An Investigation of Automated Physicochemical Property Modelling of Aqueous Strong Electrolyte Solutions and Their Mixtures

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This thesis is presented for the degree of Doctor of Philosophy of Murdoch University
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I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.

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Abstract

An investigation is described into the thermodynamic modelling of aqueous electrolyte solutions. Solutions relevant to environment and industry are emphasised. Computational facilities are described that automate the processing of physicochemical property data. Various computer models for predicting the thermodynamic quantities of aqueous solutions are developed. Used together these facilities allow data to be assessed and harmonised in a more effective manner than existing methods. Considerable attention is paid to the popular Pitzer theoretical framework but other frameworks are also studied, especially the application of so-called ‘mixing rules’ to describe multicomponent solutions from the properties of their individual solute components.

The thermodynamic properties of strong electrolyte solutions under ambient conditions are well described by Pitzer equations provided a sufficient number of accurate data are available. However, extending the pressure and temperature ranges reveals fundamental limitations. Gaps or large errors (which are inevitable over large dimensional spaces) cause unrealistic extrapolations and other problems requiring human intervention (e.g., highly specific and subjective judgements) to redress. Objective and robust automated modelling based on the Pitzer equations is thus precluded.

Accordingly, a selection of possible alternative theoretical frameworks are investigated. One, based on the Hückel equation for activity coefficients, has fewer empirical parameters than the corresponding Pitzer equation and its extrapolations of the apparent molar volumes and heat capacities to infinite dilution, performed for the first time in this work, are more robust. However, its correlation of activity coefficients is correspondingly less accurate.

Different mixing rules for density, heat capacity and water activity are compared with one another. These comparisons show that various rules give essentially equivalent property predictions for a range of ternary systems.

Contrasted with experimental osmotic coefficients, predictions from Zdanovskii’s rule are often within assessed experimental uncertainty, which can be up to an order-of-magnitude worse than that claimed by investigators.

Simple mixing rules, like those of Zdanovskii, therefore appear to offer advantages for future model development of multicomponent aqueous strong electrolyte solutions.
## Contents

1 Introduction ................................................. 11
   1.1 The importance of thermodynamic aqueous solution modelling ...... 12
       1.1.1 Natural waters ........................................ 12
       1.1.2 Industrial solutions .................................... 14
   1.2 Issues with modelling multicomponent electrolyte solutions ...... 18
       1.2.1 The problem ........................................... 18
       1.2.2 The present investigation ................................ 19

2 Thermodynamics of electrolyte solutions ........................... 21
   2.1 Basic thermodynamics ...................................... 21
   2.2 Theoretical frameworks for electrolyte solution thermodynamics ... 24
       2.2.1 Pitzer .................................................. 26
       2.2.2 Goldberg .............................................. 27
       2.2.3 Mean Spherical Approximation (MSA) ..................... 27
       2.2.4 MSA-NRTL (Non-random two-liquid) ....................... 28
       2.2.5 Liu, Harvey, Prausnitz (LHP) ............................ 29
       2.2.6 Helgeson-Kirkham-Flowers (HKF) ........................ 30
   2.3 Strengths and limitations of the existing theoretical frameworks ... 30
       2.3.1 Summary of theoretical frameworks ....................... 33
3 Reliable characterisation of thermodynamic properties of binary electrolyte solutions under ambient conditions

3.1 Physicochemical property data

3.1.1 Uncertainty of data

3.2 Pitzer’s equations

3.3 Obtaining model parameters

3.3.1 Solving least-squares problems

3.3.2 The Pitzer parameters

3.4 Automatic determination of concentration limit

3.5 Results

3.5.1 Comparisons with models from the literature

3.5.2 Simulating activity coefficients at nearby temperatures

3.6 Summary

4 Reliable characterisation of thermodynamic properties of binary electrolyte solutions under non-ambient conditions

4.1 Methods

4.2 Results

4.2.1 Case studies

4.3 Discussion

4.4 Implications

4.5 The Hückel equations as alternative to the Pitzer equations
5 Predicting the water activity of mixed electrolyte solutions

5.1 Introduction ................................................. 91
5.2 Theory ......................................................... 92
  5.2.1 Algorithm ............................................. 94
  5.2.2 Electrolyte concentrations in multicomponent solutions .... 96
5.3 Results ....................................................... 96
5.4 Case studies: independently measured systems ................. 104
5.5 Discussion .................................................. 112
5.6 Summary ..................................................... 114

