

A 3-parameter EoS to describe aqueous non-electrolytes at infinite dilution over a wide range of state parameters, with preliminary application to 1:1 electrolytes

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Abstract

A new equation of state (EoS) for describing the thermodynamic properties of aqueous non-electrolytes at infinite dilution is proposed. It is based on the accurate EoS for the solvent (H₂O) given by Hill (1990) and requires only three empirical parameters to be fitted to experimental data, and these are independent of temperature and pressure. Knowledge of the thermodynamic properties of the pure gas, together with these three parameters, enables prediction of the whole set thermodynamic properties of the solute at infinite dilution (chemical potential, entropy, molar volume, and apparent molar heat capacity) over a wide range of temperatures (0 - 500°C) and pressures (1 - 2000 bar), including the near-critical region. In the cases where experimental thermodynamic data are lacking, the empirical parameters can be estimated solely from the known standard-state properties of the solute. The proposed approach has been tested for non-polar (Ar, Ne, H₂, N₂, O₂, CO₂), polar (H₂S, NH₃, H₃BO₃) dissolved molecules, ion pairs (HCl, HF), and aqueous hydrocarbons (CH₄, C₂H₄, C₂H₆, C₃H₈, C₄H₁₀, C₆H₆). Some preliminary calculations show that the approach also has promise for the description of electrolytes.

Introduction

Proper thermodynamic description of neutral (uncharged) aqueous species in a wide pressure - temperature range is an important task with many practical applications in geochemistry and technology. Nevertheless, presently available thermodynamic descriptions of non-electrolytes are far less accurate than those of ionic species. For instance, the well known Helgeson-Kirkham-Flowers (HKF) equation of state (EoS) [1] provides excellent predictions of thermodynamic properties of aqueous ions over a wide range of conditions (0-600°C, 1-5000 bar). However, when extended to neutral aqueous species [2, 3], the HKF model does not predict the behaviour of non-electrolyte solutes correctly in the near-critical and supercritical regions of water [4 – 6].

This general deficiency is one of the reasons for the recent activity in the development of alternative EoS for aqueous non-electrolytes [5, 7 – 11]. The study presented here is

one such attempt. We propose a simple, low parametric EoS for aqueous non-electrolytes that is valid for a wide range of state parameters spanning ambient, near- and supercritical conditions.

Basic relations and development of the new EoS

The detailed derivation of the proposed EoS is given in our previous paper [12]. Here we shall give only a brief outline.

Proceeding from the virial EoS framework for a binary mixture, in which H₂O is the solvent (component 1) and in which a dissolved non-electrolyte is the solute (dissolved gas, component 2) at given pressure, P in bars, and temperature, T in K, the fugacity coefficient of the solute at infinite dilution, φ_2^∞ , can be expressed as (see, for example, [13])

$$\ln \varphi_2^\infty = \frac{2}{M_w} \rho_1^\circ B_{12} - \ln \frac{RT}{PM_w} \rho_1^\circ. \quad (1)$$

Here $R = 83.1441 \text{ cm}^3 \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is the gas constant, $M_w = 18.0153 \text{ g} \cdot \text{mol}^{-1}$ is the molar mass of H₂O, ρ_1° (in $\text{g} \cdot \text{cm}^{-3}$) indicates density of the pure solvent, and B_{12} stands for a virial cross-coefficient that characterizes interaction between the dissimilar molecules of the solute and the solvent. Evidently, in order to describe φ_2^∞ over a wide range of P , T conditions, we must know the dependence of B_{12} on P and T . The description of this function, in the simplest way possible, is the principal task of our study.

Prior to developing the function, some additional comments are due. Whereas the "traditional" formulation of the virial equation assumes that the second virial coefficient is independent of pressure and density (that is, B is a function of T only), our formulation treats B as a function of both P and T . Thus, to avoid any confusion, the term *virial* will no longer be used when referring to our B parameters below. It is nonetheless important to realise that our B parameters, as their original virial brethren, maintain their physical meaning as measures of close-range interactions between molecules.

