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Alkanol gas–liquid partition coefficients in squalane measured with packed columns
A revision of measurement methods

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Abstract

Retention volumes of 13 alkanols were measured at five temperatures between 30 and 60°C in a series of six columns packed with different squalane percentages on Chromosorb W previously modified with Carbowax 20M according with Aue et al.'s method [J. Chromatogr. 77 (1973) 299]. While alkanol retention times are independent of sample size when chromatographed in these packings, an important variation is demonstrated in columns packed with squalane coated on Chromosorb W DMCS under otherwise identical conditions. It is demonstrated that the intercepts of plots V_N/V_L vs. $1/V_L$ (V_N is retention volume per gram of packing; V_L is stationary phase volume per gram of packing) cannot be identified with the partition coefficient, and a method to calculate the gas–liquid partition coefficient is proposed.

Keywords: Partition coefficients; Squalane; Alkanols

1. Introduction

Measurement of infinite dilution gas–liquid partition coefficients for highly polar solutes in non-polar stationary phases by means of GLC suffers from an important experimental difficulty: sample size-dependent retention times are obtained, with dubious or null thermodynamic significance. The subject has gained in importance recently because of the role played by gas–hexadecane partition coefficients in linear free energy relationships (LFERs) [1–5]; different prescriptions have been proposed for their measurement [1,6–8], and a consensus is seemingly far from being reached.

There are, however, other fields of chromatographic investigation that have been postponed or deficiently studied because of these difficulties. To quote an example, molecular association investigations [9,10] have been limited to sparingly or moderately polar solutes, as aromatic hydrocarbons and halogenated methanes; since solutions of a complexing additive in an 'inert' solvent (usually an alkane) are employed as stationary phases, associations involving very polar solutes have seldom been studied.

Discussions in this paper shall be restricted to alkanol as solutes in alkane stationary phases. Peak

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asymmetry in these chromatographic systems obey two different origins:

1. Strong interactions between the alcohols and active sites on the solid support or capillary wall surfaces (silanol groups, metallic impurities) result in solute adsorption on the solid–stationary phase interface (SLI) or on uncoated portions of the solid (GSI). These distribution processes are characterized by highly curved isotherms whose linear portions are not even reached at the lower solute concentrations compatible with high sensitivity detectors.
2. Alkanol–alkane mixtures display strong positive non-idealities that result in solute adsorption on the gas–stationary phase interface (GLI). Linear ranges for the distribution isotherms of processes of this type are larger than those typical of adsorption on the SLI or on the GSI; non-linearity, however, starts at solute gas-phase concentrations at which the partition process still behaves linearly.

Retention in the presence of these concurrent distribution processes has been described by equations of the type [11,12]

$$V_N = K_L V_L + K'_A A_L + K'_I A_I + K'_S A_S \quad (1)$$

where V_N is the net retention volume per gram of packing, K_L is the gas–liquid partition coefficient, and V_L is the stationary phase volume per gram of packing. A_L, A_I and A_S represent the surface areas per gram of packing of the GLI, SLI and GSI, respectively, and K'_A, K'_I and K'_S are the slopes of the adsorption isotherms on the three mentioned surfaces; primes denote finite concentration, i.e. a non-linear region in the isotherm. Basic chromatographic theory tells that if infinite dilution is not attained by *any* of the distribution processes, resulting peaks shall be asymmetrical, their maxima displaying sample size-dependent retention times. Several methods to measure K_L in the presence of peak asymmetry have been proposed; their advantages and limitations have been discussed by Zhang et al. [6], who came to the conclusion that accurate measurements of thermodynamic partition coefficients demand that adsorption effects be minimized.

The use of silane-treated diatomite supports causes a decrease in the asymmetry of alkanol peaks, but not to the point of generating sample size-independent retention times; this was demonstrated in several opportunities, for instance by Cadogan et al. [13] using Sil–O–Cel HMDS/squalane packings, and by Zhang et al. [6] on using columns packed with hexadecane coated on Chromosorb P AW DMCS or on Chromosorb W HP. These last authors resorted then to hexadecane-coated fused-silica capillaries; with a few exceptions (amines, for instance), polar solutes chromatographed in these columns produced excellent peaks. Retention times were sample size independent, as demonstrated by t_R against log (peak area) plots shown for several alcohols; this or similar validation information should be demanded from all papers reporting data with thermodynamic implication.

Symmetrical peaks, however, indicate that infinite dilution has been attained for all the distribution processes, but not that adsorption effects have been suppressed. If the GLI is considered, for instance, elementary geometry indicates that $A_L/V_L \cong 1/\delta$ for a capillary coated with an uniform film with thickness δ; under these assumption $A_L/V_L \cong 34\,000$ cm^{-1} for the columns used by Zhang et al. Plots of A_L/V_L for β,β′-thiodipropionitrile (TDPN) on Chromosorb W calculated by Martire et al. [14] on the basis of previous experimental results [15,16] indicate that packings containing about 5% (w/w) of stationary phase show similar A_L/V_L values. From a comparison between fused-silica capillary and packed columns, it results that the former offer the advantage of a more inert solid surface, but GLI adsorption effects shall be similar in both types of column. Carr and co-workers rapidly perceived that their results with the capillary columns were not free from adsorption effects (although apparently they were thinking in terms of adsorption on the silica surface); polar solutes partition coefficients measured by means of a head-space technique reported a few months latter by workers of the same group [8] were smaller than those obtained in capillary columns.

