Journal of Chromatography, 455 (1988) 45–51
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 890

DETERMINATION OF PARTITION COEFFICIENTS BY HEADSPACE GAS CHROMATOGRAPHY

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(First received October 12th, 1987; revised manuscript received July 27th, 1988)

SUMMARY

Air–water partition coefficients of ethyl acetate are determined by analysis of the headspace vapor from a closed system containing ethyl acetate and sodium chloride solutions of various concentrations. Knowing the amount of ethyl acetate in the headspace, it is possible to calculate the partition coefficient. This paper describes a simple method of determining these values without gas injection valves or other specialized equipment. The values obtained are within 7% of previously published values.

INTRODUCTION

Research was conducted to model an absorption freezing vapor compression process to determine the loss of volatile flavor components. This process concentrates aqueous solutions, such as fruit juices, by freezing water in the process stream[1]. Cooling is provided by evaporating water at the triple point and the resulting water vapor is absorbed in a sodium solution of 15 to 20% (w/v) which is controlled at 0°C. This solution also absorbs volatile flavor components. To design a suitable essence recovery system, it was necessary to determine the extent of the absorption of essence in the sodium chloride solution. A static headspace technique appeared suitable to simulate the equilibrium conditions of the air–water partitioning process. Other researchers[2] have demonstrated that the concentration of volatile components in the liquid and vapor phases could be determined. These researchers used direct injection to determine the concentration of the volatile compound in the liquid phase, while a gas sampling loop was used to measure the concentration of compounds in the vapor. In this paper, we show that a headspace method using syringe injection and ethyl acetate as a model compound provided a rapid measure of the partition coefficient. With this technique, it is not necessary to inject the liquid phase, thereby avoiding contamination of the injector and the analytical column. In addition we show the differences between

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* Retired.

PTFE bottles and glass bottles for the equilibration container. The method should be adaptable to other organic compounds.

REAGENTS AND MATERIALS*

Ethyl acetate, distilled in glass, was obtained from Burdick and Jackson Labs. (Muskegon, MI, U.S.A.) sodium chloride from J. T. Baker (Phillipsburg, NJ, U.S.A.), the chromatographic column (15% Carbowax 20 M, 80/100 Chromosorb W AW) from Supelco (Bellefonte, Pa, U.S.A.), the glass serum bottles from Kimble (Neutraglass, 120 ml), the PTFE bottles from Nalgene (125 ml) and the PTFE faced silicone septa from Pierce (Rockford, IL, U.S.A.). The caps for the PTFE bottles were drilled to allow a needle to penerate the septum between the bottle and the cap.

Apparatus

Analyses were conducted with a Varian Model 3700 gas chromatograph with a flame ionization detector set at 200°C and with the range set at 10^{-11} A/mV. The chromatographic column used was a 12 ft. long, 1/8 in. outside diameter stainless-steel column packed with 15% Carbowax 20 M, 80/100 Chromosorb W AW. Operating conditions were as follows: Column temperature, 100°C; injection port, 200°C; helium carrier gas flow-rate, 15 ml/min. A Spectra-Physics 4270 integrator was used to integrate peak areas. A Unimetrics 1-ml gas--tight syringe was used for headspace sampling. A Hamilton 10-μl syringe was used for injecting the standard solutions.

Procedure

Static headspace concentrations were measured by sampling 1.00 ml of vapor from a 125-ml glass serum bottle or a 139-ml PTFE bottle containing 50.0 ml of sodium chloride (0 to 20%) solution, and varying amounts of ethyl acetate (0.42 to 6.26 mg). The glass bottles were sealed with rubber septa and the PTFE bottles were sealed with PTFE faced silicone septa. These vessels were immersed to the neck in a constant temperature bath at 0°C (±0.1°C), and allowed to equilibrate for 24 h before sampling. Standards were prepared by weighing ethyl acetate into a volumetric flask and diluting to volume with water. Volumes of 5 μl of each of the standards were injected into the gas chromatograph using a Hamilton 10-μl syringe.

