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Linear Relationships for Modeling CO_2 Absorption in Aqueous Alkanolamine Solutions in a Thermodynamically Consistent Way

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Abstract

A thermodynamically consistent model for the carbon dioxide (CO_2) absorption in aqueous alkanolamine system is of great importance in the research and development of a CO_2 capture process. To facilitate the development of thermodynamic models, linear Gibbs free energy, enthalpy, and heat capacity relationships using well-known amines as reference are used to correlate the standard reference state properties of ionic species with those of molecular species in the electrolyte system, which has been approved to provide a reliable and consistent way to estimate required parameters when there is minimal or no appropriate experimental data available. The proposed relationships have been applied to the development of an electrolyte Non-Random Two Liquid (NRTL) activity coefficient model for CO_2 absorption in aqueous 1-amino-2-propanol (A2P) solution, as an example to demonstration the methodology. With limited vapor-liquid equilibrium data and other thermodynamic properties, the parameters in the electrolyte NRTL model are identified with good accuracy.

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Introduction

With the need for reductions in greenhouse gas emissions to alleviate global climate change, carbon dioxide (CO_2) capture processes can be utilized to remove CO_2 from various gas streams. Among different methods used, CO_2 capture by absorption with aqueous solutions of alkanolamine or other solvents has become the most well-known and applicable technique. [1] Simulation and design of absorption/stripping processes requires detailed information and experimentally collected thermodynamic property and process data. However, thermodynamic property information is unavailable for some of the alkanolamines with potential for industrial processes.

Vapor-liquid equilibrium (VLE) modeling of gas-aqueous amine systems is critical for assessing process performance and system integration. Due to the large concentrations used and associated high ionic strengths, the chemical equilibria will behave non-ideally due to changes in the activity of the chemical species. This non-ideal behavior is usually described in two types of VLE models: empirical models based on the model of Kent and Eisenberg [2] and activity coefficient-based models. The former uses semi-empirical equations for the relevant reactions and the mass and charge balances. The Kent Eisenberg model requires fewer parameters than the activity coefficient-based model. The apparent equilibrium constants are usually used for calculating chemical equilibrium and any non-ideal behavior will be captured therein. The Kent and Eisenberg model is non-rigorous and favorably used to correlate the experimental data in a limited range. [3] However, as the model only gives inadequate information regarding to the thermodynamic properties, its usage in the industrial process simulation is limited.

The activity coefficient-based models, on the other hand, provide a rigorous thermodynamic framework to model aqueous electrolyte systems, where the electrolyte refers to the aqueous mixture system of ionic components. The excess Gibbs free energy-based activity coefficient models, such as Pitzer's model [4], the extended UNIQUAC model [5,6] and the electrolyte Non-Random Two Liquid (NRTL) model [7-11], are generally used to describe the activity changes in the electrolyte systems. Among these models, the electrolyte NRTL model satisfactorily represents the physical interactions of true species for aqueous and mixed solvent electrolyte systems by using binary and pair parameters. However, as the concentration of components in the electrolyte system varies over different orders of magnitude such as amine, carbamate, carbonate/bicarbonate in the CO_2 capture solution, it is often difficult to solve the chemical equilibrium equations due to computational problems. [12] Prior studies using the activity coefficient models have applied the electrolyte NRTL model to most of the industrially important CO_2 capture solvents, such as monoethanolamine (MEA) [13,14], diethanolamine (DEA) [13], *N*-methyldiethanolamine (MDEA) [15], diisopropanolamine (DIPA) [16], 2-amino-2-methyl-1-propanol (AMP) [17], triethanolamine (TEA), diglycolamine (DGA), and ammonia (NH_3) [18]. Among the applications, the equilibrium composition of the system is mostly calculated based on the minimization of the Gibbs free energy at constant pressure and temperature, where the equilibrium constants or the standard state properties are required. However, when such properties are not available in the literature or commercial process simulation databases, extensive experimental data, such as VLE data, absorption heat data, heat capacity data and speciation concentration data, is required to obtain their values via regression.

An accurate thermodynamic model should be based on sufficient experimental data and literature data, which is available for the commonly used solvents, while the thermophysical data is scarce

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for other solvents that still offer great potential. In such a case, it would be impractical to collect all the required data for the evaluation. Fortunately, the quantitative relation between the reaction reactivity and chemical structures has become a primary aim of physical organic chemistry and many different empirical correlations have been proposed during the past decades. Among these correlations, the linear free energy relationships (LFER) have proven useful and have been applied to different aqueous and mixed-solvent organic reactions. [19] The original correlation, namely the Hammett equation [20], is proposed as the following

$$\log \frac{K}{K_0} = \sigma\rho \tag{1}$$

where K and K_0 are the equilibrium constants for reactions involving benzoic acid derivatives, σ and ρ are parameters that dependent on the specific substituent and the type of reaction, respectively. Considering the relationship between the equilibrium constant and the standard Gibbs free energy change of reaction

$$-RT \ln K = \Delta G \tag{2}$$

where R is the gas constant and T is the system temperature, it is obvious that the LFER correlation can extendedly be used to correlate the standard Gibbs free energy of formation. Notably, Sverjensky and Molling [21] have correlated the standard free energy of formation for crystalline solids from aqua with the thermodynamics of their corresponding metal cations by the linear free energy equation

$$\Delta G^0_{f,M_vX} = a_{M_vX}\Delta G^0_{n,M^{2+}} + b_{M_vX} + \beta_{M_vX} r_{M^{2+}} \tag{3}$$

where a_{M_vX}, b_{M_vX} and β_{M_vX} are coefficients, $\Delta G^0_{f,M_vX}$ is the standard Gibbs free energy of formation of the solid with the chemical formula M_vX, $\Delta G^0_{n,M^{2+}}$ is the radius-based correction to the standard Gibbs free energy of formation of the aqueous cations M^{2+}, and $r_{M^{2+}}$ is the experimental ionic radii of the cations. It is of great importance if such relationships can also be applied to modeling CO_2 capture solvents

In this work, linear correlations are proposed to estimate the standard state properties of amine ions with the ideal gas properties of amine using linear correlations, where the ideal gas properties can be estimated from group-contributions [22,23]. Furthermore, the correlations are applied to the 1-amino-2-propanol (A2P) solvent to estimate some of its lacked standard state properties for use in the electrolyte NRTL model. A2P was selected as example due to it has been studied by many groups with some propriety being available in the public domain but still having incomplete database in Aspen. With the proposed correlations, a comprehensive thermodynamic representation for the A2P-H_2O-CO_2 system can be obtained with minimal experimental VLE data for CO_2 absorption in an aqueous A2P solution.

Thermodynamic framework

Chemical equilibrium

In the aqueous solution, H_2O, CO_2, and A2P undergo chemical dissociation reactions.

$$2\,\mathrm{H_2O} \leftrightarrow \mathrm{H_3O^+} + \mathrm{OH^-} \tag{4}$$

$$\mathrm{CO_2} + 2\,\mathrm{H_2O} \leftrightarrow \mathrm{HCO_3^-} + \mathrm{H_3O^+} \tag{5}$$

$$\mathrm{HCO_3^-} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_3^{-2}} + \mathrm{H_3O^+} \tag{6}$$

$$\mathrm{A2P} + \mathrm{H_3O^+} \leftrightarrow \mathrm{A2PH^+} + \mathrm{H_2O} \tag{7}$$

Additionally, A2P and the bicarbonate ion also react to form the carbamate ion.

$$\mathrm{A2P} + \mathrm{HCO_3^-} \leftrightarrow \mathrm{A2PCOO^-} + \mathrm{H_2O} \tag{8}$$

As a result of the above reactions, the liquid phase contains three molecular species $(\mathrm{H_2O}, \mathrm{CO_2}, \mathrm{A2P})$ and six ionic species $(\mathrm{H_3O^+}, \mathrm{A2PH^+}, \mathrm{OH^-}, \mathrm{HCO_3^-}, \mathrm{CO_3^{-2}}, \mathrm{A2PCOO^-})$. The extent of reaction in the aqueous solution is governed by chemical equilibria which are expressed by the thermodynamic equilibrium constant K_j:

$$K_j = \prod_i \alpha_i^{\nu_{i,j}} = \prod_i (x_i \gamma_i)^{\nu_{i,j}} \tag{9}$$

where $\nu_{i,j}$ is the reaction stoichiometric coefficient of specifies i in jth reaction, x_i is the molar fraction of specifies i, and γ_i is the activity coefficient of specifies i. The chemical equilibrium constants are calculated from the standard Gibbs free energy change of the reaction.

The equilibrium state for the aqueous system is defined as when the state of the Gibbs free energy is at the minimum at a temperature and pressure and thus the molar fraction of each species in the aqueous solution can be determined by minimizing the total Gibbs free energy of the system. The total Gibbs free energy for the electrolyte systems is given by the sum of Gibbs energies for pure solvents, molecular solutes, and ions with different reference states. For the aqueous phase reactions, both water and A2P are treated as solvents and described by the *symmetric* reference state, namely $\gamma_s(x_s \rightarrow 1) = 1$ (where s represents solvents). For molecular solute (CO_2) and ionic species, the *unsymmetric* reference state convention is used, namely $\gamma_i^*(x_w \rightarrow 1) = 1$ (where w represents water).

The Gibbs free energy contribution from solvents is calculated from the ideal gas Gibbs free energy and pure component fugacity.

$$G_s^l(T) = G_s^{ig}(T) + RT \sum_i x_i \ln \gamma_i \phi_i^l + RT \ln(\frac{p}{p^{ref}}), \qquad i = s \tag{10}$$

where $G_s^l(T)$ is the Gibbs free energy for solvents at temperature T, $G_s^{ig}(T)$ is the ideal gas Gibbs free energy for solvents at temperature T, ϕ_i^l is the liquid fugacity coefficient of pure solvent component, p is the system pressure and p^{ref} is the reference pressure (101325 Pa).