Research projects under development in our laboratory demanded for the measurement of alkanols partition coefficients in pure squalane and in mixtures with additives. Measurements could be made in capillary columns, correcting for adsorption effects by using a set of equal length and diameter columns coated with films of different δ; since A_L and A_I

differences between columns shall be negligible (at least for 0.53-mm I.D. capillaries coated with uniform films thinner than, say, 5 μm) a constant adsorption contribution can reasonably be predicted. Apart from experimental difficulties in coating such a set of capillaries, the highly convenient computation method used by Carr and co-workers [6] (see their Eq. (3)) cannot be employed in the presence of adsorption, and either the exact amount of stationary phase within each column or totally corrected retention volumes need to be measured; both options are source of considerable errors.

In view of these drawbacks it was decided to try with the ultrathin polymer film-coated diatomite supports developed by Aue et al. several years ago [17]. Sample size-independent retention times have been reported for a short number of polar solutes chromatographed in columns packed with these solids, either bare [18] or coated with a non-polar stationary phase [19]. Results obtained for a group of alkanols in columns packed with Carbowax 20M-deactivated Chromosorb W (henceforth named Chromosorb W-CWX) coated with squalane are reported in the present paper. Most of our conclusions should be applicable to any paraffinic stationary phase.

2. Experimental

Chromosorb W-CWX was prepared with minor modifications to the original method [17]: Chromosorb W 60-80 mesh was repeatedly extracted with boiling 6 *M* hydrochloric acid; acid washing was considered complete when contact with hot acid for 1 h resulted in a colorless liquid. The solid was rinsed with distilled water until neutral, dried at 120°C overnight and coated with 4% Carbowax 20M (Alltech) using chloroform as volatile solvent, with slow evaporation and occasional mixing in a glass evaporating dish. The dry support was packed in a cylindrical (20 cm×2.5 cm I.D.) Pyrex glass reactor and purged with nitrogen for 2 h in an oven at room temperature; the oven was programmed to 270°C at about 5°C/min, held there for 17 h under nitrogen (30 cm^3/min), and then cooled to room temperature. The solid was filled into glass thimbles and extracted for 30 h with methanol in a Sohxlet apparatus.

Squalane (Hewlett-Packard, used as received) was deposited on the solid support from solutions in *n*-hexane. Six different packings, containing 2.13_6, 4.00_1, 5.96_0, 8.04_3, 10.35_5 and 12.03_5% (w/w) squalane, were prepared. Coated supports were packed into columns of three sizes: stainless steel 1.5 m×0.53 cm I.D., glass 1.8 m×0.2 cm I.D. and glass 1.2 m×0.2 cm I.D. Two additional glass columns, 1.8 m×0.2 cm I.D., were packed with 5.13% (w/w) of squalane coated on Chromosorb W-CWX and on Chromosorb W DMCS 60–80 mesh, respectively. In order to prevent squalane oxidation [20] each packing was prepared with fresh portions of stationary phase, under nitrogen current, and was used for relatively short periods (less than a week) at temperatures below 70°C, using high quality nitrogen (less than 1.5 ppm, v/v, oxygen).

Chromatographic measurements were performed in a home-assembled apparatus. Column temperature was controlled to better than ±0.05°C by immersion in a water bath whose temperature was measured by means of a mercury thermometer calibrated against certified thermometers. Nitrogen was used as carrier gas; it was successively passed through a molecular sieves trap (Davidson 5A), a Brooks 8606 pressure regulator, a Brooks 8743 flow controller, and a 2 m×3.2-mm O.D. coiled copper tube immersed in the column bath. Inlet pressures were measured with a mercury manometer at a point between the copper coil and a Swagelock 1/4-in. stainless-steel 'T'; one branch of the latter was provided with a septum through which solute vapours were injected by means of Hamilton microsyringes; the column was connected to the remaining branch (1 in.=2.54 cm). Flow rates were measured with an air-jacketted soap film flowmeter. Detection was performed with a Hewlett-Packard 5750 flame ionization detection (FID) system and electrometer whose signals were fed to a Hewlett-Packard 3396A integrator. Sample size effects on peak shape and retention times were studied in a Hewlett-Packard 5880A gas chromatograph equipped with a FID system.

Samples were of the smallest size compatible with instrument noise (order of nmol); solute vapours and a small methane sample were simultaneously injected, and adjusted retention times were measured between the maxima of the solute (t_R) and the methane (t_{CH4}) peaks. Specific retention volumes were calculated by means of the equation

$$V_g^o = jF_f(273.15/T_f)[(p_o - p_w)/p_o](t_R - t_{CH4})/w \quad (2)$$

where j is James–Martin compressibility correction factor, F_f is the flow rate measured at the temperature T_f and pressure p_o of the flowmeter, p_w is the water vapour pressure at T_f and w represents the mass of squalane within the column. The use of methane as dead time marker finds its justification in the very careful measurements of Quintanilla-López et al. [21], from which a methane capacity factor between 0.007 (if neon is used as dead time marker) and 0.014 (if argon or equations proposed by the authors [21] are used) can be estimated in the packing with higher squalane loading employed in the present work. It can be shown that maximum differences between thus-calculated retention volumes and those obtained by using neon amount to 0.28 and 0.55% in case argon is employed in dead time determination.

