K-Values and Activity Coefficients of Some Mercaptans and Sulfides and a Disulfide in Hydrocarbon Solutions

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Gas liquid partition chromatography was used to determine *K*-values of five mercaptans (ethyl, *n*-propyl, *n*-butyl, *sec*-butyl, and isobutyl), three sulfides (dimethyl, methyl ethyl, and diethyl), and one disulfide (dimethyl) at infinite dilution in *n*-hexadecane at 100–140 °C and pressures to 2.5 atm. Activity coefficients in the liquid solutions were derived from the data.

Vaporization properties of sulfur compounds are of interest in connection with the engineering design of processes for the production of clean sulfur-free fuels. In this work we determined the *K*-values and activity coefficients of a number of these sulfur-containing compounds: ethyl mercaptan (ethanethiol), *n*-propyl mercaptan (1-propanethiol), *n*-butyl mercaptan (1-butanethiol), *sec*-butyl mercaptan (2-butanethiol), isobutyl mercaptan (2-methyl-1-propanethiol), dimethyl sulfide (2-thiapropane), methyl ethyl sulfide (2-thiabutane), diethyl sulfide (3-thiapentane), and dimethyl disulfide (2,3-dithiabutane).

Gas liquid partition chromatography (GLPC) was employed with liquid *n*-hexadecane supported on crushed firebrick as the stationary phase and helium as the carrier gas. GLPC is an efficient experimental technique for determining *K*-values of a number of solutes in a given solvent. The technique has been thoroughly described by a number of authors (*4, 7, 8*) and is particularly well suited for the odorous compounds considered here.

Stalkup and Kobayashi (*7*) presented the following equation for the determination of *K*-values from GLPC retention volume data:

$$K_i = \frac{nz_mRT}{p(V_{R_i} - V_g)(1 - y_1/K_1 - y_2/K_2 \ldots y_N/K_N)} \qquad (1)$$

This expression reduces to Equation 2 for the case of an infinitely dilute solute and an inert light carrier gas such as helium which is practically insoluble in the stationary phase at low pressures:

$$K_i = \frac{nz_mRT}{p(V_{R_i} - V_g)} \qquad (2)$$

Equation 2 can be expressed in terms of retention time,

$$K_i = \frac{nz_aRT_a}{p_aF_a(t_{R_i} - t_g)} \qquad (3)$$

With helium as the carrier gas $z_a = 1$ at the low pressures of this work.

As a check on our apparatus and procedure, we determined *K*-values of propane at infinite dilution in *n*-decane at 1.36 atm. Figure 1 shows the comparison of two points of ours with the data by Stalkup and Kobayashi (*7*) at the same pressure but lower temperatures. Our values lie on a smooth extension of their data.

Apparatus and Procedure

A schematic diagram of the GLPC apparatus used in this work is shown in Figure 2. A Nuclear-Chicago Model 5340-100 gas chromatograph was modified to show the flow pattern. The chromatograph was equipped with a six-port hot-wire thermal conductivity (TC) detector. After passing through the reference side of the detector, the carrier gas flows through a 12-ft presaturator column, then a conventional septum-equipped injector and into the first measurement cell of the detector. From there, flow continues through the gas-liquid partition column and back through the second measurement cell of the detector. A reference peak is produced by the TC cell immediately after injection of a solute sample. A second peak appears when the solute elutes from the partition column. The difference between the two peaks accurately measures retention time in the column. A Columbia Scientific digital integrator equipped with a timer is modified to print out peak times to a tenth of a second. Thus, no manual operation is required to mark the time of sample injection. Such an operation is a usual source of large uncertainty in retention time determination.

