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A phase transition in H₂O due to a high electric field close to an electrode

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Abstract

In this study a phase transition in H₂O due to an applied very high local electric field E at ambient conditions is predicted. We analyse the equation of state and behaviour of entropy. For $E = 10^9$ V m⁻¹ some characteristic features of local electrostriction pressure Π and of entropy change ΔS as a function of the field strength E are noted. These features are interpreted as testifying to a phase transition: water in low field \rightarrow H₂O in high field (or, in other words, H₂O compressed by the field). A consistency of the present results with recent off-specular surface X-ray scattering studies is discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Understanding the phase behaviour of water in high electric field remains one of the most interesting and important open questions in physical science. In particular, although more than a decade has elapsed since ‘solid water layer’ was first reported at the highly polar TiO₂ surface [1], a clear understanding of the underlying phase behaviour remains elusive. However, a phase transition to a H₂O phase vertically compressed to the surface of a RuO₂ electrode by a high electric field has very recently been reported [2]. In the current Letter, we apply a development of the method originating in [3] to describe the phase transition:

water in a low field \rightarrow H₂O in a high field (compressed H₂O), with the hope of describing some features present at the above-mentioned surface of a RuO₂ electrode [2], as well as similar systems [4,5]. In the latter papers [4,5] it was found for the first time by X-ray specular reflectivity measurements that the surface mass densities of H₂O at a charged Ag electrode with surface charge density $|\sigma_0| = 0.25$ C m⁻² ($E \sim 10^{10}$ V m⁻¹) were about twice as large as that corresponding to bulk water. This high density of H₂O within the double layer was attributed to electrostriction [3–5]. The very recent work [2] deals with the charged surface of RuO₂ immersed in water. The extremely high interfacial electric field ($\sim 10^9$ V m⁻¹) has led to ordered H₂O layers and phase transitions between them due to the changes in chemical potential. Some of these layers revealed also a very dense structure, namely that of ice X.

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In the present Letter we apply a thermodynamic and electrostatic approach to the phase transition in H₂O compressed by high electric field. To this aim, the equation of state and the behaviour of entropy are analysed.

2. The equation of state of H₂O in the double layer expressed in the variables T, Π, E

The interrelation between the charge surface density σ_0 of a planar system of charges and the relative mass density of the adjacent layer of molecules can be obtained from the equilibrium condition of the system with respect to the mass transport. The formulas concerning electrostriction are derived as follows [3]. During the process of the electrode charging, the local electric field performs work W on a molecule within the layer, by reorienting its dipole moment. The calculation of W is based on the equations of electrostatics taking into account the permittivity $\epsilon = \epsilon(E_{\text{on}}, N)$ (where N is the number of molecules in volume V and E_{on} is the Onsager local field strength) in the same way as in [3]. The reorientation of dipoles reduces the chemical potential by ζ_W , which is compensated by a change in the chemical potential ζ_L due to the compression work L done by the local electrostriction pressure Π reducing the specific volume. The following equation is written and solved numerically (cf. [3]):

$$\frac{V}{\epsilon_0} \left\{ \frac{\partial}{\partial \epsilon} \int_{a_1}^{b_1} \frac{\sigma}{\epsilon} d \left[\sigma \left(1 - \frac{1}{\epsilon} \right) \right] \right\} \left(\frac{\partial \epsilon}{\partial N} \right)_{T, V, \sigma} = \int_{a_r}^{b_r} \frac{\partial V}{\partial N} dP, \quad (1)$$

where d denotes the differential, $\sigma = \sigma_0 \epsilon$, the l.h.s. represents ζ_W and the r.h.s. ζ_L , respectively. The lower limit of the integral on the l.h.s. is zero ($a_1 = 0$) and its upper limit represents the value $b_1 = \sigma(1 - 1/\epsilon)$ taken upon completion of the charging process. The lower limit of the integral on the r.h.s. is the value of atmospheric pressure ($a_r = 10^5$ Pa) and the upper limit is $b_r = \Pi$. The latter represents the only unknown quantity in Eq. (1). Since the actual dependence of the volume $V = V(\Pi)$ on Π is not available, the room tem-

perature isotherms [6–8] $V = V(P)$ of H₂O under pressure P in the absence of field are applied instead. The use of data measured in the absence of the field introduces of course an approximation. Its validity can only be judged a posteriori, as has been done with a positive result in [3]. The upper limit (b_r) of the integral on the r.h.s. of Eq. (1) is matched so that this equation is fulfilled. This is equivalent to putting the pressure value b_r equal to the local electrostriction pressure value Π .

