Journal of Chromatography, 112 (1975) 319–327
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CHROM. 8438

DETERMINATION OF GAS–LIQUID PARTITION COEFFICIENTS BY MEANS OF GAS CHROMATOGRAPHIC ANALYSIS

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SUMMARY

Static methods of determining gas–liquid partition coefficients based on the gas chromatographic measurement of the change in concentration of the compound of interest in one of the phases after its equilibration with the other are considered. The methods can be used for the accurate determination of very small (a few hundredths of a unit) and large (a few thousand units) partition coefficients in dilute solutions of almost all volatile compounds. The proposed methods make use of thermostatted variable-volume vessels (glass syringes) and reduce the errors associated with adsorption on the vessel walls and injection of the liquids under study into the chromatographic column.

INTRODUCTION

The wide application of gas chromatographic methods based on the equilibrium distribution of the compounds of interest between two phases (for a review, see ref. 1) requires the knowledge of the partition coefficients (K) at extreme dilutions. Most of the available data on gas–liquid equilibrium refer to comparatively high concentrations and therefore cannot be used directly for trace determinations or for checking the theory of dilute solutions. Gas chromatography that can be used in both its dynamic (involving the study of retention parameters) and static versions based on the measurement of concentrations in equilibrated heterogeneous systems appears to be promising for the determination of partition coefficients at extremely low concentrations. The possibility of carrying out gas chromatographic determinations of partition coefficients from the retention parameters has been discussed[2]. The dynamic method is widely employed in the determination of partition coefficients in non-volatile liquids, but with volatile solvents and at low values of K the use of the dynamic method becomes impracticable. Also, it should be borne in mind that adsorption at the interface[3] and deviations from equilibrium may occur.

The static method is free from these limitations, but the limits of its applicability in extremely dilute solutions remain unclear. Three papers published in the past 10 years[4–6] reported on the use of a version of the static method for the determination of K that reduces to a gas chromatographic analysis of the gas phase before and after its equilibration with the liquid phase. After equilibrium distribution of a compound

has been attained in a closed volume, the concentrations in the liquid and gas phases are C'_L and C'_G, respectively, and the magnitude of K can be calculated from the equation

$$K = \frac{C'_L}{C'_G} = \frac{V_G (C^0_G - C'_G) + V_L C^0_G}{V_L C'_G} \quad (1)$$

where C^0_G is the initial vapour concentration of the compound in the gas phase and and V_G and V_L are the volumes of the gas and liquid phases, respectively, in the equilibrated system.

As the amounts of the compound to be determined are so small that the detector (*e.g.*, of the flame ionization type) operates in the linear region, one can use the height or area of the peak in the chromatogram in place of concentrations.

The main advantage of this method is that the analyses of the gas phase before and after introduction of the solvent are run under identical conditions and with the same injection device, which excludes systematic errors associated with the conditions of chromatographic analysis and the volume of the sample injected.

In earlier work[4–6], this technique was employed in order to obtain data on the solubility of methyl iodide and simple sulphur compounds (mercaptans, sulphides and disulphides) and to determine partition coefficients for the major classes of organic compounds, but possible sources of error associated, in particular, with the use of constant-volume vessels were not considered. In this work, we report on an evaluation of the sources of error and of the limits of applicability for the static technique considered, and describe a modified method that can be used for the precise determination of both large and small values of K.

SOURCES OF ERROR AND LIMITS OF APPLICABILITY OF THE METHOD

Constant-volume vessels can be employed only at high V_G/V_L ratios, as the introduction of a liquid into the vessel results in the compression or displacement of the gas. The need for large volumes of gas and small amounts of liquid in the method imposes a severe limitation on the compounds, particularly those with small K, for which this quantity can be determined with sufficient accuracy. It follows from eqn. 1 that

$$\frac{\Delta K}{K} = \frac{C^0_G}{C^0_G - C'_G}\left(\frac{\Delta C^0_G}{C^0_G} + \frac{\Delta C'_G}{C'_G}\right) = \left(\frac{V_G}{K V_L} + 1\right)\left(\frac{\Delta C^0_G}{C^0_G} + \frac{\Delta C'_G}{C'_G}\right) \quad (2)$$

Eqn. 2 shows that the error of the method increases with increase in the ratio V_G/V_L and with decrease in K. This equation enables one to find the lowest values of K that can be determined for a given error in K, the known error in the measurement of concentration and a given gas to liquid volume ratio. For instance, if the total error in determining K should not exceed 5%, and $(\Delta C^0_G/C^0_G + \Delta C'_G/C'_G) = 2\%$, at $V_G/V_L = 100$ (which is close to the conditions chosen in ref. 5), then it follows from eqn. 2 that this method can be recommended for compounds with K not less than 66 and, at $V_G/V_L = 500$, not less than 330.