The essential step of our approach is to find empirical P - T dependencies not directly for B_{12} , but *with respect to the known B values of the solvent (i.e. B_1)*. The simplest route to this end is to use an expression analogous to (1) for the fugacity coefficient of the pure solvent:

$$\ln \varphi_1^\circ = \frac{2}{M_w} \rho_1^\circ B_1 - \ln \frac{RT}{PM_w} \rho_1^\circ, \quad (2)$$

and to "compare" equation (1) for $\ln \varphi_2^\infty$ not directly with equation (2) for pure H₂O, but with a "scaled H₂O molecule", increased in size by $(1-\xi)$ times (ξ being a dimensionless, empirically fitted factor, as introduced by Plyasunov et al. [10]). Thus, we multiply (2)

by $(1-\xi)$ and then subtract it from (1). Using the well-known relation between Henry constant of the solute k_H (in bars) and φ_2^∞ [13]

$$\ln k_H = \ln(\varphi_2^\infty \cdot P), \quad (3)$$

we finally obtain

$$\ln k_H = (1-\xi) \cdot \ln f_1^\circ + \xi \ln \left(\frac{RT}{M_w} \cdot \rho_1^\circ \right) + 2\rho_1^\circ \cdot \Delta B_\rho, \quad (4)$$

Here $f_1^\circ \equiv \varphi_1^\circ P$ stands for the fugacity (in bars) of the pure solvent (H₂O) at given P - T conditions, $\Delta B = \Delta B_\rho \cdot M_w$, ξ is the empirical scaling factor, and $\Delta B \equiv B_{12} - (1-\xi) \cdot B_1$ stands for the difference in interaction between dissimilar molecules, versus that between "scaled" pure solvent molecules.

In order to find the appropriate P - T dependency of ΔB_ρ , we have tested diverse two- and three-parameter formulations using available experimental data on k_H for various dissolved gases at different temperatures (Ar – [14, 15]; CH₄ – [14, 16, 17]; CO₂ – [18 - 23]; N₂ – [15, 24]; H₂ – [15, 24, 25]; H₂S – [26 -30]; O₂ – [15, 31]; NH₃ – [32, 33]). It was found that the best fit within the group of two-parameter equations is given by the approximation

$$2\Delta B_\rho = a + b \left(\frac{10^3}{T} \right)^{0.5}. \quad (5)$$

Here a (in cm³·g⁻¹) and b (in cm³·K^{0.5}·g⁻¹) denote the adjustable parameters.

Taking into account the basic thermodynamic relation between k_H and the chemical potential of the dissolved component, $\mu_{2,aq}^\circ$ [13],

$$\ln(k_H) = \ln N_w - \frac{\mu_{2,aq}^\circ - \mu_g^\circ}{\tilde{R}T} \quad (6)$$

we finally obtain:

$$\begin{aligned} \mu_{2,aq}^\circ(P, T) = & \mu_g^\circ(T) - \tilde{R}T \ln N_w + (1-\xi)\tilde{R}T \ln f_1^\circ + \\ & \tilde{R}T \xi \ln \left(\frac{RT}{M_w} \rho_1^\circ \right) + \tilde{R} \left\{ T \rho_1^\circ \cdot \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right\}. \end{aligned} \quad (7)$$

In these expressions, $\mu_g^\circ(T)$ is the chemical potential of the pure perfect gas in cal·mol⁻¹ at standard pressure (1 bar), and $\tilde{R} = 1.9872$ cal·mol⁻¹·K⁻¹ is the gas constant.

Thus, our equation of state (7) contains three empirical constants that are independent of pressure and temperature: a "scaling" factor ξ , and two others (a and b) to account for the temperature dependence of ΔB_ρ (5). Equation (7) yields the correct low-density limit for all thermodynamic properties of the solute, as noted for similar equations by Plyasunov et al. [10].

Derivatives of (7) with respect to pressure and temperature provide the relations for partial molar volume, entropy and heat capacity of the dissolved component, as follows:

$$V_2^\circ \equiv \left. \frac{\partial \mu_{aq}^\circ}{\partial P} \right|_T = V_1^\circ (1 - \xi) + \xi RT \frac{1}{\rho_1^\circ} \frac{\partial \rho_1^\circ}{\partial P} + R \frac{\partial}{\partial P} \left\{ T \rho_1^\circ \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right\}. \quad (8)$$

$$S_{2,aq}^\circ \equiv \left. -\frac{\partial \mu_{aq}^\circ}{\partial T} \right|_P = S_{2,g}^\circ + (1 - \xi)(S_1^\circ - S_{1,g}^\circ) + \tilde{R} \ln N_w - \quad (9)$$

$$\tilde{R} \left(\xi + \xi \ln \frac{RT}{M_w} + \xi \ln \rho_1^\circ + \xi T \frac{1}{\rho_1^\circ} \frac{\partial \rho_1^\circ}{\partial T} \right) - \tilde{R} \frac{\partial}{\partial T} \left\{ T \rho_1^\circ \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right\}.$$

