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Mean distance of closest approach of ions: Sodium salts in aqueous solutions

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Abstract

The estimation of numerical values for the mean distance of closest approach of ions, a, of sodium salts in aqueous solutions, determined from activity and diffusion coefficients, and also from different theoretical approaches, is presented and discussed.

Keywords: Ion size; Mean distance; Solutions; Transport properties

1. Introduction

The present development of science and technology demands precise data concerning the fundamental thermodynamic and transport properties of ionic solutions [1–6]. For the interpretation of those data, and, much more important, for their estimation when no experimental information is available, we need to know parameters such as the “mean distance of closest approach of ions” represented by a (å when expressed in angstroms). There are a lot of thermodynamic data concerning electrolytes in solution, whose accurate values are required by many scientists and technologists in order to be used in different ulterior calculus or processes. Most of these data are not available from the literature and must be calculated by means of either empirical expressions or theoretical models in which the parameter a is involved. This 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 the solution which participate in the formation of an ionic atmosphere. While there is no direct method for the measurement of the parameter a, its estimation may be done by using finite-ion-size equations from measurements of the activity and diffusion coefficients in solutions.

Dufrêche et al. [7,8] developed a theory that describes simultaneously the different transport (e.g., diffusion) and equilibrium properties from low to high concentrations (1–2 mol dm^{-3}) using only the diameter of the ions as an adjustable parameter. It is possible to draw several qualitative conclusions from the systematic comparison of the magnitude of the a parameter, calculated from those equations with the results of studies of unrelated properties, such as ionic mobilities, and with the results obtained from theoretical approaches. In fact, different techniques ranging from diffraction methods (of X-ray, neutrons or electrons) to computer simulations (molecular dynamics or Monte Carlo methods) have been applied to this goal [9,10]. The available results of the ionic radius, particularly in solutions, up to the end of 1986 have been collected by Marcus in a review paper [10]. However, despite the intense work, the data available on this area are still scarce.

The objective of this paper is to present different estimations of a by using experimental and theoretical approaches for sodium salts useful, in our case, for corrosion studies in dental restorations and, in general, for researchers who have to deal with solutions of electrolytes.

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2. Estimation of *a* from experimental mean ionic activity coefficients and diffusion coefficients

The distance of closest approach, *a*, from the Debye–Hückel theory, has to be regarded as an adjustable parameter in the several semi-empirical equations for the activity coefficients, for well known reasons [1,2,11,12]. Lobo [11] estimated this parameter for a large number of electrolytes in aqueous solutions using data in Ref. [4] and Eq. (1)

$$\ln y_{\pm} = -\frac{A|Z_1 Z_2 \sqrt{I}|}{1 + Ba\sqrt{I}} + bI \tag{1}$$

where *a* and *b* are considered adjustable constants, Z_1 and Z_2 are the algebraic valences of a cation and of an anion, respectively, $y_{\pm}$ is the molality-scale mean ionic activity coefficient, and *I* is the molality-scale ionic strength. *A* and *B* are defined as

$$A \equiv (2\pi N_{\mathrm{A}} \rho_A)^{1/2} \left(\frac{e_0^2}{4\pi \varepsilon_0 \varepsilon_{r,A} kT} \right)^{3/2} \tag{2}$$

$$B \equiv e_0 \left(\frac{2 N_{\mathrm{A}} \rho_A}{\varepsilon_0 \varepsilon_{r,A} kT} \right)^{1/2} \tag{3}$$

In these equations (which are in SI units), N_{A} is the Avogadro constant, *k* is Boltzmann constant, e_0 is the proton charge, ε_0 is the permittivity of vacuum, ρ_A is the solvent density, $\varepsilon_{r,A}$ is the solvent dielectric constant and *T* is the absolute temperature. Using the SI values for N_{A}, *k*, e_0, and ε_0, and $\varepsilon_{r,A} = 78.38$, $\rho_A = 997.05$ kg/m^3 for H_2O at 25 °C and 1 atm, $A = 1.1744$ (kg/mol)$^{1/2}$, $B = 3.285 \times 10^9$ (kg/mol)$^{1/2}$ m^{-1}.

