tion of GLC and NMR data reported by us earlier.[16]

The work presented clearly indicates that a very substantial group of systems forming a new class of solutions has been identified. In view of their behavior we propose the name *diachoric* for such solutions.

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Solution and Complexing Studies. IV. Extension of Microscopic Partition Theory to Include Nonstoichiometric Complexation and Solvent Effects, and the Correlation of GLC, Uv, and NMR Data

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Abstract: It has been shown earlier that for 180 systems wherein a volatile solute (D) is partitioned at infinite dilution between a mixture of two liquids (A and S) and the gas phase, the partition coefficient (K_R) is related to those for D with pure A ($K_{R(A)}{}^0$) and pure S ($K_{R(S)}{}^0$) via the volume fraction (ϕ) relationship $K_R = \phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0$. This result has been shown to describe systems where explicit interaction of D with A may be expected, as well as for those where this is not so. Further, it applies where D, A, and S are of widely differing chemical type and molecular weight. It has also been shown that the simplest model consistent with the above behavior is that in which A and S are microscopically immiscible, hence the suggested name microscopic partition (MP) theory. We now establish that, irrespective of the detail of any specific interaction postulated to occur between D and A or S, the above equation can always be derived to describe overall behavior. Further, if for specific interaction in A there is a true interaction equilibrium quotient ($K_1{}^t$), it can be shown that $K_1{}^{\text{exptl}} = (K_1{}^t K_{R(A)}{}^{0,t}/K_{R(S)}{}^0) + (\Delta K_R{}^{0,t}\bar{V}_A/K_{R(S)}{}^0)$ where $K_{R(A)}{}^{0,t}$ and $K_{R(S)}{}^0$ are the partition coefficients of unreacted D in A and S, respectively, $\Delta K_R{}^{0,t}$ is their difference, and $\bar{V}_A$ is the molar volume of pure A. This two-term equation, which is also derived for the case of uv–visible and NMR studies, establishes that even if $K_1{}^t = 0$, a value of $K_1{}^{\text{exptl}}$ can be determined in practice and may be negative of limiting value, $-\bar{V}_A$. The equation also provides a quantitative definition of solvent effects in complexing studies. Correlation equations are also presented which define the relationship of purely solution (usually GLC) data and those of either uv–visible or NMR studies. Examples of the correlation of GLC and NMR data have been given previously; an example involving uv–visible and NMR data is given here. The origins of discrepancies in published data are indicated.

We have established in earlier parts of this series[1-3] that, for 180 mixed solvent–volatile solute systems, the infinite dilution partition coefficient between solvent and the gas phase for solute D is related to its corresponding partition coefficient in each of the binary liquids (A and S) by the equation:

$$K_R = \phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0 \tag{1}$$

where ϕ represents volume fraction. It has been shown[1] that this equation is incompatible with current theory,[1,3] but can readily be derived whether solution of D in A or in S is ideal or nonideal on the basis that, although A and S are macroscopically miscible, they are microscopically immiscible. The major consequence of this is that the local concentrations of A or S in a mixture are identical with those that each exhibits in the pure state. Correspondingly, the local

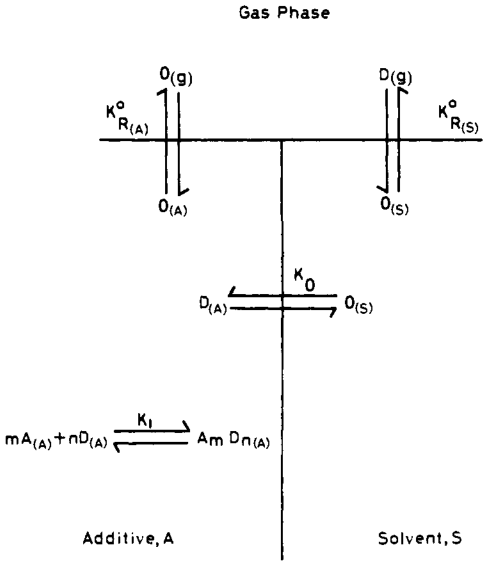

Figure 1. Diagrammatic illustration of the microscopic partition model (see text for definitions).

concentrations of D in A or D in S are also those that would be relevant to pure A or S. We have called this theory the microscopic partition theory (MP) of solution, and suggested[3] that liquid mixtures behaving according to eq 1 be called diachoric.

