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Critical comparison of gas–hexadecane partition coefficients as measured with packed and open tubular capillary columns

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ABSTRACT

The use of gas chromatography to study the thermodynamics of solute–solvent interactions is very well established. Many successful measurements using non-polar solutes have been reported. However, the investigation of the properties of even moderately polar solutes, such as acetone, on porous particles in packed beds is fraught with potential chemical problems including interfacial adsorption at the solid–gas and liquid–solid interfaces. In order to minimize, but likely not eliminate such effects, we have employed fused-silica open tubular capillary columns. This approach affords, relative to other supports, a very inert solid surface with low net area for both the solid–gas and liquid–solid interfaces. Due to the very small amount of stationary phase liquid, it is not possible to measure the absolute value of the partition coefficient. However, it is possible to obtain precise measurements of relative partition coefficients. Using the absolute value of the partition coefficient for some reference solute, obtained by alternative methods, absolute values can be computed. In this work, we show that solute retention on *n*-hexadecane is independent of solute concentration over a usefully wide range in the amount of solute injected. Where the capacity factors do vary with the amount injected, they do so in a direction consistent with a partition dominated process. Values for the partition coefficients for 105 non-polar and polar solutes in *n*-hexadecane are reported and critically compared to literature values.

INTRODUCTION

Gas–liquid chromatography (GLC) is well established as a rapid method for measuring partition coefficients and other physicochemical parameters [1,2]. The fundamentals governing the measurement of partition coefficients are straightforward. The solute capacity factor measured in a GLC experiment is directly related to the partition coefficient by the following equation:

$$k' = K\phi \quad (1)$$

where k', K, and ϕ refer to the solute capacity factor, partition coefficient and the phase ratio, respectively.

One assumption in using eqn. 1 is that only partitioning of solutes between the gas and stationary phases contributes to the measured capacity factor. This assumption has been shown to be correct for non-polar solutes with non-polar stationary phases [3–7]. However, adsorption at gas–liquid, gas–solid and liquid–solid interfaces can and do make significant contributions to the measured k' values with polar solutes on non-polar stationary phase and vice versa [3,7–15]. In such cases eqn. 1 must be modified to account for contributions from

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adsorption processes. One such modification, proposed by Jonsson and Mathiasson [16] is:

$$V_N = K_L V_L + K_S A_S + K_I A_I + K_A A_A \quad (2)$$

where $K_L V_L$, $K_S A_S$, $K_I A_I$ and $K_A A_A$ represent the contributions to the net retention volume V_N from partitioning, gas–solid, liquid–solid, and gas–liquid interfacial adsorption, respectively. It is clear that the partition coefficient cannot be calculated from the measured net retention volume and stationary phase volume (V_L) unless the contribution from these adsorption terms is negligible or can be corrected by empirical or theoretical methods. One obvious method of reducing adsorption contributions is to minimize the area of the gas–solid (A_S), liquid–solid (A_I), and gas–liquid (A_A) interfaces relative to the volume of the stationary phase.

Two different approaches have been developed to separate the contribution due to different retention processes. The first approach is to measure the specific retention volume using a series of columns with different amounts of stationary phase [17]. The specific retention volume is then plotted *versus* $1/V_L$. A "corrected" specific retention volume is said to be obtained by using the value resulting from the extrapolation of this plot to the ordinate, $1/V_L$ equal to zero. This is interpreted as being the specific retention volume obtained on an infinitely thick stationary phase which is said to "correct" for the contributions to retention from interfacial processes. This approach can easily be applied if there is a linear relationship between the specific retention volume and $1/V_L$. This can be true only with constant adsorption effects or a linear absorption contribution, where the absorption effect is so low that the infinite dilution condition can be realized for both the partition and adsorption retention processes. The situation is complicated when adsorption is non-linear, that is when the peak is tailed and the retention time and volume vary with sample size. In such cases where peaks are significantly asymmetrical, the retention volume corresponding to elution at a fixed solute gas concentration, ECP (elution by characteristic point) method [2], rather than the peak maximum volume, has been used as the basis for measurement [17]. This fixed concentration is determined by choosing a point at constant height on the diffuse side of the peak which is then used to obtain a solute's retention volume [18]. One clear disadvantage of this approach is that a series of columns have to be used under the same conditions. Another limitation of the approach is that the relationship between retention volume and the amount of stationary phase may be non-linear. The extrapolation is then much more subjective [19]. Non-linear relationships between retention volume and the volume of stationary phase have been reported [6,20]. These are attributed to cooperative adsorption effects [6] and stationary phase wetting transitions [18].

A second way to handle asymmetric peaks is to inject such a large sample that all adsorption sites become saturated. Retention is then dominated by a non-linear partition process and not by adsorption. This situation is thought to prevail when the retention time increases with sample size [19,21,22]. Retention is measured under partition dominated conditions and the partitioning contribution to retention is obtained by extrapolating the retention volume to zero sample size. The advantage of this approach is that measurements can be made on a single column. However, in order to achieve partitioning dominated retention, very large sample volumes must be used for strongly adsorbed species. Moreover, all measurements are actually made in the region where the partition coefficient becomes sample size dependent. Therefore, it is difficult to estimate the error introduced by using such large amounts of sample.

Jonsson and Mathiasson [22] proposed a similar approach by developing an equation which described retention under the assumption that a single Langmuir-type adsorption process contributes to retention. A series of retention volumes at different sample sizes are measured. The data are then fitted to their equation. The contributions from adsorption and partition processes can then be calculated by extrapolating to zero sample size. Alternatively, the contributions from adsorption and partitioning were separated by Korol *et al.* [23] by assuming a linear relation-

ship between the measured net retention volume and the reciprocal of the logarithm of the peak maximum.