$$C_{p2}^\circ \equiv -T \left. \frac{\partial^2 \mu_{aq}^\circ}{\partial T^2} \right|_P = C_{p2,g}^\circ + (1 - \xi)(C_{p1}^\circ - C_{p1,g}^\circ) -$$

$$\tilde{R} \left(\xi + 2\xi T \frac{1}{\rho_1^\circ} \frac{\partial \rho_1^\circ}{\partial T} - \xi \frac{T^2}{(\rho_1^\circ)^2} \left(\frac{\partial \rho_1^\circ}{\partial T} \right)^2 + \xi \frac{T^2}{\rho_1^\circ} \frac{\partial^2 \rho_1^\circ}{\partial T^2} \right) - \tilde{R} T \frac{\partial^2}{\partial T^2} \left\{ T \rho_1^\circ \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right\}. \quad (10)$$

Estimation of the empirical parameters (ξ , a , and b)

Calculation of thermodynamic properties of the dissolved species using equations (7) to (10) is extremely sensitive to the properties of the pure solvent. Thus, the properties of H₂O must be known with high accuracy over the entire range of state parameters. In this study the thermodynamic properties of pure water were calculated using the unified EoS given by Hill [34]. Data for ideal gaseous H₂O (steam) were taken from CODATA Key Values for Thermodynamics [35].

Having derived a modified virial-like equation of state (7-10), we now describe the fitting of the 3 empirical constants, ξ , a and b . Experimental values of V_2° at standard-state conditions were used with available experimental data on k_H of the dissolved species to estimate the three empirical parameters. The estimation procedure is iterative. In the first step the scaling factor is set to zero. The available experimental data on k_H at various temperatures and pressures are then used to calculate values of the a and b parameters by means of the least-squares method. Using these initial a and b values the ξ parameter is calculated on the basis of the known partial molar volume of the solute (V_2°) at standard-state conditions (25°C and 1 bar), according to (8). The resulting ξ value is then used to estimate a and b in the next iteration, and so on. This fitting

procedure usually needs less than 4 iterations to reach a precision of $\approx 0.03 \text{ cm}^3 \cdot \text{mol}^{-1}$ for V_2^0 at 25°C and 1 bar. The retrieved empirical parameters of the EoS for several species are given in Table 1, and the quality of the fit for some dissolved gases is illustrated in Figs. 1 to 3.

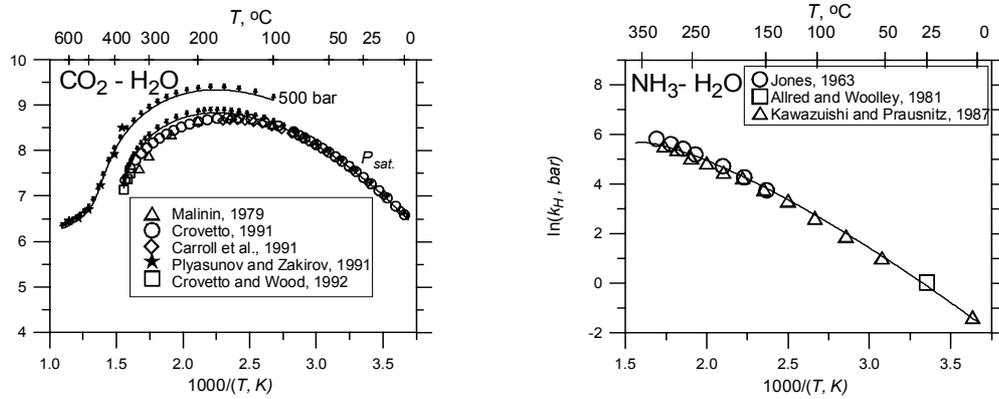


Fig. 1. Natural logarithm of Henry's constant, $\ln k_{\text{H}}$, for non-polar (CO_2) and polar (NH_3) dissolved molecules at vapour-saturated water pressure (P_{sat}) and other specified pressures, plotted against reciprocal temperature. Symbols correspond to experimental data. Continuous curves are our EoS predictions using equations 6 and 7 and data from Table 1.

