

THERMODYNAMIC MODELLING OF CONCENTRATED SULPHURIC ACID SOLUTIONS

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ABSTRACT

Acidic sulphate solutions are common in hydrometallurgy thus a proper thermodynamic description of the model for aqueous sulphuric acid is essential, if the thermodynamic equilibrium calculation are utilized in the process development and modelling.

The existing Pitzer models for aqueous H₂SO₄ are either limited up to 6 molal (37w%) sulphuric acid solution or are too complicated for practical modelling purposes, including up to 8 model parameters, with over 30 terms fitted from experimental data within.

Recently, a modified Pitzer for concentrated solutions was developed in NPL,UK. The new model uses scaled mole fractions instead of molalities and the formalism will converge to molalities in dilute solutions. Thus, the model coincides with the original Pitzer model at indefinite dilution.

The aim of this study is to test the ability of the modified Pitzer equation to model concentrated sulphuric acid solutions when using limited number of Pitzer parameters with a simple temperature dependency.

1 INTRODUCTION

The Pitzer ion interaction model, similar to the virial equation used for non ideal gases, has proved to be the most accurate thermodynamic model up to moderate concentrations in aqueous solutions [1].

The unsymmetrical mixing terms for ions with like sign but with unequal magnitude are not included in the original Pitzer ion interaction model. Harvie et al. [2] have found these terms to improve the fit for multicomponent systems and have introduced them in their modification of the Pitzer interaction model.

In original Pitzer model the third virial coefficients describing the interactions between three ions were assumed to be independent of concentration, i.e. ion strength. Archer [3] discovered that an ion strength dependent third virial parameter C describing the combined interactions between two alike cations and an anion or vice versa, will improve the fit for concentrated solutions.

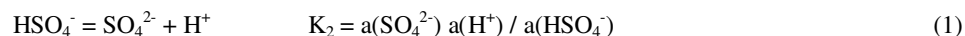
Pitzer and Simonson introduced a Margules type equation with mole fraction as concentration variable instead of molality to model aqueous solutions up to a pure salt.

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Sulphuric acid is an important chemical for the industry [4] and its thermodynamically related properties have been extensively studied especially at 298.15 K and summarized by Clegg et al.[5].

Thermodynamic modelling of sulphuric acid is complicated due to the incomplete dissociation of sulphuric acid which must be included in the thermodynamic description of aqueous sulphuric acid.



Several thermodynamic models with different K_2 equations can be found in literature and are summarised in table 1.

Table 1. Pitzer interaction models for aqueous sulphuric acid.

Author(s)	Year	Modifications ^a	Temperature range	Number of parameters	Total number of terms	Equation for K_2
Pitzer et al. [6]	1977		5-55°C	4	8	Pitzer [6]
Reardon and Beckie [7]	1987	U	5-55°C	4	9	Pitzer [6]
Hepler and Hovey [8]	1990		5-55°C	4	8	Hepler [8]
Sippola [1]	1992	U	5-55°C	4	8	Okuwaki [9]
Holmes and Mesmer [10]	1992		25-200°C	5	17	Dickson [11]
Clegg et al. [5]	1994	UA	0 -55°C	9	32	Dickson [11]
Clegg and Brimblecombe [12]	1995	M	-70 -55°C	10	40	Dickson [11]
Knopf et al. [13]	2003	A	-90 -200°C	10	34	Knopf [13]
Christov and Moller [14]	2004	U	0-200°C	5	20	Dickson [11]

^a U=unsymmetrical mixing terms; A=Archer extension; M=mole fraction scale

Recently, Sippola [15] found out that only 4 parameters with simple a temperature dependency of $(a+b/T)$ is sufficient to present the osmotic and activity coefficients in temperature range 0-55°C up to 6 molal sulphuric solution as well as more complicated models [5][12]. Several different K_2 equations were found to be able to present the studied experimental data equally well. One of them, Knopf equation [13] was found to be able to extrapolate osmotic coefficients measured by Holmes and Mesmer [8] up to 140°C within 0.001.

The aim of this study is to test the ability of the modified Pitzer equation to model concentrated sulphuric acid solutions using limited number of Pitzer parameters with a simple temperature dependency.

