

CHROM. 16,144

HEADSPACE GAS CHROMATOGRAPHIC DETERMINATION OF DISTRIBUTION COEFFICIENTS OF SELECTED ORGANOSULPHUR COMPOUNDS AND THEIR DEPENDENCE ON SOME PARAMETERS

A. PRZYJAZNY*, W. JANICKI, W. CHRZANOWSKI and R. STASZEWSKI

Institute of Inorganic Chemistry and Technology, Technical University of Gdańsk, 11/12 Majakowski St., 80-952 Gdańsk (Poland)

(First received May 16th, 1983; revised manuscript received July 13th, 1983)

SUMMARY

Using headspace gas chromatography, the distribution coefficients, K_i , of selected organosulphur compounds in air–water system as well as their temperature, ionic-strength and concentration dependences have been determined. Based on the K_i values, the detection limits for direct headspace gas chromatographic analysis with flame-ionization detection, aqueous solubilities and the Raoult-law activity coefficients have also been estimated. The detection limits were found to decrease with molecular weight within the homologous series studied. It is shown that an increase in the concentration of analytes in the gaseous phase can be most easily accomplished by elevating the temperature; the effect of ionic strength on the K_i values at 70°C was small. The dependence of the equilibrium gaseous-phase concentration on the liquid-phase concentration was found to be linear (with some exceptions) over the investigated concentration range (0.1–10 ppm). The detection limits were estimated to be in the 1–10-ppb range, thus indicating broad applicability of the direct headspace gas chromatographic analysis for organosulphur compounds. The values for the aqueous solubility and activity coefficients can be employed for physicochemical and environmental purposes.

INTRODUCTION

Headspace gas chromatographic (HS-GC) analysis is a powerful tool for solving difficult problems of trace determinations of volatile compounds, particularly in aqueous solutions. It has therefore found extensive use, especially in environmental analysis, food and agricultural sciences, forensic chemistry and biological and medical sciences. The technique is preferred if standard GC procedures cause problems with the sample matrix with respect to solubility or thermal stability. HS-GC has also found extensive application in physical chemistry, being a valuable tool for acquiring data on gas–solid and gas–liquid systems. Both the general aspects and the practical use of HS-GC have been discussed in several books^{1–3} and in a review article⁴. One of the fundamental quantities determined by means of HS-GC is the

distribution coefficient K_i of the solute, defined as the ratio of the equilibrium concentrations of the solute in the condensed and gaseous phases. As the value of the distribution coefficient depends to a large extent on a number of variables, such as temperature, concentration of the solute and composition of the sample matrix (the ionic strength generally), it cannot be applied directly in quantitative analysis by HS-GC. However, the K_i values can be employed to estimate the detection limits of various compounds in direct static headspace analysis⁵. These values may also be utilized for the determination of the Raoult-law activity coefficients of solutes and their solubilities^{4,5} as well as for calculations concerning the optimization of pre-concentration of organic compounds by means of stripping⁶. In addition, the partition coefficients can be used for the characterization of solvent properties⁷.

The analytical chemistry of organosulphur compounds is of special significance, mainly on account of the environmental effects of these compounds. Numerous papers have dealt with their determination using HS-GC⁸⁻¹⁷. The purpose of the present work was to determine the distribution coefficients of selected organosulphur compounds in an air-water system along with their temperature, concentration and ionic-strength dependences in order to estimate the detection limits when using direct HS-GC analysis with a flame-ionization detector, and to select optimal analytical conditions for this analysis. The K_i values have also been determined for artificial sea water¹⁸ on account of our interest in the analysis of sulphur compounds in marine environments. In addition, the Raoult-law activity coefficients and solubilities in water of organosulphur compounds have been calculated from the distribution coefficients and vapour-pressure data.

EXPERIMENTAL

Apparatus

A headspace vessel in which the distribution coefficients in the air-water system were determined is shown in Fig. 1. Special attention was paid to such a design of the vessel that sulphur compounds, which are highly reactive, were in contact only with glass or polytetrafluoroethylene (PTFE). Constant pressure in the system was maintained by means of a compensating syringe connected to the bottle. The measurements were carried out in four bottles which were thermostatted to $\pm 0.1^\circ\text{C}$. Bottle capacities were *ca* 600 cm³ and were determined individually. The equilibrium concentration in the gas phase was determined chromatographically by injecting 0.5 cm³ of the gas after equilibration for 90 min.

