Journal of Chromatography, 114 (1975) 47–62
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CHROM. 8355

GAS–LIQUID CHROMATOGRAPHIC DETERMINATION OF THE COMPLEXATION CONSTANT BETWEEN TWO NON-VOLATILE COMPLEXING AGENTS IN THE STATIONARY PHASE

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(Received January 23rd, 1975)

SUMMARY

A theory has been developed that makes it possible to determine the complexation constant between two non-volatile complexing molecules by gas–liquid chromatography in an inert solvent as the stationary phase by use of gaseous alkane solutes and gaseous complexing solutes. The calculations require that the constant between a complexing solute and each complexing agent be determined separately in the same inert solvent. The theory for such determinations has been presented earlier.

The theory has been used for the determination of the complexation constant for a 1:1 complex between dodecyl laurate and 1-chlorooctadecane at 50, 60 and 70 °C, with squalane as an inert solvent.

Ten complexing solutes were used in the investigations, giving ten different values of the equilibrium constant between the non-volatile complexing agents. The average values of the constant at 50, 60 and 70 °C were found to be 0.16, 0.13 and 0.26, respectively.

INTRODUCTION

Rapid development in the use of gas–liquid chromatography (GLC) for the investigation of complexing reactions in organic solutions has occurred during the past few years[1–7]. In all instances, models have been used for the calculations that involve a complexing reaction between a gaseous solute, B, and a non-volatile complexing agent, C, dissolved in an inert non-volatile solvent, S, as the stationary phase. The method is limited by the requirements that B must, at the chosen temperature, be sufficiently volatile to be eluted and that the bleeding of the stationary phase, at the same temperature, can be neglected. It has therefore not been possible to study the complexation between two non-volatile complexing agents. When different solutes, B, are chromatographed over solutions that contain two complexing agents, C and D, in an inert solvent, the contribution from the BC and BD complexes to the solubility of B will be affected by possible complexation between C and D. It is therefore possible to study the complexation between C and D in an indirect manner, as outlined under Theoretical Investigation below. If complexation constants between various solutes and two different non-volatile complexing agents, C and D, are known, it is even possible to determine the complexing constant for a CD complex. By decreasing the temperature, even at moderate temperatures, relatively volatile complexing agents can be investigated, provided that sufficiently volatile complexing solutes for injection at the chosen temperature are available.

In this work, the idea has been adapted to the system consisting of 1-chlorooctadecane and dodecyl laurate as complexing agents in the stationary phase with squalane as the inert solvent. The gaseous solutes were different benzene derivatives, alkene derivatives and alkanes. Equilibrium constants between the complexing solutes and 1-chlorooctadecane and dodecyl laurate, respectively, were determined in previous work[1,2] and the equations derived in the theoretical section below are partly based on equations from previous papers[1,3].

EXPERIMENTAL

The experimental procedures used were the same as in the earlier investigations on dodecyl laurate–squalane and 1-chlorooctadecane–squalane systems[1,2], and involved the same apparatus, glass columns, chemicals, support and column loading and the same means of determining the loading and the stationary phase densities. The flow-rate of the carrier gas (hydrogen) was about 55 ml/min, and the James and Martin factor was about 0.90. One column of 1-chlorooctadecane and dodecyl laurate, each with a molar fraction of 0.250 in squalane, was run at 50, 60 and 70 °C. The column loading was 19.79% (w/w) of organic phase on a support of Supasorb, 40–60 mesh, acid washed and treated with hexamethyldisilazane (BDH, Poole, Great Britain). A total packing of 0.62327 g was used.

All solutes previously investigated in both the 1-chlorooctadecane–squalane and the dodecyl laurate–squalane systems were used in this investigation, *i.e.*, ten complexing solutes and four alkanes (see Table II).

THEORETICAL INVESTIGATION

Equations for the behaviour of a gaseous solute, B, in a stationary phase consisting of two complexing agents, C and D, in an inert solvent, S, are derived below. The symbols used are listed at the end of the paper.

1. C and D form a 1:1 complex with B but not with each other

The equilibria and equations below need to be considered.

$$K_R = \frac{[B(A,S)]}{[B(g)]} \tag{1}$$

where A is the mixture of C and D.

$$[B(g)] = \frac{f_B^0 \, \gamma_B^\infty(A,S) \, X_B}{RT} \tag{2}$$

$$X_A = X_C + X_D \tag{3}$$

$$[\mathrm{B(A,S)}] = [\mathrm{B^0(A,S)}] + [\mathrm{BC(A,S)}] + [\mathrm{BD(A,S)}] \tag{4}$$

$$[\mathrm{B(A,S)}] = \frac{X_{\mathrm{B}} + X_{\mathrm{BC}} + X_{\mathrm{BD}}}{V^0_{\mathrm{A,S}}} \tag{5}$$

$V^0_{\mathrm{A,S}}$ is the molar volume for a mixture of C, D and S used as the stationary phase.

$$\mathrm{B} + \mathrm{C} \rightleftharpoons \mathrm{BC} \qquad K_1 \text{ (equilibrium constant)} \tag{6}$$

$$\mathrm{B} + \mathrm{D} \rightleftharpoons \mathrm{BD} \qquad K_2 \text{ (equilibrium constant)} \tag{7}$$

$$K_1 = \frac{X_{\mathrm{BC}}}{X_{\mathrm{B}}\,X_{\mathrm{C}}} \cdot \frac{\gamma^{\infty}_{\mathrm{BC(A,S)}}}{\gamma^{\infty}_{\mathrm{B(A,S)}}\,\gamma_{\mathrm{C(A,S)}}} \tag{8}$$

$$K_2 = \frac{X_{\mathrm{BD}}}{X_{\mathrm{B}}\,X_{\mathrm{D}}} \cdot \frac{\gamma^{\infty}_{\mathrm{BD(A,S)}}}{\gamma^{\infty}_{\mathrm{B(A,S)}}\,\gamma_{\mathrm{D(A,S)}}} \tag{9}$$

As B is very diluted in the stationary phase, even BC and BD are very diluted, and therefore the symbol ∞ is used to indicate infinite dilution of B, BC and BD in the stationary phase.

