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DETERMINATION OF COMPLEX ASSOCIATION CONSTANTS FROM GAS CHROMATOGRAPHIC DATA

I. BASIC RELATIONSHIPS

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SUMMARY

The basic expressions for the determination of complex association constants from gas chromatographic data in terms of the activities of the reactants are derived.

The advantage of using a reference compound in obtaining association constants is shown.

INTRODUCTION

Gas–liquid chromatography (GLC) is developing into a technique to be used in the investigation of intermolecular interactions in solution.

One of the topics that are currently being investigated is the formation of molecular complexes as a result of hydrogen bonding, charge transfer interaction, etc.

However, the equilibria involved are often formulated in terms of concentrations rather than in terms of activities[1–7]. In other cases, the reference state to which activity coefficients are related has been chosen inappropriately, so that association constants of a series of volatile compounds A with the same (involatile) compound B cannot be compared[8]. Other workers choose different reference states in the course of their derivations and use concentrations for some of the reactants and activities for others[9,10].

We therefore thought it worthwhile to present a formulation of these equilibria in terms of activities, which is both simple and rigorous. The use of a reference compound in obtaining association constants is also described.

THEORY

We can consider the formation of a complex AB from a volatile compound A and an involatile compound B. Generally, a mixture of the latter and an inert compound S is used as the stationary phase. The association equilibrium is governed by the equation:

$$K = \frac{x_{AB}}{x_A \cdot x_B} \cdot \frac{f_{AB}}{f_A \cdot f_B} \tag{1}$$

where x is the mole fraction and f is the activity coefficient. It is obvious that the activity coefficients can be related to either of two reference states:

(1) the hypothetical ideal solution in the solvent S;
(2) the hypothetical ideal solution in the solvent B.

Convention 1

Under GLC conditions, x_A is usually very small, hence its activity coefficient in the solvent S is unity.

Therefore, when a stationary phase consisting of S and one consisting of S + B are in equilibrium with a vapour phase containing A, it follows that:

$$x_{A(S)} = x_{A(S+B)} f_{A(S+B)} \tag{2}$$

Further, it can be shown that the mid-peak retention volume, V, at the mean column pressure and column temperature, corrected for the gas hold-up in the apparatus, is given by:

$$V = \frac{V_{St} C_{St}}{C_{Mob}} = \frac{N_{St} x_{St}}{C_{Mob}} \tag{3}$$

where:

V_{St} = volume of the stationary phase in the column (cm^3);
C_{St} = solute concentration in the stationary phase (mole·cm^{-3});
C_{Mob} = solute concentration in the mobile phase (mole·cm^{-3});
N_{St} = moles of stationary phase in the column;
x_{St} = solute mole fraction in the stationary phase.

The application of eqn. 3 to a stationary phase consisting of S and one consisting of S + B gives, respectively:

$$V_{A(S)} = \frac{N_{(S)} x_{A(S)}}{C_{A(M)}} \tag{4}$$

and:

$$V_{A(S+B)} = \frac{N_{(S+B)} (x_A + x_{AB})_{(S+B)}}{C_{A(M)}} \tag{5}$$

In eqns. 4 and 5, x_A, x_{AB} and C_A do not have specified values: they range from zero to a maximum mid-peak value. However, the ratios $x_{A(S)}/C_{A(M)}$ and $(x_A + x_{AB})_{(S+B)}/C_{A(M)}$ are independent of C_A when the latter is small. Therefore, the value of C_A may be chosen arbitrarily and, in particular, the values of C_A in eqns. 4 and 5 may be chosen to be equal.

Combination of eqns. 2, 4 and 5 gives:

$$\begin{aligned}\frac{V_{A(S+B)}}{V_{A(S)}} &= \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{(x_A + x_{AB})_{(S+B)}}{x_{A(S)}}\\ &= \frac{N_{(S+B)}}{N_{(S)}} \cdot \left(\frac{x_A + x_{AB}}{x_A f_A}\right)_{(S+B)}\\ &= \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{1}{f_{A(S+B)}} \cdot \left(1 + K x_B \cdot \frac{f_A f_B}{f_{AB}}\right)_{(S+B)}.\end{aligned} \tag{6}$$

For a compound A* that is closely related to A but does not yield a complex with B, it holds analogously that:

$$\frac{V_{A^*(S+B)}}{V_{A^*(S)}} = \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{1}{f_{A^*(S+B)}} \approx \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{1}{f_{A(S+B)}} \tag{7}$$

Combination of eqns. 6 and 7 yields:

$$\frac{V_{A(S+B)}}{V_{A(S)}} \cdot \frac{V_{A^*(S)}}{V_{A^*(S+B)}} = \left(\frac{V_A}{V_{A^*}}\right)_{(S+B)} \cdot \left(\frac{V_{A^*}}{V_A}\right)_{(S)} = 1 + K x_B \left(\frac{f_A f_B}{f_{AB}}\right)_{(S+B)} \tag{8}$$

or:

$$\left[\left(\frac{V_A}{V_{A^*}}\right)_{(S+B)} \cdot \left(\frac{V_{A^*}}{V_A}\right)_{(S)} - 1\right] / x_B = K \left(\frac{f_A f_B}{f_{AB}}\right)_{(S+B)} \tag{8a}$$

From eqn. 8a, K can be found by determining the left-hand side for a series of mixtures of S and B and extrapolating to $x_B = 0$.

It follows from eqn. 8, compared with eqn. 6, that the use of the reference compound A* has three advantages:

(1) Instead of absolute retention volumes, only relative retention volumes have to be determined. This means that no knowledge of inlet and outlet pressures, gas velocity and recorder chart speed is required.

