Ion Hydration and Large Electrocaloric Effect

I. Danielewicz-Ferchmin[1] and A. R. Ferchmin[2]*

Starting from a discussion of the grand potential change associated with introduction of ions into water, the electrocaloric effect for the system ion–surrounding water is calculated by means of this recent statistical approach to the problem of water in a high electric field. It is concluded that this effect is essential for the hydration of ions, in particular, for the heat of solution of salts. Consistency between the present approach and recent literature results of a density functional calculation, as well as experimental data for sequential enthalpies of hydration of doubly charged ions in the gas phase, is discussed.

1. INTRODUCTION

The heat of hydration of ions has been studied for a long time,[1] but still is the subject of many investigations.[2–5] A recent approach has been to determine the hydration reaction equilibria among ion hydrates produced by the electrospray method in the gas phase.[3] Using mass spectroscopy, the sequential enthalpies, free energies, and entropies for the hydration reaction of several doubly charged cations have been measured.[3] Also, a density functional calculation of the coordination properties of several (partly the same) doubly charged ions in an aqueous environment has recently been presented.[4] These experiments have some limitations. Only the binding enthalpies per added H_2O molecule lower than 126 kJ-mole^{-1} were accessible. The theoretical calculations[4] covered the range of high binding enthalpies (low coordination) down to about the same limiting value. Some overlap between the binding enthalpy ranges covered in Refs. (3) and (4) enabled

[1]Faculty of Physics, A. Mickiewicz University, Umultowska 85, PL-61-614 Poznań, Poland
[2]Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, PL-60-179 Poznań, Poland. E-mail: arfer@ifmpan.poznan.pl

Kebarle *et al.*[3] to state their mutual agreement whenever a comparison was possible (cf. Ref. 3, Fig. 8 therein).

Another, more traditional approach to the heat phenomena accompanying dissolution of salts in liquid water is the investigation of the properties of the products of this process. The electrocaloric effect,[6–8] seems not to have been discussed in this context. This paper is intended to fill this gap. The fact that the electrocaloric effect is closely related to electrostriction is the reason for our choice of this approach to the problem. Namely, such methods that cannot adequately quantitatively account for large electrostriction effects in high electric fields occurring close to the ions and in double layers at the electrodes should be considered as not suitable to this aim. To our knowledge, at least some computer simulations of models of water fall into this category.[9,10] A comparison[11] of several models of water accounting for electrostriction and nonlinear dielectric effect with MD computer simulations of Ref. (12) is available. We decided to apply an electrostatic and thermodynamic approach, which proved useful in treating the nonlinear dielectric effect and helped to quantitatively explain the electrostriction phenomena in an electrolyte near an electrode,[13,14] as well as various properties of hydration shells of many ions in ambient and high temperature and pressure conditions.[15,16]

The electrocaloric effect in liquids within condensers in electric fields $E \leq 10^7$ V-m^{-1} is well known. These are the highest electric fields realizable on a macroscopic scale in condensers filled with liquids. In a field of such strength, variation of permittivity ϵ [nonlinear dielectric effect[8,17]] is observed and represents a small fraction of the so-called dielectric constant. The related electrocaloric effect is very small (Table 19 in Ref. 17). This is in contrast with the case of a microscopic scale, where in the hydration shells and in double layers an electric field of a strength two or more orders of magnitude higher than the former can be present. For a field strength between nearly zero and a value within the range 10^8–10^{11} V-m^{-1}, the permittivity can vary by two orders of magnitude. This is accompanied by a huge electrostriction and electrocaloric effect. Similarly, as in the case of the huge electrostriction, the large electrocaloric effect calculation will be based on our statistical model of water (cf. Ref. 15 and references therein). In this work the electrocaloric effect is taken into account in the energy balance during dissolution of salts in water. Infinite dilution and ambient conditions are assumed throughout the paper.

2. GRAND POTENTIAL AND ELECTROCALORIC EFFECT

In this section, the grand potential Ω change associated with the emergence of ions in water will be considered. Grand potential is expressed as a function of

independent variables suitable for the phenomenon under consideration: temperature (T), volume (V), and chemical potential (ζ)

$$d\Omega = -SdT - pdV + V\epsilon_0 Ed[(\epsilon - 1)E] - n_m d\zeta \tag{1}$$

where S denotes entropy, p is pressure, ϵ_0 is the permittivity of vacuum, ϵ is permittivity, n_m is the number of moles, ζ is the chemical potential, and E is the electric field strength. In comparison with the standard expression, Eq. (1) includes the extra term $V\epsilon_0 Ed[(\epsilon - 1)E]$ representing the work done by the electric field of strength E on the medium of polarization $(\epsilon - 1)\epsilon_0 E$. Strong electric fields generated by the ionic charges decay rapidly with distance. As a consequence, the molecules within the first hydration shells are in the fields of considerably higher strength than those outside them. In other words, water surrounding an ion is placed in an electric field, whose strength depends on the distance from the ion. Since the chemical potential ζ in various parts of the system must remain the same, the inhomogeneity in electric field induces inhomogeneity in mass density of water *via* the electrostriction pressure.[6,7,14,16] The change in the grand potential $\Delta\Omega$ is expressed by the integral form of Eq. (1) taken at given temperature, volume, and chemical potential and reads

