Theoretical Prediction of the Water Activity of Standard Saturated Salt Solutions at Various Temperatures

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ABSTRACT

A theoretical approach was used to predict the water activity ($a_w$) at 15°C and 35°C of selected saturated salt solutions used as standards in the range of microbial growth ($\approx$0.57–0.97). For this purpose a rigorous thermodynamic model to predict osmotic coefficient was used. The results agreed very well with experimental measurements at 15°C and 35°C for most salts studied, which included NaBr, NaCl, (NH$_4$)$_2$SO$_4$, KCl, BaCl$_2$, and K$_2$SO$_4$. For KNO$_3$ the agreement at the higher temperature was somewhat less satisfactory and the reasons for this behavior are discussed.

INTRODUCTION

It is well known that adjustment of the water activity ($a_w$) of foods is an important method of controlling spoilage by microorganisms (Troller and Christian, 1978). This has been recognized by regulatory agencies in several countries who have incorporated the $a_w$ principle in the definition of standards for various preserved foods.

The U.S. Food & Drug Administration has adopted the water activity specification in the definition of low-acid foods (FDA, 1973) as has the FAO/WHO Codex Alimentarius Commission (FAO/WHO, 1979) and the European Community for the trade of meats products (EEC, 1976). The reliability of most $a_w$ measuring devices such as electric or fiber-dimensional hygrometers, strongly depends on proper calibration using reference sources of $a_w$. Saturated salt solutions are used by a large number of people as a convenient way to provide solutions of known $a_w$. They are reproducible reference standards because no measurement of concentration is needed and if the salts are properly chosen no interfering vapors are present (Stoloff, 1978; Gal, 1981).

Considerable data and several reviews are available on the $a_w$ of standard salt slurries (Stokes and Robinson, 1949; Wexler and Hasegawa, 1954; Young, 1967; Rockland, 1960; International Critical Tables, 1926; Labuza et al., 1976; Greenspan, 1977). Unfortunately, most reports in the literature do not agree on the exact $a_w$ of each saturated salt solution. Considerable doubt has arisen about the accuracy of water activity of saturated salt solutions in view of the recent review by Greenspan (1977). His work reflects very well the uncertainties of literature values from various workers. Recently, Resnik et al. (1984) reported the results of a world survey of $a_w$ values at 25°C of selected saturated salt solutions used as standards in the range of $a_w$ 0.57–0.97, which is of most interest to microbial growth. Their results confirmed the discrepancies between laboratories regarding the correct $a_w$ to assign to each salt. The survey was limited to 25°C but it was expected that the discrepancies would be even larger if other temperatures were considered. It is obvious that for different regulatory agencies to adopt an $a_w$ specification for foods, and for different researchers to reproduce each others $a_w$ measurements, there must be an "universal" agreement on the values to be assigned to reference standards of saturated salt solutions. This agreement should include not only 25°C but also other temperatures of interest of microbial growth.

The purpose of this study was to use a theoretical approach based on the thermodynamic properties of strong electrolyte aqueous solutions to calculate the $a_w$ of selected saturated salt solutions in the temperature range 15–35°C. The study covered the range of $a_w$ of most interest to microbial growth ($\approx$0.57–0.97). The predicted results were compared with experimental data obtained with an electric hygrometer previously calibrated with unsaturated salt solutions for which agreement on their $a_w$ at 15°C and 35°C existed.

MATERIALS & METHODS

Materials

Saturated salt solutions were prepared by mixing a large excess of each salt and distilled water and stored at 15°C (±0.2°C) or 35°C (±0.2°C) in a forced convection low-temperature incubator for various days before using. Seven reagent grade salts were used: sodium bromide, sodium chloride, ammonium sulfate, potassium chloride, barium chloride, potassium nitrate and potassium sulfate. These salts have been used extensively as reference standards of water activity in the range of interest to the present study. Unsaturated solutions of sodium chloride and lithium chloride were prepared using anhydrous reagent grade salts for calibration of the hygrometer at 15°C and 35°C.

