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Vapor pressure and water activity measurements of saturated salt solutions made with D_2O at 20°C

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Abstract

The water activity (a_w) values of 10 saturated salt solutions made with D_2O were measured in this study at 20°C: $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, KCl, $ZnSO_4$, $BaCl_2$, KNO_3, and K_2SO_4. These salts were selected because they represent a wide range of water activity values, from approximately 0.33 to 0.98. The a_w values were measured using two methods: (1) a vapor pressure manometer, and (2) an electronic chilled-mirror (AquaLab) instrument. The a_w values obtained by the manometer method were slightly, but consistently, higher than the a_w values obtained by the electronic chilled-mirror instrument. The a_w values of the saturated salt solutions made with D_2O (as measured by both methods) were also slightly, but consistently, higher than the a_w values of the same saturated salt solutions made with H_2O at 20°C. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Hygrometer calibration and material testing and conditioning often require the accurate control of humidity (Greenspan, 1977). The common methods of accurately controlling the humidity use either a humidity generator or the equilibration of a closed space with a chemical system which produces the desired equilibrium vapor pressure at a specified and constant temperature.

An especially robust method of humidity control by a chemical system is the use of binary saturated aqueous solutions (i.e. composed of a single solute and water) in which the solute is highly non-volatile, such as salts. Saturated aqueous salt solutions containing excess salt crystals are often used in the construction of isotherms for food and food ingredients (Labuza, 1984). In general, the equilibrium relative humidity (equal to water activity, a_w, divided by 100) of these saturated aqueous salt solutions decreases with increasing temperature. The excess salt crystals help to maintain the saturated aqueous salt solutions at a constant a_w during sample equilibration, where small amounts of water may be transferred from the sample to the solution. Due to the ease of its use, this is a popular method of humidity control (Greenspan, 1977; Stokes & Robinson, 1949). There are a wide variety of methods which can be used to determine the water vapor (or a_w) in equilibrium with the saturated aqueous salt solutions. These methods include the direct measurement of the vapor pressure, dew point measurement, isopiestic vapor pressure measurement, relative vapor pressure measurement, measurement with a calibrated humidity sensor, and gravimetric determination (Greenspan, 1977; Spiess & Wolf, 1987; Troller, 1989).

This study was undertaken because of the lack of literature a_w values for saturated aqueous salt solutions made with D_2O, which are often used to equilibrate samples for deuterium (^2H) nuclear magnetic resonance (NMR) spectroscopy experiments (Richardson, Baianu, & Steinberg, 1987; Schmidt, 1990; Schmidt & Lai, 1991). The objectives of this study were: (1) to measure the a_w values of 10 saturated salt solutions made with D_2O at 20°C ($MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, KCl, $ZnSO_4$, $BaCl_2$, KNO_3, and K_2SO_4), and (2) to compare the salt/D_2O a_w values to the a_w values of the same saturated salt solutions made with H_2O (salt/H_2O). These salt solutions were selected because they represent a wide range of a_w values, from approximately 0.33 to 0.98. The a_w values were measured using two methods: (1) a vapor pressure manometer, and (2) an

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electronic chilled-mirror (AquaLab) instrument. The vapor pressure manometric method gives a direct measure of the vapor pressure exerted by the sample. The a_w is calculated from the ratio of the vapor pressure of the sample to that of pure water or D_2O at the same temperature. The AquaLab is an electric hygrometer, which uses the chilled-mirror dew point technique to measure the a_w of a sample (Spiess & Wolf, 1987; Troller, 1989; Roa & Tapia de Daza, 1991). For the interested reader, research comparing the use of different water activity methods is given by Labuza et al. (1976).