By combining eqns. 1, 2, 4, 5, 8 and 9, we obtain

$$K_{\mathrm{R}} V^0_{\mathrm{A,S}} = \frac{RT}{f^0_{\mathrm{B}}\,\gamma^{\infty}_{\mathrm{B(A,S)}}\,X_{\mathrm{B}}} \cdot \left(X_{\mathrm{B}} + K_1 X_{\mathrm{B}} X_{\mathrm{C}} \cdot \frac{\gamma^{\infty}_{\mathrm{B(A,S)}}\,\gamma_{\mathrm{C(A,S)}}}{\gamma^{\infty}_{\mathrm{BC(A,S)}}} + K_2 X_{\mathrm{B}} X_{\mathrm{D}} \cdot \frac{\gamma^{\infty}_{\mathrm{B(A,S)}} \cdot \gamma_{\mathrm{D(A,S)}}}{\gamma^{\infty}_{\mathrm{BD(A,S)}}} \right)$$

$$K_{\mathrm{R}} V^0_{\mathrm{A,S}} = \frac{RT}{f^0_{\mathrm{B}}} \cdot \left(\frac{1}{\gamma^{\infty}_{\mathrm{B(A,S)}}} + K_1 X_{\mathrm{C}} \cdot \frac{\gamma_{\mathrm{C(A,S)}}}{\gamma^{\infty}_{\mathrm{BC(A,S)}}} + K_2 X_{\mathrm{D}} \cdot \frac{\gamma_{\mathrm{D(A,S)}}}{\gamma^{\infty}_{\mathrm{BD(A,S)}}} \right) \tag{10}$$

By combining eqn. 10 with eqn. 3, and

$$\gamma^{\infty}_{\mathrm{B(A,S)}} = a^{\infty}_{\gamma_{\mathrm{B(A,S)}}} \cdot t^{\infty}_{\gamma_{\mathrm{B(A,S)}}} \tag{11}$$

$$\frac{1}{a^{\infty}_{\gamma_{\mathrm{B(A,S)}}}} = \frac{1}{a^{\infty}_{\gamma_{\mathrm{B(S)}}}} + \left(\frac{1}{a^{\infty}_{\gamma_{\mathrm{B(A)}}}} - \frac{1}{a^{\infty}_{\gamma_{\mathrm{B(S)}}}} \right) \cdot X_{\mathrm{A}} \tag{12}$$

one obtains

$$K_{\mathrm{R}} V^0_{\mathrm{A,S}} = \frac{RT}{f^0_{\mathrm{B}}} \cdot \frac{1}{t^{\infty}_{\gamma_{\mathrm{B(A,S)}}}} \cdot \left[\frac{1}{a^{\infty}_{\gamma_{\mathrm{B(S)}}}} + \left(\frac{1}{a^{\infty}_{\gamma_{\mathrm{B(A)}}}} - \frac{1}{a^{\infty}_{\gamma_{\mathrm{B(S)}}}} \right) \cdot X_{\mathrm{A}} + \right.$$

$$\left. + K_1 \cdot \frac{t^{\infty}_{\gamma_{\mathrm{B(A,S)}}}\,\gamma_{\mathrm{C(A,S)}}}{\gamma^{\infty}_{\mathrm{BC(A,S)}}} \cdot X_{\mathrm{C}} + K_2 \cdot \frac{t^{\infty}_{\gamma_{\mathrm{B(A,S)}}}\,\gamma_{\mathrm{D(A,S)}}}{\gamma^{\infty}_{\mathrm{BD(A,S)}}} \cdot X_{\mathrm{D}} \right] \tag{13}$$

with

$$ {}^{t}\gamma^{\infty}_{\mathrm{B(A,S)}} \approx {}^{t}\gamma^{\infty}_{\mathrm{B(S)}} \tag{14} $$

proposed by Eon *et al.*[3], one arrives at

$$ K_{\mathrm{R}} V^{0}_{\mathrm{A,S}} = K^{0}_{\mathrm{R}} V^{0}_{\mathrm{S}} \cdot \left[1 + \left(\frac{a_{\gamma^{\infty}_{\mathrm{B(S)}}}}{a_{\gamma^{\infty}_{\mathrm{B(A)}}}} - 1 \right) \cdot X_{\mathrm{A}} + K_{1} \cdot \frac{\gamma^{\infty}_{\mathrm{B(S)}}\, \gamma_{\mathrm{C(A,S)}}}{\gamma^{\infty}_{\mathrm{BC(A,S)}}} \cdot X_{\mathrm{C}} + \right. $$

$$ \left. + K_{2} \cdot \frac{\gamma^{\infty}_{\mathrm{B(S)}}\, \gamma_{\mathrm{D(A,S)}}}{\gamma^{\infty}_{\mathrm{BD(A,S)}}} \cdot X_{\mathrm{D}} \right] \tag{15} $$

where

$$ K^{0}_{\mathrm{R}} = \frac{[\mathrm{B}^{0}(\mathrm{S})]}{[\mathrm{B(g)}]} = \frac{RT}{f^{0}_{\mathrm{B}}\, \gamma^{\infty}_{\mathrm{B(S)}}\, V^{0}_{\mathrm{S}}} \tag{16} $$

assuming that the activity coefficients for C and D are constant, which is approximately true when the behaviour of the C + D + S solution is quasi-ideal, the infinitely dilute solution of components C and D in S can be taken as the reference state and the thermodynamic equilibrium constants K^{*}_{1} and K^{*}_{2}, referring to infinite dilution in S, are obtained. This proposal was valid for complexing agents in inert solvent in earlier work[1–3]. With the activity coefficients for C and D constant, eqn. 15 will become

$$ K_{\mathrm{R}} V^{0}_{\mathrm{A,S}} = K^{0}_{\mathrm{R}} V^{0}_{\mathrm{S}} \cdot (1 + \psi X_{\mathrm{A}} + K^{*}_{1} X_{\mathrm{C}} + K^{*}_{2} X_{\mathrm{D}}) \tag{17} $$

where

$$ \psi = \frac{a_{\gamma^{\infty}_{\mathrm{B(S)}}}}{a_{\gamma^{\infty}_{\mathrm{B(A)}}}} - 1 \tag{18} $$

$$ K^{*}_{1} = \frac{\gamma^{*}_{\mathrm{BC}}}{\gamma^{*}_{\mathrm{B}}\, \gamma^{*}_{\mathrm{C}}} \cdot \frac{X_{\mathrm{BC}}}{X_{\mathrm{B}} X_{\mathrm{C}}} \tag{19} $$

and

$$ K^{*}_{2} = \frac{\gamma^{*}_{\mathrm{BD}}}{\gamma^{*}_{\mathrm{B}}\, \gamma^{*}_{\mathrm{D}}} \cdot \frac{X_{\mathrm{BD}}}{X_{\mathrm{B}} X_{\mathrm{D}}} \tag{20} $$

