A comprehensive thermodynamic study of heat stable acetic acid salt of monoethanolamine

ARTICLE INFO

ABSTRACT

The knowledge of physical properties and phase equilibrium of 2-(hydroxy)ethylammonium acetate (2-HEAA) containing systems are important when CO_2 capture processes have to be modeled accurately. The density of 2-HEAA and water + 2-HEAA was measured from 293 to 363 K each 10 K. In addition, enthalpy of fusion and the melting point of MEA and 2-HEAA were determined using a differential scanning calorimeter. SLE data for 2-HEAA, and water + 2-HEAA and MEA + 2-HEAA systems were measured with a visual method. VLE data related to the water + 2-HEAA system were measured using a static total pressure apparatus at 339 and 347 K. The VLE and SLE data of water + 2-HEAA system from both this work and the open literature were used to regress NRTL parameters. The NRTL activity coefficient model was also used to represent the SLE data of the MEA + 2-HEAA system.

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1. Introduction

The role of CO_2 as a greenhouse gas has resulted in tightening environmental regulations concerning CO_2 emissions to the atmosphere. CO_2 capture is one of the most significant means to reduce such emissions. Aqueous alkanolamine solutions have widely been used to absorb CO_2 from many gas streams such as fuel gases, natural gases and refinery gases. In a gas processing unit, CO_2 containing gas is fed to an absorber column countercurrently to a stream of the amine solution. When CO_2 encounters the amine, they react leading to CO_2 capture into the solution. In the stripper unit, CO_2 is separated from the amine solution by reducing the pressure and rising the temperature, in order to recycle the amine back to the absorber column.

Alkanolamine solutions are frequently contaminated by amine degradation products such as heat stable salts (HSS), which perturb plant operations (Lepaumier et al., 2010; Vevelstad et al., 2011). The degradation of alkanolamines is presented in the open literature (Dawodu and Meisen, 1996; Kim, 1988; Lepaumier et al., 2009) but the effects of degradation products on phase equilibria have been much less investigated. The knowledge of phase equilibria of amine degradation products + amine solutions is important for convenient thermodynamic description of real amine solutions in industrial processes. Therefore good quality data is needed for modeling and designing alkanolamine systems that contain heat stable salts.

Monoethanolamine is the most used alkanolamine for CO_2 capture from flue gases, which may contain oxygen, carbon dioxide and small amounts of NO_x and SO_x (Lepaumier et al., 2010). These gases and temperature subject monoethanolamine to three types of degradation: thermal degradation, which is significant at temperatures above 205 °C, carbamate polymerization due to CO_2, and oxidative degradation due to O_2 (Chi and Rochelle, 2002). Formic acid, acetic acid and oxalic acid form when alkanolamine fragments oxidize in the presence of oxygen in the absorption/regeneration

processes. Carboxylic acids in turn may react further with alkanolamines to form ammonium carboxylates, which are also called heat stable salts. In addition to oxygen reactions with amine, carboxylic acids may enter an amine system among the feed gas (Verma and Verma, 2009). Heat stable salts are not thermally regenerable compounds and thus they tie up the amines at the expense of the amine capacity in the CO_2 recovery processes. Heat stable salts also cause corrosion, foaming and fouling in process equipment (Lepaumier et al., 2010; Verma and Verma, 2009).

Monoethanolamine reacts with acetic acid (HAc) to form 2-(hydroxy)ethylammonium acetate (2-HEAA). Heat stable 2-HEAA salt has been studied in restricted manner and therefore only a limited amount of data on physical properties is available in the literature e.g. density (Alvarez et al., 2011; Bicak, 2004; Greaves et al., 2006; Kurnia et al., 2009; Yuan et al., 2007a,b), viscosity (Greaves et al., 2006; Yuan et al., 2007a,b), refractive index (Bicak, 2004; Greaves et al., 2006; Kurnia et al., 2009) and melting point (Bicak, 2004; Temin, 1956; Yuan et al., 2007a,b). Some vapor–liquid equilibrium data (Wang et al., 2009) for the system of water + 2-HEAA and CO_2 solubility data in 2-HEAA (Yuan et al., 2007a,b) have been published earlier. Physical properties and phase equilibrium data of 2-HEAA containing systems are important when CO_2 capture processes have to be modeled accurately.

Solid–liquid equilibrium data are necessary for developing and designing crystallization and purification processes (Domanska and Morawski, 2004). SLE data provides information about how the solution components precipitate inside process equipment. In addition, SLE data provides information about how the solution behaves at low temperatures, where it may be more difficult to determine the partial pressure over the solution. Therefore SLE data should be used together with VLE data to obtain the activity coefficients of the system components.

