Continuous Measurements of the Water Activities of the $Mg^{2+}-Ca^{2+}-Na^{+}-Cl^{-}-NO_3^{-}-SO_4^{2-}-H_2O$ System

Man Yee Choi and Chak K. Chan*

Department of Chemical Engineering, Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

Condensational growth and deliquescence are important characteristics of atmospheric aerosols. A scanning electrodynamic balance (SEDB), based on a well-characterized increase of relative humidity (RH) in the vicinity of a levitated particle in an electrodynamic balance, was used to measure the water activity of an equal molar aqueous solution of $CaCl_2 + Ca(NO_3)_2$, $MgCl_2 + CaCl_2$, $Mg(NO_3)_2 + Ca(NO_3)_2$, $NaCl + Ca(NO_3)_2$, and $NaNO_3 + Ca(NO_3)_2$ mixtures in both evaporation and growth modes. These mixtures were selected because of the lack of literature data at high concentrations. $CaCl_2 + Ca(NO_3)_2$, $MgCl_2 + CaCl_2$, and $Mg(NO_3)_2 + Ca(NO_3)_2$ mixtures neither crystallize nor deliquesce because the solutes are nondeliquescent in single particle measurements. The presence of nitrate suppresses the crystallization of NaCl, since efflorescence was not observed even at RH = 20%. The water cycles of $NaCl + Ca(NO_3)_2$ (molar ratio = 3:1) and $NaNO_3 + Ca(NO_3)_2$ (3:1) mixtures were also measured. The results show that the presence of $Ca(NO_3)_2$ lowers the deliquescence relative humidity values of NaCl and $NaNO_3$ and alters their hygroscopicity. The Zdanovskii−Stokes−Robinson (ZSR) and Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) predictions are consistent with the water activity measurements except for the $Mg(NO_3)_2 + Ca(NO_3)_2$ mixtures, for which the predictions show significant deviations from the measurements at low RH. For the $Mg(NO_3)_2 + Ca(NO_3)_2$, $NaCl + Ca(NO_3)_2$, and $NaNO_3 + Ca(NO_3)_2$ mixtures, the ZSR model prediction shows larger deviation when compared with the measurements than does the SCAPE model throughout the range of water activity studied.

Introduction

Water-soluble atmospheric aerosols, which are hygroscopic by nature, undergo size changes in moist air. Consequently, this will affect their size distribution, deposition characteristics, radiative properties, and chemical reactivity. All these properties are crucial in understanding many other relevant atmospheric processes such as air pollution,[1] fog formation and cloud physics,[2] visibility degradation,[3] meteorology, and global climate.[4] To assess accurately the role that aerosols play in these phenomena, it is important to determine the physical and chemical properties of atmospheric aerosols under varying humidities. Water activity (a_w), one of the fundamental thermodynamic properties, is important in understanding the properties and behaviors of aerosols.

In the atmosphere, the major crustal elements are aluminum, silicon, iron, calcium, and magnesium. The nitrate and chloride salts of calcium and magnesium are water-soluble species, making them hygroscopic. Aerosols containing calcium and magnesium have been found to be significant in Los Angeles[5] and areas affected by Yellow Sand particles.[6] However, much attention has been paid to sodium, ammonium, and magnesium mixtures,[7−10] while very limited data on calcium and magnesium mixtures are available in the literature.[11]

In this study, we have utilized a scanning electrodynamic balance (SEDB) to measure the water cycles (i.e. the a_w during evaporation and growth) of equal molar mixtures of selected crustal and sea salt species including $CaCl_2 + Ca(NO_3)_2$, $MgCl_2 + CaCl_2$, $Mg(NO_3)_2 + Ca(NO_3)_2$, $NaCl + Ca(NO_3)_2$, and $NaNO_3 + Ca(NO_3)_2$ mixtures, in addition to $NaCl + Ca(NO_3)_2$ (molar ratio = 3:1) and $NaNO_3 + Ca(NO_3)_2$ (3:1) mixtures. The measured results are compared to the Zdanovskii−Stokes−Robinson (ZSR) model[12,13] and the Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) model,[14,15] which are two of the most commonly used models in the prediction of a_w of atmospheric aerosols, to test their capability in the prediction of a_w of crustal species.

Methods

In this study, we employed a technique that enables the measurement of a set of water activity of singly levitated aqueous aerosols in an hour using an electrodynamic balance (EDB).[16,17] Since the principles of the EDB have been widely documented, it suffices to mention in this paper that the EDB is a very sensitive microbalance in which the mass change of individual levitated micron-sized particles can be measured. A particle absorbs an appropriate amount of water when it is in equilibrium with the ambient environment. The a_w of the droplet is equal to RH/100 (relative humidity/100), if the curvature effect can be ignored. Hence, by measuring the mass change of the levitated particle at different RH values, a set of water activity data in the form of the mass fraction of the solute (mfs = mass of solute/mass of solute and water) versus a_w can be determined. Very often, levitated droplets can be supersaturated, and therefore the measured water activity of the droplet during evaporation (decreasing RH) and growth (increasing RH) can be different at supersaturation concentrations if crystallization takes place at low RH. At

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* Corresponding author. E-mail: keckchan@ust.hk. Telephone: (852) 2358-7124. Fax: (852) 2358-0054.

