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Effect of the mean distance of closest approach of ions on the diffusion coefficient calculations in aqueous solutions of silver salts

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ABSTRACT

Diffusion coefficients of silver salts in aqueous solutions are estimated from Onsager-Fuoss and Pikal models, using different values of the mean distance of closest approach of ions, a , determined from different theoretical procedures. The influence of this parameter on the diffusion of these systems is discussed.

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R É S U M É

Les coefficients de diffusion de certains sels d'argent dans des solutions aqueuses sont estimés en partant des modèles d'Onsager-Fuoss et de Pikal, et en utilisant différentes valeurs de la distance moyenne d'approche d'ions, a , déterminée à partir de différentes méthodes théoriques. On discute l'influence de ce paramètre sur le comportement de la diffusion de ces systèmes.

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1. Introduction

The diffusion of silver salts in aqueous solutions is of great interest not only for fundamental purposes, but also for many technical fields, such as the action of corrosive media (e.g. saliva, bacterium plaque, decomposition of food) in silver dental materials [1,2], and for the impact of these electrolytes on the environment [3,4] and on biological systems (e.g. [5,6]). However, experimental data for diffusion coefficients in aqueous solutions are very scarce due to the experimental difficulties in their measurements. In fact, as far as the authors know, after careful search in the literature, only a few

experimental and theoretical diffusion coefficients, D , are available for some systems involving silver ions (e.g. [7,8]). Therefore, the calculation of these transport coefficients in dilute solutions, accordingly to the theories of Onsager-Fuoss and Pikal may provide a valuable estimation with a good approximation for symmetrical electrolytes of the type 1:1 and for polyvalent electrolytes (mainly 2:2), respectively, when no experimental data are available (e.g. [9,10]). Both theories introduce the ion size parameter a , mean distance of closest approach, but it is well known that it is not possible to accurately know the mean distance of closest approach of ions, a , in an electrolyte solution, however desirable that it would be. In this perspective, for systems containing silver ions, we propose to estimate this parameter from different methods (studies already started with some other electrolytes [9–14]), as well as to analyse its effect in the calculation of the respective diffusion coefficients D_{OF} and D_{Pikal} .

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In summary, this article reports theoretical data for differential binary mutual diffusion coefficients estimated from Onsager-Fuoss, D_{OF} , and Pikal, D_{Pikal} , for fifteen systems containing silver ion (i.e., AgF, AgBr, AgCl, AgI, AgClO₂, AgClO₃, AgClO₄, AgC₂H₃O₂, AgMnO₄, AgNO₂, AgNO₃, Ag₂SO₄, Ag₂S₂O₄, Ag₂S₂O₈ and Ag₂SeO₄) at different concentrations (that is, from 0.000 to 0.010 mol dm⁻³), and at 298.15 K. These data, calculated by using the different values of parameter a , will permit us to conclude if the accurate knowledge of that distance is critical, concerning the determination of these transport properties. In general, estimations from these theories are adequate for these electrolytes in aqueous dilute solutions ($c \leq 0.010$ mol dm⁻³), as has been shown for other similar systems (e.g. [12–14]), where the theoretical data are consistent with our experimental results (deviations < 3%, within the imprecision of this method).

2. Estimation of a by different theoretical approaches

2.1. Estimations of a values from Kielland data

The values of a have been estimated as the mean value of the effective radii of the hydrated ionic species of the electrolyte (2nd column in Table 1), using a table of ionic sizes presented by Kielland (i.e., rounded values of the effective diameter of the hydrated ion shown in the Table 1 of reference [15]). The diameters of inorganic ions, hydrated to a different extent, have been estimated by two different methods, that is, from the crystal radius and deformability, and from the ionic mobilities [15].