In part I of this series[1] we developed the general equations for the GLC case, making no specific identification of the detailed interactions occurring in A-D or D-S mixtures. We were also able to predict, from solubility data alone, the nominal stability constants reported for 98 cases of reputed charge transfer or hydrogen bonding equilibria of the type:

$$\mathrm{A} + \mathrm{D} \overset{K_{\mathrm{I}}}{\rightleftharpoons} \mathrm{AD}$$

We then correlated the GLC and NMR approaches with considerable success in part II.[2]

The majority of systems dealt with by us initially were of a type where some kind of specific interaction between D and A might be, or has been, postulated to occur. In part III,[3] however, we have established that eq 1 applies equally to systems where no specific interactions can be visualized. As pointed out by us earlier,[1] it therefore becomes a matter of importance to determine what, if anything, studies of weak complexing by partition or spectroscopic methods reveal.

In this paper we develop MP theory in more detail in order to ascertain whether or not, on this basis, true stability constants can be determined by GLC, by NMR, or by uv-visible methods, now so widely employed. This exercise is given point when it is recognized that all three methods depend on the effect of dilution of A (or D) by S, the inert solvent. In MP theory, of course, this dilution does not occur. We also now examine the generalized stoichiometric model for the interaction of D in A, and D in S, to ascertain the effects of multiple equilibria and solvation on the general relation given by eq 1.

Theory

The model relevant to what follows may be illustrated as in Figure 1. Solute D is partitioned between A and S and also between A and the gas phase and between S and the gas phase. The relevant partition coefficients (K) may be defined in terms of free (uncomplexed) D, in which case the relevant K carries the superscript t (true) or, alternatively, in terms of total D, i.e., the sum of uncomplexed and complexed D. The relevant K for this situation, which is the "experimental" value, does not have superscript t but, for compatibility with GLC nomenclature, does carry a superscript zero.

The generalized equation which describes the equilibrium complexation reaction between A and D is given by

$$n\mathrm{A} + m\mathrm{D} \overset{K_{\mathrm{I}}^{\mathrm{t}}}{\rightleftharpoons} \mathrm{A}_n\mathrm{D}_m \qquad (2)$$

where m and n are the stoichiometric reaction coefficients, and are not necessarily integral values. We can also write a similar equation to describe the solution of D in S but, as we show later, no advantage is achieved by adding this complication at this point.

The definitions corresponding to the model are as follows: (a) $K_{\mathrm{R(A)}}{}^0 = (mC_{\mathrm{comp}}{}^{\mathrm{A}} + C_{\mathrm{D}}{}^{\mathrm{A}})/C_{\mathrm{D}}{}^{g}$; (b) $K_{\mathrm{R(S)}}{}^0 = C_{\mathrm{D}}{}^{\mathrm{S}}/C_{\mathrm{D}}{}^{g}$; (c) $K_{\mathrm{R(A)}}{}^{0,\mathrm{t}} = C_{\mathrm{D}}{}^{\mathrm{A}}/C_{\mathrm{D}}{}^{g}$; (d) $K_{\mathrm{D}} = (C_{\mathrm{D}}{}^{\mathrm{A}} + mC_{\mathrm{comp}}{}^{\mathrm{A}})/C_{\mathrm{D}}{}^{\mathrm{S}}$; (e) $K_{\mathrm{D}}{}^{\mathrm{t}} = C_{\mathrm{D}}{}^{\mathrm{A}}/C_{\mathrm{D}}{}^{\mathrm{S}} = K_{\mathrm{R(A)}}{}^{0,\mathrm{t}}/K_{\mathrm{R(S)}}{}^0$; (f) $K_{\mathrm{I}}{}^{\mathrm{t}} = C_{\mathrm{comp}}{}^{\mathrm{A}}/(C_{\mathrm{A}}{}^{\mathrm{A}})^n(C_{\mathrm{D}}{}^{\mathrm{A}})^m$.

Here, C represents a molar concentration, subscripts designate a species, and superscripts designate the relevant solvent (or gas).

