Chem. Res. Chin. Univ. 2013, 29(6), 1189—1192 doi: 10.1007/s40242-013-3139-y

Mean Activity Coefficients of KCl in the KCl-$K_2B_4O_7$-H_2O Ternary System at 308.15 K by EMF Method

ZHONG Si-yao[1,2,3], SANG Shi-hua[1,2,3*] and ZHANG Jun-jie[1,3]

1. College of Materials and Chemistry & Chemical Engineering,
2. State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation,
3. Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions,
Chengdu University of Technology,Chengdu 610059, P. R. China

Abstract The mean activity coefficients of KCl in a KCl-$K_2B_4O_7$-H_2O ternary system were experimentally determined at 308.15 K by the electromotive force measurement(EMF) *via* a battery cell without a liquid junction: K-ISE|KCl(m_1), $K_2B_4O_7$(m_2)|Cl-ISE(ISE=ion selective electrode) in a total ionic strength of from 0.01 mol/kg to 1.00 mol/kg at different ionic strength fractions of $K_2B_4O_7$ with y_B=0, 0.200, 0.400, 0.600 and 0.800. K-ISE and Cl-ISE presented a good Nernst effect, which implies that this method could be used to measure the activity coefficients of an electrolyte in the above system. The Harned rule was fitted to the experimental data, the Harned coefficients and the Pitzer single-salt ion parameters of KCl were evaluated, and the relationship diagrams between the mean activity coefficient of KCl and the ionic strength fraction(y_B) were drawn. The mean activity coefficients of KCl($\gamma_{\pm KCl}$) decreased monotonically with the increase of I. The experimental results obeyed the Harned rule well.

Keywords Activity coefficient; Electromotive force measurement; Ion selective electrode; Potassium chloride; Potassium borate

1 Introduction

The activity coefficients of electrolytes in mixed aqueous electrolyte solutions have an important significance in the field of marine chemistry, salt lake chemistry, and oilfield chemistry. The activity coefficient theory of electrolyte not only is a hot-spots issue in the field of solution thermodynamic theory research both at home and abroad, but also is of importance in the field of electrochemical research, and is also a research needed on salt solution distillation, hydrometallurgy and bio-chemical engineering[1—3].

Over the past few decades, a series of ion-interaction models have been proposed to predict the activity and osmotic coefficients of each electrolyte solution. Pitzer model is one of the most famous and useful models, which is proposed by Pitzer *et al.*[4—6]. To measure the thermodynamic properties of mixed electrolyte solutions, the conductance method, freezing point depression method, isopiestic method and electromotive force(EMF) technique which are the most common methods are used. Compared with the other methods, EMF method has the characteristics of a wide range of linear response and is simple and convenient. Thus it has received much attention[7].

Recently, a huge store of underground gasfield brines had been discovered in Western Sichuan Basin of China. Particularly, the potassium ion concentration of the underground brines is up to 53.27 g/L, and the boron concentration is up to 4.994 g/L. Content of boron, potassium, and bromine in the gasfield brines far exceeds industrial grade of comprehensive utilization. Natural underground gasfield brines with the characteristic of high boron, potassium content, are a complex multi-component salt-water system[8—10]. The researches in these aspects are of great significance, such as the researches on the thermodynamic properties of boron and potassium in the gasfield brine system, and the establishment of phase equilibrium thermodynamic prediction model to guide boron and potassium optimization process and chemical production process from the underground gasfield brines. In recent years, many scholars have reported the thermodynamic properties of the salt lake brine, such as phase equilibrium of $CdCl_2$-$CdSO_4$-$CdNO_3$-H_2O system and Na-K-Mg-Cl-SO_4-NO_3-H_2O system at 298 K[11,12], the mean activity coefficients of NaCl and KCl in the NaCl-KCl-H_2O system at 308.15 K[13], LiCl in the LiCl-$Li_2B_4O_7$-H_2O system at 298.15 K[14], NaCl in the NaCl-$NaBF_4$-H_2O system at 298.15 K[15], and activity coefficients of *o*-, *m*-, *p*-xylene in aqueous salt solutions[16]. The researches about the activity coefficients of potassium electrolyte and chloride electrolyte have been made more and more. For instance, the mean activity coefficients of NaBr and amino acid in (sodium bromide+potassium phosphate+glycine+water) system at 298.15 and 308.15 K have been determined by

---

*Corresponding author. E-mail: sangsh@cdut.edu.cn

Received March 26, 2013; accepted June 20, 2013.