The ideal gas Gibbs free energy for solvents, $G_s^{ig}(T)$, is calculated with the following equation:

$$G_s^{ig}(T) = RT \sum_i x_i \ln x_i + \sum_i x_i G_i^{ig}(T), \qquad i = s \tag{11}$$

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where G_i^{ig} is the ideal gas Gibbs free energy for component i and is given by the following equation:

$$G_i^{ig}(T) = \Delta_f H_{i,T_{ref}}^{ig} - \frac{T}{T_{ref}}\left(\Delta_f H_{i,T_{ref}}^{ig} - \Delta_f G_{i,T_{ref}}^{ig}\right) + \int_{T_{ref}}^{T} C_{p,i}^{ig}(T)dT - T\int_{T_{ref}}^{T} \frac{C_{p,i}^{ig}(T)}{T}dT \quad (12)$$

where $\Delta_f H_{i,T_{ref}}^{ig}$ is the ideal gas enthalpy of formation for component i at reference temperature T_{ref} (298.15 K), $\Delta_f G_{i,T_{ref}}^{ig}$ is ideal gas Gibbs free energy of formation for component i at reference temperature, and $C_{p,i}^{ig}(T)$ is the ideal gas heat capacity. $\Delta_f H_{i,T_{ref}}^{ig}$ and $\Delta_f G_{i,T_{ref}}^{ig}$ are constants for component i, while $C_{p,i}^{ig}(T)$ is calculated with the ideal gas heat capacity polynomial. The values of the ideal gas thermodynamic properties at reference state and parameters for the ideal gas heat capacity are summarized in Table 1 and Table 2, respectively for all solution species.

The liquid fugacity coefficient of pure solvent component ϕ_i^l is calculated with

$$\phi_i^l = \frac{\phi_i^v\left(T, p_i^{*,l}\right)p_i^{*,l}\theta_i^l}{p} \quad (13)$$

where $\phi_i^v\left(T, p_i^{*,l}\right)$ is the pure component vapor fugacity coefficient at system temperature T and pure component vapor pressure $p_i^{*,l}$, and θ_i^l is the Poynting pressure correction from $p_i^{*,l}$ to p. In this work, the pure component vapor pressure $p_i^{*,l}$ is calculated with the extended Antoine equation as summarized in Table 3.

The Poynting pressure correction θ_i^l is calculated with the equation

$$\theta_i^l = \exp\left(\frac{1}{RT}\int_{p_i^{*,l}}^{p} V_i^{*,l}dp\right) \quad (14)$$

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where $V_i^{*,l}$ is the liquid molar volume for pure component i at T and p. The liquid molar volume $V_i^{*,l}$ is calculated based on the liquid density $\rho_i^{*,l}$ for pure component i

$$V_i^{*,l} = \frac{1}{\rho_i^{*,l}} \tag{15}$$

where the density is calculated with the DIPPR equation, which is summarized in Table 4. The required correlation parameters for A2P and H_2O can be retrieved from the Aspen Databank.

The Gibbs free energy contribution from the molecular solute, CO_2, is calculated with the ideal gas Gibbs free energy and Henry's constant model:

$$G_h^l(T) = G_h^{ig}(T) + RT \ln \frac{\gamma_h \left[\frac{H_h(T,p)}{\gamma_h^\infty}\right]}{p^{ref}}, \qquad h = CO_2 \tag{16}$$

where $G_h^l(T)$ is the Gibbs free energy for the molecular solute, $G_h^{ig}(T)$ is the ideal gas Gibbs free energy for the molecular solute, and $H_h(T,p)$ is the Henry's constant for the molecular solute with mixed solvent. The Henry's constant model for calculating $H_h(T,p)$ is given as

$$\ln\left[\frac{H_h(T,p)}{\gamma_h^\infty}\right] = \sum_s \omega_s \ln\left[\frac{H_{h,s}(T,p)}{\gamma_{h,s}^\infty}\right], \qquad h = CO_2 \tag{17}$$

where ω_s is the Henry's constant mixing rule weighting factor for molecular solute dissolved in mixed solvent, $H_{h,s}(T,p)$ is the Henry's constant for the molecular solute in pure solvent s. The weighing factor ω_s is calculated as

$$\omega_s = \frac{x_s\left(V_s^{*,l}\right)^{2/3}}{\sum_{s'} x_{s'}\left(V_{s'}^{*,l}\right)^{2/3}} \tag{18}$$

where $V_s^{*,l}$ and $V_{s'}^{*,l}$ are the liquid molar volumes for solvent s and s', which are calculated from the Brelvi-O'Connell model [24] with the characteristic volume for the solute and solvent as listed in Table 5. The characteristic volume for A2P is set as its critical volume, which is available in the

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Aspen Databank, and those for H_2O and CO_2 are taken from the literature [24,25]. The Henry's constant for pure solvent is calculated with a polynomial correlation and the correlation parameters used in this work are summarized in Table 6. The correlation parameters for CO_2 in water are obtained from the literature [25] and for CO_2 in A2P, and the required parameters are estimated based on the work of M. Á. Rebolledo-Morales et al. [26]

The Gibbs free energy contribution from the ionic components is calculated with the following equation:

$$G_{ca}^{l} = RT\sum_{i} x_i \ln x_i + \sum_{i} x_i G_i^{*,\infty}, \qquad i = c, a \tag{19}$$

where $G_i^{*,\infty}$ is the Gibbs free energy for an ionic component i, which is calculated as

$$G_i^{*,\infty} = H_i^{*,\infty} - TS_i^{*,\infty} + RT\ln\left(\frac{1000}{M_w}\right) \tag{20}$$

$$H_i^{*,\infty} = \Delta_f H_i^{\infty,aq} + \int_{T^{ref}}^{T} C_{p,i}^{\infty,aq}\, dT \tag{21}$$

$$S_i^{*,\infty} = \frac{\Delta_f H_i^{\infty,aq} - \Delta_f G_i^{\infty,aq}}{T^{ref}} + \int_{T^{ref}}^{T} \frac{C_{p,i}^{\infty,aq}}{T}\, dT \tag{22}$$

where $\Delta_f H_i^{\infty,aq}$ is the infinite dilution aqueous phase enthalpy, $\Delta_f G_i^{\infty,aq}$ is the infinite dilution aqueous phase Gibbs free energy and $C_{p,i}^{\infty,aq}$ is the infinite dilution aqueous phase heat capacity. The term $RT\ln(\frac{1000}{M_w})$ is added to convert the $\Delta_f H_i^{\infty,aq}$ and $\Delta_f G_i^{\infty,aq}$ based on the molality scale to the $G_i^{*,\infty}$ on the mole fraction scale. $\Delta_f H_i^{\infty,aq}$ and $\Delta_f G_i^{\infty,aq}$ are constants for component i, while $C_{p,i}^{\infty,aq}(T)$ is assumed to be constant and represented as the first term in the heat capacity polynomial. The values of the infinite dilution aqueous phase thermodynamic properties at the reference state and parameters for the ideal gas heat capacity are summarized in Table 1 and Table 7, respectively.

Vapor liquid equilibria

The distribution of molecular species of carbon between the vapor and liquid phases is governed by the phase equilibrium, which is calculated by the activity coefficient method in this work. The basic relationship for the phase equilibrium is given by

$$y_i \phi_i^v p = x_i \gamma_i \left(\frac{H_i}{\gamma_i^\infty}\right), \qquad i = \mathrm{CO_2} \tag{23}$$

where y_i is the vapor phase mole fraction, ϕ_i^v is the vapor phase fugacity coefficient, x_i is the liquid phase mole fraction, γ_i is the liquid phase activity coefficient, H_i is the Henry's constant. The PC-SAFT [27,28] equation of state is used to calculate fugacity coefficients for the vapor phase, which is widely used in the modeling of CO_2 capture with aqueous alkanolamine solutions. The PC-SAFT parameters for H_2O and CO_2 are taken from the Aspen Databank [29] and as the parameters for A2P are not available, the values for MEA, which are available in the Aspen Databank [29], are used in this work. All the binary interaction parameters used in the PC-SAFT equations are set to 0.

Activity coefficient

The electrolyte NRTL model is an excess Gibbs free energy expression to account for the liquid phase nonideality for electrolyte systems. In this model, the excess Gibbs free energy of a mixed solvent electrolyte system is represented as the sum of long- and short-range ion-ion interactions which includes local ion-molecule, ion-ion, and molecule-molecule interactions. The basic equation for the electrolyte NRTL model is given as follows

$$G_m^{*,E} = G_m^{*,lc} + G_m^{*,PDH} + G_m^{*,Born} \tag{24}$$

The activity coefficient γ_i of component i is derived from the excess Gibbs free energy with the following equation

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$$\ln \gamma_i = \frac{1}{RT}\left[\frac{\partial\left(nG_m^{E,l}\right)}{\partial n_i}\right]_{T,p,n_{j\neq i}}, \qquad i,j = m,c,a \tag{25}$$