2 THEORY

2.1 Original Pitzer equation

Pitzer introduced in 1973 an interaction model for excess Gibbs energy of aqueous solution which is based on virial coefficients similar to gas phase. After recombining virial coefficients and changing moles to molalities (m) the excess Gibbs energy divided by gas constant R, absolute temperature (T) and mass of solvent (w_w) is:

$$\begin{aligned} \frac{G^{E,m}}{w_w RT} = & f(I) + 2 \sum_c \sum_a m_c m_a \left[B_{ca} + \left(\sum_c m_c z_c \right) C_{ca} \right] \\ & + \sum_c \sum_{c'} m_c m_{c'} \left[2\Phi_{cc'} + \sum_a m_a \Psi_{cc'a} \right] + \sum_a \sum_{a'} m_a m_{a'} \left[2\Phi_{aa'} + \sum_c m_c \Psi_{aa'c} \right] \\ & + 2 \sum_n \sum_c m_n m_c \lambda_{nc} + 2 \sum_n \sum_a m_n m_a \lambda_{na} \end{aligned} \quad (2)$$

where c refers to a cation, a to an anion and n to a neutral species. B_{ca} , C_{ca} are interaction parameters for the cation c and the anion a, $\Phi_{cc'}$ and $\Phi_{aa'}$ for two different cations and anions, respectively.

Parameters $\Psi_{cc'a}$, $\Psi_{aa'c}$ are for interactions between three ions, and λ_{nc} , λ_{na} are parameters for interactions between an electrically neutral species and a cation or an anion, respectively. Function f(I) describes the long range forces between ions and is dependent on temperature and ionic strength, which is defined as:

$$I = 1/2 \sum_i m_i z_i^2 \quad (3)$$

Assuming λ and Ψ to be independent on concentration, the equations for activity and osmotic coefficients are obtained with appropriate differentiation from equation 2 and summarized in equations 4 - 7

$$\begin{aligned} \ln \gamma_M = & \left(\frac{\partial G^{E,m} / RT}{\partial n_M} \right)_{T, p, w_w, n_i, i \neq M} \\ = & z_M^2 f^{\gamma}(I) \\ & + \sum_a m_a [2B_{Ma} + ZC_{Ma}] + z_M \sum_c \sum_a m_c m_a C_{ca} + z_M^2 \sum_c \sum_a m_c m_a \left[B'_{ca} + \frac{1}{2} ZC'_{ca} \right] \\ & + \sum_c m_c \left[2\Phi_{Mc} + \sum_a m_a \Psi_{Mca} \right] + z_M^2 \sum_c \sum_{c'} m_c m_{c'} \Phi'_{cc'} + z_M^2 \sum_a \sum_{a'} m_a m_{a'} \Phi'_{aa'} \\ & + \sum_a \sum_{a'} m_a m_{a'} [m_M \Psi_{Maa'}] + 2 \sum_n m_n \lambda_{nM} \end{aligned} \quad (4)$$

$$\begin{aligned}
\ln \gamma_X &= \left(\frac{\partial G^{E,m} / RT}{\partial n_X} \right)_{T,p,w_w,n_i,i \neq X} \\
&= z_X^2 f^\gamma(I) \\
&+ \sum_c m_c [2B_{cX} + ZC_{cX}] + |z_X| \left[\sum_c \sum_a m_c m_a C_{ca} + z_X^2 \sum_c \sum_a m_c m_a \left[B'_{ca} + \frac{1}{2} ZC'_{ca} \right] \right. \\
&+ \sum_a m_a \left[2\Phi_{Xa} + \sum_c m_c \psi_{Xac} \right] + z_X^2 \sum_c \sum_{c'} m_c m_{c'} \Phi'_{cc'} + z_X^2 \sum_a \sum_{a'} m_a m_{a'} \Phi'_{aa'} \\
&+ \sum_c \sum_{c'} m_c m_{c'} [m_X \psi_{cc'X}] + 2 \sum_n m_n \lambda_{nX}
\end{aligned} \tag{5}$$

$$\ln \gamma_N = \left(\frac{\partial G^{E,m} / RT}{\partial n_N} \right)_{T,p,w_w,n_i,i \neq N} = 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na} \tag{6}$$

