

CHROM. 7792

GAS-LIQUID CHROMATOGRAPHIC INVESTIGATION OF COMPLEXATION EQUILIBRIA BETWEEN AN ALIPHATIC ESTER AND VARIOUS BENZENE DERIVATIVES AND ALKENE DERIVATIVES

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(First received April 18th, 1974; revised manuscript received July 1st, 1974)

SUMMARY

Gas-liquid chromatography has been used to study complexation between a long-chain aliphatic ester, dodecyl laurate, and solutes with π -electron systems, such as benzene derivatives and alkene derivatives. Thermodynamic values of the equilibrium constants, Gibbs free energy (ΔG), enthalpy and entropy for the complexing reaction have been calculated based on a model developed by Eon *et al.* in 1971, which was modified by taking into consideration the behaviour of non-complexing alkane solutes. A linear variation of ΔG vs. ionization potential was found for solutes with similar structures. For the aromatic solutes, dipole moments in a group of similar structures are about the same, but both the ΔG values and dipole moments differ markedly between the groups. It is therefore concluded that both charge-transfer and dipole-dipole interactions influence the complexation reaction. Investigation of the variation of entropy with enthalpy for the complexing reaction indicates different reaction mechanisms for alkylbenzenes, halobenzenes and alkene derivatives.

INTRODUCTION

Over many years, various attempts have been made to explain solution behaviour in terms of specific chemical interactions between solvents and solutes. In earlier studies, the investigation of infrared¹ and ultraviolet spectra² showed the possibility of the occurrence of specific interactions, for example between polar solvents and various ketones and esters. Subsequently, nuclear magnetic resonance spectroscopy has been an important technique for confirming the evidence for specific complexes, for example a 1:1 complex between carbonyl compounds and aromatic solvents, and it has been possible to treat weak interactions of polar molecules in terms of ordinary chemical equilibria. Further details and references to this aspect can be found in the literature^{3,4}.

During the past 10 years, gas-liquid chromatography (GLC) has become an important method for studying complexation, especially in systems that show weak interactions. With these systems, other physico-chemical measurements often fail to establish the existence of complexation. Bogoslovsky *et al.*⁵, for example, confirmed

the existence of a 1:1 complex between dimethylformamide and mesitylene by GLC when no distinct evidence for such a complex could be found by measuring the density, refractive index, viscosity or dielectric constant.

Equilibrium constants have usually been calculated from equations mentioned by Bradford *et al.*⁶ and generalized by Purnell⁷ in 1967. In 1971, Eon *et al.*^{8,9} formulated modified equations that took into consideration the different sizes of the molecules investigated. Their model was later used, for example, by Vivilecchia and Karger¹⁰ in their study of hydrogen-bonded complexes.

In most of these studies, the solvent and the complexation agent in the solution have been complicated molecules with several functional groups. The solvent has been considered to be free from self-association and from complexation with the complexing agent or the solutes.

We decided to investigate a system with squalane as solvent, dodecyl laurate as complexing agent and a wide variety of aromatic compounds and alkene derivatives as solutes. The reason for choosing squalane was that it has no functional group and therefore is not able to form complexes. It has been shown by many workers that molecules with π -electron systems, such as esters and ketones, are able to give complexes with other molecules that contain π -electrons. Dodecyl laurate has only one functional group, the ester group with a π -electron system, and it therefore might be possible to correlate the complexation constants between different solutes and dodecyl laurate with the characteristics of the ester group. The position of the ester group in the middle of the molecule makes self-association less probable. Dodecyl laurate is soluble in all proportions in squalane at the temperatures investigated. For the calculation of the numerical values of the complex constants, we used the model of Eon *et al.*⁸ with slight modifications.

THEORETICAL

In the determination of complex constants by GLC, Eon *et al.*⁸ showed that the thermodynamic equilibrium constant, K^* , between a volatile solute (B) and a complexing agent (A) dissolved in a solvent (S), considered to be inert, is given by the equation

$$K_R \cdot V_{A,S}^0 = K_R^0 \cdot V_S^0 [1 + (\psi + K^*) X_A] \quad (1)$$

where

$$K^* = \frac{X_{AB}}{X_A \cdot X_B} \cdot \frac{\gamma_{AB}^*}{\gamma_A^* \cdot \gamma_B^*}$$

where the activity coefficients γ_{AB}^* , γ_A^* and γ_B^* refer to an infinitely dilute solution of AB, A and B in the solvent S; X_A , X_{AB} and X_B are mole fractions of A, AB and B, respectively, in S; $V_{A,S}^0$, V_S^0 , V_A^0 and V_B^0 are molar volumes of solutions of A and S, pure S, pure A and pure B, respectively; K_R is the partition coefficient of the solute B in a binary mixture of A and S; and K_R^0 is the partition coefficient of the solute B with pure solvent (S) as liquid phase.

Eqn. 1 is valid provided that:

(a) the solution of A in S is quasi-ideal,

(b) $1/a_{\gamma_{B(A,S)}^\infty}$ is a linear function of X_A , and

(c) $t_{\gamma_{B(A,S)}^\infty} \equiv t_{\gamma_{B(S)}^\infty}$ is a good approximation,

where $a_{\gamma_{B(A,S)}^\infty}$ and $a_{\gamma_{B(A)}^\infty}$ are the athermal contributions to the activity coefficient for B at infinite dilution in S and A, respectively, and $t_{\gamma_{B(A,S)}^\infty}$ and $t_{\gamma_{B(S)}^\infty}$ are the thermal contributions to the activity coefficient for B at infinite dilution in a mixture of A and S and in pure S, respectively.

If condition (b) is fulfilled, then eqn. 2 is valid:

$$\psi = \frac{a_{\gamma_{B(S)}^\infty}}{a_{\gamma_{B(A)}^\infty}} - 1 \approx V_A^0/V_S^0 e^{V_B^0(1/V_A^0 - 1/V_S^0)} - 1 \quad (2)$$

If partition is the only process responsible for the solute retention, K_R can be calculated from the classical equation

$$K_R = \frac{d_{A,S}}{m} \cdot J_3^2 (t_R - t_m) d_s \cdot \frac{P_s - f}{T_s} \cdot T_c \quad (3)$$

where $d_{A,S}$ is the density of the solution of A and S, m is the mass of liquid stationary phase, J_3^2 the James and Martin factor, t_R the retention time of the solute, t_m the retention time of an unretained compound, d_s the flow-rate of carrier gas measured at the flow meter temperature T_s , P_s the outlet pressure of the column, f the water vapour pressure in the flow meter at temperature T_s , and T_c the column temperature.