Calculations

The concentration of ethyl acetate in the vapor was determined by using an external standard method. The partition coefficients were calculated with the following equations

$$K_p = M_v/M_l \tag{1}$$

where: K_p = partition coefficient; M_v = molar concentration of ethyl acetate in the vapor, mol/l; M_l = molar concentration of ethyl acetate in the liquid, mol/l.

The concentration in the vapor phase was determined by comparison of the

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* Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

headspace peak areas to the peak areas read from the standard curve. The concentration in the liquid phase was calculated from the difference between the amount of ethyl acetate in the vpor phase and the amount of ethyl acetate added.

RESULTS AND DISCUSSION

The standard curve of ethyl acetate exhibited a linear response with a correlation coefficient of 0.9934. Amounts of ethyl acetate measured ranged from 98 to 477 ng. The injection precision of the standard was 2.8% relative standard deviation (RSD).

Other researchers[3] had found that carryover in the syringe used to sample the headspace vapor was significant. We found carryover to be less than 0.1% when the plunger was removed between injections. Figs. 1 and 2 are plots of total ethyl acetate in the system *versus* peak area of the vapor injection. The linearity at each level of sodium chloride shows that the vapor phase concentration is a fixed percentage of the total ethyl acetate at each sodium chloride level. In Fig. 1 each line exhibits a positive x-intercept, due to adsorption of ethyl acetate onto the walls of the glass serum bottle[2]. Adsorption should be constant if the number of active sites on the silica surface is constant. Because each plot has approximately the same x-intercept, the number of active sites for the brand of serum bottle we used appears constant. In contrast, Fig. 2 shows no significant x-intercept indicating that there is no adsorption onto the PTFE bottle wall. This can be explained by the lack of absorption sites on the PTFE.

Fig. 3 shows a plot of the partition coefficient calculated from the raw data obtained in glass bottles. The partition coefficient was not constant at different levels of ethyl acetate. This indicates that adsorption to the serum bottle wall was significant and the data must be corrected if glass bottles are used. By subtracting an amount equal to the x-intercept from each concentration of ethyl acetate as shown in Table I,

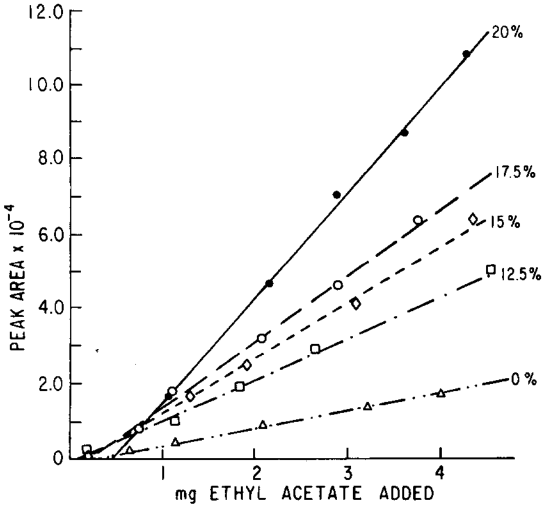

Fig. 1. Peak area response *versus* total amount of ethyl acetate in system at various concentrations of sodium chloride in glass bottles. One milliliter headspace vapor injected. Temperature of system controlled at 0°C (±0.1°C).