$$\begin{aligned}
(\phi - 1) &= - \left(\frac{1}{\sum_i m_i} \right) \left(\frac{\partial G^{E,m} / RT}{\partial w_w} \right)_{T,p,n_i} \\
&= \left(\frac{2}{\sum_i m_i} \right) \left\{ I f^\phi(I) + \sum_c \sum_a m_c m_a [B_{ca}^\phi + ZC_{ca}^\phi] + \sum_c \sum_{c'} m_c m_{c'} \left[\Phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a} \right] \right. \\
&\quad \left. + \sum_a \sum_{a'} m_a m_{a'} [\Phi_{aa'}^\phi + \sum_c m_c \psi_{aa'c}] + \sum_n \sum_c m_n m_c \lambda_{nc} + \sum_n \sum_a m_n m_a \lambda_{na} \right\}
\end{aligned} \tag{7}$$

Osmotic coefficient (ϕ) is generally used in aqueous systems instead of activity of water and is defined as:

$$\phi = - \left(\frac{1000}{M_w \sum m_i} \right) \ln a_w \tag{8}$$

where M_w is the molecular weight of water. More detailed version of the Pitzer model can be found elsewhere, for example in reference [16].

2.2 Modified Pitzer equation

Modified Pitzer equation is obtained by replacing the modified molality and ion strength defined as

$$m'_i = \frac{n_i}{\left(n_w + \sum_j n_j \right) M_w} \tag{9}$$

and

$$I' = \frac{1}{2} \sum_i \frac{n_i z_i^2}{\left(n_w + \sum_j n_j \right) M_w} \tag{10}$$

with their counterparts in equations 4-7 [17].

3 CALCULATIONS

3.1 Experimental data and methods

The experimental data used for the evaluation were chosen to be the most accurate ones and are listed in table 2. The data are almost the same as used by Pitzer et al. in 1977 [6], excluding the osmotic coefficient data by Robinson and Stokes [18].

Table 2. Experimental data included and excluded in the evaluation.

	Measurements	Temperature range (°C)	N of obs. included (total)	m (H ₂ SO ₄) (mol/kg)	Excluded molalities
Cell A [19]	Pt,H ₂ H ₂ SO ₄ PbSO ₄ ,Pb,Hg	0-50	15 (25)	0.005-0.02	All data <0.005
Cell B [20]	Pt,H ₂ H ₂ SO ₄ Hg ₂ SO ₄ ,Hg	5-55	53 (54)	0.1003-8.0	5.767 (5°C)
Cell C [21]	Pt,H ₂ H ₂ SO ₄ PbO ₂ ,PbSO ₄ ,Pt	5-55	70 (70)	0.1-7.2	
Isopiestic data [22]	Critical evaluation of several isopiestic measurements	25	36 (64)	0.2-10.0	0.1 (25°C) All data > 10

For cell A all data below 0.005 mol/kg were measured using platinum bright electrode instead of platinum black one, due to experimental difficulties, and was thus excluded [19]. For isopiestic data the lowest value of 0.1 mol/kg concentration was excluded since it deviates as much as the announced error 0.5% [22] from the corrected values of Rard [23] published in 1983.

The experimental error was evaluated for cell A and B to be 1 mV and for cell C as 0.5 mV, which are about 3 times the standard deviations obtained for these cells in an earlier evaluation [15]. The activities instead of osmotic coefficients were used in data fitting. Error estimates for activities of water are based on accuracy of 0.005 in the osmotic coefficient data.

MTDATA [24] version 4.81 was used for parameter fitting. The objective function (OF) used is

$$OF = \sum_{i=1}^N w_i [(C_i - E_i)/U_i]^2 \quad (11)$$

where

w_i = weight of the experimental value

C_i = calculated value

E_i = experimental value

U_i = uncertainty

All weights except for rejected values were set to 1.

In MTDATA there are several excess models available including Pitzer equation with Harvie et al.'s modification [2] and the modified Pitzer model used in this study.

3.2 Second dissociation constant for sulphuric acid

There are several equations in the literature for the second dissociation constant (K_2) of sulphuric acid. Four different equations (see table 3) were studied of which three of them have been found able to model the sulphuric acid equally well and the fourth one (Knopf) is superior when extrapolating data to higher temperatures [15].

Table 3. Equations for the second dissociation constant K_2 .

