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A critical point related to phase transitions in electrostricted H_2O close to an electrode

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Abstract

It is found that phase transitions should occur between two phases of H_2O with different degrees of orientational order of dipoles in a very high local field $E \sim 10^9$ V m^{-1} at temperatures in the range 273–303 K. Critical point of H_2O at $T_c^E = 308 \pm 5$ K is predicted. The analysis is based on a rigorous equation of state. The discontinuity ΔC_P of the heat capacity at the transition is calculated. A consistency of the present results with a laser temperature jump experiment at a Hg/aqueous electrolyte interface is discussed.

1. Introduction

Recently, a phase transition in H_2O in a very high field $E \sim 10^9$ V m^{-1} has been observed [1] at ambient conditions and explained as due to a high electrostriction pressure in an open system [2,3]. It is found to be a transition between two phases, $B \rightarrow A$, with different degrees of the orientational order of H_2O dipoles in the field E [2]. It is natural to ask what happens to this transition when temperature is varied. In the current Letter, it is argued on the basis of a rigorous equation of state that the phase transition of water in a high field, discovered experimentally [1] and analyzed theoretically [2,3] at ambient conditions, should extend to the temperature range 273–303 K and should have the discontinuous (first-order) character. The related region of coexistence of two phases of H_2O extends up to a *critical temperature* T_c^E. The discontinuities $\Delta\sigma$ of surface charge density at the transitions at four temperatures and ΔC_P of the heat capacity at the transition at 293 K are calculated. It is found that they should vanish at the critical temperature T_c^E. Indeed, an experiment performed by a laser temperature jump method at a Hg/aqueous electrolyte interface by Benderskii et al. [4] shows that thermal phenomena related with the transition vanish above some limiting temperature close to T_c^E.

By definition, a first-order phase transition in open systems is characterized by a finite discontinuity in the first derivative of the grand potential Ω

$$d\Omega = -S\,dT + \frac{V}{\epsilon\epsilon_o}\sigma\,dy - N d\zeta_L. \tag{1}$$

Hence, one can expect discontinuities in the surface charge density σ and entropy S:

$$\sigma = \frac{\epsilon\epsilon_o}{V}\left(\frac{\partial\Omega}{\partial y}\right)_{V,\zeta_L,T}$$

and

$$-S = \left(\frac{\partial\Omega}{\partial T}\right)_{V,\zeta_L,y}. \tag{2}$$

We have introduced the notation:

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$$y = \frac{\sigma(\epsilon - 1)}{\epsilon}, \tag{3}$$

where y is the value of the electric polarization vector per volume unit,

$$\sigma = E\epsilon\epsilon_o, \tag{4}$$

where ϵ is the permittivity, ϵ_o is the permittivity of vacuum, N is the number of molecules in the volume V, ζ_L is the chemical potential increment related with the compression work L due to the flow of molecules into the first layer at the electrode. We shall find the discontinuity $\Delta\sigma$ at the phase transition from the rigorous equation of state [5], and that of the heat capacity ΔC_P from the Clapeyron–Clausius-like equation.

2. Equilibrium condition: why do the dipolar water molecules flow into the first layer at the electrode?

The substance considered in this Letter is water placed in a local high electric field: water in the double layers at charged electrodes (cf. [5] and references therein). It forms a common system with the remaining water localized in a weak field or outside the field. Between water in the field and outside the field there is no wall (barrier), which would hinder the mass transport. The thermodynamic law describing the state of this system is the *equilibrium condition* with respect to the mass transport between the regions within and outside the field. It follows from the condition of equality of the chemical potentials:

$$\zeta^i = \zeta^o. \tag{5}$$

The superscripts i and o mark the quantities inside and outside the field, respectively. The chemical potential of a water molecule, placed in a high electric field at the expense of the work W needed for its reorientation, is reduced by ζ_W with respect to that of a molecule outside the field. Due to this local reduction in value of the chemical potential, there arises a chemical potential gradient between the subsystems '*i*' (first layer of molecules at the electrode) and '*o*' (bulk water). This gradient induces a spontaneous irreversible process: the pull of the dipoles into the field with their simultaneous orientation along the field. Each electric dipole belongs to a water molecule, hence the pull of the dipoles into the field is accompanied by a mass transport from subsystem '*o*' into '*i*'. The mass transport makes the subsystem '*i*' (first layer at the electrode) more and more dense until the compression work, denoted L or the related chemical potential increment ζ_L, compensates the increment ζ_W,

