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# Comparison of uncorrected retention data on a capillary and a packed hexadecane column with corrected retention data on a packed squalane column

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**Abstract**

Retention data obtained previously at 25°C on a hexadecane capillary column by Zhang et al. and a packed hexadecane column by Abraham et al., both uncorrected for any effects due to interfacial adsorption, were compared with retention data obtained by Poole et al. on a packed squalane column at 120°C, with the latter fully corrected for such effects. It is shown that for most solutes, the capillary and packed column data are equally compatible with the squalene corrected data, but for the solutes dimethyl sulfoxide, dimethylformamide and dimethylacetamide the packed column data are in much better accord with the corrected data than are the capillary column data. It is further shown that both sets of results at 25°C for carboxylic acids are in error, owing to dimerization. Retention volumes on Chromosorb G AW DMCS are reported at 25 and at 93°C. It is shown that at 25°C, there could be some contribution to solute retention from adsorption on the support, but that this is almost impossible at 93°C.

## 1. Introduction

Some time ago [1], we defined a new solute descriptor, log $L^{16}$, where $L^{16}$ is the solute Ostwald solubility coefficient, or gas–liquid partition coefficient, at 25°C on hexadecane. This solvent was chosen for two reasons, first because it is a well defined chemical, and second because $L^{16}$ values can be combined with gas–water partition coefficients to give water–hexadecane partition coefficients that are useful in pharmaceutical and medicinal chemistry. We first determined $L^{16}$ values for 140 solutes, using a gas–liquid chromatographic method (GLC) in which hexadecane was the stationary phase [1]. A packed column was used, with acid-washed, silanized Chromosorb G AW DMCS as the support. The log $L^{16}$ values have subsequent-

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ly proved to be very useful as a descriptor in linear free energy relationships (LFERs) and in quantitative structure–activity relationships (QSARs). Such LFERs have been used to analyse and to interpret processes including GLC retention [2–6], the solubility of vapors in soybean oil [7], polymer-probe interactions [8], the adsorption of gases and vapors on carbons [9] and on buckminsterfullerene [10] and the solubility of gases and vapors in organic solvents [11, 12]. A QSAR has been established for the effect of airborne chemicals on the upper respiratory tract irritation in mice [13]. Although the direct determination of log $L^{16}$ values on hexadecane at 25°C is restricted to the more volatile solutes, the range of log $L^{16}$ values can greatly be extended through the use of non-polar GLC phases at higher temperatures [14–16]. For example, the extensive data of Dutoit [17] on the stationary phase $C_{78}H_{158}$ at 130°C were fitted to an LFER of the form

$$I/10 = 6.669 + 8.918\,R_2 + 20.002 \log L^{16} \qquad (1)$$

$$n = 138,\ \rho = 0.9995,\ \text{S.D.} = 0.449,\ F = 67\,450$$

where $I$ is the retention index and the descriptor $R_2$ is the solute excess molar refraction [2]. In Eq. 1 and elsewhere, $n$ is the number of data points, $\rho$ is the correlation coefficient, S.D. is the standard deviation and $F$ is the Fisher $F$-statistic. Once Eqn. 1 has been set up with solutes of known $R_2$ and log $L^{16}$ values, then further log $L^{16}$ values can be calculated from known values of $I$ and $R_2$. In this way, around 1500 additional log $L^{16}$ values have been obtained [14–16].

Although the original values [1] were obtained from retention data on conventional packed columns, the further log $L^{16}$ values [14–16] were calculated from retention data on both capillary columns and conventional packed columns, usually at elevated temperatures. Recently, Zhang et al. [18], in a careful study, have re-determined log $L^{16}$ values from data on hexadecane at 25°C, using a fused-silica open-tubular capillary column. For most of 85 common solutes, there was excellent agreement between the original values and those obtained using the capillary column, but for a number of solutes there were significant deviations (see Table 1). Zhang et al. [18] attributed these differences to interfacial adsorption in the packed column, rather than to any such effect in the capillary column. Certainly, adsorption effects will be expected to be larger at 25°C than at elevated temperature, but there is no direct evidence on exactly how large such effects are, with respect to the hexadecane packed column.