	$\ln(K_2) = A + B(T/K) + C(T/K) \ln(T/K) + D(T/K)^2 + E/(T/K)$				
Equation ^a	A	B	C	D	E
Okuwaki [9]	1329.084	0.6519378	-246.01	-0.000316757	-29282
Dickson [11]	1295.687	0.5704742	-236.05043	-0.000257206	-30563.94
Hovey [8]	199.0185	---	-31.8123	---	-6658.95
Knopf [13]	-49.7086	-0.059835	10.95231	---	178.1142

a) Original log terms have been transferred to ln scale by multiplying with ln(10).

3.3 Studied parameter sets

The first four studied Pitzer parameter sets (A-D) are the same as in the earlier study [15] where parameter set A was found to be sufficient to present the activity and stoichiometric osmotic coefficient data in temperature range 0-55°C up to 6 molal sulphuric solution.

In the beginning the four parameter set A was found to be insufficient to present data up to 10 molal sulphuric acid solutions. Thus, the focus was set to 5 parameter sets and several new 5 parameter sets (E-J) were also tested. Later on, when extending the concentration range up to 15 molal sulphuric acid 5 more sets were included (K-O). The temperature dependency of all parameters is $a+b/T$.

All studied parameter sets are listed in table 4.

Table 4. Tested Pitzer parameter sets. The temperature dependency of each parameter is $a + b/T$.

Ions	$H^+ - SO_4^{2-}$			$H^+ - HSO_4^-$			$SO_4^{2-} - HSO_4^-$
Parameter set	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	θ
A	x		x	x	x		
B			x	x	x	x	
C	x		x	x	x	x	
D	x		x	x	x		x
E	x	x	x	x	x		
F	x	x	x	x		x	
G	x	x	x		x	x	
H	x	x		x	x	x	
J		x	x	x	x	x	
K			x	x	x	x	x
L		x	x	x	x		x
M	x		x	x	x	x	x
N	x	x	x	x	x		x
O			x	x	x		x

4 RESULTS

4.1 Sulphuric acid up to 10 molal solutions.

Parameter sets A-J were studied with four different equation of K_2 (see table 3). Thus, the total number of 36 parameter evaluations was executed. The values of object functions for each fit are gathered in table 5.

Table 5. The values of objective functions for each case studied ($m_{\max} = 10$ mol/kg).

Set / K_2	Dickson	Hepler	Knopf	Okuwaki
A	4.20	4.43	4.44	4.41
B	0.10	0.10	0.08	0.11
C	0.07	0.07	0.07	0.08
D	0.08	0.08	0.08	0.08
E	0.14	0.14	0.13	0.13
F	0.46	0.49	0.49	0.48
G	1.90	1.96	1.88	1.88
H	77.0	94.1	94.5	92.5
J	0.07	0.07	0.08	0.07

The standard deviations obtained and maximum deviations for each cell and stoichiometric osmotic coefficient at 25°C are shown in tables 6-9.

Table 6. Standard and maximum deviations for cell A (0.005-0.02 m, 0-50°C). Values in bold are over the estimated experimental error (1.0 mV).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
A	0.27	0.29	0.34	0.29	-0.41	-0.51	-0.72	-0.51
B	0.21	0.23	0.28	0.22	-0.47	-0.47	-0.62	-0.44
C	0.20	0.22	0.27	0.21	-0.44	-0.44	-0.61	-0.42
D	0.23	0.25	0.30	0.25	-0.47	0.47	-0.64	-0.44
E	0.22	0.25	0.29	0.24	0.47	-0.52	0.64	0.48
F	0.10	0.15	0.24	0.14	-0.20	-0.21	0.53	-0.24
G	0.22	0.20	0.27	0.17	0.46	0.41	0.56	0.39
H	1.12	0.57	1.09	0.35	-2.28	0.93	-1.77	-0.58
J	0.18	0.21	0.27	0.20	-0.41	0.42	-0.62	-0.38

Table 7. Standard and maximum deviations for cell B (0.1-8.0 m, 5-55°C). Values in bold are over the estimated experimental error (1.0 mV).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
A	0.60	0.62	0.63	0.62	0.85	1.23	1.35	1.23
B	0.35	0.36	0.31	0.37	1.43	1.45	1.12	1.52
C	0.29	0.29	0.30	0.31	0.93	1.00	0.98	1.19
D	0.31	0.30	0.29	0.31	0.95	-0.96	-0.90	0.92
E	0.26	0.26	0.27	0.27	-0.76	-0.74	-0.81	0.72
F	0.39	0.38	0.41	0.38	1.05	1.14	1.02	1.04
G	0.53	0.59	0.52	0.53	-1.43	-1.87	-1.40	-1.32
H	2.29	2.87	3.46	2.82	5.68	6.04	7.77	6.16
J	0.27	0.29	0.26	0.28	0.85	0.88	-0.86	0.93

