Two-dimensional phase transitions of water dipoles at mercury/aqueous solution interfaces

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The critical temperatures pertaining to order-disorder transitions of water dipoles at mercury/aqueous solution interfaces are estimated taking into account the hydrogen bonding considerations and surface coordination effects via Gibbs free energies. The computed values are in agreement with the experimental data deduced using Laser-induced temperature jump methods as well as empirical correlations.

The study of two-dimensional phase transitions of dipoles at electrode/electrolyte interfaces has been a fascinating topic of research for the past few decades. In view of diverse nature of interfacial interactions (short range and long range coulombic interactions, substrate effects, non-electrostatic contributions etc.), the formulation of potential dependence of surface coverages and accompanying phase transitions has been a challenging task. Consequently, simple nearest neighbour Ising models under mean field approximations have been employed to predict the capacitance-potential behaviour as well as critical temperatures of a variety of organic compounds. On the other hand, the analysis of interfacial behaviour of water dipoles at mercury electrodes in the absence of adsorption of ions and neutral molecules also poses interesting issues as regards the rationalization of the experimental data. Hence, it is worthwhile investigating the orientational transitions of water molecules at mercury electrodes using hydrogen bonding effects and structural arrangement of water aggregates. This methodology thereby serves as complimentary to different statistical mechanical versions of interfacial phase transitions. In this paper, a phenomenological thermodynamic approach is provided for estimating the critical temperatures of order-disorder transitions of water molecules at mercury/aqueous solution interfaces from Gibbs free energies and hydrogen bonding considerations.

Methods

Order-disorder transitions of water dipoles at mercury electrodes

The order-disorder transitions pertaining to water dipoles at mercury electrodes have been investigated using laser-induced temperature-jump techniques. From these experimental results, the measured temperature-coefficients were correlated with the entropy changes. Consequently, two minima have been deduced viz (i) in the temperature range 283-313 K and (ii) between 333 and 353 K. These minima have been interpreted as arising from two different arrangements of water dipoles at the temperature ranges indicated above. For example, the anti-ferroelectric orientations are postulated to exist between 283 to 313 K, a ferroelectric arrangement being favored at T > 333 K. Hence, assuming an initial state of water monomers, the first process involves the conversion of this state to a ferroelectric orientation as the temperature is increased. The two processes may be visualized as shown in Scheme 1.

It is of interest to verify whether the temperature ranges pertaining to the above transitions can be interpreted using phenomenological thermodynamic considerations.

Transition to anti-ferroelectric orientation of water dipoles at mercury electrode

As seen from Scheme 1, water dipoles existing as individual entities constitute the state I, while in state II, self aggregates of water monomers via hydrogen bonding are formed as a result of the driving force due to the applied electric field and temperature. The origin of state II consists of the adsorption of aggregates of water molecules and water dipoles getting arranged in such a manner so as to form an
anti-ferroelectric state. The Gibbs free energy change for this process ($\Delta G_I$) is given by

$$\Delta G_I = \Delta G_{\text{formation}}^{\text{aggregate}} - \Delta G_{\text{formation}}^{\text{monomer}}$$

Equivalently,

$$\Delta G_I = \Delta H_{\text{formation}}^{\text{aggregate}} - T\Delta S_{\text{formation}}^{\text{aggregate}} - \Delta H_{\text{formation}}^{\text{monomer}} + T\Delta S_{\text{formation}}^{\text{monomer}}$$

At the critical temperature $T_c$, $\Delta G_I$ is zero thereby leading to

$$T_c = \frac{(\Delta H_{\text{formation}}^{\text{monomer}} - \Delta H_{\text{formation}}^{\text{aggregate}})}{(\Delta S_{\text{formation}}^{\text{monomer}} - \Delta S_{\text{formation}}^{\text{aggregate}})}$$

Equation 3 enables the calculation of $T_c$ if the appropriate enthalpy and entropy changes are incorporated. Since these parameters essentially arise from hydrogen bonding considerations the estimation of $T_c$ is rendered possible.

The O–H–O bond enthalpies are reported as 60.25 kJ mol$^{-1}$ from NMR spectroscopic data. Since a tetrahedral arrangement of water molecules is the most stable state, $\Delta H_{\text{formation}}^{\text{aggregate}} = 4(\Delta H_{\text{formation}}^{\text{O–H–O}}) = 241.0$ kJ mol$^{-1}$. Analogously, O–H–O bond entropies have been estimated using quantum mechanical calculations as 437.23 J K$^{-1}$ mol$^{-1}$ whereby $\Delta S_{\text{formation}}^{\text{aggregate}} = 4(\Delta S_{\text{formation}}^{\text{O–H–O}}) = 1748.91$ J K$^{-1}$ mol$^{-1}$ and from tabular compilations $\Delta H_{\text{formation}}^{\text{monomer}} = -285.83$ kJ mol$^{-1}$ and $\Delta S_{\text{formation}}^{\text{monomer}} = 69.91$ J K$^{-1}$ mol$^{-1}$ for water.

