MEASURING VAPOR-LIQUID EQUILIBRIA IN SOUR GAS + GLYCOL AQUEOUS SOLUTION USING STATIC TECHNIQUES

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Introduction

Dehydration of natural gases is a frequently required gas processing. Dehydration is the process used to remove water from natural gases to prevent formation of gas hydrates/ice and condensation of water in production, transportation and processing facilities. In cryogenic processes, the presence of water increases manifold problems. In petrochemical industry, water in the gas streams may poison the catalysts. To remove water, glycols can be used. Ethylene glycol (EG) and triethylene glycol (TEG) are the most commonly used chemicals for natural gas dehydration. During the process of dehydration, the circulation of glycol aqueous solution allows absorbing given amounts of the acid gases, like CO_2, H_2S, and COS. The presence of these compounds can cause various operational and environmental problems. One prominent problem is corrosion in the dehydration units, especially at high temperatures of the regenerator. Accurate knowledge of phase behavior of the gaseous systems containing sulfur species in the presence of glycol aqueous solution is, therefore, necessary to avoid these problems. In this work, we present static experimental set ups based on the static-analytic and static-synthetic techniques designed to measure out the phase equilibria of acid/sour gas in EG aqueous solutions. Few recently obtained results are presented.

Experimental Methods for Phase Equilibria Studies

In static experimental methods, the phase equilibrium is achieved by a local phase agitator without circulation of any of the phases. There can be either one agitator in liquid phase or two agitators, one in each vapor and liquid phases. These methods can also include possibility of observing the system physically inside the equilibrium cell for any change and/or agitation. The agitators of various possible designs are either magnetically or mechanically coupled with an external motor. The size of equilibrium cell varies depending upon the nature of experimental study and fluids. There is a wide range of materials used for the construction of experimental setups, joints and O-rings. Where pressure is not very high (generally up to 15 MPa), use of transparent sapphire tube, held between the stainless steel or Titanium flanges is common. A sapphire window may be provided in high pressure (50 to 100 MPa) metallic cells where physical observations are necessary for experimental studies and sapphire tubes cannot be used because of pressure limitations and safety considerations. Ultra higher pressure cell requires other means of observations of the cell contents.

In analytic methods, phase sampling is required for compositional analysis of the phase(s). A reliable sampling and analysis technique determines the reliability and consistency of the results.

While in synthetic methods, compositions of the fluid mixture are known from prior knowledge of quantities loaded inside the equilibrium cell. Usually, mixtures are prepared gravimetrically.

Experimental Section

In this work, all phase equilibria measurements were carried out using static techniques.

Purities and Suppliers of Chemicals

EG from Sigma-Aldrich with certified purity of 99% was used without any further treatment. All gases were provided by Air-Liquide with purity of 99.9%. De-ionized, double distilled, ultra pure water was prepared by using commercial equipment (Millipore, model: direct Q5). All the solutions were gravimetrically made under vacuum after degasification.

Measuring gas solubility in EG aqueous solutions using static-analytic method

The experimental setup is explained elsewhere (Laugier and Richon, 1986). The equilibrium cell is shown in Figure 1. Briefly, the cell was made with a sapphire tube which is held between two stainless steel flanges with suitable O-rings for preventing leakages. Each flange contains point valves, for loading and cleaning the cell. The lower flange holds magnetic stirrer, protected with a Titanium (TA6V) cover to withstand corrosive environment without difficulty. External motor is capable of producing desired level of agitation in the cell. Two 100 Ω platinum resistance thermometer sensors (Pt-100) are used to measure equilibrium temperatures at lower and upper parts of the cell. The temperature measurements at two locations enable to monitor temperature gradients in the cell. The temperature sensors were calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY precision instruments). The resulting uncertainty in temperature measurements is estimated within ± 0.02 K with a second order polynomial calibration equation. The equilibrium pressures are measured by means of two Druck pressure transducers; one for low pressures (up to 2.5 MPa) and other for high pressures (up to 10 MPa). Both pressure transducers are maintained at constant temperature (higher than the maximum temperature of the study) by means of air-thermostat, which is controlled by a PID regulator (WEST instrument, model 6100). The pressure transducers were calibrated against a dead-weight pressure balance (Desgranges & Huot 5202S, CP 0.3-40 MPa, Aubervilliers, France). The pressure measurement uncertainties are estimated to be within ± 5 kPa with a second order polynomial calibration equation.

