

Scientific paper

# Calculations of Diffusion Coefficients of Iron Salts in Aqueous Solutions at 298.15 K: A Useful Tool for the Knowledge of the Structure of these Systems

Ana C. F. Ribeiro,<sup>1,\*</sup> Abílio J. F. N. Sobral,<sup>1</sup> Cecilia I. A. V. Santos,<sup>1</sup>  
Victor M. M. Lobo,<sup>1</sup> Ana M. T. D. P. V. Cabral,<sup>2</sup> Francisco J. B. Veiga<sup>2</sup>  
and Miguel A. Esteso<sup>3</sup>

<sup>1</sup> Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal

<sup>2</sup> Faculty of Pharmacy, University of Coimbra, 3000-295 Coimbra, Portugal.

<sup>3</sup> Departamento de Química Física, Facultad de Farmacia, Universidad de Alcalá 28871.  
Alcalá de Henares (Madrid)

\* Corresponding author: E-mail: [anacrib@ci.uc.pt](mailto:anacrib@ci.uc.pt)

Telef: +351-239-854460; Fax: +351-239-827703

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## Abstract

Diffusion coefficients, thermodynamic and mobility factors of iron salts in aqueous solutions are estimated from Onsager-Fuoss model. The influence of the ion size parameter  $a$ , “mean distance of closest approach of ions”, determined from different approaches, on the variation of diffusion coefficients with concentration, is also discussed. The aim of this work is to have a better understanding of the structure of these systems and of the thermodynamic behaviour of iron salts in aqueous media.

**Keywords:** Ion size, iron, diffusion, solutions, electrolytes.

## 1. Introduction

Iron salts are widely used as coagulants in water and wastewater treatment<sup>1</sup> and in some other applications often treated in hydrometallurgy.<sup>2</sup> In addition, they are components with an important role in human metabolic processes (e.g., in enzymes and in hemoglobin)<sup>3</sup> justifying the increase of the knowledge of iron metabolism during the last few years, as indicated in the literature.<sup>4-9</sup>

Thus, despite many reasons justifying the importance of these metals and their salts, the understanding of these complex systems has not yet been well established. Consequently, their characterization is very important, helping us to better understand their structure, and to model them to practical applications. While numerous studies have been carried out on the thermodynamic properties of aqueous solutions containing iron ion (e.g.,<sup>10-12</sup>), few have taken into account the diffusion behaviour of

such systems. In fact, as far as the authors know, after careful literature search, only a few experimental and theoretical  $D$  data are available for some systems involving iron ion (e.g.<sup>2, 13-16</sup>). This paper reports theoretical data for differential binary mutual diffusion coefficients estimated from Onsager-Fuoss,  $D_{OF}$ , and other parameters, for eleven systems containing iron ion (i.e.,  $\text{FeBr}_2$ ,  $\text{FeBr}_3$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{Fe}(\text{ClO}_4)_2$ ,  $\text{Fe}(\text{ClO}_4)_3$ ,  $\text{Fe}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{C}_{12}\text{H}_{22}\text{FeO}_{14}$  at different concentrations (that is, from 0.000 to 0.005 mol dm<sup>-3</sup>), and at 298.15 K. These data are a useful tool for providing information on the interactions solute-solute and solute-solvent. For their estimation, we need to know parameters such as the “mean distance of closest approach of ions”,  $a$  (Å when expressed in Angstroms). Despite considerable work has already been done, much of these data are not available from the literature, mainly due to the complexity involved in their estimation. For example, parameter,  $a$ , depends

not only on the nature of the electrolyte and its concentration, but also on the nature and concentration of the species present in solution, which participate in the formation of an ionic atmosphere. Thus, having in mind the importance of parameter  $a$  on the knowledge of  $D$ , we propose to use different methods for the estimative of this parameter, and to extend our studies concerning the computation of  $D_{\text{OF}}$  from Onsager-Fuoss model, already started with some other electrolytes.<sup>15–23</sup> Estimations from this theory are adequate for these electrolytes in aqueous dilute solutions ( $c \leq 0.005 \text{ mol dm}^{-3}$ ), as has been shown for other similar systems,<sup>15–23</sup> where the theoretical data are consistent with experimental results.