It is the purpose of this paper to present experimental data that will allow conclusions to be drawn on the possible effects of adsorption on the solid support and of interfacial adsorption, with respect to retention in packed columns with a low-polarity stationary phase. We hope in this way to obtain information on the actual origin of the discrepancies between retention data on the hexadecane capillary and packed columns.

## 2. Experimental

Specific retention volumes on the support Chromosorb G AW DMCS at the column temperature were obtained as set out before, with the usual corrections for the pressure drop across the column [1]. Data were obtained at 25°C, with the column immersed in a water-bath, and at 93°C using a conventional air oven. Specific retention volumes on squalane packed columns were obtained exactly as detailed before [19,20].

## 3. Results and discussion

Before dealing with new results, we give in Table 1 some log $L^{16}$ values that we had re-determined before Zhang et al.'s paper [18] appeared. The new values for benzyl alcohol, phenol and butylbenzene go some way to resolving the discrepancies, but the new results for the cresols are essentially the same as our original values. The log $L^{16}$ values for carboxylic acids obtained from either the capillary column or the packed column are incorrect, owing to dimerization of the acids. We have obtained log $L^{16}$ values for the acids by an indirect, non-chro-

Table 1
Some discrepancies between log $L^{16}$ values measured on capillary and packed columns

| Solute | $C(25)^a$ | $A(25)^b$ | $A(HT)^c$ |
|---|---|---|---|
| Butylbenzene | 4.714 | 4.686 | 4.730[d] |
| Benzyl alcohol | 4.162 | 4.443 | 4.221 |
| Phenol | 3.641 | 3.865 | 3.766 |
| *o*-Cresol | 4.183 | 4.242 | 4.218 |
| *m*-Cresol | 4.187 | 4.329 | 4.310 |
| *p*-Cresol | 4.254 | 4.307 | 4.312 |
| Acetic acid | 2.331 | 3.290 | 1.750[e] |
| Propanoic acid | 2.978 | – | 2.290[e] |
| Butanoic acid | 3.427 | – | 2.830[e] |
| DMF | 2.922 | 3.173 | 3.173[f] |
| DMA | 3.357 | 3.717 | 3.717[f] |
| DMSO | 3.110 | 3.437 | 3.459 |

[a] Capillary column data, Ref. [18].
[b] Packed column data, Ref. [1].
[c] Recent packed column data, at higher temperature, Ref. [16].
[d] Redetermined at 25°C.
[e] Indirect value, see text.
[f] Same as original values.

matographic, method, using gas–water partition coefficients [21] and water–hexadecane partition coefficients [22] that are corrected for dimerization. The calculated log $L^{16}$ values are given in Table 1; we have confirmed that these indirect values reproduce GLC retention data at elevated temperatures, where the acids are monomeric in the gas phase. We are left with only three outlying solutes, viz., N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) and dimethyl sulfoxide (DMSO) where the new results are the same as our original results, and where there are considerable differences between the packed column and capillary data.

Possible effects of adsorption on the inert support can be studied through measurements of specific retention volumes on the support itself. Results at 25 and at 93°C are given in Table 2. We would have liked to obtain values at 120°C but the retention volumes were too small to measure conveniently. We can use these retention volumes to calculate the contribution made by adsorption on the support to the overall retention, by assuming that the support is, say, only 90% covered. The real contribution will be