From (f)

$$C_{\mathrm{comp}}{}^{\mathrm{A}} = K_{\mathrm{I}}{}^{\mathrm{t}}(C_{\mathrm{A}}{}^0)^n(C_{\mathrm{D}}{}^{\mathrm{A}})^m \qquad (3)$$

since, in pure A, $C_{\mathrm{A}}{}^{\mathrm{A}} = C_{\mathrm{A}}{}^0$ $(=\bar{V}_{\mathrm{A}}{}^{-1})$, where $C_{\mathrm{A}}{}^0$ is the concentration of pure A, and $\bar{V}_{\mathrm{A}}$ is its molar volume. The concentration of complex, referred to the whole volume of the system, $(V_{\mathrm{A}} + V_{\mathrm{S}})$, is then

$$C_{\mathrm{comp}}{}^{\mathrm{A,S}} = \phi_{\mathrm{A}}K_{\mathrm{I}}{}^{\mathrm{t}}(C_{\mathrm{A}}{}^0)^n(C_{\mathrm{D}}{}^{\mathrm{A}})^m \qquad (4)$$

where ϕ_{A} is the volume fraction of A.

The material balance for moles of D throughout the whole system $(n_{\mathrm{D}}{}^{\mathrm{A,S}})$ is

$$n_{\mathrm{D}}{}^{\mathrm{A,S}} = n_{\mathrm{D}}{}^{\mathrm{A}} + n_{\mathrm{D}}{}^{\mathrm{S}} + mn_{\mathrm{comp}}{}^{\mathrm{A}} \qquad (5)$$

Dividing by $(V_{\mathrm{A}} + V_{\mathrm{S}})$ gives

$$C_{\mathrm{D}}{}^{\mathrm{A,S}} = \phi_{\mathrm{A}}C_{\mathrm{D}}{}^{\mathrm{A}} + \phi_{\mathrm{S}}C_{\mathrm{D}}{}^{\mathrm{S}} + mC_{\mathrm{comp}}{}^{\mathrm{A,S}} \qquad (6)$$

But the overall partition coefficient of D between the whole solvent system (A + S) and the gas phase is

$$K_{\mathrm{R}} = C_{\mathrm{D}}{}^{\mathrm{A,S}}/C_{\mathrm{D}}{}^{g}$$

Hence,

$$K_{\mathrm{R}} = \phi_{\mathrm{A}}K_{\mathrm{R(A)}}{}^{0,\mathrm{t}} + \phi_{\mathrm{S}}K_{\mathrm{R(S)}}{}^0 + \frac{m\phi_{\mathrm{A}}K_{\mathrm{I}}{}^{\mathrm{t}}K_{\mathrm{R(A)}}{}^{0,\mathrm{t}}(C_{\mathrm{D}}{}^{\mathrm{A}})^{m-1}}{\bar{V}_{\mathrm{A}}{}^n} \qquad (7)$$

whence

$$K_{\mathrm{R}} = \phi_{\mathrm{A}}K_{\mathrm{R(A)}}{}^{0,\mathrm{t}}\left[1 + \frac{mK_{\mathrm{I}}{}^{\mathrm{t}}(C_{\mathrm{D}}{}^{\mathrm{A}})^{m-1}}{\bar{V}_{\mathrm{A}}{}^n}\right] + \phi_{\mathrm{S}}K_{\mathrm{R(S)}}{}^0 \qquad (8)$$

Now, for the solvent A alone, Purnell[4] has shown that the following equation relates $K_{\mathrm{R(A)}}{}^0$ to $K_{\mathrm{R(A)}}{}^{0,\mathrm{t}}$ and $K_{\mathrm{I}}{}^{\mathrm{t}}$ for the case of $m{:}n$ complexing equilibria:

$$K_{\mathrm{R(A)}}{}^0 = K_{\mathrm{R(A)}}{}^{0,\mathrm{t}}\left[1 + \frac{mK_{\mathrm{I}}{}^{\mathrm{t}}(C_{\mathrm{D}}{}^{\mathrm{A}})^{m-1}}{\bar{V}_{\mathrm{A}}{}^n}\right] \qquad (9)$$

Hence, we see that

$$K_{\mathrm{R}} = \phi_{\mathrm{A}}K_{\mathrm{R(A)}}{}^0 + \phi_{\mathrm{S}}K_{\mathrm{R(S)}}{}^0$$

which is the equation (eq 1) previously derived by us on a more general basis and shown to have very wide applicability. Obviously, had we postulated interaction between D and S the result would have been the same, although, of course,

$K_{R(S)}{}^0$ would have been defined by a complex expression such as that for $K_{R(A)}{}^0$ in eq 9.