Eqns. 3 and 17 give

$$ K_{\mathrm{R}} V^{0}_{\mathrm{A,S}} = K^{0}_{\mathrm{R}} V^{0}_{\mathrm{S}} [1 + (\psi + K^{*}_{1}) \cdot X_{\mathrm{C}} + (\psi + K^{*}_{2}) \cdot X_{\mathrm{D}}] \tag{21} $$

ψ can be derived by means of the Flory–Huggins calculation of athermal activity coefficients for components in a solution combined with an experimental procedure for non-complexing reference solutes described earlier[1]. For infinite dilution of B, the Flory–Huggins treatment gives

$$\frac{1}{a^{\infty}_{\gamma_{B(A)}}} = \frac{V^0_A}{V^0_B}\cdot\exp\,(V^0_B/V^0_A - 1) \tag{22}$$

$$\frac{1}{a^{\infty}_{\gamma_{B(S)}}} = \frac{V^0_S}{V^0_B}\cdot\exp\,(V^0_B/V^0_S - 1) \tag{23}$$

Eqns. 18, 22 and 23 give

$$\psi_{\text{calc}} = \frac{V^0_A}{V^0_S}\cdot\exp\left[V^0_B\left(\frac{1}{V^0_A} - \frac{1}{V^0_S}\right)\right] - 1 \tag{24}$$

and, according to the previous paper[1]

$$\psi = \psi_{\text{calc}} + \Delta\psi \tag{25}$$

where

$$\Delta\psi = \frac{1}{n}\sum(\psi_{\text{exp alkane}} - \psi_{\text{calc alkane}}) \tag{26}$$

$\psi_{\text{exp alkane}}$ is determined by setting K^*_1 and K^*_2 for alkanes to zero in eqn. 17 and n is the number of alkanes used to determine the average value, $\Delta\psi$.

$V^0_{A,S}$ and V^0_A can be calculated by means of the equations

$$V^0_{A,S} = V^0_S + (V^0_A - V^0_S)\cdot X_A \tag{27}$$

and

$$V^0_A = V^0_C + (V^0_D - V^0_C)\cdot X^0_D \tag{28}$$

where X^0_D is the molar fraction of D in the C + D solution, which in this instance means initial molar fractions calculated from weighings.

K^*_1 and K^*_2 can be determined separately by mixing C with S in one investigation and D with S in another, as outlined in previous papers[1,2]. If eqn. 21 is satisfied for solutions of C and D in S, this is evidence that complexation between C and D in the stationary phase is negligible. Note that the initial molar fractions of C, D and S calculated from weighings are approximately equal to equilibrium molar fractions, as B is so diluted that the arithmetic values of X_B, X_{BC} and X_{BD} are very small.

II. C and D form a 1:1 complex with B and also a 1:1 complex with each other

Except in the rare instances where steric hindrance occurs, one usually expects complexation between two complexing agents to occur on dissolution in an inert solvent. Complexation between C and D affects molar fractions, molar volumes ($V^0_{\mathrm{A,S}}$) and the value of ψ in eqn. 17.

The equilibrium in eqn. 29 must also be taken into consideration.

$$\mathrm{C} + \mathrm{D} \rightleftharpoons \mathrm{CD} \tag{29}$$

with an equilibrium constant given by eqn. 30:

$$K = \frac{X_{\mathrm{CD_{eq}}}}{X_{\mathrm{C_{eq}}}\, X_{\mathrm{D_{eq}}}} \cdot \frac{\gamma_{\mathrm{CD(A,S)}}}{\gamma_{\mathrm{C(A,S)}}\, \gamma_{\mathrm{D(A,S)}}} \tag{30}$$

X_{C} and X_{D} must be replaced with equilibrium concentrations $X_{\mathrm{C_{eq}}}$ and $X_{\mathrm{D_{eq}}}$, and X_{A} with $X'_{\mathrm{A}} = X_{\mathrm{C_{eq}}} + X_{\mathrm{D_{eq}}} + X_{\mathrm{CD_{eq}}}$, where $X_{\mathrm{CD_{eq}}}$ is the equilibrium concentration of the CD complex formed. Eqns. 12 and 17 are changed to

$$\frac{1}{a^{\infty}_{\gamma_{\mathrm{B(A,S)}}}} = \frac{1}{a^{\infty}_{\gamma_{\mathrm{B(S)}}}} + \left(\frac{1}{a^{\infty}_{\gamma_{\mathrm{B(A)}}}} - \frac{1}{a^{\infty}_{\gamma_{\mathrm{B(S)}}}}\right)\cdot X'_{\mathrm{A}} \tag{31}$$

and

$$K_{\mathrm{R}} V^{0\prime}_{\mathrm{A,S}} = K^0_{\mathrm{R}} V^0_{\mathrm{S}} \cdot (1 + \psi' X'_{\mathrm{A}} + K^*_1 X_{\mathrm{C_{eq}}} + K^*_2 X_{\mathrm{D_{eq}}}) \tag{32}$$

The change in $V^0_{\mathrm{A,S}}$ and ψX_{A} in eqn. 17, which follows upon the complexation between C and D, is usually less than the change in X_{C} and X_{D}, and the change in $K_{\mathrm{R}} V^0_{\mathrm{A,S}}$ and $K^0_{\mathrm{R}} V^0_{\mathrm{S}} \cdot (1 + \psi X_{\mathrm{A}})$ is analogous. This is the case, for example, when equal molar fractions of dodecyl laurate and 1-chlorooctadecane are used as complexing agents in squalane as inert solvent. It is therefore possible to calculate equilibrium concentrations by an iterative procedure as described below.