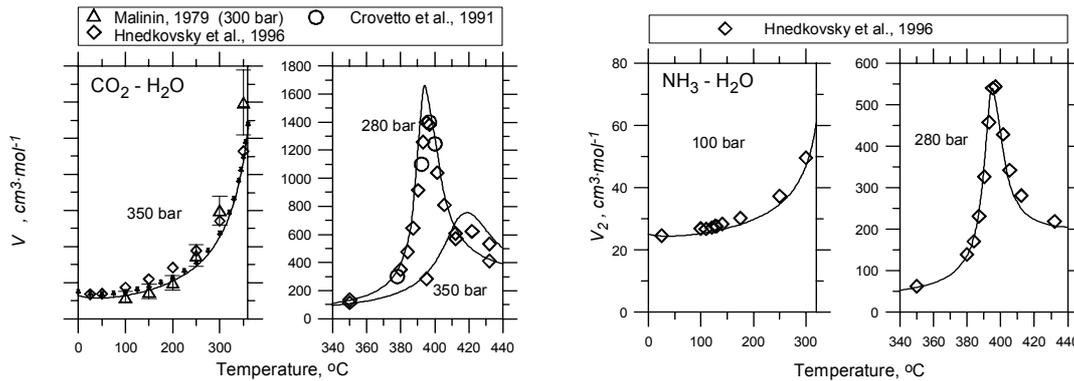


Fig. 2. Partial molar volumes of non-polar (CO_2) and polar (NH_3) dissolved molecules at subcritical (left) and supercritical (right) conditions. Symbols correspond to experimental data. Solid curves are our EoS predictions at infinite dilution (equation 8 and data from Table 1).

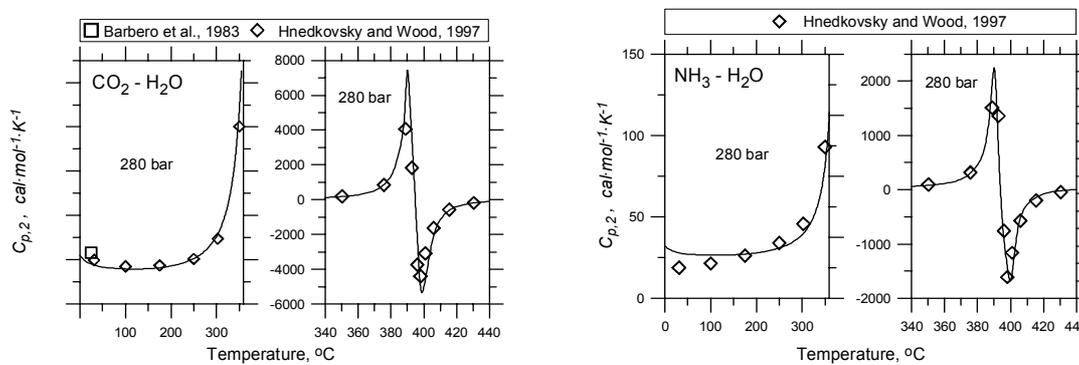


Fig. 3. Apparent molar heat capacities of non-polar (CO_2) and polar (NH_3) dissolved molecules at subcritical (left) and supercritical (right) temperatures. Symbols denote experimental data. Solid curves are our EoS predictions at infinite dilution and P, T of interest (equation 10 and data from Table 1).

The empirical parameters could be easily estimated even when high-temperature experimental data were lacking. It can be seen that equations 7 to 10 are linear with respect to the empirical parameters ξ , a , and b . Thus, the parameters could be readily obtained using only known standard-state $\mu_{2,aq}^0$, $S_{2,aq}^0$, and V_2^0 values of the dissolved species. Data for aqueous species retrieved on the basis of known standard-state properties are also given in Table 2, and the quality of corresponding description is illustrated in Fig. 4, 5 for aqueous $B(OH)_3$.