Supported by the Open Fund of State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Chengdu University of Technology, China(No.PLC201204), the National Natural Science Foundation of China(Nos.41373062, 40973047) and the Specialized Research Fund for the Doctoral Program of Higher Education of China(No.20125122110015).

electrochemical measurement[17], the activity coefficients of $\{y\mathrm{KNO_3}+(1+y)\mathrm{K_2HPO_4}\}$(aq.) system at T=298.15 K have been measured by the isopiestic vapor pressure method[18], the activity coefficients of ($NaCl+KCl+LiCl+H_2O$) at T=298.15 K have been experimentally measured by the hygrometric method[19], the activity coefficients of $CaCl_2$ in glycine+water and alanine+water mixtures at 298.15 K[20], and the osmotic and activity coefficients of $\{y\mathrm{KCl}+(1+y)\mathrm{K_2HPO_4}\}$(aq.) system at T=298.15 K have been determined by the isopiestic vapor pressure method at T=298.15 K[21]. In our previous work, the mean activity coefficients of KBr in a KBr-K_2SO_4-H_2O ternary system and NaBr in a $NaBr$-$Na_2B_4O_7$-H_2O ternary system at 298.15 K have been determined by EMF method[22,23]. So far, no report has been found for the studies on mean activity coefficients of KCl in KCl-$K_2B_4O_7$-H_2O ternary system at 308.15 K by EMF method.

In the present work, we studied the KCl-$K_2B_4O_7$-H_2O system at 308.15 K. The mean activity coefficients of KCl in the mixed aqueous solutions of KCl and $K_2B_4O_7$ were respectively determined by EMF measurement at the total ionic strengths of 0.01, 0.02, 0.05, 0.10, 0.20, 0.50, 1.00 mol/kg, the Harned coefficients and the Pitzer single-salt ion parameters of KCl were evaluated, and the relationship diagrams between the mean activity coefficient of KCl and the ionic strength score(y_B) were drawn.

2 Experimental

2.1 Chemicals

KCl(analytical reagent) and $K_2B_4O_7\cdot 4H_2O$(analytical reagent) used in this work were first dried in an oven at 393.15 K for 2 h, then stored in desiccators before use. Deionized water through secondary reverse osmosis with the conductivity less than 10^{-6} S/cm was used for the preparation of all the solutions and the cleaning of electrodes.

2.2 Apparatus

The apparatus used in this experiment were an AL104 electronic balance(Mettler-Toledo Group) with an accuracy of 0.1 mg; a Pxsj-216 ion meter(INESA Scientific Instrument Co., Ltd.) with a precision of ±0.1 mV; a JB-1 blender(INESA Scientific Instrument Co., Ltd.); a Bilon-HW-05 constant temperature water-bath with an external circulation system for the circulation of water to keep the temperature constant and a precision of 0.1 K; a 401 potassium ion selective electrode; a PCl-1-01 chlorine ion selective electrode; a 232-01 reference electrode.

K-ISE was soaked for 30 min in a 10^{-2} mol/L KCl aqueous solution, and washed with deionized water to a blank potential around −160 mV, static reading was performed on testing. Cl-ISE was soaked for 2 h in a 10^{-3} mol/L NaCl aqueous solution. Reference electrode was a double junction saturated calomel electrode with the salt bridge filled with a G. R. grade saturated solution of potassium chloride, and the foreign salt bridge was filled with a 0.1 mol/L lithium acetate solution.

2.3 Determination of Activity Coefficients

The mean ionic activity coefficients values of KCl in the mixture were determined by the EMF *via* the following bi-ISE cell without transference:

$$\mathrm{K^+\text{-}ISE|KCl}(m_1),\ \mathrm{K_2B_4O_7}(m_2)|\mathrm{Cl^-\text{-}ISE} \qquad \text{(I)}$$

in which m_1 and m_2 are the molalities of KCl and $K_2B_4O_7$ in the mixture, respectively.