Retention volumes were measured not less than four times at each of five temperatures in the 30–50 or 40–60°C intervals, according to solute volatility. Density of squalane, measured by pycnometry between 30 and 60°C, was fitted to the equation ρ (g/cm^3) $= 0.81949 - 6.0899 \times 10^{-4}\ t$, where t is expressed in °C. Values returned by this equation were compared to bibliographic results [22–24] at several temperatures. The largest discrepancy (0.0017 g/cm^3) occurred at 40°C, but differences smaller than 0.001 g/cm^3 were observed for the rest of the temperatures; incidence of these differences on the final results is negligible.

3. Results and discussion

n-Butanol corrected retention times, t'_R, measured at 45°C in two columns (glass, 1.8 m × 0.2 cm I.D., 5.13% (w/w) of squalane on Chromosorb W-CWX and on Chromosorb W DMCS, respectively) are plotted as a function of sample size in Fig. 1; t'_R values were corrected for slight flow rate and packing contents differences. Samples were microsyringe injected; their sizes ranged from a few microlitres to 1 cm^3 of head-space vapours (room temperature), plus some liquid samples injected by means of a 1-mm^3 microsyringe. Very reproducible t'_R values are obtained in the column containing Chromosorb W-CWX for samples rendering peak areas smaller than 10^6 area counts, corresponding to about 400 mm^3 of vapour (a very large sample in terms of thermodynamics measurements); mean retention time and standard deviation for results within that range are 1.504 and 0.002 min, respectively. A very notorious drop in t'_R is observed in the same sample size range for the column prepared with Chromosorb W DMCS. This difference between both columns is attributable to the existence of a large number of non-derivatized silanol groups on the surface of the silanized support, and to a very efficient covering of active sites by the Carbowax 20 M treatment. Retention times rise steeply in both columns when overloaded with very large samples. Zhang et al. [6] have attributed this behaviour to solute–solute association in the liquid phase; we are more prone to think in terms of lateral interactions between alcohol molecules adsorbed on the GLI. Results for *n*-pentanol, plotted in Fig. 2, follow the same pattern; mean retention time and standard deviation within the constant range are 4.080 and 0.006 min, respectively.

Results obtained with four alcohols at 45°C in a 1.5 m × 0.53 cm I.D. column packed with 4.00_1% (w/w) squalane on Chromosorb W-CWX shown in Fig. 3 demonstrate constant t'_R values for samples from 2 to 500 mm^3 of head-space vapour. A different panorama is depicted in Fig. 4, corresponding to ethanol chromatographed in the same conditions, and a similar drop in t'_R was observed with methanol. The reasons for such a sharp cut between the behaviours of methanol and ethanol on one side and the rest of the alcohols on the other cannot be given for the moment.

Summarizing the results of this first part of the work, it can be stated that all the distribution processes will operate within their respective Henry law regions when alkanol samples (excepting methanol and ethanol) of the sizes usually employed in thermodynamics measurements are injected in columns packed with Chromosorb W-CWX coated with squalane.

There has been in the past much debate about the form in which squalane (and other high-molecular-mass alkanes) distribute on the surface of silanized supports and the relative importance of liquid surface contribution to the retention of polar solutes [25,26].

