The Hála Constraint in the Wilson Model :

Is It Valid And/Or Useful For Ion Exchange Equilibria?

John Provis
David Shallcross

Department of Chemical and Biomolecular Engineering

The University of Melbourne

dcshal@unimelb.edu.au

THE UNIVERSITY OF MELBOURNE

Goal : To accurately model multi-component ion exchange equilibria.

Use equilibrium data from the constitutive binary ion exchange systems.

So for 4-component system of A – B – C – D we need equilibrium data for the A – B, A – C, A – D, B – C, B – D and C – D binary systems.

For A – B binary system : $z_b \; A^{\pm z_a} + z_a \; \underline{B^{\pm z_b}} \Leftrightarrow z_b \; \underline{A^{\pm z_a}} + z_a \; B^{\pm z_b}$

Equilibrium constant defined in terms of activities: $K_{AB} = \left(\frac{a'_A}{a_A}\right)^{z_b} \times \left(\frac{a_B}{a'_B}\right)^{z_a}$

But how do we calculate the activities in the solution and exchanger phases?

Solution phase activity coefficients:

1) assume solution phase is ideal
2) apply Debye-Hückel equation
3) Meissner and Kusik electrolyte solution model
4) Pitzer electrolyte solution model

Exchange phase activity coefficients:

1) assume exchange phase is ideal
2) apply Wilson model
3) apply twin-exchange site model of Melis

Solution phase activity coefficients:

1) assume solution phase is ideal
2) apply Debye-Hückel equation
3) Meissner and Kusik electrolyte solution model
4) Pitzer electrolyte solution model

Vo and Shallcross tested these four models using extensive equilibrium data for the H^+ – Na^+ – K^+ – Mg^{2+} – Ca^{2+} system

Comparison shows the Pitzer model provides most accurate prediction of 3-cpt, 4-cpt and 5-cpt equilibrium data from constitutive binary data.

Vo and Shallcross, *J. Chem. Eng. Data* **2005**, *50*, 1995-2002

Exchanger phase activity coefficient prediction:
Wilson model

Wilson proposed model in 1964.

Wilson model first proposed to model exchange phase non-idealities by Elprince and Babcock (1975).

Smith and Woodburn (1978) applied Wilson model with Debye-Hückel equation in solution phase.

Shallcross et al. (1988) applied Wilson model with Pitzer model in solution phase.

Mehablia et al. (1992) applied Wilson and Pitzer models but decoupled fitted-parameters.

Ion Exchange Equilibria and the Wilson model

If the Wilson model is used to account for the non-idealities in the exchanger phase then the equilibrium behaviour of each binary system may be fitted by three parameters: K_{AB}, Λ_{AB} and Λ_{BA}.

K_{AB} is the equilibrium constant

Λ_{AB} and Λ_{BA} are the Wilson binary interaction parameters.

The activity coefficient of component k in the exchanger phase in an N-component system may be calculated from the Wilson binary interaction parameters:

$$\ln \gamma_k = 1 - \ln\left(\sum_{j=1}^{N} y_j \Lambda_{kj}\right) - \sum_{i=1}^{N} \frac{y_i \Lambda_{ik}}{\sum_{j=1}^{N} y_j \Lambda_{kj}}$$

Ion Exchange Equilibria and the Wilson model

The original formulation of Wilson was presented in terms of a parameter $A_{j/i}$, defined by:

$$A_{j/i} = 1 - \left(\frac{\bar{V}_j}{\bar{V}_i} \right) e^{-\frac{g_{ji} - g_{ii}}{k_B T}}$$

$\bar{V}_j$ molar volume K_B Boltzmann constant T absolute temperature

g_{ij} is proportional to the interaction energy between i and j.

$$\Lambda_{ij} = 1 - A_{j/i}$$

Wilson also noted that $g_{ij} = g_{ji}$

The Hála Equation

When applied to a 3-component system the Hála Constraint is:

$$\frac{\Lambda_{jk}}{\Lambda_{kj}} = \left(\frac{\Lambda_{ik}}{\Lambda_{ki}}\right)\left(\frac{\Lambda_{ji}}{\Lambda_{ij}}\right)$$

or $\Lambda_{ij}\Lambda_{jk}\Lambda_{ki} = \Lambda_{ik}\Lambda_{kj}\Lambda_{ji}$

For binary systems this reduces to: $\Lambda_{ij}\Lambda_{ji} = 1$

Data from Vo for 5-component ion exchange equilibria.