Measurement of $a_w$

The $a_w$ of the six saturated salt solutions at 15°C and 35°C was measured using a Novasina Humidity-TH2 Thermoconstanter hygrometer (Novasina AG, CH-8050 Zürich, Switzerland). This instrument has a built-in accurate temperature control device which maintains the sensor and the sample at constant temperature in the range 0-50°C. The hygrometer was operated following the procedure described in detail by Kitic et al. (1986). Each $a_w$ measurement represents the average of three determinations. As shown previously (Kitic et al., 1986), three replicates are enough to obtain a precision of ±0.005 $a_w$ when using the Novasina Thermoconstanter for measuring the $a_w$ of saturated salt solutions in the range of interest of this study. To measure the $a_w$ of saturated salt solutions at 15°C and 35°C the instrument was first calibrated at these temperatures using other standards for which agreement exists on their $a_w$ at 15°C and 35°C. Chirife and Resnik (1984) and Kitic et al. (1986) proposed the use of unsaturated solutions of NaCl and LiCl as isopiestic standards for calibration of $a_w$ measuring devices at various temperatures and showed that there was excellent agreement between their values of $a_w$ on the exact value of the $a_w$ of these solutions; thus these values were used for the calibration of the Novasina Thermoconstanter at 15°C and 35°C. Table 1 shows the data used for the calibration; at least six points were used at each temperature. NaCl solutions are useful as standards only for, values of $a_w$ of about 0.75 and above (saturation value); for this reason LiCl solutions were used as standards for lower $a_w$ values. Equilibration times for measuring $a_w$ of each saturated salt were previously determined and ranged between 30–90 min.
RESULTS & DISCUSSION

Theoretical prediction of the $a_w$ of aqueous strong electrolyte solutions

The thermodynamic properties of aqueous strong electrolyte solutions have been extensively studied both experimentally and theoretically. Excellent examples may be found in the standard monographs by Harned and Owen (1958) and Robinson and Stokes (1965) or in the more recent works of Scatchard (1968), Scatchard et al. (1970), Pitzer (1973) and Bromley (1973). One of the most useful and accurate theoretical models to predict the $a_w$ of salt solutions is that of Pitzer (1973), (Pitzer and Mayorga, 1973). Pitzer (1973) developed a system of equations (ion-interaction model) for the thermodynamic properties of strong electrolytes which yield agreement within experimental error up to concentrations of several mol/kg (in numerous cases very close to saturation). It is interesting to note that the fit was particularly good for 1-1 and 2-1 electrolytes, which are the ones of concern in the present study.

The osmotic coefficient, $\phi$, is defined as

$$\phi = \frac{-55.51 \ln a_w}{v_1 n_1}$$

(1)

where $v_1$ is the number of particles into which each solute of molality $m_1$ dissociates. The osmotic coefficient is given by the equations developed by Pitzer (1973) as:

$$\phi - 1 = \frac{Z_M Z_X}{Z_X} \frac{2m_2 v_X}{v} B_{MX} + m^2 \frac{2(5v_0 + v_1)}{v} C_{MX}$$

(2)

where, $v_0$, $a_w$, and $X$ are the number of M and X ions in the formula and $Z_M$ and $Z_X$ give their respective charges in elec-
dependence of $\beta^{(0)}$, $\beta^{(1)}$ and $C_{MX}$ for NaCl solutions are given as:

$$
\beta^{(0)} = q_1 + q_2 \left( \frac{1}{T_R} - \frac{1}{T} \right) + q_3 \ln \left( \frac{T}{T_R} \right) + q_4(T - T_R) + q_5(T^2 - T_R^2)
$$

$$
\beta^{(1)} = q_6 + q_7(T - T_R) + q_8(T^2 - T_R^2)
$$

$$
C_{MX} = q_{11} + q_{12} \frac{T}{T_R} + q_{13} \ln \left( \frac{T}{T_R} \right) + q_{14}(T - T_R)
$$

where $T_R$ is 298.15°C and the values of the parameters $q_1$ to $q_{14}$ are given in Table 3. These values, along with Eq. (3), (4), (5), (2) and (1) allow a rigorous and accurate prediction of the $\alpha_w$ of NaCl solutions for the whole concentration range (up to saturation) and any desired temperature. The values of the Debye-Hückel parameters (Eq. 2) at different temperatures are given by Ananthaswamy and Atkinson (1984) and those of $b$ and $\alpha$ are taken as temperature independent.

Recently, Holmes and Mesmer (1983) applied the ion-interaction model of Pitzer (1973) to aqueous solutions of the alkali metal chlorides to 250°C. Their resulting set of equations provide a thermodynamic description within the accuracy of the reported experimental data. The parameters $\beta^{(0)}$, $\beta^{(1)}$ and $C_{MX}$ are described by arbitrary functions of temperature, $f(T)$ of the form

$$
f(T) = p_1 + p_2 \left( \frac{1}{T} - \frac{1}{T_R} \right) + p_3 \ln \left( \frac{T}{T_R} \right) + p_4(T - T_R) + p_5(T^2 - T_R^2) + p_6 \ln(T - 260)
$$

where $p_1$, $p_2$, $p_3$, $p_4$, $p_5$, and $p_6$ are parameters.