Table 2
Values of log $V_G$ on Chromosorb G AW DMCS at 25 and 93°C

| Solute | Log $V_G$ | |
|---|---|---|
| | 25°C | 93°C |
| Octane | −0.02 | |
| Nonane | 0.47 | |
| Decane | 0.95 | −0.41 |
| Undecane | 1.36 | −0.33 |
| Dodecane | | 0.04 |
| Tridecane | | 0.28 |
| Tetradecane | | 0.56 |
| Pentadecane | | 0.83 |
| Hexadecane | | 1.13 |
| Heptadecane | | 1.45 |
| Octadecane | | 1.68 |
| Nonadecane | | 1.94 |
| Diiodomethane | 0.49 | −1.21 |
| Dibutyl ether | 1.11 | −0.72 |
| Tetrahydrofuran | 0.79 | |
| Pentan-2-one | 0.75 | |
| Heptan-2-one | 1.41 | |
| Octan-2-one | | −0.18 |
| Nonan-2-one | | 0.10 |
| Nonan-5-one | | −0.14 |
| Decan-2-one | | 0.28 |
| Butyl propanoate | 1.25 | −0.81 |
| Pentyl acetate | 1.32 | |
| Methanol | | −1.21 |
| Ethanol | 0.51 | |
| Propan-1-ol | 0.88 | |
| Butan-1-ol | 1.20 | |
| Heptan-1-ol | | −0.05 |
| Octan-1-ol | | 0.22 |
| Octan-2-ol | | −0.13 |
| Decan-1-ol | | 0.79 |
| TFE | | −0.73 |
| HFIP | 0.55 | −1.19 |
| Triethylamine | | −0.47 |
| DMF | [a] | 0.05 |
| DMA | [a] | 0.17 |
| DMSO | [a] | 0.38 |
| Benzene | | −1.01 |
| Toluene | | −1.01 |
| Ethylbenzene | | −0.85 |
| Propylbenzene | 0.61 | |
| Butylbenzene | 1.19 | |
| Chlorobenzene | 0.27 | |
| 1,2-Dichlorobenzene | 0.94 | |
| 3-Chlorotoluene | | −0.99 |
| 4-Chlorotoluene | 0.60 | −0.99 |
| Iodobenzene | 0.93 | |
| Acetophenone | | −0.88 |

*(Continued on p. 128)*

Table 2 *(continued)*

| Solute | Log $V_G$ | |
|---|---|---|
| | 25°C | 93°C |
| Benzonitrile | | −0.21 |
| Aniline | | −0.20 |
| Phenol | 2.23 | |
| *m*-Cresol | | 0.37 |
| 2-Isopropylphenol | | 0.37 |
| 3-Isopropylphenol | | 0.66 |
| 3-Chlorophenol | | 0.80 |
| Pyridine | | −0.48 |

[a] These compounds were not eluted at 25°C.

some fraction of this, depending on the actual percentage covered. Results of calculations on these lines are given in Table 3. It is clear that for most solutes there will be a negligible contribution from adsorption on the support, but with alcohols, especially hexafluoropropan-2-ol (HFIP) and possibly also trifluoroethanol (TFE), there could be some contribution. In the event, there is good agreement between the packed column and capillary column results for HFIP. However, we observed that the three "key" solutes, DMF, DMA and DMSO, all failed to elute from the support at 25°C, so that it does seem possible that adsorption on the support could lead to log $L^{16}$ values that are too large.

We cannot calculate possible support effects at 120°C in the same way, because the log $V_G$ values were too small to determine. However, a rough estimate suggests that for 90% coverage, the contribution from adsorption on the support to retention on a squalane packed column is 0.8% and 0.4% for 5% and 10% loadings, respectively, with the solute DMSO. For DMF and DMA the contribution is even less, and for the other solutes studied it is also negligible. These results are in agreement with the study by Condor et al. [23], who showed that at low loadings of squalane on silanized Chromosorb P, adsorption of ethyl acetate at the support surface was substantial, but that this decreased with increasing temperature.

Table 3
Percentage contribution to retention volume by adsorption on Chromosorb G AW DMCS at 25°C assuming 90% support coverage

| Solute | 5% loading | 10% loading |
|---|---|---|
| Octane | 0.03 | 0.01 |
| Decane | 0.03 | 0.01 |
| Pentan-2-one | 1.46 | 0.69 |
| Propan-1-ol | 8.94 | 4.24 |
| HFIP | 21.10 | 9.98 |
| Butylbenzene | 0.04 | 0.02 |
| Chlorobenzene | 0.04 | 0.02 |
| Phenol | 3.38 | 1.60 |

Having to hand the log $V_G$ values on Chromosorb G AW DMCS at 25 and 93°C, we can analyse them through our general solvation equation in the usual way [24]. The solute descriptors are those previously listed [24], and the found regression equations are

$$\log V_G(25) = -2.43 - 0.30R_2 + 0.35\pi_2^H + 2.13\Sigma\alpha_2^H + 2.05\Sigma\beta_2^H + 0.69 \log L^{16} \quad (2)$$

