

Measurement of VLE (TP_x or TP_{xy} data) for hydrogen sulfide + (dimethylsulfide or ethylmethylsulfide or carbon disulfide) and methane solubilities in (dimethylsulfide or ethylmethylsulfide or methylmercaptan or ethylmercaptan)

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Abstract

VLE data (gas solubilities (TP_x data) or complete TP_{xy} data) were measured for the following systems:

- hydrogen sulfide (H₂S) + dimethylsulfide (DMS) at 278, 293, 313, and 333 K.
- H₂S + ethylmethylsulfide (EMS) at 293 and 313 K.
- H₂S + carbon disulfide (CS₂) at 273, 298, 323, and 348 K.
- methane (CH₄) + DMS at 253, 273, 293, and 313 K.
- CH₄ + EMS at 248, 273, 293, and 313 K.
- CH₄ + methylmercaptan (MM) at 243, 258, 273, 293, and 298 K.
- CH₄ + ethylmercaptan (EM) at 273, 293, and 313 K.

These data were used to establish new binary interaction parameters for the predictive Soave–Redlich–Kwong (PSRK) group contribution of state. The extension of the PSRK parameter matrix allows now to perform reliable phase equilibrium calculations for systems with any hydrocarbons and sulfur compounds. The mean relative deviation of PSRK compared to the experimental data for the bubble point pressures is less than 2% and the mean absolute deviation for the vapor phase composition is 0.03 in terms of mole fraction.

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1. Introduction

The idea of the study presented here was born while being faced with a large demand from gas processing industry for partition coefficients of sulfur compounds in solvents containing volatile hydrocarbons and hydrogen sulfide. Experimental studies mainly performed by ARMINES and funded by Gas Processors Association (GPA) in the project 876 [1,2] and after

in the project 986 provided a large VLE database for multicomponent systems, whereas almost no data are available for the binary subsystems with respect to the sulfur compounds. The attempt of a correlation in order to enable at least interpolations did not allow a reliable and consistent representation of the total set of experimental data, because in most cases several equation of state (EoS) binary interaction parameters had to be fitted to VLE data of multicomponent systems, whereby the data were available only at very limited composition.

A group contribution approach (predictive Soave–Redlich–Kwong: PSRK [3–7]) should then be applied to compare the experimental data from GPA project 876 with

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predicted values using PSRK. The advantage of this approach is that any compound could be considered and not only the investigated sulfur compounds. Unfortunately the direct calculation was not possible, because a major part of the required group interaction parameters were not available, namely between the methane and the sulfide groups, the methane and the thiol groups, the H₂S and the sulfide groups and the H₂S and the CS₂ groups. The initially missing interaction parameters between the H₂S and the COS groups were established in a previous work [8].

Prior to the acquisition of experimental data a number of assumptions were introduced in order to allow calculations and explore the potential of PSRK for the given problem. If the group interaction parameters for the methane group were missing, the corresponding values for the alkane group were used. If the group interaction parameters for the sulfur groups were missing, the interaction parameter values were set to zero. A comparison of the available experimental data for binary, ternary and quaternary systems with PSRK predictions showed promising agreement. The accuracy of the existing experimental data (K -values mainly for sulfur trace compounds, $K_i = y_i/x_i$) from GPA project 876 was assumed to be indicated by the dispersion of deviations between experiment and calculation, e.g. about 30% when CH₄ and H₂S were involved, and about 20% when they

were not present. The reliability of the prediction was assumed to be roughly indicated by the mean value of deviations, e.g. 25% when including CH₄ and H₂S containing systems, and 9% when CH₄ and H₂S were excluded. These results provided the idea to investigate systems with CH₄ and H₂S in combination with sulfur compounds in order to establish reliable interaction parameters.

2. Experimental

The chemicals were purchased from the following commercial suppliers with the given purities in terms of % GC: CH₄ from Airgaz (purity 99.95%), H₂S from Air Liquide (purity 99.5%), DMS from Acros (purity >99%), EMS from Aldrich (purity >99%), MM from Aldrich (purity 99.5%), EM from Merck (purity >99%) and CS₂ from Merck (purity >99.9%).

