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Short Communications

A Static Technique for the Determination of Partition Coefficients by Gas Chromatography

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Studies of the solubility of volatile compounds in solvents of high molecular weight are of interest from two points of view. They contribute to the knowledge of the thermodynamics of solutions and they are important in establishing the validity of the theory of gas-liquid chromatography.

A static technique based on measurements in equilibrated heterogeneous systems of the partition coefficient, K, between liquid phase and gas phase has been developed. In this technique the adsorption of the solute on the solid support surface or liquid surface are negligible in contrast to measurements with the GLC-technique. In a number of papers [1-7] versions of the static method are described. In all but one [7] the determination of K is reduced to a gas chromatographic analysis of the gas phase before and after equilibration with the liquid phase. In these methods the desorption of the solute molecules from the walls of the vessel, when the liquid phase is added, introduces an additional source of error. Berezkin *et al.*[7] performed the analysis on both phases after equilibration, and reached a coefficient of variation of 3.5 %. A similar technique was used in this work but with better standardization of the experimental conditions, the precision was significantly improved.

Experimental. Apparatus. The vessel in which the equilibrium was attained (Fig. 1), is a 1000 ml glass bottle with a teflon-lined septum. Inside the bottle a small open container was positioned a few centrimeters below the septum so that liquid samples could be taken with a micro-syringe with a needle length of 5 cm. The small container was fixed to a bent glass rod which was fused to the vessel. A part of the liquid was also placed as a thin layer at the bottom of the vessel in order to facilitate equilibration. The large volume of the vessel was chosen in order to minimize the reduction of the pressure when the gas phase is sampled.

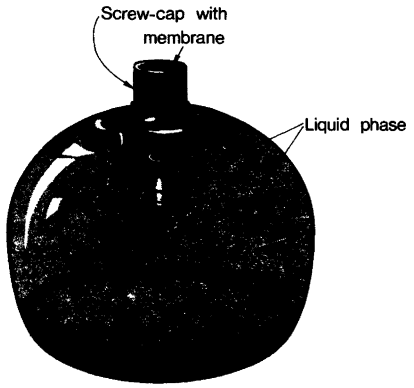

Fig. 1. Equilibrium vessel for the determination of the partition coefficient.

The vessel was loaded with about 15 ml of the liquid phase and flushed with dry nitrogen before it was closed. The solute was added *via* the teflon-lined septum with a micro-syringe (less than 30 μl). The partition coefficient is a constant only when Henry's law is valid. The linear region is observed at concentrations less than 0.3 % according to Berezkin *et al.* The present work has been performed at solute concentrations in the region of 0.02 – 0.2 %. The vessel was immersed in a thermostatically controlled waterbath and equilibrium was attained after about 24 h. This slow approach to equilibrium depends not only on the slow diffusion in the liquid phase but also on the time needed for obtaining homogeneous temperature in a litre of gas. The time can be reduced with an effective stirring system. The pressure of the vessel was adjusted to the ambient with dry nitrogen *via* a needle through the septrum.

The concentration of the solute in the vapour and liquid phases was measured with a Varian Gas Chromatograph, model 3700, with FID. The peak areas in the chromatogram were determined with a Varian digital integrator, model 481. One of the injection ports was exchanged for a six-port gas sampling valve mounted in the column oven. The volume of the gas sampling loop was 0.262 ± 0.002 ml with 95 % confidence and it was determined by filling it with a lead nitrate solution which was titrated with EDTA.

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To ensure that the valve was filled with a homogeneous gas sample, it was flushed with 5 ml of the sample gas. A waiting time of 10 s before injection was found to be appropriate to obtain temperature and pressure equilibrium. The temperature of the column oven, and thus the sample loop, was kept approximately the same as for the equilibrium vessel. Two columns were used, one connected to the six-port valve for the measurements of the gas phase, and the other connected to a conventional injection port for the measurements of the liquid phase. Both columns were connected to the same FID to ensure the same sensitivity. The columns were of stainless steel (2 m long, 2 mm i.d.) packed with 60 – 80 mesh Chromosorb AW-HMDS coated with 15 % Carbowax 1540. The carrier gas was nitrogen with a flow-rate of 30 ml/min. All chemicals had a stated purity in excess of 99 % and were not further purified.