From eqn. 1 follows a linear variation of $K_R \cdot V_{A,S}^0$ with X_A . The quotient between the slope and the intercept of the line gives $(\psi + K^*)$.

ψ can be calculated through eqn. 2 from known values of the molar volumes. For non-complexing solutes, for example saturated hydrocarbons, ψ can also be determined experimentally ($\psi_{\text{cpt.}}$) from eqn. 1, as in this case $K^* = 0$. It will be seen in a later section that $\psi_{\text{cpt.}}$ can be used to obtain more realistic values of ψ even for solutes with $K^* \neq 0$.

Once K^* has been determined at two or more temperatures, the thermodynamic quantities ΔG^{r*} , ΔH^{r*} and ΔS^{r*} for the complexation reaction $A + B \rightleftharpoons AB$ can be determined from the classical equations

$$\Delta G^{r*} = -RT \ln K^* \quad (4)$$

$$\ln K^* = \frac{-\Delta H^{r*}}{R} \cdot \frac{1}{T} + \frac{\Delta S^{r*}}{R} \quad (5)$$

where ΔG^{r*} is the Gibbs free energy, ΔH^{r*} the enthalpy and ΔS^{r*} the entropy of the complexation reaction at infinite dilution in S.

EXPERIMENTAL

The GLC measurements were performed with equipment developed by Jönsson¹¹. We investigated 20 solutes (see Table I) at three different temperatures and

TABLE I
SOLUTES INVESTIGATED

<i>Aromatics</i>	<i>Aliphatic hydrocarbons, chlorinated aliphatic hydrocarbons</i>	<i>Non-aromatic oxygen-containing compounds</i>
<i>p</i> -Xylene	Cyclohexane	Di- <i>n</i> -butyl ether
Toluene	Methylcyclohexane	Ethyl acetate
Benzene	Ethylcyclohexane	Amyl acetate
Fluorobenzene	<i>n</i> -Heptane	Ethyl methyl ketone
Chlorobenzene	<i>cis</i> -2-Heptene	
Benzotrifluoride	<i>trans</i> -2-Heptene	
Octafluorotoluene	Trichloroethene	
Methoxybenzene	Tetrachloroethene	

with a stationary phase containing complexing agent at seven mole fractions. Squalane (Perkin-Elmer, Norwalk, Conn., U.S.A.) was used as the solvent and dodecyl laurate (Eastman, New York, N.Y., U.S.A.) as the complexing agent. Stationary phases were prepared over the entire mole fraction range.

Columns

Glass columns, 520 mm long and 3 mm I.D., containing about 0.60 g of packing were used. Supasorb, 40–60 mesh, acid washed and hexamethyldisilazane treated (BDH, Poole, Great Britain), was used as the support. The amount of organic stationary phase used was about 20% (w/w), coated on the support by dissolution in light petroleum (b.p. 40–60°) and mixing followed by evaporation of the light petroleum under a stream of air. The packing was finally heated at 80° for 4 h. Because an error in the amount of packing greatly influences the partition coefficients, we standardized a procedure for control of the amount of packing in each column by means of weighing before and after each step in the experimental procedure. The amount of organic phase in the packing was determined by combustion and ashing of the organic phase in the packing in a furnace, which was slowly heated from room temperature to 750–800° and was maintained at this temperature for 2 h. One reference sample of pure support and one sample of packing with a known amount of organic phase of about the same composition as the investigated column packing were always heated together with the column packing. In this way, we could correct for support losses and also for possible incompleteness of the ashing. However, with the chosen procedure, the ashing reaction was complete for all column packings within the experimental error of the method. The support losses were between 0.20 and 0.25% in all instances. The amount of organic phase in each column packing determined in this way was compared with values obtained from weighings of the same column packing (see Table V). The average difference between these two values was 0.5%. The ashing values were used for the calculations.

Procedure

Hydrogen was used as the carrier gas, at a flow-rate of about 55 ml/min. Seven columns with different mole fractions were run at 50°, 60° and 70° and for each temperature the column variables were measured. Pressure, pressure drop and flow-

rate were measured with an accuracy of 0.1%; the J -factor calculated from the pressure drop over the column was 0.93–0.96. The flow-rate was measured before and after each of the 21 runs and the average difference between these two measurements was less than 0.4%, and the average value for each run was used in the calculations. The temperature was maintained within $\pm 0.01^\circ$ of the desired value. A flame ionization detector was used, and a helium sample was used for the determination of the dead volume in the system. Helium gives a signal caused by its dilution of the hydrogen carrier gas.

The solutes were injected in the gas phase and the sample sizes were of the order of 10^{-2} – 10^{-3} μ mole. The retention time was determined in three different runs for each solute on each column and at each temperature, which gives 63 measured retention times for each solute. Injection of solutes, separately or in mixtures, had no detectable effect on their retention volumes. No significant variation of the retention time with variation of the amount of solute injected could be seen except for ethyl acetate, amyl acetate and ethyl methyl ketone.

RESULTS

Calculations of K_R from eqn. 3 are possible only if the retention is caused by a pure partition process. As we used a high liquid loading and a hexamethyldisilazane-treated support, the contribution to the retention from adsorption at the liquid–solid interface can be neglected for all of the solutes when the non-polar or weakly polar mixtures of squalane and dodecyl laurate are used as stationary phases. This is in agreement with the findings of, for example, Littlewood and Willmott¹² for stationary phases of pure squalane, squalane mixed with polar compounds and different polar and non-polar compounds such as ethers, esters, alkenes and halogenated hydrocarbons as solutes.

There is also the possibility of adsorption at the gas–liquid interface. According to Martire¹³ and Pecsok and Gump¹⁴, non-polar solutes are most strongly adsorbed at the surface of polar stationary phases and polar solutes most strongly at the surface of non-polar stationary phases, and the adsorption of non-polar solutes at non-polar stationary phases is negligible. Polar oxy-compounds in particular have been found to give adsorption effects at the gas–liquid interface. For example, strong adsorption of acetone at the surface of pure squalane was found by Pecsok and Gump¹⁴.

