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Experimental investigation of hydrogen sulfide solubility in aqueous sulfolane solution

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ABSTRACT

New experimental data are presented for the solubility of hydrogen sulfide in aqueous sulfolane solution which is an important topic in many areas of chemical engineering. Solvent mixtures of (SFL + H_2O) contain the composition range from $x_{SFL} = 0.0113$ to $x_{SFL} = 0.939$, temperatures from (303.15 to 353.15) K with step 10 K and total pressures up to 2.0 MPa. Henry's constant of H_2S in pure SFL, pure H_2O and mixed (SFL + H_2O) are reported on the mole fraction and molality base. Model for the Gibbs excess energy of mixed solvent is used to correlate the obtained experimental data.

1. Introduction

Physical solvents have been the subject of extensive experimental, applied and scientific research studies during the last 50 years. They are less corrosive than chemical solvents because no chemical reaction occurs between the acid gases and these solvents and they are usually used when the concentration of acid gas impurities in the total gas streams is high [1–5].

In ongoing researches on solubility of acid gases in physical organic solvents, in this work, solubility measurement of hydrogen sulfide in binary solutions of water and an organic solvent such as sulfolane (SFL), which is very applicable in solvent formulation in sour gas treating, are experimentally investigated. Hereby, the whole range of solvent compositions from pure water to the pure SFL is covered. The experimental results are used to determine Henry's constant for dissolution of hydrogen sulfide in those mixed solvents.

By applying a thermodynamic model that put forward for gas solubility in binary solvent systems [6], all the experimental data covering the whole compositions are correlated. This model has been successfully used for modeling of CO_2 solubility in some aqueous solution of physical organic solvents [7–13], and aqueous ionic liquid solution ([bmim][CH_3SO_4]) [14], as well as for NH_3 solubility in aqueous solution of methanol [15–17].

2. Experimental section

2.1. Materials

The specifications and sources of the chemicals used in this work are summarized in Table 1.

All the materials were reagent grade and used without further purification. All solvents were prepared by calibrated balance (Mettler model AE 200) with an uncertainty of ±0.001 g. The water content in sulfolane reported by supplier is lower than 0.2 mass%, and this is verified by using Karl Fischer Titration analysis (Metrohm 870 KF). The water sample was prepared using ion exchange processes, then for further purification followed by feeding through an integrated vented storage reservoir (Millipore S.A.S., 67120 Molsheim, France). The total dissolved substance (TDS) has been measured by conductivity method <10 ppm (Mettler Toledo).

2.2. Apparatus and procedure

The details of the experimental method for the measurement of gas solubility have previously been presented [18] and only a short description will be provided here.

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Nomenclature

NIST	National Institute of Standards and Technology
SRK EoS	Soave-Redlich–Kwong equation of state
R	universal gas constant
V_{gc}	volume of the gas container (or gas sample)
V_{g}	gas-phase volume in the equilibrium cell
V_{auto}	volume of the autoclave (equilibrium cell)
Z_{i} and Z_{f}	compressibility factors of the initial and final state in the gas container
T_{a}	ambient temperature
P_0	initial pressure of solution
P_{t}	total absolute pressure
P_{VP} or P^s	vapour pressure of pure solvent
$P_{\mathrm{H_2S}}$	partial pressure of H_2S at equilibrium state
$P^{\mathrm{e}}_{\mathrm{ag}}$	partial pressure of acid gas at equilibrium state
$n^{\mathrm{g}}_{\mathrm{ag}}$	amount of acid gas in the gas phase at equilibrium state
$n^{\mathrm{l}}_{\mathrm{ag}}$	amount of acid gas in the liquid phase at equilibrium state
n_{ag}	total number of moles of acid gas injected to equilibrium cell
M^*_s	molar mass of mixed solvent
$u(n_i)$	standard uncertainty of amount of species *i*
m_j	molality of component *j* ($\mathrm{mol \cdot kg^{-1}}$)
w_{Solvent}	mass of solvent charged into cell in g
ρ_{ag}	density of acid gas in gas phase at equilibrium state
ρ	density of charged solution ($\mathrm{g/cm^3}$)
x_{H2S}	mole fraction of loaded gas
$\tilde{x}_{\mathrm{s}}$	mole fraction of solvent constituent in gas-free liquid mixture
T_{c}	the critical temperature
P_{c}	the critical pressure
$h^{(0)}_{\mathrm{H},x}$	the Henry's law constant on mole fraction base
$h^{(0)}_{\mathrm{H},m}$	the Henry's law constant on molality base
$f_{\mathrm{H_2S}}(T,p)$	fugacity of H_2S in gas phase
γ	the activity coefficient
$V^{\infty}_{\mathrm{H_2S}}$	molar volume of dissolved gas at infinite dilution

The double wall equilibrium cell was connected to a water recirculation bath (model T 2500 PMT Tamson) with temperature stability within ±0.02 K and the temperature was measured using a model TM-917 Lutron digital thermometer with a 0.01 K resolution equipped with a Pt-100 sensor inserted into the cell. The equilibrium cell pressure was measured using a model PA-33X KELLER pressure transmitter sensor in the range of (0–25) bar, which was accurate to within 0.1% of full scale, and that of the gas container was measured using a Baroli type BD SENSORS digital pressure gauge in the range of (0–25) bar, which was accurate to within 0.1% of full scale.