The sampling was carried out for each phase using an electromagnetic online micro sampler, ROLSI™ developed in our research group, with movable sampling position, shown in Figure 2. The details of the sampling device can be found elsewhere (Guilbot et al. 2000). Over the years, many modifications have been done in the original device. The major differences from the latest model used in this study and the one reported by Guilbot et al. (2000) include the improvements in material of construction for making it suitable for corrosive systems, a mobile capillary coupled with an external position controller to move sampling point anywhere on the vertical axis of the capillary to position it in either phases, less variation in size of each sample for analyzing as many samples as one wants, operation by electromagnetic means rather than pneumatic means, more robustness and increased operational life. Certain optional features of the sampler enable it to extend its applicability for corrosive and viscous systems. The micro sampler is a compact device without any dead volume which consists of a capillary with internal diameter less than 0.02 mm, movable in upward and downward directions, by using the joy stick type position controller without introducing any leakage within working range of the experimental set up.

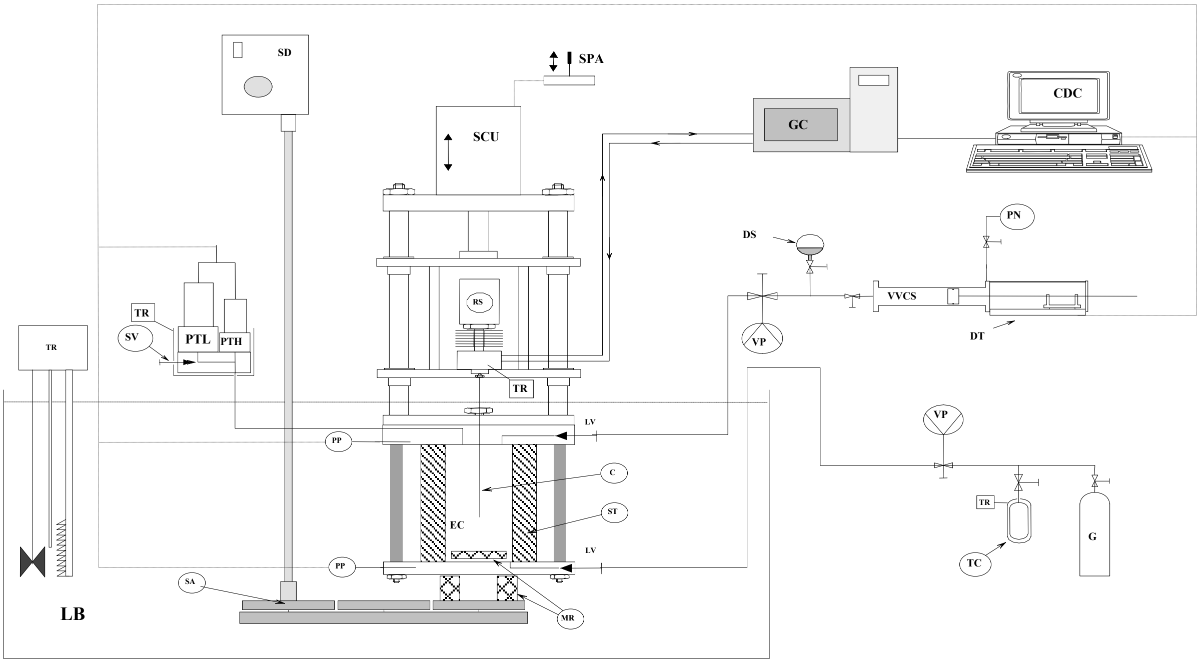

Figure 1. Flow diagram of the static-analytic apparatus.

Descriptions:- C: Capillary; CDC: Central Desktop Computer; DS: Degassed Solution; DT: Displacement Transducer; EC: Equilibrium Cell; G: Gas Cylinder; GC: Gas Chromatograph; LB: Liquid Bath; LV: Loading Valve; MR: Magnetic Rod; PN: Pressurized Nitrogen; PP: Platinum Probe (temperature sensor); PT: Pressure Transducer (H: High; L: Low); RS: ROLSI™ Sampler; SCU: Sampler Control Unit; SA: Stirring Assembly; SD: Stirring Device; SPA: Sampler Position Adjustment (joy stick); ST : Sapphire Tube; SV: Separating Valve; TC: Temperature Controller; TR: Thermal Regulator; VP: Vacuum Pump; VVCS: Variable Volume Cell for Solution.