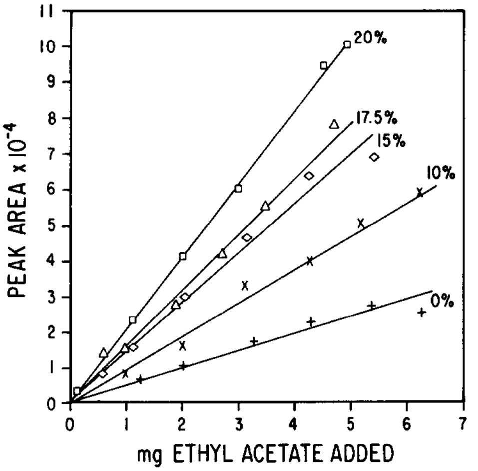

Fig. 2. Peak area response *versus* total amount of ethyl acetate in system at various concentrations of sodium chloride in PTFE bottles. One milliliter headspace vapor injected. Temperature of system controlled at 0°C (±0.1°C).

and recalculating the partition coefficients, the plots graphed in Fig. 4 are obtained. The slopes of the lines on this graph can be shown to be not statistically different than zero by a comparison of the regression coefficient to significant values of the regression coefficient at the 95% confidence level. The near zero slopes of these lines

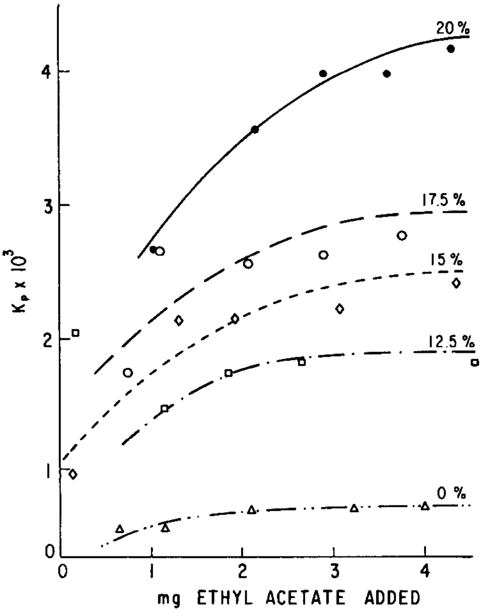

Fig. 3. Uncorrected partition coefficient *versus* total amount of ethyl acetate in system in glass bottles. Partition coefficients at different concentrations of sodium chloride were calculated from uncorrected data.

TABLE I

CORRECTIONS APPLIED TO GLASS CONTAINERS

Sodium chloride concentration (%, w/v)	*Correction (x-intercept) (mg ethyl acetate)*
20.0	−0.4597
17.5	−0.2257
15.0	−0.1741
12.5	−0.0893
0.0	−0.2341

demonstrates that the concentration of ethyl acetate has no effect on the partition coefficient. It can also be seen that the higher concentrations of sodium chloride produce a "salting-out" effect which drives the ethyl acetate out of the liquid phase into the vapor phase thus increasing the partition coefficient at higher levels of sodium chloride.

Fig. 5 shows a plot of the partition coefficient calculated from the raw data obtained in PTFE bottles. The slopes of these lines are not statistically different from zero at the 95% confidence level. Because no correction is necessary for adsorption, as is required when using glass bottles, PTFE appears to be more suitable as a container for gas samples than glass. Fig. 6 shows the variation of the natural logarithm of the

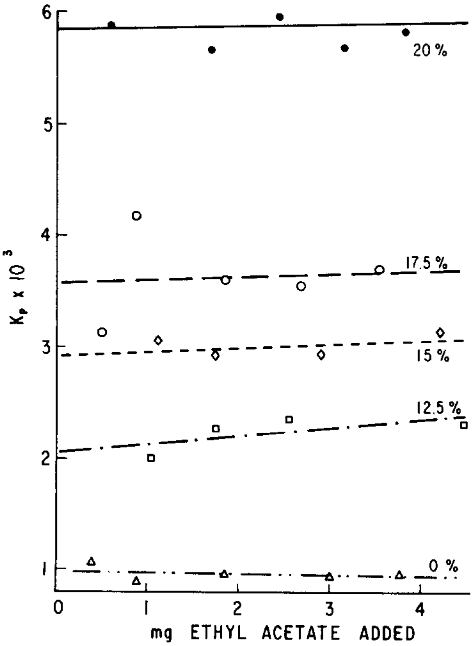

Fig. 4. Corrected partition coefficient *versus* total amount of ethyl acetate in system in glass bottles. Partition coefficients at different concentrations of sodium chloride were calculated from corrected data. The correction was applied to eliminate the effect due to adsorption of ethyl acetate onto the walls of the serum bottle.