## 2. Theory of Mutual Diffusion

### 2.1. The Onsager Fuoss Equation

As a first approach the experimental mutual diffusion coefficients at 298.15 K, we estimated diffusion coefficients,  $D_{\text{OF}}$ , by using Onsager-Fuoss model (eq. 1),<sup>24–26</sup> suggesting that  $D$  is a product of both kinetic,  $F_M$  (or molar mobility coefficient of a diffusing substance) and thermodynamic factors,  $F_T$  ( $F_T = c \partial \mu / \partial c = (1 + c \ln \gamma / c)$ ), where  $\mu$  and  $\gamma$  represent the chemical potential and the thermodynamic activity coefficient of the solute, respectively. Thus, two different effects can control the diffusion process, the ionic mobility and the gradient of the free energy,

$$D_{\text{OF}} = F_M \times F_T \quad (1)$$

where

$$F_M = (D^0 + \Delta_c + \Delta_a) = (2000RT\bar{M} / c) \quad (2)$$

with the subscripts  $c$  and  $a$  representing the cation and anion, respectively,  $\Delta_c$  and  $\Delta_a$  the first- and second-order electrophoretic terms and ( $\bar{M}c$ ) is given by equation (3)

$$\frac{\bar{M}}{c} = 1.0741 \times 10^{-20} \frac{\lambda_1^0 \lambda_2^0}{|z_1| \nu_1 A^0} + \frac{\Delta \bar{M}'}{c} + \frac{\Delta \bar{M}''}{c} \quad (3)$$

In equation (3), the first- and second-order electrophoretic terms,  $\Delta \bar{M}'/c$  and  $\Delta \bar{M}''/c$  are given by

$$\frac{\Delta \bar{M}'}{c} = \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2}{|z_1 z_2| 2(A^0)^2} \times \frac{3.132 \times 10^{-19}}{\eta_0 (\epsilon T)^{1/2}} \frac{c \sqrt{\tau}}{(1 + ka)} \quad (4)$$

and

$$\frac{\Delta \bar{M}''}{c} = \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2}{|z_1 z_2| 2(A^0)^2} \times \frac{3.132 \times 10^{-19}}{\eta_0 (\epsilon T)^{1/2}} \frac{c \sqrt{\tau}}{(1 + ka)} \quad (5)$$

where  $\tau = \sum c_i Z_i^2$  is the ionic strength,  $\eta_0$  and  $e$  are the viscosity and the dielectric constant of the solvent, respecti-

vely,  $k$  is the “reciprocal average radius of ionic atmosphere” (see e.g.,<sup>26</sup>),  $a$  is the mean distance of closest approach of ions,  $\phi(ka) = |e^{2ka} E_1(2ka) / (1 + ka)|$  has been tabulated by Harned and Owen,<sup>26</sup> and the other letters represent well-known quantities.

In this equation, phenomena such as complexation and/or ion association (e.g., short-range coulombic forces),<sup>27–29</sup> hydrolysis<sup>30</sup> and viscosity of solutions<sup>24</sup> are not taken into consideration.

### 2.2. Different Methods of Estimation of Parameter $a$ From Experimental and Theoretical Methods

There is no direct method for measuring the ion size parameter  $a$ , “mean distance of closest approach” from the Debye-Hückel theory, but it may be estimated from the data of Marcus<sup>31</sup> using two approximations. Firstly, the  $a$ -values were estimated as the sum of the ionic radii ( $R_{\text{ion}}$ ) reported by Marcus.<sup>31</sup> The  $R_{\text{ion}}$  values were obtained as the difference between the mean internuclear distance of a monoatomic ion, or the central atoms of polyatomic ions, and the oxygen atom of a water molecule in its first hydration shells ( $d_{\text{ion-water}}$ ), and the half of the mean intermolecular distance between two water molecules in liquid water ( $R_{\text{water}}$ ). Briefly,  $R_{\text{ion}} = d_{\text{ion-water}} - R_{\text{water}}$  and  $a = R_{\text{cation}} + R_{\text{anion}}$  (4<sup>th</sup> column in Table 1). In order to account for the effect of the ion hydration shell on the  $a$ -values, a second approximation considers the sum of the  $d_{\text{ion-water}}$  values reported by Marcus.<sup>31</sup> In other words, in this approach the  $a$ -values are determined as  $a = R_{\text{cation-water}} + R_{\text{anion-water}}$ . The values found are collected in the 5<sup>th</sup> column in Table 1.

