Summary

Electrodialysis (ED) is a well-established technique which enables the separation of cations and anions from electrolytes. The process takes place in a ‘stack’ which contains ion-selective membranes, placed between two electrodes. These membranes can be cation-exchange membranes (CEM) or anion-exchange membranes (AEM). An electrical current is applied to the system, while the electrolytes are circulated through the stack. Applications based on this principle are dilution and concentration of brackish solutions, membrane electrolysis and the separation of amino acids.

The application of ED which is the subject of this thesis is the production of acids and bases from salt-containing waste waters. In this process, acids and bases are produced in an ED stack from their corresponding salt, by using hydrogen and hydroxyl ions which are produced at the electrodes, or by bipolar membranes. In a co-operation between the University of Groningen and TNO Environment, Energy and Process Innovation a research project, subsidised by Senter (part of the Ministry of Economical Affairs of the Netherlands), was carried out to investigate this application. The TNO part involved the identification of industrial brine waste waters in the Netherlands, an economical evaluation and the implementation of the method for selected waste waters in laboratory and pilot plant-scale experiments. The part described in this thesis involves the mathematical modelling of acid and base production, and validation of the results by performing experiments using synthetic waste waters.

The recovery-ED model and experiments are introduced in Chapter 4, and the estimation of the model parameters is described in Chapter 2 and 3. In Chapter 2, membrane characterisation experiments are described which estimate the equilibrium properties of the ion-selective membranes. Chapter 3 describes the estimation of the Maxwell-Stefan diffusion coefficients for the relevant electrolyte-membrane systems. The diffusion parameters were obtained by modelling a (large) number of separate diffusion measurements.

From extensive characterisation experiments the fixed-charge, co-ion, counter-ion and water concentrations were determined. A thermodynamic equilibrium model was applied to the results. However, the internal activity coefficients could not be described with thermodynamic models such as the Bromley model when a homogeneous charge distribution in the membrane was assumed. For a complete two-phase description, not enough measurements were available. To overcome the problem, the experiments could be described by the equilibrium equation, extended with a heterogeneity factor, combined with the Bromley model for calculation of the
internal activity coefficients. As a result of the calculations, both the membrane-phase electrical potential, and the co-ion sorption behaviour could be modelled.

In the highly concentrated ED system, a large amount of multicomponent diffusion coefficients occur. These diffusivities are important parameters for the ED mass transfer model. A set of separate diffusion experiments was developed and performed. By modelling these experiments, for each membrane, the parameters could be calculated by means of a parameter optimisation method. It proved possible to find the diffusion coefficients, although experimental error was passed on to considerable standard deviations in some coefficients. In both cation- and anion-exchange membranes, it proved difficult to fit the co-ion/water diffusion coefficients from experiments.

The ED acid and base recovery experiments were performed with both monopolar membrane (MPM) and two types of bipolar membrane (BPM) configurations, with the salts NaCl and Na₂SO₄. The concentrations of the produced acid and base were varied between 0.5 and 5 M. The performance of the MPM’s is strongly dependent on the acid and base concentration. Higher external concentrations decrease the current efficiency. The electrical energy consumption of acid base recovery with MPM shows a minimum at around 2 M. Acid base recovery from Na₂SO₄ shows lower AEM selectivity, and higher stack potentials. This leads to a higher energy use compared to NaCl.

The BPM’s performed at high current efficiencies, between 0.96 and 0.97 in 2 M NaCl. In a stack with a large number of BPM’s, this leads to energy savings between around 20 to 50 % per mole of produced acid and base compared to the MPM configuration.

To complete the model parameter estimation, described in Chapter 2 and 3, two more parameters were determined from specially designed experiments. These were the limiting current densities and the overpotentials. It was shown that all ED experiments were carried out below the limiting current.

With the complete ED model, all acid and base recovery experiments were calculated. The model predictions of the current efficiencies show good agreement for the cation-exchange membrane and the two anion-exchange membranes. In most cases, the calculated current density was higher than the experimental results. The differences between experiment and model are caused to a great extent by deviation of the experimental current densities. The water transport is also well described by the model, except for the HCl-Nafion system. The stack potentials, calculated by the model, are generally too low compared to the experiments. This is probably caused by higher voltage drops across the anion-exchange membranes and the bipolar membranes.