We thus see that the MP theory accommodates, within its generalization, any stoichiometry of interaction in solution that may be occurring. Our general equation may thus be expected to apply where polynuclear complexing, hydrogen bonding, or any other type of solvation is postulated.

For what now follows, we shall consider only the algebraically simple case of a 1:1 interaction of A with D. In the light of the above, this will clearly illustrate any points to be made. When $n = m = 1$, eq 9 reduces to

$$K_R = \phi_A K_{R(A)}{}^{0,t}\left[1 + \frac{K_1{}^t}{\bar{V}_A}\right] + \phi_S K_{R(S)}{}^0 \qquad (10)$$

The conventional GLC equation for the evaluation of stability constants is

$$K_R = K_{R(S)}{}^0\,[1 + K_1{}^{GLC} C_A{}^{A,S}] \qquad (11)$$

Equating the foregoing then yields

$$K_1{}^{GLC} = \frac{\Delta K_R{}^{0,t}\bar{V}_A}{K_{R(S)}{}^0} + \frac{K_1{}^t K_{R(A)}{}^{0,t}}{K_{R(S)}{}^0} \qquad (12)$$

where

$$\Delta K_R{}^{0,t} = K_{R(A)}{}^{0,t} - K_{R(S)}{}^0$$

If $K_1{}^t = 0$, then obviously $K_{R(A)}{}^{0,t} = K_{R(A)}{}^0$, as expected. Further, we see that $K_{R(A)}{}^{0,t}$ and $K_1{}^t$ cannot be separated, and so cannot be separately evaluated unless either can be determined in some other fashion.

Uv–Visible. For the case of 1:1 complexing, in order to invoke the Beer-Lambert law, we require an expression for $C_{comp}{}^{A,S}$. Combining eq 6 and definitions (*e*) and (*f*) we may write:

$$C_D{}^{A,S} - C_{comp}{}^{A,S} = (C_{comp}{}^A / K_1{}^t C_A{}^A)(\phi_A + \phi_S / K_D{}^t) \qquad (13)$$

But, since the complex and A exist only in phase A, $C_{comp}{}^A / C_A{}^A = C_{comp}{}^{A,S} / C_A{}^{A,S}$ and so, on rearranging,

$$C_{comp}{}^{A,S} = \frac{K_1{}^t C_A{}^{A,S} C_D{}^{A,S} K_D{}^t}{\phi_S + \phi_A K_D{}^t + K_1{}^t C_A{}^{A,S} K_D{}^t} \qquad (14)$$

which, since the Beer-Lambert law is

$$A = \epsilon l C_{comp}{}^{A,S}$$

gives

$$\frac{C_D{}^{A,S}\epsilon l}{A} = \frac{\phi_A}{K_1{}^t C_A{}^{A,S}} + \frac{\phi_S}{K_1{}^t C_A{}^{A,S} K_D{}^t} + 1 \qquad (15)$$

Recognizing that $\phi_A / C_A{}^{A,S} = C_A{}^A = \bar{V}_A{}^{-1}$ and that $\phi_S = 1 - \phi_A$ allows some reorganization. Further, for comparability and convenience we may now drop the superscripts A,S and write only C_D and C_A, the apparent initial concentrations in the whole system. Thus, we arrive at

$$\frac{C_D l}{A} = \frac{1}{K_1{}^t K_D{}^t C_A \epsilon} + \left[1 + \frac{\bar{V}_A}{K_1{}^t} - \frac{\bar{V}_A}{K_1{}^t K_D{}^t}\right]\frac{1}{\epsilon} \qquad (16)$$

The left-hand side is the normal group of the Benesi-Hildebrand (B-H) equation and the right-hand side is, clearly, formally equivalent also. Thus, MP theory provides a rationale for the uv-visible technique.

