

Description of Vapor–Liquid Equilibria for CO₂ in Electrolyte Solutions Using the Mean Spherical Approximation

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The mean spherical approximation is used to describe the vapor pressure over aqueous solutions containing an electrolyte and carbon dioxide. Three electrolytes have been studied: NaOH, NaCl, and acetic acid. A good representation is obtained with a reduced number of parameters as compared to previous models. These parameters account for the concentration and temperature dependence of the solute sizes and the relative permittivity of solution. The numerical values of these physically interpretable parameters are in a reasonable range.

Introduction

Aqueous solutions of carbon dioxide are of considerable interest in industry, e.g., for the production of fertilizers or for the design of separation process equipment. Carbon dioxide has also become of environmental concern since the discovery of the greenhouse effect. Ways to reduce and control the amount of carbon dioxide in the atmosphere, the prediction of seawater ability to regulate atmospheric carbon dioxide (CO₂), or the introduction of pressurized carbon dioxide in geological layers require a good understanding of complex chemical solutions and reliable thermodynamic models.

These models have to describe complex systems, in which several phases and species are in equilibrium and where various components interact with each other. Electrolytes have a major influence on the equilibria, resulting in salting-in and salting-out effects on the gas solubility. In the case of the salting-in effect, the vapor pressure decreases because of the extra solubilization of gas and vice-versa for salting-out.

Vapor pressure data of carbon dioxide solutions have been reported in the literature.^{1–4} These authors measured the vapor pressure of several carbon-dioxide-containing aqueous electrolyte solutions over wide temperature ranges. The experimental data were fitted by solving the vapor liquid equilibria (VLE) equations with the help of electrolyte models such as the Pitzer model^{1–4} or the Chen and Evans model.¹ When the Pitzer model was used, up to five additional ternary salt-carbon dioxide parameters were introduced.

The mean spherical approximation model (MSA) is an analytical electrolyte model that was introduced some decades ago.^{5–8} The Ornstein–Zernike integral equation is solved with a linearized closure relation. The first version of the MSA was at the primitive level, where the solvent is taken as a continuum of relative permittivity ϵ . The ions in solution are described as charged hard spheres of equal diameter σ , which defines the

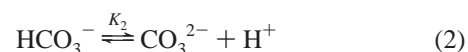
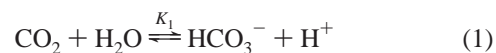
so-called “restricted level” of description. Later, the model was extended to the unrestricted level where the ions have different diameters. Applications to highly concentrated solutions at 298 K and also for higher temperatures, as well as multielectrolyte solutions, have been given in several papers.^{9–12} Associating solutes have recently been taken into account in the MSA model, with the so-called binding-MSA (BIMSA).^{13,14} A version of the MSA model with discrete solvent, the ion–dipole model, has also been studied.¹⁵

The present work is the first application of the unrestricted primitive MSA model to complex solutions including phase equilibria of more than one component. Three different types of solutions are investigated here: aqueous solutions of carbon dioxide with acetic acid (HAc), NaOH, and NaCl, in which the dissolved carbon dioxide is considered as a weak acid. These systems represent three types of mixtures: two weak acids, a weak acid and a strong base, and finally a weak acid and a salt, respectively. For these systems, the liquid phase is in equilibrium with a vapor phase containing carbon dioxide, water, and possibly acetic acid.

The first section of this paper is devoted to the description of the liquid phase and the vapor liquid equilibria (VLE). First, the chemical equilibria occurring in the carbon dioxide solutions are described. Then a description of the MSA model for the activity coefficients is given. Finally, the VLE equations are detailed. In the second section, the three different systems studied are presented. The last section is devoted to the results and discussions and also to the fitting procedure used.

Theory

Modeling of the Liquid Phase. Modeling of the Chemical Equilibria Involving Carbon Dioxide. In aqueous solutions, carbon dioxide undergoes the following reactions



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TABLE 1: Temperature Dependent Equilibrium Constants for Chemical Reactions 1–3 and for the Dimerization of the Acetic Acid (Values from Refs 2 and 24)

reaction	A_R	B_R	$10^2 C_R$	D_R
eq 1 ^a	−7742.6	−14.506	−2.8104	102.28
eq 2 ^b	−8982.0	−18.112	−2.249	116.73
eq 3 ^c	−13445.9	−22.4773	0	140.932
2 HAc $\xrightleftharpoons{K_{\text{dim}}^{\text{V}}}$ (HAc) ₂ ^d	7928.7	0	0	−19.1001

^a $K_{R,U} = 1$. ^b $K_{R,U} = 1 \text{ mol kg}^{-1}$. ^c $K_{R,U} = 1 (\text{mol kg}^{-1})^2$. ^d $K_{R,U} = 1 \text{ kg mol}^{-1}$.

where K_1 and K_2 are the equilibrium constants of the reactions 1 and 2, respectively. The dissociation of water may be written as



where K_3 is the equilibrium constant of water dissociation. The general equilibrium constant expression is given by

$$K_j = \frac{\prod a_i^{\text{P}}}{\prod a_i^{\text{R}}} \quad (4)$$

where a_i^{P} is the activity of the product i , a_i^{R} the activity of the reactant i , and K_j is the equilibrium constant of reaction j . The activity is given by the relation $a_i = m_i \gamma_i$ with m_i and γ_i being the molality and the activity coefficient of solute i , respectively. The molality of each species at equilibrium may be calculated by solving the chemical equilibria equations. The activity coefficients and the activity of solvent are calculated using the MSA model, as detailed below. The K_i values of the equilibria 1–3, taken from the literature,^{1,2} are given in Table 1. Values for K_1 , K_2 , and K_3 at 313 K are 4.53×10^{-7} , $1.02 \times 10^{-10} \text{ mol kg}^{-1}$, and $2.89 \times 10^{-14} \text{ mol}^2 \text{ kg}^{-2}$, respectively.

Description of Activity Coefficients. In the MSA model, a solute is regarded as a charged hard sphere of diameter σ immersed in a continuum characterized solely by its relative permittivity ϵ . The description of solution is made at the so-called McMillan–Mayer (MM) level,¹⁶ involving solvent-averaged ion–ion interactions (effective potential of mean force). The resulting potential is composed of a short-range potential, arising from excluded volume effects, described by the hard sphere potential (HS), and a long-range potential arising from electrostatic forces (hereafter denoted by el).

As the long-range potential is electrostatic, the MSA reduces to the Debye–Hückel limiting law at very low ionic concentration. The MSA model also has a screening parameter Γ equivalent to κ , the Debye screening parameter. These two parameters are related by the simple expression at infinite dilution: $2\Gamma \sim \kappa$.

In the MSA formalism, the thermodynamic properties may be derived from the excess Helmholtz energy per volume unit, ΔF . This energy can be split into two terms arising from the electrostatic and hard sphere interactions. If the solute associates and the corresponding chemical equilibrium is treated in the Wertheim formalism,^{17–19} a supplementary mass action law (MAL) term further adds to the excess Helmholtz energy. An advantage of the Wertheim formalism is that no supplementary

parameter and no individual activity coefficient are needed to describe the associated molecules.

The total excess MSA Helmholtz energy (to be added to the ideal part) may then be decomposed into three contributions as^{10,11,14}

$$\Delta F^{\text{MSA}} = \Delta F^{\text{el}} + \Delta F^{\text{HS}} + \Delta F^{\text{MAL}} \quad (5)$$

in which Δ means an excess quantity.

Each contribution results into an excess activity coefficient

$$\Delta \ln \gamma_i^{\text{X}} = \frac{\partial \beta \Delta F^{\text{X}}}{\partial \rho_i} \quad (6)$$

with $\text{X} = \text{el}, \text{HS}, \text{MAL}$ and ρ_i being the number density of species i (number of particles per volume unit), and into a contribution to the osmotic coefficient

$$\Delta \phi^{\text{X}} = \rho_t \frac{\partial}{\partial \rho_t} \left[\frac{\beta \Delta F^{\text{X}}}{\rho_t} \right] \quad (7)$$

with $\rho_t = \sum_i \rho_i$ (the summation being made over all solutes) and where the derivation is performed at constant mole fraction of each solute ($\rho_i/\rho_t = \text{constant}$).

