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## Solubility of H<sub>2</sub>S in ammonium-based ionic liquids

José M.M.V. Sousa<sup>a,b,\*</sup>, Tânia E. Sintra<sup>c</sup>, Abel G.M. Ferreira<sup>b</sup>, Pedro J. Carvalho<sup>c</sup>, Isabel M.A. Fonseca<sup>b</sup>

<sup>a</sup> Polytechnic Institute of Coimbra, Coimbra Institute of Engineering, Rua Pedro Nunes – Quinta da Nora, 3030-199 Coimbra, Portugal

<sup>b</sup> University of Coimbra, CIEQPF-Chemical Process Engineering and Forest Products Research Centre, Department of Chemical Engineering, Rua Sílvio Lima – Pólo II, 3030-790 Coimbra, Portugal

<sup>c</sup> CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

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### ABSTRACT

This work is inserted in a research program that consists mainly in the experimental and theoretical study of gas/liquid solubility in ionic liquids (ILs). In this study the experimental data of hydrogen sulfide solubility in ammonium-based ionic liquids, namely 2-hydroxyethylammonium acetate [2-HEA][Ace], bis(2-hydroxyethyl)ammonium acetate [B-2-HEA][Ace] and 2-hydroxyethyldiethylammonium hydrogen diacetate [2-HEDEA][H(Ace)<sub>2</sub>], were determined using a volumetric method in the 298 K to 318 K temperature range and at atmospheric pressure. The ionic liquids are functionalized with the OH group in the ammonium-based cations, in order to study the influence of hydroxyl group in the formation of hydrogen bonds between the IL-IL and IL-gas. The data gathered is modelled with the Cubic Plus Association Equation of State (CPA EoS), considering the association schemes four-sites (4C) for hydrogen sulfide and two-sites (2B) for the ILs ([2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>]).

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### 1. Introduction

This study aims to measure the temperature dependence, at atmospheric pressure, of the hydrogen sulfide (H<sub>2</sub>S) solubilities in three ionic liquids (ILs), namely 2-hydroxyethylammonium acetate ([2-HEA][Ace]), bis(2-hydroxyethyl)ammonium acetate ([B-2-HEA][Ace]) and 2-hydroxyethyldiethylammonium hydrogen diacetate ([2-HEDEA][H(Ace)<sub>2</sub>]).

Hydrogen sulfide is one of the most abundant sulfur containing compounds in natural gas and in light and middle distillate oil fractions. Because of its undesirable high toxicity and corrosiveness, hydrogen sulfide must be removed from industrial gas and oil streams [1].

Ionic liquids (ILs) are low-melting salts with extremely low vapor pressures, high thermal and chemical stability, and tunable solvent properties for many organic and inorganic compounds. These remarkable properties position ILs as environmentally benign solvents feasible for a large number of applications, including gas solubility and separation, cellulose processing, catalysis, extraction, and high-temperature pyrochemical processing, *etc.* [2,3]. However, the high viscosity of the ILs is usually a limiting step for the dissolution of the gas and ultimately on a separation

unit sizing [4,5]. The properties of the ILs can be tuned by changing the ions according to the desired properties, from a very large set of possible combinations [6]. Thus, one of the areas of research interests in the absorption of acidic gases, like CO<sub>2</sub> or H<sub>2</sub>S is to formulate ionic liquids with desirable properties concentrated on the following aspects: (1) the design and synthesis of ILs, especially the task-specific ILs for enhanced absorption performance by functionalization with amine or other groups; (2) the measurement and estimation of physical/chemical properties of the multi-component systems containing the IL and the gas, and the development of suitable thermodynamic models; (3) the investigation of the transport properties, absorption kinetics, and the mechanism for gas capture with functionalized ILs [7].

In the past few years, a growing number of imidazolium-based ILs have been evaluated for H<sub>2</sub>S solubility as a function of temperature and pressure [1,8–19]. However, experimental data for the solubility of hydrogen sulfide outside of imidazolium-based ionic liquids are surprisingly scarce if one takes into consideration their enhanced, in mole fractions, CO<sub>2</sub> solubility [20–23].

In the present work, the volumetric method with an automated apparatus [24] is used to determine the solubility of H<sub>2</sub>S in ammonium-based ionic liquids as a function of temperature and at atmospheric pressure. The H<sub>2</sub>S solubility was modeled using the Cubic Plus Association Equation of State (CPA EoS) showing high accuracy of the CPA equation of state to describe the phase equilibria solubility data.

\* Corresponding author at: Polytechnic Institute of Coimbra, Coimbra Institute of Engineering, Rua Pedro Nunes – Quinta da Nora, 3030-199 Coimbra, Portugal.

E-mail address: [sousa@isec.pt](mailto:sousa@isec.pt) (J.M.M.V. Sousa).

## 2. Experimental

The experimental technique used in this work is based on a volumetric method. The apparatus used for the determination of solubility was described in detail elsewhere [24]. This procedure has shown to be highly accurate and precise in the past for various gases and solvents, making it a preferable choice [25,26].