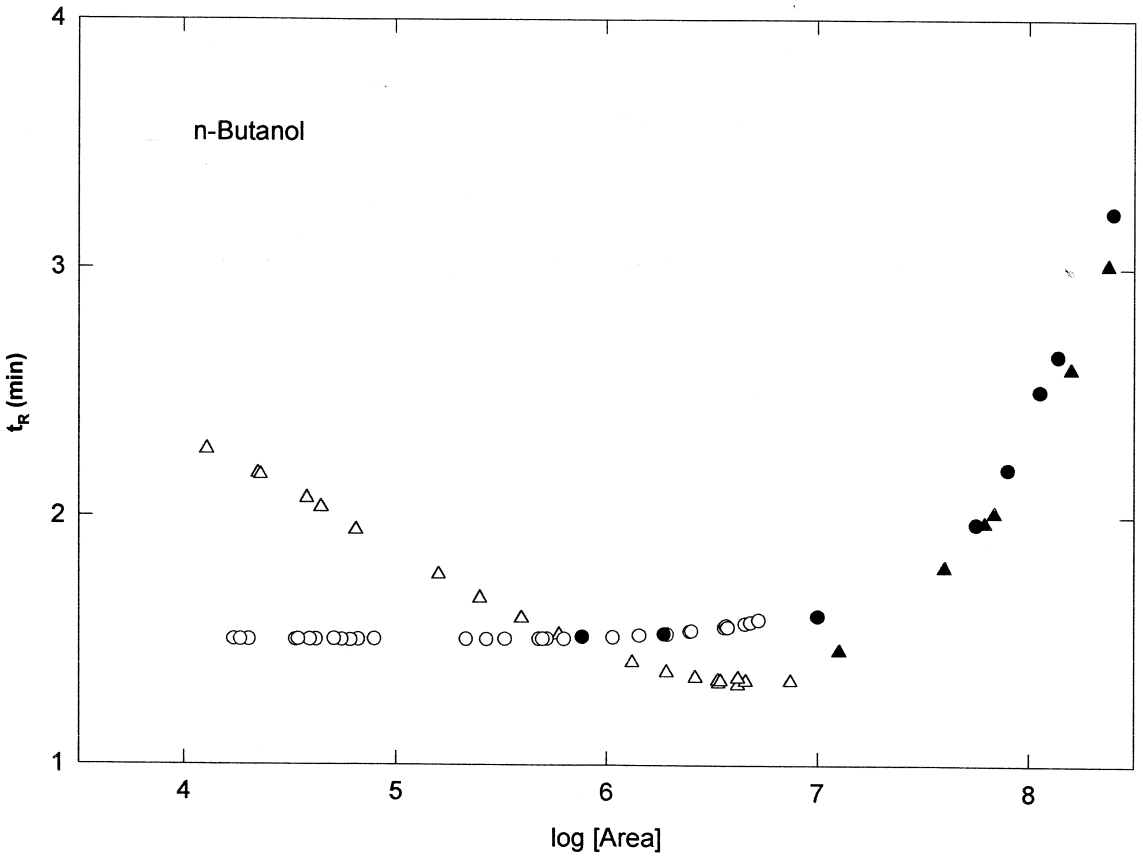

Fig. 1. Effect of injected sample size, as represented by the peak area counts, on the retention time of *n*-butanol. Circles: column packed with 5.13% (w/w) squalane on Chromosorb W-CWX. Triangles: column packed with 5.13% squalane on Chromosorb W DMCS. Empty symbols: vapour samples. Filled symbols: liquid samples.

The origin of the controversy lies in the application of the concept of critical surface tension of wetting, γ_c, developed by Zisman [27]: γ_c of a trimethylsiloxy- or poly(methylsiloxane)-treated glass has been estimated in 21–24 mN/m [27], and a similar value can be assumed for silanized Chromosorb; these surfaces will thus not be wetted by squalane, whose surface tension is 27 mN/m at 30°C [28]. Non-derivatized silicas, however, are high surface free energy solids, with critical surface tensions of wetting of about 45 mN/m [23]; γ_c is also high for poly(ethylene oxide), about 43 mN/m [29], and a high critical surface tension of wetting can be predicted for Carbowax-modified siliceous solids, unless strong non-additive effects are present. Squalane will distribute similarly on the surfaces of non-derivatized and of Carbowax-modified solid supports, following the generally accepted model of a thin film and a capillary condensate, as proposed by Giddings [30]. Contributions from adsorption on the GSI can be neglected for liquid-phase loadings exceeding 0.2–0.4% (w/w). Infinite dilution plus total coverage of the support surface enable Eq. (1) to written in the simplified form

$$V_N = K_L V_L + K_A A_L + K_I A_I \quad (3)$$

Available surface area data for coated Chromosorb W [14–16] show a considerable drop for very low loadings (in consequence of the filling of small pores), with A_L decreasing smoothly and linearly as the concentration of stationary phase increases above