A Hewlett-Packard Model 5830A gas chromatograph equipped with a flame-ionization detector was used for GC analysis. The chromatographic conditions were as follows: column, 2.4 m \times 2 mm I.D. stainless steel; packing, 10% Dexsil 300 GC or 10% DEGS on Chromosorb W AW DMCS, 80-100 mesh; carrier gas, argon at 20 cm³/min; temperatures, injector and detector at 130°C, column depending on compound investigated.

Materials

The solvent used for the preparation of stock solutions: dimethyl sulphoxide (DMSO) (Reachim, U.S.S.R.) was purified by vacuum distillation. All organosulphur compounds (E. Merck, F.R.G.) were of analytical-reagent grade except for dimethyl

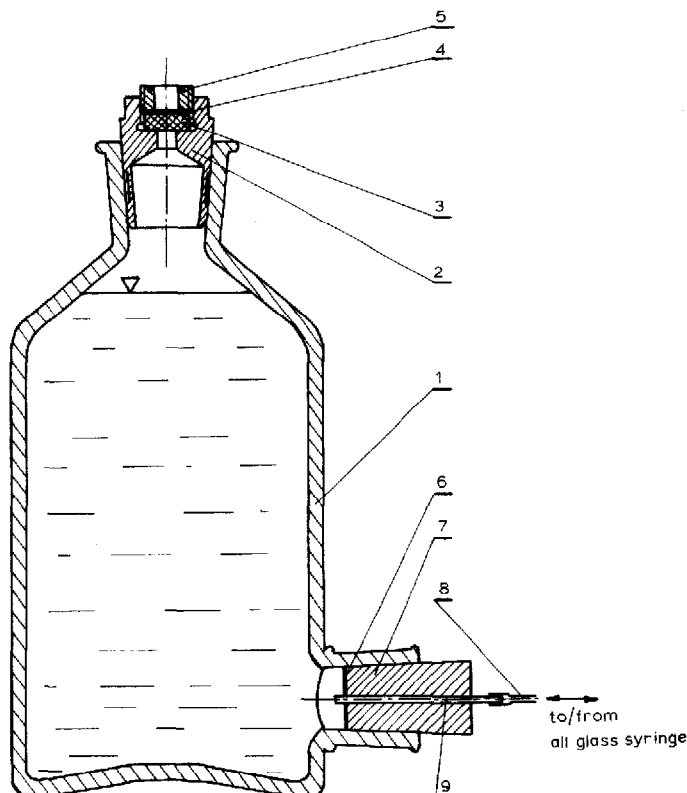


Fig. 1. Headspace vessel in which gas-liquid equilibria were studied: 1 = glass bottle; 2 = PTFE stopper; 3 = silicone rubber septum with lower surface covered with PTFE foil; 4 = washer; 5 = septum fixing screw; 6 = PTFE foil; 7 = rubber stopper; 8 = silicone rubber tubing connecting headspace vessel with 20-cm³ compensating syringe; 9 = glass tubing.

sulphide which was synthesized from methyl iodide and sodium sulphide and purified by fractional distillation. The stock solutions of sulphur compounds (*ca.* 3000 ppm, w/w) were prepared in dimethyl sulfoxide (DMSO) and their concentration was checked periodically.

Procedure

Model solutions of sulphur compounds in distilled and artificial sea water were prepared from the stock solutions. Their concentrations were approximately equal to 10, 1 and 0.1 ppm. In order to prepare solutions of varying ionic strength ($I = 1, 2, 3$ and 4), a suitable volume of saturated solution of sodium sulphate was added to the bottles. After preparing an appropriate solution, the bottle was stoppered and the gas phase was obtained by introducing an injection needle through a septum and withdrawing 15 cm³ of the solution with the compensating syringe. Subsequently, the bottles were placed in a thermostat for 90 min and the equilibrium composition of the gas phase was determined gas chromatographically by injecting four times 0.5 cm³ of the gas with a 1-cm³ gas-tight syringe. The temperature dependence of the distribution coefficients was studied by determining their values at 25, 35, 45 and

70°C. Quantitative GC analysis was performed by a calibration method based upon injection of 1 μl of the appropriate stock solution onto the GC column.