$$\Delta\Omega = W \tag{2}$$

The work W is done by the electric field of strength given by

$$E = \frac{q}{4\pi\epsilon\epsilon_0 x^2} \tag{3}$$

Here q is the elementary charge (16×10^{-20} C), x is the reduced distance from the center of the ion $x = r \times |Z|^{-1/2}$, r denotes the distance from the center of the ion, and Z is the number of excess elementary charges of an ion (valence). For field strength values as high as those generated by the ions, the permittivity ϵ depends on the field strength (Fig. 1). We shall introduce the following notation

$$\sigma = \frac{q}{4\pi x^2} \tag{4}$$

$$y = \sigma\left(1 - \frac{1}{\epsilon}\right) \tag{5}$$

The work W done by the field E on water in volume V is:

$$W = \frac{V}{\epsilon_0}\int_0^{y_1} \frac{\sigma}{\epsilon}\, dy \tag{6}$$
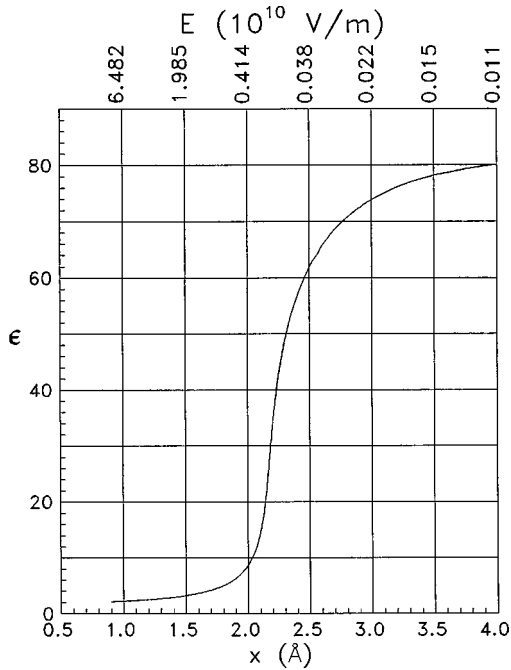
Fig. 1. Permittivity ϵ (Eq. 15) as a function of the reduced
distance $x = r \times |Z|^{-1/2}$ from the ion (lower scale) and as
a function of electric field strength E (upper scale).

where y is defined in Eq. (5), y_1 is the value at distance r_1 of the first hydration
shell, or

$$W = \frac{V}{\epsilon_0} f \tag{7}$$

where

$$f = \int_0^{y_1} \frac{\sigma}{\epsilon} dy \tag{8}$$

The entropy change ΔS in the process in question is:

$$\Delta S = \frac{\partial}{\partial T} \Delta \Omega = \frac{V}{\epsilon_0} \left(\frac{\partial f}{\partial T} \right)_{V, E, \zeta} \tag{9}$$

The quantity f (see Eq. 8) depends on temperature *via* $\epsilon(T)$. Equation (9) takes

the form:

$$\Delta S = \frac{V}{\epsilon_0} \left[\left(\frac{\partial f}{\partial y} \right) \left(\frac{\partial y}{\partial \epsilon} \right) \right]_{T,V,\zeta} \left(\frac{\partial \epsilon}{\partial T} \right)_{V,E,\zeta} \tag{10}$$

From the latter equation, it is possible to derive the expression for the heat ΔQ absorbed by the dielectric substance during an electric field change related to the appearance of the ion inside the dielectric:

$$\Delta Q = T\Delta S = \frac{TV}{\epsilon_0} \left[\left(\frac{\partial f}{\partial y} \right) \left(\frac{\partial y}{\partial \epsilon} \right) \right]_{T,V,\zeta} \left(\frac{\partial \epsilon}{\partial T} \right)_{V,E,\zeta} \tag{11}$$

If $(\partial \epsilon / \partial T)_{V,E,\zeta} < 0$, which is usually the case, we have $\Delta Q < 0$ and $\Delta S < 0$. Thus, heat is evolved by the dielectric and given off to the heat bath. At the same time, the entropy decreases, that is, the field orders the dipoles of the system. The release of heat by the dielectric as a consequence of an isothermal change in the applied field is called the isothermal electrocaloric effect. The heat due to this effect will be found from Eq. (11). The product of the derivatives:

$$\left[\left(\frac{\partial f}{\partial y} \right) \left(\frac{\partial y}{\partial \epsilon} \right) \right]_{T,V,\zeta} \tag{12}$$

is calculated in a way similar to previous work (Ref. 16):

$$\left(\frac{\partial f}{\partial y} \right)_{T,V,\zeta} = \frac{\sigma}{\epsilon} \tag{13}$$

and

$$\left(\frac{\partial y}{\partial \epsilon} \right)_{T,V,\zeta} = \left(\frac{\partial \sigma}{\partial \epsilon} \right)_{T,V,\zeta} \left(1 - \frac{1}{\epsilon} \right) + \frac{\sigma}{\epsilon^2} \tag{14}$$

The derivatives $(\partial \sigma / \partial \epsilon)_{T,V,\zeta}$ and $(\partial \epsilon / \partial T)_{V,E,\zeta}$ will be calculated below.

