

Aerosol size and relative humidity: Water uptake by mixtures of salts

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ABSTRACT

The water uptake by salt mixtures at large relative humidities is discussed. Numerous results of measurements of the lowering of water vapour pressure over multicomponent electrolyte solutions have been evaluated to obtain a simple mixture rule. Results from literature and own measurements were used. It turns out that for a given relative humidity the water uptake of a mixture of salts is almost equal to the sum of the water uptakes of the pure components of the mixture when separate from each other. This rule holds for the most cases at relative humidities larger than approximately 0.85 to 0.9 with an accuracy better than 10 to 15%. A second rule with a smaller range of application is discussed in the paper.

1. Introduction

The atmosphere is an aerosol with humid air as the dispersion medium and particles as the dispersed phases. The latter are called the atmospheric aerosol particles. There are widely different structures and chemical compositions of the atmospheric suspensoids and, in addition, the particles are not distributed uniformly in the atmosphere. This results from the non-uniform sources and sinks of the atmospheric particles. Among these, coagulation plays an important role in bringing different particles together. Coagulation on the one hand forms structurally complicated particles, on the other reduces chemical differences. In this way the particles with radii (equivalent volume radii) between 0.01 and 1 μm become agglomerates. These particles play an important role in cloud, fog and radiation physics. The dry particles consist of both anorganic and organic matter being partly water soluble. The water soluble part usually is a salt mixture.

Moreover, solid and liquid phases exist side by side within the particles. At zero relative humidity the liquid phase may consist of organic matter. As the relative humidity increases water vapour condenses on the particles. Thus the sizes of the

particles increase with relative humidity. Finally, when the air is nearly saturated with water vapour, most of the atmospheric particles consist mainly of water. When the relative humidity decreases water evaporates from the particles and thus they shrink. The response of the particles on changes of relative humidity must be known when solving problems of fog, cloud and radiation physics, especially when the air is nearly saturated with water vapour. In this context, the water taken up by salt mixtures in equilibrium with moist air is the most important feature. In the present paper this problem is discussed under the aspect of meteorological application.

Multicomponent electrolyte solutions have been considered both experimentally and theoretically by many authors of physical chemistry, e.g. Robinson and Stokes (1945), Harned and Owen (1958), Harned and Robinson (1968), Pitzer and Kim (1974). But despite of all these efforts no simple model exists which is accurate enough for meteorological application. Winkler and Junge (1972) proved a simple rule with own measurements. They found that the mass of water taken up by a number of salt mixtures at a specific relative humidity is not equal to the sum of the masses of water taken up by the pure components alone at

the same relative humidity. More recently Hänel (1976) discussed a number of examples of salt mixtures for which this rule holds with remarkable accuracy at relative humidities larger than about 0.75 to 0.9. He could also give physical reasons for the validity of this simple mixture rule. Thudium (1978) developed another simple mixture rule for multicomponent salt mixtures. This rule agrees with that by Hänel (1976) when the relative humidity is larger than about 0.95. In this paper we want to discuss the validity of both mixture rules for the water uptake by multicomponent electrolytes on the basis of a large number of measurements from literature and own research. Our own measurements cover those mixtures being expected to occur in atmospheric aerosol particles and in addition some of the systems measured by Winkler and Junge (1972).

2. Theory

2.1. The basic equation

A model has been developed by Hänel (1976) for the equilibrium state of a particle in humid air. This model correlates relative humidity with the equilibrium size of the particle or the equilibrium mass of water condensed on the particle. Compared to other models (for references see Hänel, 1976) it has the advantage that all inherent properties of numerical importance can be measured directly on samples of aerosol particles with sufficient accuracy. The appertaining experimental methods have been developed or improved by the authors (Hänel, 1976; Schreiber, 1977) and Thudium (1976, 1978).