According to the isothermal invariant points data of KCl-$K_2B_4O_7$-H_2O system at 273.15 and 323.15 K, we can roughly predict the range of the isothermal invariant point of the system at 308.15 K, that was, a selected range of the total ionic strength of the mixed solution from 0.01 to 1.00 mol/kg, from low to high concentration close to saturation. The ionic strength fractions of $K_2B_4O_7$ in the mixed solution(y_B) were respectively 0.800, 0.600, 0.400, 0.200, 0.000. The y_B was calculated *via* the following formula:

$$y_\mathrm{B}=3m_2/(m_1+3m_2) \tag{1}$$

According to the Nernst equation, the following expression is obtained:

$$E=E^0+k_\mathrm{KCl}\ln\alpha_{\mathrm{K^+}}\cdot\alpha_{\mathrm{Cl^-}}=E^0+k_\mathrm{KCl}\ln m_1(m_1+m_2)\gamma^2_{\pm\mathrm{KCl}} \tag{2}$$

where E is the EMF of the cell; E^0 is the standard potential of the cell; $k_\mathrm{KCl}=RT/F$[R is the gas constant(8.314 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$), T is the temperature(K), F is the Faraday constant(96500 C/mol)]; is the Nernst theoretical slope, $\alpha_{\mathrm{K^+}}$ and $\alpha_{\mathrm{Cl^-}}$ denote the activities of K^+ and Cl^-, respectively. $\gamma_{\pm\mathrm{KCl}}$ denotes the mean activity coefficient of KCl. In order to obtain the standard electrode potential E^0, another cell was designed as follows:

$$\mathrm{K^+\text{-}ISE|KCl}(m_0)|\mathrm{Cl^-\text{-}ISE} \qquad \text{(II)}$$

in which m_0 is the molality of KCl. EMF of the cell (II) is also expressed by the Nernst equation:

$$E_0=E^0+k_\mathrm{KCl}\ln\alpha_{0\pm\mathrm{KCl}}=E^0+k_\mathrm{KCl}\ln m_0^2\gamma^2_{0\pm\mathrm{KCl}} \tag{3}$$

where E_0 is the EMF of this cell, $\alpha_{0\pm\mathrm{KCl}}$ denotes the activity of KCl, $\gamma_{0\pm\mathrm{KCl}}$ denotes the activity coefficient of KCl. According to the Harned rule[24,25], $\gamma_{\pm\mathrm{KCl}}$, $\gamma_{0\pm\mathrm{KCl}}$ and y_B has the following relation:

$$\ln\gamma_{\pm\mathrm{KCl}}=\ln\gamma_{0\pm\mathrm{KCl}}-\alpha_{\pm\mathrm{KCl}}y_\mathrm{B}-\beta_{\pm\mathrm{KCl}}y_\mathrm{B}^2 \tag{4}$$

where $\alpha_{\pm\mathrm{KCl}}$ and $\beta_{\pm\mathrm{KCl}}$ represent the Harned interaction coefficients related only to the total ionic strength at a given pressure and temperature. This equation describes the mean activity coefficients of KCl in pure solution and mixture changed with y_B when the total ionic strength is held constant. In this cell, the activity coefficients for the single electrolyte KCl are estimated by Pitzer model[26]:

$$\begin{aligned}\ln\gamma_\pm={}&-A^\varnothing\left[\frac{\sqrt{I}}{1+b\sqrt{I}}+\left(\frac{2}{b}\right)\ln\left(1+b\sqrt{I}\right)\right]+m\left\{2\beta^{(0)}+\right.\\&\left.\left(\frac{2\beta^{(1)}}{a^2I}\right)\left[1-\left(1+a\sqrt{I}-\frac{a^2I}{2}\right)\exp\left(-a\sqrt{I}\right)\right]\right\}+1.5m^2C^\varnothing\end{aligned} \tag{5}$$

where $A^\varnothing$ is the Debye-Hückel coefficient for osmotic coefficient dependent on the temperature given by:

$$A^\varnothing=\left(2\pi N_0\rho\right)^{1/2}\left(\frac{\mathrm{e}^2}{4\pi\varepsilon kT}\right)^{3/2} \tag{6}$$

where N_0 is the Avogadro's constant, ρ the solvent density, e the electronic charges and ε the permittivity, I is the ionic strength, m is the concentration of the electrolyte in molality, the constants b=1.2 and a=2, $\beta^{(0)}$, $\beta^{(1)}$ and C^{Φ} are the parameters dependent on the electrolyte and temperature, and satisfy the formula described by Greenberg and Møller[27]:

$$P(T)=a_1+a_2T+a_3/\mathrm{T}+a_4\ln T+a_5/(T-263)+a_6T^2+a_7/(680-T)+a_8/(T-227) \quad (7)$$

where, a_1, a_2, a_3, a_4, a_5, a_6, a_7 *and* a_8 are fitting coefficients.