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Table 1. Experimental Conditions for Each Solution Studied

mixture	RH_1/%	RH_2/%	range of a_w studied	*T*/°C	range of lit. a_w[a]	ref
$CaCl_2 + Ca(NO_3)_2$	70[b]	10	0.20−0.70	23.1	0.457−0.972	11
(1:1)	30[c]	80	0.30−0.70			
$MgCl_2 + CaCl_2$	70[b]	10	0.20−0.70	23.0	N/A	N/A
(1:1)	30[c]	80	0.30−0.70			
$Mg(NO)_2 + Ca(NO_3)_2$	70[b]	10	0.20−0.70	22.1	0.6409−0.9771	11
(1:1)	30[c]	80	0.30−0.70			
$NaCl + Ca(NO_3)_2$	80[b]	20	0.30−0.80	22.3	N/A	N/A
(1:1)	20[c]	80	0.20−0.70			
$NaNO_3 + Ca(NO_3)_2$	80[b]	20	0.30−0.80	22.2	N/A	N/A
(1:1)	20[c]	80	0.20−0.70			
$NaCl + Ca(NO_3)_2$	80[b]	20	0.80−0.30	22.3	N/A	N/A
(3:1)	20[b]	80	0.20−0.70			
$NaNO_3 + Ca(NO_3)_2$	80[b]	20	0.80−0.30	22.1	N/A	N/A
(3:1)	20[c]	80	0.20−0.70			

[a] N/A = not available. [b] Evaporation study. [c] Growth study.

subsaturated concentrations, the measured a_w is identical, as dictated by equilibrium.

Compared with the conventional use of the EDB in which the RH is changed in discrete steps, our current technique involves the continuous scanning of RH, which reduces the time of measurement by an order of magnitude. Hence, we call the technique scanning EDB (SEDB). The experimental procedures are described in detail in refs 16 and 17. All measurements were made at 22 to 23 °C. In each individual study, the temperature varied less than 0.2 °C. Deviations in water activity within such small temperature changes are not expected to be significant. The error in the determination of RH depends on the flow rate of the feed stream, and it is estimated to be ±0.86% at RH = 40 to 80%. Table 1 summarizes the experimental conditions of each system studied.

Bulk water activity measurements were also made to provide the reference state concentrations for the calculation of mfs in the SEDB measurements. The water activities of bulk solutions were measured using an AquaLab water activity meter (Model 3TE, Decagon Devices, USA), and the procedures used in measuring the a_w (with accuracy of ±0.003) of the bulk solutions were described in detail by Peng and Chan.[18] All bulk measurements were made at 22 °C.

Results and Discussion

In this work, the water activities in both the evaporation and growth modes of Ca, Mg, and Na salt mixtures were measured and the results were then compared with the ZSR and SCAPE models. The ZSR model[12,13] is a simple mixing rule and is defined by the following empirical relation:

$$\sum_i \frac{m_i}{m_{0,i}} = 1$$

where m_i is the molality of species *i* in a multicomponent solution at a certain water activity and $m_{0,i}$ is the molality of the single component solution at the same water activity as that of the multicomponent solution.

The SCAPE model[14,15] is a rigorous thermodynamic model that estimates the state and composition of atmospheric inorganic aerosols between the gas and aerosol phases. It can be used to estimate some other important thermodynamic properties, for example, equilibrium constants, ionic activity coefficient, water activity, and deliquescence relative humidity (DRH). The inputs of the SCAPE model are the ambient temperature and compositions of the aerosol. Hygroscopic data on binary solutions are in the database of the model. In the SCAPE model, the activity coefficients of the system can be calculated using the Bromley, Kusik, and Meissner (KM) or Pitzer methods. The water content of the aerosol is then calculated by the ZSR equation with the consideration of the activity coefficients. Since all the activity coefficient calculation methods give almost identical predictions for the noncrystallizing and nondeliquescing mixtures studied, the SCAPE predictions using the Pitzer method are presented in Figures 1−5. For systems that partially crystallized at low RH, predictions using the KM and the Pitzer methods are compared. The comparisons of the model predictions with the measurements are shown in Table 2. The measured data in this study are summarized in Tables 3−7.

