The Water Activity of Aqueous Solutions in Equilibrium with Ice

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A thermodynamic derivation is presented to show that the water activity of aqueous solutions in equilibrium with ice is independent of the nature of the solute. In addition, recent data of ice nucleation in $MgCl_2$ solutions are compared to water-activity-based ice nucleation theory.

The formation of ice from supercooled metastable aqueous solutions is important for many atmospheric, biochemical, and physiological processes. Recently, Miyata et al.[1] have published an extensive data set of homogeneous ice nucleation temperatures (T_f) in aqueous solutions of alkali chlorides, alkali acetates, $MgCl_2$, and $AlCl_3$. In addition, they demonstrated an interesting relationship between these T_f-values and the cationic radius of the various salts. At the end of their article, they referred to a paper that we have recently published.[2] In that paper we showed from experimental data that the homogeneous nucleation of ice from supercooled aqueous solutions is independent of the nature of the solute, but depends only on the water activity of the solution, a_w. In addition, a constant offset between the water activity at the ice nucleation temperature, a_w, and the water activity of a solution in equilibrium with ice at the same temperature, a_w^i, was observed, with $a_w - a_w^i = 0.305$ over the entire temperature range investigated. Our data analysis provides strong evidence that the kinetic (non-equilibrium) ice nucleation process is driven entirely by thermodynamic (equilibrium) quantities.

Miyata et al.[1] stated that these conclusions were derived under two important assumptions: (1) the melting point depression is dependent only on a solute concentration but is independent of its nature, and (2) all salts are fully dissociated. Based on their experimental data Miyata et al.[1] concluded that these assumptions and, therefore, also our conclusions are not quantitatively valid. However, neither of the two assumptions above have been used in our derivation of the water-activity-based ice nucleation theory.[2] In the following I try to clarify how we arrived at our conclusions by addressing both of the above statements. In addition, data by Miyata et al.[1] are compared with predictions from our theory.

Statement (1): This assumption is valid for ideal solutions only[3] and does not apply to the highly concentrated non-ideal solutions in Miyata et al.[1] and Koop et al.[2] Therefore, we have used a different approach using water activities instead. By doing so we arrived at the result that the water activity of a solution in equilibrium with ice is independent of the nature of the solute. This can be demonstrated on the basis of the following thermodynamic considerations:

At atmospheric pressure, water vapor can be treated to a very good approximation as an ideal gas. Hence, the chemical potential of water in the gas phase, $\mu_w(g)$, at a water partial pressure p_w is defined as[3]

$$\mu_w(g) = \mu_w^*(g) + RT\ln\left(\frac{p_w}{p^*}\right) \tag{1}$$

where R is the ideal gas constant, T is absolute temperature, and $\mu_w^*(g)$ is the chemical potential of the hypothetical ideal gas at standard pressure $p^* = 1$ bar. For our purposes, we are interested in the chemical potentials of water in the condensed phase, i.e., the chemical potential of water in pure liquid water, $\mu_w^0(l)$, in a liquid aqueous solution, $\mu_w(l)$, and in pure solid ice, $\mu_w^0(s)$. At equilibrium between each of the condensed phases and the gas phase, the water chemical potentials in the two phases are equal:

$$\mu_w^0(l) \equiv \mu_w(g) = \mu_w^*(g) + RT\ln\left(\frac{p_{w,l}^0}{p^*}\right) \tag{2}$$

$$\mu_w(l) \equiv \mu_w(g) = \mu_w^*(g) + RT\ln\left(\frac{p_{w,l}}{p^*}\right) \tag{3}$$

$$\mu_w^0(s) \equiv \mu_w(g) = \mu_w^*(g) + RT\ln\left(\frac{p_{w,s}^0}{p^*}\right) \tag{4}$$

Here, $p_{w,l}^0$ is the water vapor pressure over pure liquid water, $p_{w,l}$ is the water vapor pressure over a liquid aqueous solution, and $p_{w,s}^0$ is the water vapor pressure over ice. We can rearrange Eqs. 2 and 3 by eliminating $\mu_w^*(g)$ such that

$$\mu_w(l) = \mu_w^0(l) + RT\ln\left(\frac{p_{w,l}}{p_{w,l}^0}\right) \tag{5}$$

According to Raoult's law the vapor pressure ratio in Eq. 5 is equal to the mole fraction of water in an ideal solution, $x_w = (p_{w,l}/p_{w,l}^0)$. However, Raoult's law is not obeyed in real solutions, but its form can be preserved by defining the water activity $a_w \equiv (p_{w,l}/p_{w,l}^0)$ such that Eq. 5 becomes

$$\mu_w(l) = \mu_w^0(l) + RT\ln(a_w) \tag{6}$$

Equation 6 is generally applicable for aqueous solutions under all conditions. At equilibrium between ice and an aqueous solution (at the ice melting point of the solution), the water chemical potentials are equal in both phases:

$$\mu_w(l) \equiv \mu_w^0(s) \tag{7}$$

and from Eqs. 3 and 4 it follows that the water vapor pressures over such a solution is equal to the water vapor pressure over ice:

$$p_{w,l} = p_{w,s}^0 \tag{8}$$

Replacing Eq. 8 into Eq. 5 yields

$$\mu_{\mathrm{w}}(l) = \mu_{\mathrm{w}}^{0}(l) + RT\ln\left(\frac{p_{\mathrm{w,s}}^{0}}{p_{\mathrm{w,l}}^{0}}\right) \tag{9}$$

and with Eq. 6 we finally arrive at

$$a_{\mathrm{w}}^{\mathrm{i}} = \frac{p_{\mathrm{w,s}}^{0}}{p_{\mathrm{w,l}}^{0}} \tag{10}$$