We are now considering an electrically neutral spherical particle with an outer layer being completely liquid in equilibrium with the surrounding moist air. Then the relative humidity f of the air is equal to the equilibrium relative humidity over the curved particle surface and is expressed by

$$f = a_w \exp \left[\frac{2\sigma}{\rho_w R_w T r} \right] \quad (1)$$

Here a_w is the water activity, σ the surface tension of the curved particle surface, ρ_w the bulk density of pure water, R_w the specific gas constant of pure water, T the absolute temperature, and r the radius of the particle.

Equation (1) is an approximation holding good for both a particle in the atmosphere and a particle in a closed laboratory system where no dry air is present. Thus it is permissible to transfer experimental results from such a system to the atmosphere and vice versa.

In eq. (1) a_w is the water activity, i.e. the equilibrium relative humidity over a plane surface ($r \rightarrow \infty$) of the same material the liquid cover of the particle consists of. This allows measurements to be made on samples of aerosol particles for which $r \rightarrow \infty$ can be assumed, and then the use of these results for computation of the response of the particle to relative humidity in the atmosphere. This technique is applicable when both the chemical composition and the structure of the sample and the particle are the same in dry state, i.e. at $f = 0$. For atmospheric aerosol particles the water activity a_w and the (equivalent volume) radius r are

$$a_w = \left[1 + \mu \frac{m_o}{m_w} \right]^{-1} \quad \text{and} \quad r = r_o \left[1 + \frac{\rho_o}{\rho_w} \frac{m_w}{m_o} \right]^{1/3} \quad (2a)$$

m_w/m_o is the water uptake per unit mass of dry, water-free substance, μ the linear mass increase coefficient of the particle, and ρ_o the mean bulk density of the dry particle. For a multicomponent electrolyte solution we have

$$a_w = \left[1 + \bar{\mu}_s \frac{m_s}{m_w} \right]^{-1} \quad \text{and} \\ r = r_o \left[1 + \frac{\rho_s}{\rho_w} \frac{m_w}{m_s} \right]^{1/3} \quad (2b)$$

m_w/m_s is the water uptake per unit mass of the dry, water-free multicomponent electrolyte, $\bar{\mu}_s$ the mean linear mass increase coefficient of the mixed electrolyte, and ρ_s its mean bulk density in dry state.

At infinite dilution, i.e. $a_w \rightarrow 1$, the linear mass increase coefficients μ and $\bar{\mu}_s$ have finite limiting values.

Equations (2a) and (2b) correlate water activity with water uptake per unit mass of dry substance by the linear mass increase coefficient alone. Both a_w and m_w/m_o (m_w/m_s) can be measured. Therefore μ ($\bar{\mu}_s$) can be determined by measurement and secondly can be regarded arbitrarily as a function of a_w or m_w/m_o (m_w/m_s). Like every thermodynamic property the linear mass increase

coefficient is temperature dependent. This dependence is zero at infinite dilution and increases with decreasing water activity.

2.2. The first mixture rule

The first mixture rule is the extension of an equation being valid for the water activity $a_w = 1$ to water activities smaller than 1 (Hänel 1976). It reads

$$\bar{\mu}_s(a_w) = \sum_i \mu_{si}(a_w) \frac{m_{si}}{m_s} \quad (3a)$$

μ_{si} is the linear mass increase coefficient of the pure component i and m_{si} its mass in dry state. It is $m_s = \sum_i m_{si}$.

Combination of the first equation of (2b) with (3a) yields

$$m_w(a_w) = \sum_i m_{wi}(a_w) \quad (3b)$$

This means that the mass of water condensed on the mixed electrolyte is equal to the sum of masses of water condensed on the pure components when separate from each other. Equation (3b) also can be derived from a relation for so-called "semi-ideal" mixtures which has been used by Tang (1976). Semi-ideality means that the components (solutes) independently interact with water (the solvent). Consequently, the interaction between the ions formed from each component is considered, but there is no interaction between those ions the components do not have in common, i.e. in an aqueous solution of NaCl and KCl interactions between Na^+ and Cl^- as well as K^+ and Cl^- are considered, but no interactions between Na^+ and K^+ . However, it is difficult to judge to which extent the interactions between Na^+ (K^+) and Cl^- originating from KCl (NaCl) are considered. The idea of semi-ideality is applicable also to non-electrolyte solutions.