The variables measured directly from the apparatus are the displaced gas volume in the gas burette due to the gas dissolution ( $\Delta V$ ), the mass of solution ( $m_s$ ), the equilibrium pressure ( $P$ ) and the temperature ( $T$ ). Being the uncertainties of the solubility data determined using the error propagation law and considering the experimental uncertainties are: temperature,  $10^{-2}$  K; pressure, 10 Pa; mass,  $10^{-7}$  kg; volume of dissolved gas,  $10^{-6}$  m<sup>3</sup> [24].

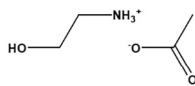
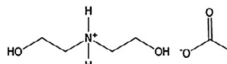
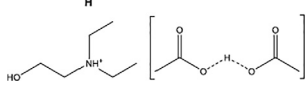
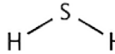
The H<sub>2</sub>S was supplied by Praxair with 0.99 mol fraction purity. The ionic liquids 2-hydroxyethylammonium acetate ([2-HEA][Ace]), bis(2-hydroxyethyl)ammonium acetate ([B-2-HEA][Ace]) and 2-hydroxyethyldiethylammonium hydrogen diacetate ([2-HEDEA][H(Ace)<sub>2</sub>]) were synthesized by us following well-established protocols, *via* proton exchange reaction between amines and acetic acid [27,28]. Briefly, a solution of acetic acid in ethanol was added dropwise to a stirring solution of amine (ethanolamine, diethanolamine or diethylethanolamine) in ethanol, with an equimolar ratio of amine and acid, at 0 °C and under N<sub>2</sub> atmosphere. The resultant solution was stirred at room temperature and under N<sub>2</sub> atmosphere overnight, producing the respective protic alkanol ammonium ionic liquid. Finally, ethanol was removed under reduced pressure and the obtained compound was dried under vacuum (0.1 Pa, 301 K) for at least 48 h. The structure of all ILs synthesized was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, showing the high purity level of all the ionic structures after their synthesis, as reported in the ESI. As can be seen by the <sup>1</sup>H NMR spectra the [2-HEDEA][H(Ace)<sub>2</sub>] presents the 1:2 (cation:anion) proportion due to the formation of an azeotrope during the distillation purification step [29].

The ionic liquids and H<sub>2</sub>S are presented in Table 1, along with their full name, abbreviations, water content, mole fraction purity and chemical structures. In order to decrease the water content and volatile compounds to negligible values, the ILs were degasified by applying vacuum (0.1 Pa), moderate temperature (313 K) and stirring for a period never shorter than 48 h. The [2-HEA][Ace], [[B-2-HEA][Ace], [2-HEDEA][H(Ace)<sub>2</sub>] ILs presented a water content lower than 200 ppm, determined by a Metrohm 831 Karl Fischer coulometer using the analyte Hydranal<sup>®</sup>-Coulomat AG from Riedel-de-Haën.

The ionic liquids were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra using dimethylsulfoxide (DMSO) as a deuterated solvent (Supporting Information).

**Table 1**

Ionic liquids and H<sub>2</sub>S name, abbreviations, chemical structure, water content (ppm) and mole fraction purity ( $x$ ). The vacuum treatment for the ILs purification was also used.

Name	Abbreviation	Chemical Structure
2-hydroxyethylammonium Acetate (water content = 160 ppm <sup>a</sup> ; $x > 0.90^b$ ) Synthetized	[2-HEA][Ace]	
bis(2-hydroxyethyl)ammonium acetate (water content = 112 ppm <sup>a</sup> ; $x > 0.99^b$ ) Synthetized	[B-2-HEA][Ace]	
2-hydroxyethyldiethylammonium hydrogen diacetate (water content = 195 ppm <sup>a</sup> ; $x > 0.95^b$ ) Synthetized	[2-HEDEA][H(Ace) <sub>2</sub> ]	
Hydrogen sulfide ( $x > 0.99$ ) Supplied by Praxair	H <sub>2</sub> S	

<sup>a</sup> Determined by Karl Fischer coulometer titration; <sup>b</sup> Determined by NMR.

### 2.1. Gas solubility calculations for ionic liquids

The volume of gas displaced due to dissolution ( $\Delta V$ ) and the amount of gas absorbed in moles ( $n^G$ ) can be related through a second-order truncated virial equation of state

$$\frac{Pv_{mix}^G}{RT} = 1 + \frac{B_{mix}P}{RT} \quad (1)$$

where  $P$  is the total pressure of gas,  $R$  the universal gas constant,  $v_{mix}^G$  the molar volume of the gas mixture that equals  $\Delta V / n^G$ ,  $T$  is the temperature and  $B_{mix}$  is the second virial coefficient of the binary mixture given by:

$$B_{mix} = y_1^2 B_{11}(T) + y_2^2 B_{22}(T) + y_1 y_2 B_{12}(T) \quad (2)$$

where  $y_1$  and  $y_2$  represent the mole fraction composition in the vapor phase, and subscripts 1 and 2 the liquid solvent (IL) and the gas solute, respectively.  $B_{11}(T)$ ,  $B_{22}(T)$  and  $B_{12}(T)$  are the second virial coefficients of pure components 1 and 2, and the second cross virial coefficient, respectively. For the temperature range studied, the calculations are simplified due to the extremely low vapor pressure of the ILs at atmospheric pressure. Therefore, the ILs are postulated as strictly non-volatile solvents and consequently  $y_1 \approx 0$ ,  $y_2 \approx 1$ ,  $B_{mix}(T) \approx B_{22}(T)$ ,  $P \approx P_{H_2S}$  and  $n^G \approx n_2$ . Therefore, Eq. (1) is rewritten where  $n_2$  and  $B_{22}(T)$  are stated as:

$$n_2 = \Delta V / (RT / P_{H_2S} + B_{22}(T)) \quad (3)$$

$$B_{22}(T) = \sum_{i=0}^3 c_i T^{-i} \quad (4)$$

The parameters  $c_i$  of Eq. (4) for H<sub>2</sub>S were retrieved from reference [30]. The number of moles of the solvent,  $n_1$ , at the end of each experiment is evaluated from the difference between the total solution mass,  $m_s$ , and the mass of solute absorbed,  $m_2 = n_2 M_2$ :

$$n_1 = (m_s - n_2 M_2) / M_1 \quad (5)$$

Finally, the mole fraction solubility of H<sub>2</sub>S in ILs ( $x_2$ ) is calculated from  $x_2 = n_2 / (n_1 + n_2)$  and the Henry's constant,  $H_{2,1}^{sp}(T, P)$  is obtained from  $H_{2,1}^{sp}(T, P) = P / x_2$ .

The solubility of gases dependency on temperature given by Eq. (6) is related with the partial molar enthalpies ( $\Delta \bar{h}_2$ ), and entropies ( $\Delta \bar{s}_2$ ) of solution as follows:

$$R \ln x_2 = A + \frac{B}{T} \quad (6)$$

$$\Delta \bar{h}_2 = RT \left( \frac{\partial \ln x_2}{\partial \ln T} \right)_p = -B \quad (7)$$

$$\Delta\bar{s}_2 = R \left[ \left( \frac{\partial \ln x_2}{\partial \ln T} \right)_p + \ln x_2 \right] = A \quad (8)$$

Values for  $\Delta\bar{h}_2$  and  $\Delta\bar{s}_2$  in each H<sub>2</sub>S/(ionic compound) system are calculated from the parameters of Eq. (6) obtained through a least squares fit.

### 3. Gas/Liquid equilibria modelling

The contact of a gas with a liquid imposes changes of enthalpy and entropy along with a decrease in gas volume as dissolution takes place until an equilibrium state is reached. Mathematically, the gas–liquid equilibrium condition for the solute can be expressed as a stationary point of Gibbs function, *i.e.* iso-fugacity condition:  $f_2^G = f_2^L$ . To model gas and liquid fugacity of H<sub>2</sub>S ( $f_2^G$  and  $f_2^L$ , respectively) and calculate their solubility in the ILs, is employed the Cubic-Plus-Association equation of state (CPA EoS) to model the phase equilibrium.

The Cubic-Plus-Association (CPA) EoS equation of state proposed by Kontogeorgis et al. [31] is used to calculate the fugacity coefficients. This equation of state can be written using the following expression for the residual Helmholtz energy:

$$A = A^{cubic} + A^{assoc} \quad (9a)$$

where  $A^{cubic}$  and  $A^{assoc}$  are the cubic and association term of the Helmholtz energy given by:

$$A^{cubic} = -\frac{a}{b} \ln(1 + b\rho) - RT \ln(1 - b\rho) \quad (9b)$$

$$A^{assoc} = RT \sum_i x_i \sum_{A_i} \left[ \ln(X_{A_i}) - \frac{X_{A_i}}{2} + \frac{1}{2} \right] \quad (9c)$$

$$g(\rho) = \frac{1}{1 - 1.9\eta} \quad (9d)$$

$$\eta = \frac{1}{4} b\rho \quad (9e)$$

Here,  $A^{cubic}$  is evaluated from a Soave-Redlich-Kwong equation of state (SRK EoS) where  $a$ ,  $b$  and  $\rho$  are the energy parameter, co-volume parameter and the molar density, respectively.  $X_{A_i}$  represents the fraction of molecule  $i$  not bonded at site  $A$ ,  $x_i$  is the mole fraction of component  $i$  and  $g$  the simplified hard-sphere radial distribution function [32].

In the association contribution,  $X_{A_i}$ , is related with the association strength,  $\Delta^{A_i B_j}$ , between sites belonging at different molecules, *e.g.* site  $A$  on molecule  $i$  and site  $B$  on molecule  $j$ , and is defined as:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \quad (10)$$

where the association strength,  $\Delta^{A_i B_j}$ , is expressed as:

$$\Delta^{A_i B_j} = g(\rho) \left[ \exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (11)$$

The  $\varepsilon^{A_i B_j}$  and  $\beta^{A_i B_j}$  are the association energy and volume, respectively,  $b_{ij} = (b_i + b_j)/2$ , where  $b_i$  is the temperature independent co-volume parameter of component  $i$ . Thus, for pure non-associating compounds the CPA EoS requires only three model parameters, the co-volume parameter  $b$ , and the parameters  $a_0$  and  $c_1$  involved in the Soave-type temperature dependency  $a(T)$ :

$$a(T) = a_0 [1 + c_1 (1 - T_r)]^2 \quad (12)$$

For associating compounds, the model has two additional pure compound parameters, the association energy,  $\varepsilon$ , and the association volume,  $\beta$ . The three or five parameters are obtained by fitting vapor pressure and liquid density data, carried by the minimization of the objective function (*OF*), taking into account the association scheme that provides the number and type of association sites for each associating compound [31].