$$-\zeta_W = \zeta_L. \tag{6}$$

3. Rigorous equation of state

When ζ_W and ζ_L are explicitly written, the equilibrium condition of the system with respect to the mass transport (Eq. (6)) takes the form of a thermodynamic (rigorous) equation of state for our subsystem '*i*' ([5], Eq. (43) therein):

$$-\frac{N^o}{\epsilon_o}\left[\left(\frac{\partial f}{\partial y}\right)\left(\frac{\partial y}{\partial \epsilon}\right)\right]_N \left(\frac{\partial \epsilon}{\partial N}\right)_\sigma = \frac{1}{v^o}\int_{P^o}^{\Pi} v(P)\,\mathrm{d}P. \tag{7}$$

For a given temperature, the only unknown quantity in Eq. (7) is the electrostriction pressure Π. We have introduced the notation: N^o for Avogadro number, v for molar volume of H_2O, P for pressure, P^o for atmospheric pressure and

$$f = \int_0^y \frac{\sigma}{\epsilon}\mathrm{d}y. \tag{8}$$

Putting Π as the upper limit of the integral on the rhs. of Eq. (7) is equivalent to admitting that the external pressure applied without electric field would produce water compression comparable to that due to the local electrostriction pressure. This equivalence is confirmed with a good accuracy in [6]. Detailed expressions for the partial derivatives on the lhs. of Eq. (7) are presented in [7]. The data of permittivity $\epsilon = \epsilon(E)$ for $273 < T < 313$ K needed to solve Eq. (7) have been taken from [8] and the values of $v(P)$ for the temperatures investigated from [9]. The solutions of this equation have the form of isotherms $\Pi(\sigma)$.

4. Phase diagram

As a result of solving Eq. (7), we have obtained the five isotherms $\Pi(\sigma)$ at 273, 283, 293, 303 and 313 K shown in Fig. 1. The 10 K temperature difference between consecutive isotherms followed the data available in literature [9]. As a consequence, the value of the critical temperature could only be predicted with the accuracy of ±5 K. The diagram obtained is similar to the well-known pressure–volume diagram for the liquid–vapour coexistence region. Both single- and two-phase regions appear as areas in this diagram. In the single-phase region the isotherms are drawn as dotted lines, in the two-phase region they have the form of straight horizontal segments (solid lines). The solid boundary line is plotted which separates the two-phase region from the single-phase region. One notices in the plot the surface charge density discontinuities at Π_t at given temperatures. The change $\Delta\sigma$ of the surface charge density at the transition is equal to the length of the horizontal segment $\Pi_t = \text{const.}$ of the electrostriction pressure isotherm. The values of Π_t at various temperatures and the related limits of the discontinuity of σ are given in Table 1.

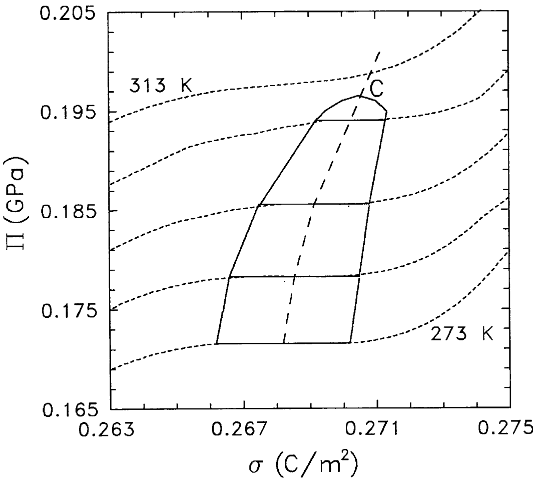

Fig. 1. Five isotherms, plotted every 10 K for temperatures 273–313 K, of electrostriction pressure Π (GPa) as a function of surface charge density σ (C m^{-2}). The isotherms are represented by dotted lines in the single-phase region and have the form of straight horizontal segments (solid lines) in the two-phase region. A dashed line going through the centers of these segments is extrapolated up to its intersection with the 313 K isotherm. The critical point C is situated at the highest part of the two-phase region boundary (solid line) between 303 and 313 K.