To a first approximation, $V^{0\prime}_{\mathrm{A,S}} = V^0_{\mathrm{A,S}}$ and $\psi' X'_{\mathrm{A}} = \psi X_{\mathrm{A}}$. $X_{\mathrm{C_{eq}}}$ and $X_{\mathrm{D_{eq}}}$ are calculated from eqn. 32, where K_{R} is determined by GLC with a C + D + S solution and K^0_{R} with pure S solution as the stationary phase. K^*_1 and K^*_2 are determined from separate GLC investigations with C + S solutions and D + S solutions as stationary phases. From the calculated values of $X_{\mathrm{C_{eq}}}$ and $X_{\mathrm{D_{eq}}}$, it is possible to calculate $X_{\mathrm{CD_{eq}}}$, the new average molecular weight of the C + D + CD + S solution and the C + D + CD solution, and $V^{0\prime}_{\mathrm{A,S}}$, X'_{A} and ψ' through eqns. 33, 34 and 35:

$$M'_{\mathrm{av}} = X_{\mathrm{C_{eq}}} M_{\mathrm{C}} + X_{\mathrm{D_{eq}}} M_{\mathrm{D}} + X_{\mathrm{CD_{eq}}} M_{\mathrm{CD}} + X_{\mathrm{S}} M_{\mathrm{S}} \tag{33}$$

$$V^{0\prime}_{\mathrm{A,S}} = \frac{M'_{\mathrm{av}}}{d_{\mathrm{A,S}}} \tag{34}$$

$$M^{0\prime}_{\mathrm{av}} = X^0_{\mathrm{C_{eq}}} M_{\mathrm{C}} + X^0_{\mathrm{D_{eq}}} M_{\mathrm{D}} + X^0_{\mathrm{CD_{eq}}} M_{\mathrm{CD}} \tag{35}$$

where $X^0_{C_{eq}}$, $X^0_{D_{eq}}$ and $X^0_{CD_{eq}}$ are equilibrium molar fractions of C, D and CD in a C + D + CD solution. The values of $X^0_{C_{eq}}$, $X^0_{D_{eq}}$ and $X^0_{CD_{eq}}$ can be determined from $X_{C_{eq}}$, $X_{D_{eq}}$ and $X_{CD_{eq}}$ by assuming that the quotient $\gamma_{CD}/\gamma_C\gamma_D$ of the activity coefficients for C, D and CD is the same in C + D + CD + S and C + D + CD solutions.

$$V^{0'}_A = \frac{M^{0'}_{av}}{d_A} \tag{36}$$

$$X'_A = X_{C_{eq}} + X_{D_{eq}} + X_{CD_{eq}} \tag{37}$$

$$\psi' = \psi'_{calc} + \Delta\psi' \tag{38}$$

$$\psi'_{calc} = \frac{V^{0'}_A}{V^0_S} \cdot \exp\left[V^0_B\left(\frac{1}{V^{0'}_A} - \frac{1}{V^0_S}\right)\right] - 1 \tag{39}$$

$$\Delta\psi' = \frac{1}{n}\sum\left(\psi'_{exp\,alkane} - \psi'_{calc\,alkane}\right) \tag{40}$$

In eqn. 40, $\psi'_{exp\,alkane}$ is determined as before by setting K^*_1 and K^*_2 for alkanes to zero in eqn. 32 and n as before is the number of alkanes used to determine the average value of $\Delta\psi'$.

The density of solutions that contain moderately complexing components is usually unaffected by the complexation and it can therefore be calculated from densities or molar volumes of pure components and initial molar fractions. This is the case, for example, when dodecyl laurate or 1-chlorooctadecane is used either alone or in combination with complexing agents in squalane.

If the initial molar fractions calculated from weighings are X_C, X_D and X_S in a C + D + S solution and X^0_C and X^0_D in a C + D solution, it follows from values of $V^0_{A,S}$ and V^0_A calculated from eqns. 27 and 28 that

$$d_{A,S} = \frac{X_C M_C + X_D M_D + X_S M_S}{V^0_{A,S}} \tag{41}$$

and

$$d_A = \frac{X^0_C M_C + X^0_D M_D}{V^0_A} \tag{42}$$

Of course, $d_{A,S}$ and d_A can also be determined experimentally, *e.g.*, by picnometric measurements. The calculated values of $V^{0'}_{A,S}$, ψ' and X'_A are used in eqn. 32 to give new values $X'_{C_{eq}}$ and $X'_{D_{eq}}$ of $X_{C_{eq}}$ and $X_{D_{eq}}$, and the iterative procedure is repeated.

The calculations can be considerably simplified if one makes solutions with equal molar fractions of C and D in S. With X_C and X_D equal, $X_{C_{eq}}$ and $X_{D_{eq}}$ will also be equal, and eqn. 32 can then be written as

$$K_R V^{0'}_{A,S} = K^0_R V^0_S \cdot [1 + \psi' X'_A + (K^*_1 + K^*_2)\cdot X_{C_{eq}}] \tag{43}$$

$X_{C_{eq}}$ determined from the iterative procedure should be independent of the choice of the complexing solute, B. If several solutes are investigated, one can use the average $X_{C_{eq}}$ value in each step for the next iteration, and use the difference between two consecutive average values of $X_{C_{eq}}$ as a criterion for stopping the iterative procedure.

With $X_{C_{eq}}$ calculated and the initial number of moles of C, D and S calculated from the weighings, $X_{CD_{eq}}$ can be calculated and eqn. 30 will give the value of $K\cdot\gamma_{C(A,S)}\cdot\gamma_{D(A,S)}/\gamma_{CD(A,S)}$.