$n = 22$, $\rho = 0.9650$, S.D. = 0.144, $F = 43.3$

$$\log V_G(93) = -2.89 - 0.46R_2 + 0.59\pi_2^H + 1.18\Sigma\alpha_2^H + 0.66\Sigma\beta_2^H + 0.51 \log L^{16} \quad (3)$$

$n = 45$, $\rho = 0.9634$, S.D. = 0.221, $F = 100.7$

where $\pi_2^H$ is the solute dipolarity/polarizability, $\Sigma\alpha_2^H$ is the solute overall or effective hydrogen-bond acidity and $\Sigma\beta_2^H$ is the solute overall or effective hydrogen-bond basicity. Although the equations are not very good, they are reasonable for gas–solid processes. The significant points are that (1) the support is considerably basic ($a = 2.13$ and 1.18) and is considerably acidic ($b = 2.05$ and 0.66), and (2) both basicity and acidity decrease markedly with increase in temperature. Thus any solute–support effects will also decrease with increase in temperature.

The problem of interfacial adsorption in packed columns is also less at elevated temperature, as found experimentally by Poole and coworkers [25–29], who determined the extent of interfacial adsorption in various systems

[19,20,25–30] using a well known procedure [31,32]. In this method, retention volumes for a given solute are obtained at several loadings of a particular stationary phase. Extrapolation of the retention volumes to infinite stationary phase volume yields the partition coefficient for the gas–stationary phase, free from any interfacial effects. The method requires (i) that the adsorption isotherm is linear, (ii) that the contribution from adsorption remains essentially constant as the loading is altered (constant surface area) and (iii) that the solute is at infinite dilution. Conditions (i) and (iii) can be fulfilled by the use of low solute concentration, and tested by the observation of symmetrical peak shape. Condition (ii) can be tested by the observation of a linear extrapolation of retention data against $1/V_L$, where $V_L$ is the volume of the stationary phase. These conditions were always found to hold [19,20,25–30]. The procedure [31,32] used by Poole and co-workers will also eliminate effects from adsorption on the support, although as we have seen these will be very small at elevated temperature. In Table 4 we give the percentage contribution by adsorption to the total retention for DMSO, DMA and DMF, obtained as above, on a squalane packed column at 120°C. As found for adsorption on the support, above, these results show that at temperatures above about 100°C there is a negligible contribution from interfacial adsorption even for the three very polar solutes, DMSO, DMA and DMF, on the non-polar squalane phase.

A comparison of percentage contribution by adsorption for a number of solutes and solvents [29] is given in Table 5. Together with previous work [23], these results show that interfacial effects in non-polar packed columns can be eliminated by using high loadings of the non-polar phase and particularly by working at elevated temperatures.

In this way, we determined gas–squalane partition coefficients at 120°C that are corrected for any interfacial adsorption for a number of solutes common to the sets of Abraham et al. [1] and Zhang et al. [18], including the key solutes DMSO, DMA and DMF [33–35]. It is now possible to compare these fully corrected data at 120°C with the uncorrected data obtained on the packed and capillary columns at 25°C. The gas–squalane partition coefficients, as log $K$ values, are given in Table 6, denoted as $P(120)$. Also in Table 6 are the log $L^{16}$ values from the 25°C data on the capillary column, $C(25)$, and on the packed column, $A(25)$, and log $L^{16}$ values obtained by the back-calculation method from retention data at higher temperatures, $A(HT)$. Finally, the best set of log $L^{16}$ values from

Table 4
Percentage interfacial adsorption on squalane with Chromosorb W AW DMCS support

| Temperature (°C) | Solute | Phase loading (%) | | | |
|---|---|---|---|---|---|
| | | 8.8 | 12.6 | 15.5 | 20.2 |
| 120 | DMSO | 1.6 | 0.9 | 1.2 | 0.6 |
| | DMA | 0.9 | 0.7 | 0.6 | 0.4 |
| | DMF | 1.9 | 1.2 | 1.0 | 0.8 |
| 100 | DMSO | 8.4 | 4.2 | 5.7 | 4.0 |
| | DMA | 8.2 | 4.2 | 5.5 | 4.0 |
| | DMF | 8.4 | 4.3 | 5.7 | 4.0 |
| 80 | DMSO | 17.3 | 11.3 | 8.7 | 7.9 |
| | DMA | 17.2 | 11.1 | 8.7 | 7.8 |
| | DMF | 17.3 | 11.2 | 8.8 | 7.8 |
| 60 | DMSO | 31.3 | 23.4 | 15.0 | 16.2 |
| | DMA | 31.3 | 23.2 | 15.7 | 16.0 |
| | DMF | 31.2 | 23.1 | 16.0 | 15.6 |

