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Note

VAPOUR–LIQUID EQUILIBRIUM DATA FOR SOME ALKANE + SULPHUR COMPOUND SYSTEMS

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Measurements are reported for the distribution ratios for very small amounts of some sulphur compounds between the vapour and liquid phases of liquefied methane, ethane or propane. Data are scarce for these systems and the aim is to provide some measurements with which to assess the equation-of-state methods used by petroleum industries to predict such equilibria. The results are expressed as K values, where K is defined by

$$K = \frac{\text{ppm of sulphur compound in the vapour phase}}{\text{ppm of sulphur compound in the liquid phase}}$$

For the very low concentrations studied here, K is independent of the concentration of the liquid phase.

EXPERIMENTAL

The two aspects of the experiments are: (a) the attainment of equilibrium between a liquid alkane containing 500 ppm of sulphur compound and its vapour; and (b) the withdrawal of samples of the phases for analysis by a gas chromatograph equipped with a flame photometric detector (FPD) which responds linearly to sulphur compounds.

The apparatus comprises a vapour-recirculation system based on a design by Street and Calado [1], and this is immersed in a conventional bath cryostat as outlined by Hong and Kobayashi [2]. The only significant changes were those made in the sampling system. Each phase is bled to the gas sampling loop of the chromatograph via 0.15-mm ID stainless-steel tubing and a low-internal-volume valve; the liquid sample completely vaporises en route. The vapour phase is withdrawn from a section of the recirculation system which is far from the liquid surface to avoid contamina-

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TABLE 1

Experimental and calculated *K* values

System	*T* (K)	*p* (bar)	Mean *K* ±95% confidence limits	Number of measurements	*K* from RKS equation
CH_4 + COS	174.4	27.0	$(5.70 \pm 0.70) \times 10^{-2}$	21	4.5×10^{-2}
C_2H_6 + COS	277.0	26.1	$(5.50 \pm 0.80) \times 10^{-1}$	27	5.0×10^{-1}
+ C_2H_5SH	275.3	25.2	$(1.05 \pm 0.15) \times 10^{-1}$	17	7.7×10^{-2}
+ $CH_3SC_2H_5$	275.3	25.2	$(3.40 \pm 0.65) \times 10^{-2}$	17	2.9×10^{-2}
+ $(CH_3)_3CSH$	275.3	25.2	$(3.55 \pm 0.55) \times 10^{-2}$	17	2.8×10^{-2}
C_3H_8 + C_2H_5SH	284.4	6.6	$(1.70 \pm 0.25) \times 10^{-1}$	13	1.2×10^{-1}
+ $CH_3SC_2H_5$	284.4	6.6	$(4.75 \pm 1.35) \times 10^{-2}$	13	3.6×10^{-2}
+ $(CH_3)_3CSH$	284.4	6.6	$(4.70 \pm 1.15) \times 10^{-2}$	13	3.5×10^{-2}

tion by vaporised liquid. The FPD was calibrated by taking samples from a 50-ppm mixture of sulphur compound + alkane using a set of calibrated gas sampling loops with volumes ranging from 0.1 to 1 cm^3. In an actual experiment, the 0.1 cm^3 loop was used to sample the liquid phase (approx. 500 ppm) and a larger loop for the vapour phase (15–250 ppm), ensuring that both analyses fell on the calibration plot. A 2 m × 3 mm Teflon column packed with Chromosil 330 separated all the mixtures except C_2H_6 + COS, which required a packing of Chromosorb 105.

Preliminary experiments determined the times required for phase equilibrations, and further experiments established that equilibrium phase concentrations were independent of the vapour recirculation rate and that K values were the same for 300- and 500-ppm mixtures.

RESULTS

The results are summarised in Table 1. Of the two previous studies of the system $C_3H_8 + C_2H_5SH$, one [3] used wet chemical methods to analyse similar thiol concentrations and obtained $K = 0.31$ at 284.4 K; the other [4] used a gas chromatograph with an FPD and obtained $K = 0.19 \pm 0.02$, which is in statistically reasonable agreement with Table 1. The CH_4 + COS phase diagram has been determined [5] but at temperatures above 298 K, where CH_4 is a supercritical fluid.

Table 1 includes K values calculated by the widely-used Redlich–Kwong–Soave (RKS) equation of state [6] using only the critical temperatures and pressures and the acentric factors for the pure components. Given that such equations are least reliable for polar substances, the typical agreement to within 25% with experiment is surprisingly good.

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