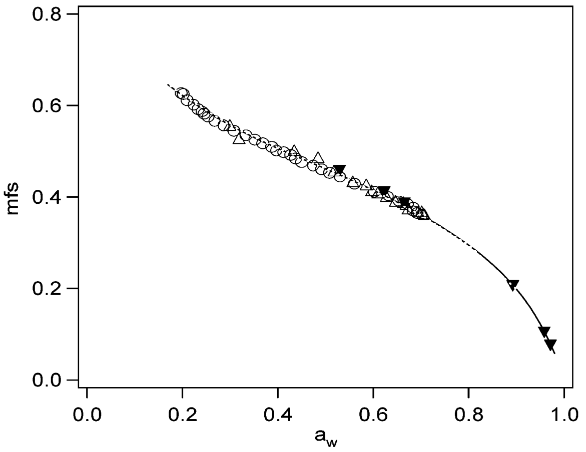

Figure 1. Water cycle of the $CaCl_2 + Ca(NO_3)_2$ = 1:1 mixtures: —, ZSR; ▼, Platford;[11] △, particle 1 (evaporation); ○, particle 2 (growth); - - -, SCAPE. ZSR and SCAPE represent the predictions by the ZSR equation and the SCAPE model.

Figure 1 shows the water cycle, that is, the water activity data from both evaporation and growth studies, of the $CaCl_2 + Ca(NO_3)_2$ (molar ratio = 1:1) mixtures. Platford[11] measured the osmotic coefficient of this mixture up to a total ionic strength of 23.36 mol kg^{-1} with molar ratios ranging from 0 to 2. The water activities of equal molar $CaCl_2 + Ca(NO_3)_2$ mixtures are interpolated from these bulk data. As both $CaCl_2$ and $Ca(NO_3)_2$ behave as nondeliquescent salts in levitated particle studies, this mixture does not crystallize. The measured data (for both evaporation and growth) are consistent with the bulk data from Platford[11] and the prediction from the ZSR and SCAPE models with a standard deviation of ±0.006 and ±0.005 for the evaporation study and ±0.008 and ±0.008 for the growth study, respectively. The single component data for

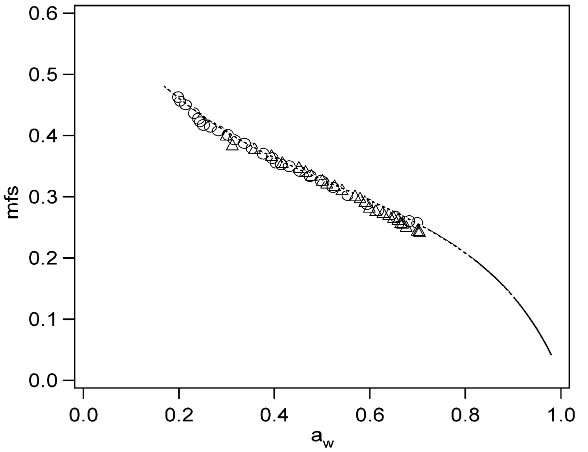

Figure 2. Water cycle of the $MgCl_2 + CaCl_2 = 1:1$ mixtures: —, ZSR; ○, particle 1 (evaporation); △, particle 2 (growth); - - -, SCAPE. ZSR and SCAPE represent the predictions by the ZSR equation and the SCAPE model.

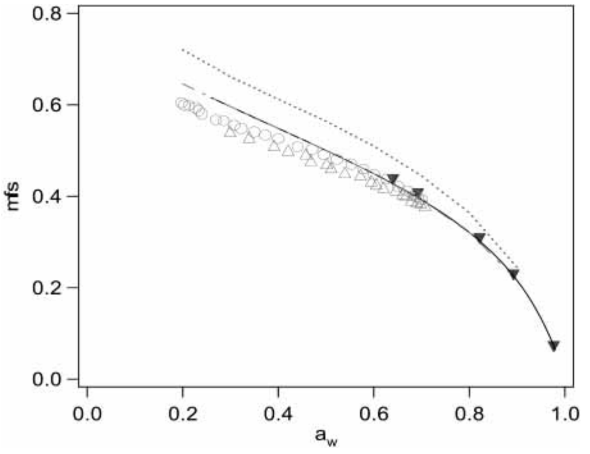

Figure 3. Water cycle of the $Mg(NO_3)_2 + Ca(NO_3)_2 = 1:1$ mixtures: —, ZSR; ▼, Platford;[11] ○, particle 1 (evaporation); △, particle 2 (growth); - - -, SCAPE 1; — - —, SCAPE 2. ZSR represents the predictions by the ZSR equation, and SCAPE 1 and SCAPE 2 represent the predictions by the SCAPE model based on the original version and the updated version, respectively.

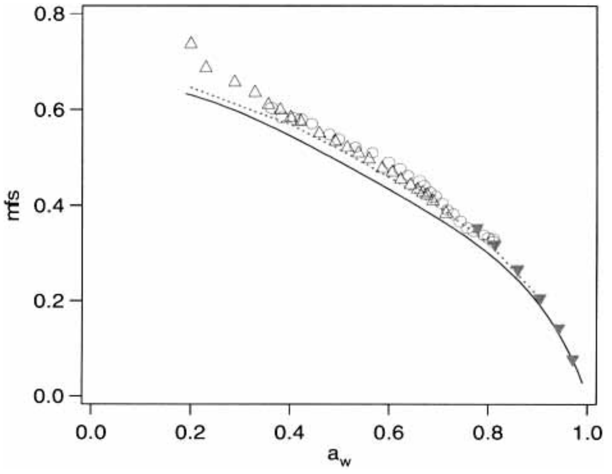

Figure 4. Water cycle of the $NaCl + Ca(NO_3)_2 = 1:1$ mixtures: —, ZSR; ○, particle 1 (evaporation); △, particle 2 (growth); - - -, SCAPE; ▼, bulk data (this study). ZSR and SCAPE represent the predictions by the ZSR equation and the SCAPE model.

