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Vapor-Liquid Equilibrium Data for the Systems H_2S-MDEA-H_2O and CH_4-H_2S-MDEA-H_2O at High Solvent Concentrations and High Pressures

Eirini Skylogianni[1], Diego D. D. Pinto[1], Hanna K. Knuutila[1]*, Christophe Coquelet[2]
[1]Norwegian University of Science and Technology (NTNU), Trondheim, Norway
[2]Mines ParisTech, Fontainebleau, France

INTRODUCTION

Trouble-free operations and stringent environmental requirements in the oil and gas industry demand the removal of, among other, acidic constituents from natural gas. The presence of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) increases corrosion, creates safety hazards for operations and results in an export gas of lower value. The most commonly used technology for acid gas removal is chemical absorption into aqueous amine-based solvents. When the selective removal of H_2S over CO_2 is desired, tertiary amines are preferred since hydrogen sulfide reacts instantaneously through a proton transfer while carbon dioxide cannot react directly with the amine (Versteeg et al., 1996). In our work, aqueous solutions of N-methyldiethanolamine (MDEA) are studied. This amine demonstrates high selectivity for H_2S over CO_2, degradation resistance, lower losses by vaporization because of its low vapor pressure and lower energy requirements during regeneration thanks to its low enthalpy of reaction (Kohl and Nielsen, 1997).

OBJECTIVE

Vapor-liquid equilibrium (VLE) data over a wide range of pressures, temperatures and concentrations of the various solvents used for acid gas removal are essential for the development of the thermodynamic models employed during the design and operation of the absorption and regeneration units. Plenty of equilibrium data is already available in the literature for the system CO_2-MDEA-H_2O, at various MDEA concentrations, pressure and temperature conditions. Moreover, the effect of the co-existence of carbon dioxide and hydrogen sulfide to the acid gas solubility into an MDEA solution has also been studied. However, few experimental measurements of the solubility of pure H_2S into aqueous amine solutions have been performed. In addition to this, to the authors' best knowledge, there are not any available data for high MDEA concentrations (MDEA > 50 wt. %). The objective of this work is, therefore, to provide experimental data for the system H_2S-MDEA-H_2O at pressures, temperatures and concentrations that have not been studied so far in the literature with focus on high pressures. When needed, methane will be used for pressurization in order to simulate the natural gas composition. Therefore experimental data for the system H_2S-CH_4-MDEA-H_2O will be also provided. Such data can be used to verify and/or extend existing models and predict the thermodynamic behavior of the system accurately.

APPARATUS

A high-pressure equilibrium cell developed by Laugier and Richon (1986) and manufactured by ARMINES, a subsidiary of MINES ParisTech, is used for the experimental measurements

* Corresponding author. E-mail address: hanna.knuutila@ntnu.no

of vapor-liquid equilibrium. A static-analytic method is employed utilizing two ROLSI capillary samplers for fluid sampling (Guilbot et al., 2000), one for the vapor phase and one for the liquid phase. The VLE apparatus is designed for measurements with acid gases and organic sulfur compounds with different solvents and it allows for measurements at a pressure range of 0 – 10000 kPa and temperature range of 243 – 473 K. The analysis of the vapor and liquid phase samples is performed by means of gas chromatography. The apparatus is connected to a gas chromatographer which allows for the automatic sampling and analysis of the two phases. Figure 1 shows a schematic of the apparatus (Dicko et al., 2010).