3. A STATISTICAL MODEL OF WATER

As already shown [Section 2, Eq. (11)], the expression for the heat ΔQ related to the electrocaloric effect contains the derivative $\partial \epsilon / \partial T$. Locally, at the ions, neither this quantity nor ϵ itself are known from experiment. Hence, the necessity of a theoretical approach arises. In the statistical model approach to the permittivity of hydrogen bonded liquids (including water) proposed earlier (see Ref. 15 and references therein) at relatively low temperatures (close to the melting temperature; this includes the ambient temperature), the mean cosine $\langle \cos \theta \rangle$ of the angle θ

between the direction of the external field E and the electric dipole moment μ of the molecule has to be expressed by the hyperbolic tangent and not the Langevin function.[18] In the hydration shells, the strengths of the electric field (Coulomb field) are so high that the linear approximation to $\langle \cos \theta \rangle$ is no longer sufficient, and the mean cosine has to be expressed by the full tanh function and not the first term in its expansion in a power series. The relation between the permittivity ϵ and the electric field strength is, according to the Onsager field model, expressed as

$$\frac{\epsilon - n^2}{\epsilon} = \frac{N B x^2}{V} \langle \cos \theta \rangle \tag{15}$$

where N denotes the number of molecules in volume V, n is the refractive index, $\langle \cos \theta \rangle = \tanh(\Xi)$ and

$$\Xi = \frac{A}{T x^2 (\epsilon + n^2/2)} \tag{16}$$

$$A = \frac{\mu q (n^2 + 2)}{8 \pi k \epsilon_0} = 1.186 \times 10^{-15} (\text{m}^2 \cdot \text{K}) \tag{17}$$

$$B = \frac{4 \pi \mu (n^2 + 2)}{3q} = 5.96 \times 10^{-10} (\text{m}) \tag{18}$$

(See Section 6 for discussion concerning the Onsager field in discrete systems.) Introducing to Eq. (17) the expression for σ Eq. (4), one can write

$$\Xi = \frac{\mu \sigma (n^2 + 2)}{k T \epsilon_0 (2\epsilon + n^2)} \tag{19}$$

where μ is the permanent dipole moment of a water molecule, and k is the Boltzmann constant. Note that σ is defined as a function of x (cf. Eq. 4), which, in turn, depends on ϵ (Eqs. 15 and 19). The derivative $(\partial \sigma / \partial \epsilon)_{T,V,\zeta}$ is obtained from Eq. (15) and takes the following form:

$$\left(\frac{\partial \sigma}{\partial \epsilon} \right)_{T,V,\zeta} = \frac{\frac{q}{4 \pi x^4} \left[n^2 \left(\epsilon + n^2/2 \right)^2 + \frac{N A B \epsilon^2}{T V (\cosh \Xi)^2} \right]}{\frac{N A B \epsilon^2 (\epsilon + n^2/2)}{T V x^2 (\cosh \Xi)^2} - \left(\epsilon + n^2/2 \right)^2 \frac{N B \epsilon^2 \tanh \Xi}{V}} \tag{20}$$

Taking into account that

$$\tanh(\Xi) = \frac{e^{\Xi} - e^{-\Xi}}{e^{\Xi} + e^{-\Xi}} \tag{21}$$

we obtain, from Eq. (15), the following:

$$\frac{2A}{T x^2 (\epsilon + n^2/2)} = \ln \left(\frac{N B x^2}{V} \frac{\epsilon}{\epsilon - n^2} + 1 \right) - \ln \left(\frac{N B x^2}{V} \frac{\epsilon}{\epsilon - n^2} - 1 \right) \tag{22}$$

From the latter implicit formula of permittivity as a function of temperature, the derivative $\partial\epsilon/\partial T$ will be found for various field strengths (different x). After some algebra, one arrives at the formula:

$$\left(\frac{\partial\epsilon}{\partial T}\right)_x = -\frac{\epsilon + n^2}{T(1 - \gamma V n^2)} + \left(\frac{\partial n}{\partial T}\right)\frac{2n[\epsilon - 1 - \gamma V \epsilon(\epsilon + 2)]}{(n^2 + 2)(1 - \gamma V n^2)}$$
$$-\alpha_p(x)\frac{\gamma V \epsilon(\epsilon - n^2)}{1 - \gamma V n^2} \tag{23}$$

where

$$\gamma = \frac{2gx^4 T(\epsilon + n^2/2)^2}{a[V^2(\epsilon - n^2)^2 - g^2 x^4 \epsilon^2(n^2 + 2)^2]}, \quad a = \frac{\mu q}{4\pi k\epsilon_0}, \quad g = \frac{4\pi N\mu}{3q} \tag{24}$$