$CaCl_2$ and $Ca(NO_3)_2$ used in the calculation of both the ZSR and SCAPE predictions were obtained from Cohen[19] and Stokes and Robinson.[20]

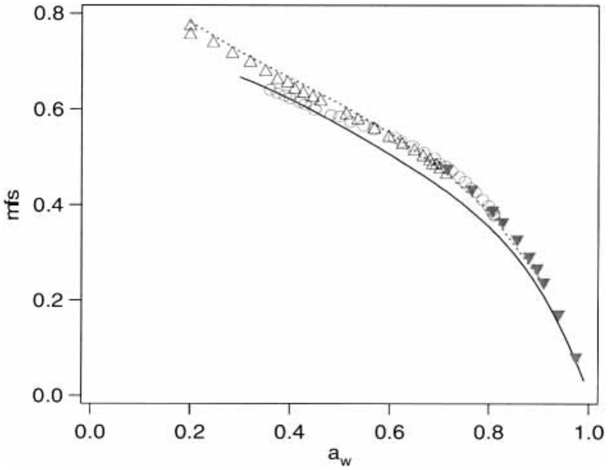

Figure 5. Water cycle of the $NaNO_3 + Ca(NO_3)_2 = 1:1$ mixtures: —, ZSR; ○, particle 1 (evaporation); △, particle 2 (growth); - - -, SCAPE; ▼, bulk data (this study). ZSR and SCAPE represent the predictions by the ZSR equation and the SCAPE model.

Figure 2 shows the results of the $MgCl_2 + CaCl_2$ (1:1) mixtures. The ZSR model was used to estimate the reference state concentration in the mfs calculations, because water activity data for this mixture are not available in the literature. Like the $CaCl_2 + Ca(NO_3)_2$ (1:1) mixtures, the $MgCl_2 + CaCl_2$ (1:1) mixtures do not exhibit crystallization nor deliquescence. The measured data agree well with both the ZSR and SCAPE predictions with a standard deviation of ±0.006 for the evaporation study and ±0.008 for the growth study, respectively. The a_w data on $MgCl_2$ used in the SCAPE model are from Goldberg and Nuttall,[21] but the data used in the ZSR model in this paper are from Ha and Chan.[8]

Figure 3 shows the water cycle of the $Mg(NO_3)_2 + Ca(NO_3)_2$ (1:1) mixtures. Platford[11] measured the osmotic coefficients of this mixture up to a total ionic strength of 18.09 mol kg^{-1} with molar ratios ranging from 0 to 2. Water activities of equal molar $Mg(NO_3)_2 + Ca(NO_3)_2$ mixtures are interpolated from these bulk data. The ZSR model gives accurate predictions only at low concentrations. Beyond $a_w = 0.6$, the ZSR predictions begin to deviate slightly from the evaporation and growth measurements with standard deviations of ±0.031 and ±0.028 for evaporation and growth studies, respectively. The SCAPE 1 predictions, based on the original version of the SCAPE model[14,15] in which a_w data for $Ca(NO_3)_2$ are used for those of $Mg(NO_3)_2$ because of "lack of data", do not agree with the measurements with a standard deviation of ±0.084 and ±0.088 for evaporation and growth studies. The SCAPE 2 predictions, which use the latest a_w data on $Mg(NO_3)_2$ measured by Ha and Chan,[8] agree with the measurements with a standard deviation of ±0.033 and ±0.029 for evaporation and growth studies.

Figure 4 shows the water cycle of the $NaCl + Ca(NO_3)_2$ (1:1) mixtures. Bulk data from this study were used to determine the reference state concentration. NaCl-containing mixtures usually crystallize at $a_w \approx 0.40$ in single particle levitation studies, but here the crystallization of NaCl was suppressed by the presence of $Ca(NO_3)_2$. Suppression of the crystallization of NaCl by nitrates has been reported by Chan et al.,[9] including the fact that $NaCl + Mg(NO_3)_2$ (1:1) mixtures do not crystallize even at $a_w \approx 0.20$, while 3:1 mixtures crystallize at $a_w \approx 0.45$. The SCAPE predictions (standard deviation = ±0.020 and ±0.032 for evaporation and growth studies) agree well with the bulk data and give better predictions than the ZSR