The 20 solutes investigated can thus be divided into two groups, one consisting of the three polar oxy-compounds ethyl acetate, amyl acetate and ethyl methyl ketone, for which liquid surface adsorption can be expected, and one consisting of the 17 other relatively non-polar compounds with no expected adsorption effects on the non-polar or weakly polar stationary phases.

Tewari *et al.*¹⁵ investigated stationary phases of saturated hydrocarbons, and most of the 17 relatively non-polar solutes used in our investigation as solutes, and they found no adsorption effects. The same behaviour was found by Meen *et al.*¹⁶ and Eon *et al.*⁹ for aromatic phthalate esters and several solutes investigated in the present work.

The absence of adsorption effects for the 17 solutes was also verified experimentally by the following observations. As the 17 solutes showed no variation of the retention time with the amount injected, the condition for infinite dilution is achieved

for partition effects. The retention behaviour also indicates either infinite dilution for adsorption effects at the gas-liquid surface, or the absence of such surface adsorption. In order to distinguish between these two possibilities, we used the three polar oxy-compounds as reference solutes. When injected in the same amounts (10^{-2} – 10^{-3} μ mole) as the other 17 solutes, the polar oxy-compounds showed a variation of retention time with the amount injected. This variation must be considered to be due to adsorption effects. Even if the amounts injected are small, it is not surprising that infinite dilution for adsorption effects at the gas-liquid interface is not achieved, because according to Martire¹³ a solute can be 100 times more concentrated at the surface than in the bulk. The lack of such variation for the 17 other solutes indicates that adsorption effects for these solutes can be neglected.

With suitable reference solutes, it should generally be possible to ascertain whether or not adsorption effects for a group of solutes can be neglected, allowing the calculation of partition coefficients for these solutes directly from eqn. 3.

K_R was calculated from eqn. 3 for the 17 solutes and a linear relationship between $K_R \cdot V_{A,S}^\circ$ and X_A was found (see Fig. 2). This is also expected according to eqn. 1 when adsorption can be neglected and the other conditions for eqn. 1 are fulfilled. The three polar oxy-compounds were also injected at about constant concentration on to each of the seven columns with different mole fractions of dodecyl laurate in squalane, and apparent values of K_R were calculated from eqn. 3. In contrast to the linear behaviour for the 17 solutes, a plot of $K_R \cdot V_{A,S}^\circ$ vs. X_A gives curves with a minimum. The polarity of the stationary phase changes from non-polar to weakly polar when the mole fraction of dodecyl laurate is increased. As the liquid surface adsorption is highest for a polar solute on a non-polar stationary phase, the adsorption effects will decrease for the polar oxy-compounds with increasing mole fraction of dodecyl laurate. On the other hand, the effect of the complexation between the solutes and dodecyl laurate will increase for higher mole fractions of dodecyl laurate. It seems reasonable that these two opposite influences give rise to the observed relationship between $K_R \cdot V_{A,S}^\circ$ and X_A . In the determination of complexation constants for the polar oxy-compounds, the contribution of partition to the total retention must therefore be determined by varying the amount of liquid phase on each of the columns. This type of solute will be further investigated.

Application of eqn. 1 to our system

Investigation of condition (a) for eqn. 1. The variation of the molar volume of the solution with the mole fraction of one of the components should be linear for a quasi-ideal solution, as pointed out by Eon *et al.*⁸. The molar volumes for mole fractions of 0, 0.30207, 0.49799, 0.69993 and 1 of dodecyl laurate in squalane were calculated according to eqn. 7 in the paper by Eon *et al.*⁸ from picnometer measurements of the densities at 50°, 60° and 70° (see Table II). An excellent linear correlation between molar volume and mole fraction was obtained for each temperature, allowing molar volumes for mole fractions 0.09993 and 0.84564 to be calculated from the regression lines. For 60°, the correlation coefficient is -0.99996 . The molar volumes given by the regression lines have been used in further calculations. Calculated densities of squalane at 50°, 60° and 70° agree with those determined by Cadogan *et al.*¹⁷.

Bogoslovsky *et al.*⁵ studied the dependence of $\log K_R$ on mole fraction for a solute

TABLE II

DENSITIES (g/ml) OF BINARY MIXTURES OF DODECYL LAURATE AND SQUALANE

Temperature (°C)	Mole fraction of dodecyl laurate in squalane				
	0	0.30207	0.49788	0.699993	1
50	0.7904	0.8020	0.8111	0.8196	0.8361
60	0.7831	0.7953	0.8044	0.8130	0.8291
70	0.7767	0.7888	0.7984	0.8064	0.8221

in a binary stationary liquid phase from a thermodynamic point of view. They obtain a third-power polynomial dependence of $\log K_R$ on the mole fraction of one of the phase components. When the stationary phase behaves as an ideal solution, the expression is reduced to

$$\log K_{R1(2,3)} = (A_{21} + 2A_{13} - A_{12} - C) X_2^2 + (A_{13} - A_{21} - C) X_2 + (-A_{13} - \log P_{01}) \quad (6)$$

where $K_{R1(2,3)}$ is the partition coefficient of a solute 1 in a binary stationary phase of components 2 and 3; X_2 is the mole fraction of component 2 in 3; A_{ij} and C are constants characterizing the paired interactions of molecules i and j of different shapes; and P_{01} is the vapour tension of the pure solute. In our system, eqn. 6 can be written as

$$\log K_R = a_2 X_A^2 + a_1 X_A + a_0 \quad (7)$$

where X_A is the mole fraction of dodecyl laurate in squalane and a_2 , a_1 and a_0 are constants. A plot of $\log K_R$ vs. X_A for some representative solutes at 60° is shown in Fig. 1. The points give a straight line, which is in agreement with early results¹⁸, but a careful examination shows that the fit of the experimental points to a parabolic curve

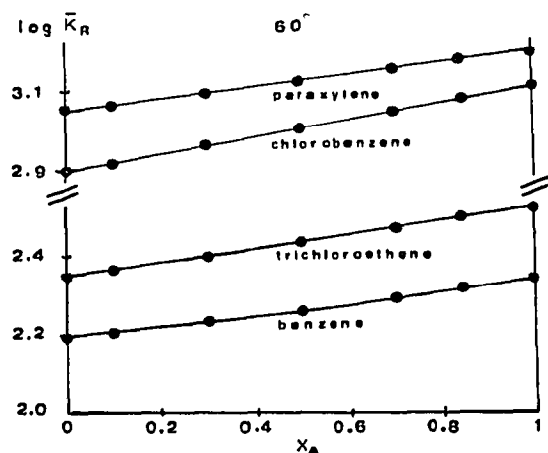


Fig. 1. Relationship between the logarithm of the partition coefficient, \bar{K}_R , and mole fraction of dodecyl laurate in squalane, X_A , at 60° for some solutes.