Then the activity and osmotic coefficients are given by

$$\ln \gamma_i = \Delta \ln \gamma_i^{\text{el}} + \Delta \ln \gamma_i^{\text{HS}} + \Delta \ln \gamma_i^{\text{MAL}} \quad (8)$$

$$\phi = 1 + \Delta \phi^{\text{el}} + \Delta \phi^{\text{HS}} + \Delta \phi^{\text{MAL}} \quad (9)$$

by virtue of the relations $\phi^{\text{ideal}} = 1$ and $\ln \gamma^{\text{ideal}} = 0$.

Experimental data for the thermodynamic coefficients are measured at the Lewis–Randall (LR) level, on the molality scale. In principle, the calculated values of the coefficients have to be converted from the MM level to the LR level, which requires the knowledge of the solution density.¹¹ Because of the lack of information on these data, and because this correction is generally small in the concentration range studied, it will be neglected here.

The number density, ρ_i , of a species i was calculated using the relation (in the SI unit system)

$$\rho_i = N_{\text{AvO}} c_i$$

with

$$c_i = m_i d(T)$$

where N_{AvO} is the Avogadro constant, c_i is the molar concentration of species i (in units of mol m^{-3}), m is its molality (in mol kg^{-1}), and $d(T)$ is the temperature-dependent density of CO₂-free solution (in kg m^{-3}), estimated using a formula proposed in the literature.²⁰

In the following, a detailed summary of each contribution to the thermodynamic coefficients is given.

Electrostatic Contribution. Expressions for the contribution ΔF^{el} have been given in several papers in the case of the restricted (where all ions have the same diameter)^{5–7} and unrestricted (where each ion has a specific diameter)^{8–10} primitive model. The general unrestricted primitive model equation for the excess Helmholtz energy (per volume unit) is¹⁰

$$\beta\Delta F^{\text{el}} = -\lambda \sum_i \left(\frac{\Gamma z_i + \eta \sigma_i}{\rho_i z_i (1 + \Gamma \sigma_i)} \right) + \frac{\Gamma^3}{3\pi} \quad (10)$$

$$\lambda = \frac{\beta e^2}{4\pi\epsilon_0\epsilon}$$

$$\eta = \frac{1}{\Omega} \frac{\pi}{2\Delta} \sum_i \frac{\rho_i \sigma_i z_i}{1 + \Gamma \sigma_i}$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_i \frac{\rho_i \sigma_i^3}{1 + \Gamma \sigma_i}$$

$$\Delta = 1 - \frac{\pi}{6} \sum_i \rho_i \sigma_i^3$$

where $\beta = 1/k_B T$ (with k_B the Boltzmann constant and T the temperature), e is the proton charge, ϵ_0 is the permittivity of a vacuum, and ϵ is the “effective” dielectric constant of solution. z_i and σ_i are the charge and the diameter of ion i , respectively. Γ is the above-mentioned MSA screening parameter, given by the following equation:

$$\Gamma^2 = \pi\lambda \sum_i \rho_i \left[\frac{z_i - \eta \sigma_i^2}{1 + \Gamma \sigma_i} \right]^2 \quad (11)$$

This equation is easily solved by iteration taking for Γ the initial value of $\Gamma_0 = \kappa/2$, with κ the Debye screening parameter

$$\kappa = (4\pi\lambda \sum_i \rho_i z_i^2)^{1/2} \quad (12)$$

Extension of the model to highly concentrated electrolyte solutions can be made by assuming a linear concentration dependence for the cation diameter and for the inverse of the permittivity¹⁰

$$\sigma_+ = \sigma_+^{(0)} + \sigma_+^{(1)} c_s \quad (13)$$

$$\epsilon^{-1} = \epsilon_w^{-1} (1 + \alpha c_s) \quad (14)$$

where c_s is the concentration of salt. The anion diameter is assumed to be constant and equal to its crystallographic value for simple ions.¹⁰

Because eqs 6 and 7 are the derivatives of the excess Helmholtz energy with respect to the number density, the concentration dependence of both MSA parameters, σ_+ and ϵ , has to be taken into account. This leads to the following results:¹⁰

$$\Delta \ln \gamma_i^{\text{MSA}} = -\lambda \left[\frac{\Gamma z_i^2}{1 + \Gamma \sigma_i} + \eta \sigma_i \left(\frac{2z_i - \eta \sigma_i^2}{1 + \Gamma \sigma_i} + \frac{\eta \sigma_i^2}{3} \right) \right] + \sum_j \rho_j q_j \frac{\partial \sigma_j}{\partial \rho_i} + \beta \Delta E^{\text{MSA}} \epsilon \frac{\partial \epsilon^{-1}}{\partial \rho_i} \quad (15)$$

$$\Delta \phi^{\text{MSA}} = -\frac{\Gamma^3}{3\pi\rho_i} - \lambda \frac{2\eta^2}{\pi\rho_i} + \frac{1}{\rho_i} \sum_i \rho_i q_i D(\sigma_i) + \frac{\beta \Delta E^{\text{MSA}}}{\rho_i} \epsilon D(\epsilon^{-1}) \quad (16)$$

where

$$q_i = \lambda \left[\frac{\Gamma^2 z_i^2}{(1 + \Gamma \sigma_i)^2} + \eta \frac{\eta \sigma_i^2 (2 - \Gamma^2 \sigma_i^2) - 2z_i}{(1 + \Gamma \sigma_i)^2} \right] \quad (17)$$

and $D(A) = \sum_k \rho_k \partial A / \partial \rho_k$ which yields using eqs 13 and 14

$$D(\sigma_+) = \sigma_+ - \sigma_+^{(0)} \quad (18)$$

$$\epsilon D(\epsilon^{-1}) = 1 - \epsilon/\epsilon_w \quad (19)$$

Hard-Sphere Contribution. The Boublik–Mansoori–Carnahan–Starling equation was used for the HS excess Helmholtz energy (per volume unit)¹⁰

$$\frac{\pi}{6} \beta \Delta F^{\text{HS}} = \left(\frac{X_2^3}{X_3^2} - X_0 \right) \ln(1 - X_3) + \frac{3X_1X_2}{1 - X_3} + \frac{X_2^3}{X_3(1 - X_3)^2} \quad (20)$$

where

$$X_n = \frac{\pi}{6} \sum_i \rho_i \sigma_i^n \quad (21)$$

Proper use of eqs 6 and 7, taking care again for the diameter concentration dependence, leads to¹⁰

$$\Delta \ln \gamma_i^{\text{HS}} = -\ln(1 - X_3) + \sigma_i F_1 + \sigma_i^2 F_2 + \sigma_i^3 F_3 + \sum_j Q_j \rho_j \frac{\partial \sigma_j}{\partial \rho_i} \quad (22)$$

$$\Delta \phi^{\text{HS}} = \frac{X_3}{1 - X_3} + \frac{3X_1X_2}{X_0(1 - X_3)^2} + \frac{X_3^2(3 - X_3)}{X_0(1 - X_3)^3} + \frac{1}{\rho_i} \sum_j Q_j \rho_j D(\sigma_j) \quad (23)$$

with

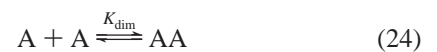
$$Q_i = F_1 + 2\sigma_i F_2 + 3\sigma_i^2 F_3$$

$$F_1 = \frac{3X_2}{1 - X_3}$$

$$F_2 = \frac{3X_1}{1 - X_3} + \frac{3X_2^2}{X_3(1 - X_3)^2} + \frac{3X_2^2}{X_3^2} \ln(1 - X_3)$$

$$F_3 = \left(X_0 - \frac{X_2^3}{X_3^2} \right) \frac{1}{1 - X_3} + \frac{3X_1X_2 - X_2^3/X_3^2}{(1 - X_3)^2} + \frac{2X_2^3}{X_3(1 - X_3)^3} - \frac{2X_2^3}{X_3^3} \ln(1 - X_3)$$

Mass Action Law. Let A and B be two species leading to the following reactions: A dimerizes to yield AA, and B associates with A to form AB:



with K_{dim} and K_{asso} the equilibrium constants of these two reactions. These two reactions will be used below for the HAC/CO₂ system.

