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Thermodynamic modelling of carbon dioxide solubility in aqueous amino acid salt solutions and their blends with alkanolamines

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A B S T R A C T

In this study, two thermodynamic approaches, namely explicit model and modified Kent-Eisenberg model are presented for the accurate determination of carbon dioxide solubility in aqueous solutions of amino acid salts with different levels of complexity. Both models were further extended to the correlation of carbon dioxide solubility in aqueous blends of amino acid salts with alkanolamines. Firstly, the explicit model consists of a single mathematical equation. Its structure is computationally simple and derived from equilibrium thermodynamics theory. Secondly, the modified Kent-Eisenberg model utilizes detailed reaction mechanism for development of a polynomial equation, that is solved by combining all non-idealities in two correction factors. Both models suitably determined the thermodynamics of carbon dioxide loaded aqueous amino acid salt solutions and their blends with alkanolamines. The results were in good agreement with experimental data for representative amino acid salt solutions (potassium and/or sodium salts of lysine, glycine, proline, sarcosine, serine, threonine, alanine, phenylalanine, amino-butyric acid, glutamine and asparagine) and their blends with alkanolamines (2-amino-2-methyl-1-propanol and piperazine) for range of process parameters. For carbon dioxide solubility in aqueous amino acid salt solutions, the AARE% for explicit and modified Kent-Eisenberg model was 13.85% and 13.84%, respectively. For carbon dioxide solubility in aqueous blends of amino acid salt and alkanolamine solutions, the AARE% for explicit and modified Kent-Eisenberg model was 18.25% and 17.25%, respectively. Both models use a small number of adjustable parameters. This indicates that generated parameters are able to accurately predict the carbon dioxide solubility at other process conditions, with minimum computational intricacy.

1. Introduction

Removal of carbon dioxide from process streams has become mandatory, because of its global warming potential and process nuisance. Various techniques have been utilized for carbon dioxide separation. Absorption via chemical solvents have gained relatively extensive application in industry due to their prevalence and operational provenance [1]. Amino acid salt solutions are the new class of evolving solvents for the separation of carbon dioxide from fuel and flue gas streams. These solvents absorb carbon dioxide by chemical reaction and are potentially capable of replacing conventional solvents, like alkanolamines [2]. Amino acid salts have been shown to provide environmental benefits, technical efficacy, thermal stability and improved process safety over their contemporaries [3,4].

Solutions of amino acid salts are usually prepared by mixing an amino acid with a strong alkali (preferably sodium or potassium

hydroxide) in an aqueous medium. Amino acids exhibit a zwitterion behaviour. Addition of a strong alkali activates the amine group by removal of proton from ammonium group that leaves the amino acid molecule with a net negative charge, as shown in Eq. (1) [5].

$$^-OOC - R - NH_3^+ \overset{-H^+}{\rightleftarrows} {}^-OOC - R - NH_2$$

Neutral Medium   Basic Medium   (1)
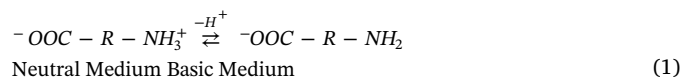
Theoretically, this amino acid's structure in basic medium is capable of reaction with carbon dioxide molecule, similar to the behaviour of alkanolamines. A variety of amino-acid salts have been evaluated for the removal of carbon dioxide with good carbon dioxide absorption capacity and are claimed to be superior than conventional solvents like alkanolamines [6]. Most of these investigations are concentrated on phase equilibrium studies. Nevertheless, the published experimental phase equilibrium data are highly limited, keeping in view the large

Nomenclature

Roman Symbols

A–E	adjustable parameters for explicit model
A_{MT}	Total amino acid salt concentration, mole/litre
A_{LK}	Total alkanolamine concentration, mole/litre
CO_2	carbon dioxide
CO_3^{-2}	carbonate
f_a, f_b, f_{am}, f_{bm}	correction parameters for modified KE model
H_2O	water
H^+	hydrogen ion
HCO_3^-	bicarbonate
H_{CO2}	Henry's constant for carbon dioxide, atm.litre/mole
KOH	potassium hydroxide
K^+	potassium ion
k_1	equilibrium constant of protonation of amino acid for explicit model
k_2	equilibrium constant of bicarbonate formation for explicit model
k_3	equilibrium constant of dissociation of potassium hydroxide for explicit model
k_4	equilibrium constant of dissociation of alkanolamine for explicit model
k_a	equilibrium constant of deprotonation of amino acid for modified KE model
k_b	equilibrium constant of carbamate hydrolysis of amino acid for modified KE model
k_{ax}	apparent equilibrium constant of deprotonation of amino acid for modified KE model
k_{bx}	apparent equilibrium constant of carbamate hydrolysis of amino acid for modified KE model
k_c	equilibrium constant of dissociation of carbon dioxide for modified KE model
k_d	equilibrium constant of dissociation of bicarbonate ion for modified KE model
k_e	equilibrium constant of dissociation of water for modified