TABLE III

VALUES OF PARTITION COEFFICIENTS, PRODUCTS OF PARTITION COEFFICIENTS AND MOLAR VOLUMES, AND $(\psi + K^*)$ CALCULATED FROM REGRESSION LINES FOR DIFFERENT SOLUTES, AT 60°

Solute	Mole fraction of dodecyl laurate in squalane														
	0	0.09993		0.30207		0.49788		0.69993		0.84564		1.00			
	\bar{K}_R	$\bar{K}_R \cdot V_{AS}$	\bar{K}_R	$\bar{K}_R \cdot V_{AS}$	\bar{K}_R	$\bar{K}_R \cdot V_{AS}$	\bar{K}_R	$\bar{K}_R \cdot V_{AS}$	\bar{K}_R	$\bar{K}_R \cdot V_{AS}$	\bar{K}_R	$\bar{K}_R \cdot V_{AS}$	\bar{K}_R	$\bar{K}_R \cdot V_{AS}$	$(\psi + K^*)$
<i>p</i> -Xylene	1119	604.2	1148	608.6	1240	633.5	1316	648.0	1413	668.8	1488	683.3	1559	693.1	0.154
Toluene	424.4	229.1	435.7	231.0	466.8	238.6	498.7	245.6	535.8	253.5	565.6	259.8	592.8	263.6	0.158
Benzene	153.7	82.99	157.3	83.38	169.7	86.74	180.7	88.96	195.2	92.36	206.6	94.87	216.8	96.38	0.171
Fluoro- benzene	150.4	81.20	156.1	82.75	170.8	87.30	186.7	91.94	205.6	97.29	221.0	101.5	236.0	104.9	0.302
Chloro- benzene	789.1	426.1	820.9	435.3	913.0	466.6	997.4	491.1	1105	522.7	1184	543.8	1271	564.9	0.334
Benzotri- fluoride	174.1	94.01	184.2	97.66	206.2	105.4	230.0	113.3	256.6	121.4	279.0	128.2	300.3	133.5	0.427
Octafluoro- toluene	96.93	52.33	104.5	55.43	119.9	61.28	134.2	66.06	149.0	70.49	160.5	73.71	166.8	74.14	0.426
Methoxy- benzene	1325	715.5	1386	735.1	1547	790.7	1746	859.6	1962	928.5	2138	982.1	2329	1036	0.464
Di- <i>n</i> -butyl ether	1202	648.7	1218	646.1	1245	636.3	1263	622.0	1298	614.4	1320	606.3	1308	581.7	-0.095
Cyclohexane	194.7	105.1	192.9	102.3	191.8	98.03	189.8	93.43	189.0	89.42	187.8	86.27	184.3	81.93	-0.214
Methyl- cyclohexane	353.5	190.8	351.8	186.6	351.2	179.5	348.0	171.3	346.5	168.0	344.7	158.3	338.5	150.5	-0.201
Ethyl- cyclohexane	981.5	529.9	973.4	516.2	970.7	496.1	965.0	475.2	960.6	454.6	954.1	438.2	937.4	416.8	-0.207
<i>n</i> -Heptane	273.7	147.8	271.9	144.2	271.0	138.5	269.2	132.6	267.7	126.7	266.5	122.4	261.4	116.2	-0.207
<i>cis</i> -2-Heptene	282.2	152.4	282.1	149.6	286.0	146.2	288.3	142.0	291.8	138.1	294.6	135.3	293.3	130.4	-0.137
<i>trans</i> -2- Heptene	269.4	145.5	269.0	142.6	272.3	139.2	275.4	135.6	278.9	132.0	281.0	129.1	280.1	124.6	-0.136
Trichloro- ethene	222.5	120.1	230.7	122.4	250.8	128.2	270.9	133.4	273.9	139.1	311.9	143.3	328.3	146.0	0.222
Tetrachloro- ethene	695.6	375.6	703.7	373.2	730.6	373.4	754.0	371.3	783.1	370.6	803.7	369.2	818.2	363.8	-0.018

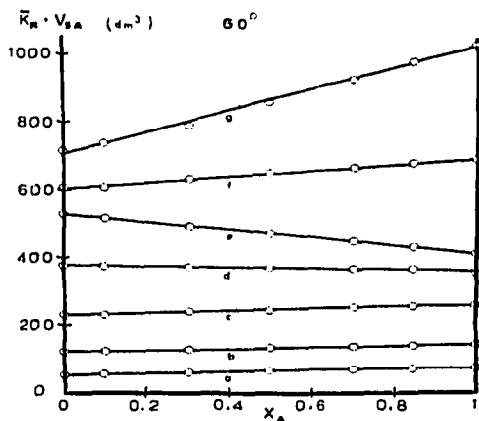


Fig. 2. Variation of $\bar{K}_R \cdot V_{SA}$ with mole fraction, X_A , of dodecyl laurate in squalane at 60° for some solutes. a, Octafluorotoluene; b, trichloroethene; c, toluene; d, tetrachloroethene; e, ethylcyclohexane; f, *p*-xylene; g, methoxybenzene.

is even better. The results of the investigation of condition (a) suggest that only weak interactions can exist between the components of the stationary phase.

Investigation of condition (b) for eqn. 1. The postulate that $1/\bar{a}_{\nu}^{\infty}$ vs. X_A is linear for different solutes has been tested for our system by calculations according to eqns. 17 and 18 in the paper of Eon *et al.*⁸ The absolute value of the correlation coefficients for the regression lines obtained with different solutes are very close to unity in all instances. For the most unfavourable case, that is, the solute with the largest molar volume, the correlation coefficient at 60° is -0.999990 .

