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Determinations of gas–liquid partition coefficients using capillary chromatographic columns. Alkanols in squalane

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ABSTRACT

This study focused on an investigation into the experimental quantities inherent in the determination of partition coefficients from gas–liquid chromatographic measurements through the use of capillary columns. We prepared several squalane – (2,6,10,15,19,23-hexamethyltetracosane) – containing columns with very precisely known phase ratios and determined solute retention and hold-up times at 30, 40, 50 and 60 °C. We calculated infinite dilution partition coefficients from the slopes of the linear regression of retention factors as a function of the reciprocal of the phase ratio by means of fundamental chromatographic equations. In order to minimize gas–solid and liquid–solid interface contributions to retention, the surface of the capillary inner wall was pretreated to guarantee a uniform coat of stationary phase. The validity of the proposed approach was first tested by estimating the partition coefficients of n-alkanes between n-pentane and n-nonane, for which compounds data from the literature were available. Then partition coefficients of sixteen aliphatic alcohols in squalane were determined at those four temperatures. We deliberately chose these highly challenging systems: alcohols in the reference paraffinic stationary phase. These solutes exhibited adsorption in the gas–liquid interface that contributed to retention. The corresponding adsorption constant values were estimated. We fully discuss here the uncertainties associated with each experimental measurement and how these fundamental determinations can be performed precisely by circumventing the main drawbacks.

The proposed strategy is reliable and much simpler than the classical chromatographic method employing packed columns.

1. Introduction

Dynamic gas–liquid chromatography (GLC) is an established method for determining relevant thermodynamic quantities including infinite dilution activity coefficients and gas–liquid partition coefficients (K_L) of volatile compounds in nonvolatile solvents [1,2].

Since GLC's inception, the chromatographic measurements of K_L have mainly been carried out by using packed columns. Although almost all separations today are performed with capillary columns, the use of that format for physicochemical measurements has been quite limited [3–5] for two principal reasons. First, several solvents of interest cannot be immobilized onto the inner walls of the capillary; second, chromatographers are used to calculating partition coefficients from the measurement of solute net or specific retention volumes. These quantities are derived from the measurements of flow-rate, which determination is not accurate when wall-coated columns are used because of the difficulties in reliably measuring very small volumetric flow-rates.

Nonetheless, infinite dilution partition coefficients can be directly calculated from retention times, without conversion to retention volumes, provided that the column phase ratio (β) is known. When capillary columns prepared by the static method are used, β can be exactly calculated at any temperature from a knowledge of the conditions used to fill the capillary tubes in addition to the liquid phase density at the same temperature [6]. The main advantage of a capillary column lies in the simplicity of its geometry and the inertness of the inner capillary after a proper pretreatment as compared to any porous and thus tortuous, support used to prepare packed columns. A simple estimation of the solid surface for a 10-m × 250-μm i.d. capillary tube gives an inner area as low as 0.008 m^2. In contrast, any packed column of normal dimensions has an area of more than 1–2 m^2. This difference of more than 2 orders of magnitude implies a significant reduction of the possibilities for adsorption onto gas– and liquid–solid interfaces. Moreover, since peaks eluted from capillary columns

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are significantly narrower, their maximum position is more distinctly defined. In addition, narrower peaks are necessarily taller, and thus much smaller injection amounts are required for obtaining a measurable signal.

In principle, the possibility of adsorbing the solute onto the solid surface (packing support or the silica wall) or onto the gas–liquid interface should be considered. This question is of special concern when a large surface is available [7–10]. If adsorption in a given interface occurs, the retention volumes will be the result of both partition and adsorption. In this circumstance, skewed peak profiles are commonly observed [3,11–13]. Zhang et al. [3] discussed different methods to measure K_L when peaks are asymmetric and reached to the conclusion that a diminution in the adsorption effects is necessary in order to acquire accurate measurements of K_L.

The first condition to be fulfilled for obtaining symmetric peaks is the injection of a sample amount within the infinite dilution region for all the sorption phenomena. The observation of symmetrical peaks, however, indicates that infinite dilution has been attained for all the sorption processes, but not that adsorption effects are absent, and therefore, even when symmetric peaks are observed, potential interfacial effects may still exist.

The aim of the present work was to discuss how capillary columns of exactly measured phase ratios can be used to determine gas–liquid partition coefficients, even when significant gas–liquid interfacial adsorption is present. Thus, we determined the partitioning of aliphatic alcohols in a typical nonpolar stationary phase, such as squalane, with wall-coated columns. This was a challenging system to test the suitability of capillary columns in obtaining accurate solution thermodynamic data, since gas–liquid interface adsorption concurrent with the partitioning process must be taken into account.