and α_p is the thermal expansion coefficient. The values of n and $\partial n/\partial T = 8 \times 10^{-5}$ K^{-1} were taken from Ref. (19). The values of α_p were taken from Ref. (20). For local electrostriction pressures Π (cf. Ref. 16) exceeding 10^8 Pa, we applied the values of α_p extrapolated from the data of Ref. (20). We shall profit from the dependence of permittivity ϵ and its temperature derivative $\partial\epsilon/\partial T$ on the reduced distance x. The former of these relations, calculated from Eq. (15), is shown in Fig. 1. The expression $\partial\epsilon/\partial T$, obtained from Eq. (23), is shown in Fig. 2 as a
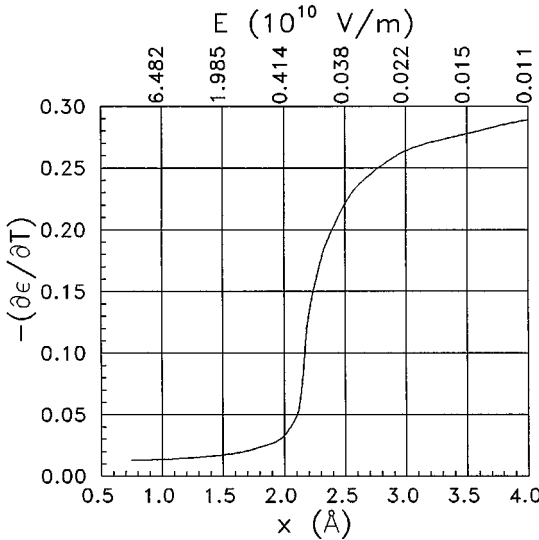

Fig. 2. Negative derivative $-(\partial\epsilon/\partial T)$ (Eq. 23) as a function of the reduced distance $x = r \times |Z|^{-1/2}$ from the ion (lower scale) and as a function of electric field strength E (upper scale).

Fig. 3. Heat ΔQ released as a result of the isothermal elec-
trocaloric effect (Eq. 11) in water as a function of the re-
duced distance $x = r \times |Z|^{-1/2}$ from the ion (lower scale)
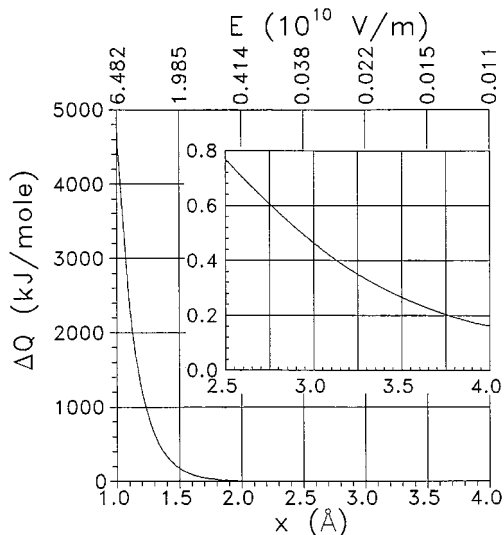and as a function of electric field strength E (upper scale).
Insert reproduces a part of the plot on an expanded scale.

function of the reduced distance $x = r/\sqrt{Z}$ from the center of an ion bearing Z ex-
cess elementary charges. Figure 3 shows the relation thus obtained of $\Delta Q = T \Delta S$
[(Eq. 11)] as a function of the reduced distance x. To each value of x, corresponds
a Coulomb field strength E (cf. Eq. 3 and the upper scale in Fig. 3). For all cations
discussed here, $x_1 < 2$ and for anions $x_1 > 3$, where x_1 are the reduced radii of
the first hydration shells. For $x < 2$, water is placed in the field of a strength $E >
4 \times 10^9$ V-m^{-1}, its permittivity $\epsilon < 10$ (cf. Fig. 1), and local electrostriction pres-
sure $\Pi > 1$ GPa (cf. Ref. 16). For $x > 2.4$, water is placed in the field of strength
$E < 4 \times 10^8$ V-m^{-1}, its permittivity $\epsilon > 60$ (cf. Fig. 1) and local electrostriction
pressure $\Pi < 0.1$ GPa (cf. Ref. 16). Here, water is only weakly ordered.[16]

4. HEATS OF SOLUTION OF SALTS IN WATER

In this section, three contributions to the integral enthalpy ΔH of solution
are dealt with. *First*, is the energy U_L released on forming one mole of the ionic
solid from the gaseous ions called the crystal or lattice energy[21,22] of a compound
MA_Z:

$$M^{Z+}(\text{gas}) + ZA^-(\text{gas}) - U_L = MA_Z(\text{solid}) \qquad (25)$$
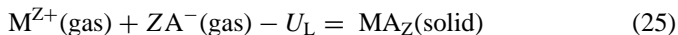
where M^{Z+} denotes a Z-charged metal cation, A^- is an anion, and MA_Z is the chemical formula of the salt.