Table 2. Comparisons of the Predictions of the ZSR Equation and SCAPE Model with Measurements in mfs

	max. deviation/abs value[a]				standard deviation			
	ZSR		SCAPE		ZSR		SCAPE	
mixture	evaporation	growth	evaporation	growth	evaporation	growth	evaporation	growth
$CaCl_2 + Ca(NO_3)_2$ (1:1)	0.013	0.021	0.010	0.018	0.006	0.008	0.005	0.008
$MgCl_2 + CaCl_2$ (1:1)	0.012	0.015	0.013	0.015	0.006	0.008	0.006	0.008
$Mg(NO)_2 + Ca(NO_3)_2$ (1:1)	0.050	0.054	0.114[b]	0.120[b]	0.031	0.028	0.084[b]	0.088[b]
			0.051[c]	0.054[c]			0.033[c]	0.029[c]
$NaCl + Ca(NO_3)_2$ (1:1)	0.059	0.113	0.032	0.094	0.042	0.051	0.020	0.032
$NaNO_3 + Ca(NO_3)_2$ (1:1)	0.052	0.110	0.046	0.024	0.036	0.049	0.024	0.010
$NaCl + Ca(NO_3)_2$ (3:1)[d]	0.020	N/A[e]	0.013	N/A	0.014	N/A	0.009	N/A
$NaNO_3 + Ca(NO_3)_2$ (3:1)[d]	0.028	N/A	0.063	N/A	0.010	N/A	0.035	N/A

[a] Standard deviation = $\{\Sigma[(\text{mfs}_{\text{model}} - \text{mfs}_{\text{meas}})/\text{mfs}_{\text{model}}]^2/(N - 1)\}^{0.5}$, where $\text{mfs}_{\text{model}}$ = mfs calculated from models, mfs_{meas} = mfs from measurement, and N = number of experimental data. [b] Compared with SCAPE 1. [c] Compared with SCAPE 2. [d] Only involves aqueous data (i.e. noncrystallized) and compared with SCAPE 1. [e] Not available.

Table 3. Water Activity Data of $CaCl_2 + Ca(NO_3)_2$ = 1:1 Mixtures

evaporation		growth		evaporation		growth	
mfs	a_w	mfs	a_w	mfs	a_w	mfs	a_w
0.360	0.703	0.557	0.300	0.502	0.398	0.363	0.705
0.363	0.693	0.528	0.319	0.510	0.388	0.362	0.708
0.368	0.685	0.502	0.435	0.517	0.370		
0.375	0.685	0.486	0.485	0.525	0.352		
0.390	0.655	0.457	0.518	0.534	0.334		
0.401	0.633	0.433	0.558	0.545	0.309		
0.412	0.602	0.427	0.586	0.556	0.288		
0.430	0.560	0.414	0.597	0.566	0.268		
0.444	0.530	0.409	0.610	0.575	0.254		
0.453	0.509	0.401	0.628	0.581	0.246		
0.460	0.492	0.391	0.647	0.587	0.242		
0.468	0.474	0.388	0.664	0.591	0.235		
0.476	0.450	0.384	0.669	0.602	0.225		
0.483	0.437	0.374	0.674	0.612	0.212		
0.492	0.428	0.368	0.695	0.624	0.204		
0.498	0.412	0.368	0.702	0.627	0.199		

Table 4. Water Activity Data of $MgCl_2 + CaCl_2$ = 1:1 Mixtures

evaporation		growth		evaporation		growth	
mfs	a_w	mfs	a_w	mfs	a_w	mfs	a_w
0.256	0.701	0.401	0.300	0.370	0.378	0.293	0.590
0.259	0.684	0.385	0.313	0.379	0.354	0.283	0.600
0.266	0.655	0.379	0.359	0.387	0.338	0.277	0.613
0.277	0.619	0.368	0.395	0.393	0.317	0.274	0.628
0.287	0.594	0.356	0.417	0.401	0.303	0.271	0.640
0.301	0.553	0.348	0.452	0.408	0.284	0.266	0.651
0.315	0.523	0.342	0.466	0.414	0.267	0.263	0.660
0.326	0.498	0.335	0.478	0.418	0.253	0.258	0.666
0.334	0.476	0.327	0.501	0.422	0.246	0.257	0.669
0.342	0.453	0.322	0.510	0.428	0.243	0.251	0.677
0.350	0.432	0.318	0.526	0.437	0.233	0.245	0.700
0.353	0.416	0.312	0.542	0.450	0.215	0.245	0.703
0.356	0.403	0.302	0.570	0.456	0.204	0.243	0.705
0.363	0.397	0.298	0.580	0.463	0.200		

Table 5. Water Activity Data of $Mg(NO_3)_2 + Ca(NO_3)_2$ = 1:1 Mixtures

evaporation		growth		evaporation		growth	
mfs	a_w	mfs	a_w	mfs	a_w	mfs	a_w
0.392	0.701	0.380	0.708	0.525	0.400	0.471	0.502
0.397	0.694	0.386	0.699	0.533	0.374	0.478	0.469
0.401	0.687	0.388	0.691	0.540	0.350	0.493	0.459
0.410	0.672	0.392	0.680	0.548	0.324	0.500	0.421
0.420	0.653	0.401	0.668	0.555	0.308	0.511	0.392
0.437	0.627	0.406	0.661	0.564	0.288	0.529	0.340
0.447	0.599	0.414	0.647	0.566	0.270	0.541	0.300
0.458	0.578	0.420	0.621	0.580	0.242		
0.469	0.553	0.426	0.606	0.587	0.235		
0.480	0.523	0.433	0.596	0.593	0.228		
0.490	0.496	0.446	0.572	0.597	0.215		
0.502	0.471	0.452	0.540	0.598	0.205		
0.507	0.441	0.462	0.511	0.603	0.199		

model (standard deviation = ±0.042 and ±0.051 for evaporation and growth studies).