The local interaction contribution is derived from the NRTL theory based on the like-ion repulsion and local electroneutrality assumptions and three types of interactions exist in the electrolyte system: the first type is the interaction of a central molecular species with other species in the immediate neighborhood; the other two types are central cationic or anionic species in the center with molecular species and oppositely charged ionic species in the immediate neighborhood. The corresponding excess Gibbs free energy can be given as follows:

$$\begin{aligned}\frac{G_m^{ex,lc}}{nRT} = & \sum_m X_m\left(\frac{\sum_i X_i\, G_{im}\tau_{im}}{\sum_i X_i\, G_{im}}\right) + \sum_c X_c\left(\frac{\sum_{i\neq c} X_i\, G_{ic}\tau_{ic}}{\sum_{i\neq c} X_i\, G_{ic}}\right) \\ & + \sum_a X_a\left(\frac{\sum_{i\neq a} X_i\, G_{ia}\tau_{ia}}{\sum_{i\neq a} X_i\, G_{ia}}\right)\end{aligned} \tag{26}$$

where the subscripts $m, c,$ and a represent the molecular, cationic, and anionic species, respectively, and thus the corresponding terms in Equation (26) are for the contributions when molecular, cationic, and anionic species are at the center, respectively. The local binary quantities G and τ are related to each other by the following equation

$$G = \exp(-\alpha\tau) \tag{27}$$

where α is the nonrandom factor parameter. In this model, the asymmetric binary interaction energy parameters τ and symmetric non-random factor parameters α are adjustable binary parameters. For molecule-molecule interactions, the required binary parameters are given directly by the adjustable parameters, while for the interactions involving cations and anions, the binary parameters are calculated from the adjustable parameters by applying the composition-average mixing rule. [9,11]

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The unsymmetric Pitzer-Debye-Hückel model and the Born equation are used to represent the contribution of the long-range ion-ion interactions.

$$\frac{G^{ex,PDH}}{nRT} = -\frac{4A_\varphi I_x}{\rho} \ln\left[\frac{1+\rho I_x^{1/2}}{1+\rho (I_x^0)^{1/2}}\right] \tag{28}$$

with

$$A_\varphi = \frac{1}{3}\left(\frac{2\pi N_A}{v_S}\right)^{1/2}\left(\frac{Q_e^2}{\varepsilon_S k_B T}\right)^{3/2} \tag{29}$$

where n is the total mole number of the solution, A_φ is the Debye-Hückel parameter, I_x is the ionic strength, ρ is the closest approach parameter, N_A is the Avogadro's number, v_S is the molar volume of the solvent, Q_e is the electron charge, ε_S is the dielectric constant of the solvent, and k_B is the Boltzmann constant. The Born term corrects the Debye-Hückel term for the change of the reference state from the mixed solvent composition to aqueous solution and is given as the following

$$\begin{aligned}\frac{\Delta G^{\mathrm{Born}}}{nRT} &= \frac{Q_e^2}{2k_B T}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)\sum_i \frac{x_i z_i^2}{r_i} 10^{-2} \\ &= \frac{N_A Q_e^2}{2RT}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)\sum_i \frac{x_i z_i^2}{r_i} 10^{-2}\end{aligned} \tag{30}$$

where ϵ_w is the dielectric constant of water, r_i is the Born radius of species i and R is the gas constant.

The molar volume v_s and the dielectric constant ε_s for mixed solvents are calculated based on the respective values of the single solvent with a composition average mixing rule proposed by Chen and Song [9]. The dielectric constants of pure solvent species are represented with a polynomial expression as summarized in Table 9.

Model parameters

The parameters associated with the thermodynamic model are summarized in Table 10. Most of the parameters are taken from the Aspen databank if the corresponding parameters exist. The ideal gas heat capacity C_p^{ig} for A2P is estimated with the Benson method provided by Aspen Property Constant Estimation System (PCES) and the infinite dilution standard state parameters for $\mathrm{A2PH^+}$ and $\mathrm{A2PCOO^-}$ are estimated with the linear correlations proposed in the current work.

The Henry's constant for CO_2 in H_2O and NRTL binary parameters for CO_2-H_2O binary, as well as the characteristic volume for CO_2 and H_2O are taken from the literature [24,25]. The NRTL binary parameters for A2P-H_2O binary and the PC-SAFT pure component parameters for A2P are fixed to those of MEA due to their similarity, which are taken from the literature [14]. The dielectric constant for A2P is also fixed to that of MEA, which is available in the Aspen databank [29]. All the PC-SAFT binary parameters for molecule-molecule pairs are fixed to 0. Other parameters, such as the Henry's constant for CO_2 in A2P and some of the NRTL binary parameters for molecule-electrolyte pairs, are identified by regressing the parameters to the experimental data by using the Data Regression System (DRS) of Aspen Plus process simulator. The objective function is minimized by the adjustment of the model parameters so that the simulation subject to the vapor-liquid equilibrium constraints for CO_2 and chemical equilibrium constraints for all reactions are included in the model.

The Henry's constant for the molecular solute with mixed solvent can be calculated from those in the pure solvents using Equation (17). Then, the Henry's constants for CO_2 in H_2O and CO_2 in A2P are required. The dissolution of CO_2 in H_2O has been studied extensively [25], while research on the physical solubility of CO_2 in A2P is limit and the required parameters are not available. Therefore, the work of M. Á. Rebolledo-Morales et al. [26] is used to estimate the Henry's constant for CO_2 in A2P. The characteristic volume parameters for the Brelvi and O'Connell model are

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taken from the Aspen databank. The values of these parameters are summarized in Table 5 and Table 6.

In an electrolyte system, the interactions can be categorized as molecule-molecule, molecule-electrolyte, and electrolyte-electrolyte pair interactions. For each of these interactions, both α and τ exist for different component species, which contribute to a great number of interaction parameters to be formulated for the electrolyte system. Therefore, it is unpractical to determine all these parameters with available experimental data. Considering that some species are present in the electrolyte system with low concentrations, not all these interaction parameters contribute significantly to the representation of VLE.

In this work, all molecule-molecule and electrolyte-electrolyte binary interaction parameters are defaulted to zero and for molecule-electrolyte binary interactions, default value of (8, -4) in Aspen Plus for the electrolyte NRTL model are used. The non-random factor is fixed at 0.2. Subsequently, the asymmetric NRTL interaction parameters between A2P and H_2O are fixed to the corresponding parameters of MEA and the asymmetric electrolyte NRTL parameters that significantly affect the representation of VLE are regressed against the experimental VLE data. Therefore, only the interactions between H_2O and ($A2PH^+$, HCO_3^-), H_2O and ($A2PH^+$, $A2PCOO^-$), as well as those between A2P and ($A2PH^+$, $A2PCOO^-$), CO_2 and ($A2PH^+$, $A2PCOO^-$), are considered in this work. The asymmetric binary parameters, τ, are temperature dependent and are fitted to the following correlation

$$\tau_{ij} = c_{ij} + \frac{d_{ij}}{T} \tag{31}$$

where c_{ij} and d_{ij} are correlation parameters. The interaction parameters are obtained by regressing the correlation parameters in Equation (31) with the experimental VLE data for A2P-H_2O-CO_2 system and the obtained parameters are summarized in Table 11 and Table 12.

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Model development (Methodology to estimate the missing data)

To develop a thermodynamic model for CO_2 absorption in aqueous solution with extensive measured data available but still incomplete thermodynamic dataset, Zhang et al. [14] calculated the standard state thermodynamic property parameters with chemical equilibrium constants obtained from literature and then used these values as the initial guess to fit experimental data. The selected experimental VLE data, enthalpy of absorption, heat capacity, and species concentration were used to regress these parameters. However, it is difficult to apply this method to those amines for which experimental data is limit. Regression of the parameters against limited experimental data may cause uncertainties that propagate through the calculation of the equilibrium and lead to unreliable results.

Contrary to the standard state thermodynamic property parameters for aqueous amine ions, the corresponding parameters for pure amine molecules are generally available. Furthermore, these pure component properties have been estimated with some group-contribution methods, which is extensively investigated in literature. [22,23] In this work, a relationship between the thermodynamic properties of a solvent molecule and its aqueous ions is developed to predict the unavailable thermodynamic data from the known properties.

As discussed in the previous section, the ideal gas reference state is used for the molecular species and the aqueous infinite dilution reference state is used for ionic species. For aqueous ions with a similar radius, Equation (3) can be reduced and rearranged to

$$\Delta_f G_i^{\infty,aq} = a_{\Delta G}\, \Delta_f G_i^{ig} + b_{\Delta G} \tag{32}$$

where $\Delta_f G_i^{ig}$ is the ideal gas Gibbs free energy of formation for the bulk molecules, $\Delta_f G_i^{\infty,aq}$ is the infinite dilution Gibbs free energy of formation for ionic species, and a, b are correlation parameters. As the ideal gas Gibbs free energy of formation is usually available in the literature or can be estimated based on the group-contribution method, it would be of great significance to estimate the infinite dilution parameters from the ideal gas parameters using Equation (32).

To verify the correlation, the ideal gas Gibbs free energy for TEA, DEA, DIPA, DGA, MDEA, MEA, AMP, and NH_3, and the corresponding aqueous phase infinite dilution parameters for their protonated and carbamate ions are retrieved from Aspen Plus (Table 13). As shown in Figure 1, good linearity is observed for the relationship between infinite dilution Gibbs free energy and ideal gas Gibbs free energy. The correlation parameters for the Gibbs free energy are given in Table 16. It is also found that the enthalpy of formation shows similar systematic relationship as the Gibbs free energy of formation. As shown in Figure 2, a linear relationship also exists between the aqueous infinite dilution and ideal gas enthalpy of formation, and thus can be correlated by the following equation

$$\Delta_f H_i^{\infty,aq} = a_{\Delta H}\, \Delta_f H_i^{ig} + b_{\Delta H} \tag{33}$$

The relationship is also verified with the components used for the case of Gibbs free energy of formation. The ideal gas and aqueous infinite dilution reference state enthalpy of formations are shown in Table 14 and the obtained correlation parameters are given in Table 16.

Considering the relationship between enthalpy and heat capacity, it is natural to assume that there exists a correlation for the ideal gas and aqueous infinite dilution heat capacities. However, the ideal gas heat capacity is represented with a polynomial expression with temperature, and the relationship is not as straightforward. Therefore, the ideal gas heat capacity at 298.15 K is used in this work. It is also assumed that the aqueous infinite dilution heat capacity is constant, which is commonly used in literature for representing the aqueous infinite dilution heat capacity. Similar with Gibbs free energy and enthalpy, a linear correlation is proposed as given in Equation (34).

