

# Amino Acid Salts for Carbon Dioxide Capture: Evaluating L-Proline at Desorber Conditions

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## S Supporting Information

**ABSTRACT:** Vapor–liquid equilibrium (VLE) measurements for unloaded and CO<sub>2</sub>-saturated aqueous potassium salt solutions of L-proline have been performed using a high-pressure equilibrium cell. The solubility of CO<sub>2</sub> has been determined at temperatures of 363, 393, and 403 K in 3 and 4 mol dm<sup>-3</sup> aqueous solutions. The CO<sub>2</sub> partial pressures ranged from 3.0 to 358 kPa. In addition, the VLE data for CO<sub>2</sub>-free and CO<sub>2</sub>-saturated 3 mol dm<sup>-3</sup> aqueous potassium sarcosinate solutions are presented for the same range of temperatures. The vapor pressures of the considered compounds have been determined at temperatures from 353 to 403 K. The reboiler duty required for stripping CO<sub>2</sub> from potassium L-proline solutions has been computed by the summation of the desorption enthalpy of CO<sub>2</sub>, sensible heat, and evaporation heat associated with co-produced regenerator overhead water vapor. A new approach to calculate the latter contribution is presented. The calculated energy requirements for L-proline are in the range reported in the literature for other amino acid salts.

## 1. INTRODUCTION

Nowadays, carbon dioxide (CO<sub>2</sub>) is widely recognized as a major greenhouse gas contributing to long-term climate changes. On the basis of technologies available today, post-combustion removal of CO<sub>2</sub> by use of absorption with chemical solvents, such as (alkanol)amines and amino acid salts (AAS), is considered to be the most cost-effective and viable option for a large-scale CO<sub>2</sub> capture from flue gases. In the amine-based gas-cleaning units, it is the regeneration of the CO<sub>2</sub>-loaded liquid that mainly determines the operational costs of the process. This cost is due to a large amount of heat required to reverse the amine–acid gas reaction, to bring rich solvent from the absorber (after feed–product heat exchange) to regenerator conditions and energy for evaporating the co-produced regenerator overhead water vapor. This reboiler duty can be measured experimentally in pilot plant units,<sup>1–3</sup> and it can be estimated by rigorous column modeling using dedicated software and advanced thermodynamic models<sup>4</sup> or estimated by the summation of above-mentioned components of the overall regeneration energy, determined separately.<sup>5,6</sup>

To obtain an (initial) indication of the energy required for a regenerative amine-based process, the latter procedure is often applied. Lee et al.<sup>2</sup> evaluated the regeneration energy and degree of CO<sub>2</sub> removal for aqueous solution of monoethanolamine (MEA) as a function of process parameters in a bench-scale CO<sub>2</sub>-capture process. For the verification of experimental results, the regeneration energy was also computed by the summation of the enthalpy of reaction, sensible heat, and heat of water vaporization using their process data. The calculated reboiler duty was in good agreement with the data from the bench-scale tests, within 6%. Song et al.<sup>6</sup> estimated the reboiler duty for CO<sub>2</sub> absorption in aqueous solutions of MEA and sodium salt of glycine as the sum of these three terms. The physicochemical properties and heat-associated data required in the calculations were determined experimentally. No informa-

tion is given, however, on the method of establishing the H<sub>2</sub>O/CO<sub>2</sub> overhead (reflux) ratio, which is a crucial parameter in this type of calculation.

In the present work, an estimation method to calculate the reboiler duty is presented with a new approach to determine the H<sub>2</sub>O/CO<sub>2</sub> overhead ratio. This ratio of partial pressures of water vapor and CO<sub>2</sub> in the gas phase at the desorber outlet (top) is referred to here as the “reflux ratio”. To validate the model developed in this work, the reboiler duty for stripping CO<sub>2</sub> from aqueous 5 M MEA solution was calculated with the current method and compared to the data obtained with the module available in the Aspen Plus, version 8.0 (referred to here as the working Aspen Plus example). After that, the energy requirements for potassium L-proline solution have been computed and compared to the literature numbers found for other AAS.

While a number of publications on the experimental CO<sub>2</sub> solubility data can be found for (alkanol)amines, the literature data for CO<sub>2</sub>–AAS–H<sub>2</sub>O systems is relatively scarce and in majority dealing with the absorption side. Table 1 summarizes the conditions of the CO<sub>2</sub> solubility measurements for AAS solutions as reported in the literature. The vapor–liquid equilibrium (VLE) data, with and without CO<sub>2</sub> in the system, are needed in the reboiler duty calculation. In the present work, the VLE curves of CO<sub>2</sub>-saturated 3 and 4 mol dm<sup>-3</sup> aqueous solutions of potassium salt of L-proline were obtained for the CO<sub>2</sub> partial pressure range of 3.0–358 kPa. The experimental procedures followed were validated using potassium salt of sarcosine. The VLE data for 3 mol dm<sup>-3</sup> sarcosinate solution in the CO<sub>2</sub> partial pressure range of 3.3–253 kPa were measured. For both amino acids, the experiments were carried out at

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Table 1. Literature Sources for the VLE Data of CO<sub>2</sub>–AAS–H<sub>2</sub>O Systems

solvent	C <sub>m</sub> (mol dm <sup>-3</sup> )	T (K)	p <sub>CO<sub>2</sub></sub> (kPa)	source
potassium taurate	0.5–3, 4 <sup>a</sup>	298 <sup>a</sup>	0.107–7.396	Kumar et al. <sup>7</sup>
	1	313	0.208–5.286	
sodium glycinate	1–3.5	303–323	0.1–214	Song et al. <sup>8</sup>
	3.5	313–393	0.1–400	Song et al. <sup>6</sup>
potassium glycinate	0.1–3	283–351	0.54–63.4	Portugal et al. <sup>9</sup>
potassium threonate	1	313	1.03–42.0	Portugal et al. <sup>9</sup>
potassium sarcosinate	3.5	313–353	0.029–14.585	Aronu et al. <sup>10</sup>
	3.5	373–393	38.1–1051	
potassium serinate	1	313–373	0.1–400	Song et al. <sup>11</sup>
potassium DL-methioninate	0.5	353	1280–8570	Kumelan et al. <sup>12</sup>
potassium L-proline	0.5–2	298–313	0.51–70.1	Majchrowicz and Brillman <sup>13</sup>
	3 <sup>a</sup>	285 <sup>a</sup> , 298–323	2.02–35.4	