The upper limit of the value of K that can be determined in this way depends

on the possibility of measuring accurately the residual concentrations, C'_G, of the compound in the gas after introduction of the liquid. If the accuracy of measuring the ratio C^0_G/C'_G is maintained at the level of a few per cent as the magnitude of the ratio proper increases up to about 100, then, as evident from eqn. 2, when $V_G/V_L = 100$ one can determine K up to 10^4, and when $V_G/V_L = 10$, values of K up to 10^3.

Desorption of the compound from the walls as they come into contact with the liquid introduced into the vessel may represent an additional source of error. The errors associated with adsorption on the walls become particularly noticeable with slight changes of concentration in small volumes of the gas phase.

DETERMINATION OF PARTITION COEFFICIENTS IN VARIABLE-VOLUME VESSELS

The above disadvantages of the method can be removed if equilibration of the compound of interest between the liquid and gas is carried out in variable-volume vessels made of low-sorption material, *e.g.*, in glass syringes with volumes up to 100 ml. The device proposed for this purpose is shown in Fig. 1*. A thermostatted glass syringe permits the collection of a gaseous (or liquid) sample for subsequent injection into the chromatograph at constant pressure without driving the system out of equilibrium. When a solvent is introduced into a variable-volume vessel at constant pressure, eqn. 1 simplifies to

$$K = \frac{V_G}{V_L} \cdot \frac{C^0_G - C'_G}{C'_G} \tag{3}$$

In addition, the use of such a device removes the limitation on the amount of the liquid introduced into the air–vapour mixture, which substantially increases the range of partition coefficients that can be determined. Indeed, reduction of the ratio V_G/V_L to about 1 permits the limit of accurately determined values of K to be reduced

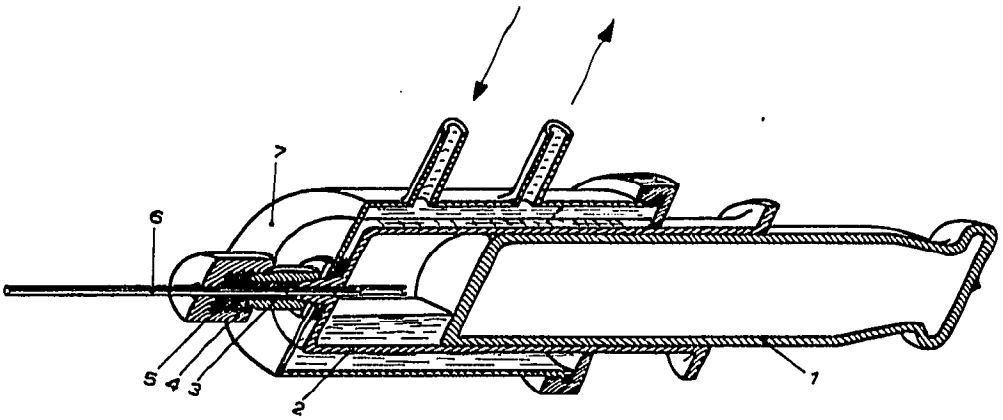

Fig. 1. Variable-volume device for injection of equilibrated air–vapour mixtures into chromatographic column. 1, Plunger of 50–100-ml glass hypodermic syringe; 2, syringe cylinder; 3, PTFE bush; 4, rubber plug sealing bush fixed rigidly to the syringe; 5, elastic rubber plug; 6, steel or PTFE capillary tube connecting the syringe to the chromatograph injection unit; 7, Perspex thermostatting jacket.

* This device is described in detail in another paper[11].

to about 1. Another advantage of this device is the possibility of taking into account adsorption on the walls and of introducing the corresponding correction into the calculation of the partition coefficients. Adsorption losses that occur when an air–vapour mixture is admitted into the syringe can be found by measuring the change in concentration in the gas (or liquid) sample introduced into the vessel whose adsorptivity is to be determined. It can be readily achieved by means of two syringes connected with a double-ended needle.

One syringe (A) of volume 100 ml is filled with an air–vapour mixture with a concentration of the compound C^0. The area of the peak, I^0, in the chromatogram corresponding to this concentration is then determined, and the gas from syringe A is subsequently transferred through the double-ended needle into syringe B. Prior to this, the dead volume in the bore of syringe B filled with air is flushed out with the air–vapour mixture from syringe A. The peak area, I', for the gas in syringe B is determined in a manner similar to that for syringe A. If C^0 is known or pre-set and the volume of the transferred gas, V_g, is known, then the amount of compound adsorbed, q, on unit surface area of the walls of syringe B can be derived from the expression

$$q = \frac{C^0 V_g}{S}\left(\frac{I^0 - I'}{I^0}\right) \tag{4}$$

where S is the surface area of the walls of the vessel.