Table 5
Comparison of percentage interfacial adsorption for various solutes and stationary phases

| Temperature (°C) | Solute | Stationary phase[a] | | | | |
|---|---|---|---|---|---|---|
| | | SQ | OV-17 | CW-20M | TCEP | DEGS |
| 121 | Tridecane | 1.5 | 0.6 | 4.5 | 21.7 | 26.9 |
| | Oct-2-yne | 2.1 | 0.6 | 5.9 | 7.1 | 11.2 |
| | Methyl octanoate | 0.9 | 0.4 | 3.7 | 1.9 | 7.3 |
| | Benzonitrile | 2.6 | 0.6 | 2.9 | 1.2 | 5.3 |
| | Heptan-1-ol | 2.6 | 0.6 | 1.9 | 2.0 | 6.6 |
| | Heptan-2-one | 1.0 | 0.8 | 1.8 | 3.3 | 7.0 |
| | Ethylbenzene | 2.8 | 0.8 | 4.7 | 12.5 | 11.4 |
| | N,N-Dimethylaniline | 2.5 | 0.5 | 2.1 | 2.8 | 12.5 |
| | DMSO | 1.2 | | | | |
| | DMA | 0.6 | | | | |
| | DMF | 1.0 | | | | |
| 81 | Tridecane | 7.0 | 2.3 | 23.0 | 47.9 | 66.3 |
| | Oct-2-yne | 7.8 | 2.1 | 11.9 | 8.3 | 32.3 |
| | Methyl octanoate | 8.1 | 2.0 | 10.9 | 10.2 | 26.5 |
| | Benzonitrile | 7.8 | 2.1 | 7.2 | 16.0 | 37.1 |
| | Heptan-1-ol | 15.5 | 2.3 | 8.9 | 5.2 | 14.7 |
| | Heptan-2-one | 8.6 | 1.4 | 7.2 | 3.9 | 9.5 |
| | Ethylbenzene | 8.1 | 2.2 | 6.6 | 12.0 | 15.2 |
| | N,N-Dimethylaniline | 8.0 | 2.1 | 5.0 | 17.2 | 34.6 |
| | DMSO | 8.7 | | | | |
| | DMA | 8.7 | | | | |
| | DMF | 8.8 | | | | |

Data from Ref. [29] and Table 4.
[a] SQ Squalane; OV-17 = poly(methylphenylsiloxane); CW-20M = poly(ethylene glycol); TCEP = 1,2,3-tris(2-cyanoethoxy-propane); DEGS = poly(diethylene glycol succinate). The phase loading is 15–16% in all cases.

packed columns at 25°C and at higher temperatures is given as $A$(All).

We start by regressing the 40 values of $A(25)$ and the 33 values of $C(25)$ against $R_2$ and $P(120)$, exactly on the lines of Eq. 1, to yield

$$A(25) = 0.355 - 0.238R_2 + 1.719P(120) \quad (4)$$
$$n = 40,\ \rho = 0.9982,\ \text{S.D.} = 0.054,\ F = 5242$$

$$C(25) = 0.270 - 0.232R_2 + 1.734P(120) \quad (5)$$
$$n = 33,\ \rho = 0.9901,\ \text{S.D.} = 0.104,\ F = 750$$

There is no doubt that the uncorrected packed column data, $A(25)$, correlate better with the corrected packed column data than do the uncorrected capillary column data, $C(25)$. In both regressions, the difficult polar solutes DMSO, DMA and DMF are included (see Table 6). A referee pointed out that Eqs. 4 and 5 are not exactly matched, with respect to either the number or type of solutes. We therefore repeated regressions with the same 29 common solutes, including DMSO, DMA and DMF;

$$A(25) = 0.369 - 0.223R_2 + 1.710P(120) \quad (6)$$
$$n = 29,\ \rho = 0.9967,\ \text{S.D.} = 0.060,\ F = 1979$$

$$C(25) = 0.283 - 0.245R_2 + 1.731P(120) \quad (7)$$
$$n = 29,\ \rho = 0.9897,\ \text{S.D.} = 0.108,\ F = 620$$