If it is desired to take the infinitely dilute solution of C, D and CD in S with activity coefficients γ^*_i as a reference state, the equilibrium constant K^*, given by eqn. 44, must be determined:

$$K^* = \frac{X_{CD_{eq}}}{X_{C_{eq}}\,X_{D_{eq}}}\cdot\frac{\gamma^*_{CD}}{\gamma^*_C\,\gamma^*_D} \tag{44}$$

Dividing eqn. 44 by eqn. 30 gives the relation between K and K^*:

$$K^*/K = \frac{\gamma^*_{CD}}{\gamma^*_C\,\gamma^*_D}\Big/\frac{\gamma_{CD(A,S)}}{\gamma_{C(A,S)}\,\gamma_{D(A,S)}} \tag{45}$$

K^* can be determined either from the experimental value of $X_{CD_{eq}}/X_{C_{eq}}\,X_{D_{eq}}$ followed by a calculation of $\gamma^*_{CD}/\gamma^*_C\,\gamma^*_D$ from classical thermodynamic equations or by determining $X_{CD_{eq}}/X_{C_{eq}}\,X_{D_{eq}}$ for different initial molar fractions of C and D in S followed by an extrapolation to infinite dilution of C and D in S. The accuracy of the last method is limited by the great uncertainty in the determination of $X_{C_{eq}}$ from eqn. 43 for low initial molar fractions of X_C and X_D, as the values of $K_R V^{0'}_{A,S}$ and $K^0_R V^0_S$ in this instance will be nearly equal. It is probable that, by assuming the activity coefficients for C, D and CD to be unity on going from dilute solutions of C and D in S to infinite dilution in S, no significant errors arise in most instances. The stationary phase components, C, D and S, are of similar size and, except for the complex-forming groups, are often structurally alike. They therefore often give quasi-ideal solutions. In this instance,

$$K^*_0 = K = \frac{X_{CD_{eq}}}{X_{C_{eq}}\,X_{D_{eq}}} \tag{46}$$

Expressing the activity coefficients as products of athermal and thermal factors according to eqn. 12, and by setting the thermal factors equal to unity, which is a good approximation for quasi-ideal solutions, one can write

$$\frac{\gamma^*_{\mathrm{CD}}}{\gamma^*_{\mathrm{C}}\,\gamma^*_{\mathrm{D}}} = \frac{a^*_{\gamma_{\mathrm{CD}}}}{a^*_{\gamma_{\mathrm{C}}}\;a^*_{\mathrm{D}}} \tag{47}$$

The Flory–Huggins treatment for infinite dilution of C, D and CD in S gives, according to Eon *et al.*[3]:

$$\frac{1}{a^*_{\gamma_{\mathrm{C}}}} = \frac{V^0_{\mathrm{S}}}{V^0_{\mathrm{C}}}\cdot\exp\,(V^0_{\mathrm{C}}/V^0_{\mathrm{S}} - 1) \tag{48}$$

$$\frac{1}{a^*_{\gamma_{\mathrm{D}}}} = \frac{V^0_{\mathrm{S}}}{V^0_{\mathrm{D}}}\cdot\exp\,(V^0_{\mathrm{D}}/V^0_{\mathrm{S}} - 1) \tag{49}$$

and

$$\frac{1}{a^*_{\gamma_{\mathrm{CD}}}} = \frac{V^0_{\mathrm{S}}}{V^0_{\mathrm{CD}}}\cdot\exp\,(V^0_{\mathrm{CD}}/V^0_{\mathrm{S}} - 1) \tag{50}$$

Substitution of eqns. 48–50 into eqn. 47 gives

$$\frac{\gamma^*_{\mathrm{CD}}}{\gamma_{\mathrm{C}}\,\gamma_{\mathrm{D}}} = \frac{V^0_{\mathrm{S}}\,V^0_{\mathrm{CD}}}{V^0_{\mathrm{C}}\,V^0_{\mathrm{D}}}\cdot\exp\,(V^0_{\mathrm{C}}/V^0_{\mathrm{S}} + V^0_{\mathrm{D}}/V^0_{\mathrm{S}} - V^0_{\mathrm{CD}}/V^0_{\mathrm{S}} - 1) \tag{51}$$

If it is assumed, as before, that the density of a solution of C and D is unaffected by the formation of a CD complex, then V^0_{CD} can be estimated by means of eqn. 52:

$$V^0_{\mathrm{CD}} = V^0_{\mathrm{C}} + V^0_{\mathrm{D}} \tag{52}$$

From eqns. 51 and 52, it follows that

$$\frac{\gamma^*_{\mathrm{CD}}}{\gamma^*_{\mathrm{C}}\,\gamma^*_{\mathrm{D}}} = \frac{V^0_{\mathrm{S}}\cdot(V^0_{\mathrm{C}} + V^0_{\mathrm{D}})}{V^0_{\mathrm{C}}\,V^0_{\mathrm{D}}}\cdot\mathrm{e}^{-1} \tag{53}$$

For a system with dodecyl laurate and 1-chlorooctadecane as complexing agents in squalane, $\gamma^*_{\mathrm{CD}}/\gamma^*_{\mathrm{C}}\,\gamma^*_{\mathrm{D}}$ at 60 °C is calculated to be 1.02. For this complexation reaction, the difference (1.02 — 1) in K^* values calculated from eqns. 30, 45 and 53 or eqn. 46 is small.

TABLE I

MOLAR VOLUMES (V_i^0), MOLAR WEIGHTS (M_i) AND DENSITIES ($d_{A,S}$, d_A) FOR THE CALCULATION OF THE EQUILIBRIUM CONSTANT FOR A 1:1 COMPLEX BETWEEN DODECYL LAURATE (C) AND 1-CHLOROOCTADECANE (D) IN SQUALANE (S)

A represents a mixture of C and D with equal initial molar fractions.

Temperature (°C)	V_A^0 (l)	V_S^0 (l)	$V_{A,S}^0$ (l)	M_C (g)	M_D (g)	M_S (g)	$d_{A,S}$ (g/l)	d_A (g/l)
50	0.3920	0.5352	0.4636	368.65	288.95	422.83	810.6	838.8
60	0.3953	0.5399	0.4676	368.65	288.95	422.83	803.7	831.8
70	0.3986	0.5442	0.4715	368.65	288.95	422.83	797.1	824.9

CALCULATIONS

Equilibrium molar fractions of dodecyl laurate (C) and 1-chlorooctadecane (D) in squalane (S) were calculated from eqn. 43 by means of the iterative procedure described above. The initial molar fractions in squalane for both complexing agents were 0.250. The calculations were made with a program written in the BASIC language for the four alkane solutes and ten complexing solutes, and involved five iterative steps. The program is easy to change to any desired number of solutes and interative steps, and is available as a paper-tape copy on request. The calculations were performed on a mini-computer with a 16K memory (ALPHA LSI-2). Two sets of data were used for the calculations (Tables I and II). In Table II, the set of data is valid for a temperature of 60 °C. Similar sets of data were used at 50 and 70 °C. The same molar volumes for solutes used in an earlier paper[1] were used in these calculations. Values of $K_R^0 V_S^0$, K_1^* and K_2^* are taken from earlier papers[1,2]. The $K_R^0 V_S^0$ values are average values of the $K_R^0 V_S^0$ values given by the regression lines in the previously investigated system of dodecyl laurate and 1-chlorooctadecane in squalane.