The sensitivity of this method of determining adsorption losses representing the difference $I^0 - I'$ depends on the ratio of the volume of gas to the surface area of syringe B. The magnitude of the difference $I^0 - I'$ increases with decrease of this ratio. Therefore, the syringe that we used as B was of 10-ml volume, *i.e.*, a syringe with the minimum volume of gas required to carry out several measurements of I'. Taking into account the amount q of the compound adsorbed, the partition coefficient can be derived from the following equation:

$$K = \frac{V_G (C_G^0 - C_G') + qS}{V_L C_G'} \tag{5}$$

It should be noted that such a calculation is valid only if the adsorption on the walls from the solution is assumed to be much less than that from the gas phase. If this is not so, the sorption on the walls from solution can be evaluated by using the above method. Then the quantity q in eqn. 5 will represent the difference in the amounts of the compound in question adsorbed per unit area of dry and solvent-wetted walls of the vessel. In our experiments with carbonyl and aromatic compounds, the amount of the compound of interest (qS) adsorbed in 100-ml syringes did not exceed 1.8% of ($C_G^0 V_G$). This figure lies within the error limits of determining $I^0 - I'$ and hence was not taken into account in the calculation of K.

The use of a glass syringe to determine K by introducing a solvent into the air–vapour mixture raises the possibility of the solvent entering the gap between the plunger and the cylinder. With ordinary hypodermic syringes, such a loss of liquid would be almost impossible to take into account as the liquid that enters this gap is a solution of indeterminate concentration rather than a pure solvent. This volume

can range from 0.05 to 0.2 ml. Therefore, when working at $K > 100$, which requires the introduction of small volumes of solvent (less than 1 ml), this source of error becomes substantial. However, it can be excluded by employing a PTFE precision plunger that fits to the cylinder with virtually no gap.

The initial concentration, C_G^0, of the air–vapour mixture is set by introducing into a dry, clean syringe a few millilitres of a volatile compound or a known volume of gas containing the vapour of this compound. The syringe is thermostatted for not less than 20–30 min. In the course of thermostatting, the gas is mixed thoroughly by shaking it with PTFE grains. A few samples of gas are injected from the syringe into the chromatograph, and the corresponding peak areas in the chromatograms are determined. In order to achieve this, a steel or PTFE capillary tube (component 6 in Fig. 1) connecting the inner cylinder space with the thermostatted gas sampling valve is led into the cylinder (1) through an air-tight seal (5). The equilibrated gas displaced by the plunger from the syringe fills the injection loop of the gas sampling valve. With a loop volume of 0.5 ml and connecting tubes 1 mm in diameter and 30 mm in length, the gas in the loop is completely replaced after the passage of 2–3 ml of the mixture under analysis. The solvent is introduced into the variable-volume device by means of syringes through the elastic rubber plug (5). The amount of liquid introduced is determined accurately from the difference in the weight of the syringe. At the moment of admission of liquid, the plunger (1) should be in the position corresponding to the precisely known volume of the cylinder (2). This position is set by means of special gauges that limit the travel of the plunger. After the introduction of the liquid, the system is maintained under constant mixing for 1 h so as to establish equilibrium distribution. The gas phase is then injected into the chromatograph and the peak area corresponding to the concentration C_G' is determined. The peak areas corresponding to the concentrations C_G^0 and C_G' and the volumes of the liquid and gas permit the partition coefficient to be calculated by means of eqn. 3.

EXPERIMENTAL

The analyses were carried out on a Tsvet Model 102 chromatograph under the

TABLE I

CONDITIONS OF GAS CHROMATOGRAPHIC ANALYSIS

Parameter	*Compound analyzed*		
	Hydrocarbons	*Carbonyl compounds*	*Sulphur compounds*
Stationary phase	Polyethylene glycol adipate	Polyethylene Polyox-100	Polyethylene glycol adipate
Amount of stationary phase (%)	20	20	15
Solid support and grain size (mesh)	Spherochrome I, 60–80	Spherochrome I, 60–80	Celite C-22, 80–100
Column length (m)	3	2	2
Temperature (°C)	100	90	90
Carrier gas flow-rate (ml/min)	60	50	50

conditions specified in Table I. The peak areas in the chromatograms were calculated with the aid of a TR-2213 digital integrator.