Figure 5 shows the water cycle of the $NaNO_3 + Ca(NO_3)_2$ (1:1) mixtures. Bulk data from this study were used to determine the reference state concentration. The SCAPE predictions agree well with the bulk data. Like the cases of the $NaCl + Ca(NO_3)_2$ (1:1) mixtures, crystallization was not observed for this mixture, although $NaNO_3$ usually crystallizes at RH = 20 to 30% (ref 7) but sometimes it becomes very supersaturated and does not crystallize even at RH = 0.5%. The SCAPE model predictions are consistent with the measured results, with a standard deviation of ±0.024 and ±0.010 for evaporation and growth studies, although small deviations at about $a_w = 0.40$ were found. The ZSR predictions, with a standard deviation of ±0.036 and ±0.049 for evaporation and growth studies, give larger deviations than the SCAPE predictions for this mixture.

Figure 6 shows the water cycle of the $NaCl + Ca(NO_3)_2$ (3:1) mixtures. Since no literature data are available, the SCAPE model was used to estimate the reference state concentration, as it has shown accurate predictions for equal molar $NaCl + Ca(NO_3)_2$ mixtures. Equal molar mixtures of this system did not effloresce at RH < 20%, as has been shown previously. For the 3:1 mixture, particle 1 partially crystallized at about RH = 52%, as indicated by a sudden jump in mfs. This was probably caused by the crystallization of NaCl, as it saturates at a higher RH than $Ca(NO_3)_2$ does. The particle was still hygroscopic after partial crystallization, because of the presence of the aqueous $Ca(NO_3)_2$ solution in the particle. The measured data agree well with the ZSR predictions before partial crystallization, and the standard deviation between the model predictions and the measured data before partial crystallization is ±0.014. However, the SCAPE model gives accurate predictions for both the aqueous (with standard deviation of ±0.009) and partially crystallized particles. The SCAPE 1 curve in Figure 6 was obtained by suppressing the formation of solid in the aerosol phase, and it is therefore applicable only to the evaporation experiments. SCAPE 2 and 3 were calculated by performing the full aqueous−solid equilibrium calculations using the Pitzer and the KM models, respectively. Calculations using the Bromley model are not shown in Figure 6 for clarity, because it gives results similar to those of the KM model. Although these three models give the same predictions for aqueous particles, they perform differently in predicting the aqueous−solid equilibrium. Generally speaking, the KM and Bromley models perform better at lower a_w, while the Pitzer model performs better at higher a_w. However, the Pitzer and Bromley models give more accurate predic-

Table 6. Water Activity Data of NaCl + $Ca(NO_3)_2$ = 1:1 and 3:1 Mixtures

NaCl + $Ca(NO_3)_2$ = 1:1				NaCl + $Ca(NO_3)_2$ = 3:1			
evaporation		growth		evaporation		growth	
mfs	a_w	mfs	a_w	mfs	a_w	mfs	a_w
0.291	0.811	0.365	0.714	0.264	0.811	0.336	0.710
0.298	0.811	0.390	0.688	0.270	0.810	0.364	0.700
0.299	0.800	0.402	0.676	0.270	0.809	0.377	0.685
0.305	0.791	0.406	0.667	0.273	0.804	0.379	0.681
0.312	0.770	0.413	0.657	0.278	0.799	0.385	0.677
0.318	0.758	0.422	0.643	0.284	0.791	0.391	0.675
0.331	0.744	0.432	0.623	0.295	0.777	0.405	0.671
0.346	0.730	0.447	0.606	0.306	0.764	0.418	0.665
0.355	0.718	0.454	0.586	0.316	0.753	0.428	0.660
0.367	0.706	0.473	0.559	0.329	0.740	0.446	0.652
0.381	0.695	0.485	0.538	0.338	0.728	0.458	0.644
0.390	0.683	0.496	0.516	0.349	0.713	0.481	0.631
0.401	0.670	0.508	0.491	0.360	0.701	0.498	0.618
0.410	0.661	0.523	0.459	0.368	0.690	0.511	0.608
0.422	0.638	0.546	0.422	0.375	0.674	0.529	0.594
0.435	0.622	0.555	0.401	0.382	0.667	0.543	0.580
0.447	0.599	0.569	0.380	0.393	0.650	0.558	0.568
0.466	0.566	0.578	0.356	0.404	0.631	0.583	0.541
0.476	0.533	0.603	0.329	0.413	0.614	0.601	0.524
0.492	0.498	0.621	0.288	0.425	0.598	0.611	0.507
0.501	0.480	0.650	0.230	0.432	0.574	0.626	0.495
0.521	0.445	0.690	0.200	0.449	0.550	0.634	0.481
0.528	0.423			0.456	0.524	0.642	0.473
0.529	0.409			0.587	0.506	0.655	0.455
0.532	0.385			0.597	0.485	0.677	0.424
0.549	0.364			0.621	0.440	0.688	0.397
				0.623	0.417	0.711	0.362
				0.630	0.401	0.739	0.329
				0.637	0.374	0.783	0.288
				0.640	0.358	0.817	0.204
						0.841	0.202

