CHAPTER 8

CONCLUSIONS

In this chapter a summary of the results presented in this thesis is given with the intention to discuss implications and suggest topics for further research.

Double layer models

- Excess charges are present in the inter-phase region. Charges in one phase induce an opposite charge in the next phase. There are two layers of charge, the double layer. The Helmholtz model describes the polarised interface as an ideal electrical capacitor. The distance between the charged layers is about one nm so the electrical field is in the order of $10^9$ V/m.

- Experimental differential capacity data for mercury electrodes shows that $C$ is a weak function of both $\phi$ and $c_{ion}$. The Helmholtz model predicts a capacity that is constant.

- The Gouy-Chapman model was to be an improvement but it gravely overestimates the influence of $\phi$ and $c_{ion}$. It predicts that the capacity becomes infinite at mild conditions already.

- The Stern model in essence combines the Helmholtz and the Gouy-Chapman models. For the high salt concentrations of 0.5 N KCl used in this work, the Stern model is almost identical to the Helmholtz model and therefore it provides no real improvement.
• Even if contact adsorption of ions is included in the Stern model, it remains impossible to completely predict experimental capacity versus potential curves. This is true for both high frequency capacity measurements and for DC methods. The differential capacities measured for graphite and Ambersorb in chapter 5 showed broad and shallow depressions around zero potential, where the Stern model predicts a local and deeper depression (the GC contribution). Perhaps inhomogenities and surface groups in the carbon matrix smear out the point of zero potential to a range of zero potential. The carbon materials used however are very homogeneous by nature.

• The dielectric constant decreases if a strong field is present. A limiting value of 5 for water is reported by Bockris and Reddy (1970b) and Kortüm (1965).

• Applying the constant limiting value for the dielectric constant of hydration water molecules in the way it is done by Bockris and Reddy is not correct. These limiting values are reached only if large potentials are applied so their model gives to low capacities if small potentials are applied.

• The alternative is to use a field dependent dielectric constant by applying the complete Langevin equation instead of its Taylor approximation. The Kirkwood formula was used to calculate from molecular properties such as the dipole moment ant the polarisability the dielectric constant.

• Kirkwood constants of 5 for water and various alcohols and 2 for aceton (under normal conditions) followed from molecular properties. Molecules with large dipoles had lower constants. For use in the double layer model, the Kirkwood constant had to be lowered to 1.5 to be able to fit experimental capacity data. The presence of the solid surface is assumed to lower the amount of neighbours for water resulting in a lower $K_{KW}$.

The mechanism of electrosorption

• It is assumed that adsorption takes place inside the double layer. The equivalent electrical view on electrosorption is the movement of a slab of
material inside a charged capacitor. Using thermodynamics, changes in the adsorption constant as a function of potential can be related to changes in the required work of adsorption.

- The difference in dielectric constants of the solute and solvent molecules is the main driving force for electrosorption. The energy of a charged capacitor is given by \( \frac{1}{2}C\phi^2 \). The system can reduce its energy by interchanging molecules with a low dielectric constant for those with a high dielectric constant. The energy of the capacitor increases but the connected potential source decreases its energy to a larger extend.

- The potential dependent adsorption equilibrium is used together with a Langmuir-Freundlich isotherm to fit experimental electrosorption data. The standard Langmuir isotherm cannot accurately fit adsorption data of organic compounds on activated carbon.

**Electrosorption data from literature**

- The complete collection of electrosorption data available in literature can be plotted in two small graphs without problems.

- The quality of the literature data is poor. The number of data points per series is no more than three or four. Measurements are limited to one branch of the potential so trend extrapolations to obtain a bell shape have a large degree of uncertainty. It is difficult to compare data series because relative conditions and experimental set-ups differ.

- By introducing a bed efficiency constant and assuming a loss of potential in the liquid phase, the electrosorption model could fit the reported electrosorption data series.

**Electrosorption data determined in this work**

- The batch method for measuring adsorption equilibrium is a fast method as multiple points can be determined in one run. The method cannot be used for other than open circuit conditions. Although the data obtained from this method is in the same order of magnitude as reports
from literature, the experimental results are considered poor due to large scattering.

- The continuous method is slower due to smaller mass transfer and only one isotherm point can be measured at the same time. The results are good, scattering is relatively low (10%) and runs can be reproduced. The method can be used for electrosorption isotherms.

- Accurately determining the influence of the potential on the isotherm has proven a difficult task. No large effects have been measured, or at least, could not be reproduced. Small effects are hard to find due to the type of (analysing) method used. Adsorption is determined by monitoring depletion of the bulk phase. If the experimental procedures are not extremely accurate the resulting errors are big and suppress any electrosorption effects.

- Large effects of the potential on the adsorption of benzyl alcohol on Ambersorb 572 have been measured but these turned out to be due to unaccounted for chemical reactions occurring in the system.

- Large effects of the potential on the isotherm found in literature for phenol on activated carbon (McGuire et al., 1985) and for benzyl alcohol on activated carbon (Bán, 1998) could not be reproduced.

