J. Chem. Thermodynamics 90 (2015) 242–250

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Molar excess enthalpy (H_m^E) for systems of aqueous piperazine derivatives

Saeed Poozesh, Aravind V. Rayer, Amr Henni *

Acid Gas Removal Laboratory, Faculty of Engineering and Applied Science, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

ARTICLE INFO

Article history:
Received 1 July 2014
Received in revised form 5 May 2015
Accepted 8 June 2015
Available online 11 July 2015

Keywords:
Molar excess enthalpy
Aqueous alkanolamine
NRTL
UNIQUAC
UNIFAC

ABSTRACT

Molar excess enthalpies (H_m^E) of aqueous1-methyl piperazine (1-MPZ), 4-(2-hydroxy ethyl) morpholine (4,2-HEMO), 1,4-dimethyl piperazine (1,4-DMPZ), 1-(2-hydroxyethyl) piperazine (1,2-HEPZ), 3-morpholinopropyl amine (3-MOPA), morpholine (MO) were reported at three different temperatures T = (298.15, 313.15, and 323.15) K and over the entire range of mole fractions. The Redlich–Kister (RK) equation was used to correlate the experimentally measured H_m^E values as a function of mole fractions. The molar enthalpies of amines and water at infinite dilutions were determined from the RK coefficients. Among the studied solution theory models to correlate the experimental data, the modified UNIFAC (UNIversal Functional groups Activity Coefficient, Dortmund) model exhibited the lowest percentage of average absolute deviations from the experimental data, followed by the NRTL (Non-Random Two Liquid) model and the UNIQUAC (UNIversal QUAsi Chemical) model. Among the six amines studied, the {1-MPZ + water} system exhibited the highest values of molar excess negative enthalpies followed by {3-MOPA + H_2O}, {1,2-HEPZ + H_2O}, {MO + H_2O}, {1,4-DMPZ + H_2O} and {4,2-HEMO + H_2O} systems.

1. Introduction

Piperazine is considered one of the most promising solvent for acid gas removal as an additive to conventional solvents such as diethanolamine (DEA), methyldiethanolamine (MDEA), and 1-amino-2-methyl-1-propanol (AMP) because of its high acid gas loading capacity along with its high reaction rate [1]. Because of its cyclic and diamine characteristics, the reactivity and solubility of piperazine are higher than other amines. The reaction kinetics, mass transfer and solubility of carbon dioxide in a single or mixed aqueous solution of piperazine have been studied by various researchers [2–10]. Kadiwala *et al.* [8] concluded that piperazine had a capacity for CO_2 in the ratio of three moles of CO_2 per mole of piperazine, at high pressures which is almost three times higher than the capacity of "standard" monoethanolamine (MEA) at high pressure.

Morpholine is a secondary cyclic amine that can be utilized as an acid gas extraction medium. Cyclic amines or morpholines are used in conjunction with the monoalkyl ether of a polyhydric alcohol to absorb hydrogen sulfide from a gas stream. Specifically, n-methyl, n-ethyl, n-propyl or n-butyl morpholine were contemplated for acid gas removal [11]. Burgoyne *et al.* [12] described a process that utilized morpholine compounds for the removal of acid gases such as H_2S, COS and CO_2 from a gas stream at high pressures and with low heat of absorption. They characterized the regeneration of these solvents to be performed simply and with a minimum of energy consumption. In addition, morpholine solutions have low vapor pressures and therefore there is the possibility to use lesser amounts of solvent in the scrubbing-regeneration process which would lead to a reduction in the storage, the amount of the required solvent, and the size of the wash trays, reducing therefore capital and operating costs [12].

Molar excess enthalpy (H_m^E) values for the above mentioned aqueous solutions are required for testing the feasibility of existing solution theories as well as for formulating new theories. (H_m^E) values are necessary for modeling multistage, multi-component equilibria in absorption and stripping columns. Different solution models and theories have to be developed to obtain coefficients which are crucial to model the solubility of gases in aqueous solutions.

Therefore, in this study, three cyclic amines with similar structures such as piperazine (1-methylpiperazine (1-MPZ), 1,4-dimethylpiperazine (1,4-DMPZ), 1-(2-hydroxyethyl)piperazine, (1,2-HEPZ), and three cyclic amines with similar structures based on morpholine (morpholine, MO; 4-(2-hydroxyethyl) morpholine (4,2-HEMO), and 3-morpholinopropyl amine (3-MOPA) have been selected and studied. Molecular structures of the

* Corresponding author. Tel.: +1 306 585 4960; fax: +1 306 585 4855.
E-mail address: amr.henni@uregina.ca (A. Henni).

http://dx.doi.org/10.1016/j.jct.2015.06.006
0021-9614/

studied amines are given in figure 1.Till now, there are no literature values for (H^E_m) for {1-MPZ (1) + H_2O (2)}, {4,2-HEMO (1) + H_2O (2)}, {1,4-DMPZ (1) + H_2O (2)}, {1,2-HEPZ (1) + H_2O (2)}, {3-MOPA (1) + H_2O (2)} and {MO (1) + H_2O (2)} systems.

2. Experimental

2.1. Chemicals

Alkanolamines used in this study were purchased from Sigma–Aldrich with a mass purity of 99% for DEA, 99% for MDEA, 99% for 1-MPZ, ⩾99% for 4,2-HEMO, 98% for 1,4-DMPZ, 98% for 1,2-HEPZ, 98% for 3-MOPA and 99.5+% for MO. They were used without further purification. Tin and Indium, used in this study for the temperature calibration, were purchased from Sigma–Aldrich with a purity of 99.99% and 99.999%, respectively.

