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GAS–LIQUID CHROMATOGRAPHIC INVESTIGATION OF COMPLEXATION EQUILIBRIA BETWEEN 1-CHLOROOCTADECANE AND VARIOUS BENZENE DERIVATIVES AND ALKENE DERIVATIVES

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SUMMARY

Equilibrium constants at 50, 60 and 70°C, enthalpies and entropies for complexation reactions between 1-chlorooctadecane and various benzene derivatives and alkene derivatives have been determined at infinite dilution in squalane. The calculations were performed with a model used earlier for the determination of complexation constants between dodecyl laurate and the same solutes. A comparison is made between dodecyl laurate and 1-chlorooctadecane which shows that the complexation constant between a solute and the former is in general greater than that for the latter. As the dipole moments for 1-chlorooctadecane and dodecyl laurate are about the same, the difference in the constant values is largely attributed to charge-transfer contributions in the dodecyl laurate–solute complexes.

INTRODUCTION

In a previous paper[1], the complexation constants between an aliphatic ester (dodecyl laurate) and various aromatic and alkene solutes were determined. It was suggested that the model used for the calculation of the constants could also be used in the investigation of other complexation reactions with complexing agents, in the stationary phase, which contains one functional group other than the ester group. This paper deals with the complexation between a haloalkane (1-chlorooctadecane) as complexing agent in the stationary phase and most of the solutes used in the previous investigation[1]. The reason for choosing 1-chlorooctadecane was the fact that a complexation could be expected to depend almost entirely on dipole–dipole interactions. In the previous investigation, the results showed that both charge-transfer and dipole–dipole interactions were responsible for the complexation in the different ester–solute complexes. It therefore seemed interesting to compare the behaviour of the two different functional groups with respect to charge-transfer and dipole–dipole interactions.

EXPERIMENTAL

The gas–liquid chromatographic (GLC) measurements were performed with the apparatus described elsewhere[2], which was expected to give a relative standard deviation of 0.8–0.9% for the values determined for the partition coefficient for a solute between the stationary phase and the gas phase. The experimental procedures, *e.g.*, phase preparations and column packings, conditioning and loading determinations and flow measurement, were the same as in the previous investigation of dodecyl laurate[1]. Squalane (Perkin-Elmer, Norwalk, Conn., U.S.A.) was used as an inert solvent for 1-chlorooctadecane in the stationary phase and Supasorb, 40–60 mesh, acid washed and treated with hexamethyldisilazane (BDH, Poole, Great Britain) as the support. 1-Chlorooctadecane (Fluka, Buchs, Switzerland; puriss grade) was further purified by passage through a column of silica gel with *n*-hexane as eluent. The fractions collected were investigated by GLC on a 5% SE-30 glass column (1.5 m × 1.6 mm) with Varaport 30, 100–120 mesh (Varian, Palo Alto, Calif., U.S.A.) as the support at a column temperature of 180°C. The remaining impurities determined by GLC were estimated to be less than 0.2%. A tailing effect in the chromatogram of the starting material, probably depending on hydrogen-bonding compounds such as alcohols, disappeared after the purification. Five columns with molar fractions 0, 0.2562, 0.4954, 0.7463 and 1 of 1-chlorooctadecane in squalane, with a packing of about 0.65 g and a loading of about 20% (w/w), were prepared and run at 50, 60 and 70°C. For the different columns and temperatures, the *J*-factor, calculated from the pressure drop, varied between 0.92 and 0.96 and the hydrogen carrier gas flow-rate between 53 and 56 ml/min.

Solutes were injected in about equal amounts (10^{-2}–10^{-3} μmole) and no significant variation in retention time with variation in the amount injected was observed, except for ethyl acetate. Referring to the previous discussion[1], this result indicates that adsorption effects for the other solutes can be neglected and the partition coefficient for these solutes can be calculated in the usual way (eqn. 3 in ref. 1), assuming that partition is the only mechanism responsible for the retention.