Employing these values in Eq. (3), $T_c$ is obtained as 313.20 K and is in good agreement with the experimental data of 313 K, deduced from the Laser-induced temperature jump methods.$^{11-13}$

**Transition from anti-ferroelectric to ferroelectric state of water dipoles**

In this process, a transition to ferroelectric state occurs as a result of the change in the applied electric field and temperatures wherein the coordination to Hg electrode via the oxygen atom of water dipoles is encountered. (The alignment of water dipoles with the mercury surface via one of their hydrogen atoms is precluded in view of the high affinity of Hg for coordination with oxygen). Consequently, the interaction energetics associated with the electrode surface needs to be incorporated. Thus,

$$\Delta G_{\text{II}} = \Delta G_{\text{formation with coordination}}^{\text{aggregate}} - \Delta G_{\text{formation}}^{\text{aggregate}}$$

Since $\Delta G_{\text{II}}$ vanishes at $T = T_c$, we obtain

$$T_c^{\text{II}} = \frac{(\Delta H_{\text{formation}}^{\text{aggregate}} - \Delta H_{\text{formation with coordination}}^{\text{aggregate}})}{(\Delta S_{\text{formation}}^{\text{aggregate}} - \Delta S_{\text{formation with coordination}}^{\text{aggregate}})}$$

In this case, the bond enthalpy due to Hg–O coordinations as well as the corresponding entropy changes need to be taken into account. The enthalpy and entropy changes involved in the Hg–O bond formation is reported as 221.0 kJ mol$^{-1}$ and 663.7 J K$^{-1}$ mol$^{-1}$ respectively.$^{15}$
\[ \Delta H^\text{formation}_{\text{aggregate with coordination}} = 4(\Delta H^\text{formation}_{O-H-O}) + (\Delta H^\text{formation}_{Hg-O}) = 462.0 \text{ kJ mol}^{-1} \]

... (6)

and

\[ \Delta S^\text{formation}_{\text{aggregate with coordination}} = 4(\Delta S^\text{formation}_{O-H-O}) + (\Delta S^\text{formation}_{Hg-O}) = 2412.6 \text{ J K}^{-1} \text{ mol}^{-1} \]

... (7)

The critical temperature \( T_c'' \) in this case is estimated as 333 K which is in agreement with the experimental data of 333 K deduced from laser-induced temperature jump studies.\(^{11-13}\)

**Discussion**

The foregoing analysis has provided a method of estimating the critical temperatures for the order-disorder transitions of water dipoles at mercury electrodes. An alternate approach of estimating the same in the case of condensing nucleobases has been demonstrated recently via a linear correlation between the experimental critical temperatures and enthalpies of formation of self-aggregates taking into account surface-coordination effects. The resulting linear regression equation is given by

\[ T_c = (0.177 \pm 0.0091)\Delta H^\text{cond} + (259.59 \pm 3.27) \]

... (8)

where \( \Delta H^\text{cond} \) denotes the enthalpy change involved in the formation of the aggregates of the nucleobases under consideration. However, this regression equation has been deduced from the experimental data whereas in the present analysis, the transition temperatures have been estimated via Gibbs free energies. In a fortuitous manner, the required enthalpy changes \( \Delta H^\text{cond} \) ca 241.0 kJ mol\(^{-1}\) and 462.0 kJ mol\(^{-1}\) occur within the range of 200 kJ mol\(^{-1}\) to 600 kJ mol\(^{-1}\) wherein the regression equation is valid. Hence, substituting \( \Delta H^\text{cond} \) as 241 kJ mol\(^{-1}\) and 462 kJ mol\(^{-1}\) as estimated here, the critical temperatures \( T_c' \) and \( T_c'' \) are obtained as 302.25 ± 5.46 K and 321.81 ± 6.47 K respectively, in gross agreement with the experimental value of 313 K and 333 K corresponding to the processes I and II depicted in Scheme 1.

It may be pointed out here that the foregoing analysis is based on phenomenological thermodynamic considerations whereas a microscopic description of interfacial phase transitions would require detailed incorporation of potential functions in the presence of external electric field. Further, it may be essential to consider the fraction of hydrogen bonds involved in the tetrahedral structure of water molecules as in the case of ice-type models so as to achieve a more realistic description of phase transitions of water at electrode surfaces. These will enable a more rigorous estimate of the critical temperature as well as new insights into the order–disorder transitions occurring at electrode surfaces.

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**References**