2.3. Another form of the first mixture rule

The water activity can be expressed with another formulation physically equivalent to eq. (2a). In the case of a mixed electrolyte it is

$$a_w = \exp \left[-\bar{\phi} \bar{\vartheta} \frac{M_w}{\bar{M}_s} \frac{m_s}{m_w} \right] \quad (2c)$$

where $\bar{\phi}$ is the mean practical osmotic coefficient of the mixed electrolyte, $\bar{\vartheta}$ the mean number of moles

of ions per mole of the mixture, M_w the molar weight of water, and \bar{M}_s the mean molar weight of the mixture. The limiting value of $\bar{\phi}$ for infinite dilution is $\lim_{\bar{\phi} a_w \rightarrow 1} \bar{\phi} = 1$ as it is defined for pure electrolytes. An equivalent formulation of the mixture rule (3b) in terms of the practical osmotic coefficient is

$$\bar{\phi}(a_w) = \sum_i \phi_i(a_w) \frac{\mathfrak{M}_i}{\mathfrak{M}} \quad (3c)$$

where the ϕ_i are the practical osmotic coefficients of the components. \mathfrak{M}_i is the "total molality" of component i and \mathfrak{M} the "total molality" of the mixed electrolyte. \mathfrak{M}_i and \mathfrak{M} are defined as the molalities of all the ions and molecules originating in component i and in the mixed electrolyte, respectively.

2.4. The second mixture rule

A second mixture rule of formal simplicity was given by Thudium (1978). It reads

$$\bar{\phi}(\mathfrak{M}) = \sum_i \phi_i(\mathfrak{M}) \cdot \frac{\mathfrak{M}_i}{\mathfrak{M}} \quad (4)$$

This mixture rule has the advantage that the practical osmotic coefficients at a given concentration, here the total molality of the mixed electrolyte, are used. This gives numerical facilitations in some cases. This second mixture rule, however, inhibits larger errors than the first one at moderate to large concentrations. This may be due to the idea leading to eq. (4) namely that the interionic interaction is governed by the total molality of the mixed electrolyte. Using $\phi_i(\mathfrak{M})$ this is supposed to be true even for the interaction between the ions of the components. There exists a third mixture rule for the practical osmotic coefficient by Chen (1974). This rule, however, is physically incorrect (Thudium, 1978) and gives too large errors.

3. Discussion of the mixture rules

3.1. General remarks

The validity of both mixture rules will be tested by comparison of computed and measured mean linear mass increase coefficients (first rule) and mean practical osmotic coefficients (second rule) of multicomponent electrolyte solutions. A large

quantity of measurements has been taken from literature, most of the references are compiled by Robinson and Stokes (1945), Harned and Owen (1958), Harned and Robinson (1968), and Pitzer and Kim (1974). Additional own measurements were necessary because the electrolyte mixtures for which experimental data exist in the physico-chemical literature usually do not meet the chemical composition and complexity of electrolyte mixtures found in atmospheric particles. The microbalance system developed by Hänel (1976) has been used for these measurements. Within this system the activity of water is known with an accuracy of ± 0.0005 – 0.001 the mass with an accuracy of ± 1.5 – $2 \mu\text{g}$. Comparison of measured linear mass increase coefficients of sodium chloride with those deduced from Robinson and Stokes (1959) showed differences smaller than $\pm 1.3\%$ in the range of water activity $0.760 \leq a_w \leq 0.952$. All our measurements have been taken in the range of water activity $a_w \leq 0.95$. Measurements at water activities $0.95 < a_w \leq 1$ are not necessary, since in this range the mixture rules give the best results (compare Tang, 1976; Hänel, 1976; Thudium, 1978).

