An Equation of State for Electrolyte Solutions

(Single Volatile Weak Electrolytes in Water)

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CONTENTS

Introduction

- Application of thermodynamic properties of volatile weak electrolytes in aqueous solutions
  - Fertilizer industry, food industry, chemical industry, environmental engineering

- Historical approach
  - based on Pitzer's equation (1973) ：
    Edwards et al. (1975,1978)
  - based on NRTL theory
    charge-charge & charge-molecule interaction :
    Cruz and Renon (1978,1979)
    Chen and Evans (1986)
    Chen et al (1979, 1980)

Introduction

  - PHC equation ：
    Daumn et al (1986)
- Perturbation theory (Jin & Donohue, 1988)
  - Charge-charge interaction
  - Charge-molecule interaction
  - PACT (Perturbation Anisotropic Chain Theory) :
    4 parameters (s,q,ε,c)
    - Neutral molecules : PACT fitting (vapor pressure & liquid density)
    - Ion molecules : calculated by ionic radius and polarizability
- No adjustable parameters determined by fitting the equation to experimental data

Thermodynamic Analysis

- Vapor-liquid equilibria

$$f_i^{v}(T,P) = f_i^{l}(T,P)$$

$$f_{el,m}^{v} = y_{el}\varphi_{el}^{v}P$$

$$f_{el,m}^{l} = m_{el,m}\gamma_{el,m}H_{el}$$

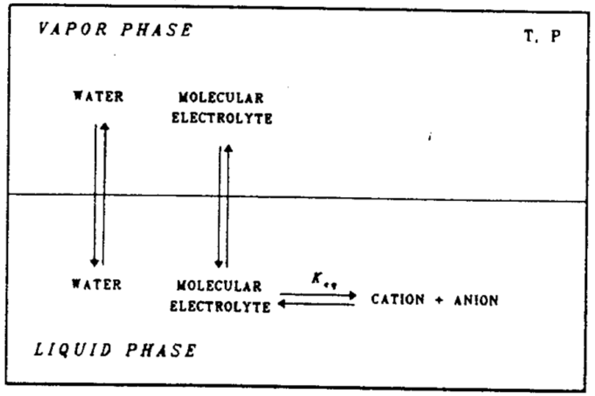

Figure 1. Schematic illustration of vapor–liquid equilibria for an aqueous solution containing single volatile weak electrolyte at temperature *T* and pressure *P*.

- Henry's Constant , H

$$H_{el} = \lim_{m_{el,m}\to 0} \frac{y_{el}\varphi_{l}^{v}P}{m_{el,m}} = \lim_{m_{el,m}\to 0} \varphi_{el}^{l}P$$

Thermodynamic Analysis

- Overall mass balance

$$m_{el,b} = m_{el,m} + \frac{m_{+} + m_{-}}{v}$$

- Dissociation

$$K_{eq} = \frac{m_{+}^{v+} m_{-}^{v-}}{m_{el,m}} \frac{\gamma_{\pm}^{v}}{\gamma_{el,m}}$$

- Charge balance

$$\sum_{i} z_i m_{ion,i} = 0$$

Equation of State

- EoS can be obtained from Helmholtz free energy

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

- Helmholtz free energy
  - Perturbed Anisotropic Chain Theory (Vimalchand et al,1985)

Ideal gas contribution

Attractive term

$$A = A^{IG} + A^{REP} + A^{ATT}$$

Repulsive term
Carnahan and Starling (1972)