2.2. Estimation of a values from Marcus data

From the data of Marcus (Table XIII of reference [16]), two approximations were considered to obtain the a

values of silver salts in aqueous solution. Firstly, the a values were determined as the sum of the ionic radii (R_{ion}) reported by Marcus [16]. The R_{ion} values were obtained as the difference between the mean internuclear distance between a monoatomic ion, or the central atoms of a polyatomic ion, and the oxygen atom of a water molecule in its first hydration shell ($d_{ion-water}$) and the half of the mean intermolecular distance between two water molecules in the bulk liquid water (the mean radius of a water molecule, $R_{water} = (1.393 \pm 0.002) \times 10^{-10}$ m [16]; this value was determined after considering the packaging effect produced by the electrostriction phenomenon derived from the strong electrical field near the ion [16]. That is, $R_{ion} = d_{ion-water} - R_{water}$ and $a = R_{cation} + R_{anion}$. These values are summarized in the third column in Table 1. For the determination of interparticle distances, $d_{ion-water}$, different methods were used, such as diffraction methods (X-ray diffraction, neutron diffraction, X-ray absorption fine structure-EXAFS- measurements and others) and computer simulations methods (molecular dynamics and Monte Carlo methods).

Having in mind the effect of the ion hydration shell on the a values, a second approximation considers the sum of the $d_{ion-water}$ values reported by Marcus [16] was also done. In this approach, the a values are determined as $a = d_{cation-water} + d_{anion-water}$. The values found are collected in the fourth column in Table 1.

2.3. Molecular mechanic studies (MM+)

Molecular mechanic studies are a valuable tool to interpret atom or ion dynamic relations. They are faster to achieve and adequate to evaluate dynamic processes involving dozens of molecules, like solvation changes around cations and anions and reasonable mean distances of approach between species in solution

Table 1

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

Electrolyte	Kielland [15]	Marcus [16] $a = R_{cation} + R_{anion}$	Marcus [16] $a = d_{cation-water} + d_{anion-water}$	Molecular mechanics (MM+) [17]	
				^a Vacuum	^b Periodic box of water molecules
AgF	3.0	2.3	5.0	3.5	3.9
AgBr	–	3.0	5.8	3.7	3.4
AgCl	–	2.8	5.6	3.8	3.5
AgI	–	3.3	6.1	4.0	3.7
AgClO ₂	3.4	–	–	3.2	3.2
AgClO ₃	3.0	–	–	3.3	3.4
AgClO ₄	3.0	3.4	6.1	3.3	3.3
AgC ₂ H ₃ O ₂	3.5	–	–	4.6	3.8
AgMnO ₄	3.0	–	–	3.3	3.6
AgNO ₂	2.8	–	–	3.3	3.4
AgNO ₃	2.5	2.8	5.6	3.4	3.3
Ag ₂ SO ₄	3.3	3.4	6.2	3.3 ^c	3.3 ^c
Ag ₂ S ₂ O ₄	–	–	–	3.8 ^c	4.7 ^c
Ag ₂ S ₂ O ₈	3.3	–	–	3.4 ^c	4.1 ^c
Ag ₂ SeO ₄	–	3.6	6.4	3.3 ^c	3.7 ^c

^a The values indicated represent the distance between the centres of cation and anion in vacuum after MM+ geometry optimization by energy minimization.

^b The values indicated represent the distance between the centres of cation and anion in a box of 216 water molecules, after global geometry optimization by energy minimization by MM+ in HyperChem 7.5, taking into account the solvation process.

^c Average of four distances from all Ag⁺ to all O⁻ in the anion.

taking into account all solvent molecules within a reasonable distance from the solute ions. Among the Molecular Mechanic methods [17], MM+ developed to be a reference in the area. Consequently, we use it to investigate both the dynamic process of water solvation and the distribution of water molecules around the electrolytes which are discussed in this paper.

The results obtained are summarized in the last columns in Table 1. The values indicated in the fifth column represent the distance between the centres of cation and anion in vacuum after MM+ geometry optimization by energy minimization. The sixth column represent the same calculations inside a periodic box of 216 water molecules, taking into account all the 216 molecules and the ions. Geometry optimization by energy minimization calculations were performed in a HP Evo dc7700 workstation using the MM+ force field in HyperChem 7.5 software package from Hypercube Inc., 2000, USA. The geometry optimizations used a Polak-Ribiere conjugated gradient algorithm for energy minimization in vacuum or water, with a final gradient of 0.1 kcal/Å³mol. The periodic box of water molecules comprises 216 water molecules in all calculations.

3. Estimations of diffusion coefficients from Onsager-Fuoss, D_{OF} , and Pikal models, D_{Pikal}

The description of the theories of the Onsager and Pikal is adequately described in the literature [18–22], and, consequently, we only report the main points on the method of computation of the diffusion coefficients of silver salts in aqueous solutions.