2. Theory

For a solute i distributed between liquid and vapor phases, the equilibrium condition is given by the equality of the fugacities in both phases or, at moderate pressures:

$$y_i P = \gamma_i x_i P_i^o \tag{1}$$

where y_i and x_i are the solute molar fractions in the gas and liquid phases, respectively, γ_i is the solute liquid-phase activity coefficient in the molar fraction scale, P is the total pressure, P_i^o is the solute saturated vapor pressure at temperature T. In Eq. (1), the interactions of the solute molecules with the carrier-gas molecules can be considered negligible in open tube GLC measurements at low gas inlet pressure [14,15]. At pressures affording ideal gas behavior, the partial pressure of the solute is related to the concentration of solute in the gas phase, C_i^g. Thus, the left-hand side of Eq. (1) can be equaled to

$$y_i P = C_i^g RT \tag{2}$$

Similarly, at $x_i \to 0$, the right-hand side of Eq. (1) can be written as

$$\gamma_i x_i P_i^o = \gamma_i^\infty C_i^L v^l P_i^0 \tag{3}$$

where γ_i^∞ is the solute infinite dilution activity coefficient, v^l is the liquid molar volume and C_i^L is the molar concentration of solute i in the liquid. The infinite dilution partition coefficient K_L, defined as the ratio between C_i^L and C_i^g is easily obtained from Eqs. (2) and (3):

$$K_L = \frac{C_i^L}{C_i^g} = \frac{RT}{P_i^0 \gamma_i^\infty v^l} \tag{4}$$

Several methods to measure either K_L or γ_i^∞ data have been proposed, with the most widely used being GLC. In a chromatographic gas–liquid system, the solute retention volume is mainly a result of the partition process. Other retention mechanisms, however, are also known to take place. These additional simultaneous processes are mainly owing to strong interactions of certain solutes at gas–liquid (GL), solid–liquid (SL) and gas–solid (GS) interfaces of any system. Thus, solute retention in the presence of these concurrent distribution processes is described by [7,8,16]:

$$V_N = K_L V_L + K_A A_L + K_I A_I + K_S A_S \tag{5}$$

where V_N represents the net retention volume, V_L is the stationary phase volume, A_L, A_I, A_S represent the surface areas of the GL, SL and GS interfaces, respectively; and K_A, K_I and K_S are the adsorption isotherm slopes of the three above-mentioned processes. Whenever thoroughly deactivated solid supports are used with highly loaded columns, the last two terms in Eq. (5) can be ignored, so that:

$$V_N \cong K_L V_L + K_A A_L \tag{6}$$

Traditionally, K_L is estimated from the intercept of plots V_N/V_L against $1/V_L$, using a set of packed columns with different stationary phase loadings.

Since:

$$\frac{V_N}{V_M} = \frac{t_R}{t_M} - 1 = k \tag{7}$$

in which equation, t_R and t_M are retention time for the solute as well as a for a nonretained analyte, respectively, k denotes the solute retention factor, and V_M the hold-up volume, the following expression can be written by combining with Eq. (6):

$$\frac{t_R}{t_M} - 1 = K_L \left(\frac{V_L}{V_M}\right) + K_A \left(\frac{A_L}{V_M}\right) \tag{8}$$

where the ratio (V_L/V_M) is the reciprocal of the column phase ratio, β.

3. Experimental

3.1. Instrumentation and materials

Chromatographic measurements were performed in an HP6890 (Agilent) gas chromatograph equipped with flame-ionization detection and manual-injection port. The data were acquired by means of the software Clarity (DataApex, Czech Republic).

Fused silica capillary tubing of 250 μm i.d., provided by MicroQuartz (München, Germany), was used to construct the chromatographic columns. Carbowax 20M was obtained from Alltech (Alltech, Deerfield, IL, USA) and the solvents from Merck KGaA (Darmstadt, Germany). The squalane (HP, Avondale, PA, USA) was used as received; solutions in dichloromethane, at the concentrations given in Table 1, were prepared avoiding air contact to prevent oxidation [21]. The density of squalane within the same temperature interval had been measured previously by pycnometry [9]. Data had been fitted to the equation ρ_s $(g\,cm^{-1}) = 0.8195(\pm 5 \times 10^{-4}) - 6.0899(\pm 1 \times 10^{-5}) \times 10^{-4} t$, where t is the temperature expressed in °C.

All the solutes were analytical-reagent grade and they were used as received from the supplier. Solutes were contained in 2.5-mL vials with a valve cap, and kept at room temperature, and injected with Hamilton syringes at least three times. Four temperatures, in the 30–60 °C range, were used. Retention times were measured at the peak maximum with a precision of 0.001 min. The extracolumn volume was negligible for the column dimensions used in this work.