6 A comparative investigation of mixing rules for property prediction in multicomponent electrolyte solutions

6.1 Theory ....................................................... 117
  6.1.1 Apparent molar volume and heat capacity ............... 117
  6.1.2 Water activity ........................................ 119
  6.1.3 Binary endpoint conditions ............................ 121
6.2 Methods .................................................... 123
6.3 Results ...................................................... 125
  6.3.1 Comparison of practical solvent partitions .......... 125
  6.3.2 Comparison of the ionic strength and water activity mixing rules ............................................. 130
6.4 Discussion ............................................... 134
6.5 Summary ................................................... 136

7 Conclusions and future directions

139
A Numerical aspects of the Pitzer equations

A.1 Sensitivity analysis
A.2 Correlation analysis

B Optimisation of binary electrolyte solutions under ambient conditions

C Finding the Zdanovskii mixing path

C.1 Initialising the binary solution concentrations
C.2 Efficient calculation of the derivatives
C.3 Efficient solution of the linear equation system

D Data visualisation

E Calculation of the Debye-Hückel coefficients

Bibliography
List of Figures


3.2 Experimental and calculated values of well-characterised properties at 25 °C using the Pitzer parameters from Algorithm 3.1 for alkali metal chloride and sulfate salts. 49

3.3 Experimental (points) and calculated (lines) activity coefficients (as ln $\gamma_\pm$) at 25 °C using the Pitzer parameters from Algorithm 3.1 for alkaline earth salts. 50

3.4 Exemplar electrolytes for which Algorithm 3.1 determines that the Pitzer equations (solid lines) do not represent data at high concentrations. 51

3.5 Comparison between activity coefficient data (as ln $\gamma_\pm$) for NaOH(aq) and various Pitzer models at 25 °C. 52

3.6 Differences between experimental activity coefficients (as ln $\gamma_\pm$) for NaOH(aq) and values calculated from the present model. 53

3.7 Experimental and calculated values of the apparent molar relative enthalpy of NaCl(aq) at 25 °C. 54

3.8 Experimental and calculated values of the apparent molar relative enthalpy of CaCl$_2$(aq) at 25 °C. 54

3.9 Experimental and calculated values of the apparent molar heat capacity of HCl(aq) at 25 °C. 55

3.10 Experimental and calculated values of the apparent molar heat capacity of HNO$_3$(aq) at 25 °C. 56
3.11 Experimental and calculated values of the apparent molar heat capacity of \( \text{La(ClO}_4\)\text{)}_3(aq) \) at 25 °C. ................................................. 56

3.12 Experimental and calculated values of the apparent molar volume of \( \text{CaCl}_2(aq) \) at 25 °C. ............................................................. 58

4.1 Activity coefficients for NaCl(aq) (as \( \ln \gamma \pm \) ) calculated from the model of Pitzer et al. [84PPB]. ................................................................. 64

4.2 The standard state apparent molar heat capacity \( \phi C_p^\circ \) calculated from the NaCl(aq) model of Archer [92Arc]. ................................................................. 65

4.3 Differences between experimental apparent molar volumes for MgCl\(_2\)(aq) at high pressure and values calculated from the present model. ........ 68

4.4 Quartile plot of the differences between experimental apparent molar volumes of \( \text{CaCl}_2(aq) \) and values calculated by the present model at high pressure. ................................................................. 69

4.5 Differences between experimental apparent molar volumes for \( \text{CaCl}_2(aq) \) at high pressure and values calculated from the present model. 70

4.6 Differences between experimental apparent molar volumes for KI(aq) and values calculated from the present model against temperature. 71

4.7 Comparison between \( \phi V^\circ \) for individual electrolytes and values based on additivity of the component ions. ............................................. 72

4.8 Experimental and calculated values of the apparent molar volumes of (a) Li\(_2\)SO\(_4\)(aq); and (b) Cs\(_2\)SO\(_4\)(aq), at \( T = 25 \) °C. ......................... 73

4.9 Apparent molar volumes of NaCl(aq) at \( T = 300 \) °C calculated from the models of Rogers and Pitzer [82RoP] (solid lines) and Archer [92Arc] (dashed lines). ......................................................... 75

4.10 Differences in apparent molar volumes between Pitzer et al. [84PPB] (dot-dashed line) or Archer [92Arc] (long-dashed line) and the present model for NaCl(aq) at \( p = 200 \) bar. ......................................................... 76