RESULTS AND DISCUSSION

The equation for calculating the distribution coefficient from the GC data, known concentration of a standard solution and the volumes of liquid and gaseous phases was derived in the following manner. The distribution constant is defined as

$$K_i = \frac{c_{iL}}{c_{iG}} = \frac{c_{iL0} - \frac{c_{iG} V_G}{V_L}}{c_{iG}} \quad (1)$$

where c_{iL} and c_{iG} are the equilibrium concentrations of the analyte i in the liquid and gaseous phases, respectively, V_L and V_G are the volumes of these phases and c_{iL0} is the initial concentration in the liquid phase, calculated from

$$c_{iL0} = \frac{c_{iS} V_{iS}}{V_L} \quad (2)$$

where c_{iS} and V_{iS} are the concentration and volume of the standard solution introduced to the HS vessel. A large V_L/V_G ratio ($\cong 39$) permits the approximation $c_{iL0} = c_{iL}$ (the amount of the analyte transferred from the liquid to the gaseous phase even for K_i values smaller than 1 does not exceed 3%). Hence,

$$K_i = \frac{c_{iL0}}{c_{iG}} = \frac{c_{iS} V_{iS}}{V_L c_{iG}} \quad (3)$$

The concentration c_{iG} is determined chromatographically:

$$c_{iG} = \cot \alpha A_{iG} \cdot \frac{1}{v_G} \quad (4)$$

where A_{iG} is the average peak area in the analysis of the gaseous phase over the investigated model solution, v_G is the volume of the headspace gas taken for analysis and $\cot \alpha$ is a calibration factor equal to

$$\cot \alpha = \frac{c_{iS} v_S}{A_{iS}} \quad (5)$$

where A_{iS} and v_S are the average peak area and the injected volume of the stock solution used in the calibration. Combination of eqns. 3, 4 and 5 yields the final formula:

$$K_i = \frac{V_{iS} A_{iS} v_G}{V_L A_{iG} v_S} \quad (6)$$

It follows from thermodynamic considerations that the temperature dependence of the distribution coefficient should be approximately linear if plotted in the coordinate system $\log K_i = f(1/T)$. Therefore, the values of K_i determined at 25, 35, 45 and 70°C were used to fit the experimental data to the linear regression curve

$$\log K_i = b \cdot \frac{1}{T} + a \quad (7)$$

by means of a least-squares method. An exemplary plot of this relationship for thiophene solutions is shown in Fig. 2. Two families of straight lines can be distinguished, corresponding to the systems air-distilled water (lines 1, 3 and 5) and air-artificial sea water (lines 2, 4 and 6). Within the families, the K_i values are similar, the largest difference occurring for the highest concentration. The results of analogous investigations for twelve organosulphur compounds are summarized in Table I. Using the regression parameters b and a , the distribution constants can be calculated for any temperature within the 25–70°C range. The values of the coefficient of determination, r^2 , approach unity, indicating a good correlation of the experimental data