Table 1
Capillary column characteristics.

Column	Length (m)	C_0[a] (mg mL^{-1})	T = 30 °C			T = 60 °C		
			β	d_f[b] (μm)	A_L/V_M[c] (cm^{-1})	β	d_f[b] (μm)	A_L/V_M[c] (cm^{-1})
1	28	1.34	595	0.105	160.1[d]	583	0.107	160.1[d]
2	19.5	2.72	294	0.212	160.3	287	0.218	160.3
3	16.6	3.94	202	0.308	160.4	198	0.316	160.4
4	9.5	4.93	162	0.385	160.5	158	0.396	160.5
5	5.5	6.31	126	0.493	160.6	123	0.508	160.7

[a] Concentration of the squalane solution used to fill the capillary tube at room temperature.
[b] Film thickness, $d_f = (d_c/2)[1 - \beta/(\beta+1)^{0.5}]$, where dc is the column diameter.
[c] Estimated from geometry: $A_L/V_M = (d_c - 2d_f)/(d_c/2 - d_f)^2$.
[d] Overestimated significant figures were kept to demonstrate the negligible differences between columns and temperatures.

3.2. Capillary inner surface treatment

In order to measure reasonable elution times, fused-silica tubes of different length (*cf.* Table 1) were prepared. Thin films of Carbowax were coated onto the column wall in a solution of 4% (w/v) Carbowax 20M in methylene chloride; and after a heating of 300 °C for 16 h, the excess was exhaustively extracted sequentially with the solvents methanol, acetone, and methylene chloride. Finally, the capillary was dried for 3 h under a low nitrogen flow.

3.3. Column coating

The traditional static-coating procedure consists in a vacuum-evaporation of the solvent from one open end of the capillary [17]. In these preparations, we evaporated the solvent of the coating solution by heat, introducing the open end of the coil into a home-made oven by rotating the column around the axis of its coil. The oven temperature is maintained only few degrees above the solvent boiling point. As the capillary tube is screwed into the oven, the solvent evaporates and escapes through the open end. This procedure leaves a thin film of stationary phase whose thickness can be easily estimated. A major advantage of this static method [18] is that the column phase ratio can be determined accurately at each temperature from the equation [6,19]:

$$\beta = \frac{\rho_s(T)}{C_0} \exp[\alpha_{Si}(T - T_0)] - 1 \quad (10)$$

where $\rho_s(T)$ represents the stationary phase density at temperature T, C_0 is the concentration of the solution of stationary phase used to fill the capillary at the temperature T_0 (expressed as (w/v)), and α_{si} denotes the thermal expansion coefficient of the silica wall of the capillary. The significant figures attainable for C_0 and ρ_s determine the level of precision in the estimation of β. The accuracy of C_0 can be increased if a large amount of coating solution is prepared, leaving the quality of the $\rho_s(T)$ measurement as the limiting condition in the accuracy of the phase ratio determination.

4. Results and discussion

4.1. Capillary surface pretreatment

The column inertness influences its final efficiency and thermal stability as well the quality of the chromatographic peaks from which the thermodynamic properties will be calculated. The procedure followed in this study involved a nonextractable layer of Carbowax 20M that was formed on the inner column surface [20]. The quality of this deactivation procedure was checked by injection of the alcohols before and after heat treatment. The asymmetries of all peaks were dramatically decreased to values smaller than 1.2 before the squalane coating.

Coating can be accomplished by either static or dynamic methods. The static-coating method has generally been considered to be superior in that it produces more efficient columns. In this study, we used a previously proven method of static coating [4] followed by evaporation of the solvent controlling both the oven temperature and the rapidity with which the column entered the oven.

After the coating, the degree of symmetry of an eluted peak was used to evaluate potential interfacial adsorption. If the condition of infinite dilution is not reached for all distribution processes that take place during the retention, asymmetric peaks will be obtained and/or retention times will be injection size-dependent. The condition of infinite dilution can be verified by quantifying the peak retention time against peak sizes as shown in Fig. 1 for four alcohols at 50 °C. Constant retention times for samples were obtained over a wide range of head-space volumes (about 2–600 μL), thus indicating that all distribution processes were operating within their respective Henry's law regions.