Table 7. Water Activity Data of $NaNO_3$ + $Ca(NO_3)_2$ = 1:1 and 3:1 Mixtures

$NaNO_3$ + $Ca(NO_3)_2$ = 1:1				$NaNO_3$ + $Ca(NO_3)_2$ = 3:1			
evaporation		growth		evaporation		growth	
mfs	a_w	mfs	a_w	mfs	a_w	mfs	a_w
0.375	0.811	0.467	0.713	0.396	0.811	0.487	0.710
0.380	0.810	0.479	0.700	0.405	0.804	0.493	0.706
0.386	0.807	0.486	0.693	0.423	0.792	0.496	0.693
0.398	0.799	0.487	0.685	0.442	0.772	0.501	0.684
0.411	0.787	0.496	0.680	0.461	0.757	0.508	0.681
0.426	0.773	0.505	0.666	0.479	0.744	0.518	0.678
0.436	0.763	0.516	0.649	0.494	0.730	0.539	0.672
0.449	0.752	0.529	0.625	0.507	0.716	0.556	0.665
0.459	0.740	0.545	0.597	0.524	0.697	0.569	0.658
0.471	0.725	0.561	0.568	0.538	0.683	0.588	0.643
0.480	0.713	0.581	0.535	0.550	0.669	0.611	0.624
0.487	0.701	0.592	0.512	0.562	0.651	0.629	0.608
0.498	0.690	0.619	0.461	0.583	0.627	0.649	0.590
0.509	0.670	0.627	0.445	0.597	0.605	0.666	0.564
0.524	0.646	0.636	0.426	0.619	0.568	0.686	0.546
0.533	0.623	0.644	0.409	0.636	0.532	0.699	0.528
0.541	0.608	0.658	0.395	0.652	0.504	0.713	0.505
0.559	0.567	0.664	0.374	0.668	0.481	0.720	0.478
0.566	0.547	0.681	0.351	0.685	0.443	0.741	0.447
0.574	0.520	0.701	0.320	0.708	0.414	0.762	0.414
0.584	0.498	0.719	0.284	0.710	0.386	0.776	0.386
0.589	0.481	0.741	0.246	0.719	0.360	0.826	0.301
0.599	0.448	0.758	0.200			0.902	0.200
0.610	0.430	0.776	0.200				
0.614	0.420						
0.623	0.400						
0.628	0.390						
0.633	0.375						
0.641	0.360						

tions of the "completely deliquesced" point of this mixture. Unlike the aqueous NaCl solution, which shows an abrupt drop in mfs during deliquescence, this mixture (particle 2 in Figure 6) gradually absorbed water in the RH range of 20 to 68%. Afterward, the mfs dependence followed the ZSR predictions again, which means that the droplet had become completely deliquesced. This mixture started to "deliquesce" at RH = 57.5% (i.e., the point where the particle starts to absorb a significant amount of water). It should be noted that the DRH of the mixture (68%), that is, the "completely deliquesced" point, was lower than the theoretical DRH of NaCl, which is consistent with the theoretical analysis of Wexler and Seinfeld[22] that the DRH of one electrolyte is lowered by the addition of a second electrolyte. $Ca(NO_3)_2$ behaved as a nondeliquescent salt in these single particle experiments.

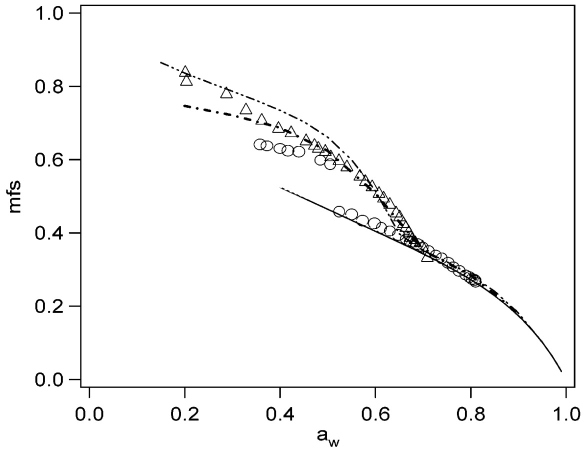

Figure 6. Water cycle of the NaCl + $Ca(NO_3)_2$ = 3:1 mixtures: —, ZSR; ○, particle 1 (evaporation); △, particle 2 (growth); - - -, SCAPE 1; — - —, SCAPE 2; — - - —, SCAPE 3. ZSR represents the predictions by the ZSR equation. SCAPE 1, SCAPE 2, and SCAPE 3 represent the predictions by the SCAPE model with no solid calculation and with solid calculation using the Pitzer model and the KM model, respectively.