Table 8. Standard and maximum deviations for cell C (0.1-7.2 m, 5-55°C). Values in bold are over the estimated experimental error (0.5 mV).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
A	0.74	0.76	0.78	0.76	-0.33	-1.79	-1.83	-1.79
B	0.16	0.16	0.14	0.17	-0.41	-0.41	-0.30	-0.46
C	0.15	0.14	0.13	0.14	-0.42	-0.31	-0.24	-0.27
D	0.14	0.15	0.15	0.15	-0.35	-0.37	-0.43	-0.36
E	0.22	0.22	0.19	0.20	-0.77	-0.82	-0.69	-0.69
F	0.33	0.33	0.33	0.33	0.68	-0.71	0.69	0.67
G	0.58	0.59	0.55	0.55	-1.19	1.11	1.08	-1.10
H	2.77	3.02	3.44	3.03	-5.94	-6.22	7.36	-6.63
J	0.14	0.14	0.16	0.14	-0.33	-0.34	-0.41	-0.30

Table 9. Standard and maximum deviations for stoichiometric osmotic coefficient (0.2-10.0 m, 25°C). Values in bold are over the estimated experimental error (0.005).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
A	0.020	0.020	0.020	0.020	-0.053	-0.054	-0.054	-0.054
B	0.001	0.001	0.001	0.001	-0.003	-0.003	-0.003	-0.003
C	0.001	0.001	0.001	0.001	0.003	0.003	0.003	0.003
D	0.001	0.001	0.001	0.001	-0.002	-0.002	-0.003	0.002
E	0.002	0.002	0.002	0.002	-0.005	-0.005	-0.005	-0.005
F	0.005	0.005	0.005	0.005	-0.012	-0.013	-0.013	-0.013
G	0.012	0.012	0.012	0.012	0.033	0.033	0.033	0.033
H	0.087	0.096	0.093	0.095	-0.210	-0.226	-0.202	-0.218
J	0.001	0.001	0.001	0.001	0.003	0.003	-0.002	0.003

The three best parameter sets are C, D and J; the last outperforming slightly the two other sets. Set C is slightly better than D but fails to fit cell B with Okuwaki's equations within experimental error. However, it is interesting that the 4 parameter set B is better than the rest of the five parameter sets.

There is little difference in predicted values of the three best parameter sets which is demonstrated in table 10. Since differences in the predicted values are well below the experimental error it is not possible to dictate which one of these parameter sets is the best.

Table 10. Differences in predicted values by parameter sets C, D and J.

	K ₂ equation				Experimental Error
	Dickson	Hepler	Knopf	Okuwaki	
Cell A, mV	0.10	0.11	0.10	0.10	1.0 mV
Cell B, mV	0.32	0.33	0.28	0.34	1.0 mV
Cell C, mV	0.26	0.35	0.31	0.38	0.5 mV
ϕ_{stoich}	0.002	0.002	0.002	0.002	0.005

All studied equations for K₂ fit the data equally well with parameter sets C, D and J so it is not possible to resolve which one is the best K₂ equation (see table 11).

Table 11. Standard deviations for the best parameter sets C, D and J.

Set / K_2	Dickson	Hepler	Knopf	Okuwaki
C	0.07	0.07	0.07	0.08
D	0.08	0.08	0.08	0.08
J	0.07	0.07	0.08	0.07

When comparing the results it can be concluded that the cation-anion Pitzer parameters C^ϕ between the hydrogen and sulphate ion is the most essential one in modelling the sulphuric acid-water binary since omitting it will ruin the fit as can be seen from the results of parameter set H. Moreover, the best sets, namely sets B, C, D and J all share the above mentioned C^ϕ parameter but also the interaction parameters $\beta^{(0)}$ and $\beta^{(1)}$ between H^+ and HSO_4^- ions.

4.2 More concentrated sulphuric acid solutions

Since several parameter sets and K_2 equations can equally well model the sulphuric acid solutions up to the concentration of 10 mol/kg the concentration range was increased by including water activity data up to 15 mol/kg at 25°C including 10 more data points in the experimental data.