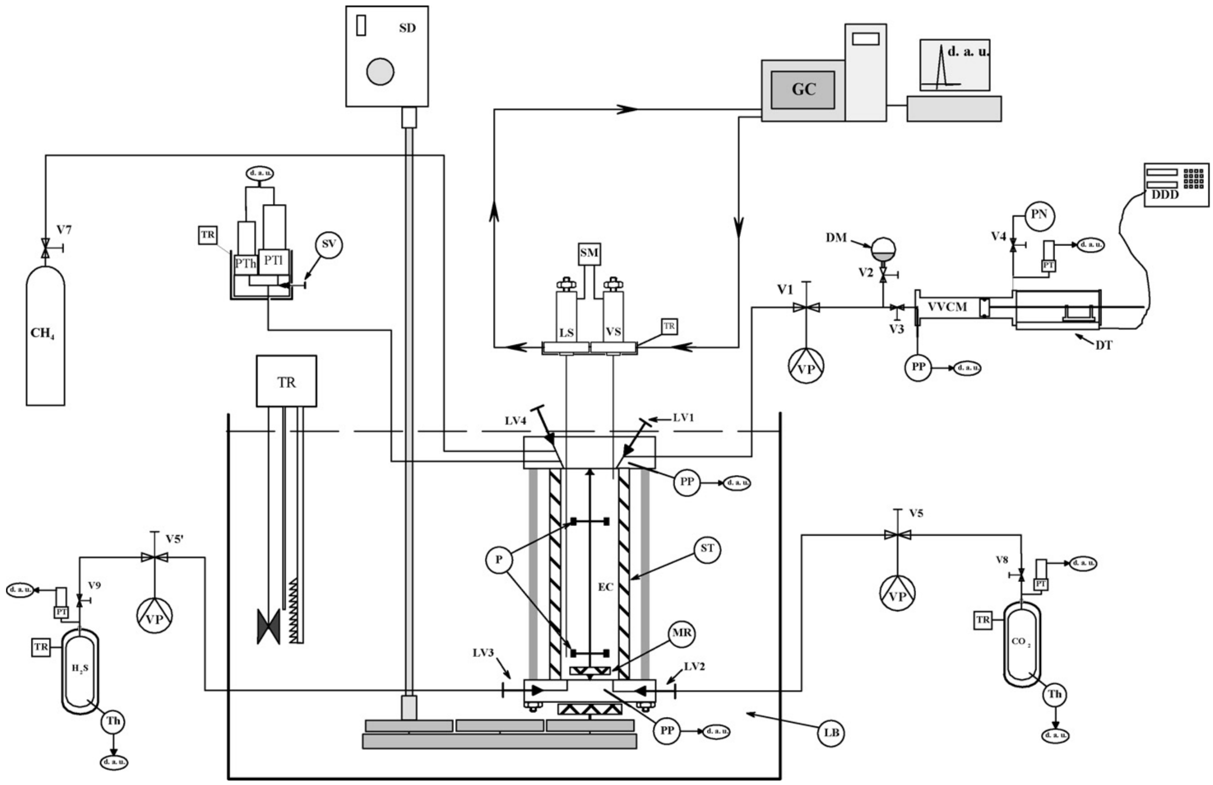

Figure 1: Flow diagram of the equipment. d.a.u.: data acquisition unit; DDD: displacement digital display; DM: degassed mixture; DT: displacement transducer; EC: equilibrium cell; GC: gas chromatograph; LB: liquid bath; LS: liquid sampler; LV_i: loading valve; MR: magnetic rod; P: propeller; PP: platinum probe; PN: pressurized nitrogen; PT: pressure transducer; PTh: pressure transducer for high pressure values; PTl: pressure transducer for low pressure values; SD: stirring device; SM: sample monitoring; ST: sapphire tube; TR: thermal regulator; Th: thermocouple; V_i: valve; VP: vacuum pump; VS: vapor sampler; VVCM: variable volume cell for mixture.

RESULTS

In this paper, we are going to present experimental vapor-liquid equilibrium data for the system H_2S-MDEA-H_2O and CH_4-H_2S-MDEA-H_2O at different loadings of the solution and at conditions relevant to the operating conditions of the absorber and the stripper (up to 100 bar and up to 120°C). A 50 wt.% MDEA solvent will be used for validation by comparing with available data from the literature, as well as two highly concentrated solvents, i.e. 70 wt. % and 90 wt. % MDEA, will be studied. A comparison of the new data and the predicted values from a thermodynamic model will be also presented.

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