Clearly, accurate measurements of thermodynamic partition coefficient demand that adsorption effects be minimized. Theoretically, this can be done by deactivating the support or minimizing the adsorption surface area. Unfortunately, the methods typically used for the deactivation of support materials produce surfaces that are not completely inert under all conditions. This is primarily attributed to difficulties in covering all adsorption sites on the support surface. In addition, active metal impurities present in the support material can contribute to adsorption. These impurities are very difficult to remove. Even PTFE, which is commonly believed to be inert, is active [24–27]. While glass bead supports have much lower surface areas than do diatomaceous supports their ability to hold the stationary phase is limited. Therefore, they are no better than deactivated white diatomite supports [20,22].

In this study we attempted to measure the gas–hexadecane partition coefficient of 105 solutes, spanning a wide range of functional groups, dipolarity and hydrogen bonding ability. Abraham *et al.* [28] collected literature data for most of the solutes given here as well as a great many others. Our incentive for remeasuring the gas–hexadecane partition coefficients is twofold. First, this molecular property is a very valuable explanatory variable in many linear solvation energy relationships and in a series of related studies we felt that a number of the data reported previously had to be in error [29]. Second, the data set reported by Abraham *et al.* was obtained from a variety of sources, by a variety of methods including gas chromatography on packed columns, head space analysis, and by extrapolations from measured values for lower members of a homolog series. We felt that it would be advisable to use data obtained by a single method on a single type of column in order to minimize differential contributions from determinate errors or at least make these errors internally consistent. Given the strong tendency for interfacial adsorption both at the gas–liquid and the solid interface when a non-polar stationary phase such as *n*-hexadecane is used we felt that the polar solutes would be particularly prone to systematic error.

In preliminary work using porous supports, despite the fact that different supports and deactivation methods were tested, interfacial adsorption was always very evident. We were unable to find a support and/or deactivation method that significantly reduced adsorption for polar and hydrogen bonding solutes. Therefore, we pursued a method that minimized the surface area available for adsorption. Here, we report on the use of deactivated fused-silica capillary columns coated with *n*-hexadecane. To our knowledge, this is the first report using a relatively volatile liquid as a stationary phase for capillary gas chromatography. Fused-silica capillaries were chosen for their high purity (low level of metallic impurities) and nearly inert surface [24,30–34]. It has been shown that the tubing wall can contribute to the retention of solutes when measurements are made at low temperatures (<100°C). Fused silica was the least sorptive of five commercially available tubing materials that we tested in a previous study [24]. An important advantage of a capillary column is the larger ratio of liquid phase volume-to-surface area relative to that of a bed packed with porous particles. Depending on the film thickness the volume-to-area ratio for a capillary column can be more than two orders of magnitude greater than for a packed column [35]. In addition, it should be possible to obtain a more homogeneous surface and a more uniform coating of a non-polar liquid on a capillary column compared to a porous particulate support.

EXPERIMENTAL

Instrument and materials

A modified Hewlett-Packard 5750 gas chromatograph was used for all measurements. As prescribed by Laub and Pecsok [1] and Conder and Young [2], great efforts were taken to modify the instrument so that high precision measurements could be made. The oven temperature controller was replaced with a YSI (Yellow Springs Instruments, Yellow Springs, OH, USA) Model 72 proportional temperature

controller. A high-resistance heater was substituted for the original low-resistance, high-power heater. This allowed for much tighter control of the oven temperature. The oven was cooled by an air cooling vortex cooler (Model 3210; Exx-air, Cincinatti, OH, USA). This device is able to cool the oven well below room temperature [36]. Auxiliary air was forced into the oven to provide additional convection in order to minimize temperature gradients across the oven. The temperature was controlled to better than ±0.05°C (as measured with a National Bureau of Standards-calibrated thermometer which is readable to the nearest 0.001°C) with a gradient of ±0.2°C across the oven (as measured by a calibrated thermistor). The largest change in the temperature across the oven occurred at the heated injection port and the detector. Essentially, we attempted to isolate these portions of the instrument from the column oven. In addition, the effects of temperature gradients can be minimized by decreasing the diameter of each column coil, thereby increasing the number of coils [37]. The helium carrier gas flow was controlled by two precision pressure regulators (Model 8286; Porter Instruments, Hatfield, PA, USA) attached in series with a flow controller (Model 8744, Brooks) all of which were thermostatted to 35°C (±0.5°C) in a forced air oven using a YSI Model 71A temperature controller [1,2]. During use, the capillary was operated at an inlet pressure of approximately 2.0 p.s.i. (1 p.s.i. = 6894.76 Pa); however, the overall backpressure on the flow controller was 15–20 p.s.i. due to the use of a packed pre-column placed upstream of the injector. The purpose of this packed pre-column was twofold, one of these is described below and the other was to increase the backpressure on the flow controller so as to stabilize its output flow. Typical column dead times during use were 1.06 min, as determined by methane. Problems with using methane as a marker of the dead volume for *n*-hexadecane at 25°C are discussed below. Connection of the capillary to the oven was made with a commercial on-column injection conversion kit from Restek. The deactivated fused-silica capillary column had an I.D. of 0.530 mm (Alltech Assoc.). Chromatograms were recorded with a Hewlett-Packard 3390 integrator and the peak maximum was used as the measure of retention time. A capillary column rinse kit (J&W Scientific) was used to coat the capillary column.

n-Hexadecane (99 + %, $H_2O < 0.005\%$) was obtained from Aldrich and kept over P_2O_5. All other chemicals were obtained from commercial sources and used as received. All support materials used in the packed column studies were obtained from Supelco.