With the exception of the term involving $p_6$ this equation is identical with the form used by Silvester and Pitzer (1977). The values of the parameters $p_1$, $p_2$, $p_3$, $p_4$, $p_5$, and $p_6$ for aqueous solutions of potassium chloride are listed in Table 4; they allow a very accurate calculation of the $\alpha_w$ of KCl solutions for the whole concentration range (up to saturation) at any temperature.

Silvester and Pitzer (1978) gave the change with temperature of the activity and osmotic coefficients. They reported results for 84 electrolytes of 1-1, 2-1, 3-1 and 2-2 valence types. The parameters allow the convenient calculation of properties at other temperatures not too different from 25°C. The values of $\beta^{(0)}$, $\beta^{(1)}$ and $C_{MX}$ at temperatures not too different from 25°C (i.e., 15°C or 35°C as is the case in the present paper) can be approximated by

$$
f(T) = f(25°C) + \frac{\partial f}{\partial T}(25°C)\Delta T
$$

where $f(T)$ is the value of the function at temperature $T$. The values of the corresponding derivatives for the salts of interest to the present study are given in Table 5. The most important conclusion is that for almost all salts considered here the temperature derivatives are relatively small. Thus, for NaBr, NaCl, KCl, BaCl$_2$, and K$_2$SO$_4$ where $\beta^{(0)}$ and $\beta^{(1)}$ at 25°C had a magnitude of about 0.05 or a few tenths (Table 2), the derivations

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Salt & $\beta^{(0)}$ (10$^{-4}$) \tabularnewline
\hline
NaBr & 1.709 \tabularnewline
NaCl & 1.709 \tabularnewline
(NH$_4$)$_2$SO$_4$ & 2.75 \tabularnewline
KCl & 2.95 \tabularnewline
BaCl$_2$ & 3.85 \tabularnewline
KNO$_3$ & 4.15 \tabularnewline
K$_2$SO$_4$ & 5.95 \tabularnewline
\hline
\end{tabular}
\caption{Table 5—Parameters of the temperature derivatives in Eq. (7) for some selected salt solutions}
\end{table}
a_{w} OF SALT SOLNS AT VARIOUS TEMPS...

Table 9—Prediction of the a_{w} of selected saturated salt solutions at 15°C and 35°C neglecting the effect of temperature on the thermodynamic parameters of the ion-interaction model

<table>
<thead>
<tr>
<th>Salt</th>
<th>a_{w} (15°C)</th>
<th>a_{w} (35°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBr</td>
<td>0.601 ± 0.002</td>
<td>0.522 ± 0.008</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.752 ± 0.001</td>
<td>0.750 ± 0.001</td>
</tr>
<tr>
<td>(NH_{4})<em>{2}SO</em>{4}</td>
<td>0.808 ± 0.002</td>
<td>0.798 ± 0.002</td>
</tr>
<tr>
<td>KCl</td>
<td>0.856 ± 0.002</td>
<td>0.830 ± 0.001</td>
</tr>
<tr>
<td>BaCl_{2}</td>
<td>0.910 ± 0.001</td>
<td>0.885 ± 0.002</td>
</tr>
<tr>
<td>KNO_{3}</td>
<td>0.944 ± 0.001</td>
<td>0.907 ± 0.002</td>
</tr>
<tr>
<td>K_{2}SO_{4}</td>
<td>0.979 ± 0.000</td>
<td>0.972 ± 0.000</td>
</tr>
</tbody>
</table>

* Pitzer (1973)

* Fluctuations in the predicted a_{w} values arise from the standard deviation of the solubility data.