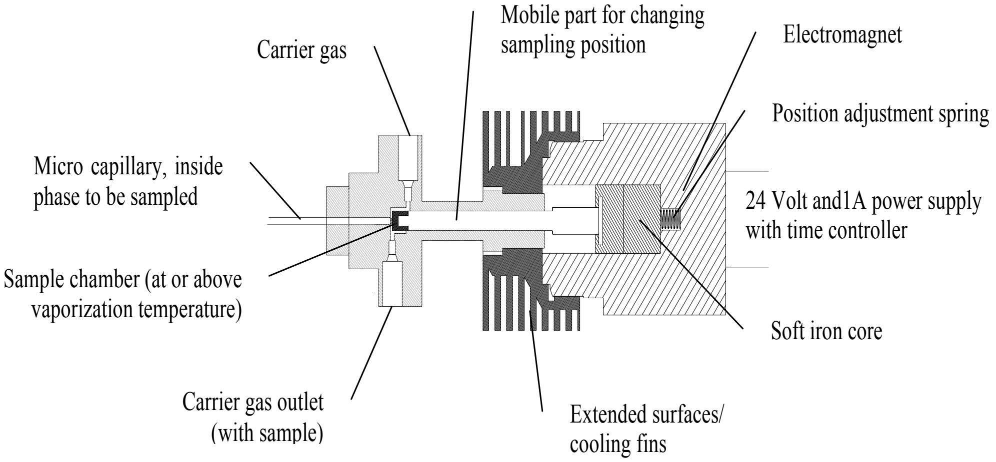

Figure 2. Flow diagram and parts of the movable position online sampler (ROLSI™).

The capillary of the sampler is connected to sample chamber through an aperture. The sample chamber is connected with a gas chromatograph (GC) through sample transfer lines. A gas chromatograph GC (Varian model CP-3800) was chosen for online phase analysis. Helium was chosen as a carrier gas. To obtain a maximum sensitivity of the detector (thin peaks), the carrier gas flow rate was adjusted. Because of the suitability, the Thermal Conductivity Detector (TCD) was used for analysis. The TCD continuously measures the difference of the thermal conductivity of the carrier gas in analytical column (containing the sample) and the reference flow.

For calibration of TCD, the compounds were simply injected in the chromatograph via the GC injector with appropriate syringes. Calibration curves for different compounds were then obtained, i.e., a relationship between the response of the detector in terms of peak area and moles of injected quantity for gas and water. Comparison between injected quantities and calculated quantities (after adjustment of the parameters of polynomial expressions) allows estimating the calibration uncertainty. Experimental uncertainties on mole numbers of each compound are estimated to be within ± 2.5% for water and ± 1.5% for the gases. It was assumed that the concentration of glycol remains constant.

The equilibrium cell and its loading lines were evacuated prior to the introduction of fluids. After introducing degassed liquid, the cell was pressurized with the gas (nitrous oxide or hydrogen sulfide) to a pressure level corresponding to the pressure of the each measurement. Strong agitation was achieved by stirring mechanism; the temperature of the cell was adjusted from liquid bath in which cell was lowered and waited for pressure stability. When both temperature and pressure were stable, sampling was stated. Only aqueous phase was analyzed to measure solubility. For each equilibrium condition, at least 7 samples of aqueous phase were withdrawn using the online micro sampler and analyzed to check for measurement repeatability.

Measuring gas solubility in EG aqueous solutions using static-synthetic method

The schematic diagram of the static-synthetic apparatus with constant volume cell consists of sapphire tube is illustrated in Figure 3. The cell, which was provided with an appropriate stirring mechanism, was immersed in a thermo-regulated constant temperature liquid bath that maintained the desired temperature. The temperature inside the cell was measured using two 100 Ω platinum resistance thermometer sensors at upper and lower flanges and connected to a data acquisition unit. Two precise pressure transducers connected to the data acquisition unit were used to measure pressures in the cell. The pressure measurement uncertainties are estimated to be within ± 5 kPa with a second order polynomial calibration equation. The data acquisition unit was connected to a central desktop computer through the appropriate interfaces. This system allowed real-time data acquisition, storage, and treatment of temperatures and pressures data throughout the experimental runs. The apparatus was coupled with a gas reserve with known pressure, temperature and volume, hence, enabling to calculate the amount of gas transferred in the equilibrium cell precisely.

In other word:

Total number of gas moles transferred into the equilibrium cell = (initial gas moles present in the gas reserve) – (final gas moles present in the gas reserve), that is:

$$n_{gas}^{T} = n_{gas}^{Ini.\mathrm{Res}.} - n_{gas}^{Fin.\mathrm{Res}.} \qquad (1)$$

where n_{gas}^{T}, represent total moles of gas transferred from the reserve into the equilibrium cell, $n_{gas}^{Ini.\mathrm{Res}}$ represents moles of gas initially present in the gas reserve and $n_{gas}^{Fin,\mathrm{Res}}$ represents moles of gas finally present in gas reserve after equilibrium cell loading. The quantity of the gas in the reserve before and after loading can be calculated using an appropriate equation of state (EoS). A suitable gas property package (ALLPROPS, HWHYD, ProSim Component Plus) can be used to calculate molar densities while precise knowledge of volumes enables to calculate the gas quantities. The volumes of gas reserve and equilibrium cell including transfer lines were carefully calibrated using standard method. The liquid solution was introduced in the equilibrium cell using a liquid variable volume cell, enabling precise volume measurement.