Table 1
Transition electrostriction pressure Π_t and the limits of the surface charge density σ discontinuity at four temperatures

T (K)	Π_t (GPa)	σ (C m^{-2})
273	0.1714	0.2662–0.2702
283	0.1781	0.2666–0.2705
293	0.1854	0.2675–0.2708
303	0.1940	0.2692–0.2713

Note that an increase (say, at 293 K) in the surface charge density σ within certain limits indicated in Table 1 (in this case, from 0.2675 to 0.2708 C m^{-2}) does not change the value of the electrostriction pressure ($\Pi_t = 0.1854$ GPa). At Π_t and at any value of σ comprized within this range two phases coexist.

The temperature which is the limit above which the phase transition is not possible is called the critical temperature. The highest point C of the two-phase region boundary between 303 and 313 K represents the newly introduced critical temperature T_c^E (cf. Fig. 1). The critical point ($\Pi_c = 0.196 \pm 0.002$ GPa, $T_c^E = 308 \pm 5$ K) lies at the intersection of the boundary (solid line) and the extrapolated (dashed) line joining the centres of the horizontal segments of four different isotherms. It is termed 'electric' critical point to discern it from the usual one related with the water–vapour system.

5. Change in heat capacity ΔC_P at the phase transition

We shall calculate ΔC_P on the basis of an expression stemming from an equation analogous to the well-known Clapeyron–Clausius one. Appearing of the discontinuity ΔC_P is one of the thermal phenomena related with the entropy discontinuity. By laser temperature jump method, thermal phenomena have been observed at the mercury/aqueous electrolyte interface [4]. It was reported by the authors [4] that these phenomena accompanied a phase transition related with the surface charge density $\sigma \sim 0.3$ C m^{-2}. Values of ΔC_P equivalent to several J (mole K)$^{-1}$ have been found. We shall now calculate ΔC_P within our approach and compare it with the experiment mentioned above. To this aim, on the basis of the data given in Table 1, the coexistence line of the phases B and A shall be plotted in the Π–T plane (Fig. 2). The phase B represents ordinary water, outside the field or in a low field. The phase A is orientationally ordered and compressed by the high field (more precisely, by the high electrostriction pressure). The critical point, marked C, is situated at the end of the coexistence line (see Fig. 2). In Fig. 2, the broken line represents the tangent to the coexistence line at the point ($\Pi_t = 0.1854$ GPa, $T = 293$ K). From the slope of this tangent, the change in heat capacity at constant pressure at the transition between the phases B and A has been calculated, following the Clausius–Clapeyron-like equation:

$$\frac{\mathrm{d}\Pi}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}, \tag{9}$$

where the local electrostriction pressure Π plays the role of the mechanical pressure P. For the phase transition calculated in this work $\Delta V = 0$ [5]. In adiabatic conditions, Eq. (9) can be expressed, making use of the well-known thermodynamic identities between partial differential coefficients [10], as:

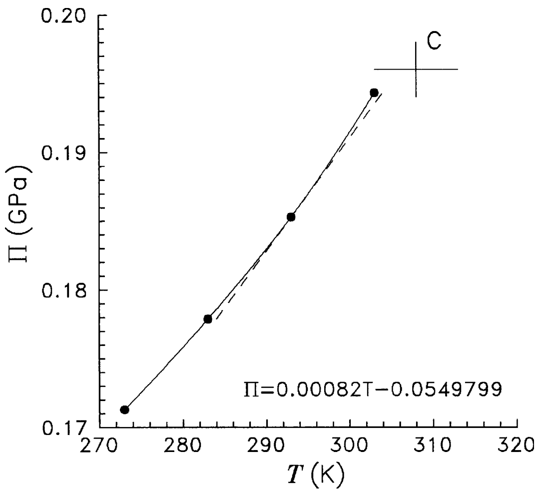

Fig. 2. The full line represents the coexistence line of phases A and B in the (Π,T) plane. The critical point C (at the intersection of the error bars) is situated at the end of the coexistence line. The broken line represents the tangent to the coexistence line at the point (0.1856 GPa, 293 K). The equation of the tangent line, $\Pi = \Pi(T)$, is written in the figure.