Five parameter sets from earlier section, namely B-E and J, were first studied. In earlier stage it became evident that the parameter set B does not cope with more concentrated solutions and the θ parameter between bisulphate and sulphate ions is also essential for concentrated sulphuric acid solutions. Thus, parameter set B was replaced with two five parameter set K and L (table 4).

Two six parameter sets were also tested: Set M obtained by merging sets D and K and set N by merging sets D and L. Finally, a parameter set O including only the four most significant parameters was tested, too (see table 4).

The values of object functions for each fit are gathered in table 12.

Table 12. The values of objective functions for each case studied ($m_{\max} = 15$ mol/kg).

Set / K_2	Dickson	Hepler	Knopf	Okuwaki
C	0.29	0.30	0.31	0.32
D	0.11	0.11	0.11	0.11
E	0.34	0.35	0.32	0.33
J	0.22	0.23	0.23	0.22
K	0.12	0.12	0.12	0.12
L	0.18	0.18	0.18	0.19
M	0.11	0.11	0.11	0.11
N	0.11	0.11	0.11	0.11
O	0.18	0.18	0.19	0.18

The six parameter set M and N do not fit the data better than the best five parameter set hence these parameter sets are neglected. It is worth noticing that the parameter set O of the four most significant parameters performs equally or better when compared to any sets without any of those parameters included in set O.

The standard deviations obtained and maximum deviations for each cell and stoichiometric osmotic coefficient at 25°C are shown in tables 13-16.

Table 13. Standard and maximum deviations for cell A (0.005-0.02 m, 0-50°C). Values in bold are over the estimated experimental error (1.0 mV).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
C	0.21	0.24	0.30	0.23	-0.47	-0.48	-0.65	-0.46
D	0.23	0.26	0.30	0.26	-0.48	-0.48	0.67	0.46
E	0.19	0.22	0.27	0.21	0.44	0.47	0.61	-0.42
J	0.20	0.23	0.29	0.22	-0.43	-0.41	0.64	-0.38
K	0.22	0.25	0.29	0.25	-0.48	-0.47	-0.64	-0.45
L	0.25	0.28	0.32	0.27	-0.50	-0.52	-0.68	0.47
O	0.25	0.28	0.32	0.27	0.49	-0.51	0.71	-0.48

Table 14. Standard and maximum deviations for cell B (0.1-8.0 m, 5-55°C). Values in bold are over the estimated experimental error (1.0 mV).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
C	0.33	0.33	0.34	0.35	1.30	1.21	1.40	1.48
D	0.32	0.32	0.30	0.31	1.00	-0.93	-0.93	-0.93
E	0.28	0.28	0.29	0.29	-0.79	-0.83	-0.85	-0.75
J	0.27	0.25	0.31	0.26	-0.82	-0.76	0.94	-0.86
K	0.31	0.30	0.29	0.31	0.95	0.91	-0.81	0.95
L	0.35	0.34	0.34	0.36	1.18	-1.08	-1.05	1.15
O	0.36	0.32	0.33	0.33	1.24	0.98	1.02	1.00

Table 15. Standard and maximum deviations for cell C (0.1-7.2 m, 5-55°C). Values in bold are over the estimated experimental error (0.5 mV).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
C	0.21	0.21	0.20	0.22	-0.59	-0.62	-0.45	-0.45
D	0.14	0.14	0.15	0.15	-0.28	-0.31	-0.30	-0.31
E	0.30	0.31	0.28	0.29	-0.97	-0.97	-0.81	-0.87
J	0.19	0.22	0.19	0.19	-0.61	-0.76	-0.55	-0.58
K	0.14	0.14	0.14	0.14	-0.27	-0.26	-0.24	-0.28
L	0.19	0.18	0.18	0.19	-0.41	0.41	-0.45	-0.47
O	0.17	0.17	0.17	0.17	0.34	-0.36	0.30	0.36

Table 16. Standard and maximum deviations for stoichiometric osmotic coefficient (0.2-15.0 m, 25°C). Values in bold are over the estimated experimental error (0.005).