Coating of the capillary column

A dynamic coating method was determined to give the most uniform coating and was used throughout [38–40]. The column was first washed with about 20 ml of the following solvents: methanol, acetone, chloroform and *n*-pentane. After purging the column with dry nitrogen, the column was installed in the oven and the temperature raised to 150°C. The columns was held at this temperature with the helium flow on for at least 8 h. It was then cooled to room temperature and removed. One end of the column was connected to a 10 ft. × 0.320 mm I.D. fused-silica capillary (1 ft. = 30.48 cm). The other end was connected to the washing kit which was pressurized by dry nitrogen. The pressure during the coating process was controlled by a precision pressure regulator in order to deliver a constant flow of *n*-hexadecane to the capillary. About 10 ml of *n*-hexadecane solution in *n*-pentane was forced through both columns. The second column served as a restrictor and ensured a smooth flow of the coating solution through the capillary and prevented an increase in the stationary phase thickness towards the end of the analytical capillary [40–42]. Tight control of the flow of coating solution is necessary in order to control the film thickness and prevent "puddling" of the stationary phase [40,43]. The amount of *n*-hexadecane in the coating solution was varied from 8, 22, 50 to 100% (w/w) to determine conditions that would provide the thickest possible stable film. The best overall performance was obtained with 22% *n*-hexadecane when it was coated at a pressure of 12 p.s.i. and a velocity of about 1.1 cm/s. After the

coating solution passed through the column, pentane was removed by purging the column with helium for approximately 40 min. The column was then installed in the oven at 25°C under a flow of helium until a steady baseline was obtained. To reduce stationary phase loss, a "pre-saturation" tube was installed before the injection port [44,45]. This saturated the carrier gas with *n*-hexadecane. Loss of *n*-hexadecane throughout the experiment was monitored via measurement of the retention of *n*-hexane. Its retention was measured repeatedly each day and minimally after each third solute was examined. All data were corrected for the loss of stationary phase.

Loading of *n*-hexadecane onto porous supports was accomplished by immersing the support in a mixture of *n*-hexadecane and *n*-pentane. *n*-Pentane was slowly removed by applying a vacuum via a rotary-evaporator. All support mesh sizes were 60–80. Chromosorb P AW DMCS (acid-washed, dimethyldichlorosilane deactivated Chromosorb P) and Chromosorb W HP were washed with acetone and dried at 150°C overnight before use. Chromosorb T was washed with acetone and isopropanol and then dried in a vacuum oven at 80°C overnight before use. Coating of Chromosorb T followed the procedure by Kirkland [27] to avoid "clump" formation. These materials were packed into both stainless-steel and glass columns. The glass columns were taken through an extensive on-column silanization procedure at 150°C. Repetitive injections of a commercially available silylation reagent, Silyl 8 (Pierce), was performed until no change in the retention time or peak symmetry was observed [46,47]. This was taken as the point of minimal surface activity.

Determination of the partition coefficients

It is difficult to measure directly the amount of stationary phase in a capillary column especially when a volatile stationary phase is used and the evaporation rate is significant. In order to avoid making this measurement, *n*-hexane was used as a standard solute and we assumed that the partition coefficient reported by Abraham *et al.* [28] was correct. The partition coefficient for any solute can then be computed as:

$$K_x = K_{n\text{-hexane}} \cdot \frac{t_{R,x} - t_m}{t_{R,n\text{-hexane}} - t_m} \quad (3)$$

where t_R and t_m denote the retention time of any species and the dead time of the column under the same conditions, respectively. Clearly an estimate of the dead time is needed. The dead time was obtained by the method of Peterson and Hirsch [48]. This method is based on the assumption that within an homolog series there is a linear relationship between the logarithm of the corrected retention time and the solute's carbon number. About 1 μl of gas phase above a mixture of *n*-pentane, *n*-hexane and *n*-heptane was injected into the column and the dead time was calculated using the following equation:

$$t_m = \frac{t_{C6} - (t_{C5}t_{C7})}{2t_{C6} - (t_{C5} + t_{C7})} \quad (4)$$

where t_{C5}, t_{C6}, and t_{C7} refer to retention times of pentane, hexane and heptane, respectively. The dead time calculated in this manner is preferred to the retention volume of methane because methane is retained by *n*-hexadecane, its gas–liquid partition coefficient is 0.48 at 25°C [28]. In addition, it has been pointed out that the retention time of methane cannot be used when the column temperature is below 100°C [1]. The linearity between logarithm of the corrected retention times and carbon number of a homologue series is the basis for a more complex method using many members of a homologue series [49]. We decided to use the three alkanes mentioned above because they are all well retained and eluted in a reasonable time frame. Typical dead-times using the three-alkane approach were approximately 1.03 min. This is significantly less than the observed retention time for methane (1.06 min).

It is possible that our choice of Abraham *et al.*'s value for the gas–liquid partition coefficient of *n*-hexane in *n*-hexadecane as a normalizing factor could introduce an error in the partition coefficients reported here. In order to ensure that we are normalizing against the most accurate data available, we have compared this value against several literature values which are

believed to be extremely reliable. McGlashan and Williamson [50] studied the infinite dilution activity coefficient of *n*-hexane in *n*-hexadecane as a function of temperature and composition by the static vapor pressure method. They covered the temperature range 20–60°C in 10°C increments and the mol fraction of *n*-hexane was varied from 0.012 to 0.90. We have interpolated their data to 25°C using their lowest concentration results and have converted the activity coefficient to the gas–liquid partition coefficient using the vapor pressure of *n*-hexane. Cruickshank *et al.* [51] and Chien *et al.* [52] have also determined the infinite dilution activity coefficient at several temperatures using high-precision packed-column GC. In addition, we have made two separate measurements of the partition coefficient of *n*-hexane in *n*-hexadecane by headspace GC [53,54]. The average partition coefficient for *n*-hexane from all of these measurements is 466.1 and the standard error is 1.99 (relative standard deviation 0.42%). Abraham *et al.*'s reported value is 465.6. It is as accurate as any data that are available for this solute. Based on these data, we feel the use of *n*-hexane as a normalization factor should not compromise the accuracy of the partition coefficients reported in this work.