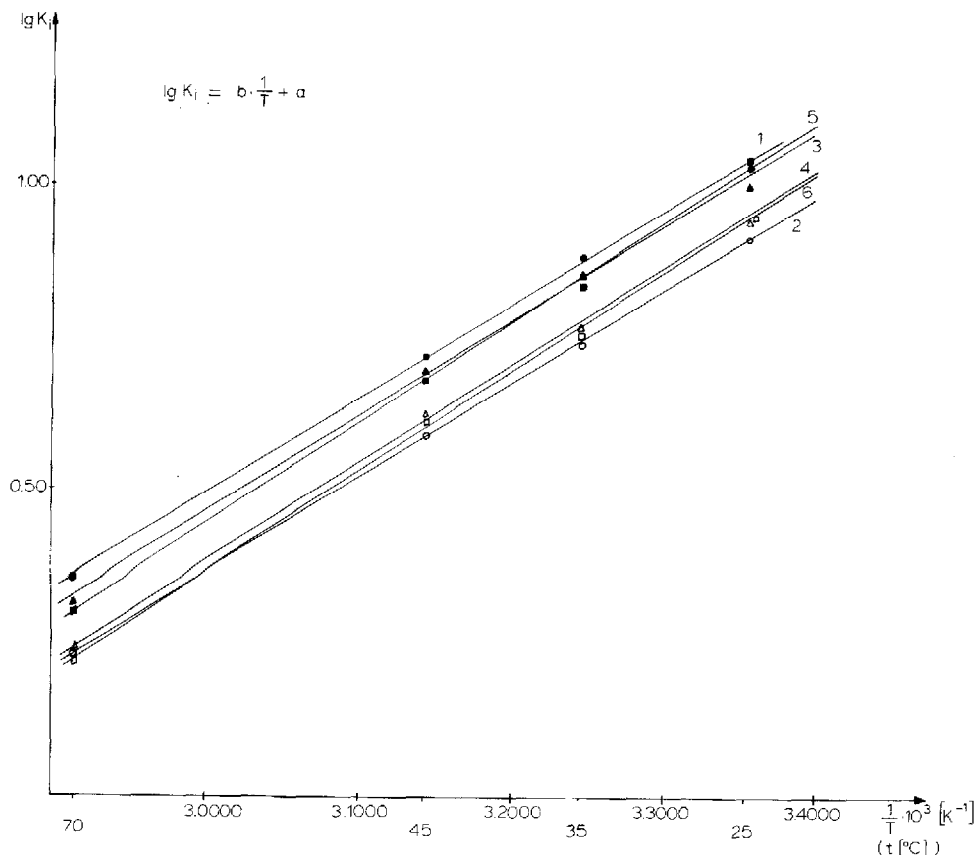


Fig. 2. The effect of temperature on the distribution coefficient of thiophene for distilled (DW) and artificial sea water (ASW) at various concentration levels: ●, [DW] = 10.4 ppm; ○, [ASW] = 10.4 ppm; ▲, [DW] = 1.04 ppm; △, [ASW] = 1.04 ppm; ■, [DW] = 0.104 ppm; □, [ASW] = 0.104 ppm.

TABLE I

TEMPERATURE, CONCENTRATION AND IONIC-STRENGTH DEPENDENCE OF THE DISTRIBUTION COEFFICIENTS OF SELECTED ORGANOSULPHUR COMPOUNDS

Compound	Concentration (ppm by weight)	Type of water or ionic strength*	Distribution coefficient K_i at 25°C**	Regression parameters***		
				b	a	r ²
Dimethyl sulphide	10	DW	13.72	1637.3	-4.354	0.9986
	10	ASW	10.75	1550.3	-4.168	0.9995
	1	DW	13.42	1635.6	-4.358	0.9998
	1	ASW	11.21	1575.4	-4.234	0.9999
	1	1	11.95	1669.1	-4.521	0.9976
	1	2	8.45	1701.4	-4.780	0.9964
	1	3	6.11	1486.8	-4.201	0.9981
	1	4	4.45	1386.5	-4.002	0.9913
	0.1	DW	14.29	1598.2	-4.205	0.9987
0.1	ASW	11.52	1618.4	-4.367	0.9996	
Diethyl sulphide	10	DW	11.79	1939.7	-5.434	0.9993
	10	ASW	8.97	1836.0	-5.206	0.9989
	1	DW	14.33	2175.4	-6.140	0.9990
	1	ASW	9.92	1932.5	-5.485	0.9985
	1	1	9.93	2006.6	-5.733	0.9989
	1	2	6.75	1900.3	-5.544	0.9887
	1	3	3.88	1540.4	-4.577	0.9908
	1	4	2.89	1437.8	-4.362	0.9480
	0.1	DW	14.54	1926.8	-5.300	0.9987
0.1	ASW	11.46	2055.5	-5.835	0.9998	
Di-n-propyl sulphide	10	DW	8.66	1656.5	-4.618	0.9999
	10	ASW	6.13	1901.4	-5.590	0.9909
	1	DW	7.55	1954.8	-5.678	0.9990
	1	ASW	5.34	2022.1	-6.054	0.9947
Diisopropyl sulphide	10	DW	7.67	2089.4	-6.123	0.9995
	10	ASW	5.09	1951.4	-5.838	0.9991
	1	DW	7.00	2000.3	-5.864	0.9997
	1	ASW	4.63	1888.5	-5.668	0.9986
	0.1	DW	7.41	2059.8	-6.038	0.9997
	0.1	ASW	4.70	2024.2	-6.117	0.9999
Dimethyl disulphide	10	DW	22.22	1657.1	-4.211	0.9997
	10	ASW	16.07	1609.0	-4.191	0.9809
	1	DW	24.66	1854.4	-4.828	0.9971
	1	ASW	15.83	1674.5	-4.417	0.9743
	1	1	20.19	1650.3	-4.230	0.9923
	1	2	13.45	1805.0	-4.925	0.9989
	1	3	10.11	1873.3	-5.278	0.9855
	1	4	8.83	1640.8	-4.557	0.9982
Diethyl disulphide	10	DW	16.06	1608.9	-4.190	0.9971
	10	ASW	11.98	1776.8	-4.881	0.9894
	1	DW	15.30	1865.0	-5.071	0.9971
	1	ASW	10.33	1797.3	-5.014	0.9957