From a table of ionic sizes presented by Kielland,<sup>32</sup> we have also estimated values of  $a$ , as the mean value of the effective radii of the hydrated ionic species of the electrolyte (2<sup>nd</sup> column in Table 1). The diameters of inorganic ions, hydrated to a different extent, have been calculated by two different methods, that is, from the crystal radius and deformability, accordingly to Bonino’s equation for cations,<sup>32</sup> and from the ionic mobilities.<sup>32</sup>

Molecular modelling studies are also important tools to estimate these parameters. Molecular mechanics (MM) studies are a valuable tool to interpret atom or ion dynamic relations. They are simpler than *ab initio* calculations and yet gave very close results. For that reason they are adequate to evaluate dynamic processes like solvation changes and mean distances of approach between species in solution. Among the MM methods,<sup>33</sup> MMFF94<sup>34</sup> is a reference in the area and was used in this study. The results obtained are summarized in the third column in Table 1.

## 3. Results and Discussion

Table 1 summarizes  $a$  values of 11 iron salts in aqueous solutions, determined from different experimental

techniques and/or theoretical approaches, and shows that, at least, one estimation of this parameter was done for every electrolyte.

Table 1 also shows that, in general,  $a$  values for some salts obtained by molecular mechanic studies (MMFF94) are approximately equal to those obtained from the sum of their ionic radii in solution (or crystal-lattice spacing), and smaller than the sum of the mean ion water internuclear distances (5<sup>th</sup> column of Table 1) and than those obtained from Kielland's data. The small differences among them are justified and acceptable, having in mind the limitations of each method. In fact, considering that in aqueous solution the ions are generally hydrated,  $a$  may be greater than the sum of the crystallographic radii of the ions, and less than the sum of the radii of the hydrated ions ( $a = d_{\text{cation-water}} + d_{\text{anion-water}}$ ); however, it is most probably less than this last limit because the hydration shells may be crushed. The smaller differences between values from Kielland method and Marcus' data ( $a = d_{\text{cation-water}} + d_{\text{anion-water}}$ ), can be explained by the limitations of Kielland equations, once they involve ionic mobilities (or phenomenological coefficients), which are rigorously valid only at very high dilution. Under those circumstances, the ion-ion and hydrodynamic interactions (not considered in this model) can actually influence the phenomenological coefficients and ionic mobilities and, consequently, lead to obtain non real values of parameter  $a$ .

**Table 1.** Summary of values of the mean distance of closest approach ( $a/10^{-10}$  m) for iron salts in aqueous solutions, estimated from experimental data, ionic radius and other theoretical approaches

Electrolyte	Kielland <sup>32</sup>	Molecular mechanics MMFF94 <sup>34</sup> a)	Marcus <sup>31</sup> b)	Marcus <sup>31</sup> c)
FeBr <sub>2</sub>	4.5	2.4	2.7	5.5
FeBr <sub>3</sub>	–	2.4	–	–
FeCl <sub>2</sub>	4.5	2.3	2.5	5.3
FeCl <sub>3</sub>	6.0	2.2	2.4	5.2
Fe(ClO <sub>4</sub> ) <sub>2</sub>	4.8	2.1	3.1	5.8
Fe(ClO <sub>4</sub> ) <sub>3</sub>	6.3	2.1	3.0	5.7
Fe(NO <sub>3</sub> ) <sub>2</sub>	4.5	2.3	2.5	5.3
Fe(NO <sub>3</sub> ) <sub>3</sub>	6.0	2.2	2.4	5.2
FeSO <sub>4</sub>	5.0	2.2	3.1	5.9
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	6.5	2.1	3.1	5.8
C <sub>12</sub> H <sub>22</sub> FeO <sub>14</sub>	–	2.0	–	–

$$^a) a = d_{\text{cation-anion}} \quad ^b) a = R_{\text{cation}} + R_{\text{anion}} \quad ^c) a = d_{\text{cation-water}} +$$