Measurement precision

All the partition coefficients reported here were based on at least two measurements for highly retained solutes and three measurements for the rest of the data set. In order to study interfacial adsorption, a series of different sample sizes were used for all polar solutes. When a sample size dependence was observed, four to eight measurements were made using different amounts of solute and the average of the values within the sample size independent region was used to determine the partition coefficient. Repeated measurements of solutes that gave asymmetric peaks were run several times on different days; a deviation of less than ±1% was observed. Despite the fact that we repeatedly measured the retention time of methanol no data are given here since its capacity factor was so low that we deemed the result unreliable. Acetaldehyde, 1,1,1,3,3,3-hexafluoroisopropanol and 2,2,2-trifluoroethanol, the three least retained species reported here, all had capacity factors of less than 0.05.

RESULTS AND DISCUSSION

Preliminary experiments using packed columns

Initial studies were undertaken using deactivated Chromosorb P AW DMCS loaded with 25% *n*-hexadecane as the packing material which was packed into 1/4 in. I.D. (1 in. = 2.54 cm) stainless-steel tubes. Polar solutes such as ketones, alcohols and nitromethane all exhibited severely asymmetric peaks whose retention times depended strongly on sample size. Small amounts of polar solutes could not be detected due to the severity of adsorption. The smallest detectable acetone peak had a retention time approximately four times that observed with a much larger sample. This clearly indicates that when Chromosorb P is used as the support, even after steps have been taken to deactivate the surface, retention of polar solutes is mainly due to adsorption and not partitioning.

In an attempt to decrease the effect of adsorption we switched to Chromosorb W HP which has a lower active metal content and lower surface area than does Chromosorb P AW DMCS. As expected, a significant decrease in peak asymmetry and a reduced dependence of retention on sample size was realized, however, adsorption effects were still very significant. For example, on a 15% (w/w) loaded support the retention time of the smallest detectable acetone peak was 37% higher than that obtained with a much larger sample.

Based on previous studies on the adsorptive strengths of different tubing surfaces [24] we switched from stainless-steel tubing to deactivated glass tubes. Deactivation using Silyl 8 was performed in order to further deactivate an already coated column [46]. A significant improvement was observed for polar solutes injected immediately after the Silyl 8 treatment. However, the decrease in activity towards polar solutes disappeared within a few hours. This leads us to believe that the silanization agent acted to block active sites on the various surfaces by physical adsorption rather than by chemical

reaction. This type of tubing and support material were abandoned due to their activity towards polar solutes.

Chromosorb T, a porous PTFE support, is commonly held to be inert towards polar solutes. When it was loaded with 20% (w/w) *n*-hexadecane, no apparent peak asymmetry or tailing was observed with alcohols and higher ketones. However, repeated measurements at the lowest detectable amount of acetone still gave retention times that were 2% higher than those obtained with a larger amount of solute. Polychloroalkanes showed significant tailing and irreproducible retention on this material. These observations confirm previous reports of the activity of this support towards polar solutes [24–27]. Additionally, nitromethane was irreproducibly retained and double peaks were obtained whereas the same solute gave a single peak on other supports. In addition, most stationary phases have a higher surface tension than PTFE and therefore do not evenly wet its surface. Based on these results, we rejected the premise that PTFE is an inert support and abandoned its further use in this study.

Partition coefficient measurement using capillary columns

Effect of coating concentration and speed. To minimize the adsorption terms in eqn. 2 relative to the partition terms it is necessary that a thick uniform coating of *n*-hexadecane be present on the column wall. This minimizes the amount of available fused-silica surface and decreases the surface-to-volume ratio, which favors solute partitioning. A column coated with an 8% *n*-hexadecane solution coated under 10 p.s.i. pressure gave a very even coating (as observed through the tubing wall with a microscope). The coating was assumed to be even, if beads were not observed and the intensity of light when directed through the tubing wall did not vary. The calculated film thickness, based on the retention of benzene, was only approximately 0.11 μm. We found that a thicker film, approximately 0.23 μm, which was still uniform could be achieved by increasing the concentration of the coating solution to 22% *n*-hexadecane and using a coating pressure of 12 p.s.i. However, increasing the solution concentration to both 50 and 100% *n*-hexadecane solutions gave non-uniform films which were only about 0.29 μm thick. Soon after the coating was completed the films made from the more concentrated solutions exhibited "pooling" and "beading" of the *n*-hexadecane. It is known that the ability of a phase to wet the tubing wall [55] and the viscosity [56] of the coating solution are critical in coating stable, uniform films on fused-silica surfaces. It is also possible that the solvent, *n*-pentane, acts as a transient wetting agent by reducing the surface energy of the capillary surface which then allowed *n*-hexadecane to coat as a thin uniform film on the tubing wall. A very uniform film with a maximum thickness of 0.29 μm was obtained using 22.5% (w/w) *n*-hexadecane solutions and coating at a pressure of 12 p.s.i. These were considered to be the optimum coating conditions. It appears that the film thickness is controlled by the coating conditions at lower concentrations of *n*-hexadecane, and by the wettability and viscosity of *n*-hexadecane at higher concentrations [55,56]. Columns prepared under optimum conditions were reasonably stable over a relatively long period of time. However, upon injecting high-boiling polar liquids, a few small "puddles" were observed near the head of the column. This problem was minimized by injecting the head-space vapor above a warm solution of the polar solutes.

The lifetime of a column was limited by the loss of stationary phase. Since the phase ratio is constantly decreasing, it was measured every few hours using a standard mixture of *n*-pentane, *n*-hexane and *n*-heptane as described above. A long term study over eight consecutive days indicated a constant loss rate of approximately 2% per day under the use conditions described here.

