

# Frequency-dependent resistance behavior of porous quartz beds

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# Frequency-Dependent Resistance Behavior of Porous Quartz Beds

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Frequency-dependent resistance measurements have been performed on porous beds consisting of monodisperse quartz particles. At low electrolyte concentrations the resistance shows a maximum as a function of frequency. The frequency at which this maximum occurs is independent of particle size. It depends on the temperature in an Arrhenius-like fashion. This is explained by a combination of convective charge transport and conduction through the Stern layer. © 1989 Academic Press, Inc.

## 1. INTRODUCTION

Recently a new pore model for describing the electrokinetic and hydrodynamic behavior of porous beds was introduced (1–4). The model described the above-mentioned phenomena well when complications such as surface conductance were absent. However, when conditions were such as to expect the occurrence of surface conductance, it was not possible to describe the experiments well with the model (including contributions due to the diffuse double layer). Two possible causes were suspected:

a) the linearization of the Poisson–Boltzmann equation introduced in the model is a serious approximation under these circumstances;

b) conduction through the Stern layer might occur.

Separation of the overall conductance of a plug into a volume current contribution and a surface current contribution is difficult. It may be effected for systems of simple geometry (see, e.g. Ref. (5)), but for plugs with pores

of complicated forms it requires the introduction of an effective length of the pores (6).

In order to obtain insight into these phenomena frequency-dependent measurements were performed.

In the past attention has been focused mainly on the dependence of the permittivity on frequency (7–13). However, because the resistance could be measured more accurately than the capacity and the frequency-dependence of the resistance gives similar information, as obtained from capacitance measurements, we focused attention on the resistance.

## 2. EXPERIMENTAL

The resistance and capacity were measured of various porous beds consisting of monodisperse particles and filled with KCl solution (pH = 5, pKCl: 1, 3, and 5) as a function of the frequency. The beds were prepared as described in Ref. 1 and 2. The measurements were performed with a Wayne Kerr Universal Bridge B224 connected to a General Radio 1316 oscillator and a General Radio 1238 detector. In order to measure the frequency accurately a Fluke 1900 A multimeter was used.

Use was made of a compensation method in which the capacity and the resistance of the system were compensated by the Wayne Kerr

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bridge. The capacity was not used in the calculations as its value was very low. There was also hardly any self-induction, so if the Springer circuit (12) is assumed to be valid the impedance is nearly equal to the resistance. Measurements were restricted from 500 Hz up to 10,000 Hz as outside these boundaries it was impossible to perform measurements accurately with the apparatus available.

Care was taken that the beds were properly thermostated as it was observed that small temperature fluctuations decreased the accuracy of the measurements.

It made no difference whether blackened or blank Pt electrodes were used. If no porous bed was placed between the electrodes but only an electrolyte solution, no influence of the frequency was observed at any electrolyte concentration. These observations exclude electrode polarization or any other dependence of the results on the measuring equipment.

Except for the two largest particle sizes, the surface roughness of the quartz samples was determined as the ratio of the Krypton adsorption surface area and the surface area determined by microscopy. The determination of the microscopic surface area is described in Ref. (1). The Krypton adsorption surface area is determined by measuring the adsorption and desorption isotherm of Krypton on the quartz samples according to the B.E.T. method (25–28). The reason that Krypton was taken instead of nitrogen was that the surface area was too small for a proper surface area measurement by nitrogen adsorption.

### 3. RESULTS AND DISCUSSIONS

There was no influence of the frequency on the resistance at pH = 5, pKCl = 3 and pH = 5, pKCl = 1 for all particle sizes. However, at pH = 5, pKCl = 5, there was a marked influence of the frequency on the resistance. At these concentrations the frequency-dependence of the resistance showed the characteristics described below for five different beds, composed of solid particles of different sizes, and at a number of different temperatures.

This excludes the possibility that the frequency-dependent behavior described is of an accidental rather than of a systematic nature.

A typical result at that concentration is shown in Fig. 1. Similar data have been reported by Sidorova *et al.* (30, 31) on diaphragms made of quartz glass fibers. These authors postulated the existence of two layers, in one of which the carriers are only slightly connected with the S/L interface, while in the other the carriers are more strongly bound; the latter might be ions of the Stern layer or counterions located in a gel-form layer at the vitreous quartz/solution interface.

The most remarkable feature of our results (Fig. 1) is that the curve has a maximum at about 5000 Hz. This corresponds to an angular frequency of 31400 cps. Table I shows that the peak resistance of the smallest particle sizes does depend on the particle size. This maximum was not reported by Sidorova *et al.* (30, 31); these authors report only an increasing conductivity (or decreasing resistance) with increasing frequency.