TABLE I (continued)

Compound	Concentration (ppm by weight)	Type of water or ionic strength*	Distribution coefficient K_i at 25°C**	Regression parameters***		
				b	a	r^2
Thiophene	10	DW	11.09	1563.6	-4.199	0.9992
	10	ASW	8.20	1548.3	-4.279	0.9999
	1	DW	10.51	1580.0	-4.277	0.9976
	1	ASW	8.95	1621.8	-4.487	0.9987
	0.1	DW	10.77	1661.9	-4.542	0.9987
	0.1	ASW	8.88	1639.7	-4.551	0.9993
2-Methylthiophene	10	DW	10.06	1651.04	-4.535	1.0000
	10	ASW	6.91	1620.3	-4.595	0.9997
	1	DW	10.04	1741.1	-4.838	1.0000
	1	ASW	7.96	1691.5	-4.772	0.9975
	0.1	DW	10.17	1886.6	-5.320	0.9957
	0.1	ASW	7.34	1727.2	-4.928	0.9995
Methanethiol	10	DW	9.88	1347.1	-3.537	0.9975
	10	ASW	7.98	903.0	-2.127	0.9707
Ethanethiol	10	DW	6.88	1486.1	-4.147	0.9997
	10	ASW	5.61	1393.7	-3.926	0.9995
<i>n</i> -Propanethiol	10	DW	5.99	1552.2	-4.428	0.9994
	10	ASW	4.72	1491.7	-4.329	0.9986
<i>n</i> -Butanethiol	10	DW	5.38	1655.9	-4.823	0.9994
	10	ASW	3.36	1623.3	-4.918	0.9970

* DW = Distilled water ($I = 0$), ASW = artificial sea water ($I \cong 0.7$), numbers (1, 2, 3, 4) indicate the ionic strength of an aqueous sodium sulphate solution.

** The K_i values determined from the linear regression curve.

*** The linear regression curve had the following form: $\log K_i = b \cdot \frac{1}{T} + a$, the parameters b and a being calculated on the basis of the K_i values determined for 25, 35, 45 and 70°C.

with the linear regression curves. It follows from Table I that, in the majority of cases, the K_i value does not depend significantly on the concentration of the studied solutions in the 10–0.1 ppm range and the differences between them result from random errors only: for comparison see the confidence intervals in the determination of K_i values (Table II). However, in several cases the observed differences are too large to be explained by random errors alone, e.g. for diethyl, di-*n*-propyl and diisopropyl sulphides. This phenomenon may be brought about by concomitant adsorption mechanisms. Although the ionic strength of the solutions has marked influence on the distribution constants, as supported by the experimental data from Table I for dimethyl and diethyl sulphides as well as for dimethyl disulphide, this effect diminishes to a large extent at higher temperatures. This is illustrated in Fig. 3 which shows the dependence of distribution coefficient of diethyl sulphide on ionic strength at 25, 35, 45 and 70°C. It follows from Fig. 3 that at 70°C the influence of ionic

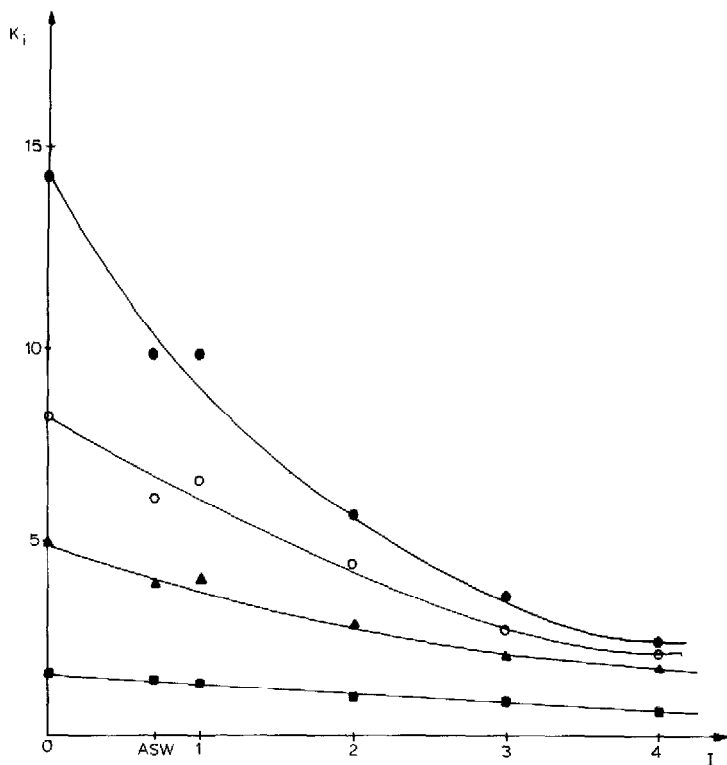


Fig. 3. The dependence of distribution coefficient of diethyl sulphide on ionic strength at various temperatures: ●, 25°C; ○, 35°C; ▲, 45°C; ■, 70°C.