The derivative $\partial \epsilon / \partial N$ stands for an expression in ϵ and σ calculated numerically from the implicit equation [3]

$$\frac{3V\sigma(\epsilon - n^2)}{N\mu\epsilon(n^2 + 2)} = \tanh \Xi, \quad (2)$$

where

$$\Xi = \left(\frac{\sigma\mu(n^2 + 2)}{\epsilon_0 k T (2\epsilon + n^2)} \right),$$

where n is the refractive index, μ is the permanent dipole moment, k is the Boltzmann constant, and T is the absolute temperature. Throughout this Letter $T = 293$ K. The dependence of ϵ and σ has been found numerically from Eq. (2) and substituted into Eq. (1). Note that in a standard theory of liquids with no hydrogen bonds, the Langevin function would replace the hyperbolic tangent in Eq. (2). Here, we follow the approach of [3,9] where a hydrogen-bonded liquid in a field at ambient conditions was conceived as being roughly two-level system-like. Solution of Eqs. (1) and (2) leads to a relation between the electrostriction pressure Π (or relative volume, i.e., inverse relative mass density d^{-1}), field strength ($E = \sigma/\epsilon_0\epsilon$) and temperature T . Eq. (1) represents an equation of state of H₂O expressed by implicit variables T, Π, E . The dependence on T is present through T -dependent permittivity $\epsilon = \epsilon(T)$ as expressed in Eq. (2) and through introducing into Eq. (1) the isotherm $V = V(P)$ for the same temperature for which ϵ is taken. The electrostriction pressure Π is equal to the upper limit of the integral on the r.h.s. of Eq. (1). The dependence on electric field strength E is present via σ and ϵ .

Hitherto, the interrelation between local density and local electric field (electrostriction) based on

the current model has been applied twice to the problem of aqueous electrolyte behaviour at a charged electrode. In [3] one looked for mass density in the first layer of H₂O molecules at the electrode given the charge density on the metal surface, applying the data taken from [7,8] and reaching a quantitative agreement with the results of [4,5]. In [10], the other way round, with the data of [4,5] at hand, the electric characteristics of the first layer of molecules at the electrode were found.

Eq. (1), as already shown in [10], enables one to calculate some state variables, given the values of other state variables. Hence, Eq. (1) does indeed represent an equation of state.

3. Local electrostriction pressure $\Pi = \Pi(E)$ in the H₂O in the double layer

The first quantity discussed in the present Letter is the electrostriction pressure $\Pi = \Pi(E)$. To find the dependence of Π on E the experimental isotherm of H₂O compressibility at $T = 293$ K was applied. A third-order polynomial fit to the data of [6] was used. Substituting this polynomial $V(P)$ into the r.h.s. of Eq. (1):

$$\int_{a_r}^{b_r} \frac{\partial V}{\partial N} dP = \frac{1}{N^0} \int_{a_r}^{b_r} V(P) dP \quad (3)$$

(where N^0 is the Avogadro number and V is the molar volume) for a range of values of σ and ϵ (and hence $E = \sigma/\epsilon_0\epsilon$), the relation shown in Fig. 1 was obtained. It is remarkable that for the field strength $E = 10^9$ V m⁻¹, in the relation $\Pi = \Pi(E)$ a short segment is seen in Fig. 1 with no variation of the electrostriction pressure ($\Pi = \text{const.}$) despite the growing E . The latter is accompanied by an increase in the number of dipoles pulled into the region within the high field (which should in turn be accompanied by an increase in the electrostriction pressure Π). Note that having the segment with no change of electrostriction pressure $\Pi = \text{const.}$ with varying E means the same as having a jump in the value of E . This is interpreted here as related to a *phase transition* of H₂O from a phase, say, B with partial orientational order to a phase A completely orientationally ordered by the

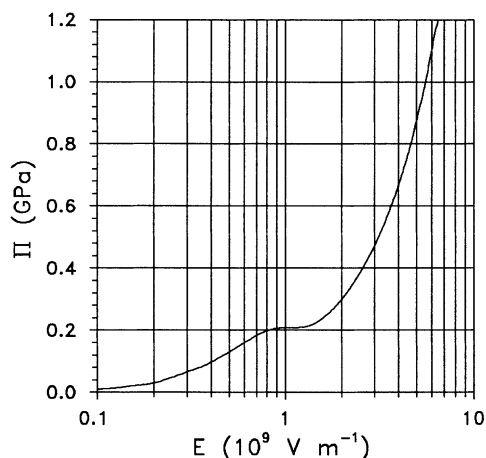


Fig. 1. Local electrostriction pressure $\Pi = \Pi(E)$ as a function of the electric field E . Note a short segment with $\Pi = \text{const.}$ at $E = 10^9$ V m⁻¹.

field E . Thus, Fig. 1 shows a phase transition with discontinuous E representing the first derivative of the Helmholtz potential, which for the systems in an electric field includes the term $E d\beta$, with β – the polarization vector.