Equation of State

- Attractive term $A^{ATT} = A^{MM} + A^{CC} + A^{CM}$

$$A^{MM} = A^{LJ} + A^{DID} + A^{DD} + A^{QQ} + A^{DQ}$$

A^{CC} : long range charge-charge interaction
perturbation expansion about a hard-sphere

$$A^{CM} = A^{CD} + A^{CID}$$

- Equation of State

$$P = P^{IG} + P^{REP} + P^{LJ} + P^{DID} + P^{DD}$$

$$+ P^{QQ} + P^{DQ} + P^{CC} + P^{CD} + P^{CID}$$

Equation of State

- Chemical potential $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$

- Properties for VLE calculation : φ_i, H, γ_i

$$\varphi_i^{(\pi)} = \frac{RT}{v^{(\pi)}P}\exp\left(\frac{\mu_i^{r(\pi)}}{RT}\right) \qquad H_i = \frac{RT}{v_w}\exp\left(\frac{\mu_i^{r(l)}(m_{el} \to 0)}{RT}\right)$$

$$\gamma_i = \frac{RT}{v^{(l)}H_i}\exp\left(\frac{\mu_i^{r(l)}}{RT}\right) \qquad \gamma_w = \frac{RT}{v^{(l)}\varphi_w^{sat}P_w^{sat}}\exp\left(\frac{\mu_w^{r(l)}}{RT}\right)$$

Determination of Parameters for Ions

- Each particle can be divided into ‘s’ equal-size : interactions between two particles can be considered as a sum of the segmental interactions of them
- Each particle has surface area ‘q’, interaction energies per unit surface area ‘ε’
- PACT contains another parameter, ‘c’
  - For simple molecules , c=1
- Parameters for Molecule

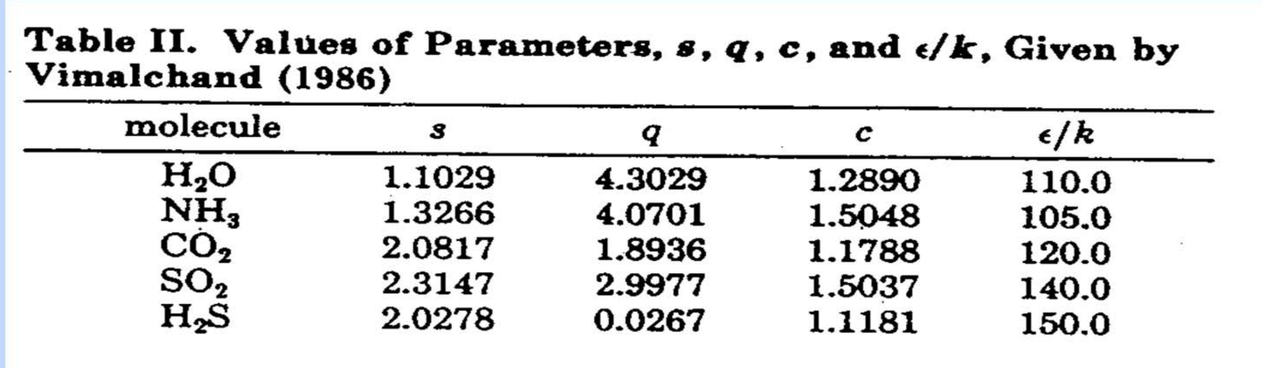

Table II. Values of Parameters, s, q, c, and ϵ/k, Given by Vimalchand (1986)

molecule	s	q	c	ϵ/k
H_2O	1.1029	4.3029	1.2890	110.0
NH_3	1.3266	4.0701	1.5048	105.0
CO_2	2.0817	1.8936	1.1788	120.0
SO_2	2.3147	2.9977	1.5037	140.0
H_2S	2.0278	0.0267	1.1181	150.0

Determination of Parameters for Ions

- Parameters for ions

$$s_{ion} = C_s \frac{r_{ion}^3}{r_{CH2}^3} \qquad q_{ion} = \frac{r_{ion}^2}{r_{CH2}^2}$$

$$\frac{\varepsilon_{ion}}{k} = 356 \frac{\alpha_{ion}^{3/2} (n_{e,ion})^{0.5}}{r_{CH2}^6}$$