4.2. Determination of partition coefficients

4.2.1. Packed columns

The assumption that gas–liquid partition is the only mechanism responsible for solute retention is implicit in most GLC measurements. Nevertheless, as has been demonstrated for several systems, partitioning in addition to other retention mechanisms occur concurrently. Traditionally, the chromatographic determination of K_L in such situations relies on the validity of Eq. (6). In this expression, two assumptions are implicit: that the solid support has been chemically treated to minimize SL interfacial adsorption and also that the relatively high stationary phase loadings used are sufficient to prevent leaving uncovered portions of the support surface available for GS adsorption. Thus, to determine K_L values, the net volume

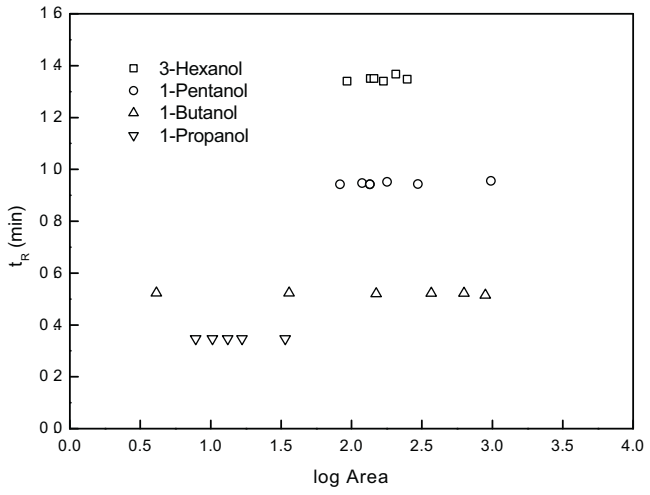

Fig. 1. Retention time constancy as a function of sample size. Analytes: (a) 1-propanol, (b) 1-butanol, (c) 1-pentanol, and (d) 3-hexanol. T = 50 °C.

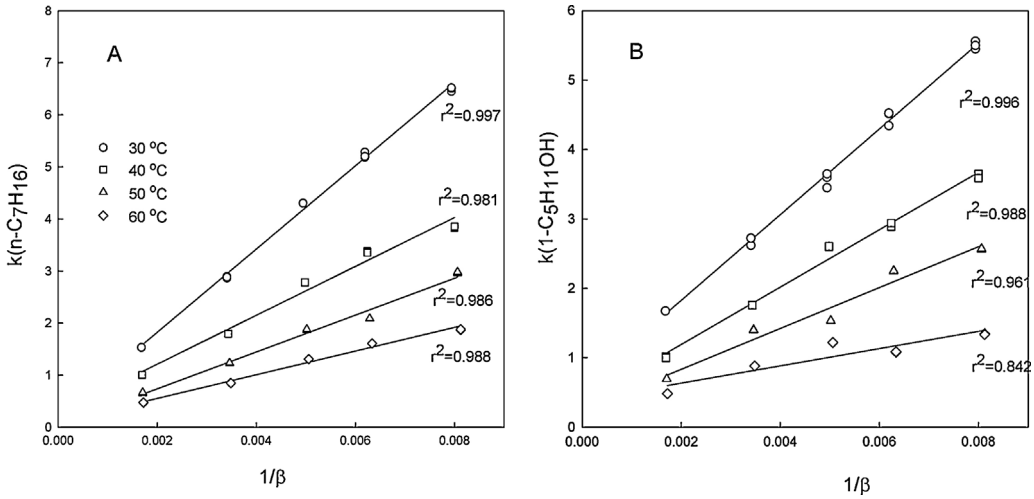

Fig. 2. Retention factors of n-heptane (A) and 1-pentanol (B) against the reciprocal of the phase ratio at four temperatures.

retention is measured on several packed columns containing different amounts of liquid, and K_L is estimated from extrapolated intercepts of V_N/V_L against $1/V_L$. These plots may or may not be straight lines, depending on the relative contribution of adsorption mechanisms. Whenever one mechanism dominates, linear extrapolations are feasible [21]. In summary, K_L determinations with packed columns depend on the experimental measurement of V_L in different columns and solute V_N in those columns, which step, in turn, requires the measurement of retention and hold-up times, volumetric flow rate at room temperature and inlet and outlet carrier-gas pressures.

4.2.2. Capillary columns

When contributions from adsorption on the SL and GS interfaces can be neglected, Eq. (8) can be used to estimate partition coefficients. Therefore, if multiple columns are prepared with different values of phase ratio, β, and if solute t_R as well as t_M data are determined, the slope of a plot of $(t_R/t_M - 1)$ *vs.* β^{-1} yields the corresponding K_L value. The nonzero intercept would indicate GL interfacial adsorption, *i.e.*, $K_A \neq 0$. This approach assumes that the A_L/V_M ratio is independent of β. On the basis of geometrical considerations, this assumption is not strictly fulfilled, but for the purpose of the present work a demonstration of the independence of the intercept from β within the studied range and the limitations imposed by our experimental errors, will be sufficient. Table 1 summarizes the physical properties of the columns in terms of β-values at the two extreme temperatures, the estimated film thickness, and the corresponding A_L/V_M ratios, with the assumption that the layer of liquid phase has been homogeneously coated. Since the differences in A_L/V_M values for these various columns are well below the experimental errors, the validity of Eq. (8) can be accepted.