The *second* contribution, the energy U, as proposed by Born[1] in 1920 (cf. also Ref. 5), is due to the transfer of an ion from vacuum to a polarizable solvent:

$$U = -\frac{N(Zq)^2}{8\pi\epsilon_0}\left(\frac{1}{r} - \frac{1}{\epsilon_1 r_1}\right) \tag{26}$$

where r is the crystallographic radius of an ion. When salt is dissolved in water, an energy equal to the difference $U_L - U$ is transferred to the solution. Born computed the energy U by setting r_1 equal to the crystallographic radius r of ions, and $\epsilon_1 = 81$. Here, we take r_1 equal to the radius of the first hydration shell (cf. Ref. 5) and, for a given value of r_1, that of ϵ_1 is found from Eq. (15). This means that we find a local value of $\epsilon_1 = \epsilon(r_1)$. A discussion of ionic radii in aqueous solutions with the dielectric saturation near the ion taken into account is due to Marcus.[23] Note that neither $\epsilon_1 = \epsilon(r_1)$ nor r_1 itself represents an adjustable parameter within the present approach (see Section 6 below for a discussion).

We are now in a position to consider the *third* contribution to the integral enthalpy ΔH of solution, the heat ΔQ related to the electrocaloric effect. On dissolving salts in water, one observes more or less strong heat effects. In the limit of high values of the rate of number of moles of water and the number of moles of salt one obtains the so-called integral enthalpy of solution ΔH (cf. Ref. 24). The latter is the enthalpy effect per one mole of salt. We admit that ΔH is expressed as follows:

$$\begin{aligned}\Delta H = U_L &+ U(M^{Z+}) + ZU(A^-) + h(M^{Z+})\Delta Q(M^{Z+})\\ &+ Zh(A^-)\Delta Q(A^-),\end{aligned} \tag{27}$$

where h is the hydration number of the corresponding ion taken in parentheses. The meaning of Eq. (27) can be expressed in the following way: The first terms in the integral enthalpy of solution ΔH are the lattice energy U_L of compound MA_Z (Eq. 25) and transfer energies $U(M^{Z+})$ of Z-charged cations M^{Z+} and $ZU(A^-)$ of Z anions A^- (Eq. 26) to the solvent. The energies in question (ΔH, U_L, U) are meant per mole of the salts or ions emerging from them after dissociation. Further terms in ΔH contain the heat absorbed ΔQ (Eq. 11) by the solution during the electric field change as a result of introducing the ions into the solvent (water). ΔQ is the heat per mole of water, hence, in Eq. (27), the heat $\Delta Q(M^{Z+})$ for the cation M^{Z+} is multiplied by the hydration number $h(M^{Z+})$ of the cation M^{Z+}, and that for the anion $\Delta Q(A^-)$ is multiplied by the product of the hydration number $h(A^-)$ of the anion A^- and the relative number Z of anions per cation in the salt (solution).

We face the following situation: In our opinion ΔQ calculated from the electrocaloric effect in this work does contribute to ΔH, which is a well-defined quantity tabulated in Ref. (24). However, it is not ΔQ itself, but the product of ΔQ and $h(M^{Z+})$, which contributes to ΔH. The point is that the literature data of the factor $h(M^{Z+})$—the value of the hydration number of the cation determined from independent experiments—reveal a large scatter of values (cf. Table II, column 5). This would lead to unacceptable differences in the calculated values of ΔH. Therefore, we decided to invert the problem. We accept the known data[24] of ΔH and calculate the less well known values of hydration numbers, taking the electrocaloric effect into account. The calculated values of hydration numbers are later subject to a comparison with the literature data. Note that on the right-hand side of Eq. (27), only the terms containing ΔQ relate to the enthalpy of the ions hydration: The field orders the dipoles of water, at the same time the entropy decreases and heat ΔQ is released by the dielectric. The remaining terms are unrelated to the ions hydration: U_L is the lattice energy of the ionic crystal absorbed during a transition from a crystal to a gas of separated ions in vacuum, and U is the energy related to the work done during the transfer of ions from vacuum into water.

5. RESULTS

Tables I and III give the terms in Eq. (27) for a number of ions. The Born transfer energy U (Eq 26) per mole of ions depends strongly on the radius r of the ion. Hence, for a part of ions, results of both Goldschmidt and Pauling radii are given. The radius r_1 of the first hydration shell is taken from the literature (as indicated in tables). The permittivity ϵ_1 in the first hydration shell and its derivative $\partial \epsilon_1 / \partial T$, as well as the heat ΔQ per mole of water, were calculated on the basis of our statistical model: Eqs. (15), (23), and (11). Tables II and IV include literature data for salts composed of the ions in question: The lattice energy of crystalline salts U_L obtained in two ways. One of them is the so-called Madelung energy.[21,22] Another one follows from the application of the Born–Fajans–Haber cycle (BFH cycle).[22] Further on, integral enthalpy of solution ΔH is given.[24] The subsequent columns of Tables II and IV present the lowest and highest literature values of hydration numbers of cations.[23,25–27]

The calculations were performed as follows: The hydration number of cations $h(M^{Z+})$ was taken as the only unknown quantity in Eq. (27):

$$h(M^{Z+}) = \frac{\Delta H - U_L - U(M^{Z+}) - Z[U(A^-) + h(A^-)\Delta Q(A^-)]}{\Delta Q(M^{Z+})} \quad (28)$$

The values of ΔH for several bromides and chlorides were taken from Ref. (24). The hydration number of the anions in question[23,25] is $h(Br^-) = h(Cl^-) = 6$. Since the anions have relatively large ionic radii, the heat ΔQ is very small