A computer program has been written for a specific electrolyte, where the values of the activity coefficients and the respective concentration were introduced. By successive calculations, where *a* varied from 1×10^{-10} to 20×10^{-10} m (1 to 20 Å) with increments of 0.01×10^{-10} m. For a given set of *a* values at each concentration, the program calculates the corresponding set of values for *b*. So, a curve of *b* against *a* is finally found at each concentration. When we extend this calculation to all concentrations for which data were available, the computer program found the best couple of *a*–*b* values that adjusts simultaneously all these concentrations for that specific electrolyte. Table 1 shows the values thus obtained.

The mutual diffusion coefficient, *D*, of an electrolyte in m^2 s^{-1} is given by

$$D = \overline{M} \left(\frac{|z_1| + |z_2|}{|z_1 z_2|} \right) \frac{RT}{c} \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c} \right) \tag{4}$$

where *R* is the gas constant in J mol^{-1} K^{-1}, *T* is the absolute temperature, z_1 and z_2 are the algebraic valences of cation and anion, respectively, and the last term in parenthesis is the activity factor, in which $y_{\pm}$ means for the mean ionic activity coefficient in the molality-scale, *c* is the concentration in mol m^{-3}, and $\overline{M}$, in mol^2 s m^{-3} kg^{-1}, is given by

$$\overline{M} = \frac{1}{N_{\mathrm{A}}^2 e_0^2} \left(\frac{\lambda_1^0 \lambda_2^0}{\nu_2 |z_2| \lambda_1^0 + \nu_1 |z_1| \lambda_2^0} \right) c + \Delta\overline{M}' + \Delta\overline{M}'' \tag{5}$$

In Eq. (5), the first- and second-order electrophoretic terms are given by

$$\Delta\overline{M}' = -\frac{c}{N_{\mathrm{A}}} \frac{(|z_2|\lambda_1^0 - |z_1|\lambda_2^0)^2}{(|z_1|\nu_1\lambda_2^0 + |z_2|\nu_2\lambda_1^0)^2} \frac{\nu_1 \nu_2}{\nu_1 + \nu_2} \frac{k}{6\pi\eta_0(1+ka)} \tag{6}$$

and

$$\Delta\overline{M}'' = \frac{(\nu_1|z_2|\lambda_1^0 + \nu_2|z_1|\lambda_2^0)^2}{(\nu_1|z_1|\lambda_2^0 + \nu_2|z_2|\lambda_1^0)^2} \frac{1}{(\nu_1+\nu_2)^2} \frac{1}{N_{\mathrm{A}}^2} \frac{k^4 \phi(ka)}{48\pi^2\eta_0} \tag{7}$$

and where η_0 is the viscosity of the water in N s m^{-2}, N_{A} is the Avogadro's constant, e_0 is the proton charge in coulombs, ν_1 and ν_2 are the stoichiometric coefficients, λ_1^0 and λ_2^0 are the limiting molar conductivities of the cation and anion, respectively, in m^2 mol^{-1} Ω^{-1}, *k* is the "reciprocal average radius of ionic atmosphere" in m^{-1} (see e.g., Ref. [2]), *a* is the mean distance of closest approach of ions in m, $\phi(ka) = |e^{2ka} E_i(2ka)/(1+ka)|$ has been tabulated by Harned and Owen [2], and the other letters represent well-known quantities [2]. In this equation, phenomena such as complexation, ionic solvation and/or ion association [13–15], and hydrolysis [16,17] are not taken into consideration. From the above equations and from our own measurements of *D*, and from other measurements, we have calculated the parameter *a*. Those values for *a* estimated by adjustment to experimental data for $c \leq 0.1$ mol dm^{-3} in order to lead to theoretical values for *D* whose deviations with respect to the experimental ones selected are less than 1–2% are shown in Table 1.

The experimental methods that were used to measure mutual differential diffusion coefficients are: conductimetric (uncertainty ±0.2%) [18–28]; Gouy and Rayleigh interferometry (uncertainty <0.1%) [21]; and Taylor dispersion (uncertainty ± 1–2%) [21]. The experimental diffusion coefficients, *D*, in aqueous solutions of electrolytes, at 25 °C, were collected from Refs. [4,21–28] and, for two cases ($NaClO_4$ and $NaClO_3$), measured recently with our technique [19,20]. They were used to calculate the values of *a* shown in Table 1, assuming the Onsager–Fuoss model Eq. (4) [5,26–28].