Considering equations (1) to (5), we have estimated  $D_{\text{OF}}$  using different values of  $a$ ,  $F_{\text{M}}$  from the average of parameter  $a$ , and  $F_{\text{T}}$  from available activity coefficient data<sup>26</sup> (Table 2). We should note that for dilute solutions, these calculations of  $D_{\text{OF}}$  are not greatly affected by the choice of  $a$ , except in the case FeSO<sub>4</sub>. In fact, almost all

$D_{\text{OF}}$  values obtained with different  $a$  values, are closer among them (deviations, in general, < 2%), and, consequently, we may use any value of the ionic size parameter  $a$  in eqs (1) to (5). In the case of FeSO<sub>4</sub>, the suggestion to use an average of  $a$  values is justified by the powerful dependence of  $D_{\text{OF}}$  on this parameter (deviations, in general, < 6%).

In general, the diffusion behaviour of these iron salts is similar, with exception of the three iron compounds – FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and C<sub>12</sub>H<sub>22</sub>FeO<sub>14</sub> – where lower values of  $D$  are observed. When the concentration increases, we see for all systems the decreasing of the diffusion coefficients,  $D_{\text{OF}}$ , and of the gradient of the free energy,  $F_{\text{T}}$ , and, the increasing of the mobility factor,  $F_{\text{M}}$ ; thus, from these facts, we can conclude that the variation in  $D$  is due mainly to the variation of  $F_{\text{T}}$  (attributed to the non-ideality in thermodynamic behaviour), and, to a lesser extent, to the electrophoretic effect in the mobility factor,  $F_{\text{M}}$  (Table 1). In fact, the values of the sum ( $\Delta_{\text{c}} + \Delta_{\text{a}}$ ), indicated in Table 2, are small and, consequently,  $F_{\text{M}}$  is almost constant in the respective concentration range.

These phenomena lead us to conclude that the behaviour of diffusion of the above systems containing iron ions in aqueous solutions at 298.15 K appears to be affected by the presence of ion-ion interactions (i.e., long-range coulombic forces). They may affect  $D$  in two ways: firstly, reducing the activity of the solute as compared with a fully dissociated electrolyte, and hence leading to lower values of  $F_{\text{T}}$  with the concentration (effect more accentuated in the cases of FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and C<sub>12</sub>H<sub>22</sub>FeO<sub>14</sub>), and secondly, increasing  $F_{\text{M}}$ , because the aggregate species resulting from these interactions<sup>27</sup> may offer less resistance to motion through the liquid. These phenomena can be explained if we consider the loss of hydration water from iron and different anions, which will lead to less resistance to motion through the liquid and, consequently, an increase of  $F_{\text{M}}$  when concentration increases.

## 4. Conclusions

No theory on diffusion in electrolyte solutions is capable of giving generally reliable data concerning the magnitude of the diffusion coefficient,  $D$ . However, for estimating purposes, when no experimental data is available, we suggest the use of Onsager-Fuoss for these electrolytes in aqueous dilute solutions (i.e.,  $c < 0.005$  mol dm<sup>-3</sup>), once for several systems they are in reasonable agreement with experimental data within 97%. In fact, for this interval of concentrations, the factors not taken into account in this model, such as viscosity, dielectric constant, hydration and association or complexation are not relevant. In these calculations, for almost indicated electrolytes, we may use any value in the literature for the ionic size parameter  $a$  in eqs (1) to (5), because slight variations in this parameter  $a$  have little effect on the final re-

Table 2.  $D_{OF}$ ,  $F_T$ ,  $F_M$ ,  $\Delta_c$  and  $\Delta_p$  of iron salts, calculated from equations (1) to (5) at 298.15 K<sup>(a)</sup>