Adsorption of polar solutes on a deactivated fused-silica capillary column. Preliminary tests of the hexadecane-coated fused-silica capillary column were performed in order to study interfacial adsorption, the sample size dependence and the reproducibility of the retention times for polar solutes. The retention time of acetone was independent of the amount of sample injected. Additionally, more highly retained polar solutes

were studied. Retention times for all solutes, except for the amines (see below), were independent of the amount of sample injected. This sample size independence typically persisted until the sample size was greater than about 10 μl of the headspace above a warmed solution. When an excessive amount of solute was injected the retention times on the capillary columns increased in contrast to the decreases observed with packed beds. A representative set of results are given in Fig. 1 for a series of alcohols. Retention times are very reproducible and do not vary with sample size until a very large amount is injected. Additionally, we intentionally overloaded the column with 1-pentanol in Fig. 2 in order to emphasize this effect. This result is consistent with the above discussion and results based on studies using headspace gas chromatography and pressure measurements of the partition coefficients [57–61]. This increase in retention times of polar solutes in *n*-hexadecane with the amount of solute injected is due to solute–solute association which increases the solute's gas–liquid partition coefficient which in turn results in an increase in the retention time. This effect is most significant for the alcohols and carboxylic acids. Acetic acid, which is known to be very highly self-associated, gave constant

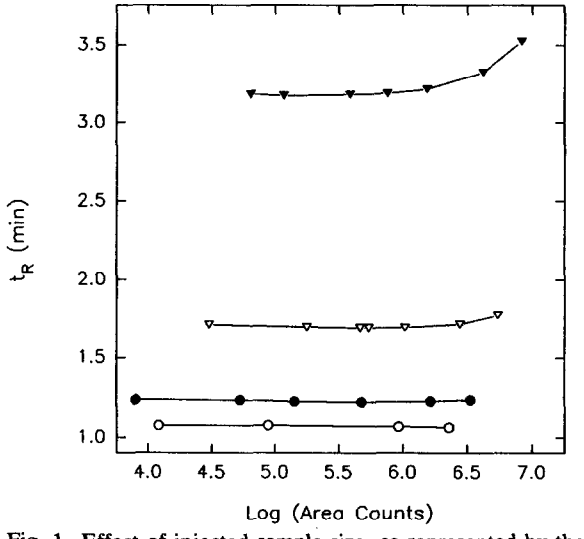

Fig. 1. Effect of injected sample size, as represented by the peak area counts, on the retention time of a series of alcohols. ○ = Ethanol; ● = 1-propanol; ▽ = 1-butanol; ▼ = 1-pentanol.

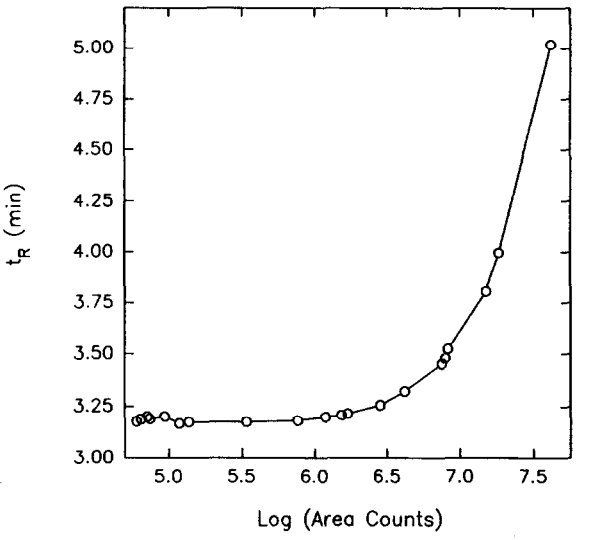

Fig. 2. Effect of injected sample size, as represented by the peak area counts, on the retention time of 1-pentanol.

retention times for small injection volumes on the capillary column whereas asymmetric peaks with varying retention times were obtained with packed columns. In summary, all of the above semi-quantitative observations lead us to believe that our measurements are made under partition-dominated conditions. Based on the above, we believe that the partition coefficients measured in this study are more reliable than those obtained with packed columns regardless of whether mixed retention processes were accounted for in the data analysis.

Although we obtained excellent peak shapes and constant retention times for most solutes, the column is definitely not completely inert. Adsorption, producing tailing peaks and sample size dependent retention, was observed for dimethylformamide, dimethylacetamide, dimethyl sulfoxide and all aliphatic amines. Aniline, pyridine and tertiary amines gave relatively better peaks, but these species were not free from adsorption contributions to retention. This is evident in the poor peak shapes and the increase in retention upon decreasing the amount injected. These observations show that the column still has some activity toward very basic solutes. We expect that the problem with amines can be significantly reduced if special attention is paid to deactivating the fused silica surface before coat-