With equal molar fractions of C and D in squalane, the equilibrium molar fractions $X_{C_{eq}}$ and $X_{D_{eq}}$ of C and D are equal. Using initial molar fractions of 0.25 for each gives the relationship between $X_{C_{eq}}$ and $X_{CD_{eq}}$:

$$X_{CD_{eq}} = \frac{1 - 4\,X_{C_{eq}}}{3} \tag{54}$$

The values of $X^0_{C_{eq}}$, $X^0_{D_{eq}}$ and $X^0_{CD_{eq}}$ necessary for performing the iterative procedure were calculated from eqns. 55–57

$$K = \frac{X_{CD_{eq}}}{X^2_{C_{eq}}} \tag{55}$$

when $X_{C_{eq}} = X_{D_{eq}}$ in eqn. 46.

$$X^0_{C_{eq}} = \frac{1}{\sqrt{K+1} + 1} \tag{56}$$

$$X^0_{CD_{eq}} = 1 - 2\,X^0_{C_{eq}} \tag{57}$$

TABLE II

DATA AT 60 °C FOR THE CALCULATION OF THE EQUILIBRIUM MOLAR FRACTIONS IN SQUALANE OF DODECYL LAURATE AND 1-CHLOROOCTADECANE

Initial molar fractions were 0.250 for both complexing agents.

V_B^0 = molar volume (l) of solute B.
K_R, K_R^0 = partition coefficients of solute on a complex-forming stationary phase and on pure squalane, respectively.
V_S^0 = molar volume (l) of pure squalane.
K_1^*, K_2 = equilibrium constants for 1:1 complexes between solute and dodecyl laurate and solute and 1-chlorooctadecane, respectively, at infinite dilution in squalane.

Solute	V_B^0	K_R	$K_R^0 V_S^0$	$K_1^* + K_2^*$
Cyclohexane	0.1137	191.1	105.6	—
Methylcyclohexane	0.1337	351.5	192.5	—
Ethylcyclohexane	0.1485	971.6	533.4	—
n-Heptane	0.1543	271.7	148.9	—
p-Xylene	0.1285	1296.9	606.8	0.638
Toluene	0.1110	491.7	230.1	0.643
Benzene	0.0934	177.7	83.2	0.659
Fluorobenzene	0.0998	180.7	81.3	0.806
Chlorobenzene	0.1057	963.2	427.4	0.877
Benzotrifluoride	0.1294	217.9	94.6	0.929
Octafluorotoluene	0.1453	120.3	53.4	0.741
Methoxybenzene	0.1128	1687.7	708.7	1.119
Trichloroethene	0.0927	257.5	121.1	0.626
Tetrachloroethene	0.1048	747.7	378.6	0.325

Eqns. 55, 56 and 57 are valid for equal initial molar fractions of C and D in squalane if the quotient $\gamma_{CD}/\gamma_C\,\gamma_D$ of the activity coefficients for C, D and CD is considered to remain unchanged on going from the C + D + CD + S solution to a C + D + CD solution. The latter restriction does not seem to be important, as the complexation in the system investigated is small and the molecules in the stationary phase are of similar structure and size.

If a thermodynamically based value is used in the determination of $X^0_{C_{eq}}$, the value of K in eqn. 56 should be replaced with $K\cdot([\gamma^0_{CD}/\gamma^0_C\,\gamma^0_D]/[\gamma_{CD}/\gamma_C\,\gamma_D])$, where γ_i^0 refers to activity coefficients in a C + D + CD solution and γ_i to activity coefficients in a C + D + CD + S solution.

TABLE III

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED (FROM EQNS. 3, 27, 28 AND 41) DENSITY VALUES AT 50, 60 AND 70 °C FOR A SOLUTION OF DODECYL LAURATE AND 1-CHLOROOCTADECANE IN SQUALANE WITH MOLAR FRACTIONS OF 0.2494, 0.2498 AND 0.5008, RESPECTIVELY

Temperature (°C)	*Density (g/l)*	
	Experimental	*Calculated*
50	810.5	810.6
60	803.7	803.7
70	797.4	797.2

However, the possible error in the determination of $X^0_{C_{eq}}$ when changes in the quotient between the activity coefficients are not taken into consideration will cause less error in the determination of $X_{C_{eq}}$ from eqn. 43. In order to illustrate this behaviour, a calculation was made by using values at 60 °C for the stationary phase investigated with *p*-xylene as the solute. Note that the only variable affected in eqn. 43 is ψ'. With $K = 0.25$ and the quotient $(\gamma^0_{CD}/\gamma^0_C\,\gamma^0_D)/(\gamma_{CD}/\gamma_C\,\gamma_D) = 1.10$ instead of 1.00, the value of $K\cdot([\gamma^0_{CD}/\gamma^0_C\,\gamma^0_D]/[\gamma_{CD}/\gamma_C\,\gamma_D])$ changes by 10%, but the change in the value of $X_{C_{eq}}$ is only about 0.9%.

The density of the stationary phase investigated was considered to be unaffected by the complexation, as stated earlier, and could therefore be calculated from eqns. 3, 27, 28 and 41.

The molar volumes for the three stationary phase components necessary for the calculations were determined earlier[1,2]. A comparison between the calculated values and those determined by picnometric measurements at 50, 60 and 70 °C for a solution of composition almost identical with that investigated by GLC is given in Table III. Table III shows very good agreement between the experimental and calculated values, which indicates that it is valid to consider the density of the stationary phase to be unaffected by complexation, as postulated above.