The heat capacities used in this work is given in Table 15 and the corresponding correlation parameters are given in Table 16.

$$C_{p,i}^{\infty,aq} = a_{C_p}\, C_{p,i}^{ig} + b_{C_p} \tag{34}$$

Note that the aqueous infinite dilution heat capacity data does not have the close linear fit as those of Gibbs free energy and enthalpy of formation, which makes it difficult to determine the required parameters with high accuracy. Nevertheless, the correlation proposed in this work still provides a good starting point for determining these parameters, which may subject to further adjustments. The thermodynamic parameters used for the estimation, as well as the estimated parameters for A2P, are given in Tables 13 – 15. With the above correlations, the infinite dilution parameters A2PH+ and A2PCOO- are obtained as shown in Table 1 and Table 7. Then, these parameters can be input to the parameters form in Aspen Plus prior to the regression.

Results

A2P-H_2O System

Although various experimental data based on different thermodynamic properties of A2P are available in literature, not all the experimental data for the A2P-H_2O system are in the tight measurement error and thus the NRTL binary parameters could not be finalized. Therefore, the NRTL binary parameters for the MEA-H_2O system are used in this work (Table 11). The stream pressure in the A2P-H_2O binary solution system is determined by the NRTL parameters and the comparison of experimental data and model results is given in Figure 4. As shown in the figure, the model results agree well with the experimental data. Hamborg and Versteeg [30] investigated the dissociation constants for A2P and MEA, and it was found that the pKa for these two alkanolamines are 9.45 and 9.44, respectively. The results suggest that the interaction between A2P and water might be very similar with that of MEA and water. Therefore, although the NRTL

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parameters are not regressed in this work, the model results are in good agreement with the experimental data. Figure 5 shows the model predictions for excess enthalpy and the overall trend of the model predictions is similar with the experimental excess enthalpy data reported by Mundhwa and Henni [31].

A2P-H_2O-CO_2 System

The equilibrium CO_2 solubility data in A2P-H_2O-CO_2 system has been measured by Rebolledo-Morales et al [26], that is available for the current regression, which covers the pressure range of 0.2 to 2436.4 kPa, measured at temperature of 313.15 K and 393.15 K with the A2P concentrations of 2.66, 3.99, 5.33 and 6.66 mol/kg. Additionally the equilibrium CO_2 solubility data over the CO_2 partial pressure range of 0 – 480 kPa at temperatures 313.15 to 393.15 K is collected in this work following the static pressure method as described in the previous work [32]. The selected temperatures, namely 313.15 K, 333.15 K, 353.15 K, 373.15 K and 393.15 K, will give detailed information regarding the evolution of VLE with temperature. As the solubility data is proprietary, the detailed data set will not be reported herein.

Figure 6 shows the comparison of experimental data obtained in this work and the model results for the A2P concentrations of 3.95 mol/kg. As the solubility data is proprietary for solvent developers, the authors would prefer not to add the y-label scale. As the main purpose of this figure is to demonstrate consistency of the model results and the experimental data, the removal of the y-axis will not change the conclusion. As shown in the figure, the model results match the experimental data reasonably well, except at low temperatures and CO_2 loadings. The reason for these inconsistences could be caused by the relatively large uncertainties of experimental data under these conditions.

The comparison between experimental data from Rebolledo-Morales et al. [26] and the model predictions is shown in Figure 7. As shown in the figure, the model predictions agree reasonably well with experimental data.

Figure 8 shows the comparison of the standard enthalpy of reaction for A2P and MEA for the amine dissociation reaction ($\Delta_r H_4^0$) and carbamate formation reaction ($\Delta_r H_5^0$). The standard enthalpy of reaction ($\Delta_r H^0$) is obtained by assuming that the standard enthalpy of reaction is a constant over a small temperature range, and thus the definite integration of the van't Hoff equation between temperatures T_1 and T_2 gives

$$\Delta_r H^0 = R\frac{\ln\frac{K_2}{K_1}}{\frac{1}{T_1}-\frac{1}{T_2}} \tag{35}$$

where K_1, K_2 are the equilibrium constants at absolute temperatures T_1 and T_2, respectively. Therefore, only the evolution of standard enthalpy of reaction with temperature is reported herein. It could be found that the evolution of $\Delta_r H_4^0$ with temperature is quite similar for A2P and MEA. Considering the similar pKa reported by Hamborg and Versteeg [30], the results seem reasonable. The evolution of $\Delta_r H_5^0$ with temperature is slightly different with that of MEA while still in a reasonable range.

<u>Conclusion</u>

In this work, the concept of linear free energy relationships (LFER) is extended to correlate the standard state properties in the electrolyte system, where three linear correlations are proposed for the Gibbs free energy of formation, enthalpy of formation and heat capacity. With these correlations, the corresponding standard state properties of ionic species can be estimated with ideal gas properties of the bulk molecule. These correlations provide a reliable and consistent way

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to estimate the standard state parameters for use in the thermodynamic modeling of CO_2 capture solvents and processes with insufficient experimental data.

Furthermore, the proposed correlations are applied to the thermodynamic modeling of CO_2 absorption in an aqueous A2P solution with the electrolyte NRTL activity coefficient model. Due to the insufficient experimental data for this system, the parameters in the model cannot be determined reliably. However, with the proposed correlations, the standard state parameters can be fixed prior to the regression. Therefore, the parameters in the electrolyte NRTL model can be identified with good accuracy. In this way, the model could provide more reliable predictions to support the process modeling and simulation of the CO_2 capture process.

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List of Figure Captions

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List of Table Captions

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Table 1 Parameters for the Reference State Thermodynamic Properties

Components	State	$\Delta_f G_{T^{ref}}$ (J/kmol)	$\Delta_f H_{T^{ref}}$ (J/kmol)	Source
A2P	ig	-1.08×10^8	-2.39×10^8	Aspen Databank[29]
H_2O	ig	-2.28572×10^8	-2.41818×10^8	Aspen Databank
CO_2	ig	-3.9437×10^8	-3.9351×10^8	Aspen Databank
H_3O^+	∞, aq	-2.37129×10^8	-2.8583×10^8	Aspen Databank
$A2PH^+$	∞, aq	-1.90×10^8	-3.55×10^8	This work
OH^-	∞, aq	-1.57244×10^8	-2.29994×10^8	Aspen Databank
HCO_3^-	∞, aq	-5.8677×10^8	-6.9199×10^8	Aspen Databank
CO_3^{2-}	∞, aq	-5.2781×10^8	-6.7714×10^8	Aspen Databank
$A2PCOO^-$	∞, aq	-4.89×10^8	-7.33×10^8	This work

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*Table 2 Parameters for Ideal Gas Heat Capacity Correlations**

Parameters	Heat capacity ($J/kmol \cdot K$)		
	A2P	H_2O	CO_2
source	Aspen Databank	Aspen Databank	Aspen Databank
C_{1i}	4796.05243	33738.112	19795.19
C_{2i}	427.816458	−7.0175634	73.436472
C_{3i}	−0.280882659	0.027296105	−0.056019384
C_{4i}	$7.68215458 \times 10^{-5}$	$-1.6646536 \times 10^{-5}$	1.715332×10^{-5}
C_{5i}		4.2976136×10^{-9}	
C_{6i}		$-4.169608 \times 10^{-13}$	

* The correlation for the ideal gas heat capacity is given by the polynomial:

$$C_{p,i}^{ig}(T) = C_{1i} + C_{2i}T + C_{3i}T^2 + C_{4i}T^3 + C_{5i}T^4 + C_{6i}T^5$$

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*Table 3 Parameters of the Extended Antoine Equation for Pure Component Vapor Pressure**

Parameters	Liquid Vapor Pressure (Pa)	
	A2P	H_2O
source	Aspen Databank	Aspen Databank
C_{1i}	46.03	73.649
C_{2i}	-7327.7	-7258.2
C_{3i}	0	0
C_{4i}	0	0
C_{5i}	-2.8942	-7.3037
C_{6i}	5.7651×10^{-19}	4.1653×10^{-6}
C_{7i}	6	2

* The equation for the extended Antoine vapor pressure model is:

$$\ln p_i^{*,l} = C_{1i} + \frac{C_{2i}}{T + C_{3i}} + C_{4i}T + C_{5i}\ln T + C_{6i}T^{C_{7i}}$$

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Table 4 Parameters for DIPPR Equation

Parameters	Liquid Molar Volume (kmol/m^3)	
	A2P*	H_2O**
source	Aspen Databank	Aspen Databank
C_{1i}	0.8321	17.863
C_{2i}	0.23132	58.606
C_{3i}	614	−95.396
C_{4i}	0.2201	213.89
C_{5i}	0	−141.26

* The DIPPR equation for A2P is:

$$\rho_i^{*,l} = C_{1i}/C_{2i}^{1+\left(1-\frac{T}{C_{3i}}\right)^{C_{4i}}}$$

** The DIPPR equation for water is:

$$\rho_i^{*,l} = C_{1i} + C_{2i}(T/T_c)^{0.35} + C_{3i}(T/T_c)^{2/3} + C_{4i}(T/T_c) + C_{5i}(T/T_c)^{4/3}$$

where T_c is the critical temperature.