The MAL reads^{13,17–19}

$$\frac{\rho_{AA}}{\rho_A^0 \rho_A^0} = K_{\text{dim}} g_{AA}^{(c)} \quad (26)$$

$$\frac{\rho_{AB}}{\rho_A^0 \rho_B^0} = K_{\text{asso}} g_{AB}^{(c)} \quad (27)$$

where ρ_k^0 , ρ_{AA} , and ρ_{AB} are the number density of “free” (nonassociated) k particles, the number density of the dimer particle AA, and the number density of the associated molecule AB, respectively. $g_{XY}^{(c)}$ is the contact value for the radial distribution function of particles X and Y.

The general expression of the excess Helmholtz energy considering one or more associations between molecules k and l is, according to Bernard and Blum¹³

$$\beta \Delta F^{\text{MAL}} = \sum_k \rho_k \ln \alpha_k + \sum_{k,l} \rho_k^0 \rho_l^0 K_{kl} \quad (28)$$

In this equation, ρ_k is the total number density of species k , and α_k is the ratio $\alpha_k = \rho_k^0 / \rho_k$. K_{kl} is the equilibrium constant for the k – l pair. For convenience, in eqs 26 and 27, we define K_{AA} and K_{AB} through the relations

$$K_{AA} = K_{\text{dim}} g_{AA}^{(c)}$$

$$K_{AB} = K_{\text{asso}} g_{AB}^{(c)} / 2$$

Assuming that A and B are neutral hard spheres, $g_{AA}^{(c)}$ and $g_{AB}^{(c)}$ are given by their value for contacting hard spheres as

$$g_{AA}^{(c)} = g_{AA}^{\text{HS}(c)}$$

$$g_{AB}^{(c)} = g_{AB}^{\text{HS}(c)}$$

The expressions for the thermodynamic coefficients are calculated with the help of eqs 6 and 7

$$\Delta \ln \gamma_i^{\text{MAL}} = \ln \alpha_i - \sum_{k,l} \rho_k^0 \rho_l^0 K_{kl} \frac{\partial \ln g_{kl}^{\text{HS}(c)}}{\partial \rho_i} \quad (29)$$

$$\Delta \phi^{\text{MAL}} = - \frac{1}{\rho_i} \sum_{k,l} \rho_k^0 \rho_l^0 K_{kl} \left(1 + \frac{\partial \ln g_{kl}^{\text{HS}(c)}}{\partial \rho_i} \right) \quad (30)$$

The contact distribution function is given by¹⁴

$$g_{ij}^{\text{HS}(c)} = \frac{1}{1 - X_3} + 3 \frac{X_2}{(1 - X_3)^2} \frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} + 2 \frac{X_2^2}{(1 - X_3)^3} \left(\frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} \right)^2 \quad (31)$$

with X_2 and X_3 defined in eq 21.

The conservation of A and B gives

$$2\rho_{AA} + \rho_{AB} + \rho_A^0 = \rho_A \quad (32)$$

$$\rho_{AB} + \rho_B^0 = \rho_B \quad (33)$$

Inserting these relations into eqs 26 and 27 leads to

$$\alpha_A = \frac{1}{1 + 2\rho_B \alpha_B K_{AB} + 2\rho_A \alpha_A K_{AA}} \quad (34)$$

$$\alpha_B = \frac{1}{1 + 2\rho_A \alpha_A K_{AB}} \quad (35)$$

Description of the Vapor Phase. Vapor liquid equilibria arise from the thermodynamic equilibrium of species between the liquid and vapor phases. The basic relation representing this equilibrium is

$$\mu_i^V = \mu_i^L \quad (36)$$

in which μ_i^L is the chemical potential of species i at temperature T and pressure P in the liquid phase and μ_i^V is its chemical potential at temperature T and pressure P in the vapor phase.

For solvent w in equilibrium between the liquid and vapor phases, the chemical potentials read

$$\mu_w^L = \mu_w^{*,L}(T,P) + RT \ln a_w \quad (37)$$

$$\mu_w^V = \mu_w^{*,V}(T,P_w^*) + RT \ln (P_w \varphi_w / P_w^* \varphi_w^*) \quad (38)$$

where a_w is the activity of w , μ_w^X denotes the chemical potential of w in phase X, P_w is the partial pressure of solvent w , and φ_w is the fugacity coefficient of solvent w in the vapor phase. The symbol * used as a superscript denotes the pure solvent reference state. The partial pressure P_i is defined by the relation $P_i = P y_i$, where P is the total pressure and y_i is the mole fraction of species i in the vapor phase.

The VLE condition, eq 36 and eqs 37, 38 yield

$$\mu_w^{*,V}(T,P_w^*) - \mu_w^{*,L}(T,P) = RT \ln a_w - RT \ln (P_w \varphi_w / P_w^* \varphi_w^*) \quad (39)$$

The standard chemical potential $\mu_w^{*,V}(T,P_w^*)$ is independent of the pressure. For pure liquid, one has²¹

$$\left. \frac{\partial \mu_w^{*,L}}{\partial P} \right|_T = v_w^* \quad (40)$$

where v_w^* is the partial molar volume of solvent w in pure solvent reference state.

The fugacity coefficients are calculated with the help of the truncated second virial equation²²

$$\ln \varphi_i = \frac{P}{RT} \left[2 \sum_{j=1}^N y_j B_{ij}(T) - \sum_{k=1}^N \sum_{l=1}^N y_k y_l B_{kl}(T) \right] \quad (41)$$

where B_{ii} is the second virial coefficient and B_{ij} ($j \neq i$) is the second cross virial coefficient. The sums in eq 41 run over all species in the vapor phase.

Equations 39 and 40 lead to the following expression for the equilibrium of solvent:

$$P_{y_w} \varphi_w = P_w^* a_w \varphi_w^* \exp \left(\frac{v_w^* (P - P_w^*)}{RT} \right) \quad (42)$$

In this equation, P_w^* may be calculated with the help of the Saul and Wagner equation.²³

For the solute, the reference state is the infinitely diluted solution, denoted by the symbol ∞ . In this case

$$\mu_i^L = \mu_i^{\infty,L} + RT \ln a_i \quad (43)$$

As in eq 40, one has

$$\left. \frac{\partial \mu_i^{\infty,L}}{\partial P} \right|_T = v_{i,w}^{\infty} \quad (44)$$

where $v_{i,w}^{\infty}$ is the partial molar volume of species i infinitely diluted in solvent w .

Now, let $H_{i,w}^P$ be the Henry's constant of species i in solvent w at the solvent saturated vapor pressure. It is defined by

$$H_{i,w}^P = \lim_{m_i \rightarrow 0} \frac{Py_i \varphi_i}{m_i} \quad (45)$$

Using eq 45 and assuming that $v_{i,w}^{\infty}$ is independent of the pressure, the resulting VLE equation for the solute, known as Henry's law, is

$$Py_i \varphi_i = H_{i,w}^P \exp\left(\frac{v_{i,w}^{\infty}(P - P_w^*)}{RT}\right) a_i \quad (46)$$

The pressure P and the mole fractions y_i of species i in the vapor phase are obtained by solving simultaneously eqs 42 and 46.

Systems studied

NaCl/CO₂/Water System. Liquid Phase. The NaCl/CO₂ system is composed of a salt and a weak acid in water. NaCl is assumed to be fully dissociated. The chemical equilibria in the liquid phase are given by eqs 1–3.