TABLE I

n-HEXADECANE GAS–LIQUID PARTITION COEFFICIENTS

Solute	Log L^{16}_{Cap} [a]	Log L^{16}_{Abr} [b]	Solute	Log L^{16}_{Cap} [a]	Log L^{16}_{Abr} [b]
n-Pentane	2.163	2.162	Acetophenone	4.458	4.483
n-Hexane	2.668 (2.670)[d]	2.668	Acetonitrile	1.537	1.560
n-Heptane	3.173	3.173	Propionitrile	1.978	1.940
n-Octane	3.677	3.677	Benzonitrile	3.913	–[c]
n-Nonane	4.176	4.182	Benzyl cyanide	4.570	–[c]
n-Decane	4.685	4.686	Acetaldehyde	1.240	1.230
Cyclopentane	2.426	2.447	Propionaldehyde	1.770	1.815
Cyclohexane	2.906	2.913	Benzylaldehyde	3.935	–[c]
2,4-Dimethylpentane	2.812	2.841	Tetrahydrofuran	2.521	2.534
2,5-Dimethylhexane	3.309	–[c]	*p*-Dioxane	2.788	2.797
Cycloheptane	3.543	3.526	Diisopropyl ether	2.561	2.559
2-Methylpentane	2.507	2.549	Diethyl ether	2.066	2.061
Ethylcyclohexane	3.767	–[c]	Dipropyl ether	2.971	2.989
2,3,4-Trimethylpentane	3.401	–[c]	Dibutyl ether	3.954	4.001
Hexene	2.571	2.547	Anisole	3.916	3.926
Benzene	2.792	2.803	Methylene chloride	1.997	2.019
Toluene	3.343	3.344	Chloroform	2.478	2.480
Ethylbenzene	3.785	3.765	Carbon tetrachloride	2.822	2.823
Propylbenzene	4.239	4.221	1,2-Dichloroethane	2.572	2.573
Butylbenzene	4.714	4.686	Chlorobutane	2.716	2.722
p-Xylene	3.867	3.858	Chloropentane	3.232	3.223
m-Xylene	3.868	3.864	Fluorobenzene	2.785	–[c]
o-Xylene	3.947	3.937	Chlorobenzene	3.630	3.640
Methanol	(0.975)[d]	0.922	Bromobenzene	4.022	4.035
Ethanol	1.556 (1.425)[d]	1.485	Iodobenzene	4.505	–[c]
n-Propanol	1.975	2.097	*o*-Dichlorobenzene	4.453	4.405
n-Butanol	2.539	2.601	*p*-Dichlorobenzene	4.405	–[c]
n-Pentanol	3.057	3.106	Dimethylformamide	2.922	3.173
n-Hexanol	3.550	3.610	Dimethylacetamide	3.357	3.717
n-Heptanol	4.067	4.115	Dimethylsulfoxide	3.110	3.437
n-Octanol	4.569	4.619	Ethylamine	1.646	1.677
2-Propanol	1.750	1.821	Propylamine	2.083	2.141
Benzyl alcohol	4.162	4.443	Butylamine	2.575	2.618
2,2,2-Trifluoroethanol	1.315 (1.116)[d]	1.224	Hexylamine	3.612	3.557
tert.-Butanol	1.994	2.018	Triethylamine	3.008	3.077
2-Methyl-1-propanol	2.381	2.399	Diethylamine	2.386	2.395
sec.-Butanol	2.322	2.338	Pyridine	2.969	3.003
Isopentanol	2.885	–[c]	Aniline	3.934	3.993
Cyclopentanol	3.107	–[c]	N-Methylaniline	4.492	–[c]
Cyclohexanol	3.594	3.671	N,N-Dimethylaniline	4.753	4.754
1,1,1,3,3,3-Hexafluoro-isopropanol	1.370	1.392	Methyl formate	1.454	1.459
2-Phenylethanol	4.552	–[c]	Methyl acetate	1.946	1.960
3-Phenylpropanol	4.663	–[c]	Ethyl acetate	2.359	2.376
4-Phenylbutanol	5.049	–[c]	Propyl acetate	2.861	2.878
Phenol	3.641	3.865	Acetic acid	2.331	3.290
m-Cresol	4.187	4.329	Propionic acid	2.978	–[c]
p-Cresol	4.254	4.307	Butyric acid	3.427	–[c]
o-Cresol	4.183	4.242	Ethyl propionate	2.860	2.881
Acetone	1.766	1.760	Nitromethane	1.839	1.892
2-Butanone	2.269	2.287	Nitroethane	2.313	2.367
2-Pentanone	2.726	2.755	Nitropropane	2.773	2.710
Cyclopentanone	3.093	3.120	Nitrobenzene	4.433	4.460
Cyclohexanone	3.580	3.616			

[a] Measured by capillary gas chromatography in this work.
[b] Reported in ref. 28.
[c] Not reported.
[d] Measured by headspace gas chromatography (see ref. 53).

ing. Methods similar to that reported by Biernacki [62] for treating the column support with sodium metanilate which is insoluble in the stationary phase, might be necessary to obtain good peak shapes with very basic compounds. However, such treatment may not produce a support which is inert to the acidic (hydrogen bond donor) solutes and was therefore not used here.

The partition coefficients for different solutes. All partition coefficients measured in this work are given in Table I along with the values reported by Abraham *et al.* [28]. Regression of these data against one another gave the following correlation:

$$\log L^{16}_{Cap} = 0.060(\pm 0.046) + 0.967(\pm 0.015) \log L^{16}_{Abr} \quad (5)$$

$n = 85$ S.E. $= 0.129$ $r = 0.9903$

Log L^{16}_{Cap} refers to the data measured in this work and log L^{16}_{Abr} refers to the values reported by Abraham *et al.* The quality of this regressions suggests that there is generally excellent agreement between the two data sets. However, there are a number of very significant outliers, all of which are either good hydrogen bond acceptors or donors. Removal of acetic acid, the single most deviant point, from the regression improves the goodness of fit:

$$\log L^{16}_{Cap} = 0.060(\pm 0.029) + 0.971(\pm 0.009) \log L^{16}_{Abr} \quad (6)$$

$n = 84$ S.E. $= 0.082$ $r = 0.9961$

We believe this excellent correlation confirms the soundness of our measurement conditions. In addition, the points that do not agree are those that are known to be problematic solutes on packed columns. A series of classwise regressions of the two data sets are presented in Table II. It is evident that within the statistics of the fit the data for the alkanes, the "select" solutes (excluding dimethylacetamide, dimethylformamide and dimethylsulfoxide), the non-hydrogen bond donor solutes, the solutes with low hydrogen bond acceptor strength, and the halogenated solutes are in essentially perfect agreement. The

TABLE II

REGRESSION ANALYSIS OF *n*-HEXADECANE GAS–LIQUID *K* VALUES

Regression of log L^{16}_{Cap} *vs.* log L^{16}_{Abr}. r = Correlation coefficient; S.E. = standard error of the fit; n = number of data points included in the regression.