Fig. 2 illustrates graphically the application of Eq. (8) to n-heptane (Fig. 2A) and to 1-pentanol (Fig. 2B) at four temperatures. The linearity is excellent for both data sets at all temperatures, which result confirms that the intercept is practically independent of the phase ratio value within the experimental range studied.

Table 2
Results of retention factor regressions for n-alkanes in squalane with the reciprocal of the phase ratio at 30, 40, 50 and 60 °C.

n-Alkane		Temperature (°C)			
		30	40	50	60
n-Pentane	K_L[a]	101 ± 4	73 ± 3	44 ± 3	43 ± 1
	Intercept	−0.003 ± 0.02	−0.007 ± 0.01	0.02 ± 0.01	−0.003 ± 0.006
	R^2	0.98	0.986	0945	0.991
	$s_{y/x}$[b]	0.023	0.016	0.019	0.007
n-Hexane	K_L	284 ± 6	193 ± 5	120 ± 6	101 ± 2
	Intercept	0.03 ± 0.03	0.01 ± 0.02	0.06 ± 0.03	0.007 ± 0.01
	R^2	0.996	0.993	0.975	0.995
	$s_{y/x}$	0.03	0.029	0.036	0.01
n-Heptane	K_L	831 ± 13	521 ± 12	324 ± 13	250 ± 5
	Intercept	0.11 ± 0.06	0.07 ± 0.05	0.13 ± 0.06	0.02 ± 0.02
	R^2	0.998	0.995	0.983	0.996
	$s_{y/x}$	0.07	0.07	0.08	0.03
n-Octane	K_L	2459 ± 43	1478 ± 28	865 ± 33	622 ± 12
	Intercept	0.4 ± 0.2	0.2 ± 0.1	0.3 ± 0.2	0.08 ± 0.05
	R^2	0.997	0.996	0.986	0.996
	$s_{y/x}$	0.23	0.17	0.19	0.07
n-Nonane	K_L	7278 ± 126	4104 ± 63	2295 ± 79	1561 ± 28
	Intercept	1.2 ± 0.6	0.8 ± 0.3	0.9 ± 0.4	0.2 ± 0.1
	R^2	0.997	0.997	0.988	0.997
	$s_{y/x}$	0.67	0.37	0.47	0.17

[a] Partition coefficients (see text) with the corresponding standard deviations of the slopes.

[b] the $s_{y/x} = [\sum (y_{ij} - \hat{y}_i)^2 / m - 2]^{1/2}$.

Table 3
Comparison of experimental K_L values for n-alkanes in squalane with literature values.

Solute	Temperature	K_L		Reference
		This work	Literature	
n-Pentane	30	101	94[a]	[33]
n-Hexane	30	284	299	[33]
	50	120	147[b]	[32]
n-Heptane	30	831	917	[33]
	50	324	395[b]	[32]
n-Octane	30	2459	2774	[33]

[a] Vacuum-microbalance technique.
[b] GLC with packed columns.

Since modifications of the typical method of measuring are proposed here, the quality of the K_L-measurements was first verified by a determination of the partitioning of n-alkanes within the temperature range of 30–60 °C. Table 2 summarizes the least-squares regression results along with the corresponding standard deviations of the slope and intercept. The standard deviations of these fits proved to be clearly quite good. The slopes correspond to the K_L-values. Relative standard deviations, $s(K_L)/K_L$, range from 0.015 to 0.075, with a mean value of 0.029. A very acceptable precision level was attained for parameters calculated from the data measured in several columns. Measurements performed on different packed columns usually gave relative standard deviations between 2 and 5% [22].

From a purely statistical point of view, a *t*-test analysis indicated that the intercepts were not significantly different from zero for any system. This criterion, however, does not necessarily mean that the "true" K_A values would be zero, but only that more results are needed to estimate them reliably. Siepman et al. [23], after conducting Monte Carlo simulations to study the interfacial adsorption of three alkanes, 1-butanol and benzene in squalane, concluded that the adsorption of the flexible chains onto the gas liquid interface existed, but the extent of the effect did not contribute significantly to the retention on nonpolar stationary phases. Similarly, the chromatographic retention of n-alkanes in columns with different film thicknesses of nonpolar poly(dimethylsiloxane) over a very wide temperature range indicated no adsorption onto the gas–liquid interface [4].