Set	Standard deviations				Maximum deviations			
	Dickson	Hepler	Knopf	Okuwaki	Dickson	Hepler	Knopf	Okuwaki
C	0.004	0.005	0.005	0.005	0.012	0.013	0.014	0.012
D	0.002	0.002	0.002	0.002	-0.004	-0.004	-0.004	-0.004
E	0.004	0.004	0.004	0.004	-0.011	-0.011	-0.011	-0.011
J	0.004	0.004	0.004	0.004	0.010	0.009	0.009	0.009
K	0.002	0.002	0.002	0.002	0.004	-0.004	0.004	-0.005
L	0.003	0.003	0.003	0.003	-0.007	-0.007	-0.007	-0.008
O	0.003	0.003	0.003	0.003	-0.006	-0.007	-0.007	-0.008

In general, the differences between K_2 -equations are small. Knopf is slightly inferior with cell A but performs well with cells B and C, especially with the best parameter sets D and K.

There is little difference in predicted values of the two best parameter sets D and K which is demonstrated in table 17. Since differences in the predicted values are well below the experimental error it is not possible to dictate which one of parameter sets D or K is the best.

Table 17. Differences in predicted values by parameter set D and K.

	K ₂ equation				Experimental Error
	Dickson	Hepler	Knopf	Okuwaki	
Cell A, mV	0.03	0.03	0.05	0.04	1.0 mV
Cell B, mV	0.18	0.20	0.22	0.22	1.0 mV
Cell C, mV	0.19	0.21	0.17	0.24	0.5 mV
ϕ_{stoich}	0.001	0.002	0.001	0.002	0.005

The extrapolating abilities of parameter sets D and K were tested by comparing the calculated stoichiometric osmotic coefficients with the Rard et al.'s data [22] at 25°C up to maximum concentration, i.e., 27 molal solution. Even though parameter set D and K can equally well present the experimental data the latter one has better extrapolating ability. There are little differences between K₂ equations. (Figure 1).

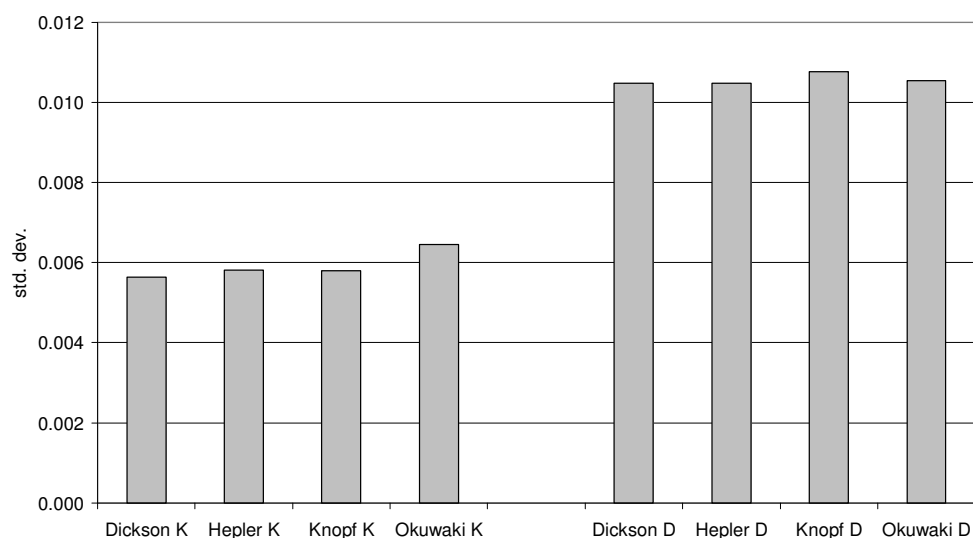


Figure 1. Standard deviations of stoichiometric osmotic coefficient data [22] at 25°C in concentration range 0.2-27 mol/kg for parameter sets D and K with studied K₂ equations. The maximum concentration used in parameter fitting was 15 mol/kg.

The parameter set K was further tested by comparing the predicted stoichiometric osmotic coefficients at 0, 25 and 50°C to the more complicated mole fraction based model by Clegg and Brimblecombe [12] for sulphuric acid up 40 mol/kg solution. Dickson et al.'s [11] equation for K₂ is used in both cases. The agreement is excellent considering that all calculated values above 15 mol/kg (25°C) and 8 mol/kg (0, 50°C) are extrapolated ones (figure 2).