TABLE IV

VALUES OF $(\psi + K^*)$ AT 50°, 60° AND 70°

Values are given with 95% confidence intervals.

Solute	$(\psi + K^*)$		
	50°	60°	70°
<i>p</i> -Xylene	0.170 ± 0.040	0.154 ± 0.016	0.128 ± 0.041
Toluene	0.178 ± 0.040	0.158 ± 0.013	0.134 ± 0.042
Benzene	0.190 ± 0.035	0.171 ± 0.020	0.143 ± 0.040
Fluorobenzene	0.337 ± 0.039	0.302 ± 0.025	0.257 ± 0.042
Chlorobenzene	0.366 ± 0.036	0.334 ± 0.018	0.292 ± 0.040
Benzotrifluoride	0.470 ± 0.046	0.427 ± 0.017	0.360 ± 0.045
Octafluorotoluene	0.507 ± 0.132	0.426 ± 0.109	0.364 ± 0.115
Methoxybenzene	0.520 ± 0.071	0.464 ± 0.049	0.407 ± 0.039
<i>cis</i> -2-Heptene	-0.140 ± 0.042	-0.137 ± 0.015	-0.141 ± 0.042
<i>trans</i> -2-Heptene	-0.142 ± 0.042	-0.136 ± 0.016	-0.141 ± 0.042
Trichloroethene	0.248 ± 0.050	0.222 ± 0.016	0.177 ± 0.050
Tetrachloroethene	-0.005 ± 0.037	-0.018 ± 0.011	-0.022 ± 0.022
Di- <i>n</i> -butyl ether	-0.084 ± 0.047	-0.095 ± 0.031	-0.086 ± 0.044
Cyclohexane	-0.222 ± 0.034	-0.214 ± 0.011	-0.213 ± 0.039
Methylcyclohexane	-0.215 ± 0.038	-0.201 ± 0.038	-0.206 ± 0.037
Ethylcyclohexane	-0.215 ± 0.039	-0.207 ± 0.014	-0.203 ± 0.038
<i>n</i> -Heptane	-0.212 ± 0.038	-0.207 ± 0.014	-0.206 ± 0.042

Investigation of condition (c) for eqn. 1. The approximation $t_{y_{B(\lambda, S)}}^{\infty} \equiv t_{y_{B(S)}}^{\infty}$ is usually good for this type of system, according to Eon *et al.*⁸. The experimental linear relationship between $K_R \cdot V_{SA}^0$ and X_A for the 17 solutes used in this work is strong evidence that this approximation is valid, because a variation of $t_{y_B}^{\infty}$ with the composition of the stationary phase would give a non-linear relationship between $K_R \cdot V_{SA}^0$ and X_A in eqn. 1.

Determination of $(\psi + K^)$.* The values of $\bar{K}_R \cdot V_{SA}^0$ (for different X_A for 17 solutes at 50°, 60° and 70°) have been used to calculate $(\psi + K^*)$. Here \bar{K}_R is the average value of three different determinations of K_R . Table III gives values at 60° for \bar{K}_R , $\bar{K}_R \cdot V_{SA}^0$ and $(\psi + K^*)$. The regression lines of $\bar{K}_R \cdot V_{SA}^0$ vs. X_A for the solutes at 50° and 70° show the same behaviour as at 60°. The regression lines for some representative solutes at 60° are given in Fig. 2.

The values of $(\psi + K^*)$ at 50°, 60° and 70°, determined from the quotient of the slope and the intercept of the regression lines and the 95% confidence interval for $(\psi + K^*)$, are given in Table IV. The confidence intervals were determined, assuming a *t*-distribution, from the confidence intervals of the slope and the intercept given with 97.5% confidence, which will give 95% confidence for the quotient. These intervals account for random errors in the experimental variables.

In order to check whether loss of stationary phase can cause a systematic error in our system, we compared the percentage of organic phase in each column packing before and after each run (Table V). The results indicate a lower percentage of organic phase after than before a run; the average relative difference is 0.7%. This difference can depend on losses when packing the column or when removing the contents, or on losses during the runs. Each column was run at three temperatures, and with a pre-conditioning period of about one quarter of the total running time and with the temperatures and the solutes run in arbitrary sequence. A loss of organic phase must also occur gradually during the runs. From the information above, we estimate a systematic error in the percentage of organic phase (determined from ashing values) to be less than 0.4%. A given percentage loss of organic phase results in about the same percentage error in K_R . If the apparent value of K_R is 0.4% too high, this will give values of $(\psi + K^*)$ that are about 0.4% too low. As $(\psi + K^*)$ has

TABLE V
COMPARISON OF PHASE CONTENT BEFORE AND AFTER RUN

Mole fraction of dodecyl laurate in squalane	Percentage of organic phase as prepared	Percentage of organic phase after run	
		Calculated from weight loss	Determined by ashing
0	20.06	19.98	20.04
0.0999	19.87	19.79	19.81
0.3021	20.86	20.89	20.75
0.4979	20.04	19.92	19.74
0.6999	20.39	20.24	20.20
0.8456	20.00	19.67	19.79
1	19.24	19.05	19.16

an average value of about 0.30 for the solutes investigated, this implies an error of less than 0.002, which is negligible.

Determination of ψ and K^* . ψ was calculated ($\psi_{\text{calc.}}$) from eqn. 2 for the 17 solutes at 50°, 60° and 70°. The necessary densities were obtained in the following way: *p*-xylene, toluene, benzene, cyclohexane, methylcyclohexane, ethylcyclohexane and *n*-heptane from API tables¹⁹; chlorobenzene, fluorobenzene, methoxybenzene and di-*n*-butyl ether through interpolation from values in Beilstein²⁰; the heptenes¹⁹ and benzotrifluoride²⁰ through extrapolation from values at 20° and 30°; trichloroethene and tetrachloroethene through extrapolation from densities at 20° with the aid of cubic expansion tables²¹; and octafluorotoluene from the density at 25° (Beilstein), assuming the same expansion coefficient as for tetrachloroethene. The variation of $\psi_{\text{calc.}}$ for each of the solutes is less than 0.001 in the temperature range 50–70°, so we consider $\psi_{\text{calc.}}$ for each solute to be constant at these temperatures. For this reason, the error in $\psi_{\text{calc.}}$ from an extrapolation of the density for a solute at 25° must be very small. The average value of $\psi_{\text{calc.}}$ at the three temperatures was used in the subsequent calculations. The plot of $\psi_{\text{calc.}}$ for a solute vs. molar volume of the solute is linear, with a linear correlation coefficient of 0.999991 (see Fig. 3).