As might have been expected, there is very little difference in the two sets of equations, and the conclusion remains the same: the uncorrected packed column data yield the better regression equation. The three solutes DMSO, DMA and DMF are not outliers in Eq. 4 (or Eq. 6), but

Table 6
Comparison of corrected log $K$ values on squalane at 120°C with sets of log $L^{16}$ values

| Solute | $P(120)$[a] | $C(25)$[b] | $A(25)$[c] | $A(HT)$[d] | $A(ALL)$[e] |
|---|---|---|---|---|---|
| Heptane | 1.64 | 3.17 | 3.17 | | 3.17 |
| Octane | 1.93 | 3.68 | 3.68 | | 3.68 |
| Nonane | 2.22 | 4.18 | 4.18 | | 4.18 |
| Decane | 2.52 | 4.69 | 4.69 | | 4.69 |
| Undecane | 2.81 | | 5.19 | | 5.19 |
| Dodecane | 3.10 | | 5.70 | | 5.70 |
| Tridecane | 3.40 | | 6.20 | | 6.20 |
| Nonanal | 2.63 | | 4.86 | | 4.86 |
| Butanone | 1.14 | 2.27 | 2.29 | | 2.29 |
| Pentan-2-one | 1.42 | 2.73 | 2.76 | | 2.76 |
| Hexan-2-one | 1.71 | | 3.26 | | 3.26 |
| Heptan-2-one | 2.00 | | 3.76 | | 3.76 |
| Octan-2-one | 2.29 | | 4.26 | | 4.26 |
| Nonan-2-one | 2.57 | | 4.74 | | 4.74 |
| Benzene | 1.51 | 2.79 | 2.79 | | 2.79 |
| Butylbenzene | 2.64 | 4.71 | 4.73 | | 4.73 |
| Butan-1-ol | 1.26 | 2.54 | 2.60 | | 2.60 |
| Pentan-1-ol | 1.62 | 3.06 | 3.11 | | 3.11 |
| Hexan-1-ol | 1.91 | 3.55 | 3.61 | | 3.61 |
| Heptan-1-ol | 2.21 | 4.07 | 4.12 | | 4.12 |
| Octan-1-ol | 2.51 | 4.57 | 4.62 | | 4.62 |
| Nonan-1-ol | 2.79 | | 5.12 | | 5.12 |
| 2-Methylpentan-2-ol | 1.59 | | 3.08 | | 3.08 |
| *Sym*-Tetrachloroethane | 2.15 | | 3.80 | | 3.80 |
| Toluene | 1.80 | 3.34 | 3.33 | | 3.33 |
| Ethylbenzene | 2.07 | 3.79 | 3.78 | | 3.78 |
| DMSO | 1.89 | 3.11 | 3.44 | 3.46 | 3.46 |
| DMF | 1.70 | 2.92 | 3.17 | | 3.17 |
| DMA | 2.02 | 3.36 | 3.72 | | 3.72 |
| Nitropropane | 1.50 | 2.77 | 2.71 | 2.89 | 2.89 |
| Pyridine | 1.64 | 2.97 | 3.00 | 3.02 | 3.02 |
| Aniline | 2.23 | 3.93 | 3.99 | 3.93 | 3.93 |
| N,N-Dimethylaniline | 2.69 | 4.75 | 4.75 | 4.70 | 4.70 |
| 1,2-Dichlorobenzene | 2.53 | 4.45 | 4.41 | 4.52 | 4.52 |
| Chlorobenzene | 2.01 | 3.63 | 3.64 | 3.66 | 3.66 |
| Bromobenzene | 2.26 | 4.02 | 4.04 | 4.04 | 4.04 |
| Dioxane | 1.50 | 2.79 | 2.80 | 2.89 | 2.89 |
| Acetophenone | 2.52 | 4.46 | 4.48 | 4.50 | 4.50 |
| Phenol | 2.05 | 3.64 | 3.86 | 3.77 | 3.77 |
| *p*-Cresol | 2.39 | 4.25 | 4.31 | 4.31 | 4.31 |
| Benzonitrile | 2.23 | 3.91 | | 4.04 | 4.04 |
| N-Methylaniline | 2.55 | 4.49 | | 4.48 | 4.48 |
| Iodobenzene | 2.56 | 4.51 | | 4.50 | 4.50 |
| Benzaldehyde | 2.23 | 3.94 | | 4.01 | 4.01 |
| Dodec-1-yne | 3.05 | | | 5.66 | 5.66 |
| Oct-2-yne | 2.06 | | | 3.85 | 3.85 |
| *cis*-Hydrindane | 2.54 | | | 4.64 | 4.64 |
| Methyl heptanoate | 2.34 | | | 4.36 | 4.36 |
| Methyl octanoate | 2.62 | | | 4.84 | 4.84 |
| Methyl nonanoate | 2.90 | | | 5.32 | 5.32 |
| Methyl decanoate | 3.18 | | | 5.80 | 5.80 |
| Methyl undecanoate | 3.46 | | | 6.29 | 6.29 |