In Table 3, we gathered K_L values from different sources, including data taken from other techniques. The divergences within that set of data proved to be reasonable: up to 20%; while the K_L values determined in this work were within the same range. Similarly, linearity between the $\ln K_L$ and the reciprocal of the temperature of the n-alkanes can be used to evaluate the consistency of the data. Although the linearity is only an approximation, it can provide a guide to detect the trends. We constructed plots of this type with our data at the four temperatures, shown in Fig. 3. We also included data at other temperatures collected from the literature that were either measured by head-space GC [24], dynamic GC employing packed columns [25–28] and estimated by Monte Carlo simulation [23]. With the exceptions of these last data, which figures fall far below the extrapolated lines, the other data points are consistent with our own.

4.3. Partition coefficients of alcohols in squalane

Table 4 gives the K_L values of sixteen aliphatic alcohols in squalane along with the corresponding standard deviations at the mentioned temperatures. The corresponding activity coefficients can be easily calculated from this set of data by using Eq. (4). The accuracy of the K_L values should in principle be estimated by comparison with data from the literature (values included in Table 4), but the few partition coefficients available differed greatly

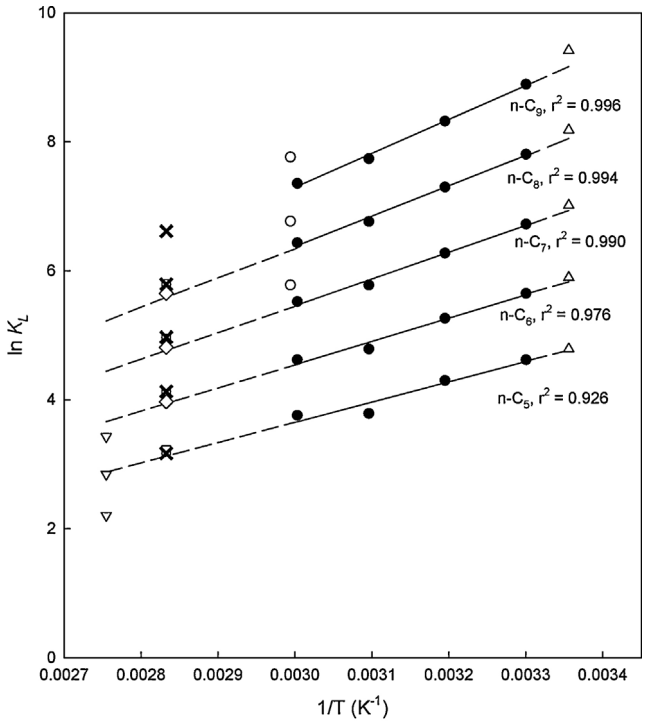

Fig. 3. Plots of $\ln K_L$ of n-alkanes as a function of $1/T$. Symbols: (●): experimental data at 30, 40, 50 and 60 °C, (△) data at 25 °C from [14]; (◯) values at 61.2 °C from [25]; (◊): values at 80 °C from [28]; (□) values at 80 °C from [26]; (×): data at 80 °C from [27]; (▽): data at 90 °C from [23].

in accuracy and reliability, even those values obtained by the same experimental method. In Fig. 4A, we plotted the $\ln K_L$ of 1-alkanols against the carbon number and extrapolated those data for comparison with the K_L values of ethanol and methanol [29]. Although, in our work these two solutes were barely retained and no reliable information could be gathered, the extrapolation (Fig. 4A) nevertheless proved quite consistent with data from the literature.

In general, our results are somewhat lower than previously reported, with the differences ranging from 5 up to as much as 20%. These presumed inaccuracies prompted us to evaluate critically the errors associated with each experimental quantity used in K_L estimations.

(a) The first source of error is related to the determination of hold-up time. The measurement of this fundamental parameter has been extensively discussed [30], and that very accurate data are obtained by non-linear regression of retention times for a solute series (n-alkanes) *vs.* the carbon number is now accepted. The estimations of t_M from the regression of retention times between n-C_5 and n-C_9 gave values whose differences were well below the experimental precision for these columns of relatively high phase ratios. At all events, the use of the retention of methane as a hold-up measurement would produce systematic negative errors in retention factors. The incidence of a wrong estimation in t_M would affect those k values obtained in the less retentive columns, and in that situation, the slopes would be even lower than those estimated in this study.

(b) The other possible error would come from the phase ratio. The filling solutions, however, were prepared with a significant weight of squalane, that was dissolved in volumetric flasks of at least 10.00-mL capacity. Similarly, the density of squalane, obtained in our laboratory earlier [9], had shown agreement (differences smaller than 0.001 g cm^{-13}) with previously measured squalane densities [31]. Thus, simple error propagation

Table 4
Partition and adsorption coefficients for alcohols in squalane at four temperatures.