The mutual diffusion coefficients at 298.15 K have been estimated by the Onsager-Fuoss and Pikal equations (Eqs. (1) and (8) [18–22]) (Table 2).

$$D = \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c}\right) (D^0 + \Sigma \Delta_n) \quad (1)$$

where D is the mutual diffusion coefficient of the electrolyte, the first term in parenthesis is the activity factor, y_{\pm} is the mean molar activity coefficient, c is the concentration in mol dm⁻³, D^0 is the Nernst limiting value of the diffusion coefficient, and Δ_n are the electrophoretic terms given by:

$$\Delta_n = k_B T A_n \frac{(z_1^n t_2^0 + z_2^n t_1^0)^2}{|z_1 z_2| a^n} \quad (2)$$

where k_B is the Boltzmann's constant; T is the absolute temperature; A_n are functions of the dielectric constant, of the solvent viscosity, of the temperature, and of the dimensionless concentration-dependent quantity (ka), k being the reciprocal of average radius of the ionic atmosphere; t_1^0 and t_2^0 are the limiting transport numbers of the cation and anion, respectively.

Since the expression for the electrophoretic effect has been derived on the basis of the expansion of the exponential Boltzmann function, because that function is consistent with the Poisson equation, we only would

have to take into account the electrophoretic term of the first and the second order ($n=1$ and $n=2$).

$$D = \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c}\right) (D^0 + \Delta_1 + \Delta_2) \quad (3)$$

The theory of mutual diffusion in binary electrolytes, developed by Pikal [22], includes the Onsager-Fuoss equation, but it has new terms resulting from the application of the Boltzmann exponential function for the study of diffusion. In other words, instead of approximating the Boltzmann exponential by a truncated power series, the calculations are performed retaining the full Boltzmann exponential. As a result of this procedure, a term representing the effect of ion-pair formation appears in the theory as a natural consequence of the electrostatic interactions. The electrophoretic correction appears now as the sum of two terms:

$$\Delta v_j = \Delta v_j^L + \Delta v_j^S \quad (4)$$

where Δv_j^L represents the effect of long-range electrostatic interactions, and Δv_j^S represents them as short-range ones.

Designated by $M = 10^{12} L/c$ is the solute thermodynamic mobility, where L is the thermodynamic diffusion coefficient, ΔM can be represented by the equation:

$$\frac{1}{M} = \frac{1}{M^0} \left(1 - \frac{\Delta M}{M^0}\right) \quad (5)$$

where M^0 is the value of M for infinitesimal concentration, and

$$\Delta M = \Delta M^{OF} + \Delta M_1 + \Delta M_2 + \Delta M_A + \Delta M_{H1} + \Delta M_{H2} + \Delta M_{H3} \quad (6)$$

The first term on the right hand in the above equation ΔM^{OF} represents the Onsager-Fuoss term for the effect of the concentration in the solute thermodynamic mobility M ; the second term ΔM_1 is a consequence of the approximation applied on the ionic thermodynamic force; the other terms result from the Boltzmann exponential function.

The relation between the solute thermodynamic mobility and the mutual diffusion coefficient is given by:

$$D = \frac{L}{c} 10^3 RT \nu \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (7)$$

where R is the gas constant, and ν is the number of ions formed upon complete ionization of one solute "molecule". From Eqs. (5) and (8), we obtain a version of the Pikal's equation more useful for estimating the mutual diffusion coefficients of electrolytes D_{Pikal} . That is,

$$D_{Pikal} = \frac{10^3 RT \nu}{M^0} \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c}\right) \left(1 - \frac{\Delta M}{M^0}\right) \quad (8)$$

From this equation, where the ion pairs are considered, it is possible to obtain a more realistic D for symmetrical polyvalent electrolytes than the Onsager-Fuoss model. However, concerning polyvalent non-symmetrical electrolytes, the full use of the Boltzmann' exponential in Pikal's development lead us to obtain D with major error,

Table 2

Estimated values of diffusion coefficients from Onsager-Fuoss and Pikal Eqs. (1) and (8), D_{OF} , and D_{Pikal} , using different values of a (Table 1) of silver salts in aqueous solutions at 298.15 K^a.