THEORETICAL

The theory was described in the previous paper[1] and only the two most important equations used for the calculations are presented here:

$$K_R \cdot V^0_{A,S} = K^0_R \, V^0_S [1 + (\psi + K^*) X_A] \tag{1}$$

$$\ln K^* = -\frac{\Delta H'^*}{R} \cdot \frac{1}{T} + \frac{\Delta S'^*}{R} \tag{2}$$

Eqn. 1 describes how to calculate the equilibrium constant, K^*, for a 1:1 complex between a gaseous solute, B, and a complexing agent, A, dissolved in an inert solvent, S, as the stationary phase. X_A is the molar fraction of A in S; $V^0_{A,S}$ and V^0_S are the molar volumes of a mixture of A and S and pure S, respectively; and K_R and K^0_R are apparent and real partition coefficients in a stationary phase with molar fraction X_A in S and pure S, respectively. The value of ψ depends on the activity coefficients of B in pure A and pure S solutions; ψ is calculated from molar volumes of A, B and S, together with an experimental determination of ψ for alkene solutes by setting $K^* = 0$ in eqn. 1. The calculation of ψ was described earlier[1]. $\psi + K^*$ can be determined from the linear variation of $K_R \cdot V^0_{A,S}$ with X_A as the quotient of the slope and the intercept of the line, and with ψ determined this will give the complexation constant, K^*.

Eqn. 2 describes a linear variation of ln K^* *versus* the reciprocal of the absolute temperature. The enthalpy, ΔH^{r*}, and the entropy, ΔS^{r*}, for the complexation reaction between a solute and A can be determined from the slope and the intercept of the line.

RESULTS

Molar volumes for solutions with different molar fractions of 1-chlorooctadecane, A, in the inert solvent squalane, S, were calculated from picnometer-measured densities for molar fractions of 0, 0.4954 and 1 of A in S at the temperatures 50, 60 and 70°C (Table I). Molar volumes at 50, 60 and 70°C for the two remaining mixtures of A and S with molar fractions of 0.2562 and 0.7463 of A were calculated from the regression line of the molar volume *versus* the molar fraction of A. The correlation coefficients for the regression lines at 50, 60 and 70°C were 0.999998, 0.999999 and 0.999998, respectively.

TABLE I

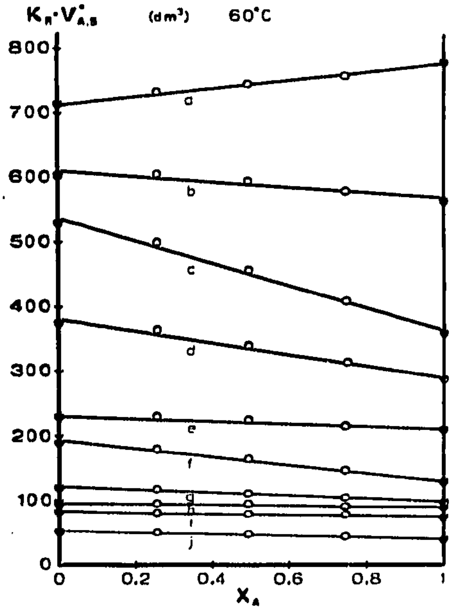
DENSITY (g/ml) FOR DIFFERENT MOLAR FRACTIONS, X_A, OF 1-CHLOROOCTADECANE, A, IN SQUALANE AT 50, 60 AND 70°C

Temperature (°C)	*Molar fraction, X_A*		
	0	*0.49535*	*1*
50	0.7900	0.8097	0.8423
60	0.7832	0.8031	0.8354
70	0.7770	0.7962	0.8284

The same molar volumes for solutes, B, as in the previous work[1] were used for the calculation of ψ. The alkane solutes used in the calculation of ψ were the same as in the previous work[1], *viz.*, *n*-heptane, cyclohexane, methylcyclohexane and ethylcyclohexane. References were given there[1] for the densities of all solutes except 1-chlorobutane and 1-chloropentane, the values of which are taken from Beilstein[3]. The variation of $K_R \cdot V^0_{A,S}$ *versus* X_A for some representative solutes are given in Fig. 1, and the variation of ln K^* *versus* $1/T$ in Fig. 2.

Values of the equilibrium constants, K^*, at infinite dilution in squalane for 1:1 complexes between 1-chlorooctadecane and various solutes at 50, 60 and 70°C, calculated by using eqn. 1, are given in Table II. This table also contains values of the enthalpy, ΔH^{r*}, and entropy, ΔS^{r*}, for the complexing reactions, calculated by means of eqn. 2.