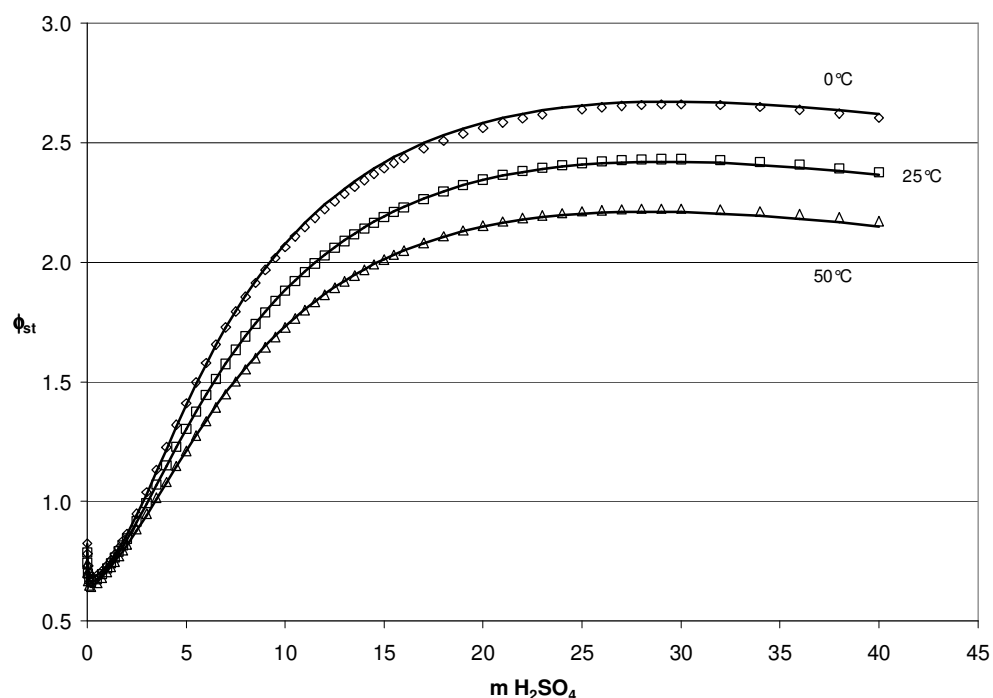


Figure 2. Stoichiometric osmotic coefficient data at 0, 25 and 50 °C predicted with parameter set K (solid line) compared to values from Clegg and Brimblecombe [12] model (dots). Dickson et al.'s [11] equation for K_2 is used in both cases. All calculated values above 15 mol/kg (25°C) and 8 mol/kg (0, 50°C) are extrapolated.

5 DISCUSSION AND CONCLUSIONS

The modified Pitzer equation was found to be able to model concentrated sulphuric acid solutions. Four Pitzer parameters were found essential in modelling the system:

- C^ϕ between H^+ and SO_4^- ions
- $\beta^{(0)}$ and $\beta^{(1)}$ between H^+ and HSO_4^- ions and
- θ between SO_4^- and HSO_4^- ions

A four parameter set consisting of these parameters can model the sulphuric acid -water system equally or better than any studied five parameter set lacking any of the essential parameters. Two five parameter sets D and K including these parameters and enhanced by $\beta^{(0)}(H^+ / SO_4^-)$ and $C^\phi(H^+ / HSO_4^-)$, respectively, were found to fit the experimental data equally well but the latter set has better ability to extrapolate the stoichiometric osmotic coefficients up to 27 mol/kg solution at 25°C. The temperature dependency of all studied parameters is $a + b/T$.

The agreement with parameter set K and the more complicated model by Clegg and Brimblecombe [12] is excellent in three studied temperatures (0, 25 and 50°C) up to 40 molal solutions when considering that the parameter set K is assessed from data not exceeding the 15 molal solution at 25°C and 8 molal in other temperature.

There is little difference in quality of the assessment between studied K_2 equations. Thus, there is no way to dictate which one is the best. Moreover, it is obvious that the correct choice of the parameters used in the assessment is much more critical than the chosen K_2 equation. The differences in predicted values by different K_2 equation with best parameter set are well beyond experimental error so it seems unlikely that the verdict on the best K_2 equation can be made by the assessment of Gibbs energy related properties like osmotic or activity coefficients for the binary system sulphuric acid-water only.

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