Greek letters

σ   standard deviation defined in eq 2

Subscripts

1   *m*-dichlorobenzene
2   aromatic hydrocarbon

Literature Cited

(1) Riddick, J. A., Bunger, W. B., "Techniques of Chemistry", Vol. II, A.

Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1970.
(2) Tanaka, R., Benson, G. C., *J. Chem. Eng. Data*, **21**, 320 (1976).
(3) Tanaka, R., Benson, G. C., *J. Chem. Eng. Data*, **22**, 291 (1977).
(4) Tanaka, R., D'Arcy, P. J., Benson, G. C., *Thermochim. Acta*, **11**, 163 (1975).
(5) Tanaka, R., Kiyohara, O., D'Arcy, P. J., Benson, G. C., *Can. J. Chem.*, **53**, 2262 (1975).
(6) Tanaka, R., Murakami, S., Fujishiro, R., *J. Chem. Thermodyn.*, **6**, 209 (1974).

Vapor–Liquid Equilibria in the System Hydrogen Sulfide–Methanethiol

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The compositions of the coexisting phases in the H_2S–CH_3SH system have been measured at a pressure of 2413 kPa (350 psia).

The purpose of the present work is to provide data useful for the design of a process for the purification of hydrogen sulfide containing small amounts of methanethiol. No data for this system are extant in the literature.

Experimental Section

Matheson C.P. grade hydrogen sulfide and methanethiol were used without further purification. The equilibrium cell consisted of a Jerguson liquid level gauge (Model 19-T-20) with a 250-cm³ tubular reservoir mounted at the top and is shown in Figure 1. A magnetic pump (*5*) was used to circulate the gas phase from the reservoir to the bottom of the Jerguson gauge. The cell and pump were housed in an air bath controlled within ±0.1 °C. The pressure of the experiments was kept at 2413 kPa by adjustment of the bath temperature. The temperature was measured by a calibrated mercury thermometer and the pressure in the cell was measured by a calibrated Heise bourdon tube gauge. The vapor sample was taken from the recirculation line and passed directly to the chromatograph for analysis. This equipment was used previously for measurements of the solubility of H_2S in DEA solutions (*3*).

A sample of the liquid was taken from the bottom of the cell and expanded into a 750-cm³ stainless steel vessel maintained at 100 °C so that the liquid sample was completely vaporized. The pressure in the vessel after sampling did not exceed 800 kPa. A sample from this vessel was then passed to the chromatograph for analysis. The chromatograph used a 6 ft long × ⅛ in. o.d. Porapak column operated isothermally at 130 °C. A thermal conductivity detector was used and response factors for the calculation of the composition were obtained from Dietz (*2*).

Results and Discussion

The experimental data are presented in Table I. Most of the data were obtained at a pressure of 2413 kPa at concentrations of hydrogen sulfide in the liquid phase greater than 80 mol %. Figure 2 shows the data for 2413 kPa on a temperature–composition diagram and smoothed data for this pressure are given in Table II.
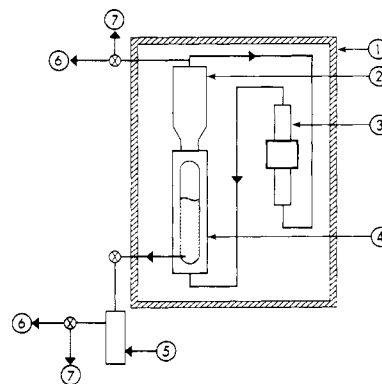

Figure 1. Schematic diagram of experimental apparatus: 1, insulated air bath; 2, vapor reservoir; 3, magnetic pump; 4, high-pressure liquid level gauge; 5, liquid sample vessel; 6, to gas chromatograph; 7, vent line.
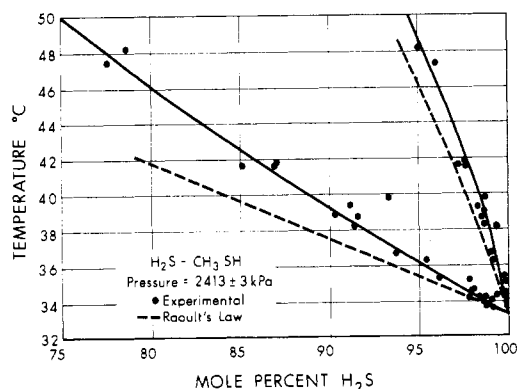

Figure 2. Vapor–liquid equilibria for H_2S–CH_3SH at 2413 kPa.