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Table 5 Brelvi-O'Connell Characteristic Volume Parameters

Parameters	Characteristic Volume (m^3/kmol)		
	A2P	H_2O	CO_2
source	Aspen Databank	Brelvi and O'Connell [24]	Yan and Chen [25]
$\nu_{1,i}$	0.278	0.0464	0.175
$\nu_{2,i}$	0	0	-0.000338

* The correlation of the characteristic volume for the Brelvi-O'Connell model is given as:

$$V_i^{BO} = \nu_{1,i} + \nu_{2,i}T$$

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*Table 6 Parameters for Henry's constant (Pa)**

Solute	CO_2	CO_2
Solvent	H_2O	A2P
source	Yan and Chen [25]	This work
$a_{h,s}$	91.344	21.9376
$b_{h,s}$	-5876.0	-1310.84
$c_{h,s}$	-8.598	0.0
$d_{h,s}$	-0.012	0.0

* The correlation for Henry's constant is given by:

$$\ln H_{h,s}(T,p) = a_{h,s} + \frac{b_{h,s}}{T} + c_{h,s} \ln T + d_{h,s} T$$

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*Table 7 Parameters for Infinite Dilution Heat Capacity Correlations**

Parameters	Heat capacity ($J/kmol \cdot K$)					
	H_3O^+	$A2PH^+$	OH^-	HCO_3^-	CO_3^{2-}	$A2PCOO^-$
source	Aspen Databank	This work	Aspen Databank	Aspen Databank	Aspen Databank	This work
C_{1i}	75291	2.03×10^5	-148500	-29260	-397100	6.10×10^4

* The aqueous infinite dilution heat capacity is assumed to be constant ($c_{p,i}^{\infty,aq} = C_{1i}$).

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Table 8 PC-SAFT Equation of State Pure Component Parameters

Parameters	A2P*	H_2O	CO_2
source	Zhang et al. [14]	Aspen Databank [29]	Aspen Databank [29]
Association energy ϵ^{AB}, K	2369.0	2500.7	0
Effective association volume k^{AB}, Å^3	0.01903	0.034868	0
Segment number m	2.9029	1.0656	2.5692
Segment energy parameter ϵ, K	306.20	366.51	152.10
Segment diameter σ, Å	3.1067	3.0007	2.5637

* The corresponding parameters for MEA are used in this work.

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*Table 9 Parameters for Dielectric Constant**

Parameters	Dielectric constant ($kmol/m^3$)	
	A2P**	H_2O
source	Aspen Databank	Aspen Databank
C_{1i}	37.72	78.51
C_{2i}	0	31989.4
C_{3i}	298.15	298.15

* The temperature dependency of the dielectric constant is given as:

$$\epsilon_i(T) = C_{1i} + C_{2i}(1/T - 1/C_{3i})$$

** The dielectric constant correlation parameters of MEA are used for A2P.

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Table 10 Model Parameters

Parameters	Components	Source
$\Delta_f G^{ig}_{T_{ref}}, \Delta_f H^{ig}_{T_{ref}}, C_p^{ig}$	H_2O, CO_2, A2P	Aspen Databank [29]
$\Delta_f G^{aq,\infty}_{T_{ref}}, \Delta_f H^{aq,\infty}_{T_{ref}}, C_p^{aq,\infty}$	$H_3O^+, OH^-, HCO_3^-, CO_3^{-2}$	Aspen Databank [29]
	$A2PH^+, A2PCOO^-$	This work
Henry's constant	CO_2 in H_2O	Yan and Chen [25]
	CO_2 in A2P	This work
NRTL binary parameters	CO_2-H_2O binary	Yan and Chen [25]
	A2P-H_2O binary	This work
	Molecule-electrolyte pairs	This work
Dielectric constant	H_2O	Aspen Databank [29]
	A2P	This work
Characteristic Volume	A2P	Aspen Databank [29]
	H_2O	Brelvi and O'Connell [24]
	CO_2	Yan and Chen [25]
PC-SAFT pure component parameters	H_2O, CO_2	Aspen Databank [29]
	A2P	This work
PC-SAFT binary parameters	Molecule-molecule pairs	This work

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Table 11 NRTL Parameters for the A2P-H_2O Binary System with $\alpha = 0.2$

Parameter	NRTL Parameters	
Component i	H_2O	A2P*
Component j	CO_2	H_2O
source	Yan and Chen [25]	Zhang et al. [14]
$c_{i,j}$	0	1.5201
$c_{j,i}$	0	0.1559
$d_{i,j}$	0	−910.30
$d_{j,i}$	0	110.80

* The corresponding parameters for MEA are used in this work.

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Table 12 Regressed NRTL Parameters for the A2P-H_2O-CO_2 System with $\alpha = 0.2$

Components i	Components j	c_{ij}	d_{ij}
H_2O	$(A2PH^+, HCO_3^-)$	0.5881	0
$(A2PH^+, HCO_3^-)$	H_2O	1.3243	0
H_2O	$(A2PH^+, A2PCOO^-)$	19.9340	−1796.2713
$(A2PH^+, A2PCOO^-)$	H_2O	−5.8913	106.6472
A2P	$(A2PH^+, A2PCOO^-)$	6.6822	0
$(A2PH^+, A2PCOO^-)$	A2P	−2.0746	0
CO_2	$(A2PH^+, A2PCOO^-)$	16.8675	0
$(A2PH^+, A2PCOO^-)$	CO_2	−6.1759	0

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Table 13 Ideal gas and infinite dilution reference state Gibbs free energies

Component	$\Delta_f G_i^{ig}$ (J/kmol)	$\Delta_f G_i^{\infty,aq}$ (J/kmol)		Source
	R0	RH+	RCOO-	
TEA	-2.9940×10^8	-4.0255×10^8		Aspen Plus
DEA	-2.2574×10^8	-3.2472×10^8	-6.2438×10^8	Aspen Plus
DIPA	-2.1500×10^8	-3.1710×10^8	-6.1980×10^8	Aspen Plus
DGA	-1.8700×10^8	-2.8512×10^8	-5.8465×10^8	Aspen Plus
MDEA	-1.6900×10^8	-2.5953×10^8		Aspen Plus
MEA	-1.0330×10^8	-1.8962×10^8	-4.9299×10^8	Aspen Plus
AMP	-8.4730×10^7	-1.6281×10^8	-4.5630×10^8	Aspen Plus
NH3	-1.6400×10^7	-7.9310×10^7	-3.7639×10^8	Aspen Plus
A2P	-1.08×10^8	-1.90×10^8	-4.89×10^8	This work

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Table 14 Ideal gas and infinite dilution reference state enthalpies

Component	$\Delta_f H_i^{ig}$ (J/kmol)	$\Delta_f H_i^{\infty,aq}$ (J/kmol)		Source
	R0	RH+	RCOO-	
TEA	-5.6145×10^8	-6.9952×10^8		Aspen Plus
DEA	-4.0847×10^8	-5.3691×10^8	-9.1808×10^8	Aspen Plus
DIPA	-4.54×10^8	-6.158×10^8	-1.006×10^9	Aspen Plus
DGA	-3.65×10^8	-5.0495×10^8	-8.8803×10^8	Aspen Plus
MDEA	-3.8008×10^8	-5.1095×10^8		Aspen Plus
MEA	-2.0670×10^8	-3.3164×10^8	-7.0747×10^8	Aspen Plus
AMP	-2.7029×10^8	-3.7812×10^8	-7.619×10^8	Aspen Plus
NH3	-4.5898×10^7	-1.3251×10^7	-4.9938×10^8	Aspen Plus
A2P	-2.39×10^8	-3.55×10^8	-7.33×10^8	This work

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Table 15 Ideal gas and aqueous infinite dilution heat capacities

Component	$C_{p,i}^{ig}$ (kJ/kmol-K)	$C_{p,i}^{\infty,aq}$ (J/kmol-K)		Source
	R0	RH+	RCOO-	
DIPA	249.651	3.5938×10^5	2.5483×10^5	Aspen Plus
DGA	163.012	2.4676×10^5	1.5441×10^5	Aspen Plus
MDEA	188.564	3.3876×10^5		Aspen Plus
MEA	84.539	2.1022×10^5	-4.9781×10^{-2}	Aspen Plus
NH3	35.554	7.9962×10^4	-3.0710×10^4	Aspen Plus
A2P	109.42	2.03×10^5	6.10×10^4	This work

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Table 16 Correlation parameters

Parameters	RH+	RCOO-
$a_{\Delta G}$	1.0054	1.0512
$b_{\Delta G}$	-8.2952×10^7	-3.8273×10^8
$a_{\Delta H}$	1.0710	1.1034
$b_{\Delta H}$	-1.0622×10^8	-4.8089×10^8
a_{C_p}	1258.7610	1414.7250
b_{C_p}	6.5423×10^4	-9.3794×10^4