Values are relative residues, R, for several systems.

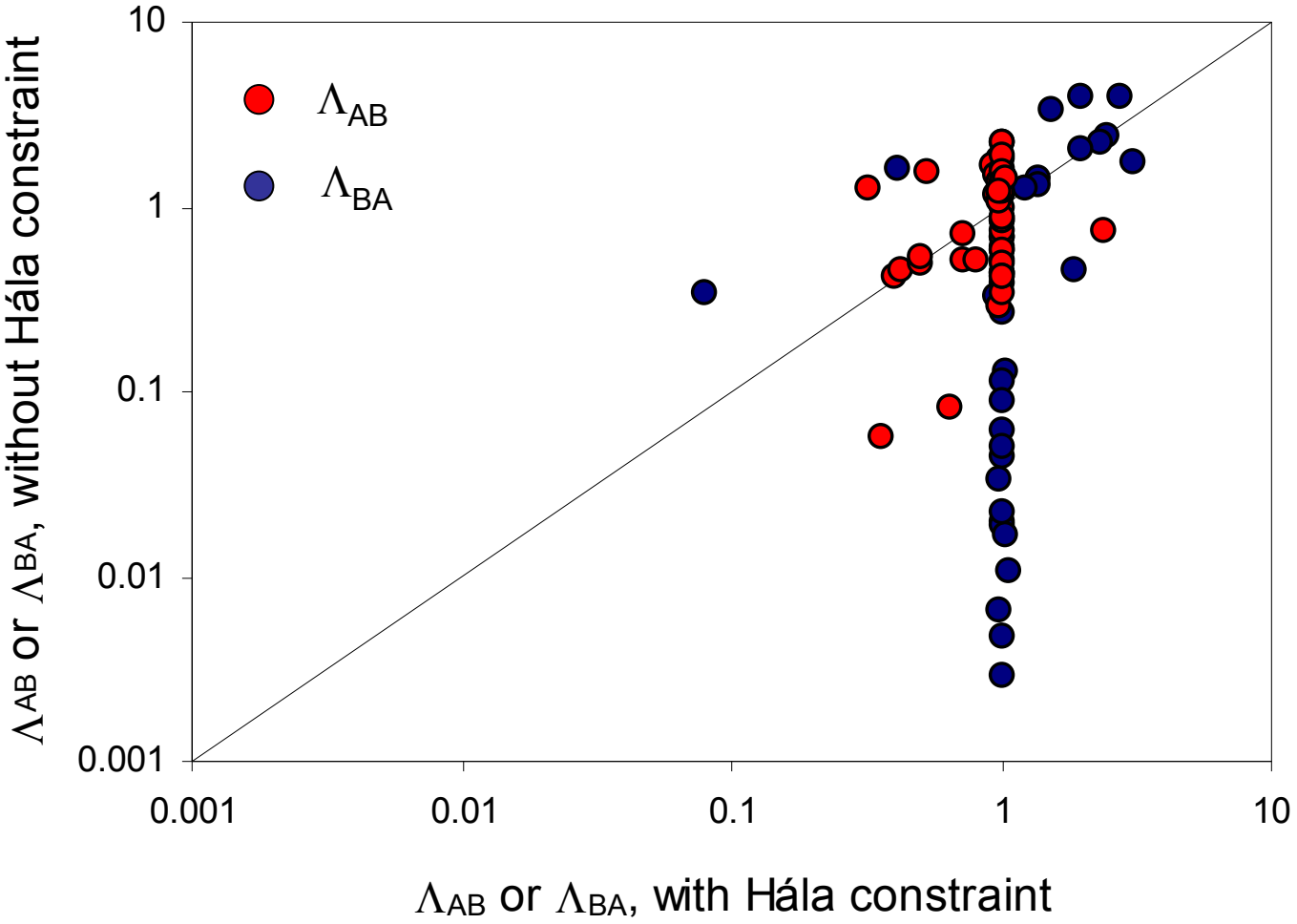
	Hála	No Hála
Na – K – H	0.00747	0.00584