In the derivation of eqns. 17 and 43, $1/a^{\infty}_{\gamma\,\mathrm{B(A,S)}}$ was substituted by the expressions given in eqns. 12 and 31, respectively. The validity of this approximation was investigated for some solutes. By setting the value of the equilibrium constant to zero and with *p*-xylene as solute, a deviation between $1/a^{\infty}_{\gamma\,\mathrm{B(A,S)}}$ calculated from

$$\frac{1}{a^{\infty}_{\gamma_{\mathrm{B(A,S)}}}} = \frac{V^0_{\mathrm{A,S}}}{V^0_{\mathrm{B}}}\cdot\exp\left(V^0_{\mathrm{B}}/V^0_{\mathrm{A,S}} - 1\right)$$

and from eqn. 12 was found to be less than 0.1% for molar fractions of $X_A \leqslant 0.50$. With a value of the equilibrium constant of 0.25 and with the same solute, a similar calculation gave a deviation of less than 0.9% for the same molar fraction range. This difference is so small that a refinement involving the replacement of eqn. 31 with a polynomial function does not seem to be necessary, especially as even the Flory–Huggins treatment of activity coefficients is approximate.

RESULTS AND DISCUSSION

The values of $X_{C_{eq}}$ obtained from the calculations for different complexing solutes are given in Table IV for the five iterative steps at 60 °C. Average values of $X_{C_{eq}}$ and standard deviations of the average value in each iterative step are also given. The value of $X_{C_{eq}}$ derived from octafluorotoluene was rejected in the *last* iterative step. However, the rejection of $X_{C_{eq}}$ for octafluorotoluene after the *first* calculation does not change the average value of $X_{C_{eq}}$ in the last step. Note that the difference between the average values of $X_{C_{eq}}$ in two consecutive steps decreases rapidly as the iterative process proceeds.

The iterations at 50 and 70 °C were carried on in the same way, and they were as satisfactory as that at 60 °C. The calculated $X_{C_{eq}}$ values at 50, 60 and 70 °C with average values and 95% confidence intervals are given in Table V.

TABLE IV

VALUES OF EQUILIBRIUM CONCENTRATIONS AT 60 °C OF DODECYL LAURATE ($X_{C_{eq}}$), AVERAGE VALUES $\bar{X}_{C_{eq}}$ OF $X_{C_{eq}}$ AND STANDARD DEVIATIONS (s) OF $\bar{X}_{C_{eq}}$ FOR THE FIVE ITERATIONS

Solute	$X_{C_{eq}}$				
	Iteration number				
	I	*II*	*III*	*IV*	*V*
p-Xylene	0.23608	0.23708	0.23695	0.23697	0.23697
Toluene	0.24129	0.24176	0.24170	0.24171	0.24170
Benzene	0.24174	0.24171	0.24171	0.24171	0.24171
Fluorobenzene	0.24593	0.24632	0.24627	0.24628	0.24628
Chlorobenzene	0.24076	0.24134	0.24126	0.24127	0.24127
Benzotrifluoride	0.24547	0.24663	0.24648	0.24650	0.24650
Octafluorotoluene	0.27000	0.27170	0.27148	0.27151	0.27151*
Methoxybenzene	0.24039	0.24126	0.24115	0.24116	0.24116
Trichloroethene	0.24771	0.24762	0.24763	0.24763	0.24763
Tetrachloroethene	0.24938	0.24868	0.24877	0.24876	0.24876
$\bar{X}_{C_{eq}}$	0.24588	0.24641	0.24634	0.24635	0.24635
s	$9.36\cdot10^{-3}$	$9.60\cdot10^{-3}$	$9.57\cdot10^{-3}$	$9.57\cdot10^{-3}$	$9.57\cdot10^{-3}$

* The value of $X_{C_{eq}}$ in step V for octafluorotoluene can be rejected by Dixon's r-test at a significance level of 0.05. In this instance, the values of $\bar{X}_{C_{eq}}$ and s are 0.2436 and $3.9\cdot10^{-3}$, respectively.

The equilibrium constants for the CD complex at 50, 60 and 70 °C were calculated by means of eqns. 54 and 55. As stated earlier, the difference between constant values calculated from eqns. 54 and 55 or 45, 53, 54 and 55 is small. Values of the complexation constants at the three temperatures and limits for the values of the constants are given in Table VI.

TABLE V

VALUES FROM THE FIFTH ITERATION OF EQUILIBRIUM CONCENTRATIONS AT 50, 60 AND 70 °C OF DODECYL LAURATE ($X_{C_{eq}}$), AVERAGE VALUES $\bar{X}_{C_{eq}}$ OF $X_{C_{eq}}$ AND 95% CONFIDENCE INTERVALS (I) FOR $\bar{X}_{C_{eq}}$

Solute	$X_{C_{eq}}$		
	50 °C	*60 °C*	*70 °C*
p-Xylene	0.2390	0.2370	0.2325
Toluene	0.2446	0.2417	0.2384
Benzene	0.2384	0.2417	0.2345
Fluorobenzene	0.2434	0.2463	0.2394
Chlorobenzene	0.2457	0.2413	0.2402
Benzotrifluoride	0.2426	0.2465	0.2480
Octafluorotoluene	(0.2639)*	(0.2715)*	0.2608
Methoxybenzene	0.2407	0.2412	0.2345
Trichloroethene	0.2509	0.2476	0.2454
Tetrachloroethene	0.2437	0.2488	0.2203
$\bar{X}_{C_{eq}}$	0.243	0.244	0.239
I	±0.003	±0.003	±0.008

* The values of $X_{C_{eq}}$ for octafluorotoluene at 50 and 60 °C can be rejected by Dixon's r-test at a significance level of 0.05 and were not used in the calculation of $\bar{X}_{C_e}$ and I.

TABLE VI

VALUES OF THE EQUILIBRIUM CONSTANT (K_0^*) AT 50, 60 AND 70 °C FOR A 1:1 COMPLEX BETWEEN DODECYL LAURATE AND 1-CHLOROOCTADECANE

Upper and lower limits of the constant at the three temperatures, calculated from the limits of the 95% confidence intervals for $\bar{X}_{C_{eq}}$ in Table V, are also given.