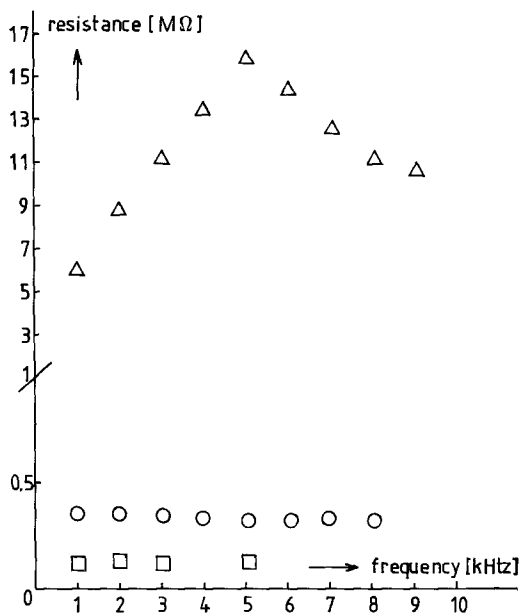


FIG. 1. The resistance as a function of the frequency. Quartz sieve fraction 36–42  $\mu\text{m}$ ;  $T = 23.5^\circ\text{C}$ .  $\square$  pH = 5, pKCl = 1;  $\circ$  pH = 5, pKCl = 3;  $\triangle$  pH = 5, pKCl = 5. For the lower resistances, the scale has been adjusted.

TABLE I  
The Peak Resistance as a Function  
of the Particle Diameter

Sieve fraction	Diameter ( $\mu\text{m}$ )	Resistance ( $10^6 \Omega$ )
315-499	200	25
100-200	100	26
80-100	57	29
43-55	32	25
36-42	28	16
10-20	13	12

Table II shows the zeta potential as computed with the von Smoluchowski equation at  $\text{pH} = 5$  for various particle sizes with KCl concentrations at  $\text{pKCl} = 5$ . The zeta potential computed at  $\text{pKCl} = 5$  is lower than at  $\text{pKCl} = 3$ .

This indicates the influence of complicating processes such as surface conductance, convective charge transport or relaxation.

It is assumed that to a first approximation only convective charge transport and ionic conduction is necessary to explain the maximum in Fig. 1.

The rising part of the curve (with increasing frequency) can be explained by convective charge transport. Because there is an inertial force due to the mass of the liquid the conduction caused by convective charge transport will decrease when the frequency is increased.

This causes the total resistance to increase as the frequency is increased. Due to a form

TABLE II

The Zeta Potential According to Von Smoluchowski in mV as a Function of the pKCl and Particle Size

Sieve fraction ( $\mu\text{m}$ )	pKCl particle size ( $\mu\text{m}$ )	pKCl		
		1	3	5
315-400	200	-11	-89	-31
100-200	100	-12	-75	-32
50-74	45	-11	-60	-30
43-55	32	-8	-55	-30
36-42	28	-7		-31
10-20	13	-8	-45	-20

TABLE III

The Specific Surface Area and Surface Roughness

Sieve fraction	Microscopic specific surface ( $10^6 \text{ m}^{-1}$ )	B.E.T. surface area per unit volume ( $10^6 \text{ m}^{-1}$ )	Surface roughness
10-20	0.435	0.907	2.08
36-42	0.206	0.290	1.41
43-55	0.187	0.239	1.28
50-74	0.137	0.233	1.70
80-100	0.105	0.152	1.45

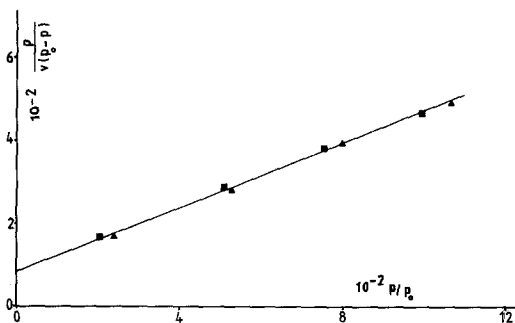


FIG. 2. Linearized B.E.T. adsorption/desorption isotherm on quartz sieve fraction 5-7.4  $\mu\text{m}$ .  $\blacktriangle$  = adsorption;  $\blacksquare$  = desorption;  $P_0$  = saturation vapor pressure of Krypton;  $V$  = equilibrium volume of gas adsorbed at pressure  $P$ .

of ionic conductance the resistance will decrease when the frequency is increased (14-18). The conduction process concerned cannot be bulk conduction, because measurements in the absence of a bed between the electrodes did not show any frequency-dependence. This also excludes electrode polarization. It cannot be surface conductance through the diffuse double layer as the frequency at which this process plays a role is in the range of  $10^5$ - $10^7$  Hz (14, 16). The process can be understood as being caused by conduction through the Stern layer, conduction through a porous surface layer (29, 30, 31), or to relaxation of the diffuse double layer. Conduction through a porous layer is probably not present in our samples as the adsorption-desorption curves of the Krypton isotherm are equal (see for a typical sample Fig. 2) and the surface roughness is small (Table III).