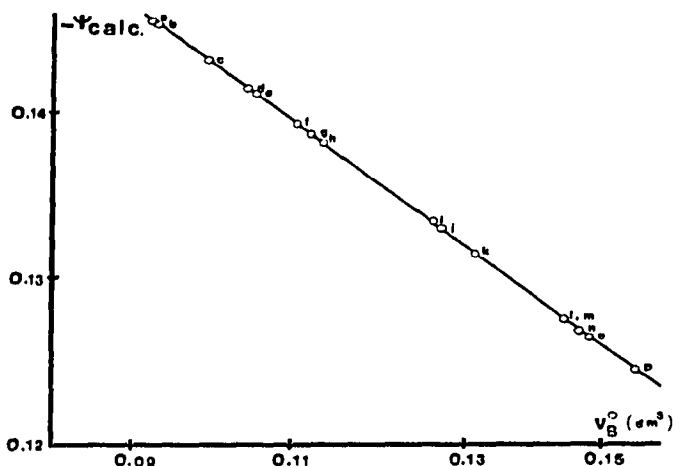


Fig. 3. Variation of $\psi_{\text{calc.}}$ with solute molar volumes, V_B^0 , at 60°. a, Trichloroethene; b, benzene; c, fluorobenzene; d, tetrachloroethene; e, chlorobenzene; f, toluene; g, methoxybenzene; h, cyclohexane; i, *p*-xylene; j, benzotrifluoride; k, methylcyclohexane; l and m, *cis*-2-heptene and octafluorotoluene; n, *trans*-2-heptene; o, ethylcyclohexane; p, *n*-heptane.

For the non-complexing solutes cyclohexane, methylcyclohexane, ethylcyclohexane and *n*-heptane, we have also determined an experimental value of ψ ($\psi_{\text{expt.}}$) at 50°, 60° and 70°, using eqn. 1 with $K^* = 0$. The value of $\psi_{\text{expt.}}$ for each solute at the three temperatures was almost constant in this instance also. Table VI gives a comparison between average values of $\psi_{\text{expt.}}$ and $\psi_{\text{calc.}}$ for these solutes. Application of $\psi_{\text{calc.}}$ to eqn. 1 would give a small negative value of K^* for the non-complexing solutes, which is not realistic. The 95% confidence intervals for $(\psi + K^*)$ are about 0.04 at 50° and 70° and 0.02 at 60° for the alkanes (Table IV). This means that

TABLE VI
COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED AVERAGE VALUES OF ψ FOR ALKANE SOLUTES

Solute	Molar volume, $\psi_{calc.}$ $dm^3 (60^\circ)$	$\psi_{expt.}$	$\Delta\psi = \psi_{expt.} - \psi_{calc.}$
Cyclohexane	0.114	-0.138	-0.216
Methylcyclohexane	0.134	-0.132	-0.207
Ethylcyclohexane	0.148	-0.126	-0.208
<i>n</i> -Heptane	0.154	-0.124	-0.208
			$\Delta\psi_{average} = -0.080$

experimental errors cannot account for the difference of 0.08 between calculated and experimental ψ values.

From Table VI it can be seen that in spite of the large differences in the molar volumes of the alkane solutes, the value of $\Delta\psi$ is almost constant. As $\psi_{calc.}$ values for the complexing solutes vary linearly with their molar volumes in the same way as $\psi_{calc.}$ values for non-complexing solutes (see Fig. 3), we consider it likely that the values of $\psi_{calc.}$ for complexing solutes are also too high and that the difference between calculated and true ψ values for these solutes are very close to $\Delta\psi$ for the non-complexing solutes.

We therefore used $\Delta\psi_{average}$ in the determination of ψ for each complexing solute through the relationship

$$\psi = \psi_{calc.} + \Delta\psi_{average}$$

From these ψ values and the values of $(\psi + K^*)$ in Table IV, we determined the values of K^* .

The variation of $\ln K^*$ vs. $1/T$ for some representative solutes is shown in Fig. 4. The values of ψ , K^* and ΔG^{r*} (from eqn. 4) at 50° , 60° and 70° , and ΔH^{r*} and

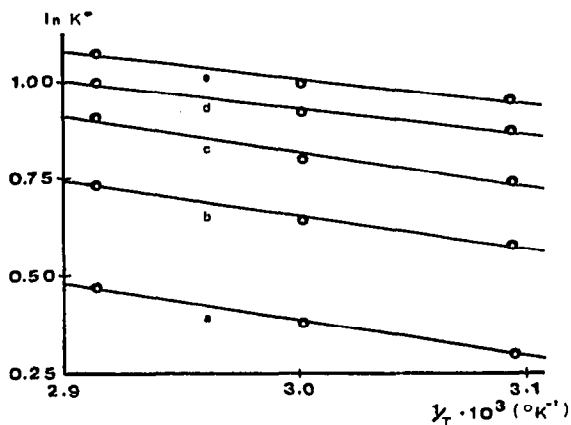


Fig. 4. Variation of the logarithm of complexation constants between dodecyl laurate and some solutes with the reciprocal of the temperature. a, Methoxybenzene; b, fluorobenzene; c, trichloroethene; d, benzene; e, *p*-xylene.

ΔS^{r*} (from eqn. 5) are given in Table VII, where an estimation of the standard deviation for ΔH^{r*} and ΔS^{r*} is also given. The confidence interval for K^* is taken to be the same as the confidence interval for $(\psi + K^*)$, as the experimental error of ψ in $(\psi + K^*)$ is small. For solutes with very low complexation constants, the experimental errors will have a greater influence on the determination of ΔH^{r*} and ΔS^{r*} .