Considering the values of the equilibrium constants K_1 , K_2 , and K_3 between 313 and 433 K, the molalities of the HCO_3^- and CO_3^{2-} ions are always smaller than 10^{-3} mol kg⁻¹ for CO₂ concentration below 1 mol kg⁻¹. Therefore, these concentrations may be neglected as compared to that of CO₂. It will be assumed that the liquid phase is composed of three species: the carbon dioxide and the ions Na⁺ and Cl⁻.

VLE. This system is composed of two volatile species, carbon dioxide and water, and one nonvolatile species, NaCl. The VLE for water is given by eq 42. For the carbon dioxide, the VLE is given by eq 46, where the subscript i is replaced by CO₂. The relation for mole fractions in the vapor phase is

$$y_w + y_{\text{CO}_2} = 1 \quad (47)$$

The set of equations (42, 46, and 47) may be solved using an iteration procedure yielding the three variables P , y_w , and y_{CO_2} .

NaOH/CO₂/Water System. Liquid Phase. This system is composed of a strong base, NaOH, and a weak electrolyte, CO₂. The NaOH is assumed to be totally dissociated. Here, eqs 1–3 are taken into account. The hydroxide anions are produced by eq 3 and by the total dissociation of NaOH in water.

The molalities of each species are calculated with the help of eqs 1–4, the mass conservation equation

$$m_{\text{CO}_2}^{\text{init}} = m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} + m_{\text{CO}_2} \quad (48)$$

where $m_{\text{CO}_2}^{\text{init}}$ is the molality of carbon dioxide introduced initially in the liquid phase, and the electroneutrality relation

$$m_{\text{Na}^+} + m_{\text{H}^+} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} \quad (49)$$

VLE. The vapor phase for this system has the same composition as for the NaCl/CO₂ system. The same iteration procedure was used for solving the equations in P , y_w , and y_{CO_2} .

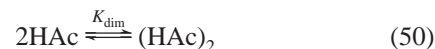
HAc/CO₂/Water System. Liquid Phase. This system involves two weak acids in water. The dissociation of the acetic acid is



where K_{HAc} is the equilibrium constant. Its value is 1.75×10^{-5} mol kg⁻¹ at 313 K.

Because the molality of the acetic acid is below 4 mol kg⁻¹ in the available data, the concentrations of HCO_3^- , CO_3^{2-} , and acetate ions may be neglected. Thus, the solution was assumed to contain only nonionic species: carbon dioxide and undissociated acetic acid.

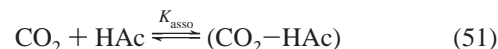
Two further assumptions were made. First, the dimerization of acetic acid was considered. It is well-known^{24,25} that this process is appreciable in concentrated acetic acid solutions. The dimerization reaction was written as follows:



where K_{dim} is the dimerization constant of acetic acid and is defined as in eqs 4 and 24. Its value, found in the literature, is discussed in the next subsection.

Unlike the NaCl/CO₂ and NaOH/CO₂ systems, the aqueous HAc/CO₂ solutions exhibit a salting-in effect for the carbon dioxide. This reveals that specific interactions exist between acetic acid and carbon dioxide. Earlier modeling of this system with the Pitzer model² also assumed CO₂–HAc interactions, taken into account through the introduction of 4 CO₂–HAc interaction parameters.

In our model, we assume that these interactions may be described with an association equilibrium between CO₂ and HAc



where K_{asso} is the association constant between carbon dioxide and acetic acid, defined as in eq 4. It is an adjustable parameter.

The two equilibria corresponding to eqs 50 and 51 have been treated within the Wertheim formalism as detailed in eqs 24–35.

VLE. There are four species in the vapor phase: water, carbon dioxide, acetic acid, and its dimer. Association between HAc and CO₂ is not assumed in the vapor phase because this is a dilute phase. The VLE equations for water and carbon dioxide remain the same as before, except for the fugacity coefficients that now take into account the mole fraction of acetic acid and its dimer. Equation 46 is used to describe the VLE of acetic acid.

The equilibrium constant for the dimerization of the acetic acid in the vapor phase is known²

$$K_{\text{dim}}^V = \frac{P_0 y_{\text{dim}} \varphi_{\text{dim}}}{Py_{\text{HAc}}^2 \varphi_{\text{HAc}}^2}$$

with φ_{HAc} and φ_{dim} the fugacity coefficients for the acetic acid and its dimer in the vapor phase, respectively. P_0 is 1 atm.

The values of the cross virial coefficients for acetic acid, $B_{\text{HAc,CO}_2}$ and $B_{\text{dim,CO}_2}$, as well as the molar volume of HAc in pure water have been set to zero, because of the lack of

TABLE 2: Cross Second Virial Coefficients and Partial Molar Volume for CO₂ at Infinite Dilution in Water Taken from Ref 2

<i>T</i> (K)	10 ⁻³ B _{CO₂,w} (dm ³ mol ⁻¹)	10 ⁻³ ν _{CO₂,w} [∞] (dm ³ mol ⁻¹)
313.15	-163.1	33.4
333.15	-144.6	34.7
373.15	-115.7	38.3
393.15	-104.3	40.8
413.15	-94.3	43.8
433.15	-85.5	47.5

TABLE 3: Henry's Constant for the Solubilities of Acetic Acid and Carbon Dioxide in Pure Water (Values Taken from Ref 2)

$\ln H_{i,w}^P(T, p_w^s)/(\text{MPa kg mol}^{-1}) = A_{i,w} + B_{i,w}/T + C_{i,w}T + D_{i,w} \ln(T)$				
<i>i</i>	<i>A_{i,w}</i>	<i>B_{i,w}/K</i>	<i>C_{i,w}/K⁻¹</i>	<i>D_{i,w}</i>
CO ₂	192.876	-9624.4	0.01441	-28.749
HAc	52.9967	-8094.25	0	-6.41203

TABLE 4: Second Virial Coefficients for Water and Carbon Dioxide Taken from Ref 2

$10^{-3} B_{i,j}/(\text{dm}^3 \text{ mol}^{-1}) = a_i + b_i (c_j/T)^{d_i}$				
<i>i</i>	<i>a_i</i>	<i>b_i</i>	<i>c_i/K</i>	<i>d_i</i>
CO ₂	65.703	-184.854	304.16	1.4
H ₂ O	-53.53	-39.29	647.3	4.3

experimental data. Note that this implies that $\varphi_{\text{HAc}} = \varphi_{\text{dim}}$. The value of the dimerization constant K_{dim}^V of acetic acid in the vapor phase is given in Table 1. The values of Henry's constants, of the cross virial coefficients and of the molar volumes in pure water are collected in Tables 2–4. Together with the relation

$$y_w + y_{\text{CO}_2} + y_{\text{HAc}} + y_{\text{dim}} = 1 \quad (52)$$

the system can be solved for *P* and for the *y_i*'s, the different mole fractions in the vapor phase. For this purpose, a Newton–Raphson procedure was used.

Results

The model parameters are the diameter of the sodium cation, σ_{Na^+} , for the solutions containing NaCl or NaOH; the diameter of the HAc molecule for those containing acetic acid; the diameter of the CO₂ molecule; and the permittivity of solution, ϵ . Following earlier work in which the MSA model was applied to the thermodynamics of ionic aqueous solutions,^{11,12} the following concentration and temperature dependencies were introduced:

$$\sigma_i = \sigma_i^{(0)} + \sigma_i^{(0,T)} \Delta T + \sum_j (\sigma_{i-j}^{(1)} + \sigma_{i-j}^{(1,T)} \Delta T) c_j \quad (53)$$

$$\epsilon^{-1} = \epsilon_w^{-1} [1 + \sum_j (\alpha_j + \alpha_j^{(T)} \Delta T) c_j] \quad (54)$$

where *j* stands for all species in solution, including the anion and species *i* itself.