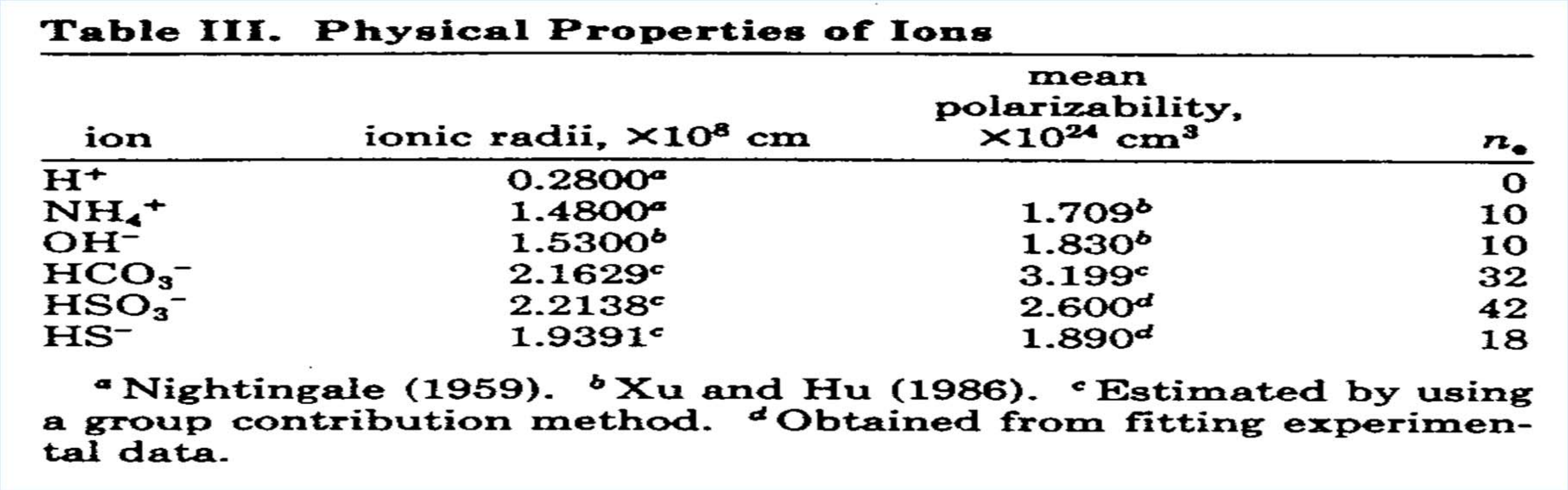

Table III. Physical Properties of Ions

ion	ionic radii, ×10⁸ cm	mean polarizability, ×10²⁴ cm³	n_e
H^+	0.2800[a]		0
NH_4^+	1.4800[a]	1.709[b]	10
OH^-	1.5300[b]	1.830[b]	10
HCO_3^-	2.1629[c]	3.199[c]	32
HSO_3^-	2.2138[c]	2.600[d]	42
HS^-	1.9391[c]	1.890[d]	18

[a] Nightingale (1959). [b] Xu and Hu (1986). [c] Estimated by using a group contribution method. [d] Obtained from fitting experimental data.