After successive injections were made of the various sulfur-containing solutes at a fixed temperature and pressure of the column, additional injections were also made of Ne, Ar,

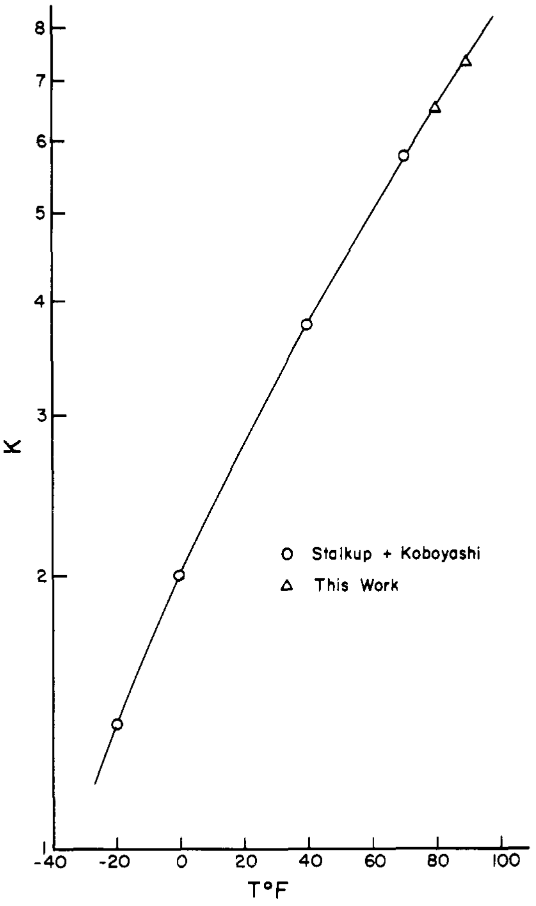

Figure 1. *K* of propane at infinite dilution in methane–*n*-decane at 1.36 atm

and Kr. The retention times of the inert gases were extrapolated to determine the retention time of a hypothetical completely insoluble gas, thus determining t_g. The procedure of extrapolation was described by Yudovich et al. (*8*).

Flow control was accomplished by a combination of a Whitey micrometering valve and a Moore constant upstream pressure flow controller to maintain a 0.20 atm pressure drop across the needle valve. Carrier gas flow rate F_a was measured with a soap bubble flow meter. Flow rates of about 40 cc/min were used.

Pressure in the GLPC apparatus was controlled by means of a Grove small-volume back pressure regulator and measured through a pressure tap at each end of the column with a mercury manometer and a Heise pressure gauge with divisions of 0.017 atm. Atmospheric pressure p_a was measured with a mercurial barometer of the U.S. Army Signal Corps type accurate to 0.1 torr.

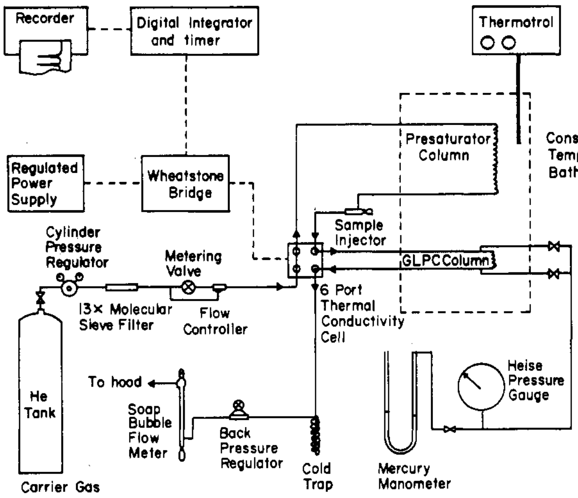

Figure 2. Schematic diagram of GLPC apparatus

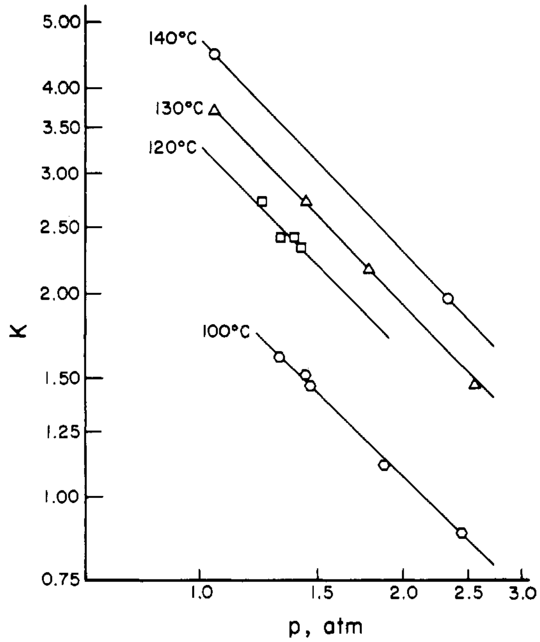

Figure 3. *K* of *n*-propyl mercaptan at infinite dilution in helium–*n*-hexadecane

Temperature in the column oven was controlled to 0.25 °C with a Hallikainen Instruments "Thermotrol" unit. Temperatures were measured with a Leeds and Northrup type K-4 potentiometer and calibrated thermocouples.