The nominal stability constant, $K_1{}^{uv}$, derived via the B-H equation is defined by the ratio, intercept/slope, of a plot of the lhs of eq 16 against $1/C_A$. Using (16) to evaluate this quantity and eliminating $K_D{}^t$ via (*e*), we find

$$K_1{}^{uv} = \frac{K_1{}^t K_{R(A)}{}^{0,t}}{K_{R(S)}{}^0} + \frac{\Delta K_R{}^{0,t}\bar{V}_A}{K_{R(S)}{}^0} \qquad (17)$$

which is obviously identical with eq 12, whence it follows that, in principle

$$K_1{}^{GLC} = K_1{}^{uv} \qquad (18)$$

Furthermore, we see that when $K_1{}^t = 0$, eq 17 reduces to the general equation[1]

$$K_1{}^{uv} = \Delta K_R{}^0 \bar{V}_A / K_{R(S)}{}^0 \qquad (19)$$

NMR. The chemical shift (δ_{obsd}) of a donor proton, partitioned according to MP theory, between two immiscible liquids, A + S, has been shown[2] to be given by the relation

$$\delta_{obsd} = \sum P_i \delta_i$$

where P_i is the probability of the proton being in the *i*th environment, and δ_i is the chemical shift when the donor is in pure *i*.

In the case of the more comprehensive model now under examination the expression becomes

$$\delta_{obsd} = P_A{}^t \delta_A{}^t + P_{AD}\delta_{AD} + P_S \delta_S{}^0 \qquad (20)$$

Since $\Sigma P_i = 1$, eq 20 can be re-formed into

$$\delta_{obsd} = P_A{}^t(\delta_A{}^t - \delta_{AD}) + \delta_{AD}$$

i.e.,

$$P_A{}^t = (\delta_{obsd} - \delta_{AD})/(\delta_A{}^t - \delta_{AD}) = \Delta/\Delta^{0,t} \qquad (21)$$

where

$$\Delta^{0,t} = \delta_A{}^t - \delta_{AD}$$

We can, alternatively, define $P_A{}^t$ in terms of moles, as earlier:

$$P_A{}^t = \frac{n_D{}^{A,t}}{n_{AD}{}^A + n_D{}^S + n_D{}^{A,t}} \qquad (22)$$

Dividing top and bottom by $[C_D{}^g(V_A + V_S)]$, and recognizing that $(V_A + V_S)^{-1} = \phi_A / V_A = \phi_S / V_S$, we find after some rearrangement and use of definitions (*a*)–(*c*), that:

$$\frac{\Delta}{\Delta^{0,t}} = P_A{}^t = \phi_A K_{R(A)}{}^{0,t} / [\phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0] \qquad (23)$$

From this point, substitution for ϕ_S, for $K_{R(A)}{}^0$ from eq 9, and for ϕ_A with $\bar{V}_A C_A$, followed by rearrangements, yields

$$\frac{1}{\Delta} = \frac{K_{R(S)}{}^0}{K_{R(A)}{}^{0,t}\bar{V}_A C_A \Delta^{0,t}} + \left[\frac{\Delta K_R{}^{0,t}}{K_{R(A)}{}^{0,t}} + \frac{K_1{}^t}{\bar{V}_A}\right]\frac{1}{\Delta^{0,t}} \qquad (24)$$

which is clearly the exact analogue of the usual equation employed to evaluate stability constants from NMR data. Again, the constant $K_1{}^{NMR}$ is evaluated from the intercept/slope quotient of a plot of $1/\Delta$ against $1/C_A$, hence,

$$K_1{}^{NMR} = \frac{K_1{}^t K_{R(A)}{}^{0,t}}{K_{R(S)}{}^0} + \frac{\Delta K_R{}^{0,t}\bar{V}_A}{K_{R(S)}{}^0} \qquad (25)$$

which is identical with the results derived for both the GLC and uv–visible cases.

Discussion

Earlier papers in this series[1-3] have established that for all the solvent-solute systems for which adequate data are available, the general relation (eq 1)