4. Changes in entropy of H₂O in the double layer

The high electric field induces in the double layer a change in entropy ΔS [11]

$$\begin{aligned} -\Delta S &= \frac{\partial W}{\partial T} \\ &= \frac{V}{\epsilon_0} \left\{ \frac{\partial}{\partial \epsilon} \int_{a_1}^{b_1} \frac{\sigma}{\epsilon} d \left[\sigma \left(1 - \frac{1}{\epsilon} \right) \right] \right\} \left(\frac{\partial \epsilon}{\partial T} \right)_{V, \sigma, \zeta} \end{aligned} \quad (4)$$

Above, the limits of the integral are the same as those on the l.h.s. of Eq. (1). From Eq. (2) relating permittivity ϵ to temperature, keeping in mind that $\tanh \Xi$ is

$$\tanh \Xi = \frac{e^{\Xi} - e^{-\Xi}}{e^{\Xi} + e^{-\Xi}} \quad (5)$$

the derivative $\partial \epsilon / \partial T$ was found for different field strengths (different σ)

$$\left(\frac{\partial \epsilon}{\partial T}\right)_\sigma = -\frac{\epsilon - n^2}{T(1 - \gamma V n^2)} + \left(\frac{\partial n}{\partial T}\right) \frac{2n[\epsilon - 1 - \gamma V \epsilon(\epsilon + 2)]}{(n^2 + 2)(1 - \gamma V n^2)} - \alpha_p(\sigma) \frac{\gamma V \epsilon(\epsilon - n^2)}{1 - \gamma V n^2}, \quad (6)$$

where

$$\gamma = \frac{6k\epsilon_0 NT(\epsilon + n^2/2)^2}{[3\sigma V(\epsilon - n^2)]^2 - [N\mu\epsilon(n^2 + 2)]^2},$$

and α_p is the thermal expansion coefficient. The values of α_p were taken from [12]. For local electrostriction pressures exceeding 10^8 Pa we applied the values of α_p extrapolated from the data of [12]. The values of the derivative $-\partial\epsilon/\partial T$ as a function of the field strength E are plotted in Fig. 2. The relation $-\Delta S$ vs. field strength E is plotted in Fig. 3. For fields of strength $E = 10^9$ V m⁻¹, the relation plotted in Fig. 3 changes its character from concave to convex with an inflection point in between. In our opinion it represents another characteristic of a transition from a only partially orientationally ordered phase B to a phase A completely orientationally ordered by the field E discussed above.

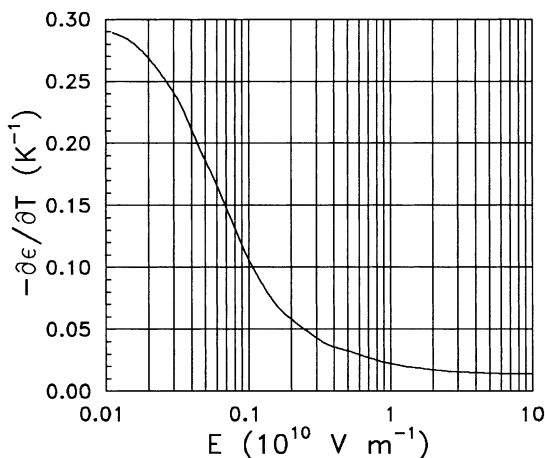


Fig. 2. The derivative $-\partial\epsilon/\partial T$ as a function of the electric field strength E .

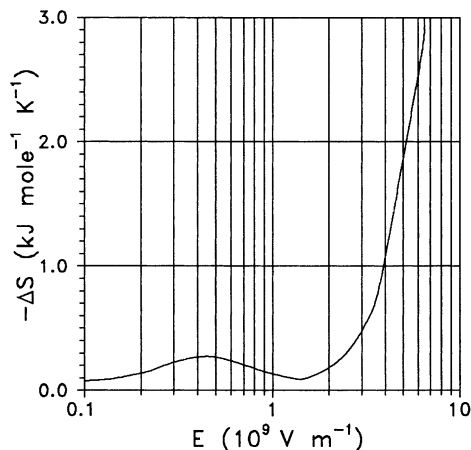


Fig. 3. Entropy change $-\Delta S$ as a function of the electric field strength E . Note an inflection point at $E = 10^9$ V m⁻¹.