3. Estimation of *a* by different theoretical approaches

3.1. Estimations of "a" values from Kielland data

From a table of ionic sizes presented by Kielland (i.e., rounded values of the effective diameter of the hydrated ion shown in the Table I of Ref. [9] with $a/10^{-10}$ m (Na^+) = 4.2 taken from data there presented), we have estimated values of *a*, as the mean value of the effective radii of the hydrated ionic species of the electrolyte (4th column in Table 1). The diameters of inorganic ions, hydrated to a different extent, have

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

Electrolyte	Activity coefficients, Eq. (1), $c \leq 1.0$ M	Diffusion coefficients, Eq. (4), $c \leq 0.1$ M	Kielland [9]	Marcus [10], $a = R_{\text{cation}} + R_{\text{anion}}$	Marcus [10], $a = d_{\text{cation-water}} + d_{\text{anion-water}}$	ab initio $d_{\text{ion-ion}}$	Molecular mechanics*		
							a)	b)	c)
NaF	–	2.5	3.9	2.2	5.0	1.9 ($d_{\text{Na-F}}$)	2.1	4.6	7.1
NaBr	4.1	–	3.6	3.0	5.7	2.5 ($d_{\text{Na-Br}}$)	2.7	5.4	7.8
NaCl	4.0	$2.5 \leq a \leq 4.0$	3.6	2.8	5.5	2.4 ($d_{\text{Na-Cl}}$)	2.6	5.2	7.7
NaI	4.2	$4.0 \leq a \leq 6.5$	3.6	3.2	6.0				
$NaBO_2$	1.2	–	–	–	–	–			
$Na_2B_4O_7$	1.3[d)]	–	–	–	–	–			
$NaBrO_3$	–	–	3.9	–	–	2.2 ($d_{\text{Na-O}}$)			
Na_2CO_3	–	2.5	4.4	–	–	2.1 ($d_{\text{Na-O}}$)			
$Na_2C_2O_4$	–	–	4.4	–	–	2.1 ($d_{\text{Na-O}}$)			
NaClO	–	–	–	–	–	2.0 ($d_{\text{Na-O}}$)			
$NaClO_2$	–	–	4.3	–	–	2.2 ($d_{\text{Na-O}}$)			
$NaClO_3$	–	2.5	3.9	–	–	–			
$NaClO_4$	–	5.5	3.9	–	–	–			
$NaHCO_3$	4.3	2.5	4.3	–	–	2.2 ($d_{\text{Na-O}}$)			
$NaHC_2O_4$	–	–	–	–	–	2.2 ($d_{\text{Na-O}}$)			
NaH_2PO_4	–	–	4.3	3.4	6.1	–			
Na_2HPO_4	–	–	4.1	–	–	–			
NaHS	–	–	3.9	–	–	2.5 ($d_{\text{Na-S}}$)			
$NaHSO_3$	–	–	4.3	–	–	2.2 ($d_{\text{Na-O}}$)			
$NaHSO_4$	–	–	–	–	–	2.2 ($d_{\text{Na-O}}$)			
$NaIO_3$	–	–	4.3	–	–	–			
$NaIO_4$	–	–	3.9	–	–	–			
Na_2MOO_4	–	–	4.4	3.6	6.4	–			
$NaNO_2$	–	–	3.6	–	–	2.2 ($d_{\text{Na-O}}$)			
$NaNO_3$	–	$2.0 \leq a \leq 3.0$	3.6	2.7	5.5	2.2 ($d_{\text{Na-O}}$)			
NaOH	3.6	$2.5 \leq a \leq 4.5$	3.9	–	–	2.0 ($d_{\text{Na-O}}$)			
Na_3PO_4	–	–	4.1	–	–	–			
$Na_4P_2O_7$	7.1[e)]	–	–	–	–	–			
Na_2S	–	–	4.6	–	–	2.4 ($d_{\text{Na-S}}$)	3.1	5.4	8.3
NaSCN	–	6.6	3.9	–	–	–			
Na_2SO_3	–	–	4.4	–	–	2.1 ($d_{\text{Na-O}}$)			
Na_2SO_4	–	2.0	4.1	–	–	–			
Na_2SeO_4	–	–	4.1	3.5	6.3	–			
Na_2WO_4	–	–	4.6	3.6	6.4	–			

*The values indicated represent the distance between the centres of cation and anion, a) without water, b) with one water molecule and c) with two water molecules between them, respectively. d) $c \leq 0.5$ M. e) $c \leq 0.2$ M.

been calculated by two different methods: from the crystal radius and deformability, accordingly to Bonino's equation for cations [9], and from the ionic mobilities [9].

