Improved Representation of the Vapor–Liquid Equilibrium of $HCl–H_2O$

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In the design of industrial absorbers for hydrogen chloride gas and HCl-rectification processes an accurate correlation of the phase equilibrium of the $HCl–H_2O$ system in the range $273 \leq T \leq 373$ K, $0 \leq m \leq 15$ mol/kg is desirable. One of the most used sophisticated molecular models for the estimation of the ionic activity coefficients is the NRTL electrolyte model of Chen et al. (1982) and Chen and Evans (1986). Assuming complete dissociation and using the interaction parameters given by Chen et al., the NRTL model is applicable only in a limited concentration range, for example, $m \leq 6$ mol/kg for HCl. Considering incomplete dissociation, the validity of the model can be increased up to 15 m by adjusting the chemical potential of the undissociated species. The three parameters of the model—the two NRTL energy parameters $\tau_{m,ca}$ and $\tau_{ca,m}$, and the chemical potential of the undissociated HCl—can be correlated very well as a function of temperature and extrapolated to higher temperatures with sufficient accuracy.

Thermodynamics

Assuming incomplete dissociation, the vapor–liquid equilibrium of a volatile electrolyte can be calculated from Henry's law:

$$p_{HCl} = m_{HCl_{(aq)}} \gamma^*_{HCl_{(aq)}} H_{HCl} \tag{1}$$

with

$$H_{HCl} = \frac{p^0}{m^*} \exp\left\{\left(\mu^*_{HCl_{(aq)}} - \mu^{ig}_{HCl}\right)/RT\right\}, \tag{2}$$

as Henry's law constant of the undissociated HCl in the aqueous solution. Due to the high degree of dissociation at low concentrations, the chemical potential of the molecular HCl in the standard state of the ideal aqueous solution of unit molality, $\mu^*_{HCl_{(aq)}}$, cannot be measured with sufficient accuracy. Therefore, $\mu^*_{HCl_{(aq)}}$ must be treated as an adjustable parameter. The chemical potential in the ideal gas state can be calculated from tabulated thermodynamic standard data as a function of temperature. According to

$$HCl(aq) \rightleftharpoons H^+ + Cl^-, \tag{3}$$

the concentration of the undissociated molecular solute in the liquid can be computed from the dissociation equilibrium

$$\frac{m_{H^+} m_{Cl^-}}{m_{HCl_{(aq)}}} \frac{\gamma^*_{H^+} \gamma^*_{Cl^-}}{\gamma^*_{HCl_{(aq)}}} = K(T) = \exp\{-\Delta g^*_R/RT\}. \tag{4}$$

The free energy of dissociation at temperature T, standard pressure p^0, and unit molality m^* is given by

$$\Delta g^*_R(T,p^0,m^*) = \mu^*_{H^+} + \mu^*_{Cl^-} - \mu^*_{HCl_{(aq)}} \tag{5}$$

The chemical potentials of all species can be estimated as a function of temperature from data in the literature (Criss and Cobble, 1964a,b; Wagman et al., 1982; Reid et al., 1987). A compilation of all thermodynamic standard data used in our calculations is given in Table 1. The molar heat capacity of HCl in the ideal gas and the vapor pressure of water are calculated as a function of temperature using the parameters given by Reid et al. (1987). To solve Eq. 4, the following relations can be used:

$$m_{H^+} = m_{Cl^-}, \tag{6}$$

$$m_{H^+} + m_{HCl_{(aq)}} = m_{HCl}. \tag{7}$$

The introduction of $\mu^*_{HCl_{(aq)}}$ as an adjustable parameter ensures the consistent representation of Henry's law constant and the dissociation constant, and is superior to the adjustment of H_{HCl} and/or $K(T)$.

The ion activity coefficients in Eq. 4 have been calculated from the NRTL electrolyte model of Chen et al. To reduce the number of adjustable parameters, the energy parameters of the undissociated HCl, that is, $\tau_{HCl_{(aq)},ca}$, $\tau_{ca,HCl_{(aq)}}$, $\tau_{HCl_{(aq)},H_2O}$, and $\tau_{H_2O,HCl_{(aq)}}$, have been set to zero. All nonrandomness factors $\alpha_{m,ca}$ and $\alpha_{ca,m}$ are fixed at 0.03 (Chen, 1986). Furthermore, the activity coefficient of the undissociated HCl, $\gamma^*_{HCl_{(aq)}}$, is set to unity. Physically incorrect, the er-

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Table 1. Standard Data ($T^\circ = 298.15$ K; $p^\circ = 0.1$ MPa)