Equation 10 reveals that the water activity of a solution in equilibrium with ice, $a_{\mathrm{w}}^{\mathrm{i}}$, is equal to the ratio of the water vapor pressure over ice to the water vapor pressure over pure liquid water. Both these vapor pressures $p_{\mathrm{w,s}}^{0}$ and $p_{\mathrm{w,l}}^{0}$ are dependent on temperature only. Hence, $a_{\mathrm{w}}^{\mathrm{i}}$ (shown as the dashed line in Fig. 1b) also depends on temperature only and neither on the solute's nature nor its concentration. Equation 10 implies that two solutions of different solutes always have the same water activity at the same ice melting point. This is the initial statement that has been used in our derivation of the water-activity-based ice nucleation theory in Koop et al.[2]

Statement (2): The degree of dissociation of salts or acids in aqueous solutions was not required for the derivation of the water-activity-based ice nucleation theory. In Fig. 1a of Koop et al.[2] we compared the experimentally observed melting points of all solutions to indicate the non-ideal behavior of the concentrated solutions. In this figure we treated all salts and acids as fully dissociated since this is a better assumption than treating them as undissociated.[3] Either way, however, the observed melting points do not follow the melting point depression law for ideal solutions. This was the reason for using water activities instead.

Based on the arguments presented above there is no direct indication that the experimental data of Miyata et al.[1] imply that our nucleation theory[2] is incorrect. In order to put our nucleation theory to a test, the freezing point data of Miyata et al.[1] have to be converted from molality to water activity first. In the following, I use the $MgCl_2$ data as an example to perform such a test. $MgCl_2$ was chosen because it was not included in our previous treatise[2] and also because it is a commonly used antifreeze.[4] In addition, high accuracy ice melting point data and room temperature water activity data over the relevant concentration range are readily available in the literature.[4–6]

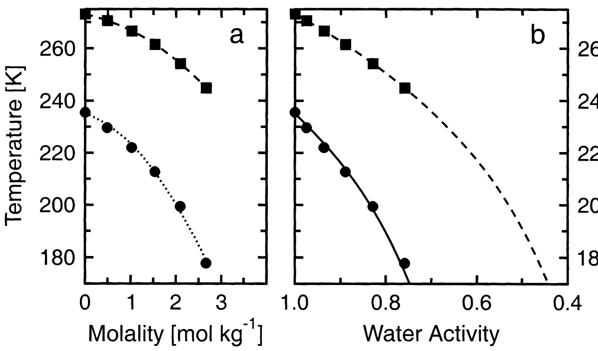

Fig. 1. (a) The ice melting points (squares) and homogeneous freezing points (circles; taken from Ref. 1) of aqueous $MgCl_2$ solutions as a function of $MgCl_2$ molality. (b) The same data as a function of the solution water activity. The dashed line is the universal ice melting point curve for aqueous solutions discussed above and the solid line is the freezing point prediction according to water-activity-based ice nucleation theory.[2] Note the constant offset between the two curves of $a_{\mathrm{w}} - a_{\mathrm{w}}^{\mathrm{i}} = 0.305$.

First, the freezing points and the corresponding concentrations were taken from Fig. 3 of Ref. 1. They are shown as circles in Fig. 1a. Then the ice melting point curve of $MgCl_2$ solutions was obtained by fitting the literature data[4,5] to a polynomial:

$$T_{\mathrm{m}} = 273.15 - 4.335\, m - 1.851\, m^2 - 0.1941\, m^3 \tag{11}$$

where T_{m} is the ice melting point in Kelvin and m is the $MgCl_2$ molality in mol kg^{-1}. From this curve (indicated by the dashed line in Fig. 1a) the melting points for the solutions used by Miyata et al.[1] were derived (squares in Fig. 1a). The corresponding water activities for these solutions at their respective melting point were calculated using Eqs. 1 and 2 in Ref. 2. At this point we have to use the only approximation in our data analysis, which is that the water activity at the freezing point is the same as that at the melting point, i.e. $a_{\mathrm{w}}(T_{\mathrm{f}}) = a_{\mathrm{w}}(T_{\mathrm{m}})$. This implies that for a fixed composition the solution water activity is independent of temperature which is a very good assumption for many salts. It was tested that this is also the case for $MgCl_2$ solutions by comparing the low temperature water activities derived from the melting points to those at 298.15 K published by Goldberg and Nuttall.[6] The change in water activity from 298.15 K to 244.85 K for the most concentrated sample was less than 1.5% which is negligible for our purposes. All other concentrations showed smaller differences.

The result of this procedure is shown in Fig. 1b. The ice freezing and melting points of $MgCl_2$ as a function of water activity are shown as circles and squares, respectively. Also shown as the solid line are the homogeneous ice freezing temperatures predicted by the water-activity-based ice nucleation theory.[2] Note that the expression employed to calculate the solid line contains no adjustable parameter. It is fair to say that the agreement between the measured freezing points by Miyata et al.[1] and the predictions by our theory[2] is very good. We are currently investigating whether the same is true for the other data sets presented by Miyata et al.[1]

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