Electrolyte	c^b	D_{OF}	D_{OF}	D_{OF}	D_{OF}	D_{OF}	D_{Pikal}	D_{Pikal}	D_{Pikal}	D_{Pikal}	D_{Pikal}
AgF		($a = 2.5$ nm)	($a = 3.0$ nm)	($a = 3.5$ nm)	($a = 3.9$ nm)	($a = 5.0$ nm)	($a = 2.3$ nm)	($a = 3.0$ nm)	($a = 3.5$ nm)	($a = 3.9$ nm)	($a = 5.0$ nm)
	0.000	1.556	1.556	1.556	1.556	1.556	1.556	1.556	1.556	1.556	1.556
	0.001	1.533	1.533	1.533	1.533	1.534	1.532	1.532	1.532	1.534	1.534
	0.002	1.524	1.524	1.525	1.526	1.526	1.523	1.523	1.523	1.526	1.526
	0.003	1.517	1.519	1.519	1.520	1.520	1.516	1.517	1.517	1.520	1.520
	0.004	1.512	1.514	1.514	1.516	1.516	1.511	1.512	1.512	1.516	1.516
	0.005	1.508	1.510	1.510	1.512	1.511	1.507	1.507	1.508	1.508	1.512
	0.008	1.500	1.506	1.501	1.504	1.502	1.497	1.498	1.498	1.499	1.504
	0.010	1.495	1.498	1.496	1.500	1.497	1.492	1.495	1.493	1.494	1.500
AgBr		($a = 3.0$ nm)	($a = 3.5$ nm)	($a = 3.7$ nm)	($a = 5.8$ nm)	–	($a = 3.0$ nm)	($a = 3.5$ nm)	($a = 3.7$ nm)	($a = 5.8$ nm)	–
	0.000	1.838	1.838	1.838	1.838		1.838	1.838	1.838	1.838	
	0.001	1.810	1.810	1.811	1.811		1.809	1.809	1.810	1.810	
	0.002	1.799	1.799	1.801	1.802		1.798	1.798	1.798	1.793	
	0.003	1.793	1.793	1.794	1.795		1.790	1.790	1.787	1.788	
	0.004	1.787	1.787	1.789	1.790		1.784	1.784	1.785	1.787	
	0.005	1.781	1.781	1.785	1.786		1.779	1.779	1.790	1.784	
	0.008	1.770	1.770	1.776	1.777		1.767	1.767	1.769	1.774	
	0.010	1.763	1.763	1.769	1.772		1.760	1.760	1.764	1.769	
AgCl		($a = 2.8$ nm)	($a = 3.5$ nm)	($a = 3.8$ nm)	($a = 5.6$ nm)	–	($a = 2.8$ nm)	($a = 3.5$ nm)	($a = 3.8$ nm)	($a = 5.6$ nm)	–
	0.000	1.821	1.821	1.821	1.821		1.821	1.821	1.821	1.821	
	0.001	1.792	1.792	1.792	1.794		1.791	1.791	1.791	1.792	
	0.002	1.782	1.782	1.783	1.784		1.780	1.781	1.782	1.783	
	0.003	1.775	1.775	1.775	1.778		1.773	1.773	1.775	1.776	
	0.004	1.769	1.770	1.770	1.772		1.767	1.767	1.769	1.771	
	0.005	1.764	1.765	1.766	1.768		1.761	1.761	1.761	1.766	
	0.008	1.752	1.757	1.759	1.759		1.749	1.749	1.750	1.757	
	0.010	1.746	1.747	1.749	1.754		1.743	1.743	1.751	1.752	
AgI		($a = 3.3$ nm)	($a = 3.7$ nm)	($a = 4.0$ nm)	($a = 6.1$ nm)	–	($a = 3.3$ nm)	($a = 3.7$ nm)	($a = 4.0$ nm)	($a = 6.1$ nm)	–
	0.000	1.825	1.825	1.825	1.825		1.825	1.825	1.825	1.825	
	0.001	1.797	1.799	1.801	1.802		1.795	1.795	1.800	1.801	
	0.002	1.786	1.788	1.795	1.796		1.785	1.785	1.794	1.795	
	0.003	1.774	1.774	1.794	1.793		1.771	1.774	1.791	1.791	
	0.004	1.769	1.769	1.789	1.790		1.766	1.766	1.788	1.789	
	0.005	1.764	1.764	1.790	1.789		1.762	1.762	1.785	1.786	
	0.008	1.757	1.757	1.787	1.786		1.754	1.755	1.784	1.782	
	0.010	1.751	1.751	1.784	1.785		1.748	1.749	1.783	1.780	
AgMnO ₄		($a = 3.0$ nm)	($a = 3.3$ nm)	($a = 3.6$ nm)	–	–	($a = 3.0$ nm)	($a = 3.3$ nm)	($a = 3.6$ nm)	–	–
	0.000	1.647	1.647	1.648			1.647	1.647	1.647		
	0.001	1.622	1.622	1.635			1.621	1.621	1.633		
	0.002	1.613	1.613	1.626			1.612	1.612	1.624		
	0.003	1.607	1.607	1.620			1.605	1.605	1.618		
	0.004	1.602	1.602	1.614			1.600	1.600	1.612		
	0.005	1.598	1.598	1.610			1.595	1.595	1.608		
	0.008	1.587	1.587	1.600			1.585	1.585	1.598		
	0.010	1.582	1.582	1.595			1.579	1.579	1.595		