$$\Re = \frac{\sum_{i=1}^{N}\left[\sum_{j}^{M}\left(\frac{\chi_{\text{Model}} - \chi_{\text{Experiment}}}{\chi_{\text{Experiment}}}\right)_j^2\right]_i}{N.M - 1}$$

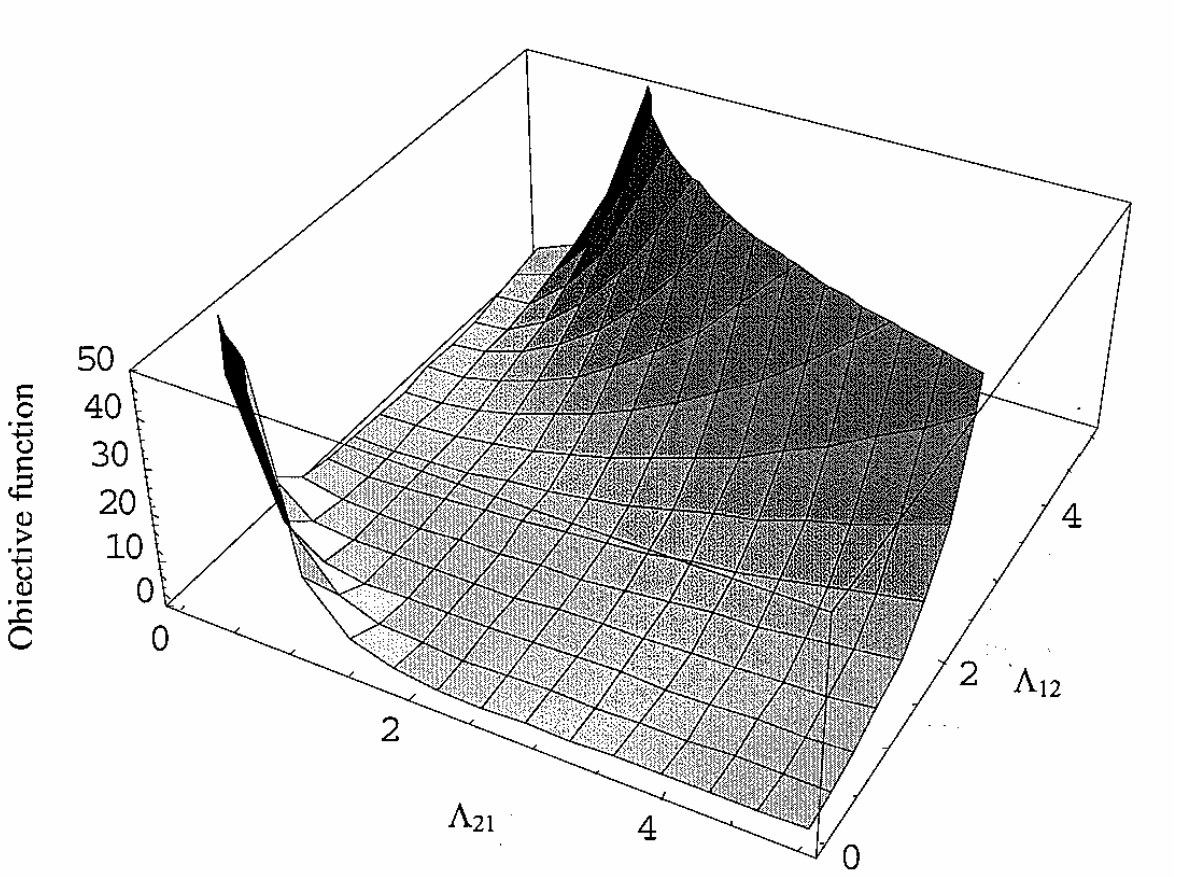
M is number of data points

N is number of exchanging ions

Using published data Allen *et al.* (1989) compared what happened when the Hála constraint was either applied or ignored.