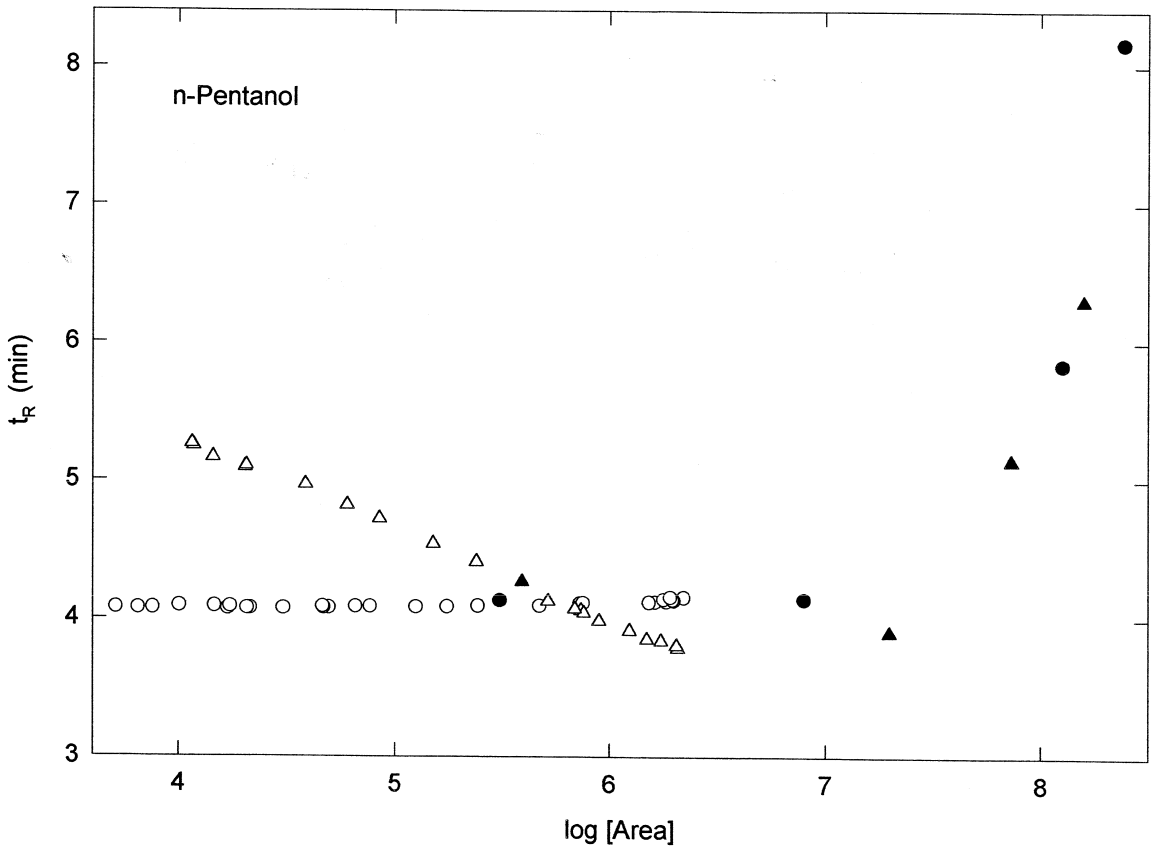

Fig. 2. Effect of injected sample size, as represented by the peak area counts, on the retention time of *n*-pentanol. Symbols as in Fig. 1.

2% (w/w). The tiny amounts of polymer present on the surface of Chromosorb W-CWX should have only minor effects, probably blocking the smallest pores; but A_L values close to those observed for the unmodified support can be predicted for loadings higher than about 2% (w/w). A_L and A_I dependence on V_L in that region can be described by the equations

$$A_L = a - bV_L \quad (4)$$

$$A_I = (1 - \rho V_L)S_I \quad (5)$$

where a and b are constants, ρ is the liquid phase density, and S_I is the solid support specific surface area. These two equations can be combined with Eq. (3) to give

$$V_N/V_L = B + C/V_L \quad (6)$$

where

$$B = K_L - (bK_A + \rho K_I S_I) \quad (7)$$

$$C = aK_A + K_I S_I \quad (8)$$

By combining Eqs. (6) and (7),

$$K_L = B + \rho C + (b - \rho a)K_A] \quad (9)$$

The former equations demonstrate that one of the two following requirements must be fulfilled in order to obtain a linear relationship between V_N and V_L:

1. A constant adsorption contribution, i.e. $K_A A_L + K_I A_I$ independent of V_L; according to Eq. (3) K_L shall be given by the intercept of a V_N/V_L against $1/V_L$ plot. This is the already mentioned case of a series of capillary columns of equal length and I.D. coated with films of different thickness; packed columns will not meet this requirement.

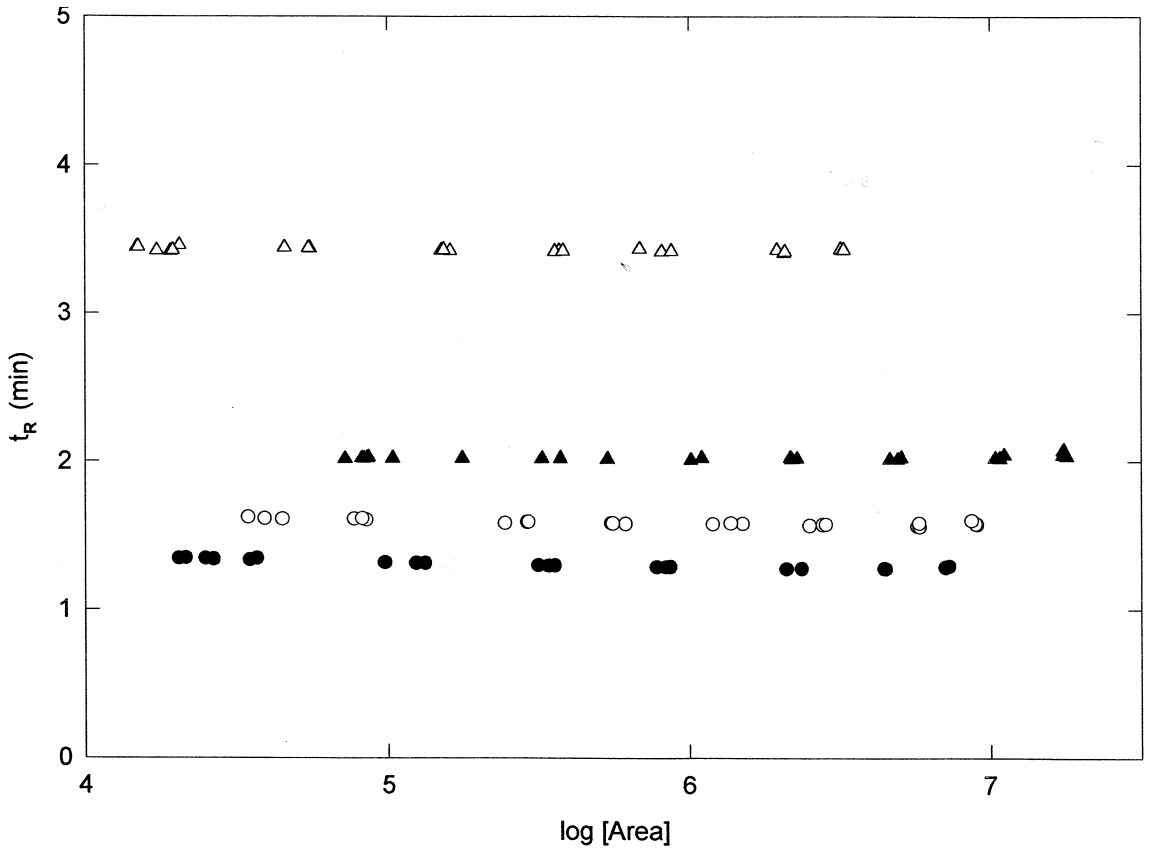

Fig. 3. Effect of injected sample size, as represented by the peak area counts, on the retention time of a series of alcohols. Column packed with 4.00% (w/w) squalane on Chromosorb W-CWX. (△) 1-Butanol; (▲) 2-methyl-2-propanol; (○) 2-propanol; (●) 1-propanol.