Table 2 (Continued)

AgC ₂ H ₃ O ₂	(a = 3.5 nm)	(a = 3.3 nm)	(a = 3.3 nm)	-	-	(a = 3.3 nm)	(a = 3.3 nm)	(a = 3.3 nm)		
0.000	1.311	1.311	1.311			1.311	1.311	1.311		
0.001	1.291	1.293	1.294			1.290	1.292	1.293		
0.002	1.284	1.285	1.287			1.282	1.284	1.285		
0.003	1.279	1.284	1.285			1.272	1.283	1.283		
0.004	1.278	1.283	1.284			1.270	1.277	1.282		
0.005	1.271	1.280	1.283			1.269	1.275	1.281		
0.008	1.263	1.279	1.280			1.261	1.274	1.277		
0.010	1.259	1.279	1.279			1.256	1.267	1.275		
AgClO ₂	(a = 3.2 nm)	(a = 3.4 nm)	-	-	-	(a = 3.2 nm)	(a = 3.4 nm)	-	-	-
0.000	1.505	1.505				1.505	1.505			
0.001	1.482	1.482				1.481	1.481			
0.002	1.474	1.474				1.472	1.472			
0.003	1.468	1.468				1.466	1.466			
0.004	1.464	1.464				1.462	1.462			
0.005	1.460	1.460				1.457	1.457			
0.008	1.451	1.451				1.448	1.448			
0.010	1.446	1.446				1.443	1.443			
AgClO ₃	(a = 3.3 nm)	(a = 3.3 nm)	-	-	-	(a = 3.3 nm)	(a = 3.3 nm)	-	-	-
0.000	1.683	1.683				1.683	1.683			
0.001	1.658	1.658				1.658	1.656			
0.002	1.648	1.648				1.647	1.647			
0.003	1.642	1.641				1.641	1.640			
0.004	1.637	1.638				1.638	1.635			
0.005	1.632	1.632				1.632	1.630			
0.008	1.622	1.622				1.621	1.620			
0.010	1.617	1.616				1.615	1.614			
AgClO ₄	(a = 3.0 nm)	(a = 3.3 nm)	(a = 3.4 nm)	(a = 6.1 nm)	-	(a = 3.0 nm)	(a = 3.3 nm)	(a = 3.4 nm)	(a = 6.1 nm)	-
0.000	1.718	1.718	1.718	1.718		1.718	1.718	1.718	1.718	
0.001	1.692	1.692	1.692	1.693		1.690	1.691	1.692	1.692	
0.002	1.682	1.682	1.682	1.684		1.681	1.682	1.683	1.683	
0.003	1.676	1.676	1.676	1.678		1.674	1.674	1.677	1.677	
0.004	1.670	1.670	1.670	1.674		1.668	1.670	1.671	1.672	
0.005	1.666	1.666	1.666	1.670		1.663	1.665	1.667	1.668	
0.008	1.655	1.657	1.658	1.662		1.652	1.655	1.659	1.659	
0.010	1.649	1.640	1.654	1.658		1.646	1.650	1.653	1.655	
AgNO ₂	(a = 3.3 nm)	(a = 3.3 nm)	(a = 3.3 nm)	-	-	(a = 3.3 nm)	(a = 3.3 nm)	(a = 3.3 nm)	-	-
0.000	1.772	1.772	1.772			1.772	1.772	1.772		
0.001	1.740	1.745	1.745			1.745	1.743	1.745		
0.002	1.736	1.735	1.729			1.730	1.733	1.734		
0.003	1.729	1.728	1.721			1.726	1.726	1.727		
0.004	1.724	1.723	1.718			1.718	1.720	1.721		
0.005	1.717	1.718	1.718			1.716	1.715	1.716		
0.008	1.705	1.706	1.704			1.704	1.711	1.709		
0.010	1.698	1.700	1.694			1.700	1.707	1.706		
AgNO ₃	(a = 2.5 nm)	(a = 2.8 nm)	(a = 3.3 nm)	(a = 3.4 nm)	(a = 5.6 nm)	(a = 2.5 nm)	(a = 2.8 nm)	(a = 3.3 nm)	(a = 3.4 nm)	(a = 5.6 nm)
0.000	1.766	1.766	1.766	1.766	1.766	1.766	1.766	1.766	1.766	1.766
0.001	1.739	1.739	1.739	1.739	1.741	1.738	1.738	1.738	1.738	1.739
0.002	1.729	1.729	1.729	1.730	1.731	1.728	1.728	1.728	1.728	1.729
0.003	1.722	1.722	1.722	1.725	1.725	1.720	1.720	1.720	1.721	1.723