3.2. Results

The results are compiled in Tables 1 and 2 where the following data are given for each mixed electrolyte: Composition of the mixture, maximum percentage deviation of the measured from the computed mean linear mass increase coefficient (first rule), maximum percentage deviation of the measured from the computed mean practical osmotic coefficient (second rule), and the pertaining range of water activity, where these maximum deviations occur.

3.2.1. *Data from the physico-chemical literature* (Table 1). There are interionic interactions between the ions of each component and between the ions of different components. The first type of interactions is completely considered in the first mixture rule but only incompletely in the second one. The second type of interactions is considered imperfectly by both mixture rules. Especially the interactions between these ions the different components have not in common are not considered. Since incomplete consideration of the interionic interactions is responsible for the error involved in a mixture rule, we expect each mixture rule to give the best results for small ionic interactions, i.e. large

mutual distances of the ions. This occurs at high dilution of the solution, i.e. large water activity, and has been confirmed by the measurements. Moreover the first rule should consider interionic interaction more perfectly than the second one. Therefore, the first rule should have the larger range of applicability, i.e. a smaller maximum error in a given range of water activity. As it can be seen from Table 1, this is true for the majority of the mixtures.

There are only a few mixtures for which the first mixture rule gives errors larger than 10% in the indicated ranges of water activity. However, these mixtures are composed of salts of no importance for atmospheric application (BaCl_2 and CsCl , CsCl and LiCl , KCl and CuCl_2) and of salts (K_2SO_4 and Na_2SO_4), which whenever they are present, contribute only small amounts to the water-soluble substance of atmospheric particles. Moreover, those salts being well known for complex ion formation (the halides of the transition metals and cupric chloride, Robinson and Stokes, 1959) are of no significance within atmospheric particles. This is important to know, since the mixture rules cannot be applied to systems with complex ion formation.

In several cases the indicated ranges of the water activity are very small. There are two reasons for this: (1) No measurements on the mixtures at smaller water activities exist. (2) Measured linear mass increase coefficients and practical osmotic coefficients of BaCl_2 , KNO_3 , NaNO_3 , NaOAc , LiOAc , and K_2SO_4 were not available for lower water activities.

3.2.2. *Confirmation of the mixture rules for atmospheric conditions* (Table 2). There were several reasons for own measurements of the water uptake of mixed electrolytes:

- (1) The mixed electrolytes, building up the water-soluble substances of atmospheric particles, generally are more complicated and of other composition than those reported in the literature.
- (2) Those cases are to be discovered for which the mixture rules give large errors.
- (3) Some measurements on mixed electrolytes by Winkler and Junge (1972) should be repeated. We wanted to investigate the statement of these authors that "the total amount of water uptake of a complex salt mixture as found in continental aerosols is not additive with respect to the individual components" being in contradiction

Table 1. *Test of the mixture rules with data from the literature (for references see Schreiber, 1977). x is the mole fraction. The maximum error is the maximum value of $100 \cdot (y_{\text{meas}}/y_{\text{calc.}} - 1)$ in the range of water activity indicated where $y = \bar{\mu}_s$ or ϕ . The maximum error occurs in the lowest part of the range of water activity indicated in the table*