Calculations and Results

- Equilibrium constant K

$$\ln K = A_1 / T + A_2 \ln T + A_3 T + A_4$$

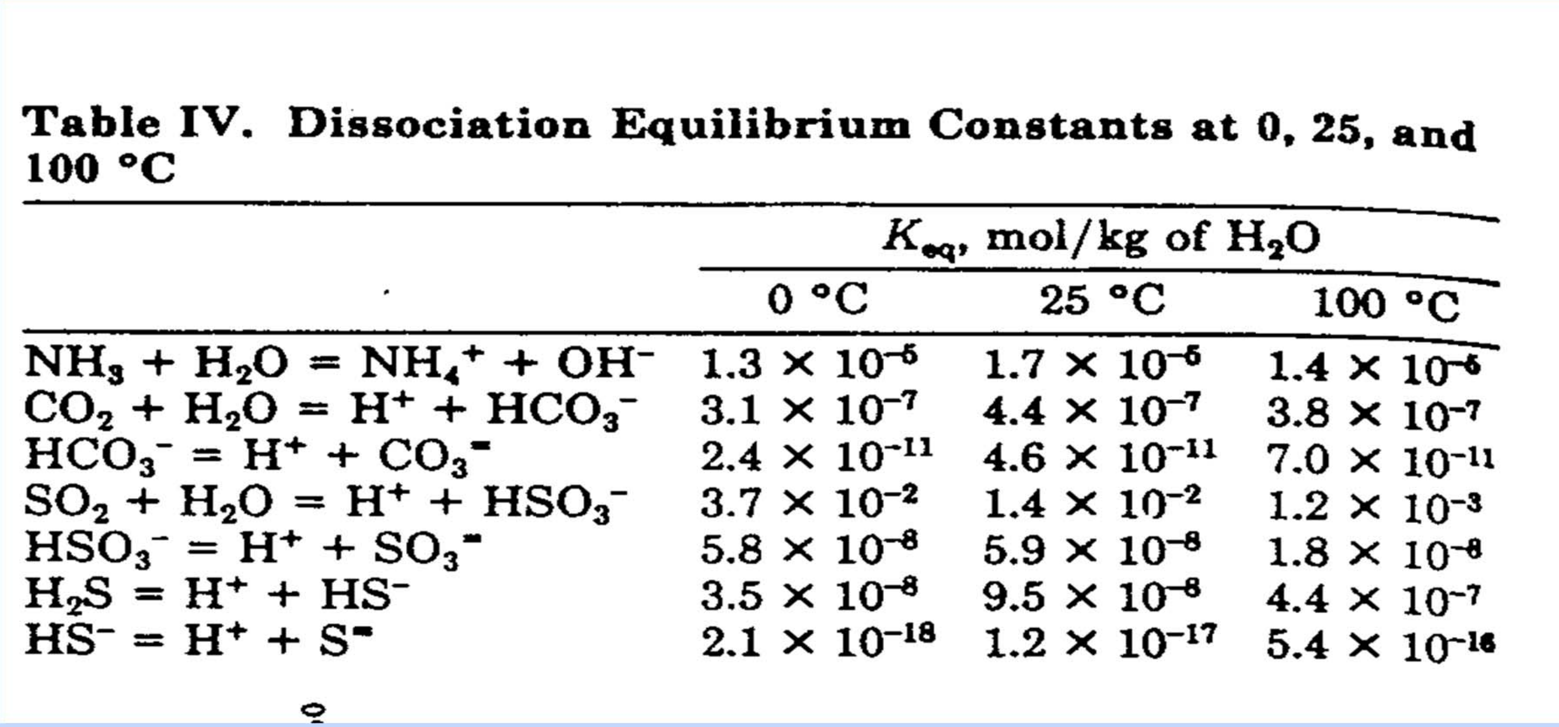

Table IV. Dissociation Equilibrium Constants at 0, 25, and 100 °C

	K_{eq}, mol/kg of H_2O		
	0 °C	25 °C	100 °C
$NH_3 + H_2O = NH_4^+ + OH^-$	1.3×10^{-5}	1.7×10^{-5}	1.4×10^{-5}
$CO_2 + H_2O = H^+ + HCO_3^-$	3.1×10^{-7}	4.4×10^{-7}	3.8×10^{-7}
$HCO_3^- = H^+ + CO_3^=$	2.4×10^{-11}	4.6×10^{-11}	7.0×10^{-11}
$SO_2 + H_2O = H^+ + HSO_3^-$	3.7×10^{-2}	1.4×10^{-2}	1.2×10^{-3}
$HSO_3^- = H^+ + SO_3^=$	5.8×10^{-8}	5.9×10^{-8}	1.8×10^{-8}
$H_2S = H^+ + HS^-$	3.5×10^{-8}	9.5×10^{-8}	4.4×10^{-7}
$HS^- = H^+ + S^=$	2.1×10^{-18}	1.2×10^{-17}	5.4×10^{-16}