The air–vapour mixtures equilibrated with the liquid were injected into the chromatographic column from a glass syringe thermostatted to within ±0.1°, using a gas sampling valve with an injection loop of volume 0.5 ml mounted in the detector thermostat and operating at 100°.

We used commercial reagents containing not less than 99% of the compound of interest, this concentration being ascertained gas chromatographically (Table I). Distilled water and glacial acetic acid were employed as solvents.

When determining the partition coefficients by the introduction of a liquid into an air–vapour mixture, the initial concentration of the compound (C_G^0) was set by diluting a known volume of saturated vapour of this compound in a glass syringe with a PTFE plunger. Syringes of volume 0.25, 1 and 2 ml were used in order to transfer 0.25–2 ml of the liquid phase into an air–vapour mixture of volume 70–100 ml. The equilibrium concentration in the liquid (C_L') varied in different experiments in the range 0.1–1%. This quantity was calculated by the equation

$$C_L' = \frac{Q\,(I^0 - I')}{V_L\,I^0} \tag{6}$$

where Q is the amount of the compound of interest in the air–vapour mixture.

In the partition coefficient measurements involving the replacement of the gas phase, the initial concentration of the compound in the liquid varied in the range 0.01–0.1% and was set by introducing 3–5 μl of the pure compound into the corresponding volume of solvent from a 10-μl syringe. The ratio V_G/V_L in these experiments ranged from 5 to 20.

RESULTS AND DISCUSSION

The technique was used for the determination of large partition coefficients. The results are listed in Table II. A comparison of our results with published data shows agreement within experimental error for the data obtained by both the static[7] and dynamic[1] methods.

TABLE II

LIQUID–GAS PARTITION COEFFICIENTS OF AROMATIC HYDROCARBONS AND KETONES

Compound	*Solvent*	*Partition coefficient*		
		Obtained by introducing liquid into air–vapour mixture	*Literature data*	
			Static method[7]	*Dynamic method*[1]
Benzene	Acetic acid	768 ± 39	—	760 ± 50
Toluene	Acetic acid	2070 ± 104	2075 ± 310	2250 ± 140
Acetone	Water	611 ± 31	—	620 ± 40
Methyl ethyl ketone	Water	440 ± 14	469 ± 70	430 ± 30

TABLE III

LIQUID-GAS PARTITION COEFFICIENTS OF BENZENE AND TOLUENE *versus* CONCENTRATION OF ACETIC ACID IN THE LIQUID PHASE AT 25°

Concentration of acetic acid in liquid phase (%)	*Partition coefficient*	
	Benzene	*Toluene*
99.73	773 ± 34	2193 ± 218
97.44	663 ± 10	1777 ± 83
95.34	582 ± 14	1514 ± 53
92.24	485 ± 16	1178 ± 76
83.93	337 ± 12	753 ± 23
76.83	202 ± 26	461 ± 32
64.60	123 ± 6	242 ± 7
56.72	65.3 ± 1.1	112.6 ± 3.7
45.86	39.3 ± 1.3	58.2 ± 3.4

The technique of determining liquid–gas partition coefficients based on introducing the solvent into the air–vapour mixture can also be employed for two- and more-component volatile liquid phases, *i.e.*, systems whose study by the dynamic method involves considerable experimental difficulties. Table III gives the partition coefficients of benzene and toluene, obtained by using acetic acid at various concentrations, which are required for the calculation of the equilibrium concentration of impurities from humid air in acetic acid[8].

Small values of K (less than 10 and down to a few hundredths), which can be obtained only poorly from the retention parameters, can be determined by a technique based on replacing with a pure gas the gas phase equilibrated with the solution of a compound. This technique consists in collecting a pre-set volume, V_L, of the liquid containing the compound of interest into a thermostatted hypodermic syringe. The gas (air in most instances) of volume V_G is collected together with the liquid and the syringe is plugged with an air-tight elastic rubber seal. After thermodynamic equilibrium between the two phases has been attained, the initial concentration of the compound in the liquid (C_L^0) or the corresponding concentration in the gas phase (C_G^0) is determined gas chromatographically. Next, the gas phase is driven completely out of the syringe, air of volume V_G is sucked into the syringe, the gas and liquid phases are equilibrated and the solution or gas above it are once again analyzed gas chromatographically, yielding the concentration C_L' or C_G^0, respectively. When these quantities are known, the value of K can be derived from the equation

$$K = \frac{C_L'}{C_L^0 - C_L'} \cdot \frac{V_G}{V_L} = \frac{C_G'}{C_G^0 - C_G'} \cdot \frac{V_G}{V_L} \tag{7}$$

The advantage of this technique is that it does not involve errors associated with the washing out of the compounds adsorbed on the walls of the vessel. Also, the compound does not need to be pure as one can use it in the form of a solution in the solvent for which the partition coefficient is to be determined. This method can obviously be employed provided that the isotherm of distribution remains linear in the concentration range C_L^0 to C_L' within experimental error.

