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PII-66. Fast Methods of Debye-Hückel Limiting Slopes Calculation Based on Iapws Equation of State of Water

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Thermodynamic modeling of aqueous electrolyte solutions is an actual practical task. The most common models used for it are Pitzer, eNRTL and eUNIQUAC models that include Debye-Hückel term containing so called Debye-Hückel limiting slopes, i.e. A_φ and its derivatives:

$$G^{DH}/(\omega_w RT) = -4A_\varphi I\ln(1+bI^{0.5})/b;\ A_\varphi = (2\pi N_a \rho M_w)^{0.5} e^3 (4\pi\varepsilon\varepsilon_0 kT)^{-1.5}/3$$

$$A_V = -4RT(\partial A_\varphi/\partial p)_T;\ A_K = (\partial A_V/\partial p)_T;\ A_H/RT = 4T(\partial A_\varphi/\partial T)_p;\ A_C = (\partial A_H/\partial T)_p$$

It requires equations for water density ρ and dielectric constant ε. There are several commonly used ones but even minor differences between them have a strong influence on A_φ first and especially second derivatives, up to 70% for A_C and A_K. The most recent and consistent to ITS-90 temperature scale are IAPWS equations [1]. They are based on Helmholtz energy equation $F(V,T)$ and calculation of $\rho(p,T)$ requires time-consuming numeric methods. Existing tables of values have large T and p steps [1,2]. The aim of this work is development of new accurate approximations for Debye-Hückel limiting slopes based on IAPWS equations for water density and dielectric constant.

Two approaches were proposed for T>273.15 K. The first one is usage of IAPWS-IF97 equation that is based on Gibbs energy expression $G(p,T)$, valid for T=273.15-623.15 K and p=0-100 MPa and gives analytical expressions for A_φ. It makes A_φ and its derivatives computation 100 times faster. Maximal relative deviations are $\varepsilon(A_\varphi)=5.9\cdot10^{-3}\%$, $\varepsilon(A_H)=0.33\%$, $\varepsilon(A_C)=4.2\%$, $\varepsilon(A_V)=0.56\%$, $\varepsilon(A_K)=7.0\%$ (see Fig.1). In [3] it is mentioned that they are "low" but no estimations are given. The second are polynomials for A_φ that are valid for 273-423 K, 0-5 MPa and with accuracy comparable to the first variant. We also suggest expressions for extrapolation of A_φ from 273-373 K to 200-573 K interval. They are required for modeling of concentrated solutions.

All methods and formulas proposed in this work are implemented in open source computer programs that can be used as a library for computation of Debye-Hückel limiting slopes.

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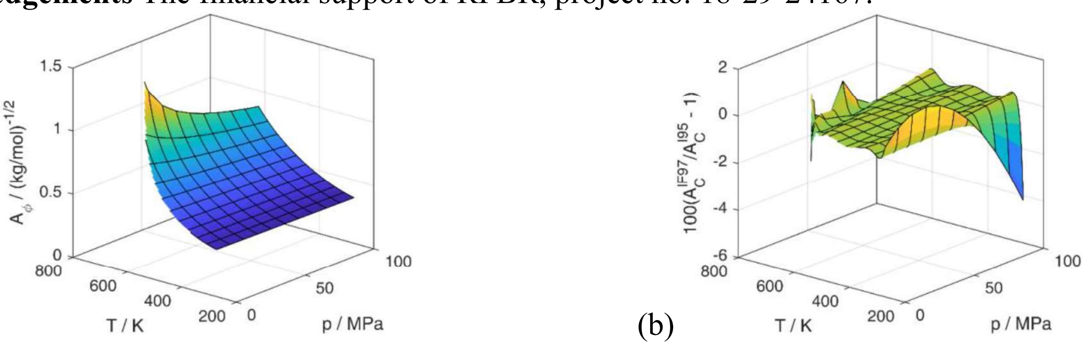

(a) (b)

Figure 1. (a) $A_\varphi(p,T)$ IAPWS95 function; (b) A_C: difference between IAPWS95 and IAPWS-IF97.

[1] D.P. Fernández, A.R.H. Goodwin et al., *J. Phys. Chem. Ref. Data*, 1997, 26, 1125.

[2] A.A. Aleksandrov, A.B. Matveev, *Teploenergetika, teplofizika: sbornik dokladov yubilejnoj nauchnoi konferencii*, MPEI, Moscow, 1998. P. 87 [in Russian].

[3] A.A. Aleksandrov, *Thermal Engineering*, 2000, 47, 561.