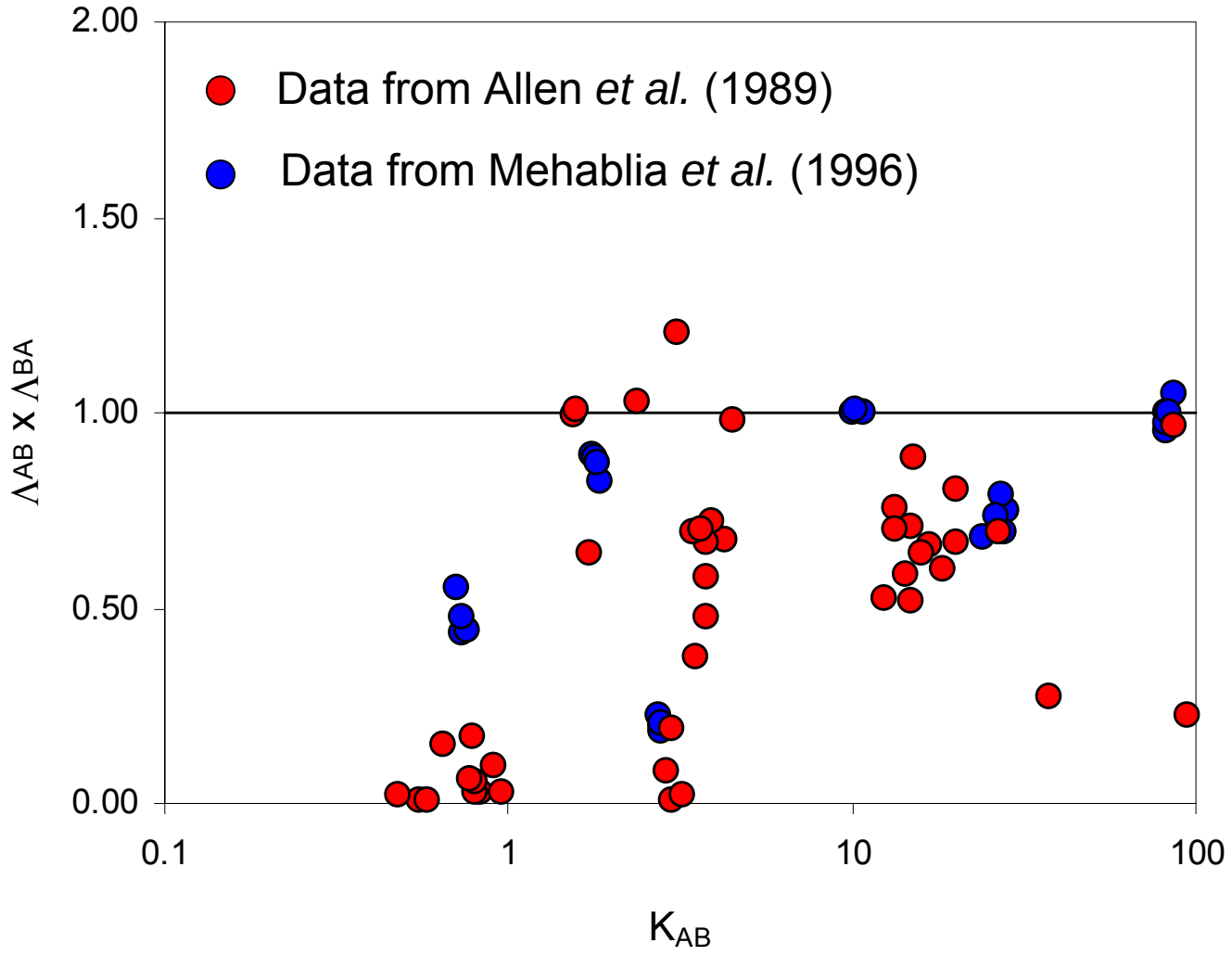


This suggests that there may have been an error in the fitting routine used to find Λ_{AB} and Λ_{BA}.



Variation of objective function with the two Wilson binary interaction parameters for the Ca – Na binary system.

Vo, PhD Thesis, University of Melbourne, 2003


2.00
1.50
1.00
0.50
0.00
0.1
1
10
100
Data from Allen *et al.* (1989)
Data from Mehablia *et al.* (1996)
$\Lambda_{AB} \times \Lambda_{BA}$
K_{AB}

Conclusions

If the Wilson model is to be applied with thermodynamic consistency then the Hála constraint must be applied.