3.2. Estimation of "a" values from Marcus data

Using the data of Marcus (Table XIII of Ref. [10]) two approximations were performed in order to obtain the a values of several salts in aqueous solution. Firstly, the a values were determined as the sum of the ionic radii (R_{ion}) reported by Marcus [10]. 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 ($d_{\text{Ion-water}}$) and the half of the mean intermolecular distance between two water molecules in the bulk liquid water (the mean radius of a water molecule, $R_{\text{water}} = (1.39_3 \pm 0.002) \times 10^{-10}$ m [10]); this value was determined after considering the packaging effect produced by the electrostriction phenomenon derived from the strong electrical field near the ion [11]. That is, $R_{\text{ion}} = d_{\text{ion-water}} - R_{\text{water}}$ and $a = R_{\text{cation}} + R_{\text{anion}}$. These values are summarized in the fifth column in Table 1. For the determination of interparticle distances, $d_{\text{ion-water}}$, 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 the Monte Carlo methods).

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 [10] was also done. In this approach the a values are determined as $a = d_{\text{cation-water}} + d_{\text{anion-water}}$. The values found are collected in the sixth column in Table 1.

3.3. Ab initio calculations

The ab initio calculations were carried out using the Gaussian 98 w (G98 w) program package [29] adapted to a personal computer. Full geometry optimizations were performed, without any structural or symmetry constraint. All calculations were performed within the Density Functional Theory (DFT) approach, using the B3LYP method [30], which includes a mixture of Hartree–Fock (HF) and DFT exchange terms. The gradient-corrected correlation functional was used [31] (parameterised after Becke [32]), along with the double-zeta split valence basis set 6-31G* [33].

Two different theoretical models could be considered for simulating the cation–anion distance in dilute aqueous solution. In a simplest one, the cation–anion distance will be optimised without considering the presence of the solvent molecules, while in a second approximation, the first-hydration shell of the cation would be considered. In the present paper, the first model was used. The calculated distances obtained are shown in column 7 of Table 1 and discussed on the basis of the corresponding experimentally predicted cation–anion distances.

3.4. Molecular mechanic studies (MM2)

Molecular mechanic studies are a valuable tool to interpret atom or ion dynamic relations. They are simpler than ab initio calculations. For that reason, they are faster to achieve and adequate to evaluate dynamic processes like solvation changes around cations and anions as equal as reasonable mean distances of approach between species in solution, involving dozens of molecules with hundreds of electrons.

Among the MM methods, MM2 developed by Ref. [34] is the 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 column in Table 1. They were obtained by considering three possibilities: a) no water molecules in between anion and cation (MM2-0), b) both ions separated by one water molecule (MM2-1) and c) two water molecules placed in between both ions (MM2-2).

4. Results and discussion

Table 1 summarized *a* values for 34 sodium salts in aqueous solution. At least, one estimation for this parameter, based on the different experimental techniques and/or theoretical approaches here considered, was done for every electrolyte.

By looking at the data in Table 1, some facts can be observed. First we note is that ab initio values are the smallest ones whereas those found from MM2-2, i.e., by considering two water molecules placed in between both ions, are the greatest ones. This is not unexpected if we have in mind that both calculus correspond to two extreme situations: the “bare” ions in contact each other and the ions aligned with two water molecules in the middle, respectively. Due to the complexity of the electrolyte solution structure, it would be expected that an intermediate situation ought to be more real.

A fair agreement seems to be given between ab initio and MM2-0 results (in both cases, a close situation of “bare” ions is considered), although these later are, in general, higher than the former ones. Nonetheless, such agreement is not observed when comparison is made between MM2-2 and Marcus’ results after considering the ion hydration shell effect ($a = d_{\text{cation–water}} + d_{\text{anion–water}}$). In effect, Marcus results are always much smaller than those and relatively close (although always slightly bigger) to the MM2-1 ones. That is, to those calculated under the supposition of only one water molecule is placed in between cation and anion. Even though in a qualitative manner only and, hence, keeping in mind all the limitations that accompany these determinations, such discrepancies would mainly be attributed to the electrostriction phenomenon, which has not been considered in MM2 calculus.