	KE model
k_f	equilibrium constant of dissociation of potassium hydroxide for modified KE model
k_g	equilibrium constant of deprotonation of alkanolamine for modified KE model
k_x	combined equilibrium constant of all reactions for explicit model
k_y	combined equilibrium constant of all reaction for explicit model of blends
k_{all}	regressed common equilibrium constant for explicit model
k_{mix}	regressed common equilibrium constant for explicit model of blends
[i]	molar concentration of specie, i mole/litre
NDP	number of data points
OH^-	hydroxide ion
P_{CO2}	pressure of carbon dioxide in vapor phase, kPa
RNH	free alkanolamine
RNH_2^+	protonated alkanolamine
RR^-NH	free amino acid
$RR^-NH_2^+$	protonated amino acid
RR^-NCOO^-	carbamate ion of amino acid
$s_1 - s_6$	adjustable parameters for modified KE model based upon process parameters
Subscript "i"	pertaining to specie, i
Subscript "AMP"	pertaining to 2-amino-2-methyl-1-propanol
Subscript "PZ"	pertaining to piperazine
T	temperature

Greek Symbols

α	carbon dioxide loading, mole of CO_2/mole of amine
$α_{calc}$	calculated carbon dioxide loading, mole of CO_2/mole of amine
$α_{expt}$	experimental carbon dioxide loading, mole of CO_2/mole of amine

variety of amino-acids and range of process parameters, e.g., temperature, pressure and solvent concentration. Table 1 presents the phase equilibrium data for carbon dioxide solubility in a variety of aqueous amino acid salt solutions. Moreover, this widened scope of thermodynamic information is further challenged by the performance assessment requisites for a laboratory tested solvent. Hence, development of a thermodynamic model is necessary for the correlation of already inadequate experimental data.

In addition to above, amino acid salts have been blended with alkanolamines to explore better reaction kinetics, increased absorption capacity and cost effectiveness. Table 2 presents the sources of phase equilibrium data for carbon dioxide solubility in a variety of aqueous blends of amino acid salt and alkanolamine solutions.

The thermodynamic modelling efforts for the aqueous amino-acid salt solutions have been limited to modified Kent-Eisenberg model and Deshmukh-Mather model. The latter being a highly complex approach is further marred by localization and large number of regressed parameters [24]. Moreover, it is hard to justify the use of such complex algorithms, when the quality of experimental data is uncertain and large variances are frequent in published literature [25]. Fig. 1 shows the variances in experimental data of potassium lysinate from various sources. Although reconciliation techniques like robust neural network winsorization [26] are available, they cannot be applied because the datasets for aqueous amino acid salt solutions are disorganized and possess incomplete information about equilibrium phase envelope.

Contrarily, modified Kent-Eisenberg model is a simple approach.

For alkanolamines, the non-idealities are conjoined in a single/dual correction parameter(s) of the model, that is a function of alkanolamine concentration, carbon dioxide loadings and/or pressure [24]. It is pertinent to note that the equilibrium constants for alkanolamine based systems are well defined and established [24]. On the other hand, the equilibrium data for amino acid salt solutions is scarce and gaps in thermodynamic information (like equilibrium constants for individual reactions, etc.) are common. Hence, the correction parameters for modified Kent-Eisenberg model used previously for the correlation of aqueous amino acid salt solutions are haphazard and does not follow a fixed pattern or convention [9,23].

Therefore, it is necessary that computationally simple modelling techniques are developed for the correlation of the said system. The developed models must be flexible enough to accommodate the new thermodynamic property data, as soon as they come available in open literature, along with extension to newer mixtures and blends. Moreover, the models should also provide a stop-gap solution towards the understanding of the separation thermodynamics of carbon dioxide loaded amino acid salts solutions.

In this study, two semi-empirical thermodynamic models are presented for the prediction of carbon dioxide solubilities in aqueous amino acid salt solutions and their blends with alkanolamines. The first model, which is referred as explicit model, hereafter, is a simple computational approach that uses a combined single correction parameter (regressed to process parameters). It consists of an abridged set of reaction equations for the correlation of carbon dioxide solubilities in a