Solute	Temperature (°C)							
	30 K_L	$K_A 10^{-4}$ (cm)	40 K_L	$K_A 10^{-4}$ (cm)	50 K_L	$K_A 10^{-4}$ (cm)	60 K_L	$K_A 10^{-4}$ (cm)
1-Propanol	61 ± 3[a]	4.5 ± 0.8	51.8 ± 0.6 58[b]	2.2 ± 0.1	38 ± 3 43.2[b] 51[c] 40.2[d]	7 ± 1	19 ± 5	0.2 ± 2
2-Propanol	34 ± 3	2.2 ± 0.7	29.5 ± 0.4 33.6	1.1 ± 0.1	16 ± 2 25.7[b] 28.4[c] 24.2[d] 26[e]	9.6 ± 0.6	–	–
1-Butanol	195 ± 5	13.5 ± 1.4	156 ± 4 181.5	6 ± 1	111 ± 7 168.6[b] 148[c,d] 118[e]	8 ± 3	56 ± 14	3.1 ± 2.5
2-Butanol	365 ± 8	–	92 ± 2 108	3.2 ± 0.4	74 ± 6 78.7[b] 93[c] 94[e]	5 ± 2	40 ± 12	–
2-Methyl-1-propanol	137 ± 3	8.2 ± 0.7	96 ± 2 127	5.8 ± 0.6	76 ± 8 91.9[b] 105.5[c] 84.4[d] 109[e]	7 ± 3	30 ± 5	6 ± 2
1-Pentanol	619 ± 12	38 ± 3	417 ± 17 521	23 ± 5	296 ± 13 354.1[b]	18 ± 4	124 ± 15	10 ± 6
2-Pentanol	353 ± 5	17 ± 1	239 ± 8 307.7	12 ± 2	178 ± 9 213[b]	11 ± 3	113 ± 9	9 ± 3
3-Pentanol	670 ± 17	22 ± 17	285 ± 15 325.4	13 ± 5	181 ± 11 225.6[b]	12 ± 4	118 ± 12	9 ± 3
2-Methyl-2-butanol	211 ± 3	8.4 ± 0.9	147 ± 5 188.3	6 ± 1	92 ± 5	16 ± 2	71 ± 8	7 ± 2
1-Hexanol	1941 ± 27	101 ± 7	1200 ± 49 1488	61 ± 13	763 ± 31 952.8[b]	45 ± 11	494 ± 24	30 ± 7
3-Hexanol	1113 ± 13	41 ± 3	679 ± 51 863.8	16 ± 21	460 ± 20 574.5[b]	25 ± 7	418 ± 76	25 ± 19
tert-Butanol	57 ± 2	2.5 ± 0.6	40 ± 1 52.3	2.2 ± 0.3	42 ± 4 44.45[c] 46[d]	2 ± 1	19 ± 2	2.2 ± 0.7
3-Methyl-3-heptanol	–	–	2737 ± 128	221 ± 57	2033 ± 81	94 ± 29	827 ± 76	125 ± 24
4-Heptanol	3133 ± 300	36 ± 28	1895 ± 65	69 ± 18	1188 ± 51	51 ± 17	828 ± 46	11 ± 12
2-Heptanol	2151 ± 130	191 ± 15	1600 ± 107	108 ± 37	1187 ± 65	60 ± 24	974 ± 93	56 ± 24
n-Heptanol	10,418 ± 59	–	3414 ± 119 4112	158 ± 33	1997 ± 111 2500[b]	116 ± 42	1267 ± 47	68 ± 13

[a] Standard deviation of the slope between retention factors and $(1/\beta)$ (see the text).
[b] From [9].
[c] From [34].
[d] From [31].
[e] From [32].

estimations indicated that the largest uncertainties in β values were 0.78% (corresponding to the column with the higher phase ratio).

(c) The K_L values measured here corresponded to the condition of infinite dilution and assuming ideal behavior of the gas phase. Thus, the inlet pressures and the amount of injected solute must correspond to these two conditions. Both requirements were systematically fulfilled as detailed above.

(d) Finally, the K_L values obtained in this study corresponded to the value of the slopes of the regression of data collected from several columns. The application of Eq. (8) is justified if the A_L/V_M is kept practically constant. Although that condition is not strictly satisfied, the errors so generated are much lower than those associated with the β values. In contrast, values of K_L obtained from the classical Martin–Berezkin linear regression [7,11,13] corresponded to extrapolations obtained from chromatographic retention volumes in columns having different amounts of liquid stationary phase. Larger errors are usually expected if K_L is extrapolated away from the experimental range, and sometimes from nonlinear plots. Moreover, certain literature data corresponded to values determined from an extrapolation of retention volumes obtained after injecting several finite samples down to a zero injection volume followed by a second extrapolation of data collected from columns with different phase loadings [32].