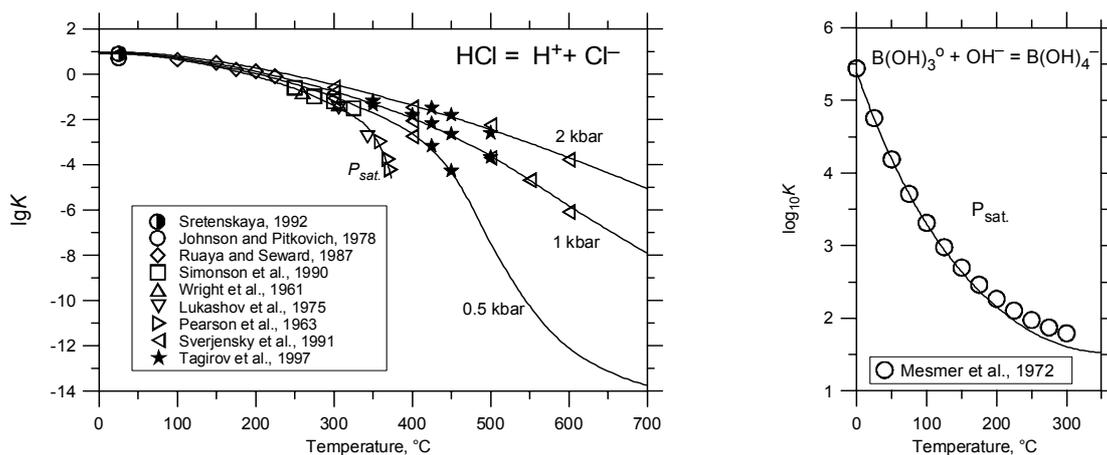


Fig. 4. Logarithm of equilibrium constants for acid dissociation reactions for HCl and boric acid as a function of temperature at specified pressures. Symbols represent experimental data, curves are theoretical predictions. Data for neutral species are taken from Tables 1 and 2 and calculated using our EoS; ionic species are calculated using the HKF EoS with data for Cl^- , and OH^- from SUPCRT92 [46], and for $B(OH)_4^-$ from Pokrovski et al. [42].

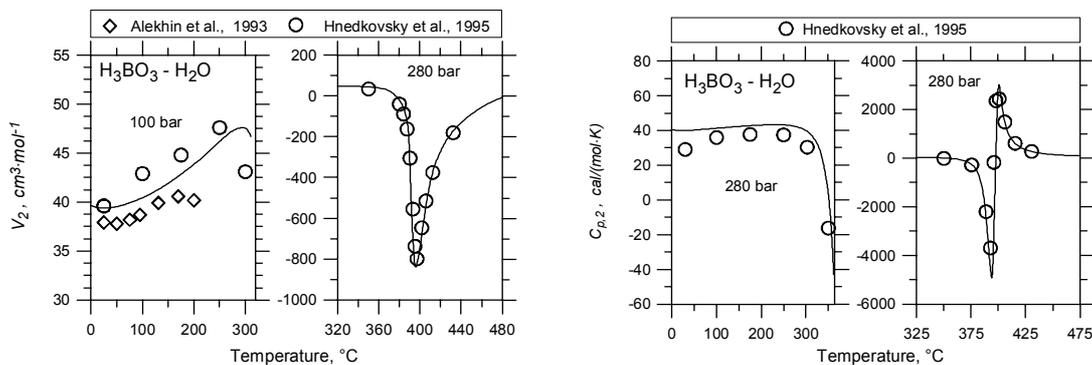


Fig. 5. Volumes and heat capacities of boric acid at subcritical (left) and supercritical (right) temperatures. Symbols denote experimental data. Solid curves are our EoS predictions at infinite dilution (equations 8 and 10, model parameters in Table 2).

Discussion

The new EoS can be viewed as a development of the semi-empirical approach derived by Japas and Levelt Sengers [44]. These authors adopted a linear relationship between ΔB and the reciprocal temperature, T^{-1} , whereas we have used an approximation (5) that provides better linearity to the T -derivative of $\ln k_H$. It is interesting to observe that

equation (15) is similar to the Redlich and Kwong equation [45], where the intermolecular parameter is set proportional to $T^{-0.5}$.

Our new EoS works well even for strongly dipolar molecules (HF_{aq} , HCl_{aq} , Fig. 4) and for boric acid ($\text{H}_3\text{BO}_{3,\text{aq}}$) (Figs. 4 and 5). The latter is known to exhibit negative divergence of V_2° and C_{p2}° near the critical point of H_2O , in contrast to most other non-electrolytes [43]. Accordance between the experimental data and our model predictions is quite fair, especially considering that the empirical parameters for $\text{H}_3\text{BO}_{3,\text{aq}}$ were retrieved solely on the basis of known standard-states properties.

We have also made a preliminary attempt to describe an aqueous electrolyte (Na^+Cl^-) using the proposed approach. Here, however, some new assumptions must be introduced.