*(Continued on p. 132)*

Table 6 *(continued)*

| Solute | $P(120)^a$ | $C(25)^b$ | $A(25)^c$ | $A(HT)^d$ | $A(ALL)^e$ |
|---|---|---|---|---|---|
| Nitrohexane | 2.39 | | | 4.42 | 4.42 |
| Nitrocyclohexane | 2.66 | | | 4.83 | 4.83 |
| Nitropentane | 2.09 | | | 3.94 | 3.94 |
| 2,6-Dimethylaniline | 2.84 | | | 5.03 | 5.03 |
| Dihexyl ether | 3.23 | | | 5.94 | 5.94 |
| Benzodioxane | 2.81 | | | 4.97 | 4.97 |
| 4-Chlorophenol | 2.67 | | | 4.78 | 4.78 |
| 2,5-Dimethylphenol | 2.66 | | | 4.77 | 4.77 |
| 2,6-Dimethylphenol | 2.62 | | | 4.68 | 4.68 |
| 3,5-Dimethylphenol | 2.71 | | | 4.86 | 4.86 |

[a] Corrected log $K$ values on squalane at 120°C, Refs. [33,35].
[b] Uncorrected log $L^{16}$ capillary values at 25°C, Ref. [18].
[c] Uncorrected log $L^{16}$ packed column values at 25°C, Ref [1].
[d] Uncorrected, back-calculated log $L^{16}$ values at higher temperature, Ref. [16].
[e] Taken log $L^{16}$ values from previous two columns.

they are in Eq. 5 (or Eq. 7). If all three are excluded from Eq. 5, we find

$$C(25) = 0.340 - 0.242R_2 + 1.716P(120) \quad (8)$$
$$n = 30,\ \rho = 0.9986,\ \text{S.D.} = 0.039,\ F = 4987$$

There is almost no statistical difference between Eqs. 4 and 8, confirming the finding of Zhang et al. [18] that for most solutes there is little to choose between the packed column and the capillary column results on hexadecane at 25°C. Hence for solutes that are not too volatile, either a packed hexadecane column at 25°C or a capillary hexadecane column at 25°C will yield reasonable values of log $L^{16}$, as found by Zhang et al. [18]. Our conclusion regarding the outliers DMSO, DMA, and DMF is not the same as that of Zhang et al. however, because we have shown that the packed column results at 25°C are in essential agreement with the fully corrected values obtained at 120°C. Zhang et al. [18] warned against the use of calculations on the lines of Eq. 1 to obtain further log $L^{16}$ values, but we can compare the back-calculated log $L^{16}$ values, as $A(HT)$, with the corrected squalane values:

$$A(HT) = 0.372 - 0.239R_2 + 1.719P(120) \quad (9)$$
$$n = 34,\ \rho = 0.9993,\ \text{S.D.} = 0.031,\ F = 11\,281$$

The excellent correlation, eqn. 9, shows that calculation using data at elevated temperatures is probably the best method of determining log $L^{16}$ values for polar solutes. Finally, we regressed the total set of log $L^{16}$ values against the corrected log $K$ values, as $P(120)$:

$$A(ALL) = 0.374 - 0.238R_2 + 1.716P(120) \quad (10)$$
$$n = 62,\ \rho = 0.9994,\ \text{S.D.} = 0.033,\ F = 22\,934$$

The regression Eq. 10 confirms that the set of log $L^{16}$ values published [24] is entirely compatible with the corrected results on squalane at 120°C.