The GLPC column was packed with 40/50 mesh acid-washed C-22 firebrick impregnated with 25 wt % loading of research grade stationary phases. Stainless-steel tubing and fittings were used throughout. One-quarter-in. tubing was used for the columns, and $\frac{1}{16}$ in. was used elsewhere to minimize dead volume. A presaturator column was used to reduce loss of stationary phase from the partition column, and frequent weighings of the partition column were made to accurately determine the amounts of stationary phase present.

With gaseous samples less than 0.4 ml and liquid samples less than 2 µl, retention time was not a function of sample volume. This is essential for Equations 2 and 3 to apply.

Experimental Results

K-values were obtained from the experimental retention time data for all the sulfur compounds studied in this work. For each sulfur compound *K*-values were determined at temperatures of 100, 120, 130, and 140 °C and at several pressures in the range of 1–2.5 atm. Dimethyl disulfide was the only exception in that it was not studied at 100 °C because of its low volatility and excessive retention time at this temperature. As an example, we show in Figure 3 the *K*-values of *n*-propyl mercaptan thus obtained. The *K*-values were reproducible to within 3% in agreement with the estimated uncertainty of the *K*-values based on a detailed analysis of the uncertainties of the experimental variables.

From plots like Figure 3, *K*-values were interpolated to a convenient intermediate pressure for calculation of activity coefficients. Table I shows the interpolated *K*-values and the corresponding pressures. Activity coefficients were derived from these *K*-values according to the following equation (*8*):

$$\gamma_i = \frac{p\phi_i K_i}{\overset{\circ}{p}_i \overset{\circ}{\phi}_i \exp\left[(p - \overset{\circ}{p}_i)\tilde{V}_i/RT\right]} \qquad (4)$$

The saturated vapor fugacity coefficient $\overset{\circ}{\phi}_i$ was taken from the generalized correlation by Lydersen et al. (*6*). Vapor pressure $\overset{\circ}{p}_i$ was taken from American Petroleum Institute Research Project 44 Tables for the mercaptans (*1*), methyl ethyl sulfide (*2*) and diethyl sulfide (*2*), and from Dreisbach (*3*) for dimethyl sulfide and dimethyl disulfide. The table values were extrapolated to higher temperatures, where necessary, on a Cox chart. The values used in the calculations are shown in Table I.

The fugacity coefficients ϕ_i of solutes in the helium elution gas deviate only slightly from 1 and were therefore set equal to 1. The liquid molal volumes $\tilde{V}_i$ were estimated from the group interaction theory of Lee et al. (*5*). The calculations of Equation 4 were highly insensitive to the values of $\tilde{V}_i$ at the relatively low pressures of interest. The exponential factor never deviated from 1 by more than 2%.

Table I shows the activity coefficient values obtained in this work. They are all less than one, but not by a great deal. Since these values are at infinite dilution, the activity coefficients at finite concentrations should be even closer to 1. We conclude that solutions of the sulfur compounds studied and paraffin hydrocarbons do not depart greatly from ideal solution behavior. Dissimilarity in the chemical nature of the sulfur compounds and paraffin molecules does not show up in greatly divergent intermolecular forces. The data should be useful for the determination of the interaction forces. A future report will present analysis of the data from a molecular structural group viewpoint.

Acknowledgment

Phillips Petroleum Co. donated the sulfur compounds.