Species	$\Delta g_{f_i}^{*\dagger}$ (kJ/mol)	$\Delta h_{f_i}^{*\dagger}$ (kJ/mol)	$c_{p_i}^{*\ddagger}$ (J/(mol·K))	$\Delta g_{f_{0i}}^{ig\dagger}$ (kJ/mol)	$\Delta h_{f_{0i}}^{ig\dagger}$ (kJ/mol)
H^+(aq)	0	0	117.23		
Cl^-(aq)	−131.228	−167.159	−247.02		
HCl(g)				−95.299	−92.307

†Wagman et al. (1982).
‡Criss and Cobble (1964b).

ror of this simplification, introduced in the calculation of the vapor pressure, is partly canceled out by the fact that the activity $m_{HCl_{(aq)}} \cdot \gamma^*_{HCl_{(aq)}}$ is needed in Eqs. 1 and 4, which are the governing equations for the phase and chemical equilibrium. The error of the assumption $\gamma^*_{HCl_{(aq)}} = 1$ therefore mainly affects the calculation of the molality of the undissociated HCl in the aqueous solution.

Results

In the range $273 \le T \le 323$ K, $0 \le m_{HCl} \le 15$ mol/kg the most accurate vapor pressure data, especially at low concentrations, are given by Fritz and Fuget (1956), who used the e.m.f. measurements of Harned and Ehlers (1932, 1933) and Åkerlöf and Teare (1937). The water vapor pressures were consistently calculated by integration of the Gibbs–Duhem equation. The data of Zeisberg (1925), published in *Perry's Handbook* (1984), show large systematic deviations at low and high concentrations as well as inconsistencies in the vapor pressures of HCl and H_2O, and cannot be correlated with sufficient accuracy by our model.

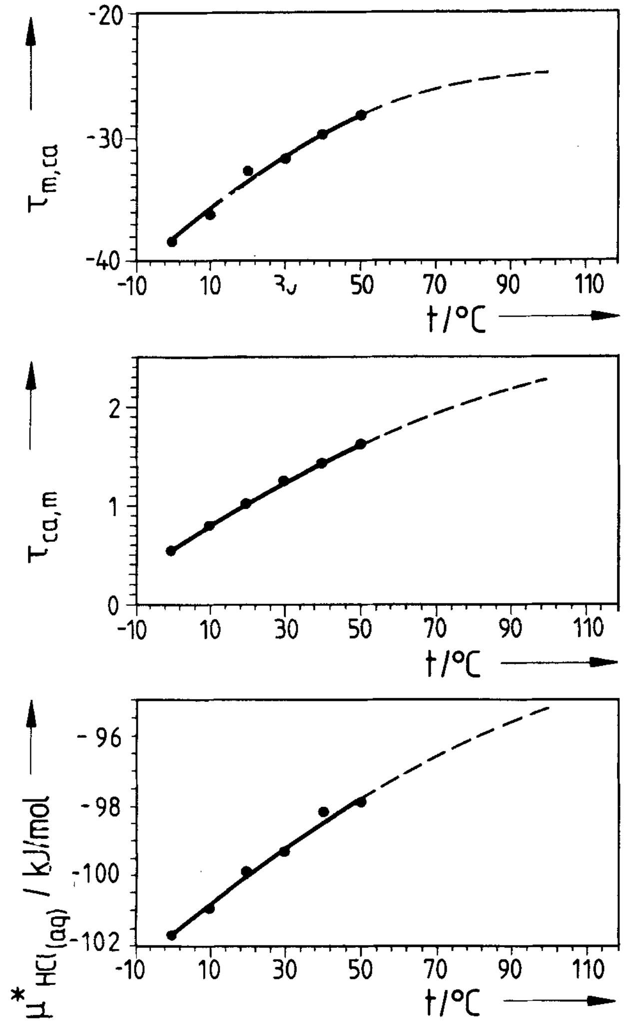

Figure 1. Temperature dependence of the three parameters $\tau_{m,ca}$, $\tau_{ca,m}$, and $\mu^*_{HCl_{(aq)}}$.

Table 2. Parameters of the Temperature Function, Eq. 8 ($\mu^*_{HCl_{(aq)}}$ in J/mol)

	a	b	c
$\tau_{m,ca}$	-0.3223557×10^2	-0.1754823×10^5	-0.1829123×10^3
$\tau_{ca,m}$	0.1156223×10^1	-0.1887221×10^4	-0.5438175×10^7
$\mu^*_{HCl_{(aq)}}$	-0.9952872×10^5	-0.7020893×10^7	-0.1528048×10^5

As shown in Figure 1, the fit to the isothermal HCl–vapor pressure data of Fritz and Fuget shows the three parameters $\tau_{m,ca}$, $\tau_{ca,m}$, and $\mu^*_{HCl_{(aq)}}$ to be smooth functions of temperature. As suggested by Clark and Glew (1966), the parameters have been correlated using the temperature function

$$\tau_{m,ca}, \tau_{ca,m}, \mu^*_{HCl_{(aq)}} = a + b\left(\frac{1}{T} - \frac{1}{298.15}\right) + c\left(\frac{298.15 - T}{T} + \ln(T/298.15)\right). \quad (8)$$