Solute class	Intercept[a]	Slope[b]	r	S.E.	n
Alkanes	−0.020 (0.023)	1.005 (0.007)	0.9997	0.019	12
Aromatic[c]	−0.070 (0.008)	1.020 (0.002)	0.99999	0.003	8
Halogenated[d]	−0.014 (0.020)	1.003 (0.007)	0.9999	0.011	7
Low β[e]	−0.012 (0.018)	1.004 (0.006)	0.9995	0.062	32
Select[f]	−0.019 (0.016)	1.002 (0.006)	0.9993	0.028	42
N-HBD[g]	−0.023 (0.013)	1.004 (0.004)	0.9995	0.027	55
HBD[h]	0.070 (0.033)	0.957 (0.011)	0.9984	0.062	26
Oxygenated[i]	0.054 (0.055)	0.967 (0.020)	0.9961	0.068	20
Amines	−0.024 (0.144)	0.982 (0.045)	0.9907	0.125	11

[a] Intercept and in parentheses the standard error of the intercept.
[b] Slope and in parentheses the standard error of the slope.
[c] Non-polar aromatic solutes only.
[d] Halogenated solutes only.
[e] Compounds having β_2^c (solute hydrogen bond acceptor basicity) values less than 0.30.
[f] Monopolar aliphatic (non-polyhalogenated) non-hydrogen bond donor solutes, excluding dimethylacetamide, dimethylformamide and dimethyl sulfoxide.
[g] All non-hydrogen bond donor solutes.
[h] Hydrogen bond donor solutes, excluding methanol.
[i] Oxygen containing solutes (carbonyl and ether functionalities), excluding alcohols.

results with the alkanes agree best, but this is hardly surprising since the column was essentially "calibrated" so as to give perfect agreement with Abraham *et al.*'s values for *n*-pentane, *n*-hexane and *n*-heptane. In contrast, there is a very slight systematic deviation observed for the aromatic solutes whereas the hydrogen bond donor, oxygenated, and amine solutes are all less retained on the capillary column relative to Abraham *et al.*'s estimates which come predominantly from measurements made with packed beds of porous particles. Interestingly, the intercept in all cases is essentially zero within the statistics of the fit.

It should be noted that the systematic differences between the gas–liquid L^{16} values reported here and those reported by Abraham *et al.* are not due to errors in estimates of the dead volume. For example, significant deviations with respect to Abraham *et al.*'s reported values are found for dimethylformamide, dimethylacetamide and dimethyl sulfoxide even though all three solutes are well within the range of retentions observed for *n*-pentane to *n*-decane, all of which agree very well with Abraham *et al.*'s values.

Agreement between the alkane and aromatic hydrocarbon series measured in this work and that of Abraham *et al.* [28] is excellent. This is expected since these solutes should not adsorb on packed beds or capillary surfaces. The differences are generally smaller than 0.02 log units, which is within the standard error reported by Abraham *et al.* [28] for a comparison of his data to headspace measurements (which are free from adsorption contributions). However, there are significant deviations for 2-methylpentane and cyclopentane. These solutes, in Abraham *et al.*'s data set, were measured by Kwantes and Rijnders [63] using copper helices as the support. Interpolation of the data for 2-methylpropane, 2-methylbutane and 2-methylhexane, reported by Abraham *et al.*, predicts a value of 2.491, which is in much better agreement with the value of 2.507 in this work than with the value of 2.549 reported by Abraham *et al.* The value reported in this work agrees very well with a recently reported value of 2.516 measured by headspace GC [54]. Additionally, the value reported for 2,4-dimethylpentane by Abraham *et al.*, 2.841, is significantly high relative to the value measured in this work, 2.812. Abraham *et al.*'s value was obtained from ref. 21 by correlation of the data obtained from experiments on *n*-heptadecane at a temperature other than 25°C. Our value agrees well with headspace measurements, 2.816 [54].

The most deviant aromatic hydrocarbon is butylbenzene. Its value is nearly 0.03 log units lower than that measured here. The value quoted by Abraham *et al.* is based on an estimate obtained by extrapolating results from lower homologues. We repeated the correlation and extrapolation and obtained a value of 4.702, which is in very good agreement with our experimental value of 4.714. Also, this data point was reported by Schantz and Martire [64] to be 4.704.

Excellent agreement was also found for halogenated alkanes. No significant deviation between the two data sets was detected.

In contrast to the behavior of the non-polar solutes, considerable systematic differences were observed for many polar solutes. In almost all instances (see below for several exceptions) the partition coefficients of polar species reported by Abraham *et al.* are larger than those observed here. This is the expected direction assuming that the data obtained with the capillary columns are not as strongly influenced by adsorption at the solid surface as are data obtained on packed columns. The gas–liquid L^{16} value for all alcohols (except methanol, ethanol and 2,2,2-trifluoroethanol) were smaller than those given by Abraham *et al.* We do not believe this is a result of interfacial adsorption in our system, but is a result of the exceedingly low retention of these solutes on the capillary column due to the lower surface area to volume ratio. Retention of these species is not significantly different than the dead volume of the column. Therefore, we believe the values listed in Table I for those solutes are in error. Alongside these values we have reported some recently measured headspace GC values for these solutes [see ref. 53] which we prefer to the capillary column measurements.

The largest differences for polar solutes were observed for benzyl alcohol, phenol and an extraordinarily large difference was observed for

acetic acid. All of these solutes are strong hydrogen bond donors. Our measurement of the partition coefficient for benzyl alcohol differs from that of Abraham *et al.* by 48%. To check, we injected a mixture of benzyl alcohol and *p*-xylene, which is known to agree well with Abraham *et al.*'s data. The partition coefficient for *p*-xylene in this particular run differed from our previously measured value and that of Abraham by less than 0.01 log units. This leads us to believe the value measured here is a better estimate of benzyl alcohol's partition coefficient than that reported by Abraham *et al.* The presence of interfacial adsorption in Abraham *et al.*'s value is probably the cause of this difference.