2. Materials and methods

Ten saturated salt solutions made with D_2O were tested in this study: $MgCl_2$, K_2CO3, $Mg(NO_3)_2$, KI, NaCl, KCl, $ZnSO_4$, $BaCl_2$, KNO_3, and K_2SO_4. The salts (Analytical Reagent Grade, AR) were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Saturated salt solutions (slurries) were prepared by mixing individual salt crystals in D_2O (99.8%, Sigma Chemical Co., St. Louis, MO, USA) with constant stirring. Salt crystals were added to the D_2O until the solution was saturated, i.e. no more salt would dissolve. In addition, excess salt crystals were added to ensure that the saturated salt solutions would remain saturated throughout the experiment. Then, the saturated salt solutions with crystals were placed into individual proximity equilibration cells (Lang, McCune, & Steinberg, 1981) and kept at a constant temperature of 20°C in a CMS Equatherm Low Temperature incubator (Curtin Matherson Scientific Inc., Houston, TX, USA) until the vapor pressure and water activity measurements were made.

A simple U-type mercury manometer (Thamas Instruments, Philadelphia, PA, USA), equipped with a coolflow refrigerated recirculator (model CFT-25, Neslab Instruments Inc., Newington, NH, USA) and a vacuum pump, was used to directly measure the vapor pressure of the saturated salt solutions made with D_2O at 20 ± 0.5°C. About 5 g of each saturated salt solution was placed into a 25-ml sample flask and sealed to the manometer. The sample flask was water-jacketed to ensure constant temperature control. The air space in the manometer was evacuated using the vacuum pump. Two thermometers, one in the water jacketed sample flask and one in the air hanging from the top of the sample flask, were used to monitor the temperature during the experiment. The system was equilibrated at constant temperature until the manometer mercury showed no change in height, usually taking 30–60 min. The accuracy in reading the difference in the two manometer legs was ± 0.1 mmHg. The vapor pressure values for H_2O (distilled–deionized, 17.25 mmHg) and D_2O (15.00 mmHg) at 20°C were used to calibrate the manometer. These vapor pressure values were obtained from Lide (1997–98). Also, a $NaCl/H_2O$ saturated salt solution with salt crystals (0.755 a_w at 20°C, Greenspan, 1977) was used to check the accuracy of the manometric method. When the vapor pressure of each saturated salt solution made with D_2O was measured, the vapor pressure value was divided by the vapor pressure of pure D_2O at the same temperature to obtain the water activity value.

An AquaLab (Model CX-2 instrument, Decagon Devices, Inc., Pullman, WA, USA) water activity meter was also used in this study to measure the a_w of the saturated salt solutions made with both D_2O and H_2O at 20°C. To maintain the desired 20°C temperature, the AquaLab water activity meter was placed in a CMS Equatherm Low Temperature incubator (Curtin Matherson Scientific Inc., Houston, TX, USA) and the a_w measurements taken inside the incubator at a constant temperature of 20 ± 0.5°C. The temperature of the incubator was measured using a standard lab thermometer. Each measurement took approximately 10–15 min to reach equilibrium. The $NaCl/H_2O$ saturated salt solution with salt crystals (0.755 a_w at 20°C, Greenspan, 1977) was used to calibrate the AquaLab instrument. The a_w values of the salt/H_2O saturated salt solutions were measured for comparison purposes.

3. Results and discussion

The vapor pressure of the $NaCl/H_2O$ saturated solution used to check the accuracy of the vapor pressure manometric method was found to be 13.00 mmHg at 20°C. The corresponding a_w value was 0.754 (13.00 mmHg divided by the vapor pressure of pure water, 17.25 mmHg), which is very close to the literature value of 0.755 ± 0.001 at 20°C reported by Greenspan (1977).

The vapor pressure (manometric method) and a_w (AquaLab) values measured in this study for the saturated salt solutions made with D_2O and H_2O at 20°C are given in Table 1. The results indicate that the measured a_w values using the vapor pressure manometric method are similar to the measured a_w values using the AquaLab water activity meter for the same saturated salt solutions made with D_2O at 20°C (Table 1). However, the manometric method consistently yielded slightly lower a_w values compared to the a_w values obtained using the AquaLab water activity meter. The average difference between the two methods was calculated to be -0.0055. A paired t-test (two-tailed) showed that the a_w values obtained by the two methods were significantly different at the 0.0001 level. However, the a_w values obtained by the two methods are probably not scientifically different, since a_w is usually only measurable to within ± 0.005.