$$OF = \sum_i^{N_p} \left( \frac{P_i^{exp.} - P_i^{calc.}}{P_i^{exp.}} \right)^2 + \sum_i^{N_p} \left( \frac{\rho_i^{exp.} - \rho_i^{calc.}}{\rho_i^{exp.}} \right)^2 \quad (13)$$

When CPA is extended to mixtures, the energy and co-volume parameters of the physical term are calculated applying the conventional van der Waals one-fluid mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \text{ where } a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (14a)$$

$$b = \sum_i x_i b_i \quad (14b)$$

When dealing with mixtures containing multiple associating components, the association term of the CPA EoS, requires combining rules for the association energy and volume parameters [33]. In order to calculate the value of the association strength, in Eq. (11), various combining rules have been investigated [34], being the Elliott combination rule used in the present work.

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad (15)$$

For estimating the binary interaction parameter,  $k_{ij}$ , the following objective function was employed using the experimental solubility data.

$$OF = \sum_i^{N_p} \left( \frac{x_i^{exp.} - x_i^{calc.}}{x_i^{exp.}} \right)^2 \quad (16)$$

The experimental solubility data at atmospheric pressure for different temperatures are presented in Section 4.1. The results for the CPA model are discussed later in Section 4.2.

## 4. Results and discussion

### 4.1. Experimental results

The solubility data for H<sub>2</sub>S in the [2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>] ionic liquids was determined in the 298.15 K to 318.15 K temperature range and at about 101.3 kPa, as presented in Table 2.

The results of Table 2 show that the solubilities for H<sub>2</sub>S increases in the order [2-HEA][Ace] < [B-2-HEA][Ace] < [2-HEDEA][H(Ace)<sub>2</sub>]. The behavior of the H<sub>2</sub>S solubilities in ammonium-based ILs shows that the solubilities increase with the free volume of the ILs cation, which indicates that the physical interactions H<sub>2</sub>S/IL appears to play the most significant role in determining the gas solubilities for H<sub>2</sub>S in the ILs reported in this paper.

To represent the temperature dependence of the mole fraction solubilities, Eq. (6), was fitted to the  $x_2$  values of H<sub>2</sub>S in [2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>]. The optimized parameters of Eq. (6), in the temperature range [298, 318] K and at 0.1 MPa, are listed in Table 3 alongside with the absolute average deviations (*AAD*) for  $x_2$ .

From Eqs. (7) and (8), negative values of  $\Delta\bar{h}_2$  and  $\Delta\bar{s}_2$  were obtained for all the systems, indicating that the solubility decreases with the increase of the temperature. This was expected due to the high solubility observed for the H<sub>2</sub>S in the ILs studied

**Table 2**

Experimental mole fraction solubilities,  $x_2$ , and mole fraction based Henry's constants,  $H_{2,1}^{sp}$ , for  $H_2S$  in [2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>] as a function of temperature,  $T$ , and total pressure,  $p$ , assumed to be the  $H_2S$  partial pressure due to low saturated vapor pressure of the ILs.

Solvent	$T$ /K	$p$ /kPa	$x_2$	$H_{2,1}^{sp}$ /MPa
[2-HEA][Ace]	298.15	102.36	0.092	1.115
	303.15	101.49	0.087	1.171
	308.15	101.69	0.083	1.228
	313.15	102.14	0.076	1.338
	318.15	102.37	0.068	1.498
[B-2-HEA][Ace]	298.15	101.19	0.122	0.829
	303.15	101.46	0.119	0.853
	308.15	102.03	0.108	0.949
	313.15	101.59	0.101	1.003
	318.15	100.90	0.093	1.087
[2-HEDEA][H(Ace) <sub>2</sub> ]	298.15	101.48	0.202	0.504
	303.15	101.19	0.194	0.521
	308.15	101.37	0.187	0.543
	313.15	102.10	0.172	0.595
	318.15	101.31	0.164	0.618

The standard uncertainties are:  $u(T) = 0.01$  K,  $u(p) = 0.010$  kPa,  $u(x_2) = 0.01$ ,  $u(H_{2,1}^{sp}) = 0.01$ .

**Table 3**

Parameters in the equation,  $R \ln(x_2) = A + B/T$ .

System	$A$ /J mol <sup>-1</sup> K <sup>-1</sup>	$B$ /J mol <sup>-1</sup>	$10^2 \cdot AAD(x_2)^1$	
$H_2S$	[2-HEA][Ace]	-57.62	11,301	1.7
	[B-2-HEA][Ace]	-54.90	11,519	1.5
	[2-HEDEA][H(Ace) <sub>2</sub> ]	-41.48	8428	1.2

$$^1 AAD(x_2) = (1/N_p) \sum_{i=1}^{N_p} |x_{cal,i} - x_{exp,i}| / (x_{exp,i}).$$

here, since for gases with larger solubilities the partial molar enthalpy of mixing (positive) tends to be smaller than the enthalpy of condensation (negative) resulting in an overall partial molar change in enthalpy that is negative. Similarly, the solute partial molar entropy of mixing ( $-R \ln(x_2)$ , assuming ideal behavior) will be smaller than the entropy of condensation for higher values of  $x_2$ . Consequently, the experimental observations agree with thermodynamic predictions and are also consistent with results verified previously by other authors [35].