2. A_L and A_I decrease linearly with V_L (Eqs. (4) and (5)); these are the cases of Chromosorb W or P coated with liquids that wet their surfaces in concentrations higher than approximately 2 and 7% (w/w), respectively. The generally accepted equality between K_L and the intercept of a V_N/V_L vs. $1/V_L$ plot is not valid in this case, as pointed out by Eqs. (7) and (9).

Specific retention volumes were fitted to the equation

$$\ln V_g^o = -\Delta H_s^o/RT + \text{constant} \quad (10)$$

where ΔH_s^o is the heat of sorption. Differences between V_g^o values calculated by means of Eq. (10) and experimental values were smaller than 0.3%; interpolation was thus accurate, and data obtained in different columns at slightly different temperatures could be corrected to a common temperature to enable further elaboration of results. V_N values at a given temperature were calculated from the corresponding V_g^o for each packing composition and least-squares fitted to Eq. (6). Values of *B*, *C* and their standard deviations at 40 and 50°C have been gathered in Table 1. The adsorption coefficient K_A and the packing constants *a* and *b* need to be evaluated to calculate K_L by means of Eq. (9).

Surface areas for TDPN on Chromosorb W or P, measured by Martin [15] and by Pecsok et al. [16] with discordant results, brought latter into agreement by Martire et al. [14] by using retention volumes in combination with statically measured K_L and K_A, remain as the best available liquid surface area data. On the basis of the expected similar liquid phase

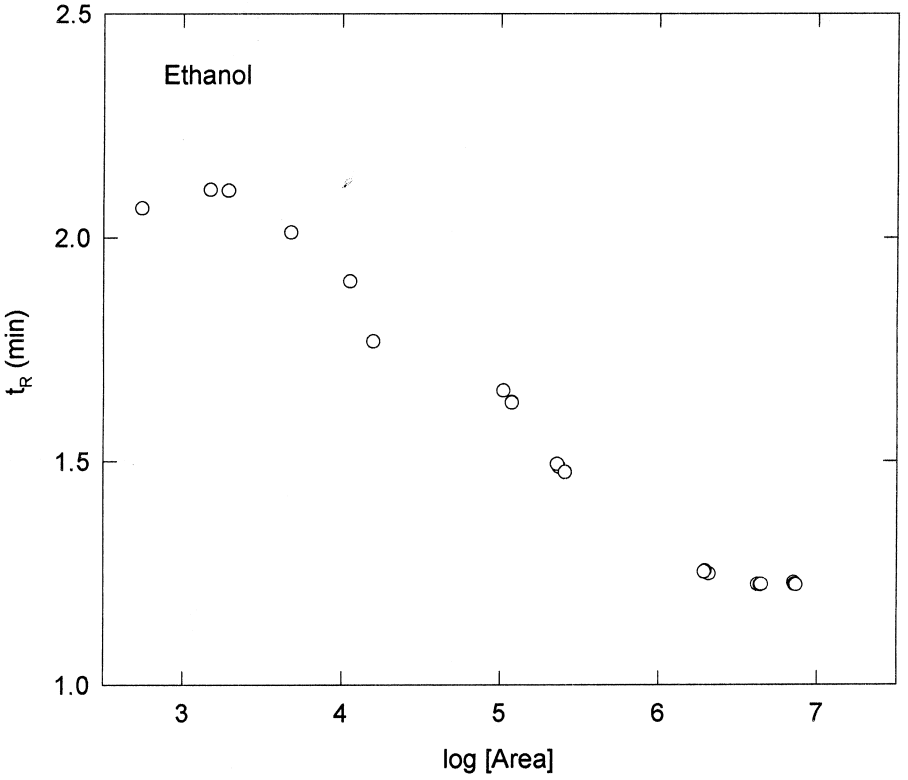

Fig. 4. Effect of injected sample size, as represented by the peak area counts, on the retention time of ethanol. Column packed with 4.00% (w/w) squalane on Chromosorb W-CWX.