TABLE 5: Values of MSA Parameters from the Fits of the Osmotic Coefficients for Pure CO₂-Free Electrolyte Solutions (See eqs 53 and 54)

salt	max. <i>m</i> ^a	temp. range	$\sigma^{(0)b}$	$10^4 \sigma^{(0,T)c}$	$10^2 \sigma^{(1)d}$	$10^5 \sigma^{(1,T)e}$	$10^2 \alpha^f$	$10^4 \alpha^{(T)g}$	AARD ^h (%)
NaCl	6	298–573 K	3.689	-6.229	-4.139	-4.720	7.154	-1.216	1.77
NaOH	10	298–473 K	3.803	0	-3.972	0	5.508	1.451	1.28

^a In units of mol kg⁻¹. ^b In units of 10⁻¹⁰ m. ^c In units of 10⁻¹⁰ m K⁻¹. ^d In units of 10⁻¹⁰ m dm³ mol⁻¹. ^e In units of 10⁻¹⁰ m dm³ mol⁻¹ K⁻¹. ^f In units of dm³ mol⁻¹. ^g In units of dm³ mol⁻¹ K⁻¹. ^h AARD = $1/n \sum_i |\phi_{\text{cal}}^{(i)} - \phi_{\text{exp}}^{(i)}| / \phi_{\text{exp}}^{(i)}$ with *n* = number of points.

In the case of the HAc solutions, they were determined in a global fit of data for ternary solutions, together with the other parameters. The cross parameters $\sigma_{i-j}^{(1)}$ and $\sigma_{i-j}^{(1,T)}$ account for the influence of species *j* on the size of species *i*; they may be calculated by fitting the pressures of the ternary systems.

It must be noticed that the CO₂ parameters $\sigma_{\text{CO}_2}^{(0)}$, $\sigma_{\text{CO}_2}^{(0,T)}$, $\sigma_{\text{CO}_2-\text{CO}_2}^{(1)}$, and $\sigma_{\text{CO}_2-\text{CO}_2}^{(1,T)}$ are specific to this species. Their values are common to the three systems studied in this work.

The vapor pressure data for the three systems studied were taken from the work of Rumpf et al.^{1,2} Pressures were measured in the range of temperature 313–433 K for different concentrations of both electrolyte and carbon dioxide.

Adjustment of Parameters Concerning the CO₂-Free Electrolyte Systems. This procedure was carried out for NaCl and NaOH for which experimental values of the osmotic coefficient up to saturation and at different temperatures are available, in contrast to the HAc solutions. Two types of parameters were adjusted: the cation diameter and the relative permittivity. Following eqs 53 and 54, these parameters are written as

$$\sigma_{\text{Na}^+}^{(b)} = \sigma_{\text{Na}^+}^{(0)} + \sigma_{\text{Na}^+}^{(0,T)} \Delta T + (\sigma_s^{(1)} + \sigma_s^{(1,T)} \Delta T) c_s \quad (55)$$

$$[\epsilon^{(b)}]^{-1} = \epsilon_w^{-1} [1 + (\alpha_s + \alpha_s^{(T)} \Delta T) c_s] \quad (56)$$

and

$$\Delta T = T - 298.15$$

where the superscript (b) stands for the binary salt/water system, *s* stands for the salt NaX (*X* = Cl or OH) $\sigma_s^{(1)} = \sigma_{\text{Na}^+-\text{Na}^+}^{(1)} + \sigma_{\text{Na}^+-X^-}^{(1)}$ and the similar relation for $\sigma_s^{(1,T)}$. In the same way, $\alpha_s = \alpha_{\text{Na}^+} + \alpha_{X^-}$ and similarly for $\alpha_s^{(T)}$. In these relations the $\sigma_i^{(0)}$, $\sigma_i^{(0,T)}$, $\sigma_s^{(1)}$, and $\sigma_s^{(1,T)}$ parameters may be determined by a fit of data for binary solutions. They were obtained by a fit of the osmotic coefficients for the electrolyte solutions.

The fits were done using a Marquardt least-squares procedure. First, $\sigma_{\text{Na}^+}^{(b)}$, $\sigma_s^{(1)}$, and α_s were adjusted by using data at 298 K. Then the remaining parameters $\sigma_{\text{Na}^+}^{(0,T)}$, $\sigma_s^{(1,T)}$, and $\alpha_s^{(T)}$ were adjusted by using the data at higher temperatures. The results are gathered in Table 5.

Adjustment of Parameters Concerning the CO₂-Containing Electrolyte Systems. NaCl/CO₂ System. In this system, the following parametrization was applied to the sodium ion diameter, the permittivity of solution, and the carbon dioxide diameter

$$\sigma_{\text{Na}^+} = \sigma_{\text{Na}^+}^{(b)} + (\sigma_{\text{Na}^+-\text{CO}_2}^{(1)} + \sigma_{\text{Na}^+-\text{CO}_2}^{(1,T)} \Delta T) c_{\text{CO}_2} \quad (57)$$

$$\epsilon = \epsilon^{(b)} \quad (58)$$

$$\sigma_{\text{CO}_2} = \sigma_{\text{CO}_2}^{(0)} + \sigma_{\text{CO}_2}^{(0,T)} \Delta T + \sigma_{\text{CO}_2-\text{NaCl}}^{(1)} c_{\text{NaCl}} \quad (59)$$

with $\sigma_{\text{Na}^+}^{(b)}$ and $\epsilon^{(b)}$ defined in eqs 55 and 56, respectively. Notice that in eq 59 $\sigma_{\text{CO}_2-\text{NaCl}} = \sigma_{\text{CO}_2-\text{Na}^+} + \sigma_{\text{CO}_2-\text{Cl}^-}$.

TABLE 6: Values of MSA Parameters from the Fit of Carbon Dioxide Solubility Pressures

species	temp. range	$\sigma^{(0)a}$	$10^3\sigma^{(0,T)b}$
CO ₂	313–433 K	3.408	−3.973
HAc	313–433 K	6.526	−10.992

^a In units of 10^{-10} m. ^b In units of 10^{-10} m K^{−1}.

Although carbon dioxide certainly influences the permittivity of solution (at least through the reduction of the concentration of water molecules), no dependence of the permittivity on the CO₂ concentration needed be considered. Because the concentration of carbon dioxide is always low, a concentration dependence for the carbon dioxide diameter was not needed. No temperature-dependent cross parameter ($\sigma_{i-j}^{(1,T)}$ in eq 53) was necessary for the CO₂ diameter.

This introduces five new parameters, as seen in eqs 57 and 59: $\sigma_{\text{Na}^+-\text{CO}_2}^{(1,T)}$, $\sigma_{\text{Na}^+-\text{CO}_2}^{(0,T)}$, $\sigma_{\text{CO}_2}^{(0)}$, $\sigma_{\text{CO}_2}^{(0,T)}$, and $\sigma_{\text{CO}_2-\text{NaCl}}^{(1)}$. They were adjusted by least-squares fit of experimental VLE data. The parameters $\sigma_{\text{CO}_2}^{(0)}$ and $\sigma_{\text{CO}_2}^{(0,T)}$ are specific carbon dioxide parameters. They are common to the three carbon dioxide systems. Values for $\sigma_{\text{CO}_2}^{(0)}$ and $\sigma_{\text{CO}_2}^{(0,T)}$ are given in Table 6. The three cross parameters $\sigma_{\text{Na}^+-\text{CO}_2}^{(1,T)}$, $\sigma_{\text{Na}^+-\text{CO}_2}^{(0,T)}$, and $\sigma_{\text{CO}_2-\text{NaCl}}^{(1)}$ are specific for the ternary system. They are specified in Table 7. The crystallographic value was taken for the diameter of Cl[−]. One finds in the literature²⁶ the value of $\sigma_{\text{Cl}^-} = 3.62 \times 10^{-10}$ m.

NaOH/CO₂ System. For this system, the MSA parameters were taken as

$$\sigma_{\text{Na}^+} = \sigma_{\text{Na}^+}^{(b)} \quad (60)$$

$$\epsilon = \epsilon^{(b)} \quad (61)$$

$$\sigma_{\text{CO}_2} = \sigma_{\text{CO}_2}^{(0)} + \sigma_{\text{CO}_2}^{(0,T)}\Delta T \quad (62)$$

Contrary to eqs 57 and 59, no cross parameter was necessary for σ_{Na^+} and for σ_{CO_2} . As stated previously, the two CO₂ parameters, $\sigma_{\text{CO}_2}^{(0)}$ and $\sigma_{\text{CO}_2}^{(0,T)}$, are the same as for the NaCl/CO₂ system.