Table 2 (Continued)

AgNO ₃	(a = 2.5 nm)	(a = 2.8 nm)	(a = 3.3 nm)	(a = 3.4 nm)	(a = 5.6 nm)	(a = 2.5 nm)	(a = 2.8 nm)	(a = 3.3 nm)	(a = 3.4 nm)	(a = 5.6 nm)
0.004	1.717	1.717	1.717	1.717	1.720	1.714	1.714	1.714	1.715	1.718
0.005	1.712	1.714	1.712	1.713	1.716	1.710	1.710	1.710	1.710	1.714
0.008	1.700	1.701	1.700	1.702	1.707	1.698	1.698	1.698	1.699	1.705
0.010	1.694	1.695	1.694	1.699	1.703	1.692	1.692	1.693	1.693	1.700
Ag ₂ SO ₄	(a = 3.2 nm)	(a = 3.4 nm)	(a = 6.2 nm)	–	–	(a = 3.2 nm)	(a = 3.4 nm)	(a = 6.2 nm)	–	–
0.000	1.393	1.393	1.393			1.393	1.393	1.393		
0.001	1.327	1.327	1.327			1.320	1.320	1.321		
0.002	1.309	1.309	1.309			1.297	1.297	1.298		
0.003	1.298	1.298	1.298			1.279	1.279	1.280		
0.004	1.290	1.290	1.290			1.264	1.264	1.265		
0.005	1.284	1.284	1.284			1.253	1.253	1.251		
0.008	1.270	1.270	1.270			1.223	1.223	1.224		
0.010	1.263	1.263	1.264			1.200	1.200	1.201		
Ag ₂ S ₂ O ₄	(a = 3.8 nm)	(a = 4.7 nm)	–	–	–	(a = 3.8 nm)	(a = 4.7 nm)	–	–	–
0.000	1.280	1.280				1.280	1.280			
0.001	1.219	1.219				1.211	1.210			
0.002	1.200	1.201				1.181	1.187			
0.003	1.187	1.189				1.159	1.167			
0.004	1.177	1.180				1.140	1.152			
0.005	1.170	1.173				1.123	1.137			
0.008	1.154	1.159				1.087	1.090			
0.010	1.146	1.153				1.059	1.062			
Ag ₂ S ₂ O ₈	(a = 3.3 nm)	(a = 3.4 nm)	(a = 4.1 nm)	–	–	(a = 3.3 nm)	(a = 3.4 nm)	(a = 4.1 nm)	–	–
0.000	1.437	1.437	1.437			1.437	1.437	1.437		
0.001	1.368	1.368	1.368			1.361	1.361	1.362		
0.002	1.345	1.345	1.345			1.334	1.334	1.336		
0.003	1.329	1.329	1.330			1.313	1.312	1.311		
0.004	1.317	1.317	1.319			1.294	1.294	1.293		
0.005	1.308	1.309	1.310			1.278	1.278	1.276		
0.008	1.286	1.286	1.290			1.243	1.244	1.241		
0.010	1.276	1.276	1.280			1.218	1.218	1.217		
Ag ₂ SeO ₄	(a = 3.3 nm)	(a = 3.6 nm)	(a = 3.7 nm)	(a = 6.4 nm)	–	(a = 3.3 nm)	(a = 3.6 nm)	(a = 3.7 nm)	(a = 6.4 nm)	–
0.000	1.360	1.360	1.360	1.360		1.360	1.360	1.360	1.360	
0.001	1.295	1.295	1.295	1.291		1.287	1.287	1.288	1.291	
0.002	1.274	1.274	1.274	1.279		1.260	1.261	1.262	1.267	
0.003	1.259	1.259	1.260	1.268		1.239	1.238	1.237	1.249	
0.004	1.247	1.248	1.249	1.260		1.218	1.218	1.218	1.234	
0.005	1.239	1.240	1.241	1.255		1.203	1.202	1.201	1.220	
0.008	1.220	1.224	1.223	1.242		1.168	1.167	1.166	1.193	
0.010	1.211	1.213	1.214	1.236		1.141	1.141	1.140	1.168	