<sup>a</sup>At these conditions, the solids precipitation is observed.

temperatures of 363, 393, and 403 K. The vapor pressures of the considered compounds were determined at temperatures from 353 to 403 K. This work is part of a set of studies aiming to identify the potential of potassium salt of L-proline as a CO<sub>2</sub> absorbent.<sup>13</sup>

## 2. MATERIALS AND METHODS

CO<sub>2</sub> (minimum of 99.99 mol %) (CAS Registry Number 124-38-9) gas used was purchased from Linde Gas. L-Proline [(S)-pyrrolidine-2-carboxylic acid, C<sub>5</sub>H<sub>9</sub>NO<sub>2</sub>, ≥98.5%] (CAS Registry Number 147-85-3), sarcosine (N-methylglycine, C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>, ≥98.0%) (CAS Registry Number 107-97-1), and KOH (≥85.0%, with the actual purity determined accurately by titration) (CAS Registry Number 1310-58-3) were purchased from Sigma-Aldrich and applied without further purification. AAS solutions were prepared by neutralizing the amino acid dissolved in deionized, double-distilled water using an equimolar quantity of potassium hydroxide. For this, the actual purity of potassium hydroxide was used. The actual concentration of the AAS solution was determined potentiometrically by titrating with a standard 1.000 mol dm<sup>-3</sup> HCl solution (CAS Registry Number 7647-01-0).

The VLE setup consisted of an autoclave made of 316 stainless steel (≈0.267 dm<sup>3</sup>), a CO<sub>2</sub> supply vessel (≈0.520 dm<sup>3</sup>), and a vacuum pump. The equilibrium cell was equipped with a high-intensity gas-inducing stirrer, digital pressure sensors, and PT100 temperature sensor (in the liquid phase). It was heated by a thermostatic oil circulator. The gas supply vessel was provided with a digital pressure sensor and PT100 temperature sensor. In all experiments, a known amount of a solution was introduced into the equilibrium cell and degassed by applying vacuum. In the vapor pressure experiment, a CO<sub>2</sub>-free solution was heated to a desired temperature. Once the system reached an equilibrium state, temperature and pressure in the autoclave were recorded. Samples were analyzed before and after each experiment to check for any concentration variation as a result of losses during evacuation or by degradation. In the CO<sub>2</sub> solubility experiments, known portions of pure CO<sub>2</sub> was added to the autoclave, after which the stirrer was started and the system was allowed to reach equilibrium. The amount of CO<sub>2</sub> absorbed by the solution was calculated from the pressure drop in the CO<sub>2</sub> supply vessel in combination with the ideal gas law corrected for the gas-phase non-ideality by applying a compressibility factor,  $Z = f(p_{\text{CO}_2}, T)$ .<sup>14,15</sup> Equilibrium reactor pressures were corrected for the solution vapor pressure to obtain the CO<sub>2</sub> partial pressure. More details about the experimental procedure and calculations used in this study can be found in the work by van Holst et al.<sup>16</sup> and Portugal et al.<sup>9</sup>

## 3. REBOILER DUTY

The heat required to regenerate a solvent solution in the stripper column of the CO<sub>2</sub>-capture process (reboiler duty, Q<sub>reb</sub>) depends upon three terms<sup>6,17,18</sup>

$$Q_{\text{reb}} = Q_{\text{sens}} + Q_{\text{des,CO}_2} + Q_{\text{vap,H}_2\text{O}} \quad (1)$$

where Q<sub>sens</sub> is the sensible heat to raise a solvent solution from the temperature of the loaded solvent downstream of the rich-lean heat exchanger to the reboiler temperature, Q<sub>vap,H<sub>2</sub>O</sub> is the heat of evaporation required to produce the stripping steam leaving the column overhead, and Q<sub>des,CO<sub>2</sub></sub> is the overall heat required to desorb CO<sub>2</sub> from the loaded solvent. All of these heat requirements are calculated in MJ kg<sup>-1</sup> of CO<sub>2</sub> leaving the process via the overhead condenser. The quantities of these three terms are calculated as follows:

$$Q_{\text{sens}} = \frac{\rho C_p \Delta T}{\Delta \alpha C_m M_{\text{CO}_2}} \quad (2)$$

$$Q_{\text{des,CO}_2} = \frac{\Delta H_{\text{des,CO}_2}}{M_{\text{CO}_2}} \quad (3)$$

$$Q_{\text{vap,H}_2\text{O}} = \frac{R \Delta H_{\text{vap,H}_2\text{O}} M_{\text{H}_2\text{O}}}{M_{\text{CO}_2}} \quad (4)$$

where Δα is the difference in CO<sub>2</sub> liquid loading between the absorber outlet (rich) and inlet (lean) and is expressed in moles of CO<sub>2</sub> per mole of solvent, R is the molar ratio of H<sub>2</sub>O/CO<sub>2</sub> in the regenerator overhead stream, ΔH<sub>des,CO<sub>2</sub></sub> is the enthalpy of desorption, ΔH<sub>vap,H<sub>2</sub>O</sub> is the heat of water evaporation, and M<sub>CO<sub>2</sub></sub> and M<sub>H<sub>2</sub>O</sub> are molar weights of CO<sub>2</sub> and water, respectively. The remaining parameters are defined in Table 2. For the heat required to strip CO<sub>2</sub> from the solution, Q<sub>des,CO<sub>2</sub></sub>, the (average) enthalpy of desorption is required and can be calculated using eqs 5 and 6.<sup>17</sup>

$$\frac{\Delta H_{\text{diff}}}{R} = \left[ \frac{\partial \ln p_{\text{CO}_2}}{\partial \left( \frac{1}{T} \right)} \right]_{\alpha} \quad (5)$$

$$\Delta H_{\text{avg}} = \frac{1}{\Delta \alpha} \int_{\alpha_{\text{lean}}}^{\alpha_{\text{rich}}} \Delta H_{\text{diff}} d\alpha \quad (6)$$