The differences between the experimental points and the regression lines for $K_R \cdot V^0_{A,S}$ *versus* X_A for different solutes at 50, 60 and 70°C are in general 1.0–1.5%



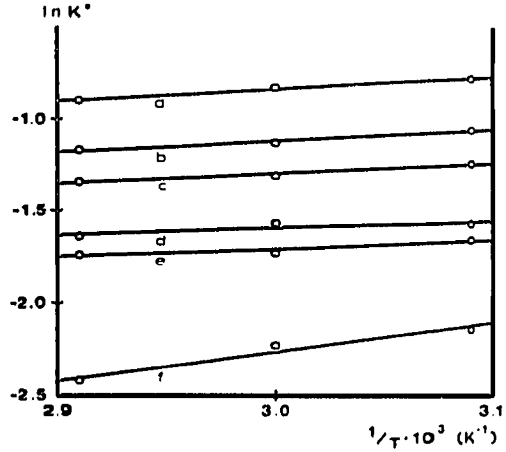


Fig. 1. Variation of $K_R \cdot V^0_{A,S}$ with molar fraction, X_A, of 1-chlorooctadecane in squalane at 60°C for some representative solutes. Solutes: a, methoxybenzene; b, *p*-xylene; c, ethylcyclohexane; d, tetrachloroethene; e, toluene; f, methylcyclohexane; g, trichloroethene; h, benzotrifluoride; i, benzene; j, octafluorotoluene.

Fig. 2. Variation of the logarithm of the complexation constants between 1-chlorooctadecane and some representative solutes with the reciprocal of the temperature. Solutes: a, methoxybenzene; b, chlorobenzene; c, *p*-xylene; d, 1-chlorobutane; e, trichloroethene; f, octafluorotoluene.

TABLE II

EQUILIBRIUM CONSTANTS, K^*, AT 50, 60 AND 70°C, AND ENTHALPY, $\Delta H'^*$, (kcal/mole) AND ENTROPY, $\Delta S'^*$, (cal/mole·°K) FOR COMPLEXATION REACTIONS BETWEEN 1-CHLOROOCTADECANE AND VARIOUS SOLUTES

Solute	K^*			$\Delta H'^*$	$\Delta S'^*$
	50°C	*60°C*	*70°C*		
p-Xylene	0.289	0.271	0.263	−1.10	− 5.88
Toluene	0.288	0.266	0.256	−1.32	− 6.57
Benzene	0.287	0.263	0.256	−1.21	− 6.26
Fluorobenzene	0.304	0.281	0.268	−1.43	− 6.81
Chlorobenzene	0.346	0.322	0.310	−1.21	− 5.86
Benzotrifluoride	0.309	0.289	0.271	−1.55	− 7.10
Octafluorotoluene	0.118	0.107	0.089	−3.09	−13.76
Methoxybenzene	0.458	0.436	0.406	−1.32	− 5.63
1-Chlorobutane	0.209	0.209	0.194	−0.77	− 5.48
1-Chloropentane	0.194	0.194	0.185	−0.55	− 4.95
Trichloroethene	0.191	0.178	0.175	−0.88	− 6.04
Tetrachloroethene	0.120	0.121	0.116	−0.33	− 5.22

for $X_A = 0$ and in general less than 1% for higher molar fractions of A. The 95% confidence intervals for K^*, calculated as described earlier[1], were about 0.06–0.09, which is a higher range than in the previously investigated system with dodecyl laurate and squalane as the stationary phase[1], where a typical value for the 95% confidence interval was about 0.04. The difference can be at least partly statistically explained in terms of the use of five columns with different molar fractions instead of seven as in the dodecyl laurate–squalane system, which makes the regression lines more sensitive to an experimental error in one of the molar fractions. However, the greater width of the interval is almost certainly due largely to chemical phenomena. The equations used in the calculation of K^* take no consideration of possible self-association between the complexing molecules in the stationary phase, which would give a non-linear variation of $K_A \cdot V^0_{A,S}$ *versus* X_A.

The existence of a small extent of self-association between 1-chlorooctadecane molecules is indicated by the values of the complexation constants determined for 1-chlorooctadecane with 1-chlorobutane and 1-chloropentane, which are 0.21 and 0.19 at 60°C (Table II). The dipole moments for all three haloalkanes are the same[4] (1.94 D). The self-association constant for 1-chlorooctadecane should therefore be considerably less than that between 1-chlorooctadecane and 1-chlorobutane, with one functional group on four carbon atoms, as the former involves interactions between molecules with one functional group on a chain of 18 carbon atoms.