Multi-component models such as the Mehablia model use the Wilson model but not the Hála constraint. The Mehablia model is therefore not physically correct. The predictions are however very good.

If the model is solely being used to predict multi-component ion exchange equilibria then the Hála constraint may be neglected.

If however we seek to extract more useful information from the actual values for Λ_{AB} and Λ_{BA} then the Hála constraint must be applied.

5th International Conference on Ion Exchange

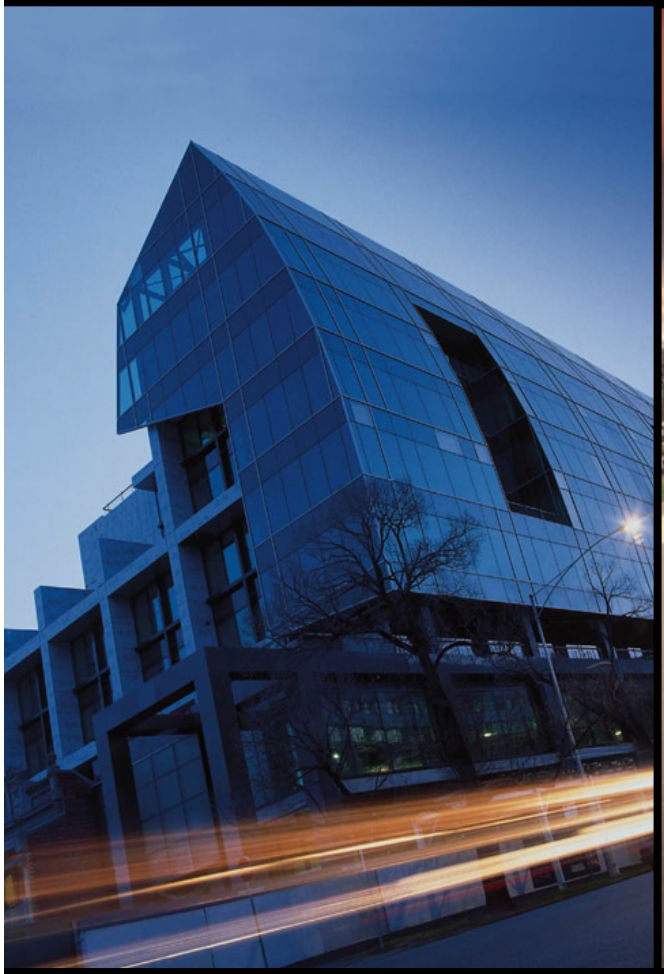
ICIE 2010

Melbourne

18-21 July 2010

www.mcmconferences.com/icie


HWT



Conference papers will be published in
Journal of Ion Exchange.

Join us in Melbourne in July 2010.