#### 4.2. CPA EoS model

To model the solubility results, the 4C association scheme, as defined by Huang and Radosz [36,37], for the  $H_2S$  was adopted. This association scheme considers the geometry of the molecule with two-sites on the sulfur atom and one additional site on each hydrogen atom is proposed. For the ILs studied in this work was adopted the two-site (2B) scheme, one-site corresponding to the

**Table 4**

Absolute average deviations of vapor pressures,  $P^\sigma$ , molar densities,  $\rho_{liq}$ , and CPA EoS components' molecular parameters,  $a_0$ ,  $c_1$ ,  $b$ ,  $\epsilon$  and  $\beta$ .

	$a_0$ /Pa m <sup>6</sup> mol <sup>2</sup>	$c_1$	105b/m <sup>3</sup> mol <sup>-1</sup>	$10^{-4} \epsilon$ /Jmol <sup>-1</sup>	$10^4 \beta$	$10^2 CE(x)^1 P^\sigma \rho_{liq}$
[2-HEA][Ace]						
Association scheme 2B	2.73	1.94	10.03	3.597	17.43	0.2
[B-2-HEA][Ace]						
Association scheme 2B	4.09	1.73	13.59	1.750	649.0	0.7
[2-HEDEA][H(Ace) <sub>2</sub> ]						
Association scheme 2B	5.80	1.80	19.95	1.615	211.0	0.2
$H_2S$						
Association scheme 4C	0.40	0.54	2.95	0.3726	474.5	0.1

$$^1 AAD(x) = (1/N_p) \sum_{i=1}^{N_p} |x_{cal,i} - x_{exp,i}| / (x_{exp,i}) \text{ with } x_i \text{ either } P^\sigma \text{ or } \rho_{liq}.$$

**Table 5**

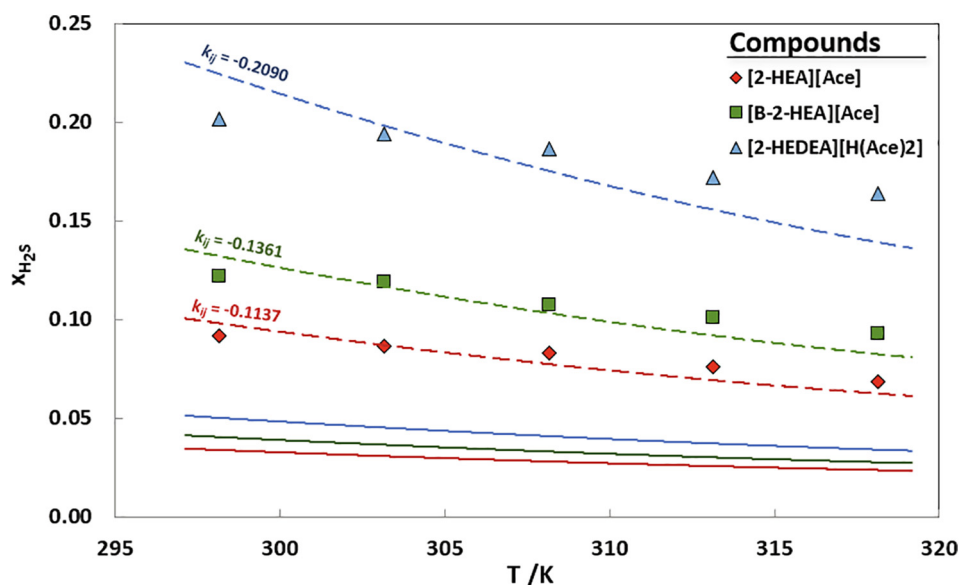
Absolute Average Deviations (AAD) of solubilities of  $H_2S$  in [2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>] ILs obtained from CPA and respective  $k_{ij}$  values, considering four-sites (4C) and two-sites (2B) association schemes for  $H_2S$  and ILs, respectively.

System	$k_{ij}$	$10^2 AAD(x)^1$
$H_2S$ /([2-HEA][Ace])	0	65.1
	-0.1137	6.5
$H_2S$ /[B-2-HEA][Ace]	0	69.2
	-0.1361	6.9
$H_2S$ /([2-HEA][H(Ace) <sub>2</sub> ])	0	77.5
	-0.2090	8.9