Table I. Data for Monovalent and Divalent Ions[a]

| | r (Å) | | r_1 (Å) | ϵ_1 | $-\partial\epsilon_1/\partial T$ (K^{-1}) | $-U$ (kJ·mol^{-1}) Eq. (26) | | ΔQ (kJ·mol^{-1}) |
	Goldschmidt	Pauling	Refs. (23, 25)	Eq. (15)	Eq. (23)	Goldschmidt	Pauling	Eq. (11)
Co^{2+}	0.82	0.75	2.11	3.2	0.017	2963	3283	193
Fe^{2+}	0.83	0.78	2.1	3.2	0.017	2927	3141	193
Mg^{2+}	0.78	0.72	2.1	3.2	0.017	3141	3437	193
Mn^{2+}	0.91	0.83	2.2	3.4	0.0175	2675	2969	124
Ni^{2+}	0.78	0.69	2.1	3.2	0.017	3141	3604	193
Zn^{2+}	0.83	0.74	2.05	3.17	0.0167	2913	3319	193
Br$^-$	—	1.96	3.4	77.5	0.276	—	351	0.3
Cl$^-$	—	1.81	3.2	76.2	0.271	—	380	0.37

[a] r, ionic radii; r_1, radius of the first hydration shell; ϵ_1, permittivity of water in the first shell; U, Born transfer energy per mole of H_2O; ΔQ, heat per mole of H_2O released as a result of the isothermal electrocaloric effect.

Table II. Data for 1:2 Salts[a]

	U_L (Ref. 22) [kJ-mole(salt)]		$-\Delta H$ [kJ-mole (salt)] Ref. (24)	$h(M^{Z+})$ Literature data Refs. (23, 25)	$h(M^{Z+})$ This work Eq. (28)			
	Madelung	BFH cycle			GM	GC	PM	PC
CoBr$_2$	2648	2629	83.8		4.8	4.9	6.5	6.6
CoCl$_2$	2709	2691	79.16	$5 \div 6$	4.8	4.9	6.5	6.6
FeBr$_2$	2464	2569	85.35		5.6	5.0	6.7	6.1
FeCl$_2$	2525	2631	80.8	$5.1 \div 6$	5.6	5.0	6.7	6.1
MgBr$_2$	2097	2440	181.17		8.1	6.3	9.6	7.9
MgCl$_2$	2326	2526	154.9	$6 \div 8.1$	7.3	6.3	8.9	7.8
MnBr$_2$	2304	2471	77.19		8.0	6.7	10.4	9.0
MnCl$_2$	2368	2537	71.92	$4.5 \div 6$	8.0	6.6	10.4	9.0
NiBr$_2$	2699	2709	82.09		5.5	5.4	7.9	7.8
NiCl$_2$	2753	2772	81.42	$5.25 \div 7.6$	5.5	5.4	7.9	7.8
ZnBr$_2$	2632	2678	69.66		3.8	3.6	5.5	5.3
ZnCl$_2$	2690	2734	69.12	$2.4 \div 7$	3.8	3.6	5.5	5.3

[a] U_L, lattice energy of the ionic solid; ΔH, integral entalpy of solution; $h(M^{Z+})$, hydration numbers of cations; GM means that the corresponding value of Born transfer energy U is based on the Goldschmidt radii and U_L according to the Madelung method; GC means that these quantities were calculated with Goldschmidt radii and BFH cycle; PM denotes the same with Pauling radii and the Madelung method; PC denotes the same with Pauling radii and BFH cycle, respectively.

Table III. Data for Trivalent Ions[a]

	r (Å) (Ref. 22)	r_1 (Å) (Refs. 26, 27)	ϵ_1 Eq. (15)	$-\partial\epsilon_1/\partial T$ (K^{-1}) Eq. (23)	$-U$ (kJ-mol^{-1}) Eq. (26)	ΔQ (kJ-mol^{-1}) Eq. (11)
La^{3+}	1.061	2.58	3.18	0.017	5118	186
Pr^{3+}	1.013	2.54	3.12	0.0166	5369	219
Nd^{3+}	0.995	2.51	3.04	0.0165	5450	245
Sm^{3+}	0.964	2.47	2.99	0.0165	5624	274
Eu^{3+}	0.950	2.45	2.94	0.0164	5699	300

[a] See footnote to Table I for definitions of symbols.

(cf. Table I and Fig. 3, insert). Hence, the value of the term $h(A^-)\Delta Q(A^-)$ is small and one does not need to estimate the uncertainty of the hydration number $h(A^-)$. This contrasts the situation with the cations, whose ionic radii are relatively small and whose heat ΔQ is large (cf. Tables I and III and Fig. 3). The product $h(M^{Z+})\Delta Q(M^{Z+})$ is a large term in Eq. (27) and the error in the number $h(M^{Z+})$ considerably affects the results. This is the reason why we have decided to determine the hydration number of cations $h(M^{Z+})$ from Eq. (28) and to compare it with the literature data collected in Tables II and IV (column 5). The latter data should be compared with those calculated from Eq. (28) and given in Table II (columns 6–9) and in Table IV (columns 6 and 7). Note that Eq. (28) leads to *almost correct* values of hydration numbers: The ranges of a part of the hydration number values obtained in this work overlap those given in literature and the remainder fall close to them. Therefore, we consider these values essentially consistent. It means that in the heat effect accompanying the dissolution of salts in water, one should take into account the isothermal electrocaloric effect, as has been done in this work.