Procedure. For each single value of the partition coefficient a number of measurements in the liquid phase was performed followed by a single determination in the gas phase. Immediately after, the pressure in the vessel was equilibrated. It was sufficient to wait 30 min between each run to obtain partition equilibrium. Differences in temperature or pressure between the vessel and the gas sample valve result either in expansion or concentration of the gas volume. To be able to relate the peak area of the solute to the concentration of the solute in the vessel, temperature and pressure of the system were strictly controlled. The temperature was measured with mercury thermometers (0.05 °C/div.) with a maximum variation of 0.1 °C and calibration traceable to NBS standards; the pressures were measured with a mercury manometer read to a precision of 0.05 mmHg.

If the gas phase is considered as ideal the solute concentration (C_g) in the equilibrium vessel is given by

$$C_g = (P_e/RT_e)x \quad (1)$$

and the injected solute concentration (C_i) by

$$C_i = (P_i/RT_i)x \quad (2)$$

P_e, T_e and P_i, T_i refer to the pressure and temperature of the equilibrium vessel and gas sampling valve, respectively. x is the molar fraction of the solute and R is the gas constant. Hence

$$C_g = (T_iP_eC_i)/(P_iT_e) \quad (3)$$

The partition coefficient is calculated from

$$K = C_l/C_g = (A_lV_gT_eP_i)/(A_gV_lP_eT_i) \quad (4)$$

A_l, V_l and A_g, V_g refer to the areas of the solute peaks and the injected volumes of the liquid and gas phases, respectively.

Results and discussion. The method was applied for n-pentane, n-heptane, diisopropyl ether and ethyl methyl ketone as solutes at 60 °C in n-octadecane as solvent. The results are summarized in Table 1. These systems were chosen in order to check the validity of a new model by Jönsson and Mathiasson[8] for calculating the partition coefficient from gas chromatographic retention data measured in the presence of strong surface adsorption effects. In experiments 1 and 2, two solutes were run simultaneously. Good agreement was obtained whether the experiments were conducted with a single solute (see Table 1; 3 – 5) or in a mixture (see Table 1; 1, 2). Provided that the total amount of solute molecules in the mixture does not exceed the region where Henry's law is valid, the partition coefficient of the volatile components of a multicomponent system can be determined.

In Table 2 the weighted means from different experiments for each solute are compared with the corresponding values of the partition coefficient given by Jönsson and Mathiasson.[8] Good agreement is obtained.

Table 1. Gas-liquid partition coefficients with n-octadecane as solvent at 60.0 °C. Values are given with 95 % confidence intervals.

Solute	Exp.	K at 60.0 °C	Number of measurements
n-Pentane	1	47.5 ± 0.2	19
n-Pentane	2	47.8 ± 0.3	28
n-Heptane	2	325 ± 2	28
Ethyl methyl ketone	3	59.5 ± 0.4	7
Ethyl methyl ketone	4	59.2 ± 0.7	26
Diisopropyl ether	1	99.6 ± 0.4	19
Diisopropyl ether	5	99.2 ± 0.3	26

Table 2. Comparison of gas-liquid partition coefficients determined by the present static technique and from gas chromatographic retention data. Solvent, n-octadecane. Values are given with 95 % confidence intervals.

Solute	K at 60.0 °C	
	This work	Ref. (8)
n-Pentane	47.7±0.2	48.2±3.9
n-Heptane	325±2	–
Ethyl methyl ketone	59.2±0.6	58.8±3.5
Diisopropyl ether	99.4±0.3	101.4±3.9

The precision of the static method is strongly influenced by the manner in which the liquid phase and especially the gaseous phase are withdrawn and injected in the gas chromatograph. The use of n-octadecane as solvent requires, however, some comment. With repeated injections the column changes slowly but continuously, as the n-octadecane is not eluted, resulting in wider peaks and base line changes and it has to be replaced after about one hundred injections. Due to the high melting point of the solvent, the temperature of the injection syringe has to be maintained above 28.2 °C. However, under these conditions the accuracy and precision of the injected volume of the liquid phase is improved compared with injections of the volatile solvents, normally used. Furthermore, the use of a gas loop injection valve is indispensable. A standard gas tight injection syringe, at least when not completely new, does not guarantee good reproducibility of the volume injected.

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