Electrolyte	$c$ b)	$D_{OF}$	$D_{OF}$	$D_{OF}$	$D_{OF}$	$F_M$ c)	$(\Delta_c + \Delta_p)$	$F_T$ d)
FeBr <sub>2</sub>	0.000	( $a = 2.4 \times 10^{-10}$ m)	( $a = 2.7 \times 10^{-10}$ m)	( $a = 4.5 \times 10^{-10}$ m)	( $a = 5.5 \times 10^{-10}$ m)	( $a = 3.8 \times 10^{-10}$ m)	( $a = 3.8 \times 10^{-10}$ m)	( $a = 3.8 \times 10^{-10}$ m)
	0.001	1.270	1.270	1.270	1.270	1.270	0.000	1.000
	0.002	1.216	1.215	1.216	1.216	1.216	0.017	0.945
	0.003	1.205	1.203	1.200	1.201	1.298	0.028	0.925
	0.004	1.195	1.193	1.190	1.192	1.306	0.036	0.911
	0.005	1.187	1.189	1.187	1.190	1.312	0.042	0.901
FeCl <sub>2</sub>	0.000	( $a = 2.3 \times 10^{-10}$ m)	( $a = 2.5 \times 10^{-10}$ m)	( $a = 4.5 \times 10^{-10}$ m)	( $a = 5.3 \times 10^{-10}$ m)	( $a = 3.6 \times 10^{-10}$ m)	( $a = 3.6 \times 10^{-10}$ m)	( $a = 3.6 \times 10^{-10}$ m)
	0.001	1.256	1.256	1.256	1.256	1.256	0.000	1.000
	0.002	1.202	1.202	1.202	1.203	1.276	0.020	0.943
	0.003	1.193	1.190	1.187	1.188	1.284	0.028	0.924
	0.004	1.182	1.179	1.177	1.179	1.293	0.037	0.910
	0.005	1.175	1.170	1.171	1.172	1.299	0.043	0.900
FeBr <sub>3</sub>	0.000	( $a = 2.4 \times 10^{-10}$ m)	e)	e)	e)	( $a = 2.4 \times 10^{-10}$ m)	( $a = 2.4 \times 10^{-10}$ m)	( $a = 2.4 \times 10^{-10}$ m)
	0.001	1.293	1.293	1.293	1.293	1.293	0.000	1.000
	0.002	1.223	1.223	1.223	1.223	1.391	0.089	0.879
	0.003	1.206	1.206	1.206	1.206	1.430	0.137	0.837
	0.004	1.197	1.197	1.197	1.197	1.474	0.181	0.807
	0.005	1.190	1.190	1.190	1.190	1.511	0.218	0.784
FeCl <sub>3</sub>	0.000	( $a = 2.3 \times 10^{-10}$ m)	( $a = 2.4 \times 10^{-10}$ m)	( $a = 5.2 \times 10^{-10}$ m)	( $a = 6.0 \times 10^{-10}$ m)	( $a = 4.0 \times 10^{-10}$ m)	( $a = 4.0 \times 10^{-10}$ m)	( $a = 4.0 \times 10^{-10}$ m)
	0.001	1.276	1.276	1.276	1.276	1.276	0.000	1.000
	0.002	1.211	1.207	1.188	1.188	1.341	0.065	0.888
	0.003	1.196	1.190	1.170	1.172	1.374	0.098	0.853
	0.004	1.187	1.180	1.162	1.165	1.400	0.124	0.830
	0.005	1.180	1.172	1.160	1.162	1.423	0.147	0.812

Table 2.  $D_{OF}$ ,  $F_T$ ,  $F_M$ ,  $\Delta_c$  and  $\Delta_p$  of iron salts, calculated from equations (1) to (5) at 298.15 K<sup>(a)</sup>(cont.)