Let us break down the process of hydration of gaseous ion, A_g (process 1 in Fig. 6) into several steps: transfer of N_A solvent molecules from the liquid to the ideal gaseous state (stage 2), "hydration" of A_g in the gaseous phase, forming a cluster, $A_{g,h} \equiv A_g \cdot (\text{H}_2\text{O})_{N_A}$ (stage 3), and transfer of the cluster from ideal gaseous to the aqueous environment A_{aq}

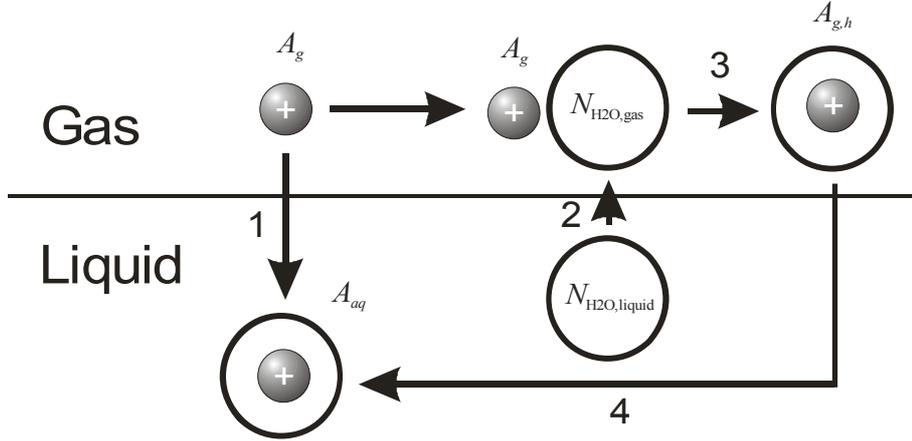


Fig. 6. Imaginary thermodynamic cycle for hydration of species A .

(stage 4). Thus, total Gibbs hydration energy of A_g is

$$\Delta_1 G \equiv \mu_{A_{\text{aq}}} - \mu_{A_g}^\circ = N_A (\mu_{w,g}^\circ - \mu_{w,l}) + [\mu_{A_{g,h}}^\circ - (\mu_{A_g}^\circ + N_A \mu_{w,g}^\circ)] + (\mu_{A_{\text{aq}}} - \mu_{A_{g,h}}^\circ). \quad (11)$$

Here $\mu_{A_{\text{aq}}}$, $\mu_{A_g}^\circ$, $\mu_{A_{g,h}}^\circ$ stand for the chemical potential of A in the aqueous, gaseous and cluster states correspondingly; $\mu_{w,g}^\circ$, $\mu_{w,l}$ are the chemical potentials of pure H_2O in the gaseous and liquid states, and the superscript "°" for μ denotes the perfect gaseous state at $P = 1$ bar. Using the proposed EoS (7) for the last stage of the process (stage 4), we finally have

$$\begin{aligned} \mu_{A_{\text{aq}}} = & \mu_{A_{g,h}}^\circ - RT \ln N_w + (1 - \xi_A - N_A) \mu_{w,l} - (1 - \xi_A) \mu_{w,g}^\circ + \\ & RT \xi_A \ln \frac{RT}{M_w} \rho_1^\circ + RT \rho_1^\circ \cdot \left[a_A + b_A \left(\frac{10}{T} \right)^{0.5} \right]. \end{aligned} \quad (12)$$

Here, as above, ξ_A , a_A , and b_A are the empirical model parameters for species A .

For the electrolyte of AB type (i.e. Na^+Cl^-), we then obtain

$$\begin{aligned} \mu_{AB_{aq}} = & \left(\mu_{A_{g,h}}^{\circ} + \mu_{B_{g,h}}^{\circ} \right) - 2RT \ln N_w + (2 - \xi - N) \mu_{w,l} - (2 - \xi) \mu_{w,g}^{\circ} + \\ & RT \xi \ln \frac{RT}{M_w} \rho_1^{\circ} + RT \rho_1^{\circ} \cdot \left[a + b \left(\frac{10}{T} \right)^{0.5} \right], \end{aligned} \quad (13)$$

where $N \equiv N_A + N_B$, and $\xi \equiv \xi_A + \xi_B$. Derivation of (13) leads to the following modifications of (8, 10) for partial molar properties of the electrolyte

$$V_{AB_{aq}}^{\circ} = V_1^{\circ} (2 - \xi - N) + \xi RT \frac{1}{\rho_1^{\circ}} \frac{\partial \rho_1^{\circ}}{\partial P} + R \frac{\partial}{\partial P} \left\{ T \rho_1^{\circ} \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right\}. \quad (14)$$

$$\begin{aligned} C_{p_{AB_{aq}}}^{\circ} = & C_{p_{AB_{g,h}}}^{\circ} + (2 - \xi - N) C_{p_{w,l}} - (2 - \xi) C_{p_{w,g}} - \\ & \tilde{R} \xi \left(1 + 2T \frac{1}{\rho_1^{\circ}} \frac{\partial \rho_1^{\circ}}{\partial T} - \frac{T^2}{(\rho_1^{\circ})^2} \left(\frac{\partial \rho_1^{\circ}}{\partial T} \right)^2 + \frac{T^2}{\rho_1^{\circ}} \frac{\partial^2 \rho_1^{\circ}}{\partial T^2} \right) \\ & - \tilde{R} T \frac{\partial^2}{\partial T^2} \left\{ T \rho_1^{\circ} \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right\}. \end{aligned} \quad (15)$$