5. Properties of the two phases of H₂O: that ordered orientationally by the field E (phase A), and that not completely ordered orientationally (phase B)

On the basis of the arguments presented we predict a phase transition under the action of electric field in the model of water formulated in [3,9]. It remains to describe the physical picture underlying this transition, in particular the properties of the phases on both sides of the transition point. Let us note that not all properties of H₂O can be deduced on the basis of the present thermodynamic and electrostatic approach. For example, from thermodynamic considerations we are not able to draw any conclusions as to the spatial structure of the compressed phase or whether it is a liquid or solid. The properties of phases A and B that can be deduced are plotted in Fig. 4: permittivity ϵ and relative volume d^{-1} of H₂O as a function of the field strength E . The dependence of $d^{-1}(E)$ has been obtained by introducing into Eq. (3) the data of $V(P)$ taken from [7,8] and by performing a graphical integration (cf. [3, Fig. 3]). Phase A of H₂O in fields of strength $E \geq 10^9$ V m⁻¹ is orientationally ordered at a molecular level: the mean value of the cosine of the angle θ between the directions of the dipole moments of H₂O molecules and the direction of the field: $\langle \cos \theta \rangle = 1$ (cf. [3, Table 1]), $\epsilon < 29$, and H₂O gets

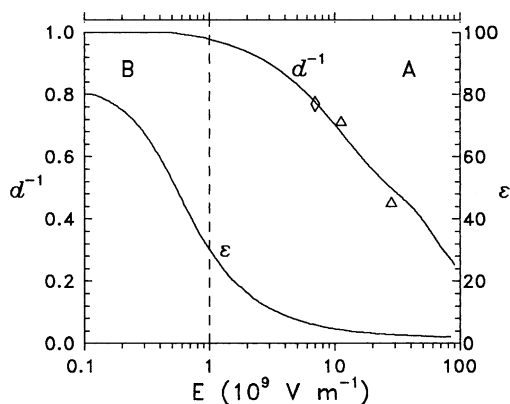


Fig. 4. Relative volume d^{-1} (left-hand scale) and permittivity ϵ (right-hand scale) of H_2O as a function of the field strength E . The triangles (Δ) correspond to the density values of H_2O in the first layer of molecules at the electrode found experimentally in [4]. The diamond (\diamond) corresponds to the density value in the second layer of molecules for $E = 7 \times 10^9 \text{ V m}^{-1}$ (cf. [4,10]). The vertical dashed line is plotted for the field strength $E = 10^9 \text{ V m}^{-1}$ corresponding to the phase transition $B \rightarrow A$.

compressed: $d^{-1} < 1$. The two triangles (Δ) in Fig. 4 correspond to H_2O densities in the first layers of molecules at the electrode, found experimentally [4]: one for the surface charge density at an electrode $|\sigma_0| = 0.1 \text{ C m}^{-2}$ ($E = 11.3 \times 10^9 \text{ V m}^{-1}$), the other one for $|\sigma_0| = 0.25 \text{ C m}^{-2}$ ($E = 28.2 \times 10^9 \text{ V m}^{-1}$). In the present interpretation both belong to the phase A of H_2O compressed by the field. For the latter surface charge density also the second layer of H_2O molecules at the electrode ($E = 7 \times 10^9 \text{ V m}^{-1}$) belongs to phase A, as it follows from the calculation [10] based on the experimental data of [4] (cf. [10, Table 1]). This is represented by a diamond (\diamond) in Fig. 4.

Water in fields of strength lower than $E \leq 10^9 \text{ V m}^{-1}$ represents phase B – orientational order is incomplete: $\langle \cos \theta \rangle < 1$ (cf. [3, Table 1]), $\epsilon < 29$, and there should be no observable compression: $d^{-1} \sim 1$.

The problem of behaviour of H_2O in a very high electric field concerns also the hydration shells around ions see, e.g., [13–15]. A discussion of that problem within the framework of the present approach is deferred to another paper.

6. Conclusion

Previously, it had been established that H_2O in a very high electric field ($> 10^9 \text{ V m}^{-1}$), in particular in the double layer at a charged electrode [4,5] and in the first hydration shells of ions [13,15] is compressed (electrostricted) and orientationally ordered at a molecular level. Hitherto, the problem whether H_2O compressed and orientationally ordered by the field represents a specific state of ordinary water or rather a different phase of H_2O attained through a phase transition at a specific field value has remained open. The very recent observation [2] of phase transitions in a few molecular H_2O layers at a RuO_2 electrode represents an experimental evidence that transition due to high electric field is possible. In this Letter, on the basis of a model approach previously applied to the problem of electrostriction in double layers [3,9], we present results indicating that a phase transition between partly orientationally ordered water and a different phase of H_2O orientationally ordered at a molecular level does occur at a local field strength of $E = 10^9 \text{ V m}^{-1}$. This value falls well in the range where phase transitions of H_2O due to high electric field have been observed [2].

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