DISCUSSION

Considering the values of the complexation constants given in Table VII, it can be seen that the aromatic molecules, in general, give higher values of the complexation constants than the alkene derivatives. The constants for the complexes between benzene, toluene, *p*-xylene and the ester have about half the value of the constants for the same solutes and di-*n*-propyl and di-*n*-butyl tetrachlorophthalate reported by Cadogan and Purnell²² and Eon *et al.*⁹, respectively. Di-*n*-butyl ether gives a complex with the ester which depends on the interaction between lone-pair electrons on the oxygen atom and the ester group in dodecyl laurate. The same type of interaction between molecules containing lone-pair electrons has recently been investigated gas chromatographically by Hsueh-Liang Liao *et al.*²³. They investigated three haloalkanes as solutes and di-*n*-octylmethylamine as complexing agent in the stationary phase and determined association constants. The values of these constants are higher than the value of the constant for di-*n*-butylether and dodecyl laurate, which may be due to stronger dipole-dipole interactions.

We have studied the relationships between ΔG^{r*} values and ionization potentials and dipole moments for the complex-forming solutes. The ionization potentials give information about the ease of electron transfer from the solutes to the ester, which can be expected to affect the magnitude of the ΔG^{r*} values. The dipole moments of the solutes should influence the contribution of dipole-dipole interactions to the magnitude of the ΔG^{r*} values.

The relationship between ΔG^{r*} and ionization potential for solutes can be seen in Fig. 5. The ionization potentials and dipole moments for the solutes and the references from which they are collected are given in Table VIII. The ionization potential for the 2-heptenes is calculated from the value for 1-heptene, assuming the same difference in ionization potential between 1-heptene and 2-heptene as between 1-hexene and 2-hexene, which is 0.30 eV. As the variation of ionization potential with the length of the hydrocarbon chain of the alkenes is small, the error in the calculated value cannot be large. The dipole moments used were generally determined in benzene solutions, and in instances where more than one literature value is cited we used the median value.

Both dipole-dipole interactions and charge transfer seem to contribute to the magnitudes of the complexation constants. In general, a higher value of the dipole moment for a solute is consistent with a lower ΔG value for the complexation reaction. As with the aromatic solutes, the ΔG^{r*} values for the two halogenated alkene derivatives decrease with increasing dipole moment.

The variation of ΔG^{r*} with ionization potential, I_p , for aromatic solutes, is linear for benzene and the alkylbenzenes with electron donating inductive, $+I$, as well as for chlorobenzene, fluorobenzene and methoxybenzene with electron donating mesomeric, $+M$, and electron withdrawing inductive, $-I$, substituents, and probably

TABLE VII

ψ VALUES, EQUILIBRIUM CONSTANTS, K^* , GIBBS FREE ENERGY, ΔG^* , (kcal/mole), ENTHALPY, ΔH^* (kcal/mole), AND ENTROPY, ΔS^* (cal/mole/°K), FOR COMPLEXATION REACTIONS WITH DODECYL LAURATE
 s_{IH}^* and s_{IS}^* are estimations of the standard deviations for ΔH^* and ΔS^* , respectively, calculated from estimations of the standard deviations for the slope and the intercept of the regression line.

Solute	ψ	K^*		ΔG^*			ΔH^*		ΔS^*		s_{IH}^*	s_{IS}^*
		50°	60°	70°	50°	60°	70°	50°	60°	70°		
<i>p</i> -Xylene	-0.213	0.383	0.367	0.341	0.616	0.663	0.733	-1.28	0.21	-5.85	0.02	0.02
Toluene	-0.219	0.397	0.377	0.353	0.593	0.646	0.710	-1.29	0.10	-5.82	0.01	0.01
Benzene	-0.225	0.415	0.396	0.368	0.564	0.613	0.681	-1.32	0.19	-5.83	0.01	0.01
Fluorobenzene	-0.223	0.560	0.525	0.480	0.372	0.426	0.500	-1.70	0.18	-6.39	0.01	0.01
Chlorobenzene	-0.221	0.587	0.555	0.513	0.342	0.390	0.455	-1.48	0.16	-5.64	0.01	0.01
Benzotrifluoride	-0.213	0.683	0.640	0.573	0.244	0.295	0.379	-1.94	0.31	-6.74	0.02	0.02
Octafluorotoluene	-0.208	0.715	0.634	0.572	0.215	0.302	0.381	-2.46	0.07	-8.30	0.01	0.01
Methoxybenzene	-0.219	0.739	0.683	0.626	0.194	0.252	0.319	-1.83	0.08	-6.26	0.01	0.01
<i>cis</i> -2-Heptene	-0.208	0.068	0.071	0.067	1.73	1.75	1.84	-0.15	0.65	-5.78	0.05	0.05
<i>trans</i> -2-Heptene	-0.207	0.065	0.071	0.066	1.75	1.75	1.85	0.18	1.0	-4.81	0.08	0.08
Trichloroethene	-0.226	0.474	0.448	0.403	0.479	0.531	0.619	-1.78	0.34	-6.98	0.03	0.03
Tetrachloroethene	-0.222	0.217	0.204	0.200	0.980	1.05	1.10	-0.90	0.26	-5.82	0.02	0.02
Di- <i>n</i> -butyl ether	-0.197	0.113	0.102	0.111	1.40	1.51	1.50	-0.21	1.2	-5.05	0.15	0.15

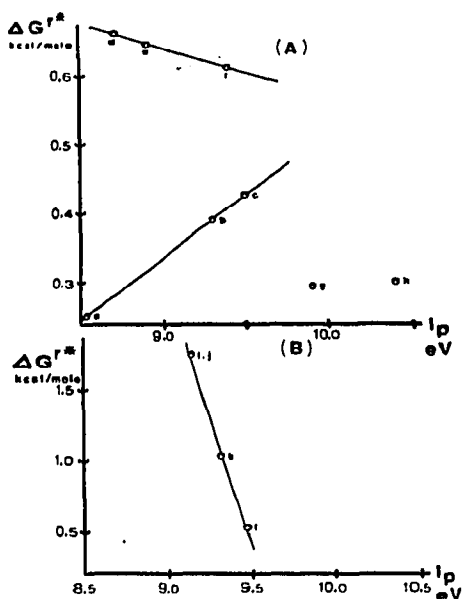


Fig. 5. Plot of ΔG^{r*} at 60° vs. ionization potential, I_p , for some solutes. A, aromatic solutes; B, alkene derivatives. a, Methoxybenzene; b, chlorobenzene; c, fluorobenzene; d, *p*-xylene; e, toluene; f, benzene; g, benzotrifluoride; h, octafluorotoluene; i and j, *cis*-2-heptene and *trans*-2-heptene; k, tetrachloroethene; l, trichloroethene.