Table 2. Input Parameters for the Reboiler Duty Calculation

solvent properties	
density	$\rho$
heat capacity	$C_p$
enthalpy of desorption	$\Delta H_{des,CO_2}$
process parameters	
solvent concentration	$C_m$
mole fraction of water in the solution	$x_{H_2O}$
rich liquid loading	$\alpha_{rich}$
lean liquid loading	$\alpha_{lean}$
reboiler temperature	$T_{reb}$
condenser temperature	$T_{cond}$
temperature approach determined by HEX	$\Delta T$
pressure drop (bottom–top of stripper)	$\Delta P$

In eq 4,  $R$  is the quantity of stripping vapor (moles of  $H_2O$ ) provided per mole of  $CO_2$  produced. This ratio is estimated via the ratio of partial pressures of water vapor and  $CO_2$  in the gas phase at the desorber outlet (top). According to the literature, this ratio in commercial columns is in the range of 0.3–3.0 mol of water/mol of acid gas,<sup>17</sup> with the highest reflux found for MEA (2–3), followed by diethanolamine (DEA) (1.5) and methyldiethanolamine (MDEA) (0.3–1.0). Alternative to assuming a “typical figure” based on a thermodynamic analysis, Oexmann and Kather<sup>18</sup> proposed to estimate this ratio from

$$\frac{p_{H_2O}^s}{p_{CO_2}^*} = \frac{p_{H_2O,ref}^s}{p_{CO_2,ref}^*} \exp\left(\left[\frac{T - T_{ref}}{RT_{ref}}\right](\Delta H_{vap,H_2O} - |\Delta H_{abs,CO_2}|)\right) \quad (7)$$

A similar equation as eq 7 is given by Rochelle et al.<sup>5</sup> and describes the ratio of the  $CO_2$  equilibrium partial pressure at the absorber temperature (here  $p_{CO_2,ref}^*$ ) to that at the stripper temperature (here  $p_{CO_2}^*$ ).

In this work, another approach is used in which the  $R$  value is estimated from regeneration pressure and temperature at the top of the stripper column. The configuration of the top of the stripper column is indicated schematically in Figure 1. The following assumptions are made: (i) the feed is introduced one tray below the water wash tray, and (ii) the temperature at the feed tray is the same as the temperature of the feed itself. In this fashion, the top temperature can be calculated from a simplified

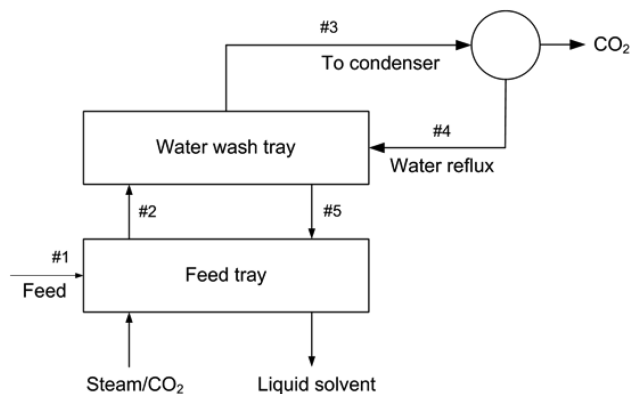


Figure 1. Top section of the regenerator column.

enthalpy balance for the water vapor and liquid streams entering and leaving the water wash tray and without the necessity of taking into account the solvent contributions. The contribution of  $CO_2$  entering and leaving the water wash tray is neglected because it contributes only around 2% of the net enthalpy input to that tray and results in less than 0.2% difference in the final reboiler duty calculated.

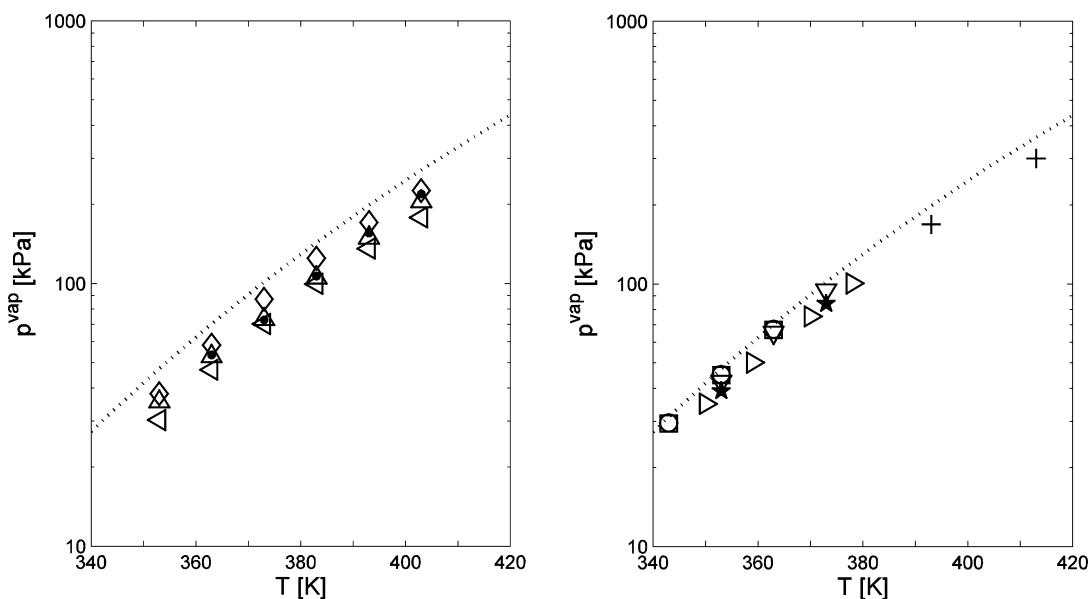
The solvent-specific properties and process parameters, required as the input for the calculation method, are listed in Table 2. Using the input parameters presented in this table, the mass and enthalpy balances for the top section of the regenerator (as presented in Figure 1) can be calculated. In this calculation, molar balances listed in Table 3 are used. Note that subscripts “ft” and “wt” stand for the feed and water wash trays, respectively. The cyclic capacity,  $\Delta\alpha$ , is defined as the difference in the rich and lean liquid  $CO_2$  loadings.