Table I. K-Values, Vapor Pressures, and Activity Coefficients

	100 °C			120 °C			130 °C			140 °C		
Compound	K	p°, atm	γ^∞	K	p°, atm	γ^∞	K	p°, atm	γ^∞	K	p°, atm	γ^∞
Ethyl mercaptan[a]	3.65	6.29	0.877	5.41	9.65	0.857	6.20	11.76	0.856	7.06	14.16	0.865
n-Propyl mercaptan[a]	1.56	2.52	0.899	2.43	4.11	0.879	2.85	5.14	0.845	3.44	6.35	0.829
sec-Butyl mercaptan[a]	0.939	1.54	0.862	1.53	2.57	0.861	1.83	3.25	0.841	2.24	4.06	0.824
Isobutyl mercaptan[a]	0.860	1.39	0.878	1.39	2.35	0.866	1.68	3.14	0.842	2.06	3.74	0.817
n-Butyl mercaptan[a]	0.670	1.05	0.904	1.145	1.81	0.905	1.38	2.33	0.875	1.73	2.95	0.859
Dimethyl sulfide[b]	3.07	5.950	0.933	4.45	9.080	0.953	5.30	11.067	0.964	6.32	13.346	0.976
Methyl ethyl sulfide[b]	1.25	2.610	0.831	2.14	4.244	0.903	2.70	5.302	0.931	3.38	6.544	0.965
Diethyl sulfide[b]	0.625	1.258	0.854	1.14	2.154	0.928	1.50	2.754	0.955	1.925	3.472	0.982
Dimethyl disulfide[b]				0.74	1.330	0.956	0.95	1.729	0.973	1.2	2.215	0.991

[a] K-values are given at 1.36 atm. [b] K-values are given at 1.70 atm.

Nomenclature

F_a = volumetric flow rate of elution gas at ambient conditions
K_i = equilibrium y_i/x_i for component i
n = mol of stationary liquid phase on column packing
p = column pressure
p_a = ambient pressure
p° = vapor pressure
R = gas constant
t_{R_i} = retention time of solute i
t_g = retention time of hypothetical "nonabsorbed" gas
T = absolute temperature
T_a = absolute ambient temperature
V_{R_i} = retention volume of component i
V_g = free gas volume
$\tilde{V}_i$ = liquid molal volume of component i
y = mol fraction in gas phase
z_m = compressibility factor of elution gas at column operating conditions
z_a = compressibility factor of elution gas at ambient conditions
γ_i = activity coefficient of component i in the liquid phase at T
ϕ_i = fugacity coefficient of component i in the elution gas at T and p
ϕ_i° = fugacity coefficient of pure vapor i at T and p_i°

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Vapor-Liquid Equilibria of Methyl Borate–Carbon Tetrachloride and Methyl Borate–Benzene Systems

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Vapor-liquid equilibrium measurements at 760 torr are reported for the methyl borate–carbon tetrachloride and methyl borate–benzene systems. Analysis of the data shows both of these systems to approach ideality. Equilibrium relations may be represented by the relative volatility equation with $\alpha_{\mathrm{MB\text{-}CCl_4}} = 1.280$ and $\alpha_{\mathrm{MB\text{-}BZ}} = 1.431$.

As a continuation of a systematic study of borate compounds initiated by one of the authors, the vapor-liquid equilibria have been measured for the two binary systems, methyl borate–carbon tetrachloride and methyl borate–benzene at a pressure of 760 ± 1 torr. An Altsheler (circulation type) still was used and is described in detail by Hala et al. (*3*). The methyl borate was purchased from Apache Chemicals, Inc. (98%), and was purified by successive fractional distillations to 99.9+% purity, giving a measured normal boiling point of 68.6 °C as compared with 68.7 °C (*6*). Analysis of the borate was by the standard mannitol–sodium hydroxide titration (*5*). Eastman Kodak spectrograde benzene and carbon tetrachloride were used. The benzene was "ACS certified" with a reported normal boiling point of 80.1 ± 0.1 °C as compared with an API-44 value of 80.1 °C (*1*). The carbon tetrachloride had a reported boiling point of 76.7 ± 0.1 °C as compared with 76.54 °C (*4*). Both the benzene and carbon tetrachloride were used as purchased.

Mixture analyses were from refractive index measurements using a Bausch and Lomb Model 33-45-03 refractome-