$$K_R = \phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0$$

applies. The systems, in a number of instances, comprised components which could be expected, or have been postulated, to interact by charge transfer, hydrogen bonding, or solvation. In other cases, no specific interaction has been or could be readily visualized. Nevertheless, we have shown that this coherence of behavior, embodied in the above equation, is an automatic consequence of MP theory regardless of the presence (*or absence*) of complexation, hydrogen bonding, or solvation in either additive *or* solvent. It must be recognized that all the solvent mixtures under discussion are relatively involatile. It might hence be argued that diachoric behavior typifies "large" molecules only. However, we have established[3] that diethyl maleate-quinoline mixtures *also* behave as diachoric solutions, as do silicone polymer mixtures. It is therefore difficult to reconcile this observation with the premise that molecular size alone is the criterion for diachoric solution behavior, since it seems no more credible to associate diethyl maleate with a silicone polymer than with some other, "smaller", molecule. We are thus led to the view that eq 1 could well be found to describe the behavior of solutions of a more "classical" kind. Unfortunately, an immediate test is precluded since the literature contains no data corresponding to infinite dilution studies of a third component in such a binary mixture. Furthermore, other than in the GLC literature, partition coefficients are rarely if ever measured or cited, since in conventional solution studies, emphasis is placed on the activity coefficient. It is worthwhile to point out that the latter has no intrinsic advantage over the former since they are always explicitly related by a simple function, and, although it is not generally stressed, the activity coefficient is defined relative to the gas phase and is, hence, a comparative quantity linking the liquid and gas phases; the partition coefficient describes this link directly. In light of the above, it seems that an area of immediate interest is a re-study of some of the "classical" solutions via the GLC molecular probe approach embodied in our investigations. We propose to attempt this in the immediate future.

Turning now to the matter of specific interactions, the foregoing has shown that, all other things being equal, the GLC, NMR, and uv-visible techniques should yield the same result for K_1^{exptl}. In practice, of course, considerable discrepancies are often noted. We will return to these later since we must deal first with the question of what, if anything, K_1^{exptl} means.

For simplicity we consider only the 1:1 interaction case and, for this, our derivation shows

$$K_1^{\mathrm{exptl}} = \frac{K_1^{\mathrm{t}} K_{\mathrm{R(A)}}^{0,\mathrm{t}}}{K_{\mathrm{R(S)}}^{0}} + \frac{\Delta K_{\mathrm{R}}^{0,\mathrm{t}} \bar{V}_{\mathrm{A}}}{K_{\mathrm{R(S)}}^{0}} \tag{26}$$

from which the following inequalities arise: $K_{\mathrm{R(A)}}^{0,\mathrm{t}} > K_{\mathrm{R(S)}}^{0}$, $K_1^{\mathrm{exptl}} > K_1^{\mathrm{t}}$; $K_{\mathrm{R(S)}}^{0} > K_{\mathrm{R(A)}}^{0,\mathrm{t}}$, $K_1^{\mathrm{t}} > K_1^{\mathrm{exptl}}$. Obviously, only when $K_{\mathrm{R(A)}}^{0,\mathrm{t}} = K_{\mathrm{R(S)}}^{0}$ can $K_1^{\mathrm{t}} = K_1^{\mathrm{exptl}}$. According to this, therefore, only rarely do experiments yield anything better than an approximation to K_1^{t}. The key feature of eq 26 is that it quantitatively describes so-called solvent effects. For strong complexes these are explicitly defined by $K_{\mathrm{R(A)}}^{0,\mathrm{t}}/K_{\mathrm{R(S)}}^{0}$, since then the second term in eq 26 is trivial. For weak complexes, the term containing $\bar{V}_{\mathrm{A}}$ may contribute significantly. Indeed, it can be responsible for values of K_1^{exptl} being zero or negative. Thus, for example, if $K_1^{\mathrm{exptl}} = 0$, the theory requires that

$$K_1^{\mathrm{t}} = -\Delta K_{\mathrm{R}}^{0,\mathrm{t}} \bar{V}_{\mathrm{A}} / K_{\mathrm{R(A)}}^{0,\mathrm{t}} \tag{27}$$

Since K_1^{t} cannot be negative, $K_{\mathrm{R(S)}}^{0} > K_{\mathrm{R(A)}}^{0,\mathrm{t}}$. The range of $\bar{V}_{\mathrm{A}}$ common to the organic liquids usually studied is 0.1-0.5 l. mol^{-1} so that, for the smallest meaningful value of K_1^{t}, ca. 0.1 l. mol^{-1}, the range of $K_{\mathrm{R(S)}}^{0}/K_{\mathrm{R(A)}}^{0,\mathrm{t}}$ demanded is only 2 to 1.2, a very reasonable situation. For a strong charge transfer or hydrogen bonded complex, K_1^{t} might be as big as 4.5 l. mol^{-1} in which case $K_{\mathrm{R(S)}}^{0}/K_{\mathrm{R(A)}}^{0,\mathrm{t}}$ must range between 50 and 10 for $K_1^{\mathrm{exptl}} = 0$. Such partition ratios between solvents are quite commonplace.