strength on K_i , and hence the detection limit, becomes considerably smaller. Therefore, the equilibrium can be shifted in favour of the gaseous phase by means of temperature alone.

The evaluation of the precision of the determination of the distribution coefficients and the estimation of the detection limits for the direct HS-GC analysis are presented in Table II. The precision is expressed in terms of the relative standard deviation, s_r , defined as

$$s_r = \frac{s}{K_i} \cdot 100\% \quad (8)$$

In addition, the confidence interval, $t \cdot \bar{s}$, at a 95% probability level is included in Table II to characterize better the uncertainty in the experimental data. The upper and lower entry for each compound represent the best and worst cases, respectively. Comparison of the precision estimates (s , and $t \cdot \bar{s}$) with the experimental conditions (temperature, type of water and concentration of solutions) permits us to conclude that the random error, which is measured by the standard deviation, does not significantly depend on the three variables. Although in two cases [for (*n*-C₃H₇)₂S and *n*-C₄H₉SH] the relative standard deviation exceeds 10%, on average, s_r was *ca.* 5%.

TABLE II

PRECISION OF DETERMINATION OF THE DISTRIBUTION COEFFICIENTS AND ESTIMATED DETECTION LIMITS

Compound	Type of water	Concentration (ppm)	<i>t</i> (°C)	\bar{K}_i^*	Number of measurements, <i>n</i>	Relative standard deviation, <i>s_r</i> (%)	Confidence interval, <i>t</i> · \bar{s} , for <i>P</i> = 95%	Detection limit (ppb)**
Dimethyl sulphide	DW	10	35	9.28	2	0.2	0.17	4
	DW	1	25	14.09	3	8.7	3.04	
Diethyl sulphide	ASW	1	25	10.26	3	0.1	0.03	2
	ASW	1	35	5.87	3	6.6	0.96	
Di- <i>n</i> -propyl sulphide	DW	1	70	1.26	3	1.6	0.05	0.8
	ASW	1	25	6.81	4	12.6	1.36	
Diisopropyl sulphide	DW	1	45	3.22	3	1.8	0.14	0.9
	DW	10	35	4.64	4	9.4	0.69	
Dimethyl disulphide	DW	10	25	26.54	3	1.5	0.99	7
	ASW	1	35	12.44	4	8.3	1.64	
Diethyl disulphide	DW	10	25	18.67	3	1.6	0.74	3
	ASW	1	70	2.09	4	9.8	0.33	
Thiophene	ASW	10	25	9.09	2	0.1	0.08	2
	DW	0.1	35	7.89	3	8.8	1.72	
2-Methylthiophene	ASW	10	35	5.10	3	2.0	0.25	1.5
	ASW	0.1	70	1.49	3	9.3	0.34	
Methanethiol	DW	10	35	6.58	4	2.5	0.26	8
	DW	10	70	2.48	4	9.5	0.37	
Ethanethiol	ASW	10	35	3.92	5	1.7	0.08	2
	DW	10	45	3.36	8	4.5	0.13	
<i>n</i> -Propanethiol	ASW	10	25	4.83	5	1.6	0.09	1.5
	DW	10	45	2.83	8	7.5	0.18	
<i>n</i> -Butanethiol	ASW	10	35	2.19	4	4.6	0.16	1
	DW	10	45	2.35	4	19.9	0.74	

* Average of experimental values.

** Calculated from K_i at 70°C averaged over concentration and ionic strength. Upper and lower entries for each compound represent the best and worst cases, respectively.

The scatter of K_i values can be ascribed mainly to errors associated with the handling of the HS samples. Nevertheless, the average K_i values seem to be reliable, as is shown by the good linearity of the temperature dependence $\log K_i = f\left(\frac{1}{T}\right)$ (see Table I).