for benzotrifluoride and octafluorotoluene with strong $-I$ substituents. The slope of the line for chloro-, fluoro- and methoxybenzene has a larger absolute value than that of the lines for the other aromatic solutes, which indicates that charge transfer contributes relatively more to the ΔG values for solutes with $+M$ substituents. This is not surprising, as the electrons from the $+M$ substituent can easily be spread over the benzene ring. In each group of solutes, where the variation of ΔG^{r*} with I_p is linear, the solutes have about the same dipole moment, with a difference of about 1 D be-

TABLE VIII

IONIZATION POTENTIALS (I_p) AND EXPERIMENTAL DIPOLE MOMENTS (μ) FOR SOLUTES

Solute	I_p (eV)	Reference	μ (D)	Reference
<i>p</i> -Xylene	8.71	24	0	28
Toluene	8.9	24	0.40	28
Benzene	9.40	24	0	28
Chlorobenzene	9.31	24	1.58	28
Fluorobenzene	9.50	24	1.47	28
Methoxybenzene	8.54	24	1.24	28
Benzotrifluoride	9.90	24	2.56	28
Octafluorotoluene	10.4	25	—	
<i>cis</i> -2-Heptene	9.15	26	—	
<i>trans</i> -2-Heptene	9.15	26	—	
Trichloroethene	9.47	27	0.95	28
Tetrachloroethene	9.32	27	0	28

tween the groups. Each group shows a marked difference in the average of the corresponding ΔG^{**} values.

For chlorobenzene, fluorobenzene and methoxybenzene, the ΔG^{**} values increase with increasing ionization potential, while for benzene and alkylbenzenes the ΔG^{**} values decrease with increasing ionization potential. Cadogan and Purnell²² reported that the ΔG values for the complexation reaction between benzene and alkylbenzenes as electron donors and di-*n*-propyl tetrachlorophthalate as an electron acceptor increase with increasing ionization potential. We found the opposite behaviour for benzene and the alkylbenzenes, which in our case indicates a different reaction mechanism. For the alkene derivatives, the variation of ΔG^{**} with ionization potential is also linear, with a high absolute value of the slope, which indicates that the complexation reaction in this instance is much more sensitive to substituents on the solutes.

Leffler²⁹, Cadogan and Purnell²², Eon *et al.*⁹ and others have pointed out that a plot of ΔS vs. ΔH for homologous derivatives is linear for a given reaction. A plot of ΔS^{**} vs. ΔH^{**} for the aromatic solutes is shown in Fig. 6A, and Fig. 6B shows the

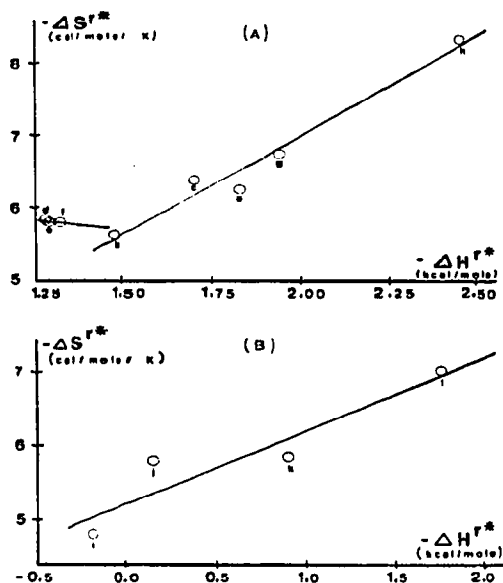


Fig. 6. Relationship between the entropy, ΔS^{**} , and the enthalpy, ΔH^{**} , of complexing reactions of some solutes with dodecyl laurate. A, aromatic solutes; B, alkene derivatives. a, Methoxybenzene; b, chlorobenzene; c, fluorobenzene; d, *p*-xylene; e, toluene; f, benzene; g, benzotrifluoride; h, octafluorotoluene; i, *trans*-2-heptene; j, *cis*-2-heptene; k, tetrachloroethene; l, trichloroethene.

corresponding plot for the alkene derivatives. The compounds studied seem to fall on three different straight lines corresponding to three different reaction mechanisms. The deviation of the points from the lines can be entirely explained by the uncertainty in the experimental determination of ΔH^{**} (see Table VII). It is interesting that the points for benzotrifluoride and octafluorotoluene occur on the same line as fluoro-, chloro- and methoxybenzene, which indicates a similarity in the geometry of the complexes between these solutes and the ester.

CONCLUSIONS

We have shown that esters can form weak complexes with alkene and benzene derivatives, and even with molecules that contain lone-pair electrons. We have also shown that the equation formulated by Eon *et al.*⁸, together with an experimental procedure for non-complexing reference solutes, leading to slight modification of the model, can be used for the determination of the complexation constants between dodecyl laurate and a wide variety of solutes.

The complexation constants seem to depend on both charge transfer and dipole-dipole interactions. The linear variation of the logarithm of the complexation constants for a solute with the reciprocal of the temperature confirms the validity of the model used. We believe that the method described for determining complexation constant can be used for several other complexation reactions. By choosing other complexing agents that are soluble in squalane, and as with dodecyl laurate, contain only one functional group, it should be possible to obtain further information about organic solution behaviour. Studies of complexation reactions in a single solvent might allow a comparison to be made between the behaviour of different functional groups in the solubility processes.

Much work remains to be carried out in this field. As inert solvents such as squalane cannot be used to dissolve all complexing agents, this can lead to binary stationary phase systems in which both the components can form complexes with the solutes and even with each other. However, with more basic knowledge about the behaviour of molecules with one functional group in inert solvents, it should be possible to treat even this type of problem, at least if the components of the binary phase can form only 1:1 complexes and if no strong self-associations are present.

ACKNOWLEDGEMENTS

The authors thank Dr. Lars Haraldson for valuable discussions concerning this work and Dr. Robert Carter for correcting the English in the manuscript.

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