Calculations and Results

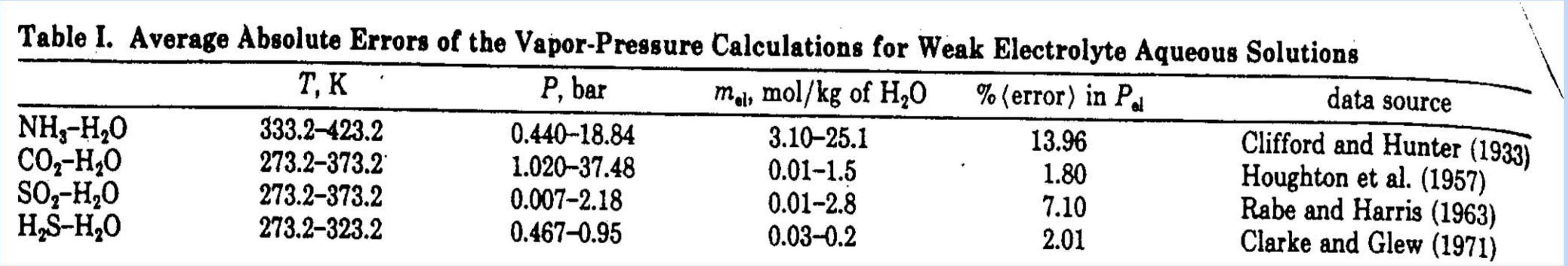

Table I. Average Absolute Errors of the Vapor-Pressure Calculations for Weak Electrolyte Aqueous Solutions

	T, K	P, bar	m_{el}, mol/kg of H_2O	% ⟨error⟩ in P_{el}	data source
NH_3-H_2O	333.2–423.2	0.440–18.84	3.10–25.1	13.96	Clifford and Hunter (1933)
CO_2-H_2O	273.2–373.2	1.020–37.48	0.01–1.5	1.80	Houghton et al. (1957)
SO_2-H_2O	273.2–373.2	0.007–2.18	0.01–2.8	7.10	Rabe and Harris (1963)
H_2S-H_2O	273.2–323.2	0.467–0.95	0.03–0.2	2.01	Clarke and Glew (1971)

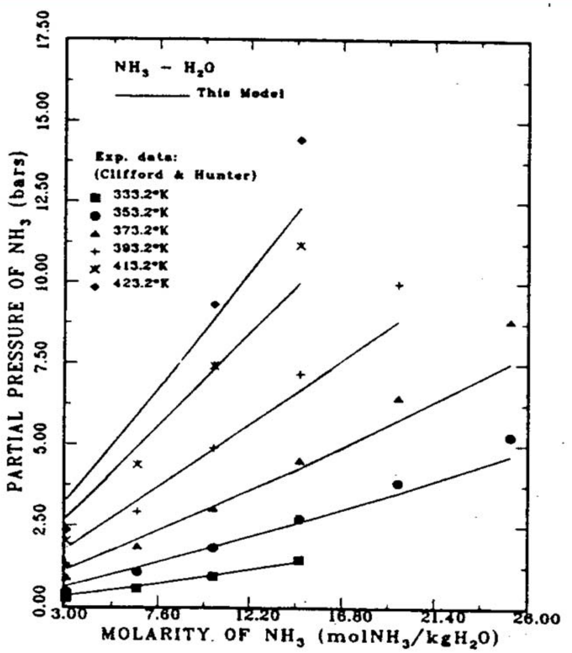

Figure 2. Calculated vapor pressures of ammonia in water at VLE compared with experimental data of Clifford and Hunter (1933).