Electrolyte	$c$ b)	$D_{OF}$	$D_{OF}$	$D_{OF}$	$D_{OF}$	$F_M$ c)	$(\Delta_c + \Delta_p)$
Fe(ClO <sub>4</sub> ) <sub>2</sub>	0.000	( $a = 2.1 \times 10^{-10}$ m)	( $a = 3.1 \times 10^{-10}$ m)	( $a = 4.8 \times 10^{-10}$ m)	( $a = 5.8 \times 10^{-10}$ m)	( $a = 4.0 \times 10^{-10}$ m)	( $a = 4.0 \times 10^{-10}$ m)
	0.001	1.190	1.190	1.190	1.190	1.190	0.000
	0.002	1.140	1.142	1.140	1.140	1.207	0.017
	0.003	1.132	1.127	1.125	1.127	1.216	0.026
	0.004	1.122	1.117	1.116	1.118	1.222	0.032
	0.005	1.115	1.107	1.110	1.110	1.228	0.038
Fe(ClO <sub>4</sub> ) <sub>3</sub>	0.000	( $a = 2.1 \times 10^{-10}$ m)	( $a = 3.0 \times 10^{-10}$ m)	( $a = 5.7 \times 10^{-10}$ m)	( $a = 6.3 \times 10^{-10}$ m)	( $a = 4.3 \times 10^{-10}$ m)	( $a = 4.3 \times 10^{-10}$ m)
	1.201	1.201	1.201	1.201	1.201	1.201	0.000

0.001	1.137	1.124	1.116	1.116	1.256	0.055
0.002	1.121	1.106	1.099	1.101	1.284	0.083
0.003	1.111	1.095	1.091	1.093	1.306	0.105
0.004	1.104	1.089	1.086	1.087	1.327	0.126
0.005	1.099	1.083	1.080	1.082	1.344	0.143
Fe(NO <sub>3</sub> ) <sub>2</sub>	( <i>a</i> = 2.3 × 10 <sup>-10</sup> m)	( <i>a</i> = 2.5 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.5 × 10 <sup>-10</sup> m)	( <i>a</i> = 5.3 × 10 <sup>-10</sup> m)	( <i>a</i> = 3.6 × 10 <sup>-10</sup> m)	( <i>a</i> = 3.6 × 10 <sup>-10</sup> m)
0.000	1.222	1.222	1.222	1.222	1.222	0.000
0.001	1.170	1.169	1.170	1.170	1.239	0.017
0.002	1.160	1.159	1.155	1.155	1.250	0.028
0.003	1.150	1.149	1.145	1.146	1.257	0.035
0.004	1.143	1.140	1.138	1.140	1.264	0.042
0.005	1.137	1.135	1.133	1.136	1.269	0.047
Fe <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>	( <i>a</i> = 2.2 × 10 <sup>-10</sup> m)	( <i>a</i> = 2.4 × 10 <sup>-10</sup> m)	( <i>a</i> = 5.2 × 10 <sup>-10</sup> m)	( <i>a</i> = 6.0 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.0 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.0 × 10 <sup>-10</sup> m)
0.000	1.237	1.237	1.237	1.237	1.237	0.000
0.001	1.172	1.168	1.150	1.150	1.298	0.061
0.002	1.157	1.151	1.133	1.134	1.329	0.092
0.003	1.147	1.141	1.125	1.128	1.347	0.110
0.004	1.140	1.137	1.120	1.120	1.373	0.136
0.005	1.135	1.129	1.115	1.115	1.393	0.156

Table 2. *D*<sub>OF</sub>, *F*<sub>T</sub>, *F*<sub>M</sub>,  $\Delta_c$  and  $\Delta_a$  of iron salts, calculated from equations (1) to (5) at 298.15 K<sup>(a)</sup> (cont.)