Our results cannot immediately be compared with the experimental results by Kebarle *et al.*,[3] who measured the sequential enthalpies (from $n = 5$ to $n = 15$,

Table IV. Data for Salts[a]

Salt	U_L (Ref. 22) [kJ-mole (salt)] Madelung	BFH cycle	$-\Delta H$ [kJ-mole (salt)] Ref. (24)	$h(M^{Z+})$ Literature data Refs. (26, 27)	$h(M^{Z+})$ This work Eq. (28) Madelung	BFH cycle
LaCl$_3$	4343	4242	137.8	9.1	9.5	10.1
PrCl$_3$	4322	4326	149.3	9.2	9.3	9.3
NdCl$_3$	4343	—	156.9	8.9	8.5	—
SmCl$_3$	4376	—	167.1	8.8	8.1	—
EuCl$_3$	4393	—	172.2	8.3	7.6	—

[a] U_L, lattice energy of the ionic solid; ΔH, integral entalpy of solution; $h(M^{Z+})$, hydration numbers of cations.

where n is the number of water molecules in the cluster) of hydration of doubly charged ions in the gas phase, since the heat ΔQ represents the mean value of the binding enthalpies of water molecules in the first hydration shell, but not the sequential enthalpies for consecutive water molecules. Also, in Ref. (3) only the binding enthalpies lower than 126 kJ-mol^{-1}, hence n values equal to or larger than 5, were experimentally accessible. Note that mean enthalpies ΔQ for molecules in the first hydration shells of doubly charged ions (Table I) do not contradict the data of Ref. (3), since their values are indeed > 126 kJ-mol^{-1}, as it should be.

Theoretical studies of the coordinative behavior of doubly charged metal ions in water are reported in Ref. (4). Let us compare the data for Mg^{2+} and Zn^{2+} in Ref. (4) and the present ones. Total binding energies for the complex $[Mg(H_2O)_6]^{2+}$ (Ref. 4, Table 2 therein) amount to ≈ 1250 kJ per 6 mole H_2O, or 208 kJ-mol^{-1}, on average. This is to be compared with our result of 193 kJ-mol^{-1} (Table I). Total binding energies for complex $[Zn(H_2O)_5]^{2+}$ (Ref. 4, Table 4 therein) amount to ≈ 1290 kJ per 5 mole H_2O, or 258 kJ-mol^{-1}, on average. This is to be compared with our 240 kJ-mol^{-1} (Table I).

6. DISCUSSION

We shall discuss statistical calculation of average quantities as applied to the present case of aqueous solutions of salts. Strong electric fields generated by the charges of the ions decay rapidly with the radial distance into water, according to the Coulomb law. As a consequence, the molecules within the first hydration shells are in the fields of a considerably higher strength than those outside them. In this way, the first hydration shells about the ions are distinguished in respect to the field from the whole solution. Taken together, the first shells form a subsystem of molecules in the same physical conditions, although they do not have a common macroscopic boundary. As briefly mentioned above, the chemical potentials of various parts of the system in equilibrium, including the set of the first hydration shells, the sets of the further more or less well-defined shells, and the rest in zero field, are equal. The subsystem of all first shells of ions of one kind forms a macroscopically large ensemble of molecules in the same physical conditions and thus can be subjected to the procedure of statistical averaging, leading to values of their thermodynamic parameters. Although dispersed in space, the set of the hydration shells can be treated in much the same way as a layer of molecular thickness in the theory of electrolytes at an electrode.[14,28] Thus, one can freely derive thermodynamic quantities concerning the dispersed in space, but otherwise macroscopic, set of hydration shells by statistical methods, as done throughout this paper.

Another point is the applicability of the Onsager field approximation, frequently conceived after textbooks as forming a part of the continuum theory (*e.g.*, Ref. 10), to discrete microscopic systems, such as those considered here. Let

us stress that this approximation in the statistical calculations appears in the literature of atomically discrete dielectric and magnetic systems, to mention only Refs. (29–31).

It can be noticed that the heat ΔQ related to the electrocaloric effect shows a dependence on the charge of the ion. Namely, it can be deduced from Fig. 3 (note that $x \sim |Z|^{-1/2}$ is equivalent to $x^{-2} \sim Z$, the excess elementary charge on the ion), or Eq. (11) together with Eqs. (4, 13, 14 and 20). The question of deviations from quadratic dependence of the hydration energy on the charge on the ion has recently been discussed by Hummer *et al.*[32]

It is a common use nowadays to put $r = r_1 = R$ in the right-hand side of Eq. (26). R is an effective mean radius "that is generally longer than the crystal ionic radius . . . [our r], but shorter than the first solvation-shell radius"[33] [our r_1]. It is called the "Born radius," and treated as an adjustable parameter (see, *e.g.*, Refs. 11, 12, 32–34). It should be noted that in the present work r and r_1 are treated as input data, known from other experiments, and not as adjustable parameters.