per kilogram water) in molecular form

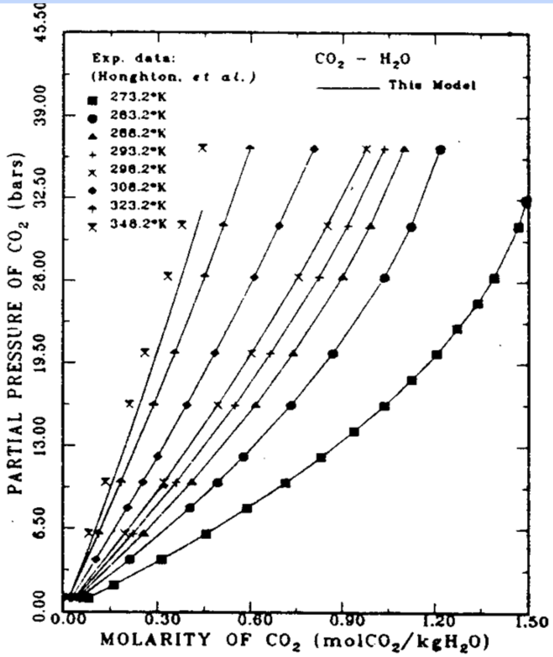

Figure 3. Calculated vapor pressures of carbon dioxide in water at VLE compared with experimental data of Houghton et al. (1957).

Calculations and Results

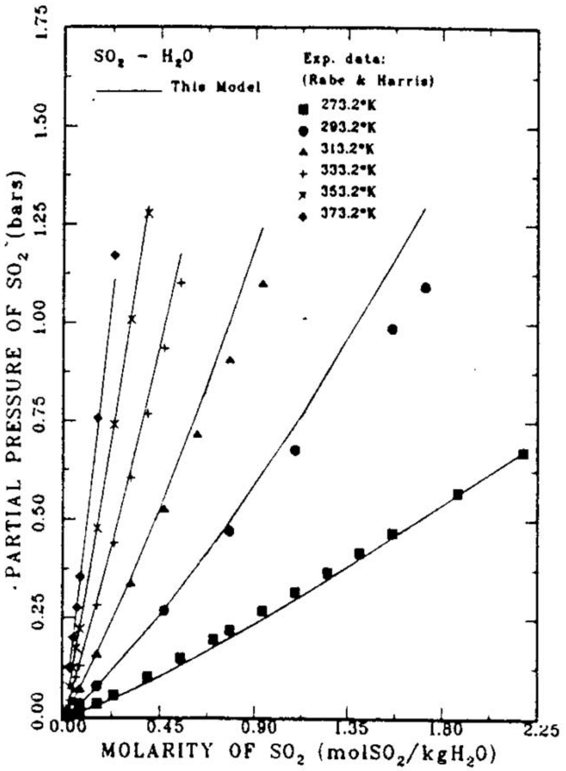

Figure 4. Calculated vapor pressures of sulfur dioxide in water at VLE compared with experimental data of Rabe and Harris (1963).

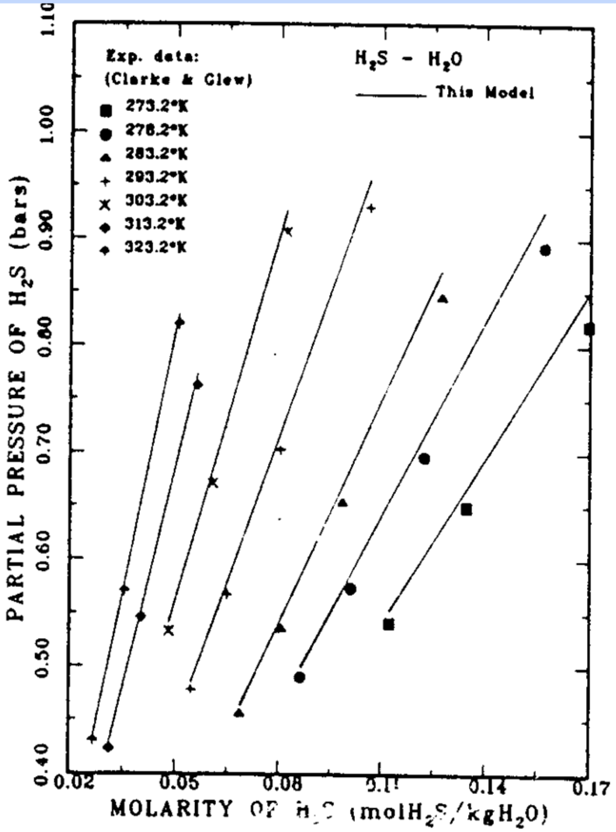

Figure 5. Calculated vapor pressures of hydrogen sulfide in water at VLE compared with experimental data of Clarke and Glew (1971).