In a simple case, a binary system forms one eutectic point on the SLE curve whereas in a more complicated case, a binary system

Nomenclature

1	N-methylene group of MEA in Figs. 1 and 3
2	O-methylene group of MEA in Figs. 1 and 3
a	N-methylene group of 2-HEAA in Figs. 1 and 3
a'	N-methylene group of 2-HEAM in Figs. 1 and 3
a	activity
$a_0, a_1, a_2, \ldots$	parameters of Eqs. (3) and (4)
a_{ij}, b_{ij}	parameters of Eqs. (7) and (8)
b	O-methylene group of 2-HEAA in Figs. 1 and 3
b'	O-methylene group of 2-HEAM in Figs. 1 and 3
A, B, AB	components
C_P	constant-pressure heat capacity (J/mol K)
G	Gibbs energy (kJ/mol)
H	enthalpy (kJ/mol)
K	equilibrium constant
obj	objective function
P	pressure (kPa)
R	gas constant (J/K mol)
T	temperature (K)
T_r	reduced temperature
w	mass fraction
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
C	the ratio 2-HEAM:2-HEAA in Eq. (1)
I	intensity

Greek letters

α	nonrandomness parameter of the NRTL activity coefficient model
γ	activity coefficient
ρ	density (kg/m^3) or as given
τ_{ij}, τ_{ji}	parameters in the NRTL model

Superscripts

$calc$	calculated
exp	experimental
fus	fusion
E	excess property
L	liquid phase
ref	the reference state of pure solid complex
S	solid phase
vap	vapor pressure
∞	infinite dilution

Subscripts

i, j	component i and j
υ	stoichiometric factor
1	component 1
2	component 2
3.09 ppm	the location of N-methylene signal of 2-HEAM in ^{1}H NMR spectrum
3.38 ppm	the location of O-methylene signal of 2-HEAM in ^{1}H NMR spectrum
3.25 ppm	the location of O-methylene signal of 2-HEAA in ^{1}H NMR spectrum
3.25 . . . 3.80 ppm	the cluster of O-methylene signals of 2-HEAA + 2-HEAM in ^{1}H NMR spectrum

forms two or more eutectic points on the SLE curve. For example, some compounds act according to the latter case by forming a solid complex with water below the freezing point and between the two eutectic points. These kinds of SLE systems have been modeled in several ways in the literature. Miller and Carpenter (1964) modeled the water-methanol system by assuming that the system consists of water, methanol and 1:1 water–methanol complex, the equilibrium constant of the complex reaction being set equal to unity. Ott and Goates (1983) used a semi-empirical polynomial equation to model the SLE data. There is also a very typical SLE model available in the literature that is used by many authors (Folas et al., 2005; Prikhod'ko et al., 2007; Tumakaka et al., 2007). In this model the freezing temperature for the complex forming part of the SLE curve is obtained by using the equilibrium constant of the complex reaction. It is also assumed that two liquid compounds react to form a pure solid complex. The model is used in this work and thus it is described in more detail in the modeling section.

The objective of this work was to prepare heat stable 2-HEAA salt, which is also called ionic liquid, from MEA and acetic acid and to investigate the salts physical properties and phase equilibria with water and MEA. 2-HEAA has not been studied extensively in the open literature and only limited experimental data are available. In this work physical properties such as melting point, enthalpy of fusion and density were measured. In addition, experimental vapor–liquid equilibrium data of the system of water + 2-HEAA were measured with a static total pressure apparatus at 339 and 347 K. Solid–liquid equilibria were investigated with differential scanning calorimeter and visual method for MEA and 2-HEAA and for two binary systems: water + 2-HEAA and MEA + 2-HEAA. The measured data were used to determine the binary interaction parameters of the NRTL activity coefficient model (Renon and Prausnitz, 1968).

2. Experimental

2.1. Chemicals

MEA and acetic acid were purchased from Sigma Aldrich. They were dried over Merck 0.3 nm molecular sieve after which the water content was determined by the Karl Fischer titration method. The purity of both compounds was >99.9 mass-%. Deuterated dimethylsulfoxide (DMSO-d$_6$, 99% deuterated) was purchased from Euriso-Top and stored over 0.3 nm molecular sieves before use to remove residual water. N-(2-hydroxyethyl)acetamide was purchased from Sigma Aldrich and was used as received.

2.2. Preparation and purification of 2-HEAA

Monoethanolamine was placed in a triple necked flask equipped with a reflux condenser, dropping funnel and N$_2$ gas. An equimolar amount of acetic acid was added dropwise into the flask and the reaction mixture was stirred vigorously with a magnetic bar. The reaction mixture was cooled in an ice bath. During the salt preparation, some of 2-HEAA underwent dehydration reaction, which yielded N-(2-hydroxyethyl)acetamide (2-HEAM) and water as side products (Supap et al., 2011). 2-HEAM gives the solution yellowish color. The reaction product solidified either during or after its preparation and was therefore heated in an oven before vacuum distillation. The temperature was set to slightly below 343 K since according to Temin (1956) the melting point of 2-HEAA is 338–339 K. 2-HEAA and 2-HEAM were separated from each other in vacuum distillation as had been done by Temin (1956). 2-HEAA was obtained as distillate and 2-HEAM remained in the bottom flask. 2-HEAA was distilled twice in order to get as pure salt as possible. The distilled 2-HEAA is a viscous and colorless liquid. It was recovered as subcooled liquid and stored at room temperature.

2.3. Characterization of 2-HEAA

The purity of 2-HEAA was determined by proton nuclear magnetic resonance (^{1}H NMR) analysis and the water content by Karl