KCl was weighed on the electronic balance, and then added to approximately 30 mL of deionized water in beakers to be respectively formulated into seven concentrations: 0.01, 0.02, 0.05, 0.10, 0.20, 0.50, 1.00 mol/kg. Beakers were stirred until the solid was dissolved, then placed in a constant temperature water-bath with external circulation under test, the temperature in the cell was maintained constant within (308.15±0.1) K. Their electromotive forces were measured according to the ascending order of concentration by K-ISE and Cl-ISE. When the value of the electromotive force shown in the ion meter changed less than 0.1 mV within 30 min, at this time, the reading was regarded as the constant during the equilibrium in the cell.

3 Results and Discussion

According to Eq.(7), the values of the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{Φ} for pure KCl at 308.15 K were calculated to be 5.33×10^{-2}, 2.32×10^{-1} and -1.35×10^{-3}, respectively. The value of A^{Φ} at 308.15 K calculated by Archer and Wang was 0.3985[28]. The activity coefficient values for pure electrolyte KCl($\gamma_{0\pm\mathrm{KCl}}$) calculated *via* Eq.(4) and Eq.(2), and the experimental E^0 values obtained are listed in Table 1. Then E^0 was plotted against $\ln\alpha_{0\pm\mathrm{KCl}}$ in order to check their linear relationship(see Fig.1).

Table 1 Electromotive force and activity coefficient of pure electrolyte KCl at 308.15 K

m_0/(mol·kg^{-1})	E_0/mV	$\gamma_{0\pm\mathrm{KCl}}$ Calculated value *via* Pitzer equation	 Calculated value *via* regression	Relative error(%)
0.010	–9.1	0.900	0.880	2.12
0.020	27.1	0.867	0.877	–1.17
0.050	70.9	0.813	0.812	0.11
0.100	104.1	0.766	0.769	–0.40
0.200	136.8	0.715	0.717	–0.29
0.499	179.8	0.650	0.654	–0.70
0.999	211.5	0.607	0.600	1.15
Mean relative error(%)			0.85	

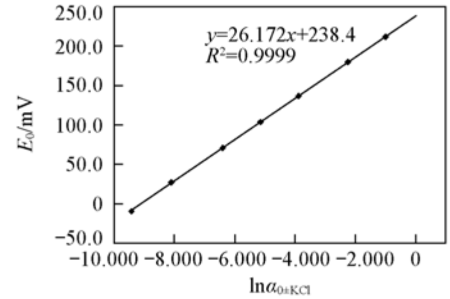

Fig.1 Plot of E_0 *vs.* $\ln\alpha_{0\pm\mathrm{KCl}}$ for calibration of potassium and chlorine selective electrode pair at 308.15 K to check their linear relationship

E^0=238.4 mV; k_{KCl}=26.17 mV.

It could be seen from Table 1 that the mean relative error between the calculated value of Pitzer equation and the calculated value of regression was 0.85%; as could be found from Fig.1, the pair of electrodes used in the experiments had a good Nernst linear response, its E^0 was 238.4 mV, k_{KCl} was 26.17 mV. So it is reliable to measure the activity coefficient by the EMF method.

On the basis of the electromotive force measured in the mixed electrolyte and E^0, k_{KCl} obtained above, the mean activity coefficient of KCl in a mixed solution was calculated *via* Eq.(2), with the correlation data shown in Table 2. Then $\ln\gamma_{\pm\mathrm{KCl}}$ was plotted against y_B.

