A New Method for the Measurement of the Water Activity or Relative Humidity by Fourier Transform Infrared Spectroscopy

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Water activity is an important property of aqueous solutions and humid solids. It can be measured via the relative humidity of a gas which is in equilibrium with the solution or solid. A new method was developed to measure the water activity via the relative humidity by fourier transform infrared (FTIR) spectroscopy. This method is based on earlier work on the measurement of the dew point of compressed humid air (Koglbauer and Wendland, *J. Chem. Eng. Data* **2007**, *52*, 1672−1677). The accuracy of the method was tested on salt fixed points which are widely used as humidity fixed points for the calibration of water activity sensors. The estimated uncertainty of the new method and the deviation of the new data from the reference values of the humidity fixed points are within the uncertainty of the reference values.

Introduction

Water activity is a very important thermophysical property of a humid condensed phase—either an aqueous solution or a humid solid such as, e.g., dried or otherwise preserved food. The water activity a_W can be expressed via the fugacitiy $f_W(T) = \phi_W p_W$ of a pure vapor in equilibrium with the humid condensed phase in relation to the fugacitiy $f_W^0(T) = \phi_W^0 p_W^0$ of saturated vapor at the same temperature T. This is written as

$$a_W(T) = \frac{\phi_W p_W}{\phi_W^0 p_W^0} \tag{1}$$

where ϕ_W and ϕ_W^0 are the fugacity coefficients of water and p_W and p_W^0 are the vapor pressures in the respective vapor phases.

The water activity can be determined experimentally by directly measuring the vapor pressure p_W of the condensed phase (e.g., Apelblat and co-workers[1]) or by isopiestic vapor pressure measurements (e.g., Rard and co-workers[2,3]) where equilibrium between the condensed phase and a solution with known water activity is achieved.

The water activity can also be measured via the relative humidity (RH) in a gas phase in equilibrium with the sample phase. The RH of a humid gas is defined as[4,5]

$$u_W(T) = \frac{p_W}{p_W^0} = \frac{x_W}{x_W^0} \tag{2}$$

and is usually measured by a dew point measurement with a chilled mirror or with a humidity sensor. In both cases, equilibrium of the humid gas with condensed water on the mirror or the sensor surface is achieved. In the first case, the vapor pressure of the condensed water on the mirror is needed. Measurements with sensors need a calibration with known standards such as, e.g., salt fixed points[4,6] or humidity generators.

The ratio of the fugacity coefficients in eq 1 can be neglected if the gas phases behave as ideal gases. In this case, the partial pressures can also be related to the vapor concentration c_W in the gas phase which is defined as moles of water per volume of humid gas. Thus, for ideal gases, the following relation is valid

$$a_W(T) = u_W(T) = \frac{p_W}{p_W^0} = \frac{x_W}{x_W^0} = \frac{c_W}{c_W^0} \tag{3}$$

In this work, we are presenting a new method to measure the water activity with FTIR spectroscopy. It has strong advantages toward the vapor pressure method, because air and other gas components in the phase above the condensed sample are completely inert for IR adsorption measurements, and toward the isopiestic method, because no reference solutions are necessary for which equilibration is slow and an analysis of the concentration is necessary. It has also advantages toward the use of humidity sensors or chilled mirrors since no calibrations with a humidity standard or humidity generator are necessary and systematic temperature errors cancel out, as will be shown.

Previously,[7,8] we have used FTIR spectroscopy to measure the vapor concentration enhancement factor $g_W(T,p)$ in compressed humid gases. It is defined very similarly to the last term of eq 3 as[7,9] $g_W(T,p) = c_{W,G}/c_W^0$ where $c_{W,G}$ and c_W^0 are the vapor concentrations in a saturated compressed humid gas and in a saturated humid ideal gas, respectively. The absorbance A of IR light by water increases linearly with the water concentration c_W in the gas phase as described by the Beer−Lambert law ($A = \varepsilon d c_W$). Thus, the relative humidity or water activity can be measured conveniently via the ratio of the absorbance A in the gas in equilibrium with the sample condensed phase to the reference absorbance A^0

$$a_W(T) = u_W(T) = \frac{c_W}{c_W^0} = \frac{A}{A^0} \tag{4}$$

since both linearity constants—the extinction coefficient ε and the path length d—are the same for both measurements which are taken at the same temperature and pressure.