The sizes of OH[−], HCO₃[−], CO₃^{2−}, and H⁺ were kept constant (concentration independent). Although the OH[−] and H⁺ diameters were taken from previous work,¹¹ the two parameters $\sigma_{\text{HCO}_3^-}$ and $\sigma_{\text{CO}_3^{2-}}$ have been fitted to the NaOH/CO₂ system, but are not specific to this system. These parameter values may be used in further modelings of carbon dioxide solutions where the dissociation of carbon dioxide has to be taken into account. Values of the anions and the hydronium diameters are collected in Table 8.

HAc/CO₂ System. As mentioned above, the interaction between the two particles was taken into account through the association constant K_{asso} (see eq 51). Nevertheless, one cross parameter was introduced in the acetic acid diameter in order to improve the accuracy of fit

Fit of Pressure

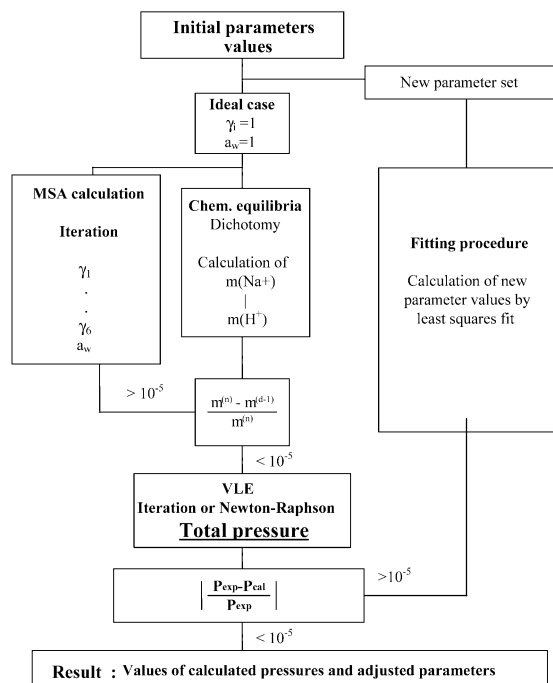


Figure 1. Diagram of the fitting procedure used for the description of CO₂ solubility pressures in aqueous electrolyte solutions.

$$\sigma_{\text{HAc}} = \sigma_{\text{HAc}}^{(0)} + \sigma_{\text{HAc}}^{(0,T)}\Delta T + \sigma_{\text{HAc}-\text{CO}_2}^{(1)} c_{\text{CO}_2} \quad (63)$$

$$\sigma_{\text{CO}_2} = \sigma_{\text{CO}_2}^{(0)} + \sigma_{\text{CO}_2}^{(0,T)}\Delta T \quad (64)$$

No further parameter was introduced for the permittivity, that is $\epsilon = \epsilon_w$.

The two CO₂ parameters in eq 64, $\sigma_{\text{CO}_2}^{(0)}$ and $\sigma_{\text{CO}_2}^{(0,T)}$, are common to the other systems studied. As in eq 62, no cross parameter was necessary for σ_{CO_2} . No temperature-dependent cross parameter ($\sigma_{i-j}^{(1,T)}$ in eq 53) was necessary for the acetic acid diameter.

For this system, four new parameters were adjusted: $\sigma_{\text{HAc}}^{(0)}$, $\sigma_{\text{HAc}}^{(0,T)}$, $\sigma_{\text{HAc}-\text{CO}_2}^{(1)}$, and K_{asso} . They were obtained by fitting the solubility pressures of carbon dioxide in the ternary aqueous solution. The values are collected in Tables 6 and 7. The maximum proportion of associated CO₂ is found to be 69% of the overall amount of carbon dioxide at 313 K.

The value for K_{dim} (see eq 50) was found in the literature. The value of 0.146 kg mol^{−1}, given in ref 25, gave better results than that of 0.0517 kg mol^{−1} from ref 24. The value of K_{dim} was therefore fixed to 0.146 kg mol^{−1}.

Fitting Procedure of the Carbon Dioxide Solutions. The adjustment procedure for the carbon dioxide, acetic acid, and cross parameters, schematized in Figure 1, is now explained.

(1) For the NaCl/CO₂ system, one calculates the γ_i 's and a_w with eqs 15, 16, 22, and 23.

TABLE 7: Cross Parameters and Results of Fits

system A + B	max. $m_{\text{CO}_2}^a$	max. m_{salt}^a	temp. range	$10^2\sigma_{\text{A-B}}^{(1)b}$	$\sigma_{\text{B-A}}^{(1)b}$	$10^4\sigma_{\text{B-A}}^{(1,T)c}$	K_{asso}^d	AARD ^e (%)
CO ₂ + NaOH	1.73	1	313–433 K	0	0	0		6.82
CO ₂ + NaCl	0.46	6	313–433 K	−0.1571	−0.01382	1.2983		3.47
CO ₂ + HAc	1.28	4	313–433 K	0	−0.21527	0	0.263	4.47

^a In units of mol kg^{−1}. ^b In units of 10^{-10} m dm³ mol^{−1}. ^c In units of 10^{-10} m dm³ mol^{−1} K^{−1}. ^d In units of dm³ mol^{−1}. ^e AARD = $1/n \sum |P_{\text{cal}}^{(i)} - P_{\text{exp}}^{(i)}|/P_{\text{exp}}^{(i)}$, with n = number of points.

TABLE 8: Values for the Ion Diameters (in Units of 10⁻¹⁰ M) Fitted with the MSA Model

$\sigma_{\text{H}^+}^a$	$\sigma_{\text{Cl}^-}^a$	$\sigma_{\text{OH}^-}^a$	$\sigma_{\text{HCO}_3^-}^b$	$\sigma_{\text{CO}_3^{2-}}^b$
5.04	3.62	3.55	4.30	5.23

^a Taken in ref 11. ^b Fitted in this work.

For the HAc/CO₂ system, the γ_i 's and a_w are calculated using eqs 15, 16, 22, 23, 29, 30, 34, and 35. For these systems, the next step is step 5 below (because eqs 1–3 are not taken into account).

For the NaOH/CO₂ system, the solution is initially assumed to be ideal: $\gamma_i = 1$.

(2) The liquid equilibria are solved with the association constants taken from the literature and eqs 4, 48, and 49, yielding the concentrations of the different species.

(3) The values of the γ_i 's are computed for the concentrations of species obtained in step 2 for a set of MSA parameters.

(4) The steps 2 and 3 are repeated until the calculated stork concentrations of each species i fulfils the criterion: $|m_i^{(n)} - m_i^{(n-1)}|/m_i^{(n)} < 10^{-5}$ where $m_i^{(n)}$ is the n th calculated molality of species i .

(5) The pressure and the mole fractions of species in the vapor phase are calculated by solving the VLE eqs 42 and 46 by using either an iteration or a Newton–Raphson procedure.

(6) Unless the criterion: $|P^{\text{calc}} - P^{\text{exp}}|/P^{\text{exp}} < 10^{-5}$ on the pressure is fulfilled (where P^{exp} is the experimental pressure and P^{calc} is the calculated one), the Marquardt least-squares procedure is repeated (steps 1–6 with another set of MSA parameters).

Discussion

Aqueous Electrolyte Solutions. The calculations for the binary NaCl aqueous solutions were carried out up to 6 mol kg⁻¹ of NaCl in the temperature range 298–573 K. In the case of NaOH aqueous solutions, the data description was done up to 10 mol kg⁻¹ and in the temperature range 298–473 K. The experimental data for the osmotic coefficients were taken from refs 27–29 for the NaCl solutions and from refs 27, 30, and 31 for the NaOH solutions. Following the recommendations of ref 32, points above 473 K from ref 31 were not used.