Mixture	Range of a_w	Maximum error of mixture rule in %	
		First eq. (3b)	Second eq. (4)
$x\text{KNO}_3 + (1-x)\text{Ca}(\text{NO}_3)_2$ $x = 0.6667$	0.94–1.0	–4.7	–12.3
$x\text{KCl} + (1-x)\text{CaCl}_2$	0.85–1.0	–3.3	–9.5
$x\text{KCl} + (1-x)\text{BaCl}_2$	0.91–1.0	–3.1	–3.7
$x\text{NaCl} + (1-x)\text{BaCl}_2$	0.90–1.0	–0.3	–0.6
$x\text{NaCl} + (1-x)\text{CaCl}_2$	0.77–1.0	+0.4	–3.2
$x\text{CaCl}_2 + (1-x)\text{MgCl}_2$	0.61–1.0	–0.9	–1.3
$x\text{NaCl} + (1-x)\text{LiCl}$	0.76–1.0	+0.8	–0.4
$x\text{NaNO}_3 + (1-x)\text{LiNO}_3$	0.87–1.0	+2.0	–2.9
$x\text{NaOAc} + (1-x)\text{LiOAc}$	0.87–1.0	+0.5	+0.6
$x\text{NaCl} + (1-x)\text{KCl}$	0.76–1.0	–2.8	–2.6
$x\text{Mg}(\text{NO}_3)_2 + (1-x)\text{MgCl}_2$	0.52–1.0	+1.1	+1.7
$x\text{Ca}(\text{NO}_3)_2 + (1-x)\text{MgCl}_2$	0.53–1.0	+5.5	+4.1
$x\text{CaCl}_2 + (1-x)\text{Mg}(\text{NO}_3)_2$	0.60–1.0	–9.7	–16.2
$x\text{Ca}(\text{NO}_3)_2 + (1-x)\text{Mg}(\text{NO}_3)_2$	0.64–1.0	–2.3	–6.9
$x\text{Ca}(\text{NO}_3)_2 + (1-x)\text{CaCl}_2$	0.53–1.0	–3.7	–10.4
$x_1\text{LiCl} + x_2\text{NaCl} + x_3\text{CsCl}$ $x_1 = x_2 = x_3 = 1/3$	0.89–1.0	–3.2	–5.4
$x_1\text{LiCl} + x_2\text{NaCl} + x_3\text{KCl}$ $x_1 = x_2 = x_3 = 1/3$	0.89–1.0	–3.0	–2.4
$x_1\text{LiCl} + x_2\text{NaCl} + x_3\text{CsCl}$ $x_1 = x_2 = x_3 = 1/3$	0.81–1.0	–4.9	–10.3
$x\text{LiCl} + (1-x)\text{BaCl}_2$	0.91–1.0	+1.1	+1.2
$x\text{BaCl}_2 + (1-x)\text{CsCl}$	0.92–1.0	+21.6	+22.1
$x\text{Na}_2\text{SO}_4 + (1-x)\text{LiCl}$	0.88–1.0	+4.3	+1.0
$x\text{Na}_2\text{SO}_4 + (1-x)\text{CsCl}$	0.85–1.0	+6.2	–7.5
$x\text{Na}_2\text{SO}_4 + (1-x)\text{NaCl}$	0.94–1.0	+2.2	+1.0
$x\text{K}_2\text{SO}_4 + (1-x)\text{KCl}$	0.98–1.0	+0.9	+0.5
$x\text{K}_2\text{SO}_4 + (1-x)\text{Na}_2\text{SO}_4$	0.98–1.0	–10.5	–1.4
$x\text{K}_2\text{SO}_4 + (1-x)\text{NaCl}$	0.98–1.0	–0.6	–1.5
$x\text{Na}_2\text{SO}_4 + (1-x)\text{KCl}$	0.91–1.0	+3.3	+3.6
$x\text{CsCl} + (1-x)\text{NaCl}$ $x = 0.1335$	0.77–1.0	–1.5	–2.6
$x = 0.2698$	0.78–1.0	–1.6	–4.2
$x = 0.3689$	0.79–1.0	–3.4	–5.7
$x = 0.4989$	0.80–1.0	–4.1	–6.5
$x = 0.6354$	0.81–1.0	–3.8	–6.0
$x = 0.7978$	0.81–1.0	–2.8	–4.4
$x\text{KCl} + (1-x)\text{LiCl}$ $x = 0.3356$	0.79–1.0	–1.8	–5.6
$x = 0.3526$	0.79–1.0	–1.8	–5.7
$x = 0.5210$	0.80–1.0	–2.0	–6.5
$x = 0.6434$	0.81–1.0	–2.2	–6.4
$x = 0.7019$	0.82–1.0	–1.8	–5.5