The parameters a, b, c are given in Table 2. Using the Gibbs–Helmholtz equation for the enthalpy at the reference state $T^\circ = 298.15$ K, $p^\circ = 0.1$ MPa, the correlation gives

Table 3. Correlation Results for the Partial Pressures of HCl and H_2O in the Range $0 \le m_{HCl} \le 15$ mol/kg

	HCl			H_2O		
T K	δ_1 %	δ_2 %	Sta %	δ_1 %	δ_2 %	Sta %
273.15	3.64	0.43	4.82	0.99	−0.81	1.20
283.15	3.34	1.59	3.90	0.44	0.12	0.60
293.15	2.71	1.22	3.29	0.46	−0.14	0.73
303.15	2.46	0.85	2.80	0.57	−0.40	0.83
313.15	2.27	−0.33	2.84	0.88	−0.76	0.99
323.15	2.34	−1.51	3.04	0.54	0.12	1.01

Experimental data from Fritz and Fuget (1956).

$$\delta_1 \equiv \frac{1}{N}\sum_i^N \frac{|p_{i,\mathrm{calc}} - p_{i,\mathrm{exp}}|}{p_{i,\mathrm{exp}}} \times 100 \qquad \text{(mean absolute relative error).}$$

$$\delta_2 \equiv \frac{1}{N}\sum_i^N \frac{(p_{i,\mathrm{calc}} - p_{i,\mathrm{exp}})}{p_{i,\mathrm{exp}}} \times 100 \qquad \text{(mean relative error).}$$

$$\mathrm{Sta} \equiv \sqrt{\frac{\sum_I^N (\Delta p_i - \delta_2)^2}{N-1}}, \qquad \Delta p_i \equiv (p_{i,\mathrm{calc}} - p_{i,\mathrm{exp}})/p_{i,\mathrm{exp}} \times 100.$$

Table 4. Correlation Results at Higher Temperatures

T (K)	m_{HCl} (mol·kg^{-1})	$p_{HCl_{calc}}$ (kPa)	$p_{H_2O_{calc}}$ (kPa)	p_{calc} (kPa)	p_{exp} (kPa)	Δp (%)
323.4	1.262	0.56170×10^{-3}	11.921	11.922	12.06	−1.14
344.5		0.31288×10^{-2}	31.542	31.545	31.55	−0.02
364.6		0.14114×10^{-1}	70.770	70.784	70.50	0.40
376.9		0.33569×10^{-1}	110.57	110.60	110.23	0.34
387.5		0.68658×10^{-1}	158.28	158.35	157.57	0.50
323.8	6.644	0.23509	8.225	8.460	8.65	−2.20
351.8		0.16020×10^{1}	29.626	31.228	31.54	−0.99
364.6		0.36412×10^{1}	49.390	53.032	53.00	0.06
375.0		0.69264×10^{1}	72.658	79.585	79.26	0.41
394.5		0.21696×10^{2}	140.91	162.60	159.89	1.69
324.1	8.567	0.11121×10^{1}	6.772	7.884	8.10	−2.67
351.8		0.65956×10^{1}	24.417	31.012	31.41	−1.27
374.2		0.24587×10^{2}	58.990	83.577	81.23	2.89
392.1		0.63971×10^{2}	110.46	174.43	162.13	7.59
323.5	10.042	0.31384×10^{1}	5.484	8.622	8.77	−1.69
350.9		0.16429×10^{2}	19.991	36.420	35.44	2.77
373.2		0.54950×10^{2}	49.240	104.19	96.60	7.86
385.6		0.10073×10^{3}	77.635	178.36	159.21	12.03
323.5	13.435	0.24391×10^{2}	3.568	27.959	27.62	1.23
346.4		0.74296×10^{2}	11.346	85.642	87.90	−2.57
359.9		0.13354×10^{3}	20.934	154.47	158.75	−2.70

Experimental data from Sako et al. (1985).

$$\mu^*_{HCl_{(aq)}}(T^\circ,p^\circ,m^*) = \Delta g^*_{f_{HCl_{(aq)}}} = -99.529 \text{ kJ/mol},$$

$$h^*_{HCl_{(aq)}}(T^\circ,p^\circ,m^*) = \Delta h^*_{f_{HCl_{(aq)}}} = -123.077 \text{ kJ/mol},$$

$$K(T^\circ) = 3.577\times10^5.$$

It is important to mention that the NRTL energy parameters of our correlation differ significantly in size and sign from those given by Chen et al. (1982).