The detection limit, c_{iLO}^{\min} , was estimated from the relationship

$$c_{iLO}^{\min} = K_i \bar{A}_{\min} \overline{\cot \alpha} \cdot \frac{1}{v_G} \quad (9)$$

assuming $v_G = 1 \text{ cm}^3$ and the minimum peak area that can be correctly integrated,

$\bar{A}_{\min} = 500$ integration units; $\overline{\cot \alpha}$ is the average calibration factor for sulphur compounds when using flame-ionization detection and K_i is the distribution coefficient at 70°C averaged over concentration and ionic strength. The values of c_{iLO}^{\min} indicate that the direct HS-GC analysis of aqueous solutions of organosulphur compounds at 70°C permits their determination in the ppb range.

The solubilities and the Raoult-law activity coefficients for aqueous solutions of organosulphur compounds were estimated in the following manner. The distribution constant of an analyte can be expressed in terms of the thermodynamic properties of the system (neglecting the quantities accounting for the effects of non-ideality of the gaseous phase and compressibility of the condensed phase)⁴:

$$K_i = \frac{RTd_L}{\gamma_i p_i^0 M_L} \quad (10)$$

where R is the perfect-gas constant, d_L is the density of the condensed phase, γ_i and p_i^0 are the Raoult-law activity coefficient and the saturated vapour pressure of component i , respectively, and M_L is the molecular weight of the condensed phase, all the above quantities referring to a temperature of the system, T . Hence, knowing R , T , d_L , M_L and p_i^0 and determining K_i , γ_i can be calculated from eqn. 10 written in the form:

$$\gamma_i = \frac{RTd_L}{K_i p_i^0 M_L} \quad (11)$$

The values of p_i^0 at 25°C were calculated from the Antoine equation using the data reported in a handbook by Boublik *et al.*¹⁹. The solubility in water, S_i , was estimated on the basis of the following equation⁵:

$$S_i = \frac{55,500 M_i}{\gamma_i} \quad (12)$$

where S_i is expressed in mg/l (ppm) and M_i is the molecular weight of compound i . This approximate relationship is valid if the activity coefficient is a constant, which is generally true for concentrations below 1% (10,000 ppm)²⁰. The values of γ_i , S_i and p_i^0 for the investigated sulphur compounds are listed in Table III. The values of γ_i and S_i at temperatures different from 25°C can be calculated employing eqns. 11 and 12 by substituting appropriate values for K_i (calculated from the data in Table I), T , d_L and p_i^0 . As expected, the value of the activity coefficient increases with molecular weight whereas the solubility in water decreases going along a homologous

TABLE III

ESTIMATED VALUES OF SOLUBILITY IN WATER AND THE RAOULT-LAW ACTIVITY COEFFICIENT FOR SELECTED ORGANOSULPHUR COMPOUNDS CALCULATED FROM THE DISTRIBUTION COEFFICIENTS AT 25°C AND OTHER RELEVANT THERMODYNAMIC DATA

Compound	b.p. (°C)	p_i^0 at 25°C (atm)	S_i at 25°C (ppm)	γ_i at 25°C
Dimethyl sulphide	37.3	0.636	22000	160
Diethyl sulphide	92.1	0.076	4100	1200
Di- <i>n</i> -propyl sulphide	142.38	0.008	310	21000
Diisopropyl sulphide	120.02	0.019	680	9700
Dimethyl disulphide	109.7	0.038	3400	1500
Diethyl disulphide	154	0.006	470	14000
Thiophene	84.16	0.105	3900	1200
2-Methylthiophene	112.56	0.035	1400	3800
Methanethiol	6.2	1.997	39000	69
Ethanethiol	35	0.694	12000	280
<i>n</i> -Propanethiol	67.7	0.203	3800	1100
<i>n</i> -Butanethiol	98.46	*	—	—

* No data available.

series. Comparison of the distribution constants for compounds belonging to one homologous series indicates that the K_i values decrease with molecular weight (Table I) and hence the concentration in the gaseous phase increases with M_i . As a result, the detection limits are lower for compounds with higher molecular weight (Table II). Although the vapour pressure decreases with increasing M_i , so does the solubility (Table III). The latter effect predominates, resulting in an overall increase in c_{iG} with increasing molecular weight for all types of compounds investigated.