^a D_{OF} and D_{Pikal} , in units of $10^{-9} \text{ m}^2 \text{ s}^{-1}$.

^b c in units of mol dm^{-3} .

as shown by a significant deviation between experimental data and these calculations in some cases [22].

4. Results and discussion

Table 1 summarizes a values for 15 silver salts in aqueous solution. At least two estimations, based on the different theoretical approaches here considered, were done for every electrolyte. From this table, in general, we verify that the values calculated from MM+ and Marcus data ($a = R_1 + R_2$), and those obtained from Kielland's, are similar, whereas those found from the other Marcus' data ($a = d_{\text{cation-water}} + d_{\text{anion-water}}$), i.e., by considering one water molecule placed between both ions, are the higher ones. It would be expected that due to the complexity of the electrolyte solution structure, an intermediate situation ought to be more real. That is, we assume that the actual value of this parameter should lie between the cited range of values, and that this may be interpreted on the basis of the collision of hydrated cations and anions, respectively, and consequently on the compaction of their hydration shells in some extension.

The D values estimated from both theories using different values of a are indicated in Table 2. For univalent electrolytes (1:1), we see that both equations give similar results and that the differences between the estimated values of D for different concentrations are not changed significantly with a (i.e., deviations < 3%). This leads us to consider that in such circumstances, there is no formation of ion pairs (phenomenon taken into account by Pikal (Eq. (8)).

Concerning polyvalent non-symmetrical electrolytes, in general, there are significant deviations between the estimated values of Onsager-Fuoss and Pikal equations for solutions of concentration, $c > 0.005 \text{ mol dm}^{-3}$ (< 10%). However, the results obtained for all the range of concentrations, from Onsager-Fuoss using different a values, are similar between them (< 1%), same situation to what happens with the values estimated by Pikal's equation. Thus, for $c < 0.005 \text{ mol dm}^{-3}$, we suggest the use of Onsager-Fuoss' equation (or Pikal's equation), but for higher concentrations, it is more convenient the use both diffusion coefficients, D . In fact, in Pikal's development, those deviations can be interpreted either as the presence of ion pairs, or eventually because of the full use of Boltzmann's exponential.

5. Conclusions

The importance of the diffusion on systems containing silver ion and the scarcity of their diffusion coefficients, well justify efforts on the respective determination by theoretical procedures. However, knowing that there is no direct method for measuring a , we present some values for this parameter estimated using different methods. For

dilute aqueous studied systems ($c < 0.010 \text{ mol dm}^{-3}$), the choice of a in calculation of D , either from Onsager-Fuoss or Pikal equations, shows us to be not relevant (i.e., slight variations have little effect on the values of D), and in those circumstances, one can say that the mean distance of closest approach does not influence the diffusion of silver salts in aqueous solutions.

Concerning symmetrical electrolytes, both equations lead us to similar values of D and, consequently, the use of Onsager-Fuoss or Pikal's models is not relevant. On the contrary, for polyvalent non-symmetrical electrolytes, we suggest the use of both equations to estimate the diffusion coefficients in dilute solutions, believing that the actual values of D should lie between them, being the choice of the parameter a not relevant, within acceptable limits.

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