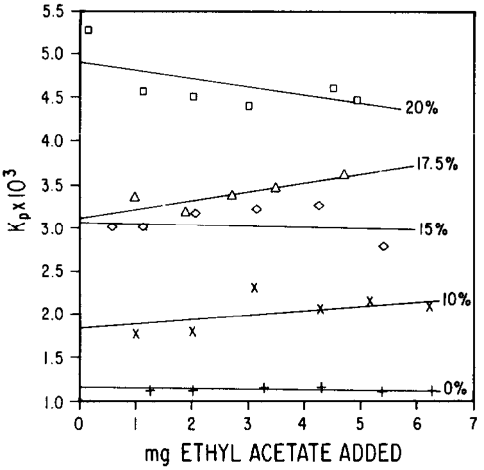

Fig. 5. Partition coefficient *versus* total amount of ethyl acetate in system in PTFE bottles. Raw data was used to calculate partition coefficients.

partition coefficient with respect to the concentration of sodium chloride in the liquid in glass and in PTFE bottles. This graph shows a linear correlation and can be used to predict the partition coefficient at various levels of sodium chloride solution at 0°C.

To check the accuracy of this method, the partition coefficient of ethyl acetate was determined at 25°C in distilled water to compare the values to previously published data. The partition coefficient obtained in glass bottles equalled $7.44 \cdot 10^{-3}$, compared to $6.94 \cdot 10^{-3}$, the value obtained by Kieckbusch and King[4] under the same conditions. The two methods show a difference of 6.95%. The partition coefficient obtained in PTFE bottles equalled $6.55 \cdot 10^{-3}$, a difference of 5.78%.

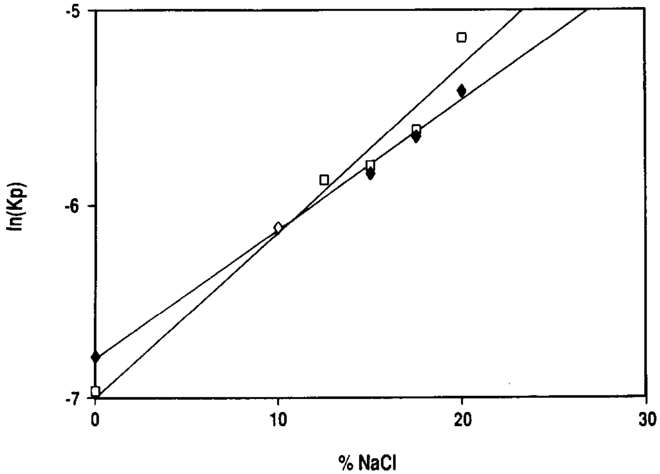

Fig. 6. Natural logarithm of the partition coefficient *versus* concentration of sodium chloride in the liquid. □ = Glass corrected; ◆ = PTFE.

The most serious problem using glass bottles is the need to apply a correction to account for the adsorption of ethyl acetate onto the walls of the serum bottle. Because brands vary, each new lot would require re-determination of the correction factor. We have shown this effect can be reduced or eliminated by using PTFE bottles which are relatively inert with respect to adsorption.

This method offers a rapid means of determining the partition coefficient of ethyl acetate with a minimum of specialized equipment and should be readily adaptable to other organic compounds. It could also be used to determine the total amount of a component in a closed system once the partition coefficient is determined for that system with the condition that the vapor and liquid volumes are accurately known. The activity coefficient can also be calculated once the partition coefficient is found.

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