If conduction through the Stern layer is important one should picture a mechanism as is shown in Fig. 3 in which ions hop across an energy barrier from one hydroxyl group to the next. This also explains why it cannot be seen at larger electrolyte concentrations as then the conduction through the Stern layer is very small compared to the bulk conductance. The concept of conduction through the Stern layer was also used by Urban *et al.* (19) to explain their anomalous surface conduction results.

Derjaguin and Dukhin (20) used this concept to explain the results of Bull and Gortner (21) who dealt with comparable particle sizes and electrolyte concentrations as in this note. Sidorova *et al.* (30, 31) leave open the question whether the firmly bound counterions responsible for the resistance decrease are present in the Stern layer, or in a gel-like surface layer as postulated by Lyklema (29). However, the latter explanation is not confirmed in our case of crystalline quartz particles by the absence of pronounced surface roughness (Table III).

Figure 4 shows that the peak frequency is approximately independent of the particle size.

This means that since convective charge transport depends on the square of the particle radius (21) the conductance mechanism also has to depend on the square of the particle radius. This is only the case for conduction through the Stern layer and relaxation due to diffusion (7). In order to discriminate between these two possibilities, measurements of the temperature-dependency of the resistance were performed.

If relaxation is important one should not expect an Arrhenius-like behavior of the peak

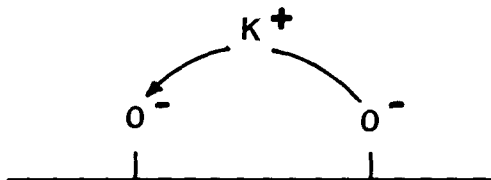


FIG. 3. An example of how the mechanism of conduction through the Stern layer is viewed.

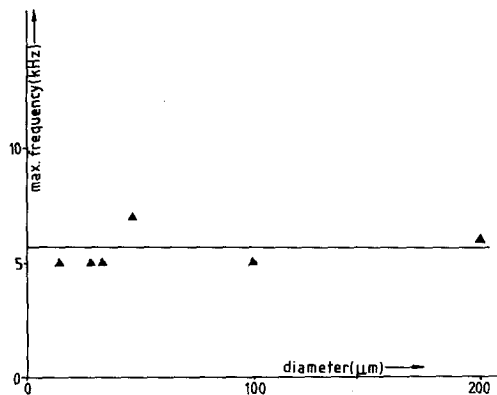


FIG. 4. The frequency at which the maximum resistance occurs versus the average particle diameter.

frequency. If, however, conduction through the Stern layer is important an Arrhenius-like behavior is expected caused by the hopping of the adsorbed ions. Such transport does not depend too much on temperature (8, 22, 23). Figure 5 shows that this is the case. Twelve experiments showed that the activation enthalpy equals  $17 \pm 3$  kJ/mole, which is quite reasonable as compared to other conduction processes (24) and which is of the same order as obtained from the conduction of adsorbed layers (7, 8). The intercept of the  $\ln \omega_c$  versus

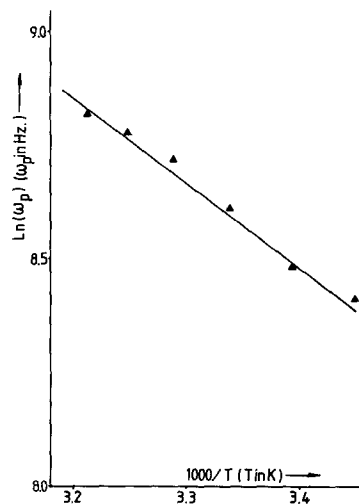


FIG. 5. The logarithmic frequency as a function of the reciprocal temperature.

1/T curves was  $15.5 \pm 1.5$  which depends on the activation entropy. The conductance mechanism through the Stern layer as assumed here should depend on the kind of conduction ion. However, no attempt was made to investigate this experimentally.

#### 4. CONCLUSIONS

Significant conduction through the Stern layer at pH = 5 and pKCl = 1 or 3 is ruled out as no frequency-dependent behavior at these concentrations occurred. Conduction through the Stern layer is possible at pH = 5 and pKCl = 5; it is explained by a hopping mechanism of ions across the quartz surface. The activation enthalpy of this process is  $17 \pm 3$  kJ/mole.

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