If, of course,

$$K_1^{\mathrm{t}} < \left[\frac{K_{\mathrm{R(S)}}^{0}}{K_{\mathrm{R(A)}}^{0,\mathrm{t}}} - 1\right] \bar{V}_{\mathrm{A}}$$

then K_1^{exptl} will appear negative with a limiting value of $\bar{V}_{\mathrm{A}}$; thus, negative values in the range -0.1 to -0.5 l. mol^{-1} might well be regarded as not unexpected. However, it must be emphasized that, if the explanation of negative K_1^{exptl} lies in the above, the theory still demands that the same result be obtained by the GLC and spectroscopic methods. In all instances so far published, negative spectroscopic data are accompanied by positive GLC results. The explanation is therefore somewhat more complex than the above, although it may be a contributory factor. We propose to publish later an account of a number of systems where all techniques yield zero or negative values of about the same magnitude.

Returning now to the matter of discrepancies in published K_1^{exptl} values, two contributory factors can immediately be identified. First, the B-H (and its variants) equation is a poor vehicle for data evaluation; even trivial experimental errors can quite remarkably affect (intercept/slope) quotient calculations. This matter has been the subject of major discussion over the years and is widely recognized: Second, the normal condition of the GLC experiment is that D is at infinite dilution, A is at some finite concentration, and S is generally in excess, whereas in contrast, in the spectroscopic experiment, A is at high (though not infinite) dilution, D is at finite concentration, and S is usually in excess. The latter situation is demanded experimentally in order to provide separation of the charge transfer band or to induce a sufficient chemical shift. Thus, the published information, as so far provided, does not relate to the same systems in terms of MP theory. Hence, since the relevant partition coefficients of D, for instance, are certainly concentration dependent, it could not be expected that substantial agreement need be observed.

Of course, it must be recognized also that there are basic assumptions and approximations involved in the spectroscopic methods which may be invalid in practice. In this case, no correlation with GLC or even between NMR and uv-visible could be expected. Finally, we must take into account the possibility envisaged in part I[1] that the solution and spectroscopic K_1^{exptl} values derive from different sources. Martire,[6] for example, has suggested that GLC (solution) data reflect not only charge transfer or other complexing, but also collisional pairing in the system, whereas the spectroscopic methods provide information regarding only the former (it is, perhaps, significant that K_1^{GLC} is normally greater than is K_1^{spect}). This possibility can be readily accommodated in MP theory simply by introducing an extra equilibrium constant into the general complexing eq 28, such that $K_1^{\mathrm{GLC}} = K^{\mathrm{spect}} + K_1^{\mathrm{coll}}$. This would only add a simple term to the correlation equations involving the GLC data which follow. Only when much more (and more accurate) information of the right sort is available can we proceed to distinguish between the above possibilities.

In part II[2] we showed that GLC and NMR data could be correlated remarkably well even though the derived values of K_1^{exptl} were in only modest agreement. We now consider a comparison of the usual forms of the GLC and NMR equations:

$$K_{\mathrm{R}} = K_{\mathrm{R(S)}}^{0}[1 + K_1^{\mathrm{GLC}} C_{\mathrm{A}}] \tag{28}$$

$$\frac{\Delta^0}{\Delta} = \frac{1}{K_1^{\mathrm{NMR}} C_{\mathrm{A}}} + 1 \tag{29}$$

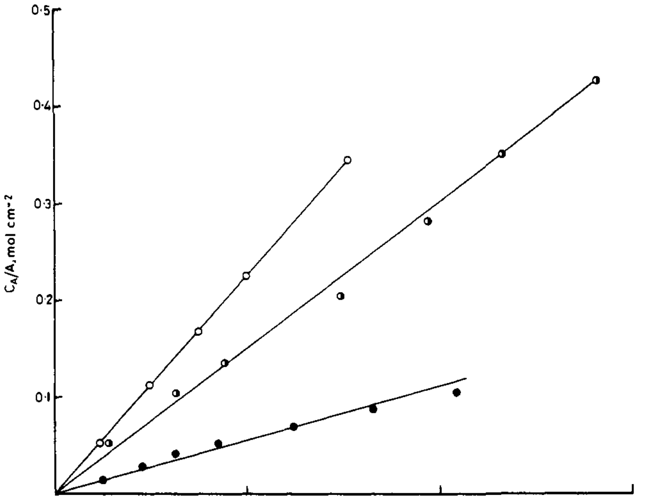

Figure 2. Plot of $C_A l/A$ vs. $1/\Delta$ for toluene and trinitrofluorenone in the solvents: di-*n*-butyl succinate (◑), di-*n*-butyl adipate (○), and di-*n*-butyl sebacate (●) at 40°C.