If the gas phase is analyzed, then from eqn. 6 it follows that

$$\frac{\Delta K}{K} = \frac{C_G^0}{C_G^0 - C_G'}\left(\frac{\Delta C_G^0}{C_G^0} + \frac{\Delta C_G'}{C_G'}\right) = \left(\frac{K V_L}{V_G} + 1\right)\left(\frac{\Delta C_G^0}{C_G^0} + \frac{\Delta C_G'}{C_G'}\right) \quad (8)$$

This expression shows that the error in the determination of K in the version based on the introduction of the gas phase decreases with increase in the ratio V_G/V_L and with decrease in K, in contrast to the above method. Therefore, small partition coefficients (less than 10) at $(\Delta C_G^0/C_G^0 + \Delta C_G'/C_G') = 2\%$ and $V_G/V_L = 20$ (which are the conditions typical for a 50–100-ml syringe) can be determined with an error that does not exceed 3%.

The technique of determining peak areas when injecting equilibrated gas into a chromatographic column and of measuring the volumes of the liquid and gas phases is similar to that used to introduce a liquid into the air–vapour mixture. The time taken to establish an equilibrium distribution of a compound between a liquid and gas (with periodic shaking) is 30–60 min.

Table IV lists the partition coefficients of simple sulphur-containing compounds and aromatic hydrocarbons between water and air obtained by replacing the gas phase equilibrated with the solution of the compound of interest. The published values for the partition coefficients of sulphur compounds were found by the method involving the introduction of a solvent into the air–vapour mixture in a constant-volume vessel. The data for the hydrocarbons were obtained by static measurements. A comparison of our results and published figures for K reveals fairly good agreement, although the published data may be considered to be only approximate as they were derived by us from the graph in ref. 4.

This work has shown that by choosing properly one of the above techniques, depending on the magnitude of K, the properties of the compound of interest and the

TABLE IV

PARTITION COEFFICIENTS OF SIMPLE SULPHUR COMPOUNDS AND AROMATIC HYDROCARBONS BETWEEN WATER (pH 2) AND AIR

Compound	*Temperature (°C)*	*Partition coefficient*		
		Obtained by replacing equilibrated gas phase	*Literature data*	
			Value	*Reference*
Ethyl mercaptan	20	5.4 ± 0.3	—	
Dimethyl sulphide	20	14.8 ± 1.4	17	4
Dimethyl disulphide	20	20.2 ± 2.0	22	4
Diethyl disulphide	20	11.4 ± 1.1	—	
Benzene	25	4.5 ± 0.15	4.3	9
			4.48	10
Toluene	25	4.7 ± 0.16	4.7	9
			4.52	10

permissible error, one can determine the liquid–gas partition coefficient over a fairly broad range extending from a few hundredths to several thousand units.

ACKNOWLEDGEMENTS

I. M. Balashova and T. Strukova participated in the experimental part of this work.

REFERENCES

1 A. G. Vitenberg, B. V. Ioffe and V. N. Borisov, *Zh. Anal. Khim.*, 29 (1974) 1795; *Chromatographia*, 7 (1974) 610.
2 M. S. Vigdergauz and R. I. Izmailov, *The Application of Gas Chromatography in the Physico-Chemical Characterization of Substances*, (in Russian), Nauka, Moscow, 1970.
3 V. G. Berezkin and V. M. Fateeva, *Zh. Anal. Khim.*, 29 (1974) 2453.
4 I. H. Williams and F. E. Murrey, *Pulp Pap. Mag. Can.*, (1966) 347.
5 P. E. Nelson and J. E. Hoff, *J. Food Sci.*, 3 (1968) 479.
6 R. A. Hasty, *Can. J. Chem.*, 46 (1968) 1643.
7 L. Rohrschneider, *Anal. Chem.*, 45 (1973) 1241.
8 B. V. Ioffe, A. G. Vitenberg and V. N. Borisov, *Zh. Anal. Khim.*, 27 (1972) 181.
9 S. P. Wasik and W. Tsang, *J. Phys. Chem.*, 74 (1970) 2970.
10 R. J. Bohon and W. F. Clauson, *J. Amer. Chem. Soc.*, 73 (1951) 1572.
11 A. G. Vitenberg, I. L. Butaeva and Z. St. Dimitrova, *Chromatographia*, in press.