For each salt, six parameters were fitted, as detailed in the preceding section. The results are given in Table 5, and a typical plot for NaOH osmotic coefficients is shown in Figure 2. The overall average absolute relative deviation (AARD) for the two salts is satisfactory, considering the simple concentration and temperature dependence relations for the diameter and the solution permittivity. The $\sigma^{(0)}$, $\sigma^{(1)}$, and α parameters are similar in magnitude to those obtained by Simonin et al.^{10,11} The slight deviations from their values are due to the absence of the McMillan–Mayer to Lewis–Randall (MM–LR) conversion in our calculations.

The negative value of $\sigma^{(1)}$ is consistent with the expectation that the effective diameter of the cation (plus hydration shell) decreases with salt concentration. The positive value of the α parameter is coherent with the experimental observation that the solution permittivity decreases with salt concentration. The negative value of $\sigma^{(0,T)}$ means a decrease of the effective diameter of the cation with temperature, as expected from thermal effects on hydration.

In the case of NaOH, the adjustment of $\sigma_{\text{Na}^+}^{(1,T)}$, $\sigma_{\text{NaOH}^-}^{(1,T)}$ and $\alpha_{\text{NaOH}}^{(T)}$ yielded a relative deviation quite comparable to the one obtained with the $\alpha_{\text{NaOH}}^{(T)}$ parameter alone. Thus, it was decided to set $\sigma_{\text{Na}^+}^{(1,T)}$ and $\sigma_{\text{NaOH}^-}^{(1,T)}$ to zero and adjust only $\alpha_{\text{NaOH}}^{(T)}$.

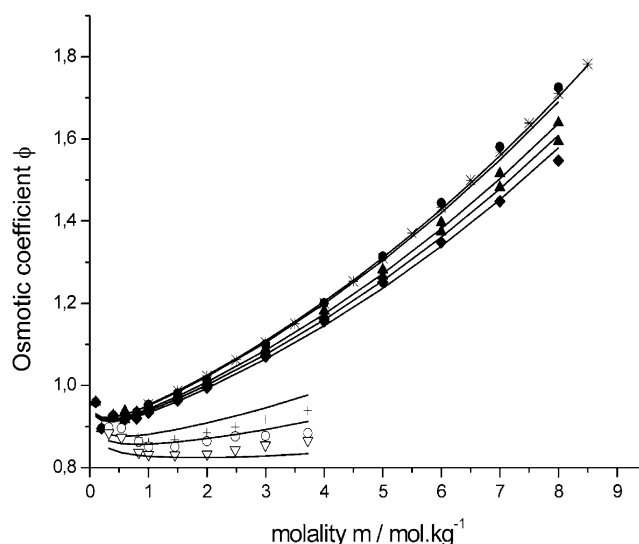


Figure 2. Plot of the osmotic coefficients for aqueous NaOH solutions, up to 8 mol kg⁻¹ and for different temperatures. Experimental values taken from refs 27–30. (*): 298.15 K. (●): 303.15 K. (▲): 323.15 K. (▼): 333.15 K. (◆): 343.15 K. (+): 423.15 K. (○): 448.15 K. (▽): 473.15 K.

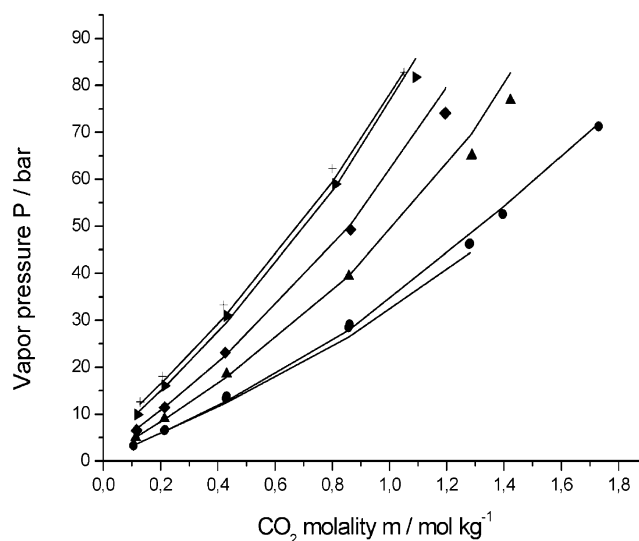


Figure 3. Plot of the pressure over HAc/CO₂ aqueous solutions at the HAc concentration of 0.9 mol kg⁻¹ up to 413 K. Experimental values taken from ref 2. (●): 313.15 K. (▲): 333.15 K. (◆): 353.15 K. (right solid arrow): 393.15 K. (+): 413.15 K.

Carbon Dioxide Solutions. The experimental pressure values were taken from the papers of Rumpf et al.^{1,2} in the temperature range 313–433 K for each solution. For the NaCl/CO₂ system, pressures were given for two different salt concentrations, namely, 4 and 6 mol kg⁻¹, and up to 0.5 mol kg⁻¹ of carbon dioxide. For the NaOH/CO₂ system, pressures were given at 1 mol kg⁻¹ of salt and up to 2 mol kg⁻¹ of carbon dioxide. Finally, for the HAc/CO₂ system, the experimental data ranged up to 1.7 mol kg⁻¹ of carbon dioxide at one acetic acid concentration of 4 mol kg⁻¹. The results of our description are given in Tables 6 and 7, and typical plots of the pressures in the three systems are shown in Figures 3–5.

The AARD value of 3.5% for the NaCl/CO₂ system is larger than the value of 1.9% obtained with the Pitzer model. However, the present MSA model introduces 11 adjustable parameters as compared to the 16 parameters for the Pitzer model. The Pitzer

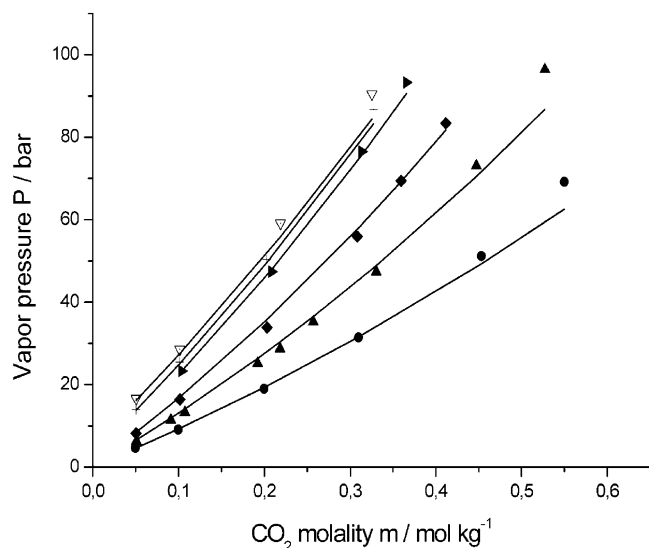


Figure 4. Plot of the pressure over aqueous NaCl/CO₂ solutions at 4 mol kg⁻¹ of the salt and up to 433 K. Experimental values taken from ref 1. (●): 313.15 K. (▲): 333.15 K. (◆): 353.15 K. (right solid arrow): 393.15 K. (+): 413.15 K. (▽): 433.15 K.

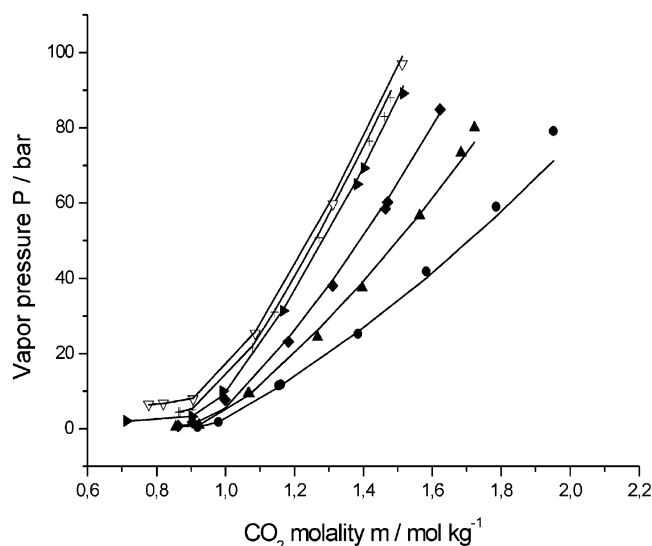


Figure 5. Plot of the pressure over aqueous NaOH/CO₂ solutions at 0.96 mol kg⁻¹ of NaOH up to 433 K. Experimental values taken from ref 2. (●): 313.15 K. (▲): 333.15 K. (◆): 353.15 K. (right solid arrow): 393.15 K. (+): 413.15 K. (▽): 433.15 K.

model needs five ternary parameters, as compared to three in the MSA model. Moreover, setting $\sigma_{\text{CO}_2-\text{NaCl}}^{(1)}$ to zero, one still obtains a satisfactory AARD value of 3.7%.