The calculated values for the solubility in water and the distribution constants were compared with literature data to verify the experimental procedure employed. Verschueren²¹ reported the following values: $S_i = 3130$ mg/l at 20°C for diethyl sulphide and $S_i = 15000$ mg/l for ethanethiol at an unspecified temperature. The respective values calculated from our data are 3270 mg/l for $(C_2H_5)_2S$ (a difference of 4.5%) and 12360 at 25°C for C_2H_5SH (a difference of ca. 18%; however, the value of 15000 mg/l is given for an unknown temperature). The value of K_i at 60°C for methanethiol reported by Field and Gilbert⁹ is equal to 3.14, whereas that calculated from the present data equals 3.21, the difference amounting to 2.2%. Hence, the data determined in the present study are in a good agreement with the literature data.

On the basis of the above discussion the following conclusions can be drawn.

(1) In a given homologous series of the sulphur compounds investigated, the distribution coefficients, and hence the detection limits, decrease with molecular weight.

(2) The increase of the amount of compound in the gaseous phase can be accomplished most conveniently by elevation of temperature; the effect of ionic strength on the K_i values at 70°C is insignificant.

(3) With some exceptions, the distribution constants do not essentially depend on the concentration of the model solutions in the investigated concentration range, thus indicating linearity of the partition isotherm.

(4) The K_i values reported in the present paper cannot be generally used for quantitative analysis by HS-GC which has to be carried out by calibration (standard-addition^{1,4} or sample-addition^{2,2} calibration); however, the estimated detection limits are in the order of 1–10 ppb, which shows the broad applicability of direct HS-GC analysis for solutions of organosulphur compounds.

(5) The estimated aqueous solubilities of sulphur compounds can partially fill the gap existing in the literature and may be employed for calculations concerning environmental pollution control.

ACKNOWLEDGEMENT

This work was supported by grant MR.I-15 from the Institute of Oceanology (Sopot) of the Polish Academy of Sciences.

REFERENCES

- 1 J. Novák, *Quantitative Analysis by Gas Chromatography*, Marcel Dekker, New York, 1975, pp. 107–156.
- 2 H. Hachenberg and A. P. Schmidt, *Gas Chromatographic Headspace Analysis*, Heyden, London, New York, Rheine, 1977.
- 3 B. Kolb (Editor), *Applied Headspace Gas Chromatography*, Heyden, London, Philadelphia, Rheine, 1980.
- 4 J. Drozd and J. Novák, *J. Chromatogr.*, 165 (1979) 141.
- 5 W. F. Cowen and R. K. Baynes, *J. Environ. Sci. Health*, A15 (1980) 413.
- 6 W. Chrzanowski and R. Staszewski, *Proc. Annual Conference of the Polish Chemical Society, Lublin, 1982*, p. 458.
- 7 L. Rohrschneider, *Anal. Chem.*, 45 (1973) 1241.
- 8 A. G. Vitenberg, B. V. Ioffe and V. N. Borisov, *Chromatographia*, 7 (1974) 610.
- 9 T. G. Field and J. B. Gilbert, *Anal. Chem.*, 38 (1966) 628.
- 10 I. H. Williams and F. E. Murray, *Pulp Pap. Mag. Can.*, 1966, p. 347.
- 11 T. T. Toan, R. Bassette and T. J. Claydon, *J. Dairy Sci.*, 48 (1965) 1174.
- 12 J. C. Miers, *J. Agric. Food Chem.*, 14 (1966) 419.
- 13 M. Kawabata, K. Ohtsuki, H. Kokura and Y. Wakahara, *Agric. Biol. Chem.*, 41 (1977) 2285.
- 14 T. Takahashi, S. Nakajima, I. Konishi, H. Miedauer and L. Narziss, *Bratnwissenschaft*, 31 (1978) 1.
- 15 O. Leppanen, J. Denslow and P. Ronkainen, *J. Inst. Brew.*, 85 (1979) 350.
- 16 G. Mazza, M. Le Maguer and D. Hadziyev, *Can. Inst. Food Sci. Technol. J.*, 13 (1980) 87.
- 17 H. Murayama, I. Kifune and T. Uemura, *Niigata Rikagaku*, 6 (1980) 11.
- 18 J. P. Riley and G. Skirrow, (Editors), *Chemical Oceanography*, Academic Press, London, New York, 1965, Vol. 1, p. 648.
- 19 T. Boublík, V. Fried and E. Hála, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam, London, New York, 1973.
- 20 B. Kolb, *J. Chromatogr.*, 122 (1976) 553.
- 21 K. Verschueren, *Handbook of Environmental Data on Organic Chemicals*, Van Nostrand Reinhold, New York, 1977.
- 22 J. Drozd and J. Novák, *Chromatographia*, 16 (1982) 309.