7. CONCLUSION

A large electrocaloric effect occurs in water in the field of strength equal to that due to the Coulomb field at a first hydration shell of doubly and triply charged cations. The heat related to this effect brings a significant contribution to the energy balance of the process of solution of salts in water. The values of the mean enthalpy ΔQ of water molecules in the hydration shells of Mg^{2+} and Zn^{2+} cations found in this work compare well with the results of recent functional density calculations.[4] Also, our ΔQ values do not contradict the experimental data of Ref. (3). The results of this paper indicate that the electrocaloric effect is the source of hydration enthalpy of ions.

REFERENCES

1. M. Born, *Z. Phys.* **1**, 45 (1920).
2. B. M. Pettitt, *Theoret. Chem. Account.* **103**, 171 (2000).
3. M. Peschke, A. T. Blades, and P. Kebarle, *J. Phys. Chem. A* **102**, 9978 (1998).
4. M. Pavlov, P. E. M. Siegbahn, and M. Sandström, *J. Phys. Chem. A* **102**, 219 (1998).
5. J. R. Bontha and P. N. Pintauro, *J. Phys. Chem.* **96**, 7778 (1992).
6. L. D. Landau and E. M. Lifshits, *Statisticheskaya Fizika* (Izd. Tekh.-Teor. Lit., Moskva, 1951), Section 25, in Russian; L. D. Landau and E. M. Lifshits, *Elektrodinamika Sploshnykh Sred* (Izd. Tekh.-Teor. Lit., Moskva, 1957), Sections 12 and 15, in Russian.
7. H. S. Frank, *J. Chem. Phys.* **23**, 2023 (1955).
8. G. J. F. Böttcher, O. C. Van Belle, P. Bordevijk, and A. Rip, *Theory of Electric Polarization*, 2nd revised edn., Vol. 1 (Elsevier, Amsterdam, 1973).
9. A. Brodsky, *Chem. Phys. Lett.* **261**, 563 (1996).
10. In-Chul Yeh and M. L. Berkowitz, *J. Chem. Phys.* **112**, 10491 (2000).
11. Jin-Kee Hyun and T. Ichiye, *J. Chem. Phys.* **109**, 1074 (1998).

12. Jin-Kee Hyun and T. Ichiye, *J. Phys. Chem. B* **101**, 3596 (1997).
13. M. F. Toney, J. N. Howard, J. Richer, G. L. Borges, J. G. Gordon, O. R. Melroy, D. G. Wiesler, D. Yee, and L. B. Sorensen, *Nature (London)* **368**, 444 (1994).
14. I. Danielewicz-Ferchmin and A. R. Ferchmin, *J. Phys. Chem.* **100**, 17281 (1996).
15. I. Danielewicz-Ferchmin and A. R. Ferchmin, *J. Chem. Phys.* **109**, 2394 (1998).
16. I. Danielewicz-Ferchmin and A. R. Ferchmin, *Physica B* **245**, 34 (1998).
17. S. Kielich, *Dielectric and Related Molecular Processes*, Vol. 1, Chapter 7, M. Davies, Senior Reporter (Chemical Society, Burlington House, London, 1972).
18. I. Danielewicz-Ferchmin, *J. Phys. Chem.* **99**, 5658 (1995).
19. B. P. Nikol'skiy, ed., *Spravochnik Khimika*, Vol. 1, 3rd corrected edn. (Izd. Khimiya, Leningrad, 1971), p. 1029 (in Russian).
20. D. Eisenberg and W. Kauzmann, *Structure and Properties of Water* (Oxford University Press, London, 1969).
21. C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), Chap. 14.
22. R. C. Weast, ed., *Handbook of Chemistry and Physics*, 67th edn. (CRC Press, Boca Raton, FL, 1986–1987).
23. Y. Marcus, *Chem. Rev.* **88**, 1475 (1988).
24. K. Schäfer, ed., *Landolt-Börnstein Numerical Data and Functional Relationships* [NS], Vol. 2 (Springer, Berlin, 1976).
25. H. Ohtaki and T. Radnai, *Chem. Rev.* **93**, 1157 (1993).
26. A. Habenschuss and F. Spedding, *J. Chem. Phys.* **70**, 3758 (1979).
27. A. Habenschuss and F. Spedding, *J. Chem. Phys.* **73**, 442 (1980).
28. S. Romanowski, W. Stasiak, and L. Wojtczak, *Electrochim. Acta* **27**, 511 (1982).
29. T. Kaneyoshi, *Progr. Theoret. Phys.* **41**, 577 (1969).
30. T. Kaneyoshi, *Progr. Theoret. Phys.* **45**, 1340 (1971).
31. D. E. Logan, Y. H. Szczech, and M. A. Tusch, *Europhys. Lett.* **30**, 307 (1995).
32. G. Hummer, L. R. Pratt, and A. E. García, *J. Phys. Chem.* **100**, 1206 (1996).
33. C. Satheesan Babu and Carmay Lim, *J. Chem. Phys.* **114**, 889 (2001).
34. Jin-Kee Hyun, C. Satheesan Babu, and T. Ichiye, *J. Phys. Chem.* **99**, 5187 (1995).