$$^1 AAD(x) = (1/N_p) \sum_{i=1}^{N_p} |x_{cal,i} - x_{exp,i}| / (x_{exp,i}).$$

positive charge in cation and the other site in the negative charge of the anion. The molecular parameters for the  $H_2S$  were adopted from the work of Panah [38]. To calculate the pure component parameters for [2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>] the liquid density data for these ILs were obtained in the literature [29,39] and the critical properties, acentric factors and boiling temperature were obtained from Valderrama et al., estimated applying the modified Lydersen-Joback-Reid method [40,41]. For these two ILs studied, vapor pressure experimental data ( $P^\sigma$ ) is unavailable and therefore it was assumed that at the reduced temperature range between 0.40 and 0.70, used to estimate the parameters,  $P^\sigma$  could be described by:  $\ln(P^\sigma/Pa) = A - B/(T/K)$ ; where parameters  $A$  and  $B$  were regressed considering  $P^\sigma = 10^{-6}$  Pa at 273.15 K and  $P^\sigma = 10^5$  Pa at boiling temperature [42]. This qualitative correlation was used to generate vapor pressure data for fitting the CPA EoS molecular parameters. The pure compounds molecular parameters, are reported in Table 4, along with the absolute average deviations (AAD) calculated for molar densities,  $\rho_{liq}$ , and estimated vapor pressure  $P^\sigma$ , after minimization of Eq. (13). Since there is a much larger uncertainty in vapor pressures than in liquid densities, it was used a weighting factor to consider the best description of liquid densities, while still providing a qualitative description the IL known negligible volatility character. Therefore, the pressure weight factor in Eq. (13), was 0.1 while that for density 0.9.

Prediction of the  $H_2S$  solubilities in the ILs ([2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>]) was carried out using the estimated pure component molecular parameters in the CPA EoS, with the binary interaction parameters  $k_{ij} = 0$  (prediction), considering the schemes 2B (two-association sites) for the ILs and four-sites (4C) association scheme for the  $H_2S$ . Furthermore, aiming an enhanced description of the systems phase diagrams a temperature independent binary interaction parameter,  $k_{ij}$ , was adjusted, allowing %AAD of 6.5, 6.9 and 8.9 for the  $H_2S$ /[2-HEA][Ace],  $H_2S$ /[B-2-HEA][Ace] and  $H_2S$ /[2-HEDEA][H(Ace)<sub>2</sub>], respectively. The  $k_{ij}$  values and global average deviations for the solubility values are presented in Table 5.



**Fig. 1.**  $pTx$  phase diagrams for the binary systems  $H_2S$  + [2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>], at 0.1 MPa. The solid and dashed lines represent the CPA EoS prediction ( $k_{ij} = 0$ ) and fit to the experimental data, respectively.

Fig. 1 shows that the CPA EoS (prediction with  $k_{ij} = 0$ ) with the scheme 2B for [2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>] and the scheme 4C for  $H_2S$  describes in the correct order the  $H_2S$  solubilities in these ionic liquids.

## 5. Conclusions

The solubility of  $H_2S$  in three ammonium-based IL solvents ([2-HEA][Ace], [B-2-HEA][Ace] and [2-HEDEA][H(Ace)<sub>2</sub>]) have been determined in the temperature range between 298 K and 318 K at about 1 atm. It was found that among the solvents, the solubilities of  $H_2S$  increases in the following order: [2-HEA][Ace] < [B-2-HEA][Ace] < [2-HEDEA][H(Ace)<sub>2</sub>]. The behavior of the  $H_2S$  solubilities in ammonium-based ILs show that the solubilities increase with the free volume of the ILs cation, which indicates that the physical interactions are the main factor in the solubility of  $H_2S$  in the ILs reported in this paper.

The CPA EoS was applied in the description of the experimental solubilities of the  $H_2S$ /[2-HEA][Ace],  $H_2S$ /[B-2-HEA][Ace] and  $H_2S$ /[2-HEDEA][H(Ace)<sub>2</sub>] systems. According to the results, CPA EoS was able to predict (with  $k_{ij} = 0$ ) in a qualitative way the solubilities between  $H_2S$ -IL systems; and show the expected order. Also the CPA EoS model allows a satisfactory description of the solubilities through the ranges of temperature and pressure selected in this work with low average deviations. A temperature independent binary interaction parameter (in the physical term) fitted to the experimental data is enough to describe the systems  $H_2S$ /[2-HEA][Ace],  $H_2S$ /[B-2-HEA][Ace] and  $H_2S$ /[2-HEDEA][H(Ace)<sub>2</sub>].

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jct.2020.106336>.