Temperature (°C)	K_*^0	*Lower and upper limits of* K_0^*
50	0.16	0.09–0.23
60	0.13	0.07–0.21
70	0.26	0.07–0.47

A study of Table V shows that the variation between the $X_{C_{eq}}$ values determined from different solutes is small, except for octafluorotoluene at 50, 60 and 70 °C and tetrachloroethene at 70 °C. The behaviour of octafluorotoluene can be explained by the unexpectedly low value of the complexation constant for the octafluorotoluene–1-chlorooctadecane complex[2], as an underestimation of K_2^* will give an overestimation of $X_{C_{eq}}$ when eqn. 43 is used. The low value for tetrachloroethene at 70 °C is probably due to an accidental error in the experimental determination of K_R. The values of $X_{C_{eq}}$ obtained from octafluorotoluene and tetrachloroethene, respectively, can be rejected with Dixon's r-test at a significance level of 0.10. In this instance, $\bar{X}_{C_{eq}} = 0.239$ and $I = 0.004$, that is, the average value is the same but the confidence interval is now considerably smaller and about the same as at 50 and 60 °C. The interval for K_0^* at 70 °C is now 0.16–0.36.

Whether the variations of $X_{C_{eq}}$ determined from the other solutes at the three temperatures are due to experimental errors, differences in the structures of the solutes or a combination of both is difficult to say. In any event, it should be borne in mind that the value of the equilibrium constant is small, which makes the determination rather uncertain, independent of the method used. The GLC measurements in this investigation give about the same precision as optical and NMR methods.

The value determined for the equilibrium constant is of the expected magnitude. The magnitudes of the constants at 60 °C between the solutes used in this investigation and dodecyl laurate and 1-chlorooctadecane were 0.20–0.68 and 0.11–0.44, respectively. As the solute molecules are considerably smaller than either of these complexing agents, it is not surprising that the equilibrium constant between a solute molecule and one of the complexing agents is in general larger than the constant between the two long-chain molecules in the stationary phase containing only one functional group each.

CONCLUSIONS

It has been shown that equilibrium constants between two non-volatile complexing agents can be determined indirectly by GLC. The method described, which avoids the previous necessity for the use of one volatile and one non-volatile complexing agent for determinations of complex constants by GLC, has further increased the usefulness of GLC for the study of complexation in organic solvents.

LIST OF SYMBOLS

A	Mixture of two complexing agents, C and D.
B	Volatile solute.
$[B^{\circ}(S)]$, $[B^{\circ}(A,S)]$	Concentration of uncomplexed solute in pure solvent S and A + S solution, respectively.
$[B(A,S)]$	Total concentration of B in an A + S solution including complexed species.
C, D	Complexing agents in the stationary phase.
BC, BD, CD	1:1 complex between B and C, B and D and C and D, respectively.
$[BC(A,S)]$, $[BD(A,S)]$	Concentration of BC complex and BD complex, respectively, in an A + S solution.
$d_{A,S}$, d_A	Density of a solution of C + D + S and of a solution of C + D, respectively.
f^0_B	Fugacity of pure B vapour in equilibrium with pure B liquid.
K_1, K_2	Equilibrium constants for the reactions between B and C in S, and B and D in S, respectively.
K^*_1, K^*_2	Thermodynamic equilibrium constants for the reaction between B and C, and B and D, respectively, using an infinitely dilute solution of each chemical species in solvent S as the reference state for chemical potentials.
K	Equilibrium constant for the reaction between C and D in a C + D + S solution.
K^*	Thermodynamic equilibrium constant for the reaction between C and D using an infinitely dilute solution of each chemical species in solvent S as the reference state for chemical potentials.
K^0_R	Partition coefficients of the solute between the pure inert solvent S and the gas phase.
K_R	Apparent partition coefficient, *i.e.*, the ratio of the total concentration of solute B (including complexed species BC and BD) in the liquid phase to the concentration in the gas phase.
M_i	Molecular weight of the species *i*.
M'_{av}, $M^{0'}_{av}$	Average molecular weights of a C + D + S solution and a C + D solution, respectively, when complexation occurs between C and D.
S	Solvent.
V^0_i	Molar volume of species *i*.
V^0_A, $V^0_{A,S}$	Molar volumes of C + D solutions and C + D + S solutions, respectively, if complexation between C and D does not occur.
$V^{0'}_A$, $V^{0'}_{A,S}$	Molar volumes of C + D solutions and C + D + S solutions, respectively, if complexation occurs between C and D.
X_i, X^0_i	Molar fraction of species *i* in a C + D + S solution and a C + D solution, respectively, if complexation between C and D does not occur.

$X_{i_{eq}}$, $X^0_{i_{eq}}$	Equilibrium molar fraction of species i in a C + D + S solution and a C + D solution, respectively, if complexation occurs between C and D.
$\bar{X}_{C_{eq}}$	Average value of the equilibrium concentration of C calculated from the complexing solutes B.
X_A, X'_A	Sum of the molar fractions of all species except S in a C + D + S solution with and without complexation between C and D, respectively.
T	Absolute temperature.
$\gamma_{i(j)}$	Activity coefficient of the species i in a j solution, where j can be pure S or a C + D + S solution (A + S solution).
${}^a\gamma_{i(j)}$, ${}^t\gamma_{i(j)}$	Athermal and thermal contributions to the activity coefficient $\gamma_{i(j)}$.
$\gamma^{\infty}_{i(j)}$	Activity coefficient for infinite dilution of species i in a j solution, where j can be pure S, a C + D solution (A solution) or a C + D + S solution (A + S solution).
${}^a\gamma^{\infty}_{i(j)}$, ${}^t\gamma^{\infty}_{i(j)}$	Athermal and thermal contributions to the activity coefficient $\gamma^{\infty}_{i(j)}$.
γ_i^*	Activity coefficient of the species i with an infinitely dilute solution of all species i in S as the reference state for the chemical potential.

ACKNOWLEDGEMENTS

The author thanks Dr. Lars Haraldson for valuable and encouraging discussions concerning this work and Dr. Robert Carter for correcting the English in the manuscript.

REFERENCES

1 L. Mathiasson and R. Jönsson, *J. Chromatogr.*, 101 (1974) 339.
2 L. Mathiasson, *J. Chromatogr.*, 114 (1975) 39.
3 C. Eon, C. Pommier and G. Guiochon, *Chromatographia*, 4 (1971) 235 and 241.
4 J. H. Purnell and O. P. Srivastava, *Anal. Chem.*, 45 (1973) 1111.
5 C. Eon and G. Guiochon, *Anal. Chem.*, 46 (1974) 1393.
6 R. J. Laub and R. L. Pecsok, *Anal. Chem.*, 46 (1974) 1214.
7 D. E. Martire, *Anal. Chem.*, 46 (1974) 1712.