Here $C_{p_{AB_{g,h}}}^{\circ} = C_{p_{A_{g,h}}}^{\circ} + C_{p_{B_{g,h}}}^{\circ}$ (the sum of heat capacities of the gaseous cluster molecules) and N (the hydration number of the electrolyte) should be assumed as additional adjustable parameters.

Equations (14, 15) with $N = 10.502$, $\xi = -10.802$, $a = 21.819$, $b = -18.017$ and $C_{p_{A_{g,h}}}^{\circ} = 75.0 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ were used to describe temperature dependencies of partial molar volumes and heat capacities of Na^+Cl^- at different pressures. The very plausible result of the description is shown in Fig. 7.

Concluding remarks

Figures 1 to 3 demonstrate that our EoS provides good predictions of the entire set of investigated thermodynamic properties (chemical potential, entropy, molar volume and heat capacity) of aqueous species at infinite dilution, over a wide $P - T$ range encompassing the H_2O critical region. The EoS works well with both non-polar (CO_2 , N_2 , etc.) and polar (NH_3 , H_2S , etc.) neutral species. In terms of the Henry constant, k_H , the standard deviations of the predictions with respect the experimental data are less than $0.05 \log_{10}$ units, and the standard deviation is about 0.08 units in the case of H_2S . The accuracies of the calculated temperature dependencies of V_2° and $C_{p_2}^{\circ}$ are good

measures of the predictive capacity of the new EoS, since the corresponding experimental data were not used in the estimation procedure.

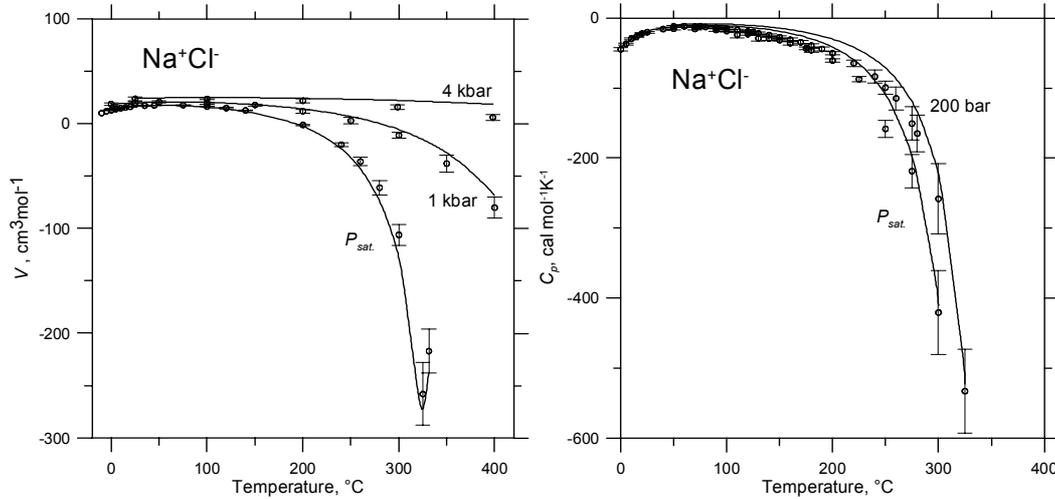


Fig. 7. Volumes (left) and heat capacities(right) of aqueous electrolyte NaCl vs. temperatures at specified pressures. Symbols denote various experimental data available on the web-site at www.kfy.vslib.cz/aqueous/download.htm. Solid curves are our EoS predictions at infinite dilution (equations 14 and 15, model parameters in the text).

Our new EoS is formulated with the same standard state as the HKF model, which is highly successful for charged species, and it is fully compatible with the SUPCRT92 database of thermodynamic properties [46]. Therefore, there are no restrictions on applying our equation to reactions involving minerals, gases and aqueous ions, in addition to uncharged species.

