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A new method of characterising liquid uptake within particles over short time periods

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Abstract

A method of measuring both the capacity and rate of absorption of liquid by powders of small particles over short time periods (of the order of a few seconds or less) is presented. The method is based on the measurement of the isothermal transient ionic current in a sample cell containing the absorbant material and the liquid. The method has been tested on solid glass beads, porous glass beads and cellulose agglomerates. Properties such as the instantaneous absorption capacity and rate can be characterised within a few seconds. No other technique is currently able to measure these fast outcomes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Absorption; Particles; Isothermal transient ionic current

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1. Introduction

The uptake of liquid is an essential parameter for various products and applications. For soft absorbant paper and sanitary products, for example, the uptake of liquid is, quite obviously, the performance-determining parameter (Hollmark, 1984). In other applications, the purpose of liquid uptake is to trigger subsequent events. This is the case in the field of pharmaceutics, where the uptake of liquid by tablets causes them to disintegrate (Van Kamp et al., 1986; Lowenthal, 1973) or enhances the absorption of drugs (Nagai et al., 1984; Morén and Edman, 1993). In all these cases it is important to gain information about the process of liquid absorption in order to allow further improvements to the products.

There are several reviews of the various methods of studying the uptake of liquid (Caramella, 1990a,b; Takahashi et al., 1997). One disadvantage of the existing methods is that they do not allow the study of very rapid liquid uptake, that occurs over seconds or even less than a second. For example, the time course of liquid absorption into small particles is very short. Similarly, for tablets, the crucial time for studying liquid uptake is before disintegration; once disintegration has occurred, further uptake of water is of no interest.

Materials can absorb liquid either by swelling or by capillary imbibition. When a material

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swells, its dimensions are enlarged and the cohesion of its units is diminished, i.e. it becomes soft and flexible. A porous tile, on the other hand, absorbs liquid without changing dimensions and the cohesion of its parts is not diminished. In materials like this, methods which characterise swelling will not register any change, even though liquid has been taken up by the porous material.

The purpose of this work is to introduce a method which — independently of the mechanism of liquid absorption — can determine *both* the capacity and the rate of absorption over a short time period. The method is based on measurements of the isothermal transient ionic current (ITIC) through a cell containing the liquid to be absorbed and the material to be investigated. The method has been tested on powders which absorb liquids by different mechanisms.

2. ITIC measurements

The ITIC technique measures the transient current after a constant field is applied across a sample cell, with other parameters, such as temperature held constant. The technique has been used to study ionic mobility in dielectric systems such as SiO_2 films (Stagg, 1977; Greeuw and Hoenders, 1984; Greeuw and Verwey, 1984), in insulating polymer films (Watanabe et al., 1985) and recently in ion conductors such as Ta_2O_5 (Strømme Mattsson and Niklasson, 1999; Strømme Mattsson et al., 1999). In this section the experimental set-up for the measurement of liquid absorption and the theory behind the use of this type of measurement to study liquid absorption is described.

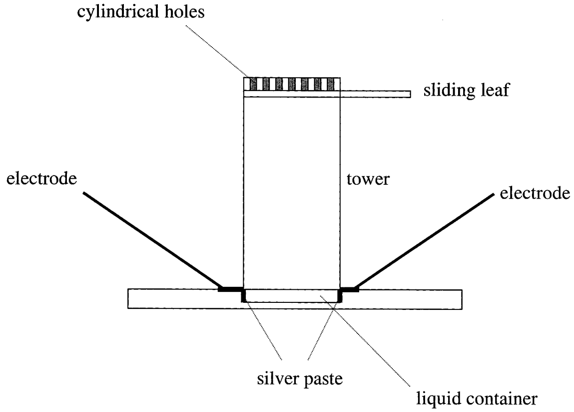

Fig. 1. Experimental set-up for liquid absorption measurement using the ITIC technique. Powder can be applied into 56 cylindrical holes (each having a volume of 1.571×10^{-3} cm^3) on top of the tower. Liquid containing a known concentration of ions is held in the liquid container. A constant potential is applied between the electrodes, and the powder is added to the liquid by sliding the leaf to the side.