One can calculate the total number of moles of acid gas injected into the equilibrium cell using the procedure adopted by Park and Sandall [19] and Hosseini-Jenab et al. [18]:

$$n_{\mathrm{ag}} = \frac{V_{\mathrm{gc}}}{RT_{\mathrm{a}}}\left(\frac{P_{\mathrm{i}}}{Z_{\mathrm{i}}} - \frac{P_{\mathrm{f}}}{Z_{\mathrm{f}}}\right) = (\rho_{\mathrm{i}} - \rho_{\mathrm{f}}) \cdot V_{\mathrm{gc}} \tag{1}$$

where V_{gc} denotes the volume of the gas container, Z_{i}, Z_{f} and ρ_{i}, ρ_{f} are the compressibility factors and molar density corresponding to the initial and final pressures, P_{i} and P_{f}, respectively, in the gas container before and after transferring gas, and T_{a} is the ambient temperature, which is equal to that in the gas container. Compressibility factors were calculated using NIST Scientific and Technical Databases [20]. Equilibration between liquid and vapour phases inside the cell were normally achieved within about 2 h after beginning of stirring and the partial pressure of gas at equilibrium in the equilibrium cell, $P^{\mathrm{e}}_{\mathrm{ag}}$, was calculated as follow:

$$P^{\mathrm{e}}_{\mathrm{ag}} = P_{\mathrm{t}} - P_{\mathrm{VP}} \tag{2}$$

where P_{t} and P_{VP} denote the total pressure and vapour pressure of solution. A key issue is the determination of the vapour pressure of the mixture solution since this value must be subtracted from the total pressure to obtain the partial acid gas pressure.

The moles of remaining acid gas in the gas phase, $n^{\mathrm{g}}_{\mathrm{ag}}$, was determined from:

$$n^{\mathrm{g}}_{\mathrm{ag}} = \frac{V_{\mathrm{g}} P^{\mathrm{e}}_{\mathrm{ag}}}{Z_{\mathrm{ag}} RT} = V_{\mathrm{g}} \cdot \rho_{\mathrm{ag}} = (V_{\mathrm{EC}} - V_{\mathrm{Liquid}}) \cdot \rho_{\mathrm{ag}} \tag{3}$$

where V_{g}, V_{EC} and V_{Liquid} are respectively the volume of gas phase, equilibrium cell and liquid phase, T is the equilibrium temperature of the cell, R is the universal gas constant and Z_{ag} and ρ_{ag} are the compressibility factor and density of acid gas at $P^{\mathrm{e}}_{\mathrm{ag}}$ and T in the gas phase, respectively.

The volume of the liquid phase, V_{Liquid}, can be calculated from the mass and density at equilibrium condition for each solution, however, this value needs to be corrected due to the dissolution of gas into the solution [21–23]:

$$V_{\mathrm{Liquid}} = V_{\mathrm{Solution}} + n^{\mathrm{l}}_{\mathrm{ag}} \cdot V^{\infty}_{\mathrm{ag}} \tag{4}$$

V_{Solution} is the volume of gas free (SFL + H_2O) solution, $n^{\mathrm{l}}_{\mathrm{ag}}$ is number of moles of acid gas in liquid phase and V^{∞}_{ag} is partial molar volume of acid gas in infinite solution.

The number of moles of gas in the liquid phase was determined from:

$$n^{\mathrm{l}}_{\mathrm{ag}} = n_{\mathrm{ag}} - n^{\mathrm{g}}_{\mathrm{ag}} \tag{5}$$

Combining Eqs. (1), (3), (4) and (5), the quantity of acid gas absorbed in liquid phase is given as follows:

$$n^{\mathrm{l}}_{\mathrm{ag}} = \frac{(\rho_{\mathrm{i}} - \rho_{\mathrm{f}}) \cdot V_{\mathrm{gc}} - (V_{\mathrm{EC}} - V_{\mathrm{Solution}}) \cdot \rho_{\mathrm{ag}}}{1 + V^{\infty}_{\mathrm{ag}} \cdot \rho_{\mathrm{ag}}} \tag{6}$$

Table 1
Specifications and sources of chemicals used in this work.

Chemical name	Molecular formula/ relative molar mass	CAS registry number	Purity	Source
Hydrogen sulfide	H_2S/34.081	[7783-06-4]	99.95% (mol%)	ROHAM GAS COMPANY
Sulfolane	$C_4H_8O_2S$/120.17	[126-33-0]	99% (mass%) (contain 0.2 mass% H_2O)	SIGMA-ALDRICH
Water	H_2O/18.015	[7732-18-5]	The total dissolved substance (TDS) < 10 ppm	ION EXCHANGE RESIN (RIPI), and MILLIPORE S.A.S., 67120 MOLSHEIM, FRANCE