(2) The amount of stationary phase in the columns need not be known.

(3) The factor $f_{A(S+B)}$, to which the right-hand side of eqn. 6 is proportional, is eliminated to a good approximation.

It is advantageous to choose the reference solvent S to be as similar to B as possible*. In that case, $f_{A^*} \approx f_A \approx 1$ in eqn. 7 and the concentration dependence of $f_A f_B / f_{AB} \approx 1$ in eqn. 8a is small.

Convention 2

Analogous to eqn. 2, it now holds that:

$$x_{A(S)} f_{A(S)} = x_{A(S+B)} f_{A(S+B)} \tag{9}$$

Combination of eqns. 4, 5 and 9 gives:

$$\begin{aligned}\frac{V_{A(S+B)}}{V_{A(S)}} &= \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{(x_A + x_{AB})_{(S+B)}}{x_{A(S)}}\\ &= \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{f_{A(S)}}{f_{A(S+B)}} \left(\frac{x_A + x_{AB}}{x_A}\right)_{(S+B)}\\ &= \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{f_{A(S)}}{f_{A(S+B)}} \left(1 + K x_B \cdot \frac{f_A f_B}{f_{AB}}\right)_{(S+B)}\end{aligned} \tag{10}$$

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* *E.g.*, when studying the hydrogen-bonding of alcohols when B is 1-chlorohexadecane, the ideal reference solvent S is hexadecane or heptadecane.

For the reference compound A*, it holds that:

$$\frac{V_{A^*(S+B)}}{V_{A^*(S)}} = \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{f_{A^*(S)}}{f_{A^*(S+B)}} \approx \frac{N_{(S+B)}}{N_{(S)}} \cdot \frac{f_{A(S)}}{f_{A(S+B)}} \qquad (11)$$

Combination of eqns. 10 and 11 gives, once again, eqns. 8 and 8a. K can now be found from eqn. 8a by determining the left-hand side for a series of mixtures of S and B and extrapolating to $x_B = 1$.

Again, it is advantageous to choose S to be as similar to B as possible.

When this convention for the activity coefficients is chosen, the association constant can be found from measurements on the stationary phases B and S only. In the solvent B, f_A, f_{AB}, f_B and x_B are unity because under GLC conditions x_A and x_{AB} are usually very small. Therefore, eqn. 8 simplifies to:

$$\left(\frac{V_A}{V_{A^*}}\right)_{(B)} \cdot \left(\frac{V_{A^*}}{V_A}\right)_{(S)} = 1 + K \qquad (12)$$

In some cases it may be impossible to use pure B as a solvent, *e.g.*, when B is solid at the chosen temperature. A well known example of this situation is the formation of a complex between olefins and a solution of silver nitrate in ethylene glycol. In these cases the mixture of B and S can be formally considered as a single-component, complex-forming solvent B'.

Further, it may be advantageous to use as the reference solvent a mixture of an inert compound C and S (in the above example, a solution of lithium nitrate or sodium nitrate in ethylene glycol). The mixture of C and S can be formally considered as a single-component, inert solvent S'.

Activity coefficients can then be related to hypothetical ideal solutions in the solvent S', or to hypothetical ideal solutions in the solvent B'.

Eqns. 1–12 still hold, with one minor exception: in eqn. 8 x_B is not unity and therefore eqn. 12 becomes:

$$\left(\frac{V_A}{V_{A^*}}\right)_{(B')} \cdot \left(\frac{V_{A^*}}{V_A}\right)_{(S')} = 1 + K\,x_B \qquad (13)$$

Comparison of conventions 1 and 2

The activity coefficients resulting from conventions 1 and 2 are completely analogous to the activity coefficient $f = f^0 \cdot f^*$, which is generally used in the characterization of electrolyte solutions. f^0 describes the "primary medium effect" and f^* the "salt effect".

The usefulness of this approach in the study of association constants by means of gas chromatography appears from the example of the formation of a complex between olefins and silver nitrate solutions in ethylene glycol.

The use of convention 2 (combined with eqn. 12) reduces the amount of experimental work required, as measurements on mixed stationary phases are not necessary.

However, convention 2 has the disadvantage that results obtained for a series of compounds B are difficult to compare, in view of the series of different reference states involved.

A further disadvantage is as follows:
when convention 1 is used, a factor:

$$\frac{f_{A^*(S+B)}}{f_{A(S+B)}}$$

is neglected in eqn. 8 (see eqns. 6 and 7). In the extrapolation to $x_B = 0$, this factor approaches to:

$$\frac{f_{A^*(S)}}{f_{A(S)}} \equiv 1,$$

as activity coefficients in the solvent S are unity, according to convention 1.

When convention 2 is used, a factor:

$$\frac{f_{A^*(S+B)}}{f_{A^*(S)}} \cdot \frac{f_{A(S)}}{f_{A(S+B)}}$$

is neglected in eqn. 8 (see eqns. 10 and 11). In the extrapolation to $x_B = 1$, this factor approaches to:

$$\frac{f_{A^*(B)}}{f_{A^*(S)}} \cdot \frac{f_{A(S)}}{f_{A(B)}} \equiv \frac{f_{A(S)}}{f_{A^*(S)}},$$

as activity coefficients in the solvent B are unity, according to convention 2. So, this factor is only approximately equal to 1 if A and A* are very closely related. If this is not so, a correction should be attempted[*].

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[*] *E.g.*, when studying hydrogen bonding of A = ethanol with B = 1-chlorohexadecane and S = hexadecane, using ethylchloride as the reference compound A*, a correction must be applied for the difference in dipole moment of A and A*[11].

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