Table 1
Intercepts (B) and slopes (C) obtained by fitting retention volumes to Eq. (5), and partition coefficients (K_L) calculated by means of Eq. (11) at 40 and 50°C

	40°C			50°C		
	$B \pm \sigma$ (B)	$C \pm \sigma$ (C)	K_L	$B \pm \sigma$ (B)	$C \pm \sigma$ (C)	K_L
1-Propanol	48.7±1.30	3.05±0.068	58.7	36.5±1.22	2.06±0.065	43.2
2-Propanol	29.4±0.31	1.26±0.016	33.6	22.8±0.30	0.87±0.016	25.7
1-Butanol	159.6±1.33	6.67±0.070	181.5	115.2±0.88	4.09±0.047	168.6
2-Butanol	99.5±0.67	2.62±0.035	108.1	73.1±0.56	1.72±0.030	78.7
2-Methyl-1-propanol	113.2±0.82	4.20±0.043	127.0	83.3±0.59	2.65±0.031	91.9
2-Methyl-2-propanol	48.8±0.31	1.05±0.016	52.3	37.2±0.27	0.71±0.014	39.5
1-Pentanol	471.2±4.70	15.2±0.24	521.3	325.4±3.82	8.79±0.203	354.1
2-Pentanol	287.6±1.80	6.13±0.096	307.7	201.0±1.21	3.77±0.065	213.3
3-Pentanol	307.8±1.90	5.34±0.102	325.4	214.8±1.39	3.31±0.074	225.6
2-Methyl-2-butanol	179.5±1.30	2.66±0.069	188.3	128.8±0.94	1.71±0.050	134.4
1-Hexanol	1355±17.7	38.8±0.93	1488	884.1±9.21	21.06±0.490	952.8
3-Hexanol	825.8±9.20	11.6±0.49	863.8	552.7±8.16	6.67±0.433	574.5
1-Heptanol	3785±63.1	99.8±3.32	4112	2331± 34.0	51.95±1.80	2500

distribution in their packings and in those used in the present work, A_L values were read after adequate enlargement on the linear region of Fig. 8(a) in Ref. [14] and fitted to Eq. (4), resulting in $a=4500$ cm^2/g and $b=14700$ cm^{-1}.

Methanol and ethanol K_L and K_A at infinite dilution in squalane were measured by Pecsok and Gump by static means [28]; unfortunately no reliable retention times could be obtained for these two alcohols in the present work. In order to compare their results with ours we made the assumption $K_A \cong C/a$; this is a rather bold assumption: it implies to neglect adsorption effects at the LSI (see Eq. (8)). Values of $\ln(C/a) \cong \ln K_A$ at 50°C corresponding to normal 1-alkanols are plotted against the number of carbon atoms, *n*, in Fig. 5; the line corresponds to the fitting of experimental results from $n=3$–7 to a second-degree polynomial. Results obtained by ex-

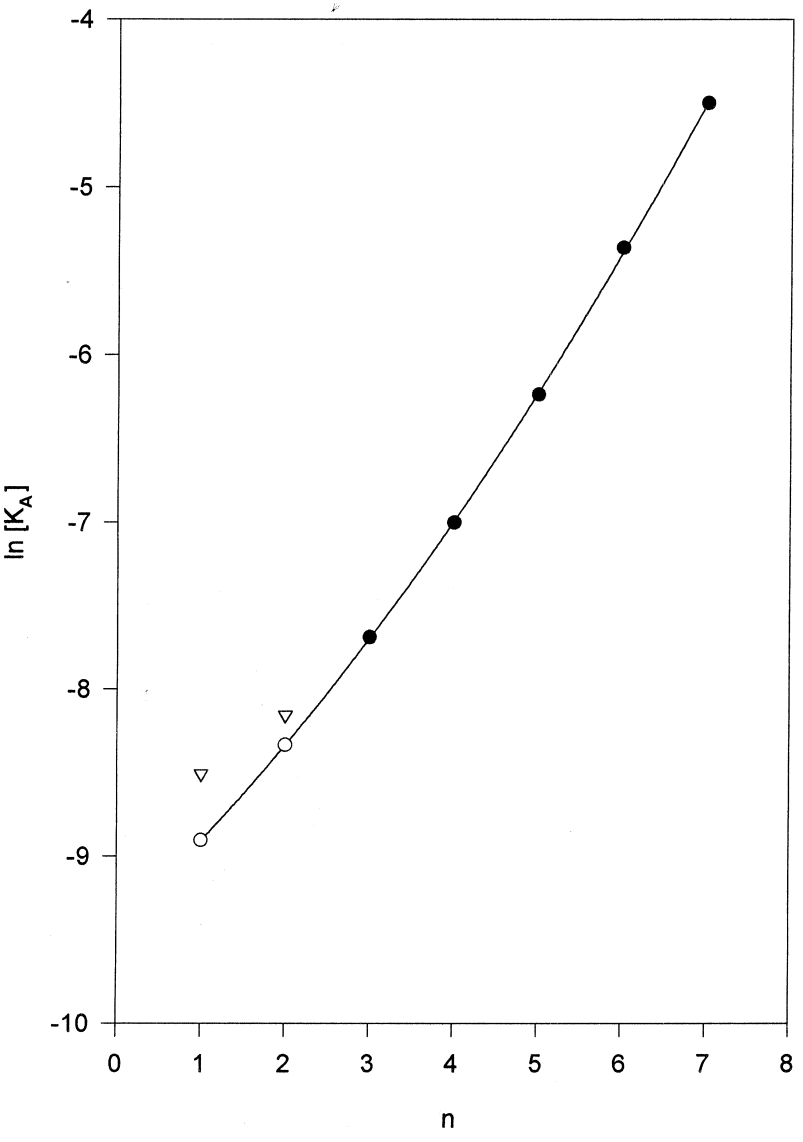

Fig. 5. $\mathrm{Ln}(C/a)=\ln K_A$ against the number of carbon atoms, *n*. (●) Experimental values; (○) extrapolated values; (▽) statically measured values (Pecsok and Gump [28]).

trapolating to $n=1$ and 2 are compared to those of Pecsok and Gump: static results are larger, but the coincidence is highly acceptable. In any case, these results indicate that effects of adsorption at the LSI are negligible in comparison to those of adsorption at the GLI; no solid support was present during Pecsok and Gump's measurements.