## References

- [1] H. Sakhaeina, A.H. Jalili, V. Taghikhani, A.A. Safekordi, Solubility of  $H_2S$  in ionic liquids 1-ethyl-3-methylimidazolium hexafluorophosphate ([emim][PF<sub>6</sub>]) and 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide ([emim][Tf<sub>2</sub>N]), J. Chem. Eng. Data 55 (2010) 5839–5845.
- [2] F.S. Liu, Z. Li, S.T. Yu, X. Cui, X.P. Ge, Environmentally benign methanolysis of polycarbonate to recover bisphenol A and dimethyl carbonate in ionic liquids, J. Hazard. Mater. 174 (2010) 872–875.
- [3] J.L. Anderson, J.K. Dixon, J.F. Brennecke, Solubility of  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $O_2$ , and  $N_2$  in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: comparison to other ionic liquids, Acc. Chem. Res. 40 (2007) 1208–1216.
- [4] M.T. Mota-Martinez, P. Brandl, J.P. Hallett, N. Mac Dowell, Challenges and opportunities for the utilisation of ionic liquids as solvents for  $CO_2$  capture, Mol. Syst. Des. Eng. 3 (2018) 560–571.
- [5] J. Leclaire, D.J. Heldebrant, A call to (green) arms: a rallying cry for green chemistry and engineering for  $CO_2$  capture, utilisation and storage, Green Chem. 20 (2018) 5058–5081.
- [6] J.D. Holbrey, K.R. Seddon, Ionic liquids, Clean Prod. Process. 1 (1999) 223–236.
- [7] G. Cui, J. Wang, S. Ahang, Active chemisorption sites in functionalized ionic liquids for carbon capture, Chem. Soc. Rev. 45 (2016) 4307–4339.
- [8] F.Y. Jou, A.E. Mather, Solubility of hydrogen sulfide in [bmim][PF<sub>6</sub>], Int. J. Thermophys. 28 (2007) 490–495.
- [9] C.S. Pomelli, C. Chiappe, A. Vidis, G. Laurency, P.J. Dyson, Influence of the interaction between hydrogen sulfide and ionic liquids on solubility: experimental and theoretical investigation, J. Phys. Chem. B 111 (2007) 13014–13019.
- [10] M.B. Shiflett, A.M.S. Niehaus, A. Yokozeki, Separation of  $CO_2$  and  $H_2S$  using room temperature ionic liquid [bmim][MeSO<sub>4</sub>], J. Chem. Eng. Data 55 (2010) 4785–4793.
- [11] A.H. Jalili, M. Rahmati-Rostami, C. Ghotbi, M. Hosseini-Jenab, A.N. Ahmadi, Solubility of  $H_2S$  in ionic liquids [bmim][PF<sub>6</sub>], [bmim][BF<sub>4</sub>], and [bmim][Tf<sub>2</sub>N], J. Chem. Eng. Data 54 (2009) 1844–1849.
- [12] A.H. Jalili, A. Mehdizadeh, M. Shokouhi, H. Sakhaeina, V. Taghikhani, Solubility of  $CO_2$  in 1-(2-hydroxyethyl)-3-methylimidazolium ionic liquids with different anions, J. Chem. Thermodyn. 42 (2010) 787–791.
- [13] A.H. Jalili, A. Mehdizadeh, M. Shokouhi, A.N. Ahmadi, M. Hosseini-Jenab, F. Fateminassab, Solubility and diffusion of  $CO_2$  and  $H_2S$  in the ionic liquid 1-