Elec-trolyte	<i>c</i> b)	<i>D</i> <sub>OF</sub>	<i>D</i> <sub>OF</sub>	<i>D</i> <sub>OF</sub>	<i>D</i> <sub>OF</sub>	<i>F</i> <sub>M</sub> e)	( $\Delta_c + \Delta_a$ )	<i>F</i> <sub>T</sub> d)
FeSO <sub>4</sub>	0.000	( <i>a</i> = 2.2 × 10 <sup>-10</sup> m)	( <i>a</i> = 3.1 × 10 <sup>-10</sup> m)	( <i>a</i> = 5.0 × 10 <sup>-10</sup> m)	( <i>a</i> = 5.9 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.0 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.0 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.0 × 10 <sup>-10</sup> m)
	0.001	0.853	0.853	0.853	0.853	0.853	0.000	1.000
	0.002	0.708	0.733	0.726	0.724	0.882	0.029	0.833
	0.003	0.688	0.698	0.688	0.685	0.908	0.055	0.780
	0.004	0.675	0.675	0.664	0.660	0.921	0.068	0.747
	0.005	0.667	0.660	0.658	0.650	0.934	0.081	0.723
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.000	( <i>a</i> = 2.1 × 10 <sup>-10</sup> m)	( <i>a</i> = 3.1 × 10 <sup>-10</sup> m)	( <i>a</i> = 5.8 × 10 <sup>-10</sup> m)	( <i>a</i> = 6.5 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.4 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.4 × 10 <sup>-10</sup> m)	( <i>a</i> = 4.4 × 10 <sup>-10</sup> m)
	0.001	0.815	0.815	0.815	0.815	0.815	0.000	1.000
	0.002	0.767	0.754	0.746	0.747	0.898	0.083	0.831
	0.003	0.762	0.746	0.737	0.737	0.943	0.128	0.788
	0.004	0.761	0.745	0.735	0.735	0.965	0.150	0.763
	0.005	0.759	0.742	0.733	0.733	0.984	0.169	0.745
C <sub>12</sub> H <sub>22</sub> FeO <sub>14</sub> <sup>b)</sup>	0.000	( <i>a</i> = 2.3 × 10 <sup>-10</sup> m)	( <i>a</i> = 2.3 × 10 <sup>-10</sup> m)	g)	g)	( <i>a</i> = 2.3 × 10 <sup>-10</sup> m)	( <i>a</i> = 2.3 × 10 <sup>-10</sup> m)	( <i>a</i> = 2.3 × 10 <sup>-10</sup> m)
	0.001	0.830	0.830	0.830	0.830	0.830	0.000	1.000
	0.002	0.793	0.793	0.793	0.793	0.844	0.014	0.940
	0.003	0.786	0.787	0.787	0.787	0.857	0.027	0.918
	0.004	0.775	0.786	0.786	0.786	0.871	0.041	0.902
	0.005	0.770	0.775	0.775	0.775	0.872	0.042	0.889
						0.877	0.047	0.878

<sup>a)</sup> *D*<sub>OF</sub>, *F*<sub>M</sub>,  $\Delta_c$  and  $\Delta_a$  in units of in units of 10<sup>9</sup> m<sup>2</sup> s<sup>-1</sup>, <sup>b)</sup> *c* in units of mol dm<sup>-3</sup>, <sup>c)</sup> *F*<sub>M</sub> = (*D*<sup>0</sup> +  $\Delta_c$  +  $\Delta_a$ ), where ( $\Delta_1 + \Delta_2$ ) represents the electrophoretic corrections (eq. 2), <sup>d)</sup> *F*<sub>T</sub> from available activity coefficient data<sup>5,6</sup>, <sup>e)</sup> There is only one estimated value for parameter *a*. <sup>f)</sup> *D*<sub>OF</sub> values have been estimated by using  $\lambda^0 = 34 \times 10^{-4}$  m<sup>2</sup> Ω<sup>-1</sup> mol<sup>-1</sup><sup>35</sup> for the equivalent conductance at infinitesimal concentration of gluconate ion, <sup>e</sup>, at 298.15 K. <sup>g)</sup> See note e).

sults of  $D_{OF}$ , with exception of the  $FeSO_4$ , where it is recommendable to use the average value of all of them. For all systems, the variation in  $D$  is due mainly to the variation of  $F_T$  (attributed to the non-ideality in thermodynamic behaviour), and, to a lesser extent, the electrophoretic effect in the mobility factor,  $F_M$ .

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## Povzetek

S pomočjo Onsager-Fuossvega modela smo določili difuzijske koeficiente železovih soli v vodnih raztopinah ter pokazali, kako vrednost razdalje najmanjšega približanja ionov, dobljena iz različnih modelov, vpliva na njihovo vrednost. Dobljeni rezultati nam dajo boljši vpogled in razumevanje strukture in lastnosti teh sistemov.