Table 2 Mean activity coefficients of KCl in KCl(m_1)-$K_2B_4O_7$(m_2)-H_2O system at 308.15 K

I/(mol·kg^{-1})	y_B	m_1/(mol·kg^{-1})	m_2/(mol·kg^{-1})	E/mV	$\gamma_{\pm\mathrm{KCl}}$	I/(mol·kg^{-1})	y_B	m_1/(mol·kg^{-1})	m_2/(mol·kg^{-1})	E/mV	$\gamma_{\pm\mathrm{KCl}}$
0.01	0.799	0.002	0.003	–53.7	0.981	0.10	0.200	0.080	0.007	95.8	0.760
0.01	0.610	0.004	0.002	–37.1	0.942	0.10	0.000	0.100	0.000	103.7	0.762
0.01	0.393	0.006	0.001	–23.9	0.917	0.20	0.800	0.040	0.053	81.7	0.654
0.01	0.218	0.008	0.001	–14.8	0.901	0.20	0.600	0.080	0.040	102.2	0.656
0.01	0.000	0.010	0.000	–9.1	0.884	0.20	0.400	0.112	0.027	115.8	0.667
0.02	0.804	0.004	0.005	–20.4	0.948	0.20	0.198	0.160	0.013	126.4	0.681
0.02	0.602	0.008	0.004	–1.1	0.909	0.20	0.000	0.200	0.000	136.5	0.713
0.02	0.403	0.012	0.003	9.8	0.887	0.50	0.800	0.100	0.133	120.3	0.550
0.02	0.204	0.016	0.001	19.1	0.871	0.50	0.600	0.199	0.100	142.1	0.564
0.02	0.000	0.020	0.000	26.0	0.861	0.50	0.400	0.299	0.067	156.9	0.586
0.05	0.798	0.010	0.013	21.7	0.826	0.50	0.200	0.399	0.033	168.7	0.613
0.05	0.600	0.020	0.010	40.3	0.804	0.50	0.000	0.500	0.000	179.1	0.644
0.05	0.400	0.030	0.007	52.4	0.794	0.99	0.800	0.198	0.264	149.9	0.486
0.05	0.199	0.040	0.003	61.7	0.791	0.99	0.600	0.397	0.199	172.4	0.505
0.05	0.000	0.050	0.000	69.6	0.794	1.00	0.400	0.597	0.133	187.7	0.529
0.10	0.800	0.020	0.027	52.6	0.751	1.00	0.200	0.798	0.067	200.3	0.560
0.10	0.600	0.040	0.020	73.3	0.755	1.00	0.000	0.999	0.000	211.9	0.603
0.10	0.399	0.060	0.013	86.3	0.758						

It can be seen from Table 2 and Fig.2 that in mixed solutions with different total ionic strengths, $\gamma_{\pm KCl}$ decreased monotonically with the increase of the total ionic strength(I); when I was constant, $\gamma_{\pm KCl}$ increased with the increase of y_B within a range of I less than 0.05 mol/kg, $\gamma_{\pm KCl}$ decreased with the increase of y_B within a range of I more than 0.05 mol/kg.

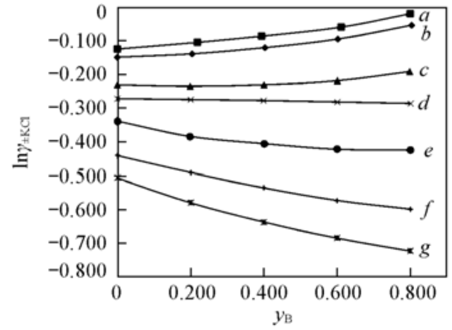

Fig.2 Plots of the mean activity coefficients of KCl at ionic strengths 0.01(*a*), 0.02(*b*), 0.05(*c*), 0.10(*d*), 0.20(*e*), 0.50(*f*) and 1.00(*g*) mol/kg *vs.* y_B in KCl-$K_2B_4O_7$-H_2O system at 308.15 K

The Harned interaction coefficients $\alpha_{\pm KCl}$ and $\beta_{\pm KCl}$ were obtained *via* Eq.(4), with the results shown in Table 3. A good correlation can be observed from Table 3, so it was concluded that the Harned rule can be applied to describing this system commendably.

Table 3 Interaction coefficients of the Harned rule

$I/(mol\cdot kg^{-1})$	$\ln\gamma_{0\pm KCl}$	$-\alpha_{\pm KCl}$	$-\beta_{\pm KCl}$	R^2
0.01	−0.122	−0.054	−0.089	0.996
0.02	−0.148	−0.018	−0.122	0.998
0.05	−0.229	0.055	−0.129	0.993
0.10	−0.271	0.011	0.007	0.993
0.20	−0.340	0.234	−0.161	0.995
0.50	−0.439	0.280	−0.100	0.999
1.00	−0.506	0.384	−0.144	0.999

4 Conclusions

The mean activity coefficients of KCl in pure solutions and in KCl-$K_2B_4O_7$-H_2O ternary system were measured experimentally at 308.15 K at potassium electrode and chlorine electrode by means of EMF method, where the total ionic strength was in a range of 0.01 to 1.00 mol/kg. The Harned interaction coefficients and values of the Pitzer parameters for pure KCl were determined in this system. The results show that the Harned rule could be well applied to this system, and this study provided further development of the thermodynamic reference data.