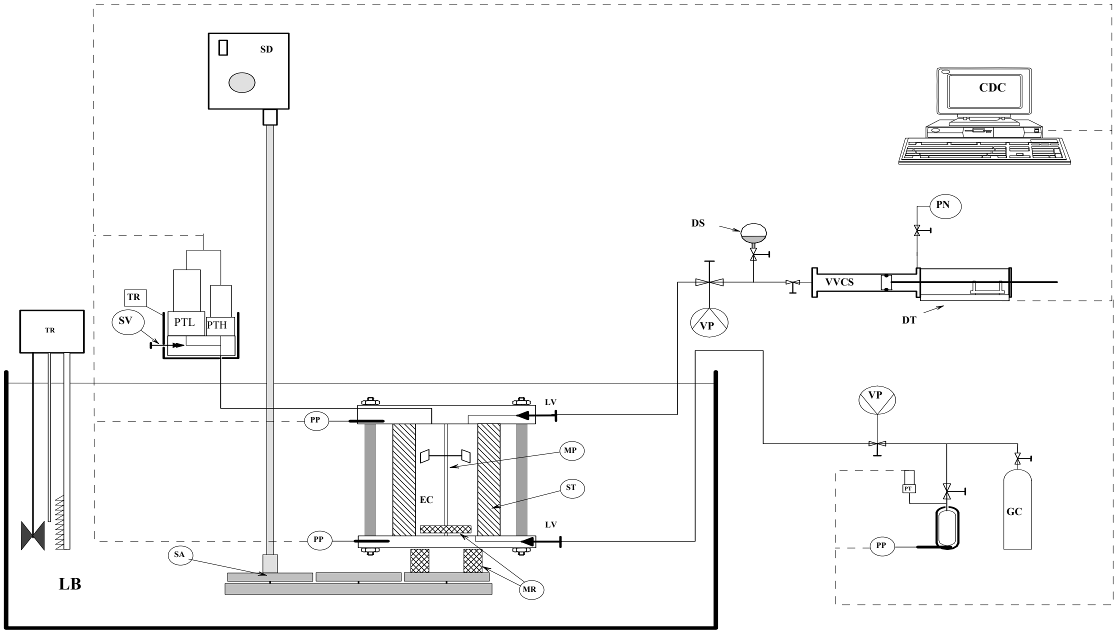

Figure 3. Flow diagram of the static-synthetic method to measure the solubility of single gas in liquids.

Descriptions:- CDC: Central Desktop Computer; DS: Degassed Solution; DT: Displacement Transducer; EC: Equilibrium Cell; GC: Gas Cylinder; LB: Liquid Bath; LV: Loading Valve; MR: Magnetic Rod; MP: Multiple Propeller; PN: Pressurized Nitrogen; PP: Platinum Probe (Temperature Sensor) ; PT: Pressure Transducer (L: Low Pressure and H: High Pressure); SA: Steering Assembly; SD: Steering Device; ST: Sapphire Tube; SV: Separation Valve; TR: Temperature Controller; VP: Vacuum Pump; VVCS: Variable Volume Cell for Solution.

The experimental volumetric properties of liquids are used in equation (3). The precise measurements of volumes of the cell and solution enabled estimation of vapor volume. Measuring equilibrium pressures at fixed temperatures enabled to calculate molar density of gas using the gas property packages as described earlier. It is assumed that liquid concentration does not change and no liquid is vaporized. This is consistent with observations while working with analytical methods.

$$n_{gas}^{L} = n_{gas}^{T} - n_{gas}^{V} \tag{2}$$

$$n_{gas}^{V} = \phi_{Solution} \times V_{Solution} \tag{3}$$

where *L* and *V* represent liquid and vapor phases, $\phi_{Solution}$ is molar density, calculated assuming ideal solution without thermal effects and $V_{Solution}$ is volume of solution entered in the solution, measured using variable volume cell. The density of mixture would be experimentally measured at the temperatures of the interest. The solubility is, therefore calculated using the following equation:

$$x_{gas} = \frac{n_{gas}^{L}}{n_{COS}^{L} + n_{EG+water}} \tag{4}$$

where x_{gas} stands for gas solubility in the liquid solution. In this way by measuring the temperature, pressure, total loadings and total volumes, we can estimate the solubility. Further details on static-synthetic method can be found elsewhere (Fischer and Wilken, 2001).