The overall calculation procedure to calculate  $R_{wt}$  and  $R_{ft}$  now involves the following steps (where subscripts “b” and “top” stand for the bottom and top conditions in the column, respectively): (1) Select reboiler temperature,  $T_{reb}$ , and a lean  $CO_2$  liquid loading,  $\alpha_{lean}$ . (2) From VLE data at  $T_{reb}$ , find the reboiler  $CO_2$  equilibrium partial pressure,  $p_{CO_2,b}$ , at the selected  $\alpha_{lean}$ . (3) The water vapor pressure at the reboiler conditions,  $p_{H_2O,b}$ , is estimated using the following equation:  $p_{H_2O,b} = p_{H_2O}^0(T_{reb})x_{H_2O}\gamma$ , where  $x_{H_2O}$  is the mole fraction for water in the solution and  $\gamma$  is the non-ideality coefficient defined as the ratio of the solution vapor pressure at zero  $CO_2$  loading,  $p^{vap}$ , and the vapor pressure for pure water at the reboiler temperature,  $p_{H_2O}^0(T_{reb})$ . (4) Calculate the total pressure at the bottom of a regenerator (maximum attainable pressure),  $P_b$ , using formula:  $P_b = p_{H_2O,b} + p_{CO_2,b}$ . (5) With pressure  $P_b$  at the bottom and the assumed pressure drop,  $\Delta P$ , over the column, the operating pressure at the top (water wash and feed trays) of the regenerator is  $P_{top} = P_{wt} = P_{ft} = P_b - \Delta P$ . (6) For the feed tray, the water vapor pressure,  $p_{H_2O,ft}$ , is calculated via  $p_{H_2O,ft} = p_{H_2O}^0(T_{feed})x_{H_2O}\gamma$  and the  $CO_2$  partial pressure is calculated via  $p_{CO_2,ft} = P_{ft} - p_{H_2O,ft}$ . The ratio  $R_{ft}$  is now  $(p_{H_2O}/p_{CO_2})_{ft}$ . (7) Use an initial guess for  $T_{wt}$  (e.g.,  $T_{wt} = T_{feed}$ ). (8) Calculate the vapor pressure of water at the water wash tray,  $p_{H_2O,wt}$  via  $p_{H_2O,wt} = p_{H_2O}^0(T_{wt})$  and the  $CO_2$  partial pressure at the top using equation  $p_{CO_2,wt} = P_{top} - p_{H_2O,wt}$ . With this,  $R_{wt} = (p_{H_2O}/p_{CO_2})_{wt}$ . (9) With  $R_{ft}$  and  $R_{wt}$  known, the flow rate and composition of all streams can be calculated using the mass and enthalpy balances from Table 3. (10) Check if the enthalpy balance over the water wash tray closes (see Table 3 and Figure 1). Adjust the value for  $T_{wt}$  (in step 7 above) and repeat steps 8 and 9 until the enthalpy balance over the water wash tray is closed (relative deviation with respect to enthalpy stream 3 <  $10^{-9}$ ).

The (minimum)  $R$  value relevant to the energy requirement calculation (see eq 4) is now the  $R_{wt}$  value for the converged solution. The optimal ratio between  $R$  actual and  $R$  minimum normally depends upon an economic analysis that compares the cost of energy (which rises with rising reflux) to a number of column trays (which declines with rising reflux), and for most commercial operations, it equals 1.1–1.5.<sup>19</sup> For the present case, it is assumed that  $R_{wt,actual}/R_{wt,minimum} = 1.2$ . Hence, via eq 4, the contribution  $Q_{vap,H_2O}$  can now be

Table 3. Mass and Enthalpy Balances for the Top Section of the Regenerator

feed (1)	known composition
CO <sub>2</sub> molar balance	$\phi_{M,CO_2} (2) = \phi_{M,amine} (1)\Delta\alpha$
	$\phi_{M,CO_2} (3) = \phi_{M,CO_2} (2)$
	$\phi_{M,CO_2} (4) = 0$
	$\phi_{M,CO_2} (5) = 0$
water molar balance	$\phi_{M,H_2O} (2) = \phi_{M,CO_2} (3)R_{fr}$
	$\phi_{M,H_2O} (3) = \phi_{M,CO_2} (3)R_{wt}$
	$\phi_{M,H_2O} (4) = \phi_{M,H_2O} (3)$
	$\phi_{M,H_2O} (5) = \phi_{M,H_2O} (2)$
enthalpy balance	$\phi_H (2) + \phi_H (4) = \phi_H (3) + \phi_H (5)$
	$\phi_H (i) = \phi_{M,H_2O} (i)H_{H_2O}^{sat,vap}(P_{top},T(i))M_{H_2O} (i = 2 \text{ or } 3)$
	$\phi_H (j) = \phi_{M,H_2O} (j)H_{H_2O}^{sat,liq}(P_{top},T(j))M_{H_2O} (j = 4 \text{ or } 5)$
temperature	$T_{feed} = T_{reb} - \Delta T$
	$T(3) = T_{wt}$ (from enthalpy balance)
	$T(4) = T_{cond}$
	$T(2) = T_{feed}$
	$T(5) = T(3)$