Table 1 shows that, in general, the values of *a* obtained by fitting experimental data of activity coefficients are greater than the sum of ionic radii in solutions (or crystal-lattice spacing) or the interatomic distances, $d_{\text{ion–ion}}$; they are close to those obtained from Kielland’s data; they are smaller than the sum of the mean ion–water internuclear distances. This fact could 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. However, for some particular electrolytes (such as $NaBO_2$ and $Na_2B_4O_7$) *a* is even smaller than the lattice spacing in the crystal which, apparently, contradicts the physical meaning of *a*. Probably, this is due to the fact that only electrostatic interactions obeying Coulomb’s law are considered in the Debye–Hückel model. In fact, the ion–ion and ion–solvent interactions, not included in this model, can be responsible for the mutual potential energy to fall at short distances, below the value that is assumed in the Debye–Hückel theory. So, the only way to use the D–H equation to adjust experimental activity coefficient data is by using a value for the distance of closest approach clearly smaller than the expected real one. Apparently, the inverse situation is verified for the electrolyte $Na_4P_2O_7$ ($a = 7.1 \times 10^{-10}$ m) having in mind all values showed for sodium salts (*a* changes between 3.6×10^{-10} and 5.3×10^{-10} m). This phenomenon can also be interpreted on the basis of the limitations of the Debye–Hückel model. Actually, under the form given by the Eq. (1), that is by taking into account just the first-order term arisen from the virial developing of the radial distribution of charge density of the ion atmosphere, activity coefficient values can be adequately fitted up to relatively low concentrations depending on the electrolyte nature. Besides, in some cases it has been proved the necessity of using additional terms which include higher-order interactions (short-range forces between like ions, triple ion interactions, etc) even at low molalities. If more virial terms are involved for the fitting, the *a* parameter will not be the only one that support the effect of the different molecular phenomena that take place in the solution and that become enhanced with concentration. Accordingly, more realistic value for the *a* parameter will be obtained.

Concerning the values of parameter a obtained by adjustment of Onsager–Fuoss' equation to the experimental data of diffusion coefficients, we see that, in most cases, results are lower than those obtained from Kielland's data and close to those obtained from the sum of ionic radii in solutions (or crystal-lattice spacing) or the interatomic distances, $d_{\text{ion-ion}}$. This not too big distance (that is, in general, approximately equal to the sum of the radii of the "bare" ions) may suggest that those cations and anions would not retain their primary hydration shell. In fact, we see that for those cases, that choice of a alters substantially their calculations of D from Eq. (4). This is not surprising if we take into account that factors as the formation of complex ions and the variety of ion pairs eventually formed [13], and the change with concentration of parameters such as viscosity, dielectric constant, hydration and hydrolysis of ions [14–17] is not considered in Onsager–Fuoss theory (Eq. (4)). Thus, those effects, not predicted in the theory of the electrophoretic effect, can be responsible for masking the real values of the parameter a. For other cases indicated in Table 1 (NaCl, NaI, $NaNO_3$ and NaOH), we should note that calculations based on Eq. (4) are not greatly affected by the choice of the ion size parameter a, within the limits indicated.

When a is calculated from Kielland's data [10] we can see, first of all, that a moderately small dispersion of the results is attained. Certainly, they all are included in the range $(3.6\text{–}4.6)\times 10^{-10}$ m. On the other hand, the values appear to be placed between the sum of Marcus ionic radii and those found from activity coefficient measurements. It is necessary to take into account that really these Kielland data result from equations involving ionic mobilities (or phenomenological coefficients) which are rigorously valid only at very high dilution. In addition, under those circumstances, the ion–ion and hydrodynamic interactions which are not considered in this model can actually influence the phenomenological coefficients and ionic mobilities and, consequently, lead to obtain non real values of the parameter a. However, they would be considered as a quite good option for a values to be used into the calculus/determination of thermodynamic quantities referred to sodium salts in aqueous solution.

5. Conclusions

It is not possible to accurately know the mean distance of closest approach of ions, a, in an electrolyte solution, however desirable that would be. We present here several estimations of a using different methods, so that the researcher who needs to use this parameter may have an idea of the possible range of values. All of them could be reasonable compromises to select an adequate value for this a parameter, depending on the necessities of its application to a given real problem. Consequently, by taking the appropriate precautions, each researcher can eventually either choose the most appropriate value for his case, or select a value from one specific method of estimation, or even use an average value of all of them or an average of the most suitable for his case. The indications given in Sections 3 and 4 may be of help for such a choice.

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