Calculations and Results

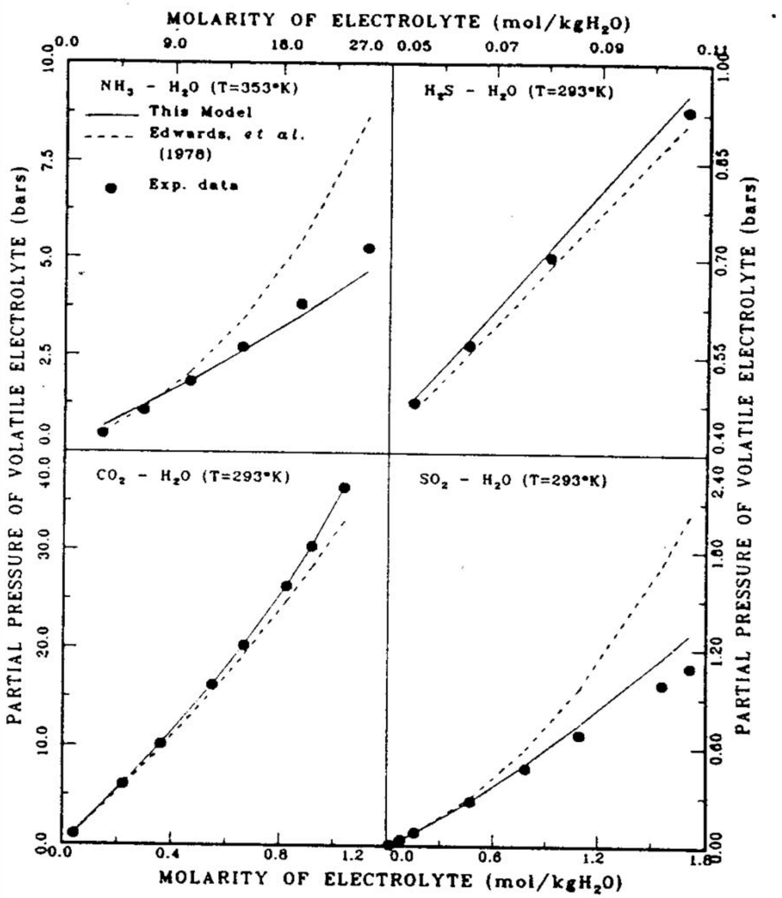

Figure 6. Comparisons of vapor pressures for four single solute systems, CO_2–H_2O, SO_2–H_2O, NH_3–H_2O, and H_2S–H_2O, calculated by using this EOS and the model of Edwards et al. (1978) with experimental data.