On the basis of these experimental findings Eq. (9) can be simplified to

$$K_L = B + (b/a)C \quad (11)$$

Partition coefficients at 40 and 50°C calculated by means of Eq. (11) can be read in Table 1. In no case is the difference between K_L and the intercept B negligible.

We have attempted to compare our results with those obtained by former authors. Partition coefficients reported by Cadogan et al. [13] several years

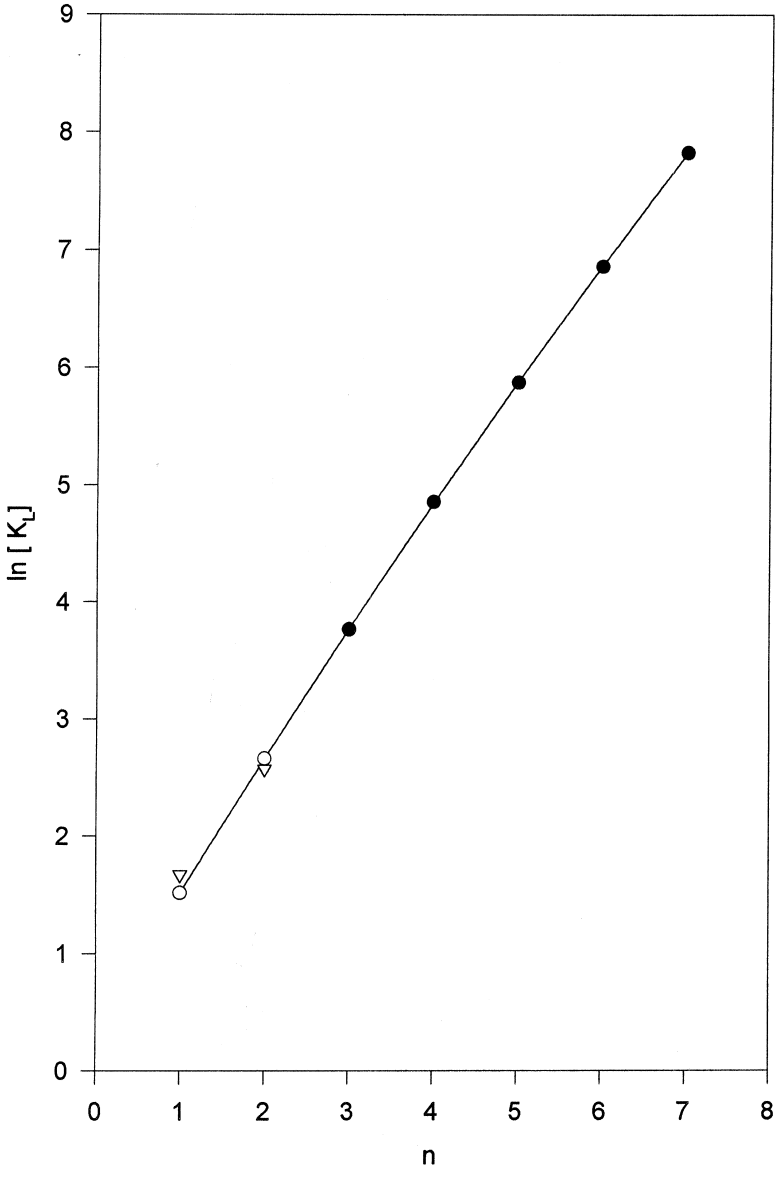

Fig. 6. Ln K_L against the number of carbon atoms, n. Symbols as in Fig. 5.

ago are between 15 and 25% larger than ours; they were calculated from asymmetrical peaks, by applying the constant finite solute concentration method of Conder [31], using Sil–O–Cel HMDS as solid support. Distribution of squalane on this surface can be complex [26,32] and this, added to operation at finite solute concentration, can be responsible for the curved V_N/V_L plots obtained by these authors.

There has been a renewed interest in infinite dilution activity coefficients of alkanol–alkane mixtures in the last years, mainly to test predictions of recent semiempirical models; two reviews have been recently published [33,34], and squalane as solvent is not mentioned in none of them. Comparison with methanol and ethanol partition coefficients measured by Pecsok and Gump is the more reliable test for our results that we were able to find. To this end Fig. 6 was drawn by following the procedure detailed in the case of Fig. 5; the results obviate any comment.

4. Conclusions

Symmetrical peaks, with sample size-independent retention times, are obtained when alkanols are chromatographed in columns packed with squalane coated on Carbowax 20M-modified Chromosorb W.

There is a linear relationship between V_N/V_L and $1/V_L$; the intercepts of these plots, however, cannot be identified with the gas–liquid partition coefficients. Physical significance of slopes and intercepts is discussed, and a method to calculate K_L is proposed.

A good agreement between methanol and ethanol K_L and K_A statically measured and those obtained by extrapolating results obtained in this work for higher normal 1-alkanols (1-propanol to 1-heptanol) is observed. This comparison indicates that effects of alcohol adsorption at the LSI are negligible in relation to those of adsorption on the GLI.

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