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Table 1. Purities of the Salts

salt	company	chemical grade	purity better than
lithium chloride	Roth	p.a.	99.0 %
magnesium chloride	Roth	p.a.,A.C.S.	99.0 %
potassium carbonate	Merck	p.a.	99.0 %
sodium chloride	Roth	p.a.,A.C.S.	99.5 %
potassium chloride	Roth	p.a.,A.C.S.	99.5 %
potassium nitrate	Roth	p.a.,A.C.S.	99.0 %
potassium sulfate	Roth	p.a.,A.C.S.	99.0 %

Table 2. Method and Settings of the FTIR Spectrometer

parameter/method	setting
IR source	MIR globar (7500 to 370) cm^{-1}
beam splitter	KBr
detector	RT-DLaTGS
aperture	6 mm
scanner velocity	20 kHz
scan time	100 scans
sample gain	× 2
apodization	four point
phase resolution	1 cm^{-1}
acquisition mode	forward−backward
phase correction	power spectrum
zero filling factor	32
integration method	peak bundle with baseline
integration range	(4150 to 2800) cm^{-1}
baseline nodes	(6000; 1000) cm^{-1}

Saturated aqueous solutions of single salts are often used as humidity fixed points for calibration of water activity sensors. Greenspan[6] has assigned, after an elaborate review, humidity values u_W to these fixed points which are still valid[4] and extensively used in connection with water activity and sorption isotherm measurements of, e.g., preserved food. Also, their water activity only depends on the temperature. Thus, the new FTIR method was tested by measurements of the water activity of saturated salt solutions (fixed points) at 25 °C. The new data have a similar or even better accuracy than the reference data of Greenspan[6] and agree with those within the given accuracies.

Experimental Section

Chemicals. Water of LC-MS grade was purchased from Roth company (Karlsruhe, Germany, type ROTISOLV). The salts are of p.a. (pro analysi) grade with purities of 99.0 % and better (see Table 1).

Method and Apparatus. Figure 1 shows schematically the view cell placed in the sample compartment of the FTIR spectrometer. The view cell has an internal diameter of 20 mm (optical diameter). It consists of two window units and a body. With different bodies, it can be extended to a range of internal length (optical path length) from (40 to 100) mm. The body and the flanges were machined from the aluminum alloy 2011 (AlCu6BiPb, DIN 3.1655) by the mechanical workshop of our institute. The body and flanges were painted with high-temperature resistant, highly elastic paint to avoid reflections of scattered IR light. The windows have a diameter of 25 mm and a thickness of 2.5 mm. Two different materials were tested, quartz and calcium fluoride (CaF_2). Quartz is chemically inert but limits the measurement to wave numbers of a maximum of 2500 cm^{-1}. Calcium fluoride allows measurements up to 1000 cm^{-1} but is slightly soluble in water (0.0017 g/100 g at 20 °C). The windows were coated with a thin film of silicon oil to prevent wetting for the quartz and formation of hydrates for calcium fluoride. The windows are each housed in a PTFE seal and a PET washer. The window units are sealed toward the body with 0.5 mm FPM 75 flat seals. A sample container (made from 0.25 mm of ETFE or PTFE foil) is placed in a groove at the bottom of the cell which is outside the optical path. The sample container can be filled externally and placed in the cell while a window unit is removed.

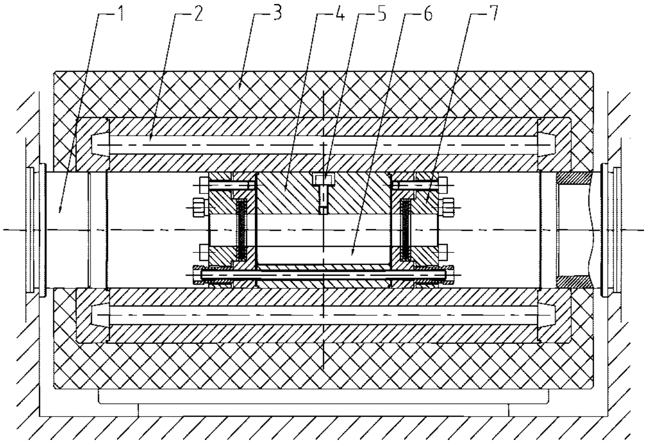

Figure 1. Schematic drawing of the measuring cell and the thermostatted jacket and their placement in the sample compartment of the FTIR spectrometer: 1, bellow; 2, thermostatted jacket; 3, insulation; 4, cell body; 5, tube connector; 6, groove for sample container; 7, window unit.

The cell is placed in a jacket which is machined from the same alumina alloy as the cell. It is divided horizontally so that it can be opened easily to replace the cell. It is connected with bellows to the compartment walls of the spectrometer. The whole optical path outside the cell (inside the bellows, the jacket, and the spectrometer) is flushed by air which was dried and cleaned from carbon dioxide by a 4 Å mole sieve.

For each measurement, the sample (saturated salt solution) was filled into the sample container which was then placed into the sample groove of the cell. The cell was placed into the thermostatted jacket in the sample compartment of the spectrometer and allowed to equilibrate for about 22 h. An IR spectrum in the gas phase inside the cell was measured three times within 20 min. Afterward, the cell was removed, emptied, flushed with dried air, and replaced. After one hour of flushing and drying the whole optical system, the background spectrum was measured. Finally, the absorbance A was calculated by integration of the absorption spectra, and an average of the three absorbance measurements was taken. The same procedure was also applied to pure water which yielded the reference absorbance A^0 and finally the water activity a_W with eq 4. The absorbance A or A^0 was measured by the FTIR spectrometer Tensor 27 (Bruker Optik GmbH, Ettlingen) which was already used for the compressed humid gas measurements.[7,8] The spectrometric method and the settings which are very similar to the one applied for the compressed gases are given in Table 2. An absorption spectrum measured with the CaF_2 windows is given in Figure 2. Again, the range between about (3550 and 4000) cm^{-1} was chosen for the measurements. The CaF_2 windows were used throughout the measurements because they allowed a better observation of the carbon dioxide absorption at 2500 cm^{-1} which is a very sensitive indicator for sufficient flushing and drying. An optical path length of 100 mm was chosen for all measurements at 25 °C.

Uncertainties. The temperature was controlled through a thermostatted bath (Julabo, Karlsruhe, Germany, type F25-HE, stability 0.01 K) and the jacket around the measuring cell and was measured by a 100 Ω platinum resistance (Pt100) thermometer and a nanovolt meter (Agilent Technologies, Englewood, CO, USA, type 34420A). The nanovolt meter was operated together with a switch unit, a 1 mA constant current

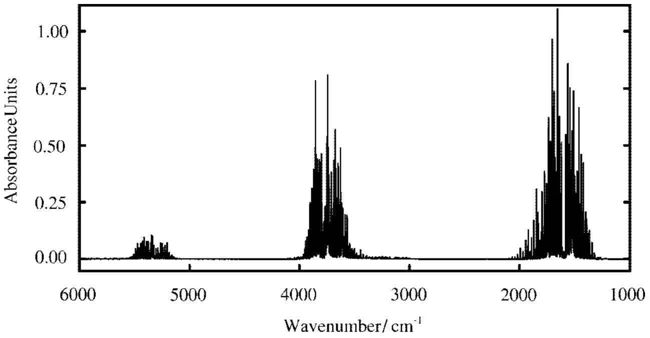

Figure 2. IR absorbance spectrum of water vapor.

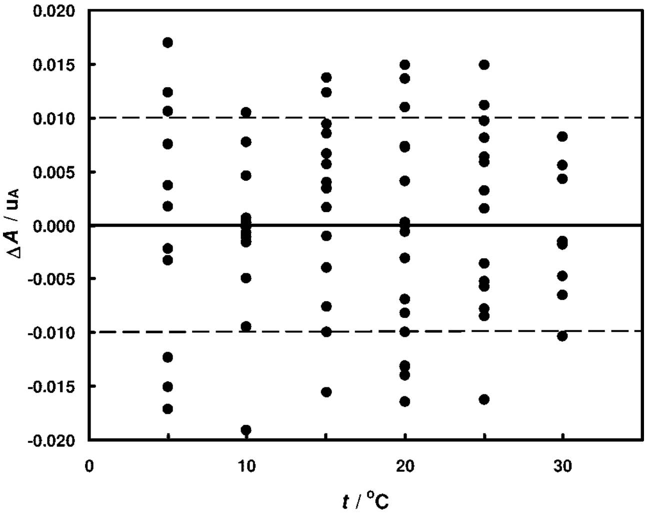

Figure 3. Deviation ΔA of the experimental A^0 values from their correlation with temperature.

load (both designed and built by the electronics workshop of our institute), and a 10 Ω Wilkins standard resistor (Tinsley, London, UK, type 5685A). The Pt100 thermometer had been calibrated prior to the measurements against a 25 Ω platinum resistance thermometer (Rosemount, USA, type 162 D, calibrated according to the International Temperature Scale of 1990 (ITS-90) at three fixed points between (−40 and 156) °C by Landesamt für Mess- und Eichwesen Thüringen, Ilmenau, Germany, uncertainty less than 2 mK). A temperature gradient in the cell of less than 0.08 K was observed. The combined standard uncertainty of the temperature measurement was estimated to be less than 0.10 K. This uncertainty has a large contribution from systematic errors but only a small contribution from stochastic errors of less than ± 0.01 K.

For the determination of the water activity a_W with eq 4, one measurement of the absorbance A and one reference measurement of A^0 are needed. Thus, the combined standard uncertainty of a_W can be derived by the error propagation law from eq 4 as

$$\Delta a_W = \sqrt{\left(a_W \frac{\Delta A^0}{A^0}\right)^2 + \left(a_W \frac{\Delta A}{A}\right)^2} \tag{5}$$

or, since the relation $a_W/A = 1/A^0$ is constant, as

$$\Delta a_W = \sqrt{\left(a_W \frac{\Delta A^0}{A^0}\right)^2 + \left(\frac{\Delta A}{A^0}\right)^2} \tag{6}$$

There are several contributions to the accuracy of the absorption measurement with FTIR from the stability of the IR source, the optical system, the detector, the background spectrum, and the positioning of the cell in the optical way. The last contribution is by far the largest mainly because of uncertainties in the horizontal position of the cell which is removed and replaced for each single filling. This contribution can not be estimated theoretically but has to be accessed via repeated measurements of identical samples. There will be also a temperature contribution to each absorption measurement. In eq 6, only stochastic errors in the temperature of less than ± 0.01 K need to be taken into account because any systematic temperature error will cancel out in eq 4 since both absorption measurements are taken at the same temperature reading. We have measured the reference absorbance A^0 with pure water samples over a temperature range from (5 to 30) °C with about five to ten independent measurements for each temperature to estimate the temperature dependence of the absorbance and the above-mentioned contributions to the stability of the FTIR measurements. The uncertainty of the absorption measurements (A and A^0) can be estimated with error propagation from contributions of the temperature fluctuations ΔA_T and the FTIR measurement ΔA_{FTIR}

$$\Delta A = \sqrt{(\Delta A_T)^2 + (\Delta A_{FTIR})^2} = \sqrt{\left(\frac{A - A(T_0)}{T - T_0}\Delta T\right)^2 + (\Delta A_{FTIR})^2} \tag{7}$$

The absorption will, according to the Lambert−Beer law, increase with temperature mostly because of the increasing vapor density. The extinction coefficient ε decreases only slightly with temperature from 180 $m^2 \cdot mol^{-1}$ at 5 °C to 165 $m^2 \cdot mol^{-1}$ at 30 °C. Thus, the temperature contribution to the uncertainty in A (first term in eq 7) is estimated to $\Delta A_T/A_T \leq 0.0004$.

A polynomial function of the fourth degree was used to correlate the experimental data of the reference absorption A^0. Deviations of the data from the correlation function are shown in Figure 3. The standard deviation (root-mean-square, rms) of the experimental data to the correlation function is 0.0096 absorbance units (u_A). The measurements were done over a period of several months which shows the stability of the spectrometer and method. The correlation function is used to determine the A^0 value in eq 4 at the temperature reading of each water activity measurement. From this repeatability of the A^0 measurements, we get a standard uncertainty ($k = 1$, confidence level 68 %) of the reference absorbance at 25 °C ($A^0 = 19.4\ u_A$) of $\Delta A^0/A^0 \leq 0.0005$. Thus, the temperature fluctuations account with $\Delta A_T/A_T \leq 0.0004$ for by far the largest contribution to the uncertainty of the absorption measurements.

We can assume that the absolute uncertainty ΔA of the absorption measurements for the salt fixed points is the same as the absolute uncertainty ΔA^0 for the reference measurements. Thus, we can use $\Delta A/A^0 = \Delta A^0/A^0 \leq 0.0005$ to estimate the uncertainty of the measured water activity with eq 6. Thus, the combined total standard uncertainty ($k = 1$, confidence level 68 %) of the a_W measurements decreases with decreasing water activity from 0.0007 at $a_W = 1.0$ to 0.0005 at $a_W = 0.1$. The expanded uncertainty ($k = 2$, confidence level 95 %) ranges from 0.0014 at $a_W = 1.0$ to 0.0010 at $a_W = 0.1$. These expanded uncertainties are mostly smaller or at least equal to the expanded uncertainties given by Greenspan for the salt fixed points at 25 °C.

Table 3. Experimental (exp) Results for the Water Activity a_W in Comparison with Reference (ref) Values for u_W from Greenspan[6] at 25 °C[a]

salt	t/°C	$a_{W,exp}$	$u_{W,ref}$	$a_{W,exp} - u_{W,ref}$	$\delta A/A^0$
lithium chloride	25.02	0.1132 ± 0.0082	0.1130 ± 0.0027	0.0002	± 0.0041
		0.1134 ± 0.0024	0.1130 ± 0.0027	0.0004	± 0.0012
		0.1130 ± 0.0010	0.1130 ± 0.0027	0.0000	± 0.0001
magnesium chloride	25.00	0.3271 ± 0.0011	0.3279 ± 0.0016	−0.0008	± 0.0002
		0.3277 ± 0.0032	0.3279 ± 0.0016	−0.0002	± 0.0016
		0.3263 ± 0.0016	0.3279 ± 0.0016	−0.0016	± 0.0008
potassium carbonate	24.97	0.4308 ± 0.0028	0.4317 ± 0.0039	−0.0009	± 0.0014
		0.4207 ± 0.0011	0.4317 ± 0.0039	−0.0010	± 0.0002
		0.4217 ± 0.0011	0.4317 ± 0.0039	0.0000	± 0.0002
sodium chloride	25.01	0.7524 ± 0.0033	0.7530 ± 0.0012	−0.0006	± 0.0016
		0.7525 ± 0.0014	0.7530 ± 0.0012	−0.0005	± 0.0006
		0.7525 ± 0.0023	0.7530 ± 0.0012	−0.0005	± 0.0011
potassium chloride	25.00	0.8421 ± 0.0013	0.8434 ± 0.0026	−0.0013	± 0.0005
		0.8418 ± 0.0033	0.8434 ± 0.0026	−0.0016	± 0.0016
		0.8413 ± 0.0041	0.8434 ± 0.0026	−0.0021	± 0.0020
potassium nitrate	25.02	0.9349 ± 0.0014	0.9359 ± 0.0055	−0.0010	± 0.0005
		0.9360 ± 0.0040	0.9359 ± 0.0055	0.0001	± 0.0019
		0.9345 ± 0.0017	0.9359 ± 0.0055	−0.0014	± 0.0007
potassium sulfate	25.01	0.9714 ± 0.0016	0.9730 ± 0.0045	−0.0016	± 0.0006
		0.9726 ± 0.0032	0.9730 ± 0.0045	−0.0004	± 0.0015
		0.9722 ± 0.0017	0.9730 ± 0.0045	−0.0008	± 0.0007

[a] Experimental results and reference values are given together with the extended standard uncertainties. Also the fluctuation $\delta A/A^0$ of the absorption measurement is given for each data point.

Results and Discussion

The accuracy of the new method was tested by measuring the water activity a_W of several salt fixed points at 25 °C. The new experimental data are given in Table 3 and compared with Greenspan's reference data[6] for the relative humidity u_W of the salt fixed points. Three independent measurements were done for each salt fixed point. For each measurement, at least three readings of the absorption were taken with about 10 min in between and averaged. The fluctuation $\delta A/A^0$ of the three absorbance readings are also given in the table as root-mean-square difference to the average value which was used to calculate a_W. Some of the data points have fluctuations $\delta A/A^0$ of about the same magnitude as the fluctuations $\Delta A^0/A^0 = 0.0005$ of the reference measurements in Figure 3, while others show larger fluctuations. The estimated standard uncertainties were calculated for each data point by eq 6. For the uncertainty of the absorption measurement $\Delta A/A^0$, either the fluctuation $\delta A/A^0$ or the estimate $\Delta A/A^0 = \Delta A^0/A^0 = 0.0005$ was taken, whichever was larger. The uncertainties of the new experimental data are given for each data point in Table 3 as extended uncertainties ($k = 2$, confidence level 95 %) and are almost always smaller than the extended uncertainties given by Greenspan. The difference between the new data and Greenspan's reference values is always clearly within the given extended uncertainties of both data sets.

Conclusions

A new method and new apparatus for the measurement of the water activity via relative humidity by FTIR spectroscopy was developed. It was tested by measurements of humidity fixed points at 25 °C which were reproduced within their experimental uncertainty. No calibration was needed. The relative humidity can be determined only by one IR absorbance measurement in the gas phase above the humidity fixed point and one reference measurement in the gas phase above pure water at the same temperature. Thus, the method has the potential to be used as a primary standard for the relative humidity.

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