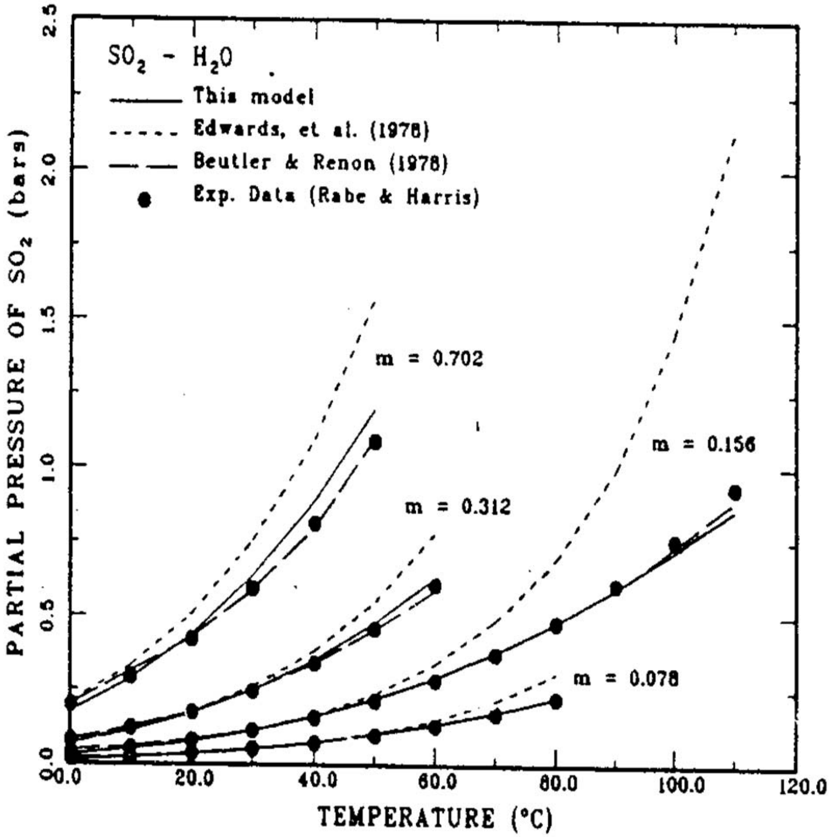

Figure 7. Comparisons of vapor pressures of sulfur dioxide in water calculated by using this model, the model of Edwards et al. (1978), and the model of Beutler and Renon (1978) with experimental data of Rabe and Harris (1963).

Calculations and Results

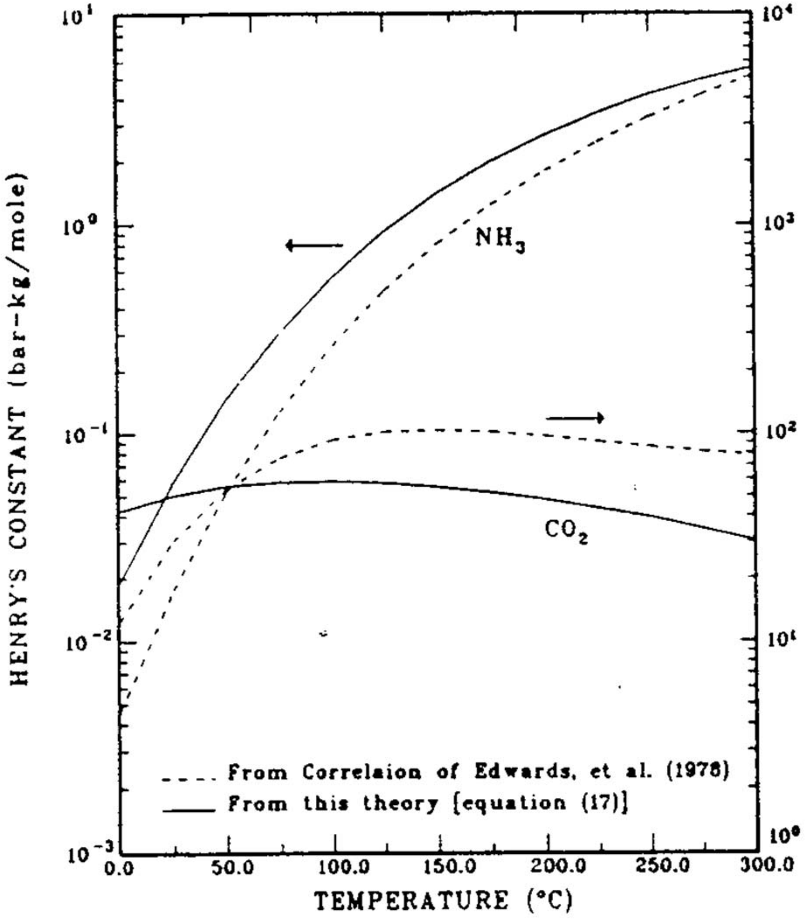

Figure 8. Calculated values of Henry's constants for NH_3 and CO_2 for temperature range of 0–300 K from this theory (eq 17) compared with those obtained from the correlation of Edwards et al. (1978).

Conclusion

- The agreement between this model and other correlations is remarkable with determining unique parameter values when regressing so many parameters from the experimental data and no adjustable parameter
- PACT EoS shows considerable promise for prediction vapor-liquid equilibrium behavior of weak electrolyte aqueous solution without any adjustable parameter