In general, for both measurement methods, the measured a_w values of the saturated salt solutions made

Table 1
Saturated salt solutions made with D_2O and H_2O, and their corresponding vapor pressure and water activity (a_w) values at 20°C

Salt	Salt/D_2O			Salt/H_2O	
	P_{AVG} (mmHg) ±SD[a]	a_w calc.[b]	a_w AquaLab ±SD[c]	a_w AquaLab ±SD[c]	a_w literature values[d]
K_2SO_4	14.6±0.2	0.973	0.980±0.003	0.969±0.003	0.976±0.005[e]
KNO_3	14.2±0.1	0.947	0.961±0.002	0.936±0.002	0.946±0.006[e]
$BaCl_2$	13.8±0.2	0.920	0.925±0.001	0.911±0.002	0.910±0.003[f]
$ZnSO_4$	13.3±0.2	0.887	0.896±0.001	0.883±0.001	0.890±0.002[f]
KCl	13.0±0.1	0.867	0.869±0.001	0.849±0.002	0.851±0.003[e]
NaCl	11.7±0.0	0.780	0.781±0.001	0.755±0.001	0.755±0.001[e]
KI	11.0±0.1	0.733	0.735±0.001	0.697±0.001	0.699±0.003[e]
$Mg(NO_3)_2$	8.1±0.1	0.540	0.544±0.000	0.540±0.002	0.544±0.002[e]
K_2CO_3	6.8±0.1	0.453	0.454±0.001	0.435±0.003	0.432±0.003[e]
$MgCl_2$	5.0±0.2	0.333	0.343±0.002	0.328±0.003	0.331±0.002[e]

[a] P_{AVG}, average vapor pressure value obtained using the manometric method;

[b] a_w calc., calculated a_w value from the ratio of P_{AVG} of the sample to P_{D_2O}, where $P_{D_2O} = 15.0$ mmHg at 20°C (Lide, 1997–98);

[c] a_w AquaLab, measured water activity value using the AquaLab water activity meter;

[d] a_w literature is the literature water activity value at 20°C.

[e] Greenspan (1977).

[f] McCune, Lang, & Steinberg (1981).

with D_2O were higher than the measured a_w values of the saturated salt solutions made with H_2O using the AquaLab water activity meter (Table 1). Specific comparisons of the salt/D_2O a_w values to the salt/H_2O a_w values for the same saturated salt solutions are as follows. The measured a_w values of the saturated salt solutions made with D_2O are higher than the measured a_w values of the same saturated salt solutions made with H_2O using the AquaLab water activity meter for all saturated salt solutions measured, with an average difference over all salt solutions ($\Delta a_w{}^1 = a_w$ AquaLab $H_2O - a_w$ AquaLab D_2O) of -0.0185 ± 0.0095. When the a_w values of the saturated salt solutions made with D_2O are compared to the literature a_w values of the saturated salt solutions made with H_2O ($\Delta a_w{}^2 = a_w$ literature $H_2O - a_w$ AquaLab $D_2O = -0.0154 \pm 0.0108$), the a_w values of the saturated salt solutions made with D_2O using both methods are higher, except for the a_w values for three samples (i.e. K_2SO_4, $ZnSO_4$ and $Mg(NO_3)_2$) obtained using the vapor pressure manometric method ($\Delta a_w{}^3 = a_w$ Literature $H_2O - a_w$ calc. $D_2O = -0.0099 \pm 0.0135$).

The difference in the a_w values between the same saturated salt solutions made with D_2O and H_2O may be due to the difference between the vapor pressure of pure H_2O (17.25 mmHg) or D_2O (15.00 mmHg) and/or the different solubility of same salts in pure H_2O or D_2O at the same temperature.

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