If no self-association occurs between dodecyl laurate molecules in the dodecyl laurate–squalane system, the confidence interval of 0.04 reflects the experimental error. As the apparatus and the experimental procedures were the same in the investigation of the 1-chlorooctadecane–squalane system, the experimental errors in the latter system should be about the same, or possibly larger as a result of the use of five columns instead of seven. The error in the constants determined between 1-chlorooctadecane and different solutes caused by self-association of 1-chlorooctadecane can then be estimated from the difference between the confidence intervals in the investigations of 1-chlorooctadecane and dodecyl laurate. With typical intervals of 0.08 and 0.04, respectively, it follows that the error caused by self-association corresponds to a confidence interval of less than 0.04.

The fact that the deviation from ideality in solutions of 1-chlorooctadecane and squalane is small is supported by the results of Heric and Coursey[5]. They determined excess molar volumes for several binary mixtures of different *n*-alkanes, and *n*-alkanes and 1-chloroalkanes. Their results showed that the excess molar volumes of mixtures of two long-chain alkanes are very small. Further, in mixtures of long-chain hydrocarbons and 1-chloroalkanes, such as *n*-hexadecane and 1-chlorooctadecane, the effect of the halogen atom is so small that molar excess volumes are the same whether *n*-hexadecane is mixed with 1-chlorooctadecane or *n*-octadecane. Squalane was used as the solvent for 1-chlorooctadecane instead of *n*-hexadecane in the present work, but this solvent is expected to show similar behaviour.

Complexation constants between dodecyl laurate and different solutes have been determined earlier[1]. As in the present investigation, these constants were also determined at infinite dilution in squalane, which makes a comparison interesting. Table III shows complexation constants at 60°C for dodecyl laurate and 1-chlorooctadecane, with common solutes in the two investigations. The complexation constants between a solute and dodecyl laurate are in general higher than the complexation

TABLE III

MOLAR FRACTION-BASED COMPLEXATION CONSTANTS AT 60°C FOR DODECYL LAURATE–SOLUTE COMPLEXES, K_1^*, AND 1-CHLOROOCTADECANE–SOLUTE COMPLEXES, K_2^*

Solute	K^*	K_2^*
p-Xylene	0.37	0.27
Toluene	0.38	0.27
Benzene	0.40	0.26
Fluorobenzene	0.53	0.28
Chlorobenzene	0.56	0.32
Benzotrifluoride	0.64	0.29
Octafluorotoluene	0.63	0.11
Methoxybenzene	0.68	0.44
Trichloroethene	0.45	0.18
Tetrachloroethene	0.20	0.12

constant between the same solute and 1-chlorooctadecane. The dipole moments for 1-chlorooctadecane (1.94 D) and dodecyl laurate should be about the same [the dipole moment for dodecyl laurate was not available, but dipole moments for similar long-chain aliphatic mono-esters, such as ethyl palmitate and butyl stearate, are 1.89 D (ref. 6)]. The higher values of the complexation constants for dodecyl laurate–solute complexes must therefore depend largely on charge-transfer contributions. The existence of both charge-transfer and dipole–dipole interactions in the dodecyl laurate–solute complexes was already suggested on the basis of results in the previous investigation[1], and is now further confirmed.

The complexation constant for octafluorotoluene at 60°C seems very low, and is similar at 50 and 70°C. This might depend on steric hindrance. The much larger negative value of ΔS^{r*} for octafluorotoluene than for other solutes also suggests this effect.

The values of ΔH^{r*} and ΔS^{r*} in Table II for the complexation reaction between 1-chlorooctadecane and different solutes vary from solute to solute in a similar manner to the values for the complexing reactions between dodecyl laurate and the same solutes[1]. Standard deviations for ΔH^{r*} and ΔS^{r*} in the present investigation are about the same as earlier[1], or in general 0.20–0.30 kcal/mole for ΔH^{r*} and 0.01–0.03 cal/mole·°K for ΔS^{r*}.

The terminology used in the investigations of systems with weak interactions between molecules is unclear, different workers using different terms to characterize essentially the same concept. Here and in the previous investigation[1], the model used for the calculations separates chemical and physical effects, and the term complexation has been used for the calculated chemical contribution. In an excellent recent paper by Martire[7], questions about complexation, association and loosely bonded "contact pairs" in different systems are thoroughly discussed.

CONCLUSIONS

It has been shown that a model[1] previously used for the calculation of complexation constants between dodecyl laurate and different benzene and alkene derivatives is also valid for the calculation of complexation constants between 1-chlorooctadecane and the same derivatives. As the same solvent, squalane, was used in both investigations, it is now possible to investigate a stationary phase with dodecyl laurate and 1-chlorooctadecane dissolved simultaneously in this solvent. Such an investigation is dealt with in the following paper[8].

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