Table 1—continued

Mixture	Range of a_w	Maximum error of mixture rule in %	
		First eq. (3b)	Second eq. (4)
$x\text{LiNO}_3 + (1-x)\text{LiCl}$			
$x = 0.3066$	0.46–1.0	+0.6	–2.6
$x = 0.4662$	0.48–1.0	+0.9	–3.1
$x = 0.6414$	0.51–1.0	+1.1	–3.2
$x\text{NaCl} + (1-x)\text{LiCl}$			
$x = 0.3301$	0.71–1.0	+0.7	+0.5
$x = 0.4833$	0.73–1.0	+0.7	–0.6
$x = 0.6608$	0.73–1.0	+0.8	–0.7
$x\text{CsCl} + (1-x)\text{KCl}$			
$x = 0.1411$	0.84–1.0	–0.3	–0.4
$x = 0.3025$	0.84–1.0	–0.6	–0.7
$x = 0.4007$	0.84–1.0	–0.6	–0.7
$x = 0.6443$	0.84–1.0	–0.7	+1.7
$x = 0.7726$	0.85–1.0	–0.5	–0.6
$x\text{CsCl} + (1-x)\text{LiCl}$			
$x = 0.3029$	0.75–1.0	+11.2	–13.4
$x = 0.4515$	0.77–1.0	+5.4	–16.0
$x = 0.5578$	0.79–1.0	+2.2	–16.5
$x = 0.7034$	0.80–1.0	–0.6	–14.7
$x = 0.8146$	0.81–1.0	–1.6	–11.3
$x\text{KCl} + (1-x)\text{MgCl}_2$			
$x = 0.6667$	0.86–1.0	–1.8	–8.4
$x\text{KCl} + (1-x)\text{BaCl}_2$			
$x = 0.6667$	0.92–1.0	–2.3	–3.1
$x\text{KCl} + (1-x)\text{MnCl}_2$			
$x = 0.6667$	0.85–1.0	–6.5	–9.8
$x\text{KCl} + (1-x)\text{CoCl}_2$			
$x = 0.6667$	0.84–1.0	–4.9	–10.3
$x\text{KCl} + (1-x)\text{NiCl}_2$			
$x = 0.6667$	0.84–1.0	–4.9	–11.7
$x\text{KCl} + (1-x)\text{CuCl}_2$			
$x = 0.6667$	0.85–1.0	–12.4	–14.2

to the first mixture rule. The reason for our doubts was the fact that sea salt, being a complicated salt mixture, too, obeys the mixture rules (Hänel, 1976; Thudium, 1978) very well.

Our measurements were performed on 16 mixed electrolytes covering the range of chemical compositions of mixed electrolytes being formed within atmospheric particles and some of the mixtures Winkler and Junge (1972) had reported. Our findings are as follows:

- (1) Several mixtures of salts contain crystal water and sometimes this crystal water cannot be

removed using physical methods. This may happen when a mixture contains considerable amounts of MgCl_2 , CaCl_2 , or MgSO_4 . In these cases the mixtures seem to take up less water than the mixture rules predict. However, whenever the mass of crystal water is subtracted from the measured “dry” substance to obtain the dry water-free substance (as is required in the theory) and secondly added to the water taken up by the electrolyte (compare Winkler and Junge, 1971) both mixture rules have a good accuracy. This is due to the fact that no distinction can be made between crystal water

Table 2. Test of the mixture rules with own measurements. The composition of the mixture is given in moles of the components. The maximum error is calculated as in Table 1