Table 9—The a_{w} of selected saturated salt solutions between 15°C and 37°C

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>NaCl</th>
<th>(NH_{4})<em>{2}SO</em>{4}</th>
<th>KCl</th>
<th>BaCl_{2}</th>
<th>K_{2}SO_{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.753</td>
<td>0.808</td>
<td>0.859</td>
<td>0.910</td>
<td>0.979</td>
</tr>
<tr>
<td>17</td>
<td>0.753</td>
<td>0.806</td>
<td>0.856</td>
<td>0.909</td>
<td>0.978</td>
</tr>
<tr>
<td>19</td>
<td>0.752</td>
<td>0.805</td>
<td>0.852</td>
<td>0.907</td>
<td>0.977</td>
</tr>
<tr>
<td>21</td>
<td>0.752</td>
<td>0.804</td>
<td>0.849</td>
<td>0.906</td>
<td>0.977</td>
</tr>
<tr>
<td>23</td>
<td>0.751</td>
<td>0.803</td>
<td>0.846</td>
<td>0.905</td>
<td>0.976</td>
</tr>
<tr>
<td>25</td>
<td>0.751</td>
<td>0.803</td>
<td>0.842</td>
<td>0.903</td>
<td>0.975</td>
</tr>
<tr>
<td>27</td>
<td>0.750</td>
<td>0.802</td>
<td>0.840</td>
<td>0.902</td>
<td>0.975</td>
</tr>
<tr>
<td>29</td>
<td>0.750</td>
<td>0.801</td>
<td>0.836</td>
<td>0.900</td>
<td>0.974</td>
</tr>
<tr>
<td>31</td>
<td>0.750</td>
<td>0.800</td>
<td>0.833</td>
<td>0.899</td>
<td>0.973</td>
</tr>
<tr>
<td>33</td>
<td>0.749</td>
<td>0.799</td>
<td>0.830</td>
<td>0.898</td>
<td>0.973</td>
</tr>
<tr>
<td>35</td>
<td>0.749</td>
<td>0.798</td>
<td>0.827</td>
<td>0.896</td>
<td>0.972</td>
</tr>
<tr>
<td>37</td>
<td>0.748</td>
<td>0.797</td>
<td>0.823</td>
<td>0.894</td>
<td>0.971</td>
</tr>
</tbody>
</table>

It was experimentally found in the literature for several salts slurry; however, as reported by Scott and Barnard (1983), the "phytochemical reasons for the decrease in a_{w} were not fully understood." The a_{w} of saturated NaCl remained almost constant between 15°C and 35°C (Δa_{w} = 0.002) and this was expected on the basis of the solubility changes and very small effect of the temperature on the characteristic parameters in the model of Pitzer (1973). It was noteworthy that the predicted a_{w} values at 15°C and 35°C were in very good agreement with the values measured with the Novasina Thermoconstatier previously calibrated with unsaturated NaCl and LiCl solutions; differences between theoretical and experimental values were only about 0.002 a_{w}. The exception was KNO_{3} for which a larger difference was observed, these differences being 0.003 at 15°C and 0.009 at 35°C. This may be attributed to the relatively large values of the temperatures derivatives (Table 5) which make more uncertain the accurate theoretical prediction of the effect of temperature. KNO_{3} also exhibited a large increase of solubility with increasing temperature; extrapolation of Pitzer's (1973) model to the saturation concentration at 35°C may be somewhat less reliable.

Labuzza et al. (1985) used the vapor pressure manometer to measure the a_{w} of saturated NaCl and KCl solutions and reported values of 0.765, 0.748 and 0.727 for NaCl and 0.846, 0.841 and 0.786 for KCl at 25°C, 30°C and 45°C, respectively. The values for NaCl were not in good agreement with the theoretical predictions or with present experimental determinations; the values for KCl at 25°C and 30°C are in better agreement but the value for 45°C seems to be somewhat low. A simplified theoretical approach was also tested to predict the effect of a temperature change (from 25°C to 15°C or 35°C) on the a_{w} of salt slurries studied in this work. For this purpose it was assumed that the effect of temperature may be accounted for by only considering the effect on solubility and neglecting the intrinsic variation of a_{w} with temperature (i.e., the temperature derivatives of ion-interaction parameters are negligible). Thus, Eq. (2) with parameters β(0), β(1), C_{MX} corresponding to 25°C was used to predict the a_{w} values at saturation concentration at 15°C or 35°C. The Debye-Hückel parameters were those at the corresponding temperature 15°C or 35°C (Ananthaswamy and Atkinson, 1984). The results are shown in Table 8. Predicted values for NaBr, NaCl, KCl, BaCl_{2} and K_{2}SO_{4} agree quite well with the values obtained with the more rigorous approach (Table 7). This method allowed the prediction of a_{w} at 15°C and 35°C of (NH_{4})_{2}SO_{4} there is a good agreement with measured values (Table 7). As found before, KNO_{3} at a higher temperature (35°C) exhibited the greatest deviation. These results indicated that for the salts studied (with the exception of KNO_{3}) the increase in solubility was the dominant factor which regulated the change in a_{w} when temperature shifted from 25°C to 15°C or 35°C.

Having demonstrated the reliability of the theoretical predictions, the different equations and solubility data were used to calculate the a_{w} of unsaturated NaCl, (NH_{4})_{2}SO_{4}, KCl, BaCl_{2} and K_{2}SO_{4} every 2°C between 15°C and 37°C (a slight extrapolation above 35°C was done because of the microbiological interest in the temperature 37°C). The results are shown in Table 9; it is believed that these data are accurate enough for almost all needs in food microbiology research or quality control. NaBr and KNO_{3} were not included here because the predictions were somewhat less accurate than those for the others. This theoretical approach may help to find ways to reach a general agreement on the a_{w} of standards used to calibrate a_{w} measuring devices.

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