4.4. Contribution of gas–liquid interfacial adsorption to retention

The intercepts of the regression between k and $1/\beta$ were determined and the K_A values along with the corresponding standard

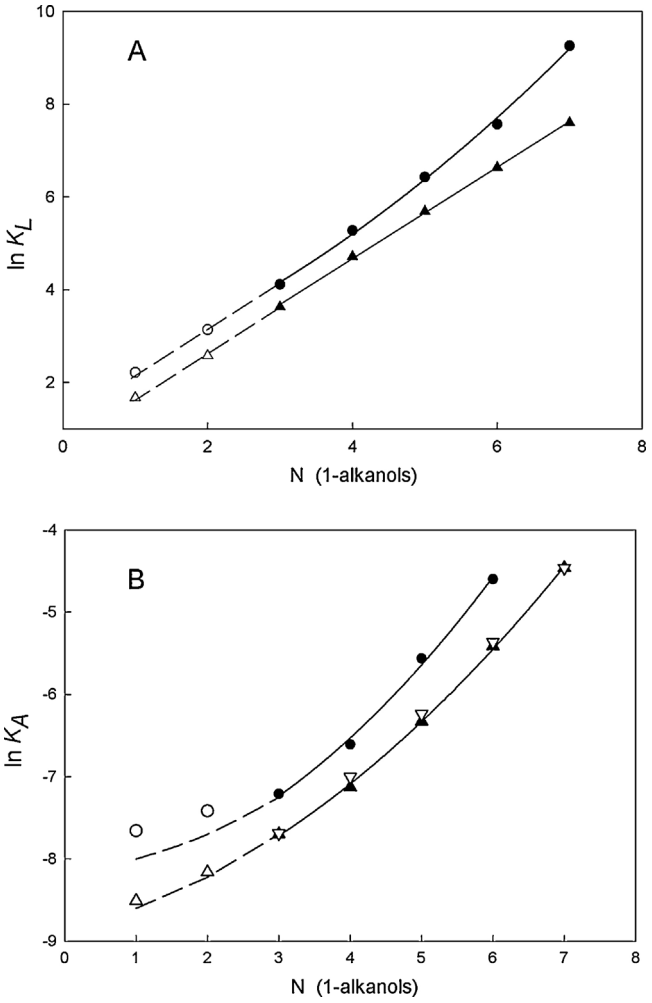

Fig. 4. Plots of (A) ln K_L and (B) ln K_A (μm) as a function of 1-alkanol carbon number. Symbols: (●) and (▲): experimental data at 30, and 50 °C, respectively; (△) and (◯) data from [29] at the same temperatures; (▽) taken from [9].

deviations calculated (Table 4). Significant adsorption effects were clearly present for systems such as these having positive deviations from the ideal solution behavior. In Fig. 4B, we plotted values of ln K_A at 30 and 50 °C corresponding to normal 1-alkanols against the carbon number. We fitted the experimental data for $n = 3$–7 to quadratic equations (solid lines) and extrapolated to $n = 1$ and 2 (dotted lines). The data of the interfacial adsorption of methanol and ethanol in squalane at 30 and 50 °C obtained from surface tension measurements [29] were included for comparison along with ln K_A data of 1-propanol to 1-heptanol at 50 °C measured with packed columns [9]. The plots indicated a quite acceptable agreement between our results, obtained from the open-tube GLC measurements, and those acquired previously.

The contribution of this adsorption onto the interfacial GL surface to chromatographic retention is more significant for columns with higher phase ratio. For instance, that contribution was, as an average, 18 ± 4% at 40 °C in the column with film thickness of 0.2-μm, whereas decrease down to 10 ± 2% in the column with 0.4-μm film thickness.

5. Conclusions

We have determined the infinite dilution partition coefficients of n-alkanes and sixteen aliphatic alcohols in squalane measured by using a series of capillary columns at four temperatures. The approach used here was based on GLC measurement of retention and hold-up times along with the phase ratio of each column at a given temperature. With a specifically deactivated inner surface, the alcohols chromatographed in squalane did not adsorb onto the silica surface. Since the systems constituted by the very polar alcohol and the nonpolar squalane were characterized by strong positive deviations from the Raoult's law, the contribution due to interfacial adsorption was very significant. This concurrent retention mechanism has been taken into account and the K_L values reported here correspond to the pure partitioning process.

We have proven that the use of capillary columns of well known phase ratios for physicochemical measurements is a reliable approach even when interfacial adsorption is present. Cumbersome corrections become unnecessary since the resulting figures lie within the experimental uncertainty. The simplicity of the equations diminished systematic errors and resulted in less complicated experimental procedures.

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