**Figure 2.** (Left) Experimental results of the vapor pressure of aqueous: ( $\diamond$ ) 2 M L-proline, ( $\triangle$ ) 3 M L-proline, ( $\nabla$ ) 4 M L-proline, and ( $\bullet$ ) 3 M sarcosinate. (Right) Literature values of the vapor pressure of aqueous CO<sub>2</sub> absorbents: ( $\star$ ) 3.5 M sarcosinate,<sup>10</sup> ( $\triangle$ ) 3.3 M glycinate,<sup>11</sup> ( $\square$ ) 2.6 M MEA,<sup>22</sup> (+) 3 M DEA,<sup>23</sup> ( $\nabla$ ) 2.6 M MDEA,<sup>24</sup> and ( $\circ$ ) 2.3 M AMP.<sup>25</sup> Dotted line stands for water by Popiel and Wojtkowiak.<sup>26</sup>

calculated. In addition, the sensible heat,  $Q_{sens}$  is calculated here using eq 8.

$$Q_{sens} = \frac{\rho C_p \Delta T}{\Delta \alpha C_m M_{CO_2}} + \frac{(\phi_H(4, T_{reb}) - \phi_H(4, T_{cond}))M_{H_2O}}{\Delta \alpha C_m M_{CO_2}} \quad (8)$$

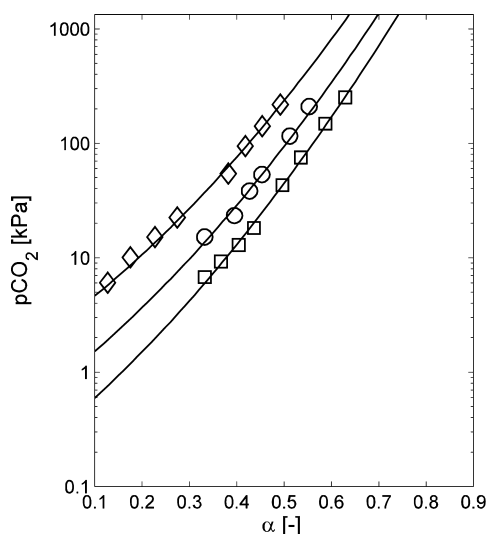
In this equation, not only is the difference in the sensible heat between the rich and lean streams taken into account but also the sensible heat effect associated with feeding the cold reflux condensate back to the column. The CO<sub>2</sub> product stream is delivered at the pressure of the top condenser, and its water content is determined by its dewpoint at these conditions.

## 4. RESULTS AND DISCUSSION

The high volatility of (alkanol)amine-based solvents results in higher wash-up costs and environmental risks,<sup>17,20</sup> whereas, in general, salt solutions are characterized by negligible vapor pressure of the active components and, thus, show minimum liquid evaporation losses.<sup>21</sup> For AAS, Aronu et al.<sup>10</sup> reported the vapor pressure of aqueous potassium sarcosinate solutions ( $C_m = 1, 2, 3.5, 3, 4,$  and  $5$  M) at temperatures of 313, 333, 353, and 373 K. In Figure 2, the measured VLE data of L-proline and sarcosine solutions at regeneration temperatures are presented. These data are compared to the  $p^{vap}$  values of other aqueous CO<sub>2</sub> absorbents. As expected, AAS are characterized by lower vapor pressures, as compared to amines. For amines, the following trend in increasing volatility was reported in the literature: tertiary < secondary < primary.<sup>23,24</sup> Nguyen et al.<sup>20</sup> related volatility of amines with molecular groups and structural

shapes. The volatility–structural relations for amines seem to be also applicable for AAS. It was reported that amines having one or more polar groups, such as amine, hydroxyl, and ether groups, tend to be less volatile because of favorable interactions with water. The presence of one or more methyl groups in the structure contributes to nonpolarity and greater volatility [e.g., 2-amino-2-methylpropanol (AMP)]. As a second-order effect, the presence of a N–CH<sub>3</sub> contribution in a straight-chain amine (e.g., sarcosine) or a C–CH<sub>3</sub> contribution in a cyclic amine correlates to lower volatility. Finally, cyclic amines (e.g., proline) appear to be less volatile than straight-chain amines (e.g., glycine).

The VLE apparatus and methodology applied were validated using potassium salt of sarcosine. The equilibrium partial pressure of CO<sub>2</sub> over aqueous solutions of potassium L-prolinate ( $C_m = 3$  and 4 M) for the CO<sub>2</sub> partial pressure range of 3.0–358 kPa and potassium sarcosinate ( $C_m = 3$  M) for  $p_{\text{CO}_2}$  ranging from 3.3 to 253 kPa was measured. The experiments were carried out at temperatures of 363, 383, and 403 K. The VLE curves obtained for potassium salts of sarcosine and L-proline are shown in Figures 3 and 4, respectively. Aronu et



**Figure 3.** Experimental results of the CO<sub>2</sub> equilibrium partial pressure over 3 M solution of potassium sarcosinate: (□)  $T = 363$  K, (○)  $T = 383$  K, (◇)  $T = 403$  K, and (—) calculated by eq 9.

al.<sup>10</sup> reported CO<sub>2</sub> partial pressure over 3.5 mol dm<sup>-3</sup> solutions of potassium sarcosinate for the  $p_{\text{CO}_2}$  range of 0.03–14.6 kPa at temperatures of 313, 333, and 353 K and for the  $p_{\text{CO}_2}$  range of 38.1–971 kPa at temperatures of 373 and 393 K. It was found that the VLE data from the present work for potassium sarcosinate are comparable to the data by Aronu et al.<sup>10</sup> The reaction enthalpy of potassium sarcosinate solution was calculated according to eq 5 and compared to the values reported by Aronu et al.<sup>10</sup> At the liquid CO<sub>2</sub> loading,  $\alpha$ , of 0.2 (mol of CO<sub>2</sub>/mol of solvent), the enthalpy of desorption is found to be 66.3 kJ mol<sup>-1</sup> of CO<sub>2</sub> and at  $\alpha = 0.4$ , the enthalpy of desorption equals 62.2 kJ mol<sup>-1</sup> of CO<sub>2</sub>. These values agree with the value of 66.7 kJ mol<sup>-1</sup> of CO<sub>2</sub> reported at  $\alpha = 0.2$  for 3.5 mol dm<sup>-3</sup> solution by Aronu et al.<sup>10</sup>

At a certain  $\alpha$  value, an increase in the system temperature results in a higher CO<sub>2</sub> partial pressure, which is common for CO<sub>2</sub>–(alkanol)amine–H<sub>2</sub>O systems. For both amino acids, the

dependence of the CO<sub>2</sub> partial pressure upon the temperature and CO<sub>2</sub> liquid loading in the temperature range studied has been expressed by eq 9, where  $a_0$ – $a_5$  are constants (see Table 4). The average relative deviation between the experimental data and the values from the fits are 7.6 and 2.2% for 3 and 4 mol dm<sup>-3</sup> L-prolinate solutions, respectively, and 2.8% for sarcosinate solution. The  $p_{\text{CO}_2}$ – $\alpha$  curves as calculated by eq 9 are included in Figures 3 and 4.