Experimental Results

H_2S Solubility in Pure Water

The first measurements were performed using static-analytic method for the (H_2S + H_2O) binary system. The data points are presented in Table 1. The data are also compared with the predictions of a comprehensive thermodynamic model, the HWHYD model, Herriot-Watt University Hydrate model (HW HYD). As can be seen, the maximum absolute deviation (*AD*) between the model predictions and experimental data is 6%. It has previously (Chapoy et al., 2005) been shown that the model is reliable within the range of data presented here for this system.

H_2S Solubility in 80 Mass% Ethylene Glycol Aqueous Solution

The experimental H_2S solubility in 80 mass% ethylene glycol aqueous solution was measured using static-analytic technique. The results are presented in Table 2. The HWHYD model has not been developed for this system.

CO_2 Solubility in 60 Mass% Ethylene Glycol Aqueous Solution

The experimental CO_2 solubility in 60 mass% ethylene glycol aqueous solutions at 0.5 MPa were measured using static-synthetic method. The results are presented in Table 3. The results are also compared with the data from Davis et al. (2002) in Figure 4. The deviations are found less than 5%. The HWHYD model has not been developed for this system.

The solubility of both the acid gases studied here decreases with increase in temperature within our study range. The results indicate that the temperature of the dehydration unit should be kept high enough to minimize the acid gas absorption in the glycol solution.

Table 1. Experimental and predicted (Using HWHYD model) solubility of H_2S in pure water (x_{H2S}).

T/K	**P/MPa**	**Experimental x_{H2S}**	**Predicted x_{H2S}**	**AD%**
293.15	0.504	0.00801	0.00823	2.7
298.25	0.52	0.00794	0.00776	2.3
303.25	0.571	0.00808	0.00783	3.1
308.15	0.597	0.00788	0.00757	3.9
318.15	0.674	0.00782	0.00736	5.9

Table 2. Experimental solubility of H_2S in 80 mass% ethylene glycol aqueous solution.

T/K	**P/MPa**	**Experimental x_{H2S}**
263.27	0.697	0.121
273.20	0.586	0.066
273.15	0.869	0.114
288.00	1.140	0.106
288.01	1.421	0.141
297.94	1.323	0.098
298.00	1.670	0.132
298.00	1.986	0.172

Table 3. Experimental solubility of CO_2 in 60 mass% ethylene glycol aqueous solution.

T/ K	**P/ MPa**	**Experimental x_{CO2}**
250.15	0.512	0.0109
273.15	0.495	0.0069
298.15	0.510	0.0039
333.15	0.502	0.0024

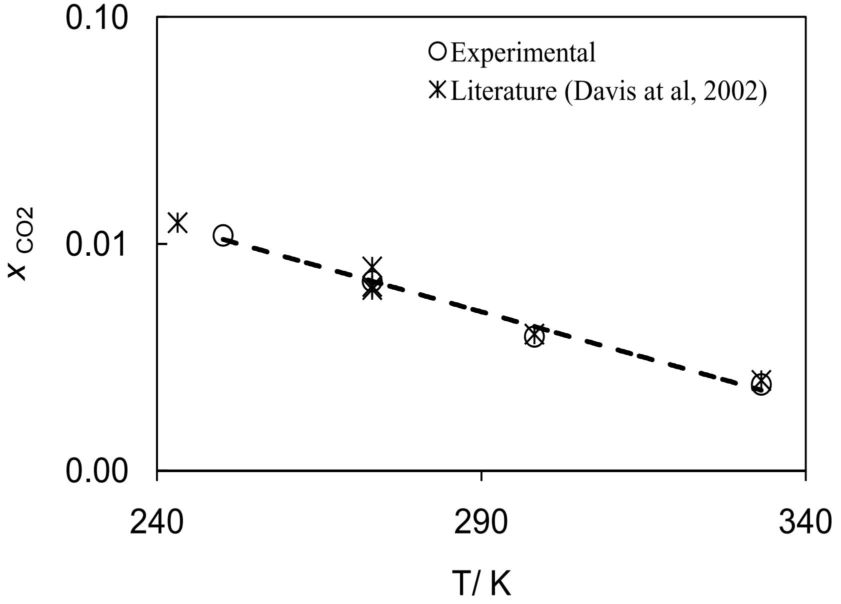

Figure 4. Experimental solubility of CO_2 in 60 mass% ethylene glycol aqueous solution (0.5 MPa). Curve: Tendency behavior; Relative deviation: < 5.

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