where $C_A = C_A{}^{A,S}$ in our earlier nomenclature. By equating $K_1 C_A$, we found[1] that

$$\Delta = \phi_A K_{R(A)}{}^0 \Delta^0 / K_R \qquad (30)$$

and a plot of values of Δ against those of $\phi_A K_{R(A)}{}^0 / K_R$ for the same value of C_A were linear, of slope Δ^0. By an identical procedure, using the B-H form of the uv-visible equation, we get

$$\frac{C_D \epsilon l}{A} = \frac{1}{K_1{}^{uv} C_A} + 1 \qquad (31)$$

from which we see that, for equal values of C_A,

$$A/C_D l = \epsilon \phi_A \Delta K_R / K_R \qquad (32)$$

A plot of the lhs against ϕ_A / K_R should therefore be linear, of slope $\epsilon \Delta K_R$, with zero intercept. Equally, of course, for pairs of data for equal C_A,

$$\Delta / \Delta^0 = A / C_D \epsilon l \qquad (33)$$

It should be noted that the GLC/NMR correlation, and a check of calculated and experimental slopes of the plots according to eq 30, were previously possible[2] since Δ^0 could there be measured since, in each case, both A and S were liquids. In the uv-visible case, however, ϵ cannot be measured independently, and a test of either eq 32 or 33 can only be based on linearity and zero intercept at this time. Such linearity, of course, could provide a basis for independent estimation of ϵ via eq 33 if both A and S were liquids since then Δ^0 could be directly determined.

Fortunately, Purnell and Srivastava[7] have reported comparative NMR and uv-visible data for the systems: aromatic hydrocarbons with trinitrofluorenone in respectively di-*n*-butyl succinate (DBSUCC), di-*n*-butyl adipate (DBA), and di-*n*-butyl sebacate (DBSEB). We show in Figure 2a representative plot of these data for toluene in the form required by eq 33; the results are obviously in good accord with the theory. However, the B-H evaluated $K_1{}^{\text{exptl}}$ values were:[7] DBSUCC (uv, 0.116; NMR, −0.019; DBA (uv, −0.030; NMR, −0.01); DBSEB (uv, −0.008; NMR, 0.053). Although the extent of disagreement of the $K_1{}^{\text{exptl}}$ values listed is not large, it is worth noting that the ratios, ϵ/Δ^0, evaluated from the B-H plots differ from those derived from Figure 2 by up to a factor of 3. This, if nothing else, emphasizes the problems of intercept evaluation of B-H plots and seems to us to indicate that eq 33 might provide a good basis for future data evaluation.

We have now shown that the concept of localized aggregation in binary mixtures provides a quantitative description of all the available data and that it can accommodate any detailed solution mechanism that may be postulated. Further, it provides a rationale for the conventional spectroscopic approaches to studies of interaction in solution and an explicit description of the hitherto vague term, "solvent effects", even to the extent of accounting for "negative" equilibrium constants. We recognize clearly that the account given up to now is still of a very general nature and that cogent arguments against local aggregation can be advanced. It seems to us, however, that it would be precipitate to introduce at this point any significant attempt at detail since the extent of the generality of our basic equation has still to be finally determined.

One last point in support of our general premise may be made. The conventional view of complexing in D/A/S mixtures (wherein D and A are molecularly dispersed) requires that the stoichiometric stability constant, being only an equilibrium quotient, should normally be concentration dependent on account of varying activity coefficients. It is a remarkable feature of the literature on weak complexing that, in contrast to expectation, B-H (or its variants) type plots are virtually always linear. This matter has been the subject of substantial discussion in the literature and never yet satisfactorily explained. In the present theory, of course, no nonlinear effects would be anticipated when D is at infinite dilution and they would be minimal even at finite concentrations. The full weight of evidence from the literature on complexing may thus be argued to support the present view.

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