The used apparatus allows to work with both the synthetic (as described in [8]) and analytical [9] methods, see Fig. 1. The principle of the synthetic method is to inject precisely known amounts of the pure components into a thermo-regulated equilibrium chamber, and to measure the system pressure as a function of global composition. These data can be treated with mass and volume balances in order to obtain the bubble point line for mixtures (TP_x-data). The analytic method allows the direct

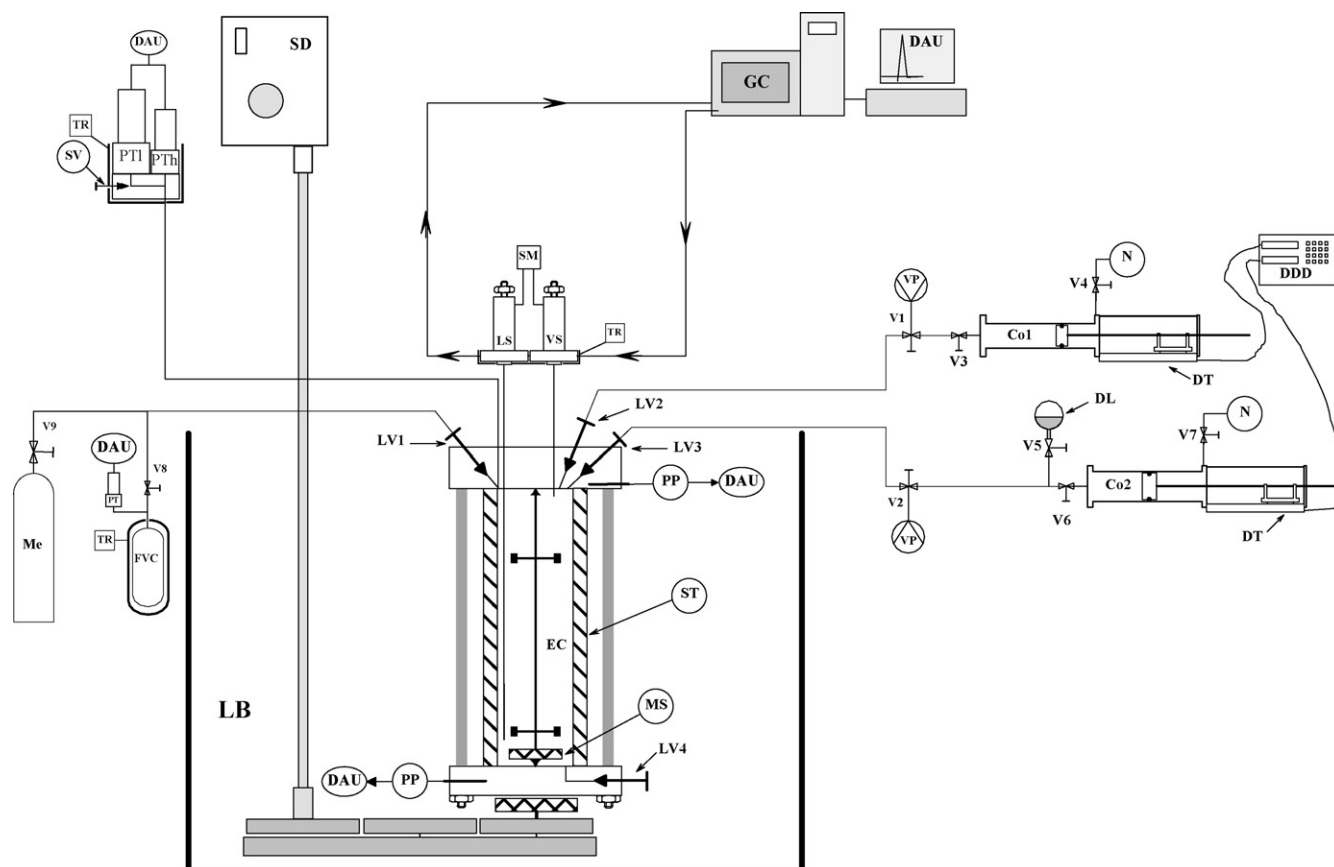


Fig. 1. Flow diagram of equipment. Co1: variable volume cell for component 1; Co2: variable volume cell for component 2; DAU: data acquisition unit; DDD: digital displacement transducer; DL: degassed liquid; DT: displacement transducer; FVC: fixed volume cell; GC: gas chromatograph; LB: liquid bath; LS: liquid sampler; LV_i loading valve *i*; Me: methane cylinder; MS: magnetic stirrer; PP: platinum probe; N: pressurized nitrogen; PTh: high pressure pressure transducer; PTI: low pressure pressure transducer; SD: stirring device; SM: sample monitoring; SV: home made shut off valve; TR: thermal regulator; V_i: shut off valve *i*; VP: vacuum pump; VS: vapor sampler.

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