# Solution and Complexing Studies. III. Further Evidence for a Microscopic Partitioning Theory of Solution

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**Abstract:** A microscopic partition (MP) model of solution interaction initially proposed by Purnell and Vargas de Andrade has been shown to allow prediction of the reputed charge transfer or hydrogen bonding complexing stability constants obtained by gas-liquid chromatography of almost 100 systems and also, for the first time, to allow correlation of the corresponding GLC and nuclear magnetic resonance spectroscopic data. We now present evidence drawn from the literature relating to a further 80 systems containing, as one component of a binary solvent mixture, dodecanol, lauronitrile, di-*n*-nonyl phthalate, di-*n*-propyl tetrachlorophthalate, and quinoline, respectively, each system with a wide range of solutes of diverse types. In every case the previously presented basic relation $K_R = \phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0$ is shown to be obeyed over the whole range $\phi_A = 0 \rightarrow 1$. $K_R$ is the infinite dilution partition coefficient of a solute (D) between a binary liquid mixture of A and S (of volume fraction $\phi_A$ and $\phi_S$) and the gas phase, while $K_{R(A)}{}^0$ and $K_{R(S)}{}^0$ are the corresponding quantities for pure A and pure S. The equation is now shown to apply equally well to systems where no specific interactions would be anticipated as to those where charge transfer or hydrogen bonding between D and A would be expected on current views. This indicates a like basis for the solution process in systems of widely diverse type and the further possibility, either that complexing interactions are of a less specific nature than has been supposed, or, indeed, as presently defined, do not occur at all. The implications for theories of solution and of complexing are discussed. The results clearly establish that a new class of nonelectrolyte solutions has been revealed and the name *diachoric* is suggested for these.

Since its inception, gas-liquid chromatography (GLC) has been widely used for the study and measurement of physico-chemical properties, ranging from activity coefficients[1,2] to vertical ionization potentials.[3] In recent years there has been a rapidly developing interest in GLC studies of "weak complexes" anticipated to involve either charge transfer or hydrogen bonding interactions.[4] Particular emphasis has been laid on the determination of equilibrium formation (stability) constants, $K_1$, due to the nominal simplicity and accuracy of the GLC technique. The two basic GLC methods used to determine $K_1$ data, and the results obtained, have recently been reviewed by Wellington[5] and by Laub and Pecsok.[6] In outline, they are as follows.

For the complexing reaction,

$$A + D \rightleftharpoons AD$$

the stoichiometric stability constant is defined as

$$K_1 = C_{AD}/C_A C_D$$

and, if such a reaction between a solute D and A, dissolved in inert solvent, S, is postulated to occur in addition to "normal" solution of D in S, Gil-Av and Herling[7] have shown that the GLC retention equation is

$$K_R = K_{R(S)}{}^0(1 + K_1 C_A) \tag{1}$$

Here, $K_R$ is the infinite dilution partition coefficient for the complex-forming donor (acceptor) solute, D, between the mixed liquid phase containing acceptor (donor) of molar concentration, $C_A$, and the gas phase. $K_{R(S)}{}^0$ is the corresponding quantity for the same solute in the pure inert liquid phase, S. The usual procedure is to employ a series of columns of varied composition and to plot values of $K_R$, calculated from retention volumes, against the corresponding value of $C_A$. $K_1$ is then evaluated from the slope and intercept of the resulting straight line.

A second method, developed by Martire and Riedl,[8] employs the following equation:

$$K_1 = \left[\frac{V_g{}^A V_g{}^C}{V_g{}^B V_g{}^D} - 1\right]\left[\frac{1}{\gamma_A \bar{V}_A}\right] \tag{2}$$

where $V_g{}^A$ and $V_g{}^B$ are the specific retention volumes of an inert (noncomplexing) solute in the pure inert and pure complexing phases, respectively, while $V_g{}^D$ and $V_g{}^C$ are the corresponding specific retention volumes of a complexing solute with the same phases. $\bar{V}_A$ is the molar volume of the pure complexing phase, and $\gamma_A$ is the relevant activity coefficient, which is given by:

$$\gamma_A = \frac{V_g{}^B MW_C}{V_g{}^A MW_N}$$

where $MW_C$ and $MW_N$ are the complexing and inert solvent molecular weights, respectively.