4.11 Differences between NaCl(aq) and KCl(aq) apparent molar volumes of Coxam et al. [91CQG] and the present models at \( p = 17.2 \) MPa. 77

4.12 Experimental and calculated values of the activity coefficients of KCl(aq) (as \( \ln \gamma \pm \)). ................................................................. 77
4.13 Osmotic coefficients from the KCl(aq) model of Pabalan and Pitzer [88PaP] at high temperatures. ............................. 78
4.14 Differences between experimental isopiestic molalities of KCl(aq) (relative to NaCl(aq) reference) [78HBM] and values calculated from models in the present work. ............................. 79
4.15 Calculated values of activity coefficients (as ln $\gamma$) from the Pitzer (dashed curves) and Hückel (solid curves) equations. ...................... 89
4.16 Calculated apparent molar volumes and heat capacities from the Pitzer (dashed curves) and Hückel (solid curves) equations. .............. 90

5.1 Water activity against concentration for exemplar electrolyte and non-electrolyte solutions at $T = 25$ °C. ............................. 93
5.2 Mixing paths between two binary solutions having equal water activity (solid line) and unequal water activities (e.g., dashed lines). ........ 93
5.3 Examples of outlying osmotic coefficient data identified by examining the residual plots for all ternary electrolyte mixtures in Table 5.1. ... 97
5.4 Examples of ternary mixtures with large, systematic deviations from the osmotic coefficient values predicted by Zdanovskii’s rule. .... 103
5.5 Differences between experimental osmotic coefficients of NaCl + MgCl$_2$ and values predicted using Zdanovskii’s rule. ...................... 106
5.6 Differences between experimental osmotic coefficients of KCl + MgCl$_2$ and values predicted using Zdanovskii’s rule. ...................... 107
5.7 Differences between experimental osmotic coefficients of NaCl + CsCl and values predicted using Zdanovskii’s rule. ...................... 108
5.8 Differences between experimental osmotic coefficients of CaCl$_2$ + MgCl$_2$ and values predicted using Zdanovskii’s rule. ...................... 109
5.9 Differences between experimental osmotic coefficients of K$_2$SO$_4$ + MgSO$_4$ and values predicted using Zdanovskii’s rule. ...................... 111
5.10 Mineral solubility diagrams calculated using Zdanovskii’s rule. ........ 113

6.1 Comparisons of density predictions made using different mixing rule endpoint conditions. ............................. 122
6.2 A particular prediction of the apparent molar volume of a ternary solution is obtained for a given partition of the solvent among the pure solutes. ................................. 124

6.3 Calculated apparent molar volumes of a ternary solution from Young’s rule using different solvent partitions/mixing paths. ................................. 125

6.4 Predictions from Young’s rule of the density difference relative to pure water vs. fraction of solvent assigned to the first solute at 25 °C. .... 126

6.5 Differences between the various density predictions and Young’s rule using the constant ionic strength endpoint condition at 25 °C. .... 127

6.6 Differences between the various density predictions and Young’s rule using the constant ionic strength endpoint condition at 100 °C. .... 128

6.7 Differences between the various osmotic coefficient predictions and the constant ionic strength endpoint condition at 25 °C. .... 129

6.8 Water activity against molality for hydrochloric acid and alkali metal chloride solutions at 25 °C. ................................. 131

6.9 Contour plots of apparent molar volumes in ternary alkali chloride solutions predicted by Young’s rule using equal ionic strength endpoint conditions minus those using equal water activity at the endpoints. . 132

6.10 Apparent molar volume difference contours (constant ionic strength predictions minus constant water activity predictions, cm³ mol⁻¹). . 133

6.11 Apparent molar heat capacity difference contours (constant ionic strength predictions minus constant water activity predictions, J(K mol)⁻¹). . 135

A.1 Pairwise correlation plots of Pitzer parameters obtained by optimising 50 synthetic osmotic coefficient datasets. ................................. 145

A.2 Pairwise correlation plots of volumetric Pitzer parameters obtained by optimising 50 synthetic apparent molar volume datasets. .... 146

D.1 User interface of the 8-ball facility allowing the FIZ database and various models to be accessed in Microsoft Excel. ................................. 160
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1. Description of the JESS optimiser for physicochemical data and case studies 2 and 3.

2. Predominantly written by the present author.

3. Description of theory, data entry and development of computing programs.

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