The deviations of the calculated vapor pressures from the data of Fritz and Fuget are shown in Table 3. The calculated partial pressures of HCl and H_2O are within experimental accuracy. The vapor pressure of water is calculated from

$$p_{H_2O} = x_{H_2O}\gamma_{H_2O}p_{s_{H_2O}} \tag{9}$$

Table 4 shows the results for the extrapolation of the correlation to temperatures up to 394.5 K. The calculated total pressures are in good agreement with the experimental data of Sako et al. (1985). The extrapolation of the temperature dependence of the parameters is superior to other empirical temperature correlations for electrolyte activity coefficients (Meissner and Peppas, 1973). The extrapolation results demonstrate the physical significance of the activity coefficient model and the assumption of incomplete dissociation.

Conclusions

Assuming incomplete dissociation and using new energy parameters, the range of application of the electrolyte NRTL model of Chen et al. can be extended to concentrations up to 15 m for HCl-H_2O. The three parameters of the model can be correlated as smooth functions of temperature. The extrapolation of the given correlation to temperatures up to 395 K give reliable results. In conclusion we recommend the new equation instead of the data in the *Perry's Handbook*.

Notation

c_p = molar heat capacity
Δg_f^0 = standard Gibbs free energy of formation
Δh_f^0 = standard enthalpy of formation
K = equilibrium constant
m = molality, moles per kg water
p° = standard pressure, 0.1 MPa
R = universal gas constant
T° = standard temperature, 298.15 K
x = mole fraction

Superscripts and Subscripts

ig = ideal gas
a = anion
c = cation
m = molecular species
$0i$ = pure component

Literature Cited

Åkerlöf, G., and J. W. Teare, "Thermodynamic of Concentrated Aqueous Solutions of Hydrochloric Acid," *J. Amer. Chem. Soc.*, **59**, 1855 (1937).

Chen, C.-C., H. I. Britt, J. F. Boston, and L. B. Evans, "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems," *AIChE J.*, **28**, 588 (1982).

Chen, C.-C., and L. B. Evans, "A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems," *AIChE J.*, **32**, 444 (1986).

Chen, C.-C., "Representation of Solid-Liquid Equilibrium of Aqueous Electrolyte Systems with the Electrolyte NRTL Model," *Fluid Phase Equilib.*, **27**, 457 (1986).

Clark, E. C. W., and D. N. Glew, "Evaluation of Thermodynamic Functions from Equilibrium Constants," *Trans. Farad. Soc.*, **62**, 539 (1966).

Criss, C. M., and J. W. Cobble, "The Thermodynamic Properties of High Temperature Aqueous Solutions. IV. Entropies of the Ions up to 200° and the Correspondence Principle," *J. Amer. Chem. Soc.*, **86**, 5385 (1964a).

Criss, C. M., and J. W. Cobble, "The Thermodynamic Properties of High Temperature Aqueous Solutions. V. The Calculation of Ionic Heat Capacities up to 200°. Entropies and Heat Capacities above 200°," *J. Amer. Chem. Soc.*, **86**, 5390 (1964b).

Fritz, J. J., and C. R. Fuget, "Vapor Pressure of Aqueous Hydrogen Chloride Solutions, 0° to 50°C," *Chem. Eng. Data Ser.*, **1**, 10 (1956).

Harned, H. S., and R. W. Ehlers, "The Dissociation Constant of Acetic Acid from 0 to 35° Centrigrade," *J. Amer. Chem. Soc.*, **54**, 1350 (1932).

Harned, H. S., and R. W. Ehlers, "The Thermodynamics of Aqueous Hydrochloric Acid Solutions from Electromotiv Force Measurements," *J. Amer. Chem. Soc.*, **55**, 2179 (1933).

Meissner, H. P., and N. A. Peppas, "Activity Coefficients—Aqueous Solutions of Polybasic Acids and their Salts," *AIChE J.*, **19**, 806 (1973).

Perry, R. H., and D. W. Green, *Perry's Chemical Engineer's Handbook*, 6th ed., McGraw-Hill, New York (1984).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases & Liquids*, 4th ed., McGraw-Hill, New York (1987).

Sako, T., T. Hakuta, and H. Yoshitome, "Vapor Pressures of Binary (H_2O—HCl, —$MgCl_2$, and —$CaCl_2$) and Ternary (H_2O—$MgCl_2$—$CaCl_2$) Aqueous Solutions," *J. Chem. Eng. Data*, **30**, 224 (1985).

Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttal, "The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units," *J. Phys. Chem. Ref. Data*, **11**, Suppl. 2 (1982).

Zeisberg, F. C., "Partial Vapor Pressure of Aqueous HCl Solutions," *Chem. Metal. Eng.*, **32**, 326 (1925).

Manuscript received Jan. 24, 1994, and revision received May 2, 1994.