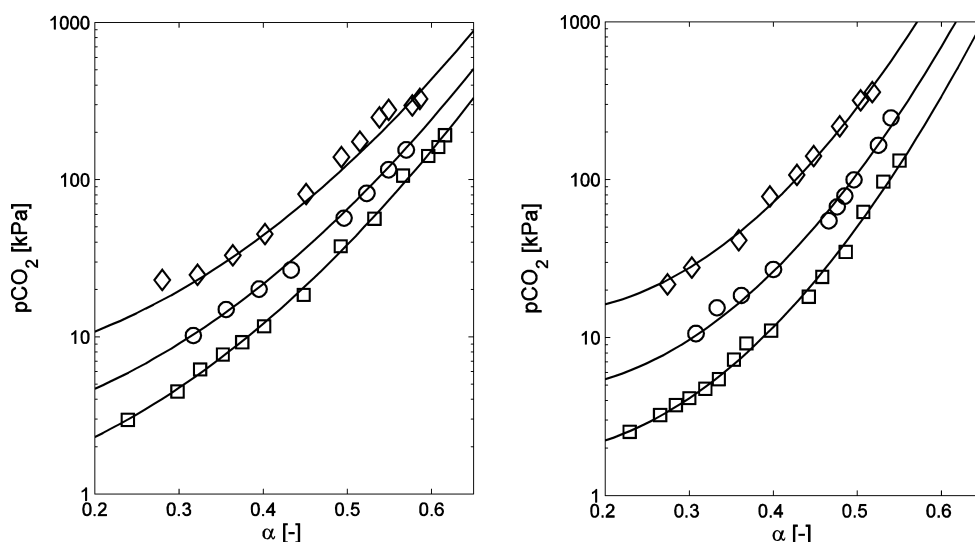
$$\ln p_{\text{CO}_2} = a_0 + a_1\alpha + a_2T + a_3\alpha^2 + a_4\alpha T + a_5T^2 \quad (9)$$

The effect of the AAS concentration on the absorption capacity of CO<sub>2</sub> for potassium L-prolinate solutions was also investigated (see Figure 4). Generally, if the main path of CO<sub>2</sub> absorption is the formation of a carbamate (primary and secondary amines), the absorption equilibria are less dependent upon the solvent concentration (up to a certain CO<sub>2</sub> liquid loading). On the other hand, if the bicarbonate formation dominates (e.g., for tertiary and some sterically hindered primary and secondary amines), the absorbent concentration significantly influences the VLE behavior of the system.<sup>18</sup> This latter pathway is, however, kinetically less favorable than the formation of a carbamate. For L-prolinate, no significant reduction in CO<sub>2</sub> solubility in 4 mol dm<sup>-3</sup> solution, when compared to the results for 3 mol dm<sup>-3</sup> solution, is found up to  $\alpha \approx 0.35$  (mol of CO<sub>2</sub>/mol of solvent). This loading increases to (approximately) 0.40 and 0.46 (mol of CO<sub>2</sub>/mol of solvent) as the absorption temperature decreases to 383 and 363 K, respectively.

In a recent version of the Aspen process simulator (Aspen Plus, version 8.0), a working example of CO<sub>2</sub> absorption in 4.5 M MEA solution is available based on a full electrolyte non-random two-liquid (NRTL) column model for the absorber and stripper. The results for the stripper were compared to the method developed in this work for 5 M MEA solution. The reboiler duty found with the method described above is in good agreement with the Aspen simulation [5.18 MJ kg<sup>-1</sup> of CO<sub>2</sub> (this work) versus 5.25 MJ kg<sup>-1</sup> of CO<sub>2</sub> (Aspen)], and also, distributions of the three energy components in eq 1 are quite similar (see Figure S.1 and Tables S.1 and S.2 of the Supporting Information). The  $R$  value for the water wash tray in the Aspen simulation equals 2.20, whereas a value of 1.86 is found with the present method. The  $R$  value for the feed tray in the Aspen simulation equals 2.38 versus 2.33 as found by the current method. More information can be found in the Supporting Information.

CO<sub>2</sub>-capture process in aqueous solutions of (alkanol)amines has been simulated and studied under different process conditions in a number of publications,<sup>3,27,28</sup> where several process parameters have been varied over a given span to study their effect on the CO<sub>2</sub> removal and reboiler duty. It has been pointed out that some major energy savings can be obtained by optimizing the CO<sub>2</sub> liquid loading level in the amine system. Therefore, this factor was studied for 3 mol dm<sup>-3</sup> aqueous solution of potassium L-prolinate by keeping the lean solvent loading constant at the value of 0.262 and increasing the rich loading. The input parameters as reported in Table S.3 of the Supporting Information were applied. Equation 9 was used to calculate the VLE data of the system. The results of this study are presented in Table 5.

It is apparent that, at a given lean CO<sub>2</sub> loading, a reduction in the rich CO<sub>2</sub> loading leads to an increase in the reboiler duty. For a theoretical maximum rich solution loading of 0.586 (mol of CO<sub>2</sub>/mol of solvent), represented by an equilibrium with the



**Figure 4.** Experimental results of the CO<sub>2</sub> equilibrium partial pressure over potassium salt of L-proline for (left) 3 M solution and (right) 4 M solution: (□)  $T = 363$  K, (○)  $T = 383$  K, (◇)  $T = 403$  K, and (—) calculated by eq 9.