- Desorption experiments suggest effects up to 20%, but these are not backed by the relevant adsorption experiments.

*The physical behaviour of packed bed electrodes*

- The response of two packed bed electrodes to a change in applied potential closely resembles that of a classic RC circuit.

- Due to its large characteristic time, charging of packed bed electrodes is a very slow process. As the charging time depends quadratically on the distance to the current collector, thin beds are required.
• The response of complex RC circuits can be determined by a Laplace transform method. This method cannot give results that contain a place dependency to account for internal electrical resistances.

• Distribution of potential in an electrode is mathematically equal to heat transfer in a slab of material (Posey and Morozumi, 1966).

• Changing the boundary conditions gives three potential distribution functions. The no losses model assumes that the carbon is much more conductive than the pores and no external resistances exist. The internal losses model assumes that the carbon matrix and the pores have about the same conductivities. The external losses model assumes that part of the applied potential is lost due to ohmic resistances in the liquid phase.

Transient current experiments

• Only the external losses model can correctly describe experimental transient current experiments. The other two models are discarded.

• Reproducibility of transient current experiments is good. By fitting them with exponential functions the values of electrical properties such as the capacity, resistances and loss factors can be obtained.

• Direct measurement of particle and bed resistances proved to be unsatisfactory as too high values were obtained.

• Moderate mechanical pressure can significantly enhance the conductivity of packed beds of carbon granules.

• The total capacity is a weak function of the applied potential. The total resistance is independent of the applied potential. Increasing the solvent concentration had no real influence.

Simulating a packed bed electrosorption unit

• Six characteristics times can be identified: Residence, adsorption, desorption, dispersion, mass transfer and double layer charging time. The
adsorption time should be larger than the charging time, the adsorption time should be 100 times larger than the residence time, the dispersion time should be 10 times larger than the residence time and the residence time should be 10 times higher than the mass transfer time. The second of these four conditions is always satisfied.

- The other three conditions can be satisfied by changing the liquid speed and the bed length, the two most important design parameters. If $u = 2 \times 10^{-6}$ m/s, $L$ can be up to 4 m and $d_p$ to 10 mm. If $u = 2 \times 10^{-5}$ m/s, $L$ can be up to 0.4 m and $d_p$ to 1 mm. If $u = 2 \times 10^{-4}$ m/s, $L$ can be up to 0.04 m and $d_p$ to 0.1 mm. The mass transfer condition is never limiting.

- If lower concentrations are used, but the total mole flow remains the same, lower characteristic times are obtained.

- The difference between co-current and counter-current configurations is small. Differences occur only for the (short) time that the bed is not yet fully charged. Counter-current gives initially a faster reduction of carbon loading.

- Incorporating a potential and surface concentration dependent capacity function in the set of equations, instead of an empirical quadratic equation does not generate large differences on the packed bed performance.

**Streaming current**

- Streaming current is a phenomenon caused by the movement of the GC excess charge due to an applied pressure difference over the packed bed.

- A theoretical value of 8.2 mA at 1 V and 1 bar was found to be 2.5 times larger in practice. A possible error in estimating the effective area could be the cause of the difference.

- Increasing the pressure or the potential gives higher charging currents. The relation is not linear as predicted by theory. Deviations are more
pronounced for smaller potentials. It is assumed that increasing turbulence causes less favourable contributions to the charging current generation.

**The relation between charge and mass transfer**

- The adsorption of benzyl alcohol on a polarised packed bed electrode of Ambersorb 572 causes transport of charge. If the relative amount adsorbing (normalised) is compared to the relative amount of charge transported (normalised) a good linear relation is found.

- Using the electrosorption model, the theoretical charge transfer associated with a certain amount of adsorption can be calculated and compared to the experimental results. For small potentials this ratio is in the order of 60%. For larger potentials it drops to 5-10%. If large potentials are applied more of the adsorbing benzyl alcohol does not lead to an electrical response.

- A large part of the surface is covered with an electrical double layer, this follows from the electrical capacity measurements. Adsorption occurs inside the double layer for small potentials and not inside the double layer for large potentials.

**Economics and feasibility**

- In chapter 3 it was found that the effectiveness of electrosorption in theory could be as good as adding methanol to the mixture. Potentials did not exceed 1.33 V to achieve the same results as rinsing with 100% methanol.

- Energy costs can be divided into two: for polarising the bed and for desorbing the adsorbed compounds. This energy depends on system configuration and conditions. It is between 4.3 and 30.7 kJ/mol and 2.6 and 15 kJ/mol respectively.

- The operation costs for four cases are compared: No regeneration, steam regeneration, methanol regeneration and electrosorption. It was found that steam regeneration is the cheapest method. Methanol regeneration and
electrosorption are almost equally expensive. No regeneration is the most expensive option. Electricity costs can be neglected, the only problem for the electrosorption alternative is the (probably) low regeneration efficiency.