References

[1] Robinson R. A., Stokes R. H., *Electrolyte Solut.*, *2nd Ed.*, Butterworth, Boston, MA, **1959**
[2] Pitzer K. S., *Accounts of Chem. Res.*, **1977**, *10*, 371
[3] Robinson R. A, Stokes R. H., *Trans. Faraday Soc.*, **1949**, *45*, 612
[4] Pitzer K. S., Mayorga G., *J. Phys. Chem.*, **1973**, *77*, 2300
[5] Pitzer K. S., Kim J. J., *J. Am. Chem. Soc.*, **1974**, *96*, 5701
[6] Pitzer K. S., *Activity Coefficients in Electrolyte Solutions*, *Second Ed.*, CRC Press, Boca Raton, FL, **1991**, 75
[7] Yan W. D., Liu W. D., Han S. J., *J. Chem. Eng. Chin. Univ.*, **1994**, *8*, 33
[8] Yuan R. Q., Cheng F. Q., *Chin. J. Salt. Lake. Res.*, **2008**, *16*, 67
[9] Song P. S., Li W., Sun B., Nie Z., Bu L. Z., Wang Y. S., *Chin. J. Inorg. Chem.*, **2011**, *27*, 801
[10] Song P. S., *J. Salt Lake Res.*, **2000**, *8*, 33
[11] Huang Y., Zou F., Ni S. J., Sang S. H., *Chem. Res. Chinese Universities*, **2011**, *27*(3), 482
[12] Huang X. L., Wang X. F., Chen L. J., *Chem. J. Chinese Universities*, **2011**, *32*(6), 1378
[13] Li Z. G., Huang H. J., Yan J., *Chin. J. Chem. Phys.*, **2002**, *15*, 476
[14] Tian H. B., Yao Y., Song P. S., *Chem. Res. Appl.*, **2000**, *12*, 403
[15] Galleguillos H. R., Graber T. A., Taboada M. E., Hernández-Luis F., *Fluid Phase Equilibria.*, **2009**, *275*, 39
[16] Xie X. M., Xie W. H., *Chem. Res. Chinese Universities*, **1988**, *4*(3), 90
[17] Dehghani M. R., Modarress H., Monirifar M., *J. Chem. Thermodynamics*, **2005**, *37*, 1305
[18] Daniela Ž. P., Jelena M., Milica D. T., Milorad M. Z., Joseph A. R., *J. Chem. Thermodynamics*, **2012**, *55*, 172
[19] Abderrahim D., *J. Chem. Thermodynamics*, **2007**, *39*, 96
[20] Zhang X. K., Zhuo K. L., Ma J. J., Liu H. X., Wang J. J., *Chem. J. Chinese Universities*, **2009**, *30*(9), 1844
[21] Daniela Ž. P., Jelena M., Milica D. T., Milorad M. Z., Joseph A. R., *J. Chem. Thermodynamics.*, **2011**, *43*, 1877
[22] Zhang J. J., Sang S. H., Zhong S. Y., *J. Chem. Eng. Data*, **2012**, *57*, 2677
[23] Zhang J. J., Sang S. H., *J. Sichuan University: Engineering Science Edition*, **2012**, *44*, 240
[24] Harned H. S., Owen B. B., *Phys. Chem. Electrolytic Solut.*, Reinhold, New York, **1958**
[25] Harned H. S., Robinson R. A., *Multicomponent Electrolyte Solut.*, Pergamon Press, London, **1968**
[26] Pitzer K. S., *J. Phys. Chem.*, **1973**, *77*, 268
[27] Greenberg J. P., Møller N., *Geochimica et Cosmochimica Acta*, **1989**, *53*, 2503
[28] Archer D. G., Wang P., *J. Phys. Chem. Ref. Data*, **1990**, *19*, 371