The main goal of this study is to determine, experimentally, H^E_m values for various cyclic amines at three different temperatures T = (298.15, 313.15, and 323.15) K. The experimentally measured (H^E_m) values are correlated as a function of mole fractions employing the Redlich–Kister (RK) equation. The molar enthalpies of alkanolamines and water at infinite dilutions were estimated using the method proposed by Maham *et al.* [13]. Three solution theory models [Non-Random Two Liquid model, NRTL; UNIversal QUAsi Chemical model, UNIQUAC, and the UNIversal Functional groups Activity Coefficient model, modified UNIFAC] were used to correlate the measured (H^E_m) values. The parameters of these three models are determined using Aspen Plus software package, which has a built-in algorithm for fitting of the experimental data called the Data Regression System (DRS).

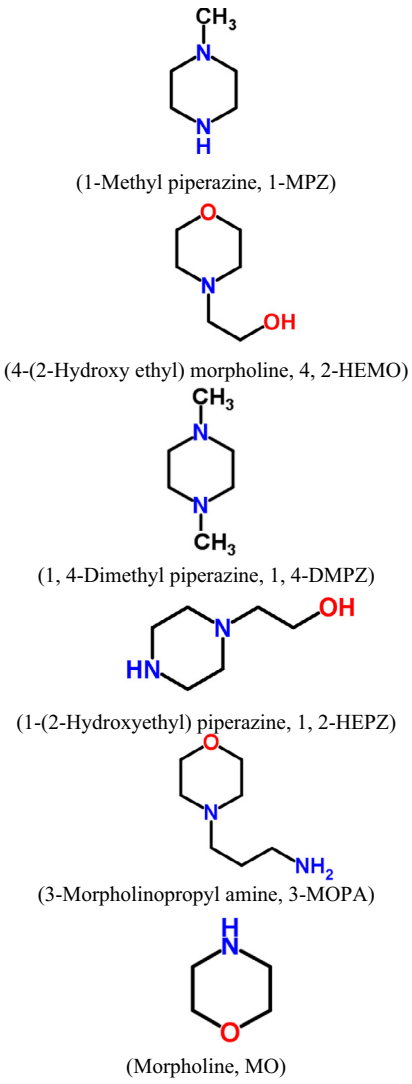

FIGURE 1. Molecular structures of the studied cyclic amines.

2.2. Apparatus and procedure

The measurements of (H^E_m) values were carried out with the C80 calorimeter manufactured by Setaram Instrumentation (Caluire, France). The C80 calorimeter works on the Tian-Calvet heat flow principle as described in detail by Calvet *et al.* [14]. The operating range of the C80 calorimeter is from ambient temperature to 573.15 K. An analytical balance Ohaus (Model AP250D, Florham Park, NJ) was used to weigh the amines and deionized (double distilled) water with a precision of ±0.1 mg (0.01 mg for weights less than 52 g). The overall possible uncertainty in the mole fractions was estimated to be less than ±0.0002 using the above mentioned precision of the analytical balance. To obtain precise measurements of (H^E_m) values, a sensitivity calibration of the C80 calorimeter was performed by Joule Effect. The calibration was performed for the entire temperature range of the C80 calorimeter i.e. T = (298.15 to 573.15) K at a scanning rate of 0.1 K/minute. The detailed description of the sensitivity calibration is given in the work published by Mundhwa [15]. The temperature calibration was performed by measuring the displayed temperature of a phase change of a substance (Indium or Tin) which has a well-documented and precise transition temperature. The detailed description of the temperature calibration was also given in reference [15].

Two identical membrane mixing cells having a volume of 5.4 ml each were used for the measurements; one was used for the measurement chamber and the other one for the reference chamber. The disadvantage of these cells is that the mole fraction cannot be accurately determined in the regions of $x_1 < 0.0250$ and $x_1 > 0.9500$ due to the fact the amount of heat flux produced at these regions are very low and difficult to integrate to get the specific heat of mixing values and by doing several experiments at these regions it was found out that the repeatability of the experimental values in these regions are not worthy enough to report. In the mixing cell, both amines and water were placed into separate sealed compartments on either side of an aluminum foil. Amine was placed on the lower a part of the mixing cell (≈2.5 ml) and water was placed on the top of the Aluminum foil in the mixing cell having a volume of 2.9 ml approximately. In the reference cell the amine and water were premixed to their final desired composition and placed in the cell. The reference cell serves to cancel out the heat supplied to maintain the isothermal conditions and the negligible heat of stirring. The actual temperatures of each measurement were within ±0.01 K of the stated temperatures T = (298.15, 313.15 and 333.15) K.

To verify the reliability of the C80 heat flow calorimeter for molar excess enthalpy measurements, two well-known and widely published systems ({MDEA (1) + H_2O (2)} and {DEA (1) + H_2O}) have been chosen from the literature to be investigated. H^E_m measurements for the systems aqueous MDEA and DEA solutions were reported by Mundhwa *et al.* [15] and Maham *et al.* [13] for mole fractions from almost 0.050 to 0.9000 at T = 298.15 K for DEA and 313.15 K for MDEA. The molar excess enthalpy values of these systems were slightly in better agreement with those measured by Maham *et al.* [13] than the work of Mundhwa *et al.* [15] as shown in tables 1 and 2. Slight deviation from our previous work (purity ⩾ 98%) may be due to the different purities of the