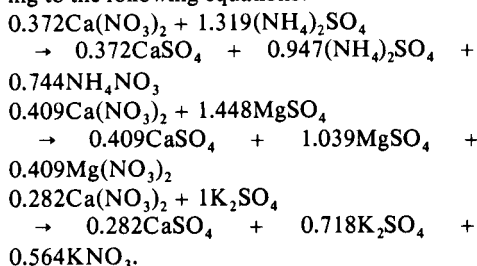
No.	Mixture	Range of a_w	Maximum error of mixture rule in %	
			First eq. (3b)	Second eq. (4)
1	5NaCl + 0.937MgCl ₂	0.76-1	-2.3	-6.3
2	5NaCl + 0.937MgCl ₂ + 8(NH ₄) ₂ SO ₄	0.85 (0.90)*-1	-5.9	-5.2
3	5NaCl + 0.937MgCl ₂ + 8(NH ₄) ₂ SO ₄ + 1K ₂ SO ₄	0.90-1	-5.4	-10.9
4	0.5(NH ₄) ₂ SO ₄ + 0.5NH ₄ NO ₃	0.85-1	+6.4	+1.9
5	0.25(NH ₄) ₂ SO ₄ + 0.75NH ₄ NO ₃	0.86-1	+8.1	+4.2
6	0.75(NH ₄) ₂ SO ₄ + 0.25NH ₄ NO ₃	0.85-1	+6.0	+3.0
7	5NaCl + 2MgCl ₂	0.76-1	-10.3	-19.6
8	5NaCl + 2MgCl ₂ + 8(NH ₄) ₂ SO ₄	0.90-1	-11.5	-27.0
9	5NaCl + 2MgCl ₂ + 8(NH ₄) ₂ SO ₄ + 1K ₂ SO ₄	0.90-1	+7.6	+4.7
10	3.093(NH ₄) ₂ SO ₄ + 4.908NH ₄ NO ₃ + 5.296NaCl + 1MgCl ₂	0.85-1	+3.3	-12.3
11	4.667(NH ₄) ₂ SO ₄ + 1.963NH ₄ NO ₃ + 5.964NaCl + 1MgCl ₂	0.85-1	+5.2	-18.5
12	1(NH ₄) ₂ SO ₄ + 1.650NH ₄ NO ₃ + 7.124NaCl + 1.261MgCl ₂	0.85-1	+10.6	+6.6
13	2.422(NH ₄) ₂ SO ₄ + 1NH ₄ NO ₃ + 10.786NaCl + 1.909MgCl ₂	0.85-1	+13.0	+9.8
14	34.536NaCl + 3.008MgCl ₂ + 1.014MgSO ₄ + 1K ₂ SO ₄	0.90-1	-2.5	+4.7
15	1.319(NH ₄) ₂ SO ₄ + 2.179NH ₄ NO ₃ + 1.063Ca(NO ₃) ₂ + 2.052NaNO ₃ + 1.448MgSO ₄ + 2.983NaCl + 1.831MgCl ₂ + 1K ₂ SO ₄	0.90-1	-4.9	+15.2
16	3.452K ₂ SO ₄ + 1MgSO ₄ + 2.832NaNO ₃ + 2.527MgCl ₂	0.90-1	-3.9	+21.2

* Lower end of the range of a_w being valid for the second mixture rule.

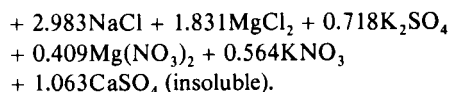
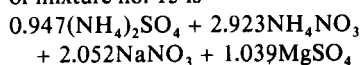
and the condensed water when all the material is dissolved (as it occurs at large water activities). Then the ratio between the numbers of the dissolved electrolyte species and the water molecules is highly responsible for the water activity. Some of the findings of Winkler and Junge 1972 can be explained easily taking crystal water into account. In Table 2 the crystal water corrections are considered.

- (2) The mixture rules would underestimate the water uptake by salt mixtures containing K_2SO_4 when dissolution of K_2SO_4 below its saturation water activity of 0.975 would not be considered. K_2SO_4 is present within the mixtures 3, 9, 14, 15, and 16. For these mixtures we have assumed that K_2SO_4 is completely dissolved at water activities ≥ 0.9 . The influence of the dissolved K_2SO_4 on the water uptake of the mixtures at $a_w \geq 0.9$ was calculated using extrapolated values of the osmotic coefficient of K_2SO_4 ($\phi_{K_2SO_4}$ ($a_w = 0.9$) = $0.66 \pm 5-10\%$, $\phi_{K_2SO_4}$ ($a_w = 0.95$) = $0.62 \pm 2-5\%$). Without consideration of the dissolution of K_2SO_4 the errors in Table 2 would shift in the positive direction, e.g. for the first mixture rule by almost 2-7% for the mixtures nos. 3, 9, 14, and 15 and by 23% for no. 16. The dissolution effect might occur for other salts too, however, we did study it only for K_2SO_4 .

