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研究论文

298.15 K $Li_2B_4O_7$-$MgCl_2$-H_2O体系热力学性质的电动势法测定及离子相互作用模型的研究

张爱芸*，姚燕

([1]河南理工大学 焦作 454000)
([2]中国科学院青海盐湖研究所 西宁 810008)
([3]黑龙江科技学院 哈尔滨 150027)

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摘要 测定了298.15 K下, 无液接电池Li-ISE | $Li_2B_4O_7$ (m_A)(aq.), $MgCl_2$(m_B)(aq.) | AgCl/Ag的电动势, 利用测定结果计算了$Li_2B_4O_7$-$MgCl_2$-H_2O体系离子强度在0.05～3 mol•kg^{-1}范围内, 不同$MgCl_2$离子强度分数的溶液中LiCl的平均活度系数, 并给出了其随离子强度I, $B_4O_7^{2-}$和Mg^{2+}浓度的变化规律. 结合以往关于该体系和$Li_2B_4O_7$-LiCl-H_2O, $Li_2B_4O_7$-H_2O体系的等压研究结果, 用迭代和多元线性回归方法对Li^+-Mg^{2+}-Cl^--$B_4O_7^{2-}$-H_2O体系的离子相互作用模型进行了研究. 具体方法为考虑了该体系在不同的总硼浓度范围H_3BO_3, $B(OH)_4^-$, $B_3O_3(OH)_4^-$和$B_4O_5(OH)_4^{2-}$四种含硼化合物的存在以及各硼化合物间的化学平衡, 以修正了的Pitzer渗透系数方程和活度系数方程为基础, 对该体系的等压法和电动势法研究结果进行最小二乘拟合, 拟合的标准偏差为0.0167, 用该模型计算的该体系的渗透系数、活度系数与实验值基本一致.

关键词 $Li_2B_4O_7$-$MgCl_2$-H_2O体系 电动势法 等压法 平均活度系数 离子相互作用模型

分类号

Thermodynamic Studies by Electromotive Force Method and Ion Interaction Model for $Li_2B_4O_7$-$MgCl_2$-H_2O System at 298.15 K

ZHANG Ai-Yun*, YAO Yan

([1] *Henan Polytechnic University, Jiaozuo 454000*)
([2] *Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008*)
([3] *Heilongjiang Institute of Science and Technology, Harbin 150027*)

Abstract Values of electromotive force of the cell without liquid junction Li-ISE | $Li_2B_4O_7$(m_A)(aq.), $MgCl_2$(m_B)(aq.) | AgCl/Ag were determinaed at 298.15 K. The mean activity coefficients of LiCl in the system with ionic strengths from 0.05 to 3 mol•kg^{-1} at different ionstrength fraction Y_B of $MgCl_2$ have been calculated, together with the tendencies of these values along with the ion strengths and the concentrations of Mg^{2+} and $B_4O_7^{2-}$2B_4O_7-$MgCl_2$-H_2O system, but also from the isopiestic studies for systems $Li_2B_4O_7$-$MgCl_2$-H_2O, $Li_2B_4O_7$-LiCl-H_2O and $Li_2B_4O_7$-H_2O. The species of boric acid H_3BO_3 and borate anions $B(OH)_4^-$ $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$ have been taken into account in different total boron concentrations. To consider the stoichiometric molality equilibrium constants for the formation of the aqueous species containing boron, Pitzer's osmotic equation and activity equation have been modified slightly to represent the system, and the ion interaction parameters have been obtained using multiple regression analysis. The standard deviation of the calculated and experimentally determined activity coefficients of LiCl in $Li_2B_4O_7$-$MgCl_2$-H_2O system was 0.0167, which reflects that the set up model for the system with boron was adaptable to this four ion system.

Key words $Li_2B_4O_7$-$MgCl_2$-H_2O system electromotive force isopiestic mean activity coefficients ion interaction model

DOI:

通讯作者 张爱芸 dr_zay2004@yahoo.com.cn