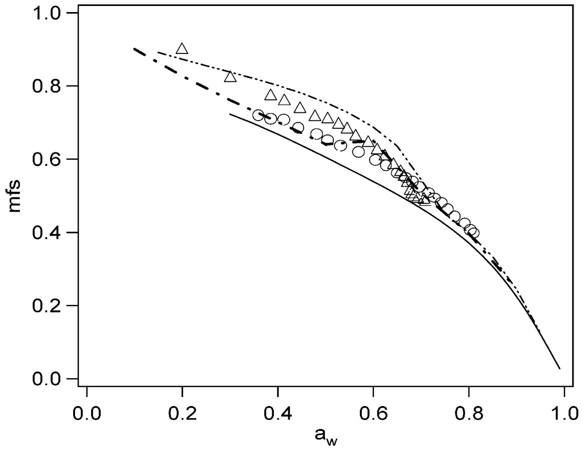

Figure 7. Water cycle of the $NaNO_3$ + $Ca(NO_3)_2$ = 3:1 mixtures: —, ZSR; ○, particle 1 (evaporation); △, particle 2 (growth); - - -, SCAPE 1; — - —, SCAPE 2; — - - —, SCAPE 3. ZSR represents the predictions by the ZSR equation. SCAPE 1, SCAPE 2, and SCAPE 3 represent the predictions by the SCAPE model with no solid calculation and with solid calculation using the Pitzer model and the KM model, respectively.

Figure 7 shows the water cycle of the $NaNO_3$ + $Ca(NO_3)_2$ (3:1) mixtures. Again, there are no literature data for this mixture. The SCAPE model was thus used to estimate the reference state concentration. This mixture did not crystallize even at about RH = 35%, as $NaNO_3$ usually crystallizes at about RH = 20 to 30% (ref 7). The particle crystallized at RH = 20%, which was the starting point of the growth experiment. Like the NaCl + $Ca(NO_3)_2$ (3:1) mixture, this mixture also showed a gradual deliquescence rather than a sharp decrease in mfs. The particle started to deliquesce at about RH = 60% and completely deliquesced at RH = 68%. The SCAPE model again gave more accurate predictions than the ZSR model did in this case. SCAPE 1 (without solid calculation) accurately predicts the mfs of this mixture in the evaporation mode, while the ZSR model underestimates the mfs of this mixture at the same a_w when compared with the measurements. SCAPE 2 (with aqueous−solid equilibrium calculation by the Pitzer model) gives accurate predictions of both the “completely deliquesced” point and the aqueous−solid equilibrium at a_w above 0.6. At a_w below 0.6, SCAPE 2 gives results similar to those of SCAPE 1. SCAPE 2 cannot predict the growth of the aerosols, but SCAPE 3 (with aqueous−solid equilibrium calculation by the KM or Bromley model) gives reasonable predictions. The measured data follow SCAPE 1 predictions after complete deliquescence. Again, the observed DRH was smaller than the theoretical DRH of pure $NaNO_3$, as expected.

Conclusions

The hygroscopic and deliquescence properties of selected crustal species mixtures of atmospheric importance were measured with the SEDB. In this study, the SEDB was applied to measure the water cycles of equal molar mixtures of $CaCl_2$ + $Ca(NO_3)_2$, $MgCl_2$ + $CaCl_2$, $Mg(NO_3)_2$ + $Ca(NO_3)_2$, NaCl + $Ca(NO_3)_2$, and $NaNO_3$ + $Ca(NO_3)_2$. All systems showed neither crystallization nor deliquescence, and the measured data agreed with the ZSR and the SCAPE predictions. After incorporation of the latest $Mg(NO_3)_2$ water activity data, SCAPE was found useful in predicting the mfs of crustal aerosols. The presence of $Ca(NO_3)_2$ suppressed the efflorescence of NaCl and $NaNO_3$ in the 1:1 mixtures. The water cycles of the NaCl + $Ca(NO_3)_2$ (3:1) and $NaNO_3$ + $Ca(NO_3)_2$ (3:1) mixtures were also measured by the SEDB, and the mixtures exhibited gradual deliquescence rather than a sharp decrease in mfs like NaCl or $NaNO_3$ alone. The addition of nondeliquescent salts lowered the DRH of the deliquescent salts. These observations hint at the complex interactions between the deliquescent salts and the nondeliquescent portion of the atmospheric aerosols during water absorption. The SCAPE model gives accurate predictions of the deliquescence RH and the deliquescence properties of crustal mixtures. However, it cannot adequately predict the hygroscopic properties of partially crystallized aerosols.

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