Phenol gave a symmetric peak and a much lower partition coefficient than that reported by Abraham *et al.* We believe this difference is due to the presence of significant interfacial adsorption in Abraham *et al.*'s value. Based on the solute's dipolarity ($\pi_2^{*,c} = 0.77$) and strong hydrogen bond donating ability ($\alpha_2^c = 0.69$) this deviation is expected. Similar solutes such as the cresols, also gave significantly lower partition coefficients than reported by Abraham *et al.* Moreover, the order of increasing partition coefficients for *m*- and *p*-cresol is reversed in our measurements relative to those of Abraham *et al.* Although the boiling point for *m*-cresol is slightly higher than that of *p*-cresol (202.2°C *vs.* 201.9°C) [65], *p*-cresol's vapor pressure at 25°C is higher than that of *m*-cresol (0.143 mmHg and 0.130 mmHg, respectively; 1 mmHg = 133.322 Pa). These observations lead us to believe the higher values in Abraham *et al.*'s compilation for these types of solutes are due to adsorption at the solid and liquid interfaces.

All three aliphatic nitro compounds studied gave very symmetric peaks. The values for nitromethane and nitroethane are lower than Abraham *et al.*'s by 0.05 log units; however, our value for nitropropane is 0.06 log units higher than Abraham *et al.*'s. Based on linearity of the partition coefficients within this homologous series we predict, from the first two members of the series, a value of 2.787 for nitropropane, which is in good agreement with the measured value of 2.773 reported here. The same estimation process was applied to Abraham *et al.*'s data from which a value of 2.842 was calculated for nitropropane, which is much larger than the experimental value of 2.710 reported by Abraham *et al.* Although we do not expect a perfect linear relationship within the series, this approach should at least give a reasonable estimate of the true value. A weak dependence of retention time on sample size was observed with nitrobenzene indicating relatively little interfacial effect. Although peak shapes were good with smaller samples, significant fronting was observed with larger sample sizes.

As mentioned above, the fused-silica surface has an affinity for basic solutes due to the presence of residual silanol groups [24]. Of the amines examined in this study, symmetric peaks were observed only for pyridine, aniline and trimethylamine. L^{16} values for all strong hydrogen bond acceptors reported here, except that of *n*-hexylamine, are smaller than those of Abraham *et al.* The sole exception, *n*-hexylamine, reported by Abraham *et al.* was estimated from the linear relationship between log L^{16} and carbon number for ethyl, propyl and butylamine. We must emphasize that, because of the strong interaction of amines with silanols on the fused-silica surface, the partition coefficients reported here for amines probably contain contributions from interfacial adsorption. These data are given because they are generally lower than the values reported by Abraham *et al.* and are therefore probably closer to the true value.

Some of the other solutes show deviations even greater than those shown by amines. The partition coefficients for dimethylformamide, dimethylacetamide and dimethyl sulfoxide are about 0.3 log units lower than those of Abraham *et al.* Even though we believe these data were obtained under conditions that are not completely partition dominated we still feel they are superior to those obtained using packed columns.

Recently, Abraham *et al.* [66] have reported a new set of log L^{16} values which were obtained by back-calculation from the GC data of McReynolds [67] and Patte *et al.* [68] using an "inverse" multiple linear regression analysis. These calculated data are used by Abraham *et al.* in an attempt to rationalize fundamental issues

regarding solute-solvent interactions as they relate to the solute parameters π_2^* (solute dipolarity/polarizability) and α_2 (solute hydrogen bond donating acidity). Their calculated log L^{16} are purported to be superior to those used by Li *et al.* [29]. Their use of the cycloalkanones as an example to support this is confusing since Li *et al.* used Abraham *et al.*'s data originally reported in refs. 28 and 69. The data for the two cycloalkanones, cyclopentanone and cyclohexanone, obtained in this work are in reasonably good agreement with Abraham *et al.*'s original data in ref. 28, as well as for cyclopentanone measured by headspace GC [53]. The log L^{16}_{Cap} values for cyclopentanone and cyclohexanone are 3.093 and 3.580, respectively, and those reported in ref. 28 are 3.120 and 3.616, respectively. In contrast, the calculated values are 3.221 and 3.792, respectively; resulting in a difference in the gas–liquid partition coefficient in excess of 25% for cyclopentanone and 50% for cyclohexanone between the three sets of data. These differences are by no means minor or systematic as claimed by Abraham *et al.* [66]. Since the experimentally measured data are in good agreement, we believe that the back-calculated estimates are in error. In support of this we choose to look at *n*-hexane for which the value of log L^{16} is well established, as discussed above. Abraham *et al.*'s back-calculated value is 2.688 ($L^{16} = 487.5$) and the average of six accurate measurements is 2.661 ($L^{16} = 466.1$); this is a 5% difference in L^{16} which is large considering the percent relative standard deviation of the six measurements is 0.42%. Therefore, we suggest that use of back-calculated log L^{16} values should be used with some caution.

CONCLUSIONS

Gas–liquid partition coefficients on a relatively volatile liquid, *n*-hexadecane, have been measured using capillary gas chromatography. Columns with a film thickness in excess of 0.2 μm were prepared so as to maximize the ratio of liquid volume to interfacial area and thereby reduce the relative contribution of interfacial adsorption to retention. The problem of measuring the amount of stationary phase was circumvented by making all measurements relative to the partition coefficient of a species (*n*-hexane) whose partition coefficient had been previously established using packed bed chromatography. The data were compared with literature values and deviations are interpreted based on the effect of interfacial adsorption. It is shown that in most instances the literature data for strong hydrogen bond donor and acceptor solutes, especially amines, are significantly influenced by interfacial adsorption effects. The data reported here are shown to be more accurate than the previously reported results.

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