The data shown in Table 5 indicate that the use of heavily loaded packed columns with non-polar phases at elevated temperatures can lead to retention data essentially free from contributions due to interfacial adsorption. The situation with capillary columns is not so clear. First, a distinction must be made between capillary columns that have chemically bonded phases and capillary columns such as that used by Zhang et al. [18], which are deactivated by heating and which are coated from solution. The latter are not inert; indeed, Zhang et al. [18] specifically noted the problem of adsorption for DMSO, DMA, DMF, aliphatic amines, aniline and pyridine on the hexadecane capillary column. There seem to be a number of disadvantages in the use of capillary columns to obtain thermodynamic data, as follows. (i) It is very difficult to

obtain absolute retention data; Zhang et al. [18] overcame this problem by using data for alkanes on a packed hexadecane column, obtained by Abraham et al. [1] as standards for a hexadecane capillary column, but this stratagem is not usually available. (ii) The problem of interfacial adsorption still exists with capillary columns; Matisova et al. [36] examined a capillary column coated with the relatively non-polar OV-101 and Apiezon L. They showed that as the film thickness increased, the Kováts retention indices of methyl alkanoates reached limiting values, but for decan-1-ol no clear limiting value was obtained, at 100 or 110°C. Gvoliany and Rixiao [37] also examined a capillary column coated with OV-101, this time at 120°C. They showed that with a film thickness of 0.3 $\mu$m, interfacial adsorption makes a ca. 20% contribution to the total retention for solutes such as octan-1-ol and methyl hexanoate. Although we are concerned with non-polar phases, it is worth pointing out that Berezkin and Korolev [38] investigated a fused-silica open-tubular column coated with the polar phase SP-2380 and found that interfacial adsorption of alkanes was so large at 85°C that Kováts retention indices could not be determined. It seems, therefore, that interfacial adsorption in capillary columns is no less a problem than in packed columns. Zhang et al. [18] quoted Lichtenthaler et al. [39] as suggesting that the volume-to-area ratio for a capillary column could be more than two orders of magnitude larger than for a packed column, which, if correct, would indicate that interfacial adsorption should be very much less with capillary columns. We calculate that for a capillary column of length 20 m, of I.D. 0.053 cm and of film thickness 0.29 $\mu$m the volume to surface area is $2.90 \cdot 10^{-5}$ cm. For a packed squalane column of length 2 m, with a 15% loading (0.27 g of squalane and 1.53 g of support) and of support surface area $10^4$ cm$^2$ g$^{-1}$, at 120°C where the density of squalane is 0.7278 g cm$^{-3}$, the volume to surface area is $2.43 \cdot 10^{-5}$ cm. The ratio between the capillary and packed columns is thus around 1.2, nowhere near the "two orders of magnitude" suggested. (iii) As clearly shown by Zhang et al. [18], the use of excessive amounts of solute can result in increased retention times through solute–solute association. Such use can also result in decreased retention times through non-equilibration of the solute with the stationary phase. A lack of linearity in the adsorption/absorption isotherm could lead to either an increase or a decrease in retention time. The overall effect will be compound specific and can result in an increase or decrease in retention time. We argue that these problems may be more severe with capillary columns as used by Zhang et al. [18] than with packed columns. In any case, it is clear that a calculated log $L^{16}$ value could be larger or smaller on the hexadecane capillary column at 25°C than on the packed hexadecane column at 25°C.

Our conclusion is that there is no advantage to be gained through the use of capillary columns to measure thermodynamic data. With non-polar stationary phases it is reasonably clear that the use of heavily loaded packed columns at temperatures above about 100°C will yield retention data free from complications due to interfacial adsorption. As regards the determination of log $L^{16}$ values for "difficult" polar solutes and for the less volatile solutes, we recommend that if packed columns are employed, then high loadings of non-polar stationary phases should be used. In any case, whatever the type of column, it is a marked advantage to work at elevated temperature.

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