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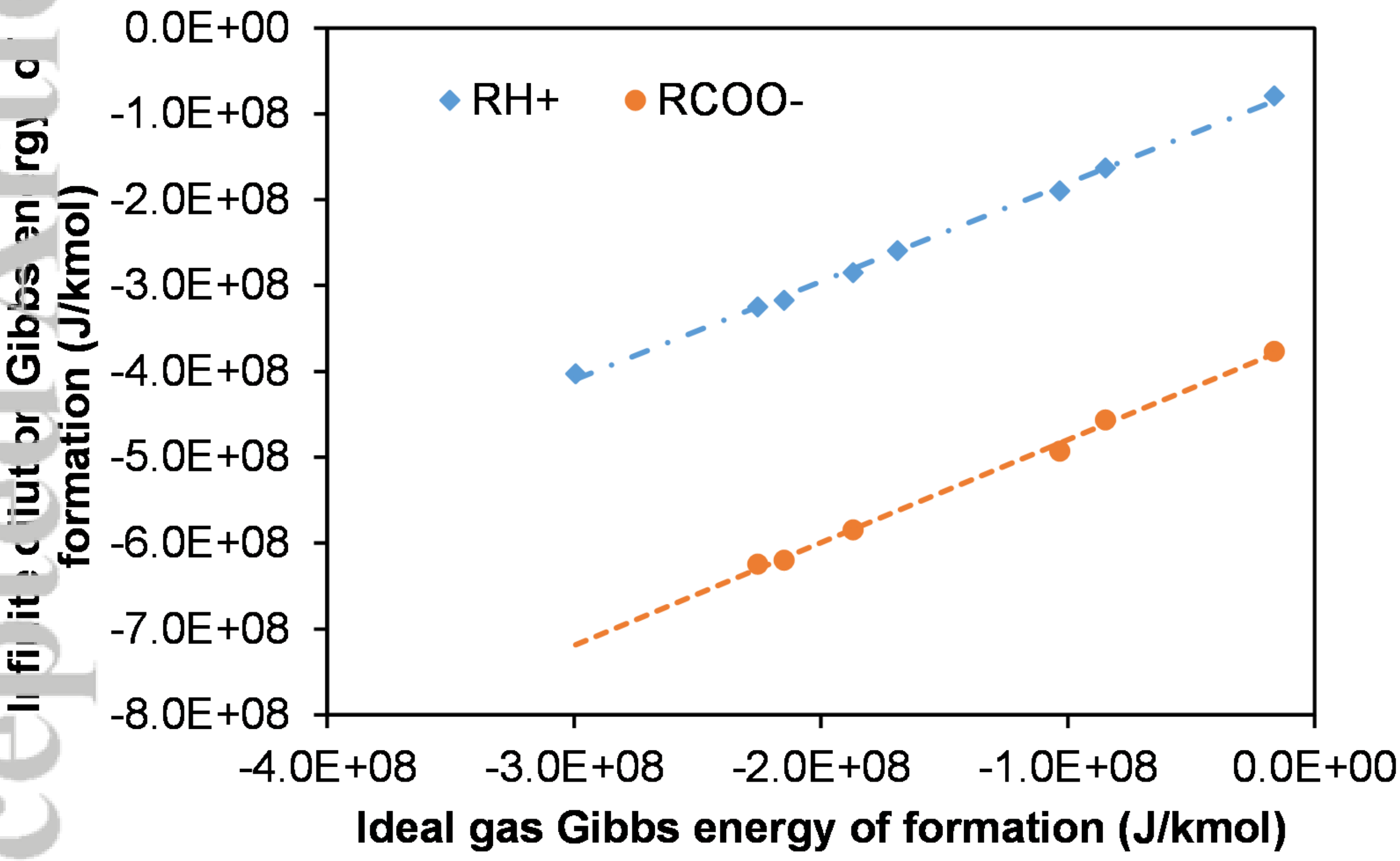

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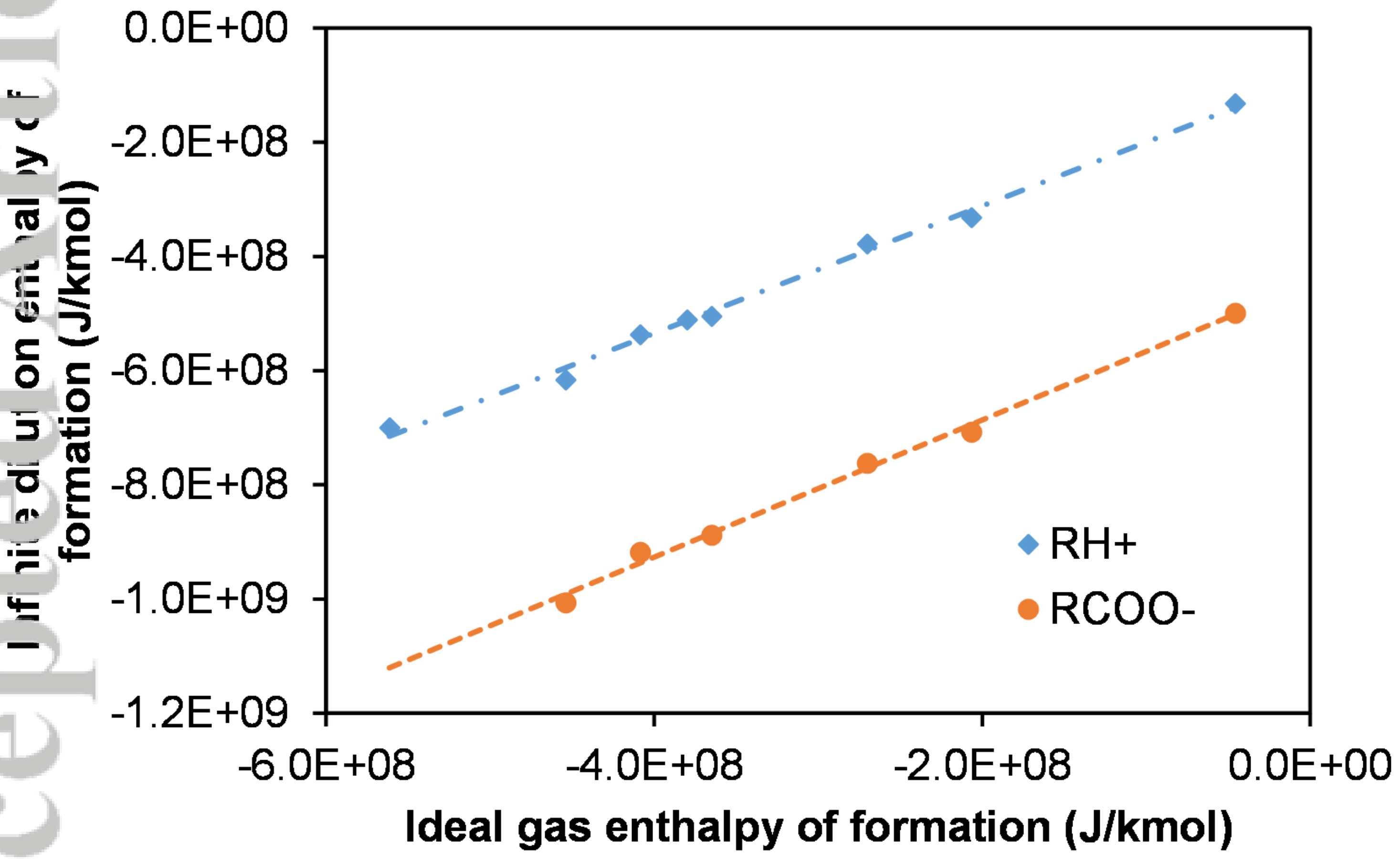

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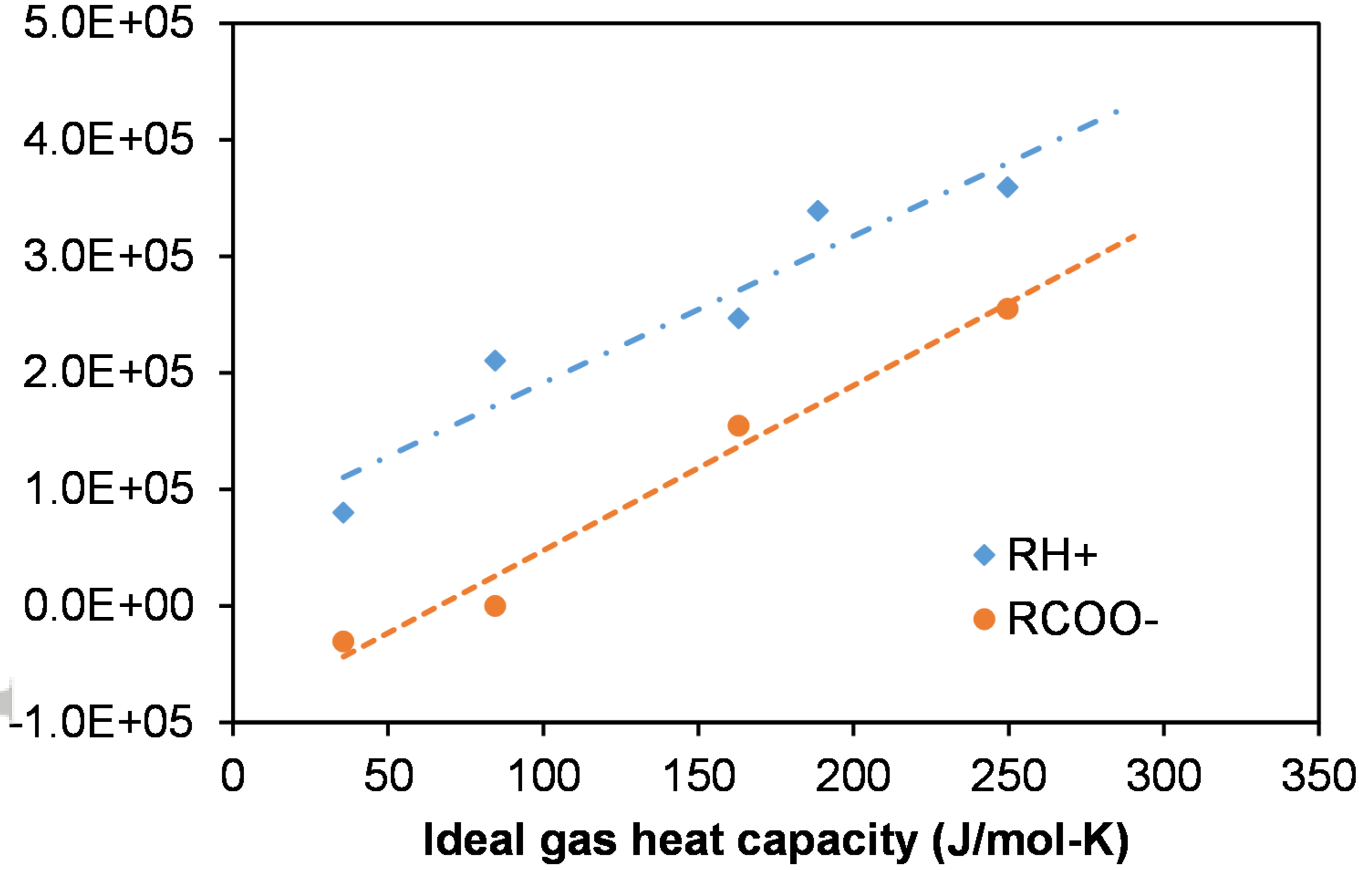

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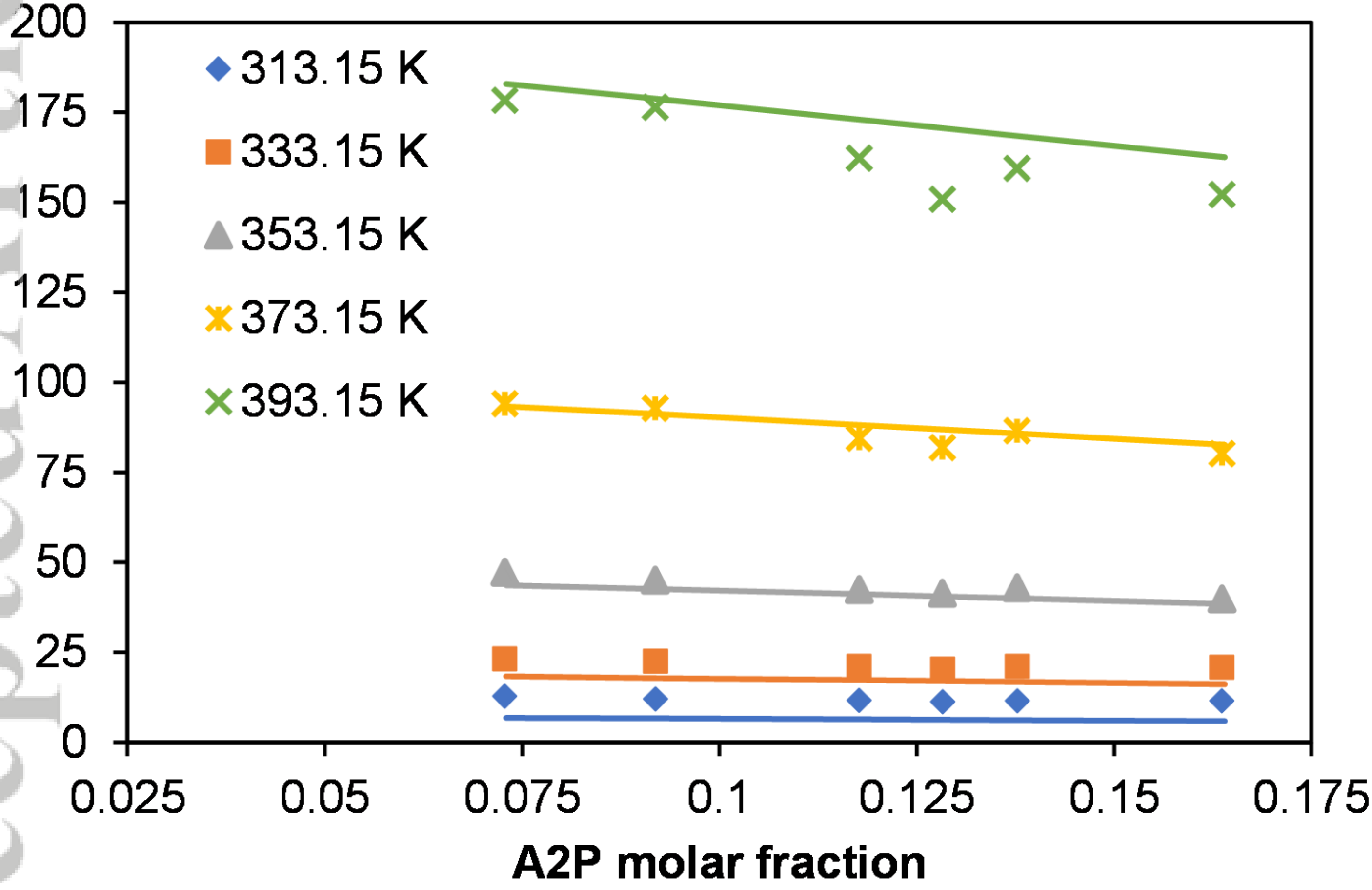

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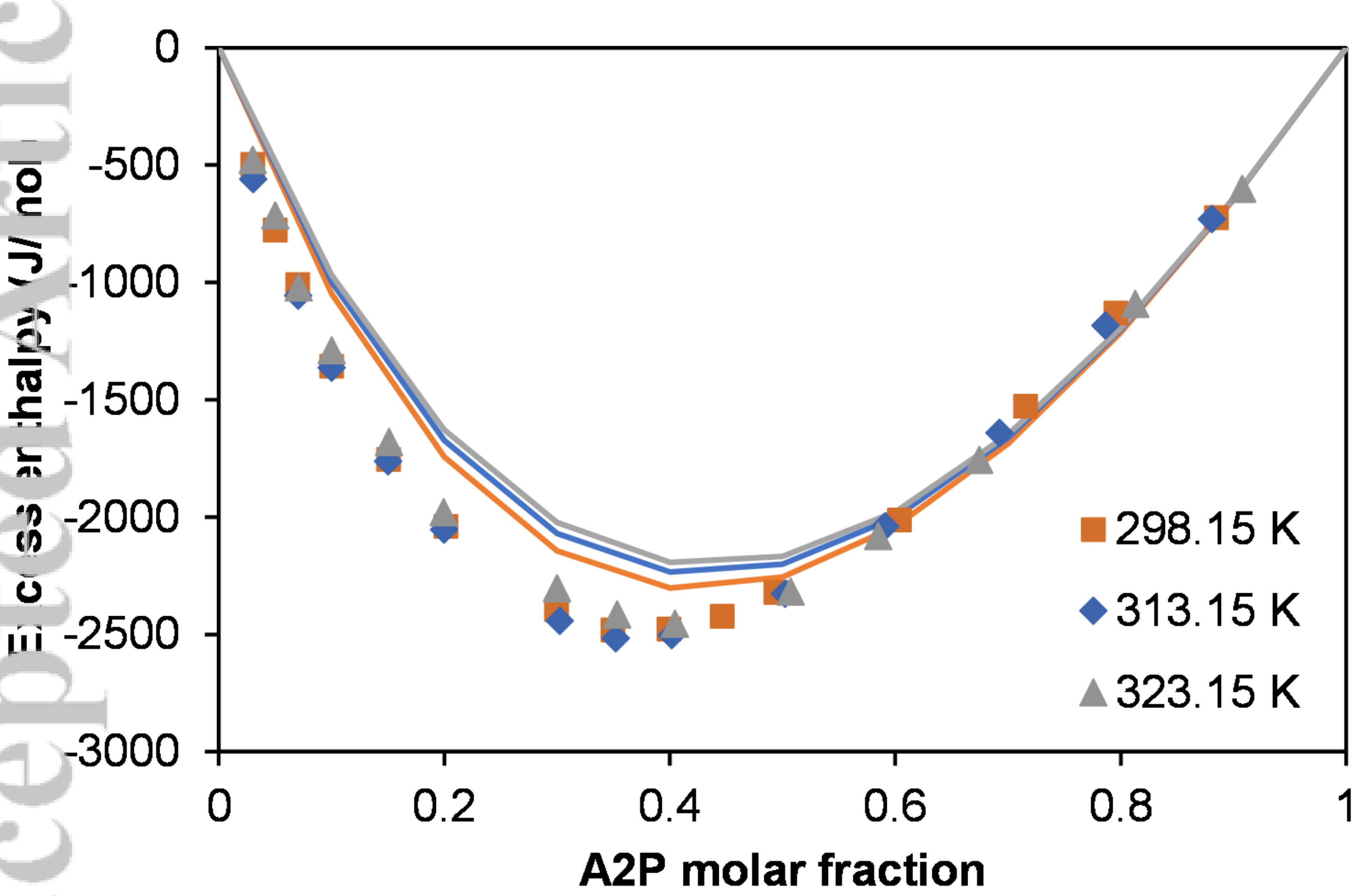

AIC_17623_Figure_5.tif

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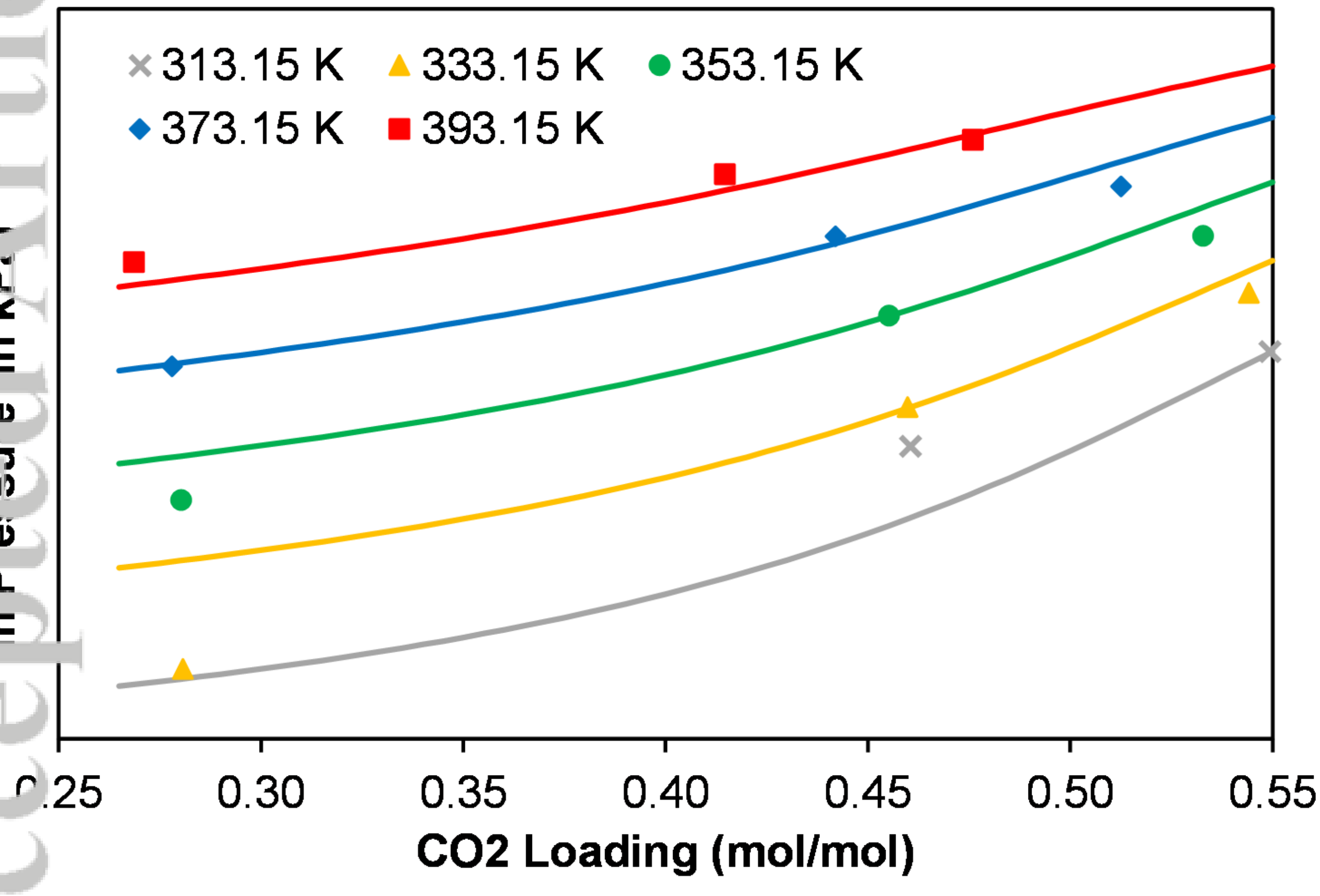

AIC_17623_Figure_6.tif

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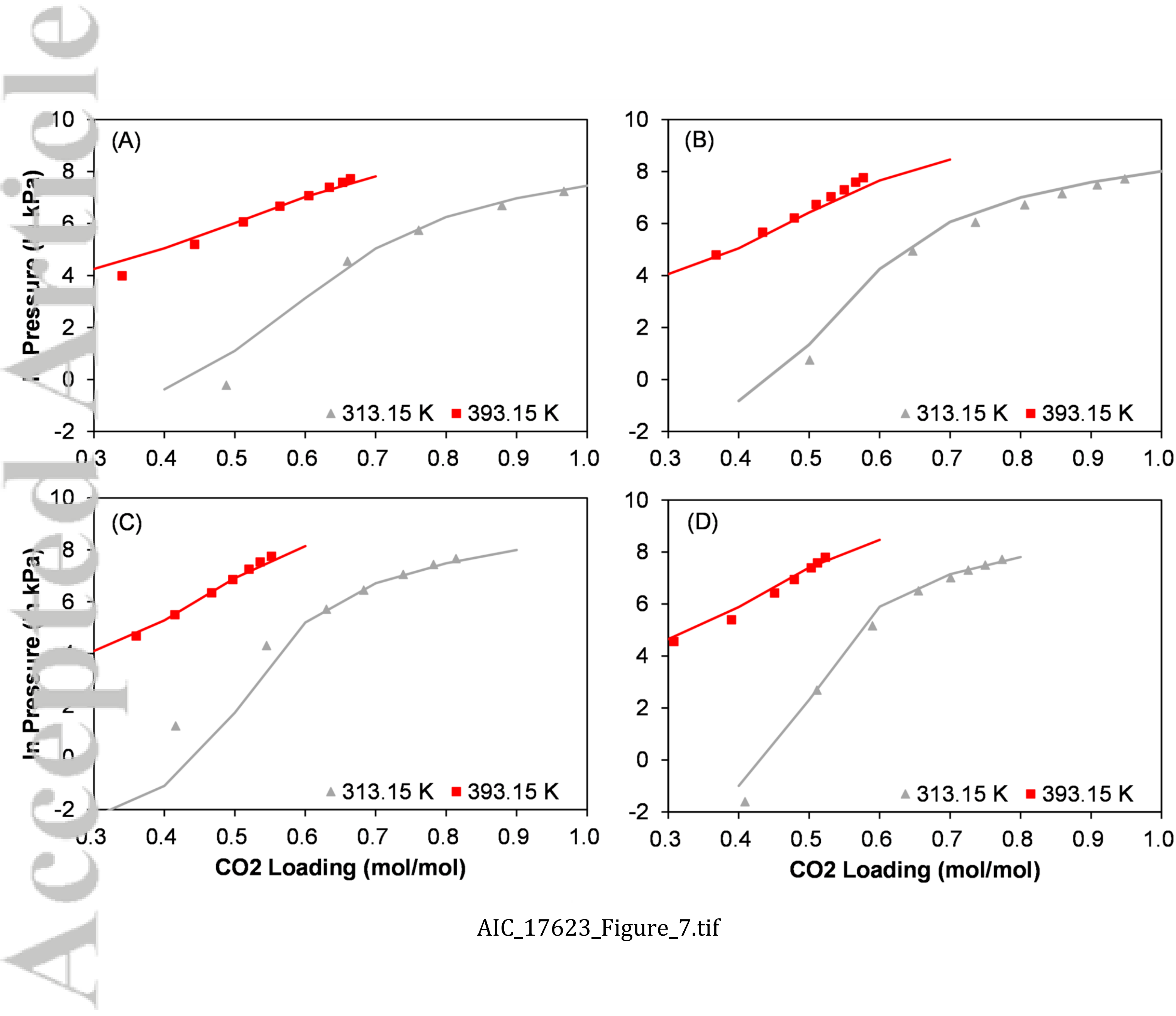

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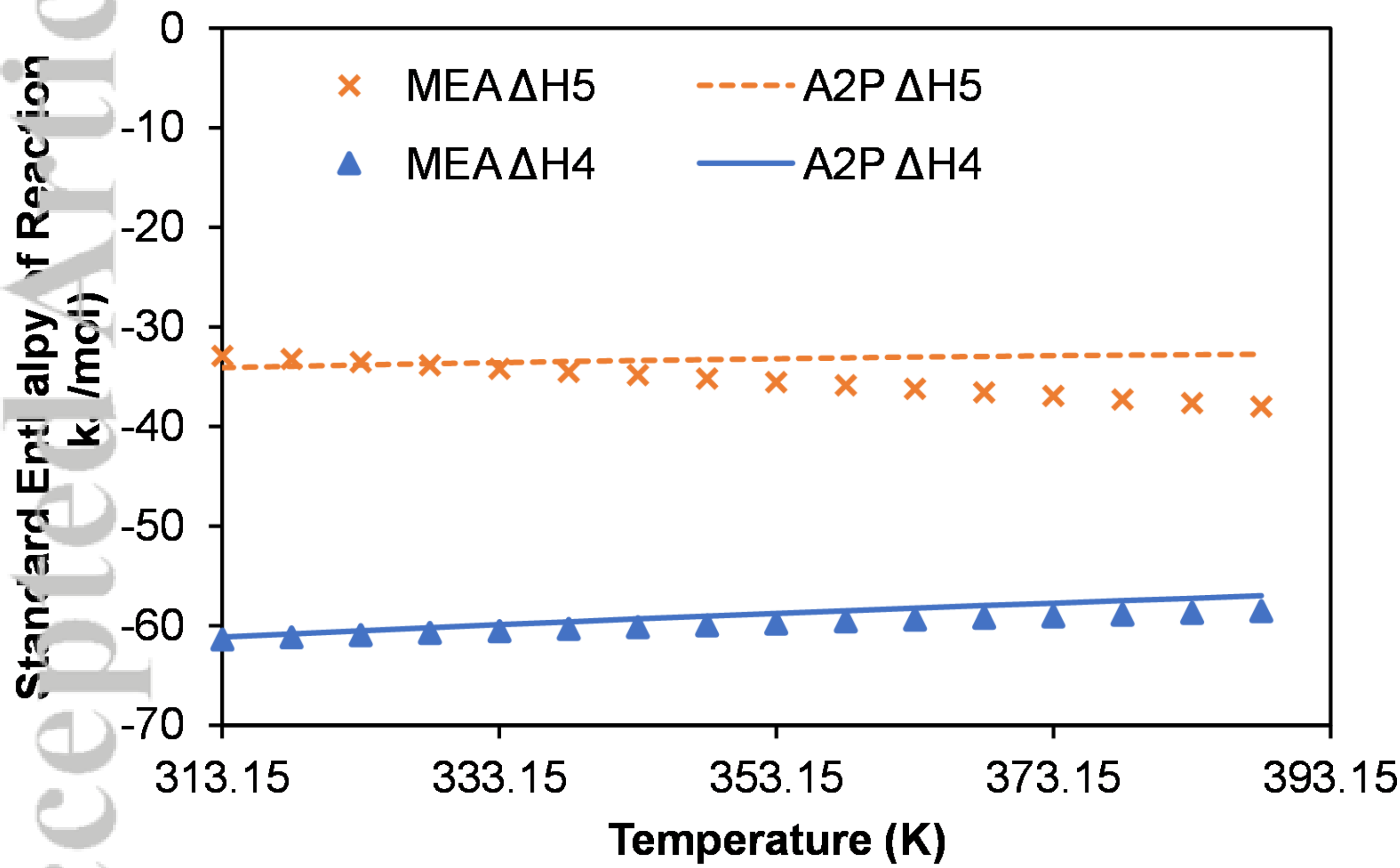

AIC_17623_Figure_8.tif

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