This latter method has the advantage of requiring the determination of only four specific retention volumes using two columns. The inert reference solvent of the Martire/Riedl technique, however, must, as a matter of principle, be as nearly identical as possible, in every respect, to the nominally complexing solvent (e.g., molecular weight, molar volume, polarizability). This restriction is not nearly as serious as might be supposed since we know from experience that, for the same systems, the stability constants obtained[9] via eq 1 are identical with those obtained via eq 2.

Charge transfer interactions have also been investigated for many years by uv-visible[10] and NMR[11] spectroscopic techniques. Attention has been turned in recent years to the problem of the negative formation constants so frequently indicated by these techniques.[12] Furthermore, uv-visible and NMR derived values of $K_1$ are commonly solvent dependent even when positive results are obtained[13] and are, in addition, often in serious disagreement with each other even when the same solvents and methods are used by the same workers in the same laboratory.[14] Data processing by one or other of the several variants of the Benesi-Hildebrand (B-H) equation introduces some improvement in reproducibility but does not significantly affect the situation.[14] It has been a common observation of recent studies that a further disagreement with GLC derived data is also usual. This state of affairs led us to a more comprehensive study than usual of the various methods as a result of which

Table I. Densities of Pure Liquids at Stated Temperature

|  | $\rho$, g cm$^{-3}$ | $T$, °C |  | $\rho$, g cm$^{-3}$ | $T$, °C |
|---|---|---|---|---|---|
| Squalane | 0.7862 | 56 | 1-Dodecanol | 0.8091 | 56 |
|  | 0.7644 | 90 | Lauronitrile | 0.8054 | 56 |
|  | 0.7580 | 100 | Di-*n*-nonyl phthalate | 0.9078 | 100 |
|  |  |  | Di-*n*-propyl tetra-chlorophthalate | 1.3274 | 90 |

we were able to show[15] that, for almost 100 systems, $K_R$ was precisely described by the equation

$$K_R = \phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0 \tag{3}$$

where $K_{R(A)}{}^0$ and $K_{R(S)}{}^0$ are the partition coefficients of solute D between pure liquids A and S, respectively, and the gas phase, and $\phi$ represents a volume fraction in the solvent mixture.

Consideration of the data led us to propose[15] a microscopic partition (MP) theory of solutions of the type under study since the commonly employed theories of the time were found to be incompatible with eq 3. Briefly, we proposed that the liquids A and S exist in their macroscopic solution as microscopically immiscible groups of like molecules. On this basis, we showed that eq 3 could be derived readily and, furthermore, would describe both ideal and nonideal solutions. In addition, using this theory as a basis, we derived[16] a general equation correlating, for the first time, and with remarkable accuracy, GLC and NMR data for a number of systems.

In our earlier publications[15,16] we developed the theoretical arguments generally and ignored the question of whether or not complexing or other specific interactions contributed to solubility. We propose to show in a subsequent paper (part IV) that the theory can readily be developed to accommodate entirely these matters and, further, to provide a detailed account of both the NMR and uv-visible methods for complexing studies, as well as correlating both with GLC. Here, we restrict ourselves to presenting further evidence in support of the MP view of solution. The data are entirely drawn from the literature and comprise some 81 systems; all those, in fact, which provide sufficient information or require only detailed density measurements, to provide a test of the theory. As will be seen, despite the remarkable range of solvents and solutes, each behaves in excellent accord with eq 3. In addition, we review briefly results described in a number of papers relating to the GLC performance of a range of mixed-solvent systems and show

Table II. $K_{R(S)}{}^\circ$ and $K_{R(A)}{}^\circ$ Values for Named Solutes and Solvents at Reported Temperatures

| No. | Name | $K_{R(S)}{}^\circ$ | $K_{R(A)}{}^\circ$ |
|---|---|---|---|
|  | A. Squalane and 1-Dodecanol at 56°C |  |  |
| 1 | Methyl alcohol | 12.5 | 110 |
| 2 | Ethyl alcohol | 23.9 | 213 |
| 3 | *n*-Propyl alcohol | 50.5 | 512 |
| 4 | Isopropyl alcohol | 26.2 | 291 |
| 5 | *n*-Butyl alcohol | 134 | 1190 |
| 6 | Isobutyl alcohol | 87.0 | 1019 |
| 7 | *sec*-Butyl alcohol | 72.6 | 751 |
| 8 | *tert*-Butyl alcohol | 38.5 | 393 |
| 9 | 1-Pentyl alcohol | 321 | 4240 |
| 10 | Isopentyl alcohol | 242 | 2988 |
| 11 | 2-Pentyl alcohol | 191 | 1926 |
| 12 | 3-Pentyl alcohol | 198 | 1795 |
| 13 | 2-Methyl-1-butyl alcohol | 259 | 2925 |
| 14 | 3-Methyl-2-butyl alcohol | 164 | 1394 |
| 15 | *tert*-Pentyl alcohol | 119 | 1006 |
| 16 | *neo*-Pentyl alcohol | 136 | 1289 |
|  | B. Squalane and Lauronitrile at 56°C |  |  |
| 1 | Nitromethane | 29.3 | 370 |
| 2 | Nitroethane | 75.8 | 759 |
| 3 | Nitropropane | 191 | 1582 |
| 4 | Ethyl cyanide | 39.0 | 367 |
| 5 | *n*-Propyl cyanide | 97.6 | 844 |
|  | C. Squalane and Di-*n*-propyl Tetrachlorophthalate at 90°C |  |  |
| 1 | Benzene | 71.8 | 156 |
| 2 | Toluene | 163 | 360 |
| 3 | Ethylbenzene | 329 | 649 |
| 4 | *p*-Xylene | 368 | 809 |
| 5 | *m*-Xylene | 373 | 780 |
| 6 | *o*-Xylene | 437 | 1044 |
| 7 | Isopropylbenzene | 524 | 934 |
| 8 | *n*-Propylbenzene | 658 | 1215 |
| 9 | 1-Methyl-3-ethylbenzene | 729 | 1333 |
| 10 | 1-Methyl-4-ethylbenzene | 742 | 1397 |
| 11 | 1,3,5-Trimethylbenzene | 849 | 1566 |
| 12 | 1-Methyl-2-ethylbenzene | 826 | 1735 |
| 13 | *tert*-Butylbenzene | 882 | 1499 |
| 14 | 1,2,4-Trimethylbenzene | 978 | 2203 |
| 15 | Isobutylbenzene | 994 | 1731 |
| 16 | *sec*-Butylbenzene | 1003 | 1669 |
| 17 | 1-Methyl-3-isopropylbenzene | 1113 | 1802 |
| 18 | 1,2,3-Trimethylbenzene | 1192 | 3051 |
| 19 | 1-Methyl-4-isopropylbenzene | 1178 | 1915 |
| 20 | 1-Methyl-2-isopropylbenzene | 1239 | 2261 |
| 21 | 1,3-Diethylbenzene | 1364 | 2259 |
| 22 | 1-Methyl-3-*n*-propylbenzene | 1416 | 2423 |
| 23 | *n*-Butylbenzene | 1441 | 2603 |
| 24 | 1-Methyl-4-*n*-propylbenzene | 1478 | 2583 |
| 25 | 1,2-Diethylbenzene | 1484 | 2769 |
| 26 | 1,3-Dimethyl-5-ethylbenzene | 1595 | 2539 |
| 27 | 1,4-Diethylbenzene | 1487 | 2469 |
| 28 | 1-Methyl-2-*n*-propylbenzene | 1560 | 3053 |
| 29 | 1,4-Dimethyl-2-ethylbenzene | 1748 | 3463 |
| 30 | 1,3-Dimethyl-4-ethylbenzene | 1833 | 3485 |
| 31 | 1,2-Dimethyl-4-ethylbenzene | 1901 | 3581 |
| 32 | 1,2-Dimethyl-3-ethylbenzene | 2164 | 4703 |
| 33 | 1,2,4,5-Tetramethylbenzene | 2508 | 5759 |
| 34 | 1,2,3,5-Tetramethylbenzene | 2618 | 5869 |
| 35 | 1,2,3,4-Tetramethylbenzene | 3169 | 8692 |
|  | D. Squalane and Di-*n*-nonyl Phthalate at 100°C |  |  |
| 1 | Benzaldehyde | 281 | 884 |
| 2 | Acetophenone | 618 | 1906 |
| 3 | Benzyl alcohol | 462 | 2233 |
| 4 | Phenol | 227 | 3068 |
| 5 | Ethoxybenzene | 416 | 745 |
| 6 | Benzene | 41.2 | 58.6 |
| 7 | Ethylbenzene | 200 | 254 |
| 8 | *n*-Butylbenzene | 830 | 980 |
| 9 | *n*-Hexane | 33.7 | 24.5 |
| 10 | *n*-Heptane | 67.2 | 49.0 |
| 11 | *n*-Octane | 140 | 97.1 |
| 12 | *n*-Nonane | 301 | 202 |
| 13 | *n*-Decane | 630 | 414 |
| 14 | *n*-Undecane | 1315 | 847 |
| 15 | *n*-Dodecane | . . . | 1734 |
|  | E. Diethyl Maleate and Quinoline at 35°C |  |  |
| 1 | Isopentane | 37.4 | 39.0 |
| 2 | *n*-Pentane | 48.1 | 57.1 |
| 3 | 3-Methylpentane | 116 | 131 |
| 4 | Cyclopentane | 116 | 167 |
| 5 | *n*-Hexane | 131 | 172 |
| 6 | Furan | 302 | 227 |
| 7 | Cyclohexane | 294 | 404 |
| 8 | *n*-Heptane | 352 | 508 |
| 9 | Cyclohexene | 505 | 713 |
| 10 | Benzene | 1239 | 1321 |
| 11 | Thiophene | 1704 | 1998 |

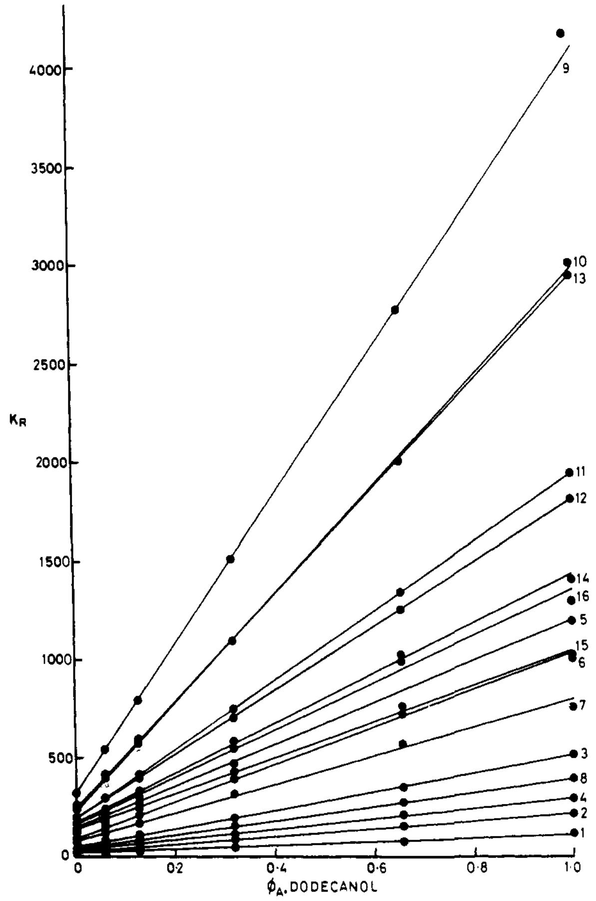

Figure 1. Plot of $K_R$ vs. $\phi_A$ for the system 1-dodecanol in squalane at 56°C. Numbers correspond to solutes listed in Table IIA.

that, although the data cannot be fully, quantitatively reduced, they, almost entirely, also show behavior in accord with the theory.

## Experimental Section

In addition to those systems reported in part I, the literature contains information for the solubility of a wide range of solutes in the binary pairs, squalane with respectively 1-dodecanol, lauronitrile, di-*n*-nonyl phthalate and di-*n*-propyl tetrachlorophthalate, which require only the addition of density measurements for our purposes. In addition, data are available for a number of solutes in diethyl maleate-quinoline[20] mixtures which, since they were given in terms of volume fraction, require no modification.

Samples of the first five liquids quoted above were obtained, variously, from B.D.H., Applied Science, and Phase Separations, and being of the highest purity obtainable were used without further treatment.

The equipment used and the method of density measurement were exactly as described by Laub and Pecsok[21] except that, for improved accuracy, the equipment was totally thermostated. Measured densities of the pure liquids agreed to within 0.1% of published values, where comparison could be made. An important observation was that in no case was any excess volume of mixing indicated by the data for the liquid mixtures.

## Results

**Density Measurements.** The measured densities of the pure liquids at the temperatures relevant to the published data to be reviewed were as listed in Table I. In every instance, the density of mixtures ($\rho_{mix}$) of squalane (S) with another liquid (A) was given to better than ±0.1% by the equation

$$\rho_{mix}^{-1} = \rho_S^{-1} + w_A(\rho_S - \rho_A)/\rho_S\rho_A$$

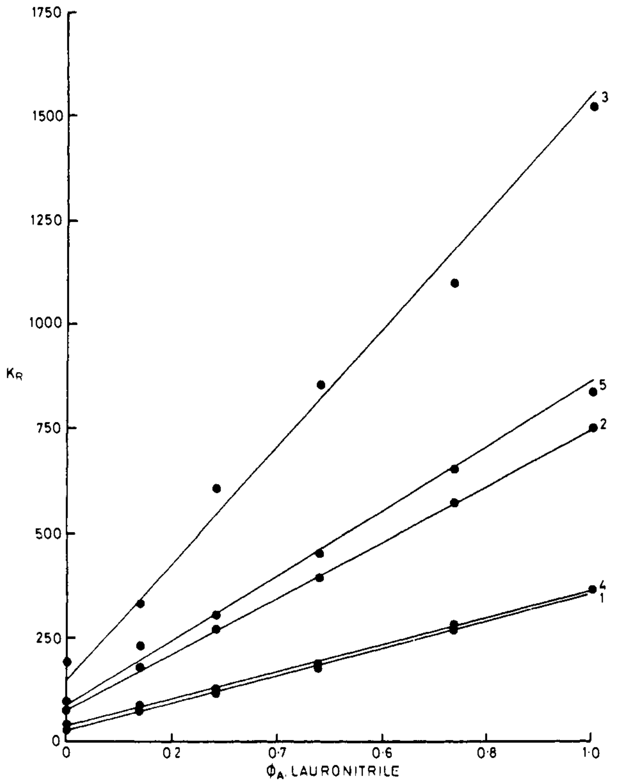

Figure 2. Plot of $K_R$ vs. $\phi_A$ for the system lauronitrile in squalane at 56°C. Numbers correspond to solutes listed in Table IIB.

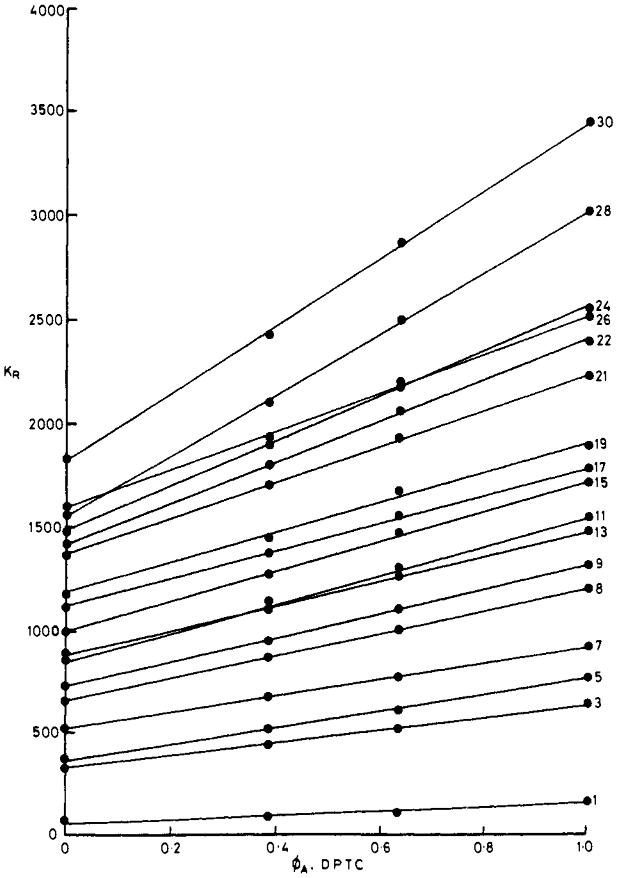

Figure 3. Plot of $K_R$ vs. $\phi_A$ for the system di-*n*-propyl