- (3) The water-insoluble $CaSO_4$ forms from some of the mixtures of electrolytes Winkler and Junge (1972) have used and from our mixture no. 15. We have considered the formation of $CaSO_4$ for mixture no. 15 assuming, that each Ca-ion from $Ca(NO_3)_2$ reacts with a SO_4 -ion from $(NH_4)_2SO_4$, $MgSO_4$, and K_2SO_4 according to the following equations:



After the formation of $CaSO_4$ the composition of mixture no. 15 is



The errors given in Table 2 for mixture no. 15 are computed for this product of reaction. The mass of $CaSO_4$ had been subtracted from the mass of the original water-free electrolyte mixture to obtain the true mass of "active" water-free electrolyte mixture.

4. Summary

The water taken up by a mixture of electrolytes at high relative humidities has been discussed. Two mixture rules describing this effect have been tested using data from the literature and from own measurements. The results are compiled in Tables 1 and 2 leading to the following conclusions:

- (1) Interpreting measurements of the water uptake by electrolyte mixtures, three effects must be considered: (a) the influence of crystal-water, (b) the formation of insoluble material, and (c) when K_2SO_4 is present the dissolution of K_2SO_4 at water activities smaller than its saturation activity.
- (2) In the majority of all cases the first mixture rule (eqs. 3a, 3b or 3c) gives better results, i.e. smaller errors, than the second one (eq. 4).
- (3) When we tolerate a maximum error of 10 to 15% in the water uptake by the electrolyte mixture the first mixture rule is applicable for water activities larger than 0.85 to 0.9. In most cases the lower limits are valid. The second mixture rule is applicable at water activities above 0.9 to 0.95. Only the system $BaCl_2$ - $CsCl$ (Table 1) shows larger errors due to complex ion formation being not of importance in atmospheric particles (see discussion). The large errors for mixtures no. 7 and 8 (Table 2) are most likely due to incorrect preparation of the mixtures.

5. Meteorological implications

Together with the approach of Hänel (1976) both mixture rules are good tools computing the relations between equilibrium radius and relative humidity for mixed particles as they are found in the atmosphere. It is possible now to use measured

data of the chemical composition of the water-soluble part of atmospheric aerosol particles for such estimates. Chemical data are available for numerous locations and weather situations.

The relations between particle equilibrium radius and relative humidity, which now can be obtained by this technique for many different aerosol types, are direct input data for numerical models of the non-equilibrium growth or shrinking of fog and cloud droplets due to condensation or evaporation of water vapour. As a consequence we are now

able to study fog and cloud formation and the generation of precipitation on a more realistic and broader basis.

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РАЗМЕР АЭРОЗОЛЬНЫХ ЧАСТИЦ И ОТНОСИТЕЛЬНАЯ ВЛАЖНОСТЬ: ПОГЛОЩЕНИЕ ВОДЫ СМЕСЯМИ СОЛЕЙ

Обсуждается поглощение воды смесями солей при высокой относительной влажности. Оцениваются многочисленные результаты измерений понижения давления водяного пара над поверхностью многокомпонентных растворов электролитов для получения простой закономерности для смеси. Используются как литературные данные, так и результаты собственных измерений.

Показано, что при данной относительной влажности поглощение воды смесью солей практически эквивалентно суммарному поглощению воды отдельными компонентами смеси. Эта закономерность выполняется при относительной влажности выше 0,85 с точностью выше 10%. В статье обсуждаются также другое правило с меньшей областью применимости.