The experimental set-up consists of a liquid container, a powder-application device and two electrodes, Fig. 1. The liquid container is a square cavity (2 × 2 cm) in a polycarbonate unit. Conductive Silver D200 from Demetron, Germany is painted on opposite walls of the liquid container and slightly over the lip of the polycarbonate unit, so as to facilitate contact with the tungsten needle electrodes. The powder application device, also in polycarbonate, consists of a hollow (2 × 2 cm) tower with a sliding leaf and a plate with 56 cylindrical holes (2 mm in diameter and 0.5 mm in height).

The liquid container is filled with liquid containing a known concentration of ions, and the powder to be investigated is applied into the cylindrical holes. A constant potential is applied between the electrodes, which are connected to an electrochemical instrument (Autolab/GPES, Eco Chemie, Utrecht, The Netherlands) that can measure the current as a function of time. Before the material is dropped onto the liquid film, the current in the cell is solely due to ions moving towards the electrodes. The ions are blocked by the electrodes, hence the current decreases. This phenomenon is called electrode polarisation. As time goes by, the current decay slows down, as shown schematically in Fig. 2 for time $t < t_0$. At t_0 the sliding leaf is pulled out and the material flows from the tower and disperses onto the liquid. Between time t_0 and t_1 the liquid is sucked into the absorbant material and the number of free charge carriers in the system is, thus, diminished. The absorption capacity and absorption rate can be obtained from the drop in current (ΔI) and the time derivative of the current response (dI/dt) between t_0 and t_1, respectively.

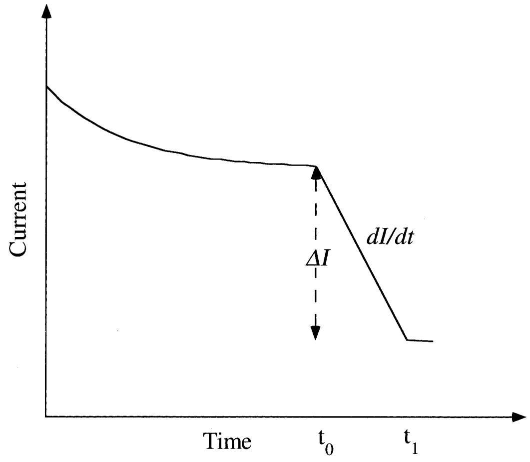

Fig. 2. Schematic response of current during liquid absorption measurement using the ITIC method. At time t_0 the powder is added onto the liquid (cf. Fig. 1). The almost instantaneous absorption process takes place between time t_0 and t_1. The current drop (ΔI) as well as the time derivative of the current ($\mathrm{d}I/\mathrm{d}t$) in the absorption step are shown in the figure.

According to basic electrodynamics, the current I conducted by a liquid containing ions can be expressed by

$$I(t) = A\sigma E = \left\{\sigma = nq\bar{\mu},\ E = \frac{U}{L}\right\} = Anq\bar{\mu}\,\frac{U}{L}. \tag{1}$$

Here A is the cross sectional area of the conducting liquid, i.e. the area of the silver electrodes in contact with the electrolyte. σ is the conductivity of the liquid, E is the applied electric field, n is the ion concentration in the liquid, q is the charge per ion, $\bar{\mu}$ is the average mobility of the ions in the liquid, U is the applied potential and L is the length of the conduction path, i.e. the distance between the electrodes. If the total number of ions in the liquid is symbolised by N_{ion}, the ion concentration in the liquid (n) equals N_{ion}/AL, and $I(t)$ can be expressed as

$$I(t) = N_{\mathrm{ion}}q\bar{\mu}\,\frac{U}{L^2}. \tag{2}$$

When a powdered material is introduced into a salty liquid, it absorbs the liquid and the number of charge carriers is diminished. The absorption capacity of the powder is calculated by using

$$\text{Absorption capacity} = \frac{m_{\mathrm{l}}}{m_{\mathrm{m}}} = \frac{V_{\mathrm{l}}\rho_{\mathrm{l}}}{V_{\mathrm{m}}\rho_{\mathrm{m}}},$$

where m_{l} is the mass of the absorbed liquid, m_{m} is the mass of the powder, V_{l} is the volume of the absorbed liquid, V_{m} is the volume of the powder, ρ_{l} is the density of the liquid and ρ_{m} is the bulk density of the powder.

The volume of the absorbed liquid, can be expressed as

$$V_{\mathrm{l}} = \frac{\Delta N_{\mathrm{ion}}}{cN_{\mathrm{A}}}, \tag{4}$$

where ΔN_{ion} is the number of ions absorbed by the powder. The number of ions per liquid volume (n) can be expressed as cN_{A}, where c is the molar ion concentration and N_{A} is the Avogadro constant. Thus, $1/cN_{\mathrm{A}}$ is the liquid volume per ion.

If the ion concentration in the liquid and the bulk density of the absorbant material are known, the absorption capacity can be measured using the decrease in current ΔI:

$$\text{Absorption capacity} = \frac{\Delta I L^2}{qU\bar{\mu}cN_{\mathrm{A}}}\,\frac{\rho_{\mathrm{l}}}{V_{\mathrm{m}}\rho_{\mathrm{m}}}. \tag{5}$$

The absorption rate is then easily obtained by replacing ΔI with the time derivative of the current:

$$\text{Absorption rate} = \frac{\mathrm{d}m_{\mathrm{l}}}{\mathrm{d}t}\,\frac{1}{m_{\mathrm{m}}} = \frac{\mathrm{d}I}{\mathrm{d}t}\,\frac{L^2}{qU\bar{\mu}cN_{\mathrm{A}}}\,\frac{\rho_{\mathrm{l}}}{V_{\mathrm{m}}\rho_{\mathrm{m}}}. \tag{6}$$

3. Materials

Solid glass beads were obtained from Kebo Laboratory, Sweden. The porous glass beads, Nucleosil, came from Macherey-Nagel, Germany. Cellulose agglomerates were produced from microcrystalline cellulose from FMC, USA, by milling, spray drying and washing (Ek et al., 1995). Tween 80, Polysorbatum, came from Kebo Laboratory, Sweden. The physical parameters of the materials are presented in Table 1.

Table 1
Physical characteristics of the materials used

Material	Bulk density[a] (kg/m^3)	Particle diameter (μm)	Porosity[d] (%)
Solid glass beads	1370	<63[b]	46.3
Porous glass beads	448	25–40[c]	82.4
Cellulose agglomerates	420	<63[a]	73.4

[a] Measured by weighing 20 ml loosely packed powders of the materials.

[b] According to Eriksson et al. (1990).

[c] According to Macherey-Nagel, D-5160 Düren, Germany.

[d] Calculated as $1-$(bulk density)/(particle density). The particle densities of the glass beads and cellulose agglomerates were 2550 kg/m^3 (Eriksson et al., 1990) and 1580 kg/m^3 (measured with a He gas pycnometer from Accu Pyc Micrometrics 1330, USA), respectively.

4. Experimental method

The liquid container was filled with 50 μl of water containing 154 mM NaCl (i.e. $c = 2 \times 154$ mM). In addition, 0.05% by weight Tween 80, a surface tension reducing substance, was added in order to ensure a planar liquid layer with no drop formation. A constant potential ($U = 1$ V) was then applied across the cell. About 20 s after the potential was applied across the liquid container, powder was dropped from the powder application device onto the water film. The amount of powder used in the experiments varied between $10 \times 1.571 \times 10^{-3}$ and $56 \times 1.571 \times 10^{-3}$ cm^3. The reason for waiting before adding the powdered material to the liquid container was that the initial ($t < 20$ s) current decay due to electrode polarisation is faster than the slower subsequent decrease, Fig. 3. The figure shows the current response of the water film. The current decay is caused by electrode polarisation; after 20 s the decrease was less than 0.25 μA/s.

5. Results

Fig. 4 shows the response of the current in an absorption experiment performed on three different powdered materials. A straight line is fitted to the current response during the water absorption step and the derivative dI/dt of this line is shown together with the magnitude of the change in current ΔI. From the figure it is obvious that the absorption process for all three powders is so rapid that the current decay due to electrode polarisation can be neglected when using ΔI and dI/dt to calculate the absorption capacity and rate. The rate and capacity of absorption of salty water were obtained from Eqs. (5) and (6). The bulk densities of the powders were obtained from Table 1 and the average mobility of sodium and chloride ions in water was assumed to be 4.87×10^{-4}/cm^2/Vs (Weast, 1974). The measurements were repeated about 10 times for each powder and the average capacities and rates of absorption are presented in Table 2. The rate and capacity in Eqs. (5) and (6) depend inversely on the mass (or volume) of powder used in the experiment. By varying the powder volume no significant variation in the measured capacities and rates was

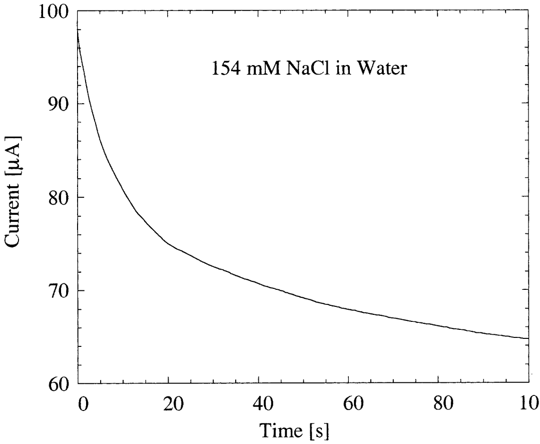

Fig. 3. Current response when the liquid container in the cell in Fig. 1 is filled with salty water. The potential across the cell is 1 V.

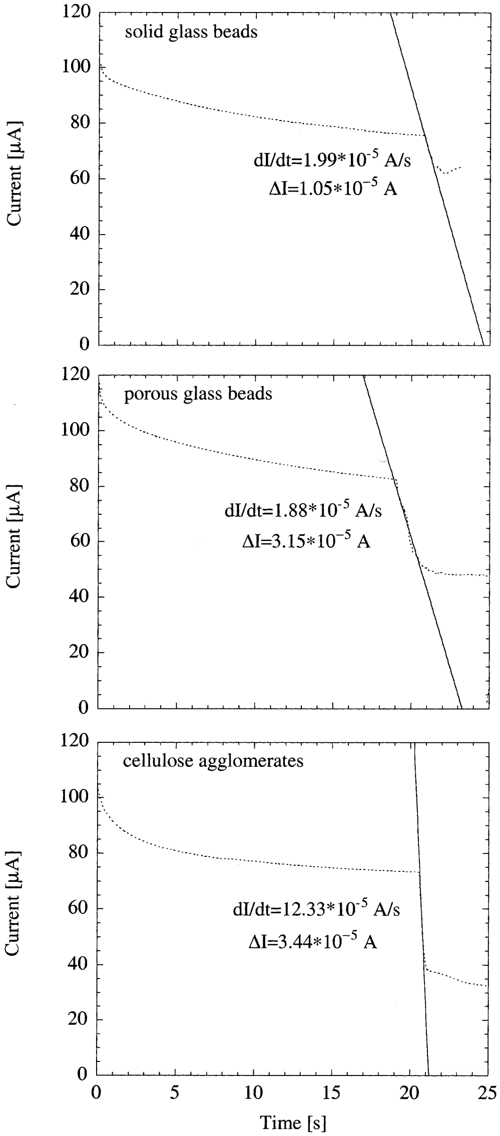

Fig. 4. The response of the current (dashed lines) during an ITIC experiment of salty water absorption by three different powders. Included in the figures are also linear curve fits (solid lines) to the regions of water absorption. The derivative of the curve fits dI/dt as well as the magnitude of the current drop ΔI in the absorption region are also shown.

found when expressed per kg (or per cm^3). Hence, the mass (or volume) dependence in the two equations was verified.

The absorption capacity of the solid glass beads was about 10% of that of the porous glass beads or the cellulose agglomerates. The rate of absorption by the cellulose agglomerates was about one order of magnitude higher than that by the (solid and porous) glass beads.

According to the derivations detailed in Section 2, the capacities and rates obtained by using ITIC should be independent of the initial volume of liquid in the liquid container. To verify this, the experiment was repeated using cellulose agglomerate powder with different amounts of water in the liquid container, Fig. 5. No dependence on the volume of water was found for volumes ranging from 30 to 300 μl.

6. Discussion

No significant variation in the measured capacities and rates (per kg) were found when significantly different powder volumes were used. This does not *only* prove the correctness of the volume (or mass) dependence in Eqs. (5) and (6), it also verifies that the length of the conduction path L is not significantly altered because of the powder introduced into the liquid container. The conduction path length appears squared in Eqs. (5) and (6), hence the capacity and rate is very sensitive to any changes in its value.

The three powders used to test the new ITIC method presented in this paper were chosen because of their fundamentally different properties as liquid absorbers. The solid glass beads have no internal pores. The only place were liquid can reside in this powder is in the cavities between the beads. The porous glass beads are a little more complex. In addition to absorption into cavities between the beads, liquid can be absorbed by capillary imbibition into internal pores. The cellulose agglomerate powder absorbs water by both these methods and also swells on contact with liquid.

It was found that the absorption capacity of the solid glass beads was about 10 times less than that of the porous glass beads (see Table 2). This suggests that only a small amount of liquid is absorbed into the cavities between particles in a powder where liquid can be transported into the interior of the particles.

Table 2
Rate and capacity of salty water absorption by various materials

Material	Capacity[a] (kg water/kg material)	S.D. (%)	Rate[b] (kg water/kg material per s)	S.D. (%)
Solid glass beads	2.4×10^{-2}	11	4.6×10^{-2}	13
Porous glass beads	0.22	7	0.13	6
Cellulose agglomerates	0.26	10	0.90	8

[a] From Eq. (5).

[b] From Eq. (6).

The rate of absorption by the porous glass beads was about three times higher than that by the solid glass beads. This may be explained by the strength of the capillary forces. The cavities between the beads are many orders of magnitude larger than the internal pores in the porous glass beads. The capillary movement is much stronger in narrower pores and thus occurs much faster in the smaller internal pores than in the larger cavities between the beads.

The absorption capacity of cellulose agglomerate powder was comparable to that of the porous glass beads. Since the particles making up the two powders were comparable in size and had approximately the same porosity, this was not unexpected. However, the cellulose agglomerate powder also absorbs liquid by swelling. When a material swells, both its internal pore system and its outer dimensions change as the liquid is absorbed. The ITIC method, as described here, traces the absorption processes that occur over a time scale of seconds; in this limited time window, the cellulose agglomerate powder does not have time to considerably change in dimension. However, some initial swelling, which almost instantaneously closes some pores and opens others, may occur; this may partly explain the much higher absorption rate in the flexible cellulose agglomerate powder as compared to in the powder of rigid porous glass beads.

7. Concluding remarks

This paper presents a method of characterising liquid uptake, which occurs over a period of a few seconds or less, by a powdered material. The method, which is an easy and convenient way to obtain information about the capacity and rate of absorption, is based on the isothermal transient ionic current technique that has been used previously to study ionic mobility in dielectric systems.

There are currently no other techniques able to measure very rapid liquid absorption properties.

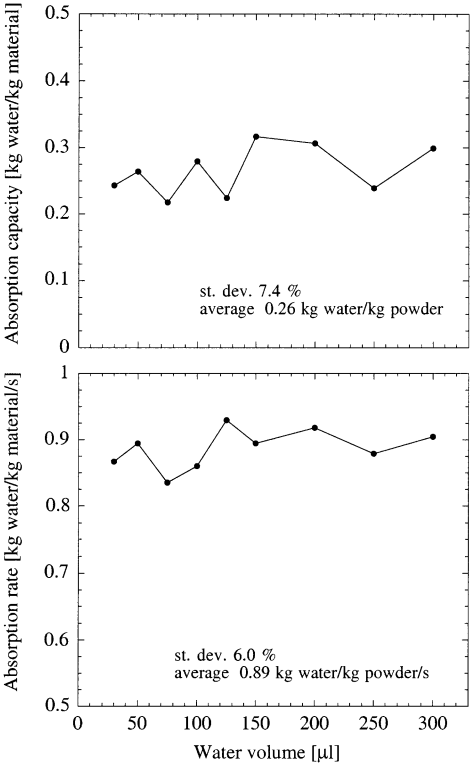

Fig. 5. Capacity and rate of absorption of salty water by cellulose agglomerate powder as a function of the amount of water in the liquid container. The average capacity and rate (plus the S.D.) are displayed.

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