Also shown on Figure 2 are dashed lines obtained by the use of Raoult's law for the calculation of the equilibria. Values of the vapor pressures for the pure compounds were obtained from the Matheson data book (*1*), and at the pressure of 2413 kPa, the corresponding temperatures for pure H_2S and pure CH_3SH are 33.3 and 126.1 °C, respectively. The results indicate a small negative deviation from Raoult's law for CH_3SH concentrations less than about 15 mol %. A *y–x* diagram for this system was

Table I. Experimental Equilibrium Data for H₂S–CH₃SH

Temp, °C	Pressure, kPa	Mol % H₂S Liquid	Mol % H₂S Vapor
37.8	2593	96.52	99.61
35.0	2426	96.72	99.82
32.2	2277	96.81	99.71
37.8	2573	96.48	99.56
35.0	2408	96.15	99.74
32.2	2250	96.10	99.93
39.0	2412	90.35	98.66
41.7	2412	85.04	97.34
47.4	2413	77.5	95.81
38.1	2413	93.89	99.24
39.4	2416	91.1	98.43
39.9	2413	93.2	98.69
35.4	2413	96.16	99.71
34.4	2415	97.8	99.94
36.4	2413	95.35	99.26
34.6	2413	97.99	99.82
34.6	2413	97.87	99.79
33.7	2414	98.76	99.95
34.3	2410	98.62	99.88
35.2	2413	97.72	99.86
33.7	2411	99.14	99.94
34.2	2412	99.0	99.92
34.3	2411	98.37	99.86
48.2	2413	78.6	94.97
41.7	2413	86.9	97.69
38.4	2413	91.34	98.62
36.8	2413	93.68	99.21
38.8	2413	91.52	98.67
41.9	2410	86.98	97.63

Table II. Smoothed Equilibrium Data for H₂S–CH₃SH at 2413 kPa

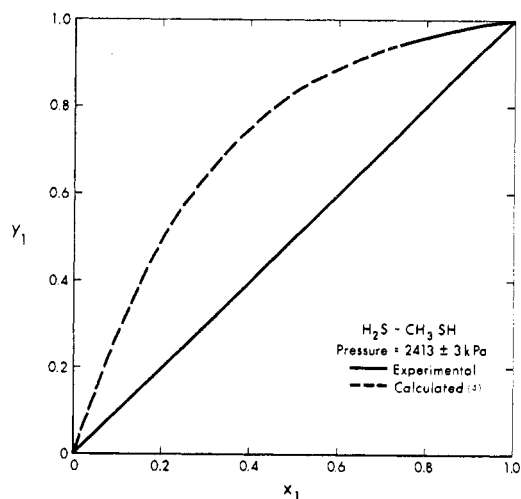| Temp, °C	Mol % H₂S Liquid	Mol % H₂S Vapor
48	77.50	95.22
46	80.22	96.05
44	83.00	96.83
42	85.95	97.60
40	88.90	98.30
38	92.08	98.95
36	95.45	99.55
34	98.76	99.94
33.5	99.68	99.99

Figure 3. Calculated and experimental phase equilibria in the system hydrogen sulfide–methanethiol at 2413 kPa.

generated using the corresponding states correlation of Mollerup (4) and is presented as Figure 3. The calculated values are in good agreement with the experimental values at high H₂S concentrations and since there is no azeotrope, the separation of hydrogen sulfide from methanethiol by distillation does not appear to present any difficulties.

Glossary

x mole fraction in liquid phase
y mole fraction in vapor phase

Subscripts

1   H₂S

Literature Cited

(1) Braker, W., Mossman, A. L., "Matheson Gas Data Book," 5th ed., Matheson Gas Products, East Rutherford, N.J., 1971.
(2) Dietz, W. A., *J. Gas Chromatogr.*, **5**, 68 (1967).
(3) Lee, J. I., Otto, F. D., Mather, A. E., *J. Chem. Eng. Data*, **18**, 71 (1973).
(4) Mollerup, J., *Adv. Cryog. Eng.*, **20**, 172 (1975).
(5) Ruska, W. E. A., Hurt, L. J., Kobayashi, R., *Rev. Sci. Instrum.*, **41**, 1444 (1970).