The performance of our new EoS is remarkably promising, considering that only 3 empirical constants need to be fitted to experimental data. Other published EoS perform equally well in some instances, but these equations contain 5 or more empirical parameters. Nevertheless, the development of our EoS is far from complete. One of the goals of this paper is to call the attention of the scientific community to the advantages of our approach, so that it may be improved by common efforts. Firstly, some discrepancies in C_{p2}° , especially at low temperatures and for large molecules, must be reduced. Secondly, the EoS cannot be used automatically to describe aqueous electrolytes. Our preliminary attempts have required the introduction of two additional parameters to describe V_2° and C_{p2}° behaviour for electrolytes. Nevertheless, we hope that using the *ab initio* calculations presented by Wood [47] to predict the properties of hydrated gaseous species, may reduce the number of adjustable parameters for electrolytes.

The new EoS is available in the form of a computer code allowing calculations in units of calories or joules, in a format which is directly compatible with the SUPCRT92 database [46]. The code can be free downloaded from the <http://www.geo.unibe.ch/Akinfiiev/index.html>.

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Tables

Table 1. Empirical parameters of the EoS (ξ , a , b ; see equations 7 to 10) for a number of dissolved gas species, estimated from the experimentally determined temperature dependence of Henry's constant. Where listed, the experimental value for partial molar volume of the solute, V_2° , at standard-state conditions was used in the fitting.

Species	V_2° ^a	Source for V_2°	ξ	a	b
	$\text{cm}^3 \cdot \text{mol}^{-1}$			$\text{cm}^3 \cdot \text{g}^{-1}$	$\text{cm}^3 \cdot \text{K}^{0.5} \cdot \text{g}^{-1}$
Ar	32.6	[36]	0.0733	-8.5139	11.9210
H ₂ S	34.9	[37]	-0.2102	-11.2303	12.6104
O ₂	33.2	[36]	0.0260	-9.7540	12.9411
N ₂	35.7	[36]	-0.0320	-11.5380	14.6278
NH ₃	24.4	[38]	-0.0955	-4.7245	4.9782
H ₂	25.2	[39]	0.3090	-8.4596	10.8301
CH ₄	37.3	[39]	-0.1131	-11.8462	14.8615
CO ₂	32.8	[37]	-0.0850	-8.8321	11.2684
C ₆ H ₆			-1.1010	-21.0084	22.9340
HCl			-0.2800	11.6420	-7.4244

(a) Partial molar volume of aqueous species at 298.15 K, 1 bar

Table 2. Empirical parameters of the EoS (ξ , a , b ; see equations 7 to 10) for a number of dissolved gas species, estimated from known standard-state properties only.

Species	$\mu_{2,aq}^{\circ}$ ^a	$S_{2,aq}^{\circ}$ ^a	V_2° ^a	ξ	a	b
	cal·mol ⁻¹	cal·mol ⁻¹ K ⁻¹	cm ³ ·mol ⁻¹		cm ³ ·g ⁻¹	cm ³ ·K ^{0.5} ·g ⁻¹
Ar	3900 ^b	14.30 ^b	31.71 ^b	0.0733	-7.6895	11.4657
Ne	4565 ^b	16.74 ^b	20.40 ^b	0.5084	1.0014	4.7976
H ₂ S	-6673 ^b	30.00 ^b	34.90 ^b	-0.2029	-13.4481	13.8821
CH ₄	-8234 ^c	20.99 ^c	37.30 ^c	-0.1196	-10.9926	14.4019
C ₂ H ₄	19450 ^c	28.70 ^c	45.50 ^c	-0.4499	-16.8037	18.8460
C ₂ H ₆	-4141 ^d	26.75 ^d	51.20 ^d	-0.6091	-16.3482	20.0628
C ₃ H ₈	-2021 ^d	33.49 ^d	67.00 ^d	-1.1471	-25.3879	28.2616
C ₄ H ₁₀	99 ^d	39.66 ^d	82.80 ^d	-1.6849	-33.8492	36.1457
C ₆ H ₆	32000 ^d	35.62 ^d	83.50 ^d	-1.9046	-39.1090	37.5421
H ₃ BO ₃	-231540 ^e	38.79 ^e	39.60 ^f	-1.0850	-3.5423	3.4693
HF	-71662 ^b	22.50 ^b	12.50 ^b	0.1008	3.0888	-3.5714
SO ₂	-71980 ^b	38.70 ^b	38.50 ^b	-0.4295	-14.5223	14.3512

(a) Standard-state properties of aqueous species at 298.15 K, 1 bar, used in the estimation procedure; $\mu_{2,aq}^{\circ}$, chemical potential at infinite dilution; $S_{2,aq}^{\circ}$, partial molar entropy; V_2° , partial molar volume; (b) [2]; (c) [40]; (d) [41], (1997); (e) [42]; (f) [43].