Concerning the NaOH/CO₂ system, the Pitzer model described the system with an AARD value of 9%. No cross parameter was introduced, meaning that the vapor pressures of the ternary system could be predicted using the results for binary systems. However, as many as 46 parameters were needed, corresponding to the three binary subsystems NaOH/H₂O, NaHCO₃/H₂O, and Na₂CO₃/H₂O. In this work, with the use of eight adjusted parameters (four parameters for the binary system CO₂/H₂O, four parameters for the binary system NaOH/H₂O, and no cross parameter), the MSA model gives an accuracy of 6.8%.

For the HAc/CO₂ system, the precision was 2% with the Pitzer model, using eight parameters (including four cross parameters). The result of this work is 4.5% with seven parameters (including two cross-parameters).

Conclusion

The overall quality of fits is satisfactory compared to the Pitzer model. Moreover, the parameters have a more direct physical meaning, and the number of parameters is reduced.

It appears that the chemical equilibria associated with the carbon dioxide reactions (eqs 1 and 2) play only a little role for the solubility of carbon dioxide, unless the supporting solution contains a base. In all other cases, it seems reasonable to neglect these equilibria, which makes the calculations much simpler.

It can be shown from the present study that the vapor phase is composed in each case of more than 98% of carbon dioxide. This is due to the very high value of the Henry's coefficient of carbon dioxide. Consequently, the activity coefficient that influences most the VLE is the carbon dioxide activity coefficient, γ_{CO_2} . It is observed that this quantity does not vary much with concentration and temperature. So, it is found with our treatment that, in the range 313–433 K, γ_{CO_2} varies from 1.6 to 2 for the system NaCl/CO₂ at 4 mol kg⁻¹ of NaCl, from 2.2 to 2.6 for the same system at 6 mol kg⁻¹ of NaCl, from 1.2 to 1.3 for the system NaOH/CO₂, and from 0.5 to 0.7 for the system HAc/CO₂.

The only system exhibiting a salting-in effect is the solution of carbon dioxide and acetic acid, with a CO₂ activity coefficient γ_{CO_2} smaller than 1. In our modeling, this system is assumed to be a mixture of uncharged hard spheres, leading to a repulsive effect, with activity coefficients γ_{CO_2} larger than unity. In contrast, the association between carbon dioxide and acetic acid introduced in our model is an attractive effect that causes the γ_{CO_2} to be decreased below 1. So, at 1.3 mol kg⁻¹ of carbon dioxide and 4 mol kg⁻¹ of acetic acid, and with a value of 0.3 for the association constant K_{asso} , the values for the activity coefficients are as follows: $\gamma_{\text{CO}_2}^{\text{HS}} = 1.98$, $\gamma_{\text{CO}_2}^{\text{MAL}} = 0.33$, yielding $\gamma_{\text{CO}_2} = \gamma_{\text{CO}_2}^{\text{HS}} \gamma_{\text{CO}_2}^{\text{MAL}} = 0.66$. Again, because the major component in the vapor phase is the carbon dioxide, the dimerization of acetic acid in the liquid phase has a negligible influence on the calculated pressures.

The two parameters $\sigma_{\text{CO}_2}^{(0)}$ and $\sigma_{\text{CO}_2}^{(0,T)}$ obtained for the carbon dioxide parameters are common to the three systems. The value of the carbon dioxide diameter at infinite dilution and 298 K, $\sigma_{\text{CO}_2}^{(0)}$, is 3.41×10^{-10} m which is reasonable considering the value of 1.22×10^{-10} m for a C=O bond. The interpretation of the parameter $\sigma_{\text{CO}_2}^{(0,T)}$ is the same as for the Na⁺ cation.

These parameter values were found to provide also a good description of the binary CO₂/H₂O mixture. In the temperature range 373–433 K, and for concentrations of carbon dioxide up to 0.5 mol kg⁻¹,³³ the model describes the pressures with a precision of 3.15% if one uses $\sigma_{\text{CO}_2}^{(0)}$ and $\sigma_{\text{CO}_2}^{(0,T)}$ given in Table 5. A plot is given in Figure 6. In this case, the activity coefficient of the carbon dioxide is slightly above 1 and decreases slowly with temperature.

The values of the anion diameters $\sigma_{\text{HCO}_3^-}$ and $\sigma_{\text{HCO}_3^{2-}}$ are consistent with the values generally found in the literature.³⁴ The carbonate anion is somewhat large, which can be explained by the solvation shell surrounding this doubly charged anion.

The HCO₃⁻ and CO₃²⁻ diameter values adjusted in the NaOH/CO₂ system may be expected to give satisfactory representation of other aqueous electrolyte systems containing carbon dioxide.

For the acetic acid, the value of the adjusted infinite dilution diameter $\sigma^{(0)}$ of 6.53×10^{-10} m seems plausible. Considering the geometrical form of the acetic acid and the size of the different bonds of the molecule, one obtains with the program MOPAC (Molecular Package) a distance of 5.1×10^{-10} m

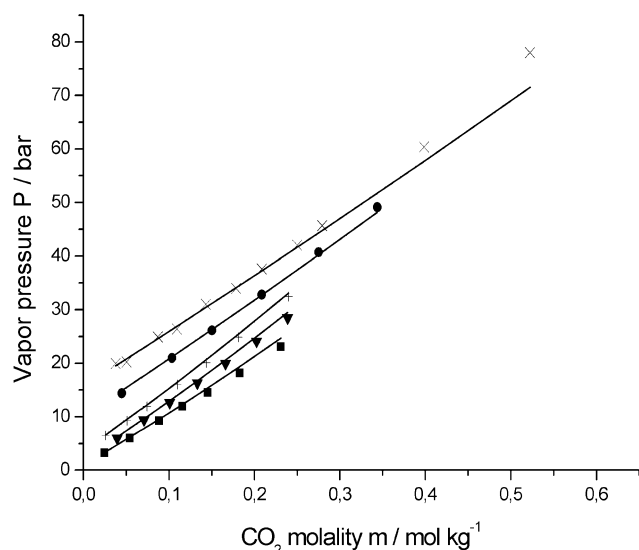


Figure 6. Plot of the pressure over aqueous CO₂ solutions up to 433 K. Experimental values taken from ref 33. (●): 373.15 K. (▼): 393.15 K. (+): 413.15 K. (■): 453.15 K. (×): 473.15 K.

between the hydrogen atom of the carboxylic acid group and the hydrogen atom of the methyl group. The value of 6.53×10^{-10} m is close to the value of 6.22×10^{-10} m found by Cartailier et al.²⁵ The concentration and temperature-dependent parameters are also coherent, as explained before.

Finally, it may be noted that the influence of salts on the CO₂ solubility pressure follows the Hofmeister series³⁵ much as the surface tension of electrolyte solutions.³⁶ This is not surprising because in both cases there is a balance between ionic hydration and the direct interaction between ions and gas molecules. Probably, both dispersion and hydration forces are responsible for this effect. In the present paper, these effects are buried in the parameters that are adjusted to the macroscopically measured pressures. In a forthcoming paper, these effects will be quantified by taking explicitly into account the influence of dispersion and hydration forces.

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