed for all temperatures.

Theoretically, an increase in temperature represents an increase in the average molecular speed of the ion, in other words, diffusion occurs faster at higher temperatures. At any given temperature, smaller molecules diffuse faster than larger molecules because the rate of diffusion depends on the molecular weight of the substance. The fast diffusion of Ba^{2+} that enables it to travel longer distances in water solutions could be attributed to its ionic radius. Among the four investigated metal ions, Ba^{2+} has the lowest value of the ionic radius; on the other hand, Ni^{3+} has the largest computed ionic radius. These results are consistent with the theory that ions with small values of ionic radius ideally should have a higher value of the diffusion coefficient due to the smaller weight of the ions.

Another parameter calculated is the hydrodynamic radii of the ions and the Stokes-Einstein equation was used to determine the effective hydrodynamic radius or Stokes radius of the ion as follows:

$$D_{ion}^{0} = \frac{kT}{6\pi\mu_B r_S} \quad (8)$$

Where k is the Boltzmann constant, T is the absolute temperature, μ_B is the viscosity of component B (in this case is water), and r_S is the effective hydrodynamic radius or Stokes radius of the ion.

From the presented results in Table 6, it is noteworthy to mention that the hydrodynamic radius of the investigated heavy metal ions (with the exemption of Ba^{2+}), decreases with an increase in temperature. The Stokes radius or hydrodynamic radius is different from the ionic radius of ions. In this experiment, Ba^{2+} has the highest value of molar conductivity even if in terms of ionic radius, it has the largest value. The explanation for this is that Ba^{2+} has the smallest value of the Stokes radius. The ionic radius is defined as the total distance from an atom's nucleus to the outermost orbital electron. Ionic radius measures the radius of a charged particle (Poling et al. 2001). The Stokes radius or the effective hydrodynamic radius of the ion is its effective radius taking into account all the water molecules it carries in its hydration sphere. Smaller ions produce stronger electric fields; thus, they are more extensively solvated than larger ions. Therefore, an ion with a smaller ionic radius may have a large hydrodynamic radius because it drags many solvent molecules through the solution as it migrates (Wilke and Chang 1955).

CONCLUSIONS

In this work, the diffusion coefficient data were determined from the measured conductivity data of the investigated systems. The Nernst-Haskell equation was used for the determination of the infinite dilution diffusion coefficient of the heavy metal chloride samples while the Nernst-Einstein equation was used to determine the self-diffusion coefficient of the ions. In addition to this, other parameters were calculated such as the pre-exponential factor, activation energy of ionic migration, and Stokes radius. Systems were studied in different concentrations at varying temperatures in order to investigate different conditions that may affect the behavior and transport of the ions. From the results, it was reported that the specific conductivity is temperature-dependent and an increase in temperature resulted in the increase of the specific conductivity values. The diffusion coefficient and the self-diffusion coefficient at infinite dilution both increased in value as the temperature increased indicating that mobility is greater at higher temperatures. The results of this study may provide sufficient information to better understand the mobility of heavy metal ions, especially in water systems.

NOMENCLATURE

Λ : molar conductivity [S-m^2/mol]
κ : electrolytic conductivity [μS/cm]
C : molar concentration [kmol/m^3]
D_{AB}^{0} : diffusion coefficient of the solute (in this case the heavy metal chloride, A, in water, B) at infinite dilution [m^2/s]
F : Faraday's constant
z_+ : charge number of the cation
z_- : charge number of the anion
Λ_+^0 : molar conductivity of the cation [S-m^2/mol]
Λ_-^0 : molar conductivity of the anion [S-m^2/mol]
D_{ion}^{0} : self-diffusion coefficient of the ion at infinite dilution [m^2/s]

Λ^{0}_{ion} : infinite dilution molar conductivity of the ion [S-m^2/mol]
z_{ion} : charge number of the ion
α_1, α_2 : empirical parameters of Eq. (5)
A : pre-exponential factor [S-m^2/mol]
E_a : activation energy of ionic migration [J/mol]
R : universal gas constant
k : Boltzmann constant
μ_B : viscosity of component B (in this case is water)
r_s : effective hydrodynamic radius or Stokes radius of the ion [m]

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