**Table 4.** Constants  $a_0$ – $a_5$  in Equation 9

solvent	$a_0$	$a_1$	$a_2 (\times 10^{-2})$	$a_3$	$a_4 (\times 10^{-3})$	$a_5 (\times 10^{-5})$
potassium L-prolinate, 3 M solution	7.40	13.08	−7.89	10.95	−31.27	16.17
potassium L-prolinate, 4 M solution	17.64	2.834	−13.62	21.36	−20.38	24.79
potassium sarcosinate, 3 M solution	11.51	16.57	−11.57	5.084	−24.31	22.12

**Table 5.** Calculated Values of the Reboiler Duty versus  $\alpha_{\text{rich}}$  for Potassium L-Proline Using Input Parameters Reported in Table S.3 of the Supporting Information<sup>a</sup>

$\alpha_{\text{rich}}$	$Q_{\text{reb}}$ (MJ kg <sup>−1</sup> of CO <sub>2</sub> )
0.400	6.26
0.425	5.94
0.450	5.71
0.475	5.53
0.500	5.39
0.525	5.28
0.550	5.19
0.586	5.08

<sup>a</sup> $C_m$ , 3 M;  $T_{\text{reb}}$ , 403 K; and  $\alpha_{\text{lean}}$ , 0.262 (mol of CO<sub>2</sub>/mol of solvent).

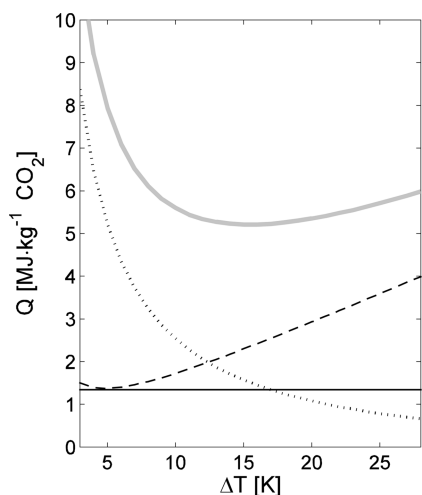
feed gas at the absorber bottom conditions, a reboiler duty of 5.08 MJ kg<sup>−1</sup> of CO<sub>2</sub> is calculated. Because this theoretical maximum cannot be attained in practical equipment, a “75–80% approach to equilibrium” is often assumed in the design of the amine plants.<sup>17</sup> For the  $\alpha_{\text{rich}}$  of 0.465, a reboiler duty of at least 5.60 MJ kg<sup>−1</sup> of CO<sub>2</sub> is required by the system, using the conditions from Table S.3 of the Supporting Information. As presented in Figure S.2 of the Supporting Information, high values of the sensible heat and heat of vaporization of water are the main reason for the high regeneration heat of L-proline, of which  $Q_{\text{sens}}$  corresponds to 30.8%,  $Q_{\text{vap,H}_2\text{O}}$  corresponds to 45.3%, and  $Q_{\text{des,CO}_2}$  corresponds to 24.0%.

The approach by Oexmann and Kather<sup>18</sup> was used to calculate the  $R$  value and further the reboiler duty of potassium L-proline solution. For the calculated ratio of 2.9, the reboiler duty of 5.64 MJ kg<sup>−1</sup> of CO<sub>2</sub> was found. The  $Q_{\text{reb}}$  and  $R$  values thus calculated are around 1% higher than the values obtained by the current method. It was observed that the  $R$  values obtained by the Oexmann and Kather method are sensitive to

the value of enthalpy of reaction inserted to their formula (eq 7). For instance, when  $\Delta H_{\text{des,CO}_2}$  is increased by 10% (which is probably within the range of experimental error) to 65 kJ mol<sup>−1</sup>, the  $R$  value increases to 4.2. This inconvenience is eliminated in the model developed in the present work. In addition, the current method allows for studying the reboiler duty of the considered acid gas absorption process for different process conditions.

The inlet temperature of the rich solution to the stripper column is determined by a performance of the rich-lean cross-flow heat exchanger. The minimum acceptable temperature approach of 10–15 K is usually used in the design of the amine-based CO<sub>2</sub> absorption systems, but with the use of more modern plate exchangers, a  $\Delta T$  of less than 5 K can be achieved.<sup>27</sup> The predicted change of the reboiler duty and the three energy contributions for potassium L-proline with  $\Delta T$  is illustrated in Figure 5. The rich liquid loading was fixed to 0.465 (mol of CO<sub>2</sub>/mol of solvent). No reduction in the reboiler duty with a decreasing  $\Delta T$  value is found. Instead, an optimum of 5.21 MJ kg<sup>−1</sup> of CO<sub>2</sub> at  $\Delta T$  equal to 15 K is reached. This finding is contrary to the conclusion by Barchas and Davis,<sup>29</sup> who stated generally that, with a more efficient cross-flow heat exchanger, much less energy for stripping CO<sub>2</sub> is needed. Finally, an influence of the pressure drop along the stripper column,  $\Delta P$ , on the reboiler duty was investigated. As  $\Delta P$  increases from a zero pressure drop to 0.1 kPa, the energy consumption of the system increases by 7.7% from 5.17 to 5.50 MJ kg<sup>−1</sup> of CO<sub>2</sub> and is further increased by 21.6% as  $\Delta P$  goes up to 0.3 kPa. A complete optimization of the system is, however, not pursued in this work.