- ethyl- 3-methylimidazolium ethylsulfate, *J. Chem. Thermodyn.* 42 (2010) 1298–1303.
- [14] H. Sakhaeinia, V. Taghikhani, A.H. Jalili, A. Mehdizadeh, A.A. Safekordi, Solubility of H<sub>2</sub>S in 1-(2-hydroxyethyl)-3-methylimidazolium ionic liquids with different anions, *Fluid Phase Equilib.* 298 (2010) 303–309.
- [15] M. Shokouhi, M. Adibi, A.H. Jalili, M. Hosseini-Jenab, A. Mehdizadeh, Solubility and diffusion of H<sub>2</sub>S and CO<sub>2</sub> in the ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, *J. Chem. Eng. Data* 55 (2010) 1663–1668.
- [16] A.H. Jalili, M. Safavi, C. Ghotbi, A. Mehdizadeh, M. Hosseini-Jenab, V. Taghikhani, Solubility of CO<sub>2</sub>, H<sub>2</sub>S, and their mixture in the ionic liquid 1-octyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide, *J. Phys. Chem. B* 116 (2012) 2758–2774.
- [17] M. Safavi, C. Ghotbi, V. Taghikhani, A.H. Jalili, A. Mehdizadeh, Study of the solubility of CO<sub>2</sub>, H<sub>2</sub>S and their mixture in the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate: experimental and modelling, *J. Chem. Thermodyn.* 65 (2013) 220–232.
- [18] A.H. Jalili, M. Shokouhi, G. Maurer, M. Hosseini-Jenab, Solubility of CO<sub>2</sub> and H<sub>2</sub>S in the ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, *J. Chem. Thermodyn.* 67 (2013) 55–62.
- [19] M. Nematpour, A.H. Jalili, C. Ghotbi, D. Rashtchian, Solubility of CO<sub>2</sub> and H<sub>2</sub>S in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, *J. Nat. Gas Sci. Eng.* 30 (2016) 583–591.
- [20] Z.-Z. Yang, Y.-N. Zhao, L.-N. He, CO<sub>2</sub> chemistry: task-specific ionic liquids for CO<sub>2</sub> capture/activation and subsequent conversion, *RSC Adv.* 1 (2011) 545–567.
- [21] M.L. Alcântara, M.L. Carvalho, V.H. Alvarez, P.I.S. Ferreira, M.L.L. Paredes, L. Cardozo-Filho, A.K. Silva, L.M. Lião, C.A.M. Pires, S. Mattedi, High pressure vapor-liquid equilibria for binary carbon dioxide and protic ionic liquid based on ethanalamines + butanoic acid, *Fluid Phase Equilib.* 460 (2018) 162–174.
- [22] R. Vijayaraghavan, T. Oncsik, B. Mitschke, D.R. MacFarlane, Base-rich diamino protic ionic liquid mixtures for enhanced CO<sub>2</sub> capture, *Sep. Purif. Technol.* 196 (2018) 27–31.
- [23] A.I. Akhmetshina, A.N. Petukhov, O.R. Gumerova, A.V. Vorotyntsev, A.V. Nyuchev, I.V. Vorotyntsev, Solubility of H<sub>2</sub>S and CO<sub>2</sub> in imidazolium-based ionic liquids with bis(2-ethylhexyl) sulfosuccinate anion, *J. Chem. Thermodyn.* 130 (2019) 173–182.
- [24] I.M.A. Fonseca, J.P.B. Almeida, H.C. Fachada, Automated apparatus for gas solubility measurement, *J. Chem. Thermodyn.* 39 (2007) 1407–1411.
- [25] J.M.M.V. Sousa, J.F.O. Granjo, A.J. Queimada, A.G.M. Ferreira, N.M.C. Oliveira, I. M.A. Fonseca, Solubility of hydrofluorocarbons in ionic liquids: experimental and modelling study, *J. Chem. Thermodyn.* 73 (2014) 36–43.
- [26] J.M.M.V. Sousa, J.F.O. Granjo, A.J. Queimada, A.G.M. Ferreira, N.M.C. Oliveira, I. M.A. Fonseca, Solubility of hydrofluorocarbons in phosphonium-based ionic liquids: experimental and modelling study, *J. Chem. Thermodyn.* 79 (2014) 184–191.
- [27] S. Sobhani, M. Honarmand, 2-Hydroxyethylammonium acetate: a reusable task-specific ionic liquid promoting one-pot, three-component synthesis of 2-amino-3, 5-dicarbonitrile-6-thio-pyridines, *C. R. Chimie* 16 (2013) 279–286.
- [28] A. Pinkert, K.L. Ang, Ken Marsh, S. Pang, Density, viscosity and electrical conductivity of protic alkanolammonium ionic liquids, *Phys. Chem. Chem. Phys.* 13 (2011) 5136–5143.
- [29] M.A.R. Martins, G. Sharma, S.P. Pinho, R.L. Gardas, J.A.P. Coutinho, P.J. Carvalho, Selection and characterization of non-ideal ionic liquids mixtures to be used in CO<sub>2</sub> capture, *Fluid Phase Equilib.* 518 (2020) 112621.
- [30] , *Virial Coefficients of Pure Gases*, Landolt-Börnstein – Group IV Physical Chemistry vol. 21A (2002) 83–109.
- [31] G.M. Kontogeorgis, E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, An equation of state for associating fluids, *Ind. Eng. Chem. Res.* 35 (1996) 4310–4318.
- [32] G.M. Kontogeorgis, I.V. Yakoumis, H. Meijer, E. Hendriks, T. Moorwood, Multicomponent phase equilibrium calculations for water-methanol-alkane mixtures, *Fluid Phase Equilib.* 158–160 (1999) 201–209.
- [33] G.M. Kontogeorgis, M.L. Michelsen, G.K. Folas, S. Derawi, N. Von Solms, E.H. Stenby, Ten years with the CPA (Cubic-Plus-Association) equation of state. Part 1. Pure compounds and self-associating systems, *Ind. Eng. Chem. Res.* 45 (2006) 4855–4868.
- [34] G.K. Folas, J. Gabrielsen, M.L. Michelsen, E.H. Stenby, G.M. Kontogeorgis, Application of the Cubic-Plus-Association (CPA) equation of state to cross-associating systems, *Ind. Eng. Chem. Res.* 44 (2005) 3823–3833.
- [35] A. Finotello, J.E. Bara, D. Camper, R.D. Noble, Room-temperature ionic liquids: temperature dependence of gas solubility selectivity, *Ind. Eng. Chem. Res.* 47 (2008) 3453–3459.
- [36] L. Ruffine, P. Mougou, A. Barreau, How to represent hydrogen sulfide within the CPA equation of state, *Ind. Eng. Chem. Res.* 45 (2006) 7688–7699.
- [37] S.H. Huang, M. Radosz, Equation of state for small, large, polydisperse, and associating molecules, *Ind. Eng. Chem. Res.* 29 (1990) 2284–2294.
- [38] H.S. Panah, Modeling H<sub>2</sub>S and CO<sub>2</sub> solubility in ionic liquids using the CPA equation of state through a new approach, *Fluid Phase Equilib.* 437 (2017) 155–165.
- [39] K.A. Kurnia, C.D. Wilfred, T. Murugesan, Thermophysical properties of hydroxyl ammonium ionic liquids, *J. Chem. Thermodyn.* 41 (2009) 517–521.
- [40] J.O. Valderrama, P.A. Robles, Critical properties, normal boiling temperatures, and acentric factors of fifty ionic liquids, *Ind. Eng. Chem. Res.* 46 (2007) 1338–1344.
- [41] J.O. Valderrama, W.W. Sanga, J.A. Lazzús, Critical properties, normal boiling temperature, and acentric factor of another 200 ionic liquids, *Ind. Eng. Chem. Res.* 47 (2008) 1318–1330.
- [42] M.S. Manic, A.J. Queimada, E.A. Macedo, V. Najdanovic-Visak, High-pressure solubilities of carbon dioxide in ionic liquids based on bis (trifluoromethylsulfonyl)imide and chloride, *J. Supercrit. Fluids* 65 (2012) 1–10.