$$\frac{\mathrm{d}\Pi}{\mathrm{d}T} = \frac{\Delta C_{\mathrm{P}}}{TV(\Delta\alpha)}, \tag{10}$$

(cf. [11] Chap. 4, Section 4). Hence,

$$\Delta C_{\mathrm{P}} = \frac{\mathrm{d}\Pi}{\mathrm{d}T} TV(\Delta\alpha), \tag{11}$$

where α is the coefficient of thermal expansion and C_{P} is the heat capacity at constant pressure. From the slope of the tangent (Fig. 2) one obtains

$$\frac{\mathrm{d}\Pi}{\mathrm{d}T} = 8.2 \quad (10^{-4}\ \mathrm{GPa\ K^{-1}}). \tag{12}$$

In order to get $\Delta\alpha$, we have plotted the relation $V = V(T)$ on the basis of the data of [9] for $P = 0.18$ GPa. This is the closest value of pressure P with respect to the electrostriction pressure $\Pi_t = 0.1854$ GPa value at 293 K, for which experimental data of $V = V(T)$ are available [9]. In the range $263 < T < 293$ K this relation has been approximated by a straight line (not shown), and in the range $293 < T < 413$ K – by another one (not shown). From the slope difference of the above lines, the value of $V(\Delta\alpha)$ has been found:

$$V(\Delta\alpha) = 0.00023 \quad \frac{10^{-3}\ \mathrm{m}^3}{\mathrm{kg\ K}}. \tag{13}$$

At $T = 293$ K we have found from Eq. (11):

$$\Delta C_{\mathrm{P}} = 1.0 \quad \frac{\mathrm{J}}{\mathrm{mole\ K}}. \tag{14}$$

The above change in heat capacity ΔC_{P} at the transition is comparable (to the order of magnitude) to the values of ΔC_{P} that have been found in the Benderskii et al. [4] work.

Note that since the phase transition vanishes above the critical point, this thermal effect should vanish above T_{c}^{E} as well. Indeed, Benderskii et al. [4] observed vanishing of the entropy and ΔC_{P} extremes, characteristic of their thermal phenomena, starting at a temperature of about 323 K, which is only slightly higher than the upper limit of the critical temperature $T_{\mathrm{c}}^{E} = 313$ K found in this work.

6. Conclusion

Previously, it had been established, that at ambient conditions H_2O in a very high field, in particular in the double layer at a charged electrode with a surface charge density $\sigma \sim 0.3\ \mathrm{C\ m^{-2}}$ undergoes a phase transition [1–3]. Hitherto, the question what happens to this transition when temperature is varied has remained open. In this Letter, a model approach previously applied to the problem of the phase transition mentioned above is extended to the range 273–313 K of temperature. We present new results indicating that there is a critical temperature, T_{c}^{E}, above which no transition in water due to the field is possible. This result is corroborated by experiment [4].

To summarize:

On the basis of the thermodynamic equation of state we have plotted the isothermal electrostriction pressure as a function of the surface charge density on an electrode in an open system containing water in a high field for 273, 283, 293, 303 and 313 K.

We have found a region of coexistence of two water phases with different degree of orientational order of the dipole moments in the high electric field.

The highest point of the two-phase region boundary in the Π–σ plane (Fig. 1) represents the newly introduced *critical point*, termed ‘electric’ critical point to discern it from the usual one present at the phase boundary line of liquid water and vapour.

The existence of the predicted phase coexistence line (Fig. 2) is confirmed by the related discontinuity in C_{P} (Eq. (14)) corresponding to that observed by Benderskii et al. [4] at the Hg/aqueous electrolyte interface.

The existence of T_{c}^{E} is confirmed by vanishing of this experimental effect above some limiting temperature [4] close to the value of $T_{\mathrm{c}}^{E} = 308 \pm 5$ K predicted in this Letter.

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