In general, aqueous AAS solutions have slightly higher desorption energy requirements than, e.g., the industry standard MEA. Erga et al.<sup>30</sup> performed the equilibrium and pilot plant tests using aqueous solutions of MEA, MDEA–



**Figure 5.** Calculated values of the total energy requirements (reboiler duty) and individual energy contributions versus  $\Delta T$  for potassium L-proline using input parameters reported in Table S.3 of the Supporting Information,  $C_m = 3$  M,  $T_{\text{reb}} = 403$  K, and  $\alpha_{\text{lean}} = 0.262$  (mol of  $\text{CO}_2$ /mol of solvent): (gray line) reboiler duty, (dashed line) sensible heat, (black line) heat of desorption, and (dotted line) heat of evaporation.

piperazine mixture, and potassium salts of sarcosine and glycine. For amino acids, the operational conditions used were as follows: a 6.0 vol %  $\text{CO}_2$  gas stream at the inlet of the absorber,  $\text{CO}_2$  absorption temperature of 313 K, 4 M solutions, stripping temperature of 413 K, and  $\Delta T$  set to 10 K. In terms of the reboiler heat demand, the amino acid systems were found to be less competitive than MEA solution.<sup>31</sup> The reboiler duties for stripping  $\text{CO}_2$  from aqueous potassium salts of glycine and sarcosine were 6.05 and 5.77  $\text{MJ kg}^{-1}$  of  $\text{CO}_2$ , respectively. In another comparison, Song et al.<sup>6</sup> calculated the regeneration energy for 30 wt % aqueous solutions of MEA and for sodium salt solutions of glycine. Other assumptions made in that study included a rich liquid loading of 0.4, a temperature difference between top and bottom of the stripper of 50 K, and a stripping temperature of 393 K. It was reported that the heat demand for glycinate ( $Q_{\text{reb}} = 5.74 \text{ MJ kg}^{-1}$  of  $\text{CO}_2$ ) is 17% higher than that for the MEA system ( $Q_{\text{reb}} = 4.75 \text{ MJ kg}^{-1}$  of  $\text{CO}_2$ ) under the same conditions. Also, in this work, for potassium salt of L-proline, the calculated reboiler duty,  $Q_{\text{reb}}$ , is higher than the value found for the MEA system. The results are in line with the numbers reported in the literature for other AAS.

## 5. CONCLUSION

VLE data for  $\text{CO}_2$ -saturated and  $\text{CO}_2$ -free potassium L-proline solutions were obtained at the stripper operating conditions. The experimental VLE data at regeneration conditions were used to calculate the reboiler duty for an absorption–desorption process. This heat duty is calculated as the sum of the desorption enthalpy of  $\text{CO}_2$ , sensible heat, and heat of vaporization. A new method to determine the latter contribution was used and tested against a full electrolyte NRTL rigorous column model. Similar to other AAS solutions, the energy required for stripping  $\text{CO}_2$  from aqueous solutions of L-proline is somewhat higher than that for the 5 M MEA reference system. With the new method, the influence of a few process parameters on the calculated reboiler duty of potassium L-proline was investigated, showing, e.g., an optimum temperature approach,  $\Delta T$ , of 15 K for the lean-rich heat

exchanger. The specific reboiler duty reduces with increasing cyclic capacity of the AAS solution. Hence, an increase in the  $\alpha_{\text{rich}}$  by precipitation during absorption<sup>13</sup> may result in further energy savings in AAS-based  $\text{CO}_2$  absorption systems.

## ■ ASSOCIATED CONTENT

### Supporting Information

System parameters for the reboiler duty calculation for the MEA case (Table S.1), total energy requirements for the MEA case (Table S.2), heat contributions to the reboiler duty for the MEA case: (left) calculated by the model ( $Q_{\text{reb}} = 5.18 \text{ MJ kg}^{-1}$  of  $\text{CO}_2$ ) and (right) calculated by the Aspen process simulator ( $Q_{\text{reb}} = 5.25 \text{ MJ kg}^{-1}$  of  $\text{CO}_2$ ) (Figure S.1), system parameters for the reboiler duty calculation for potassium L-proline (Table S.3), total energy requirements for potassium L-proline (Table S.4), and heat contributions to the reboiler duty for potassium L-proline ( $Q_{\text{reb}} = 5.60 \text{ MJ kg}^{-1}$  of  $\text{CO}_2$ ) (Figure S.2). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.5b00206.

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### Notes

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## ■ NOMENCLATURE

- $C_p$  = heat capacity ( $\text{kJ kg}^{-1} \text{K}^{-1}$ )
- $C_m$  = molar concentration of amine or amino acid ( $\text{mol m}^{-3}$ )
- $\Delta H_{\text{des,CO}_2}$  = heat of reaction ( $\text{kJ mol}^{-1}$ )
- $H_{\text{H}_2\text{O}}^{\text{sat,liq}}$  = specific enthalpy of boiling water ( $\text{kJ kg}^{-1}$ )
- $H_{\text{H}_2\text{O}}^{\text{sat,vap}}$  = specific enthalpy of saturated steam ( $\text{kJ kg}^{-1}$ )
- $\Delta H_{\text{vap,H}_2\text{O}}$  = heat of water evaporation ( $\text{kJ kg}^{-1}$ )
- $M_{\text{CO}_2}$  = molar mass of carbon dioxide ( $\text{kg mol}^{-1}$ )
- $M_{\text{H}_2\text{O}}$  = molar mass of water ( $\text{kg mol}^{-1}$ )
- $Q_{\text{sens}}$  = sensible heat ( $\text{MJ kg}^{-1}$  of  $\text{CO}_2$ )
- $Q_{\text{vap,H}_2\text{O}}$  = heat of evaporation ( $\text{MJ kg}^{-1}$  of  $\text{CO}_2$ )
- $Q_{\text{des,CO}_2}$  = heat of desorption ( $\text{MJ kg}^{-1}$  of  $\text{CO}_2$ )
- $Q_{\text{reb}}$  = reboiler duty ( $\text{MJ kg}^{-1}$  of  $\text{CO}_2$ )
- $P$  = pressure (kPa)
- $T$  = temperature (K)
- $\alpha$  = loading (mol of  $\text{CO}_2$ /mol of solvent)
- $\Phi_M$  = molar flow ( $\text{mol s}^{-1}$ )
- $\Phi_H$  = enthalpy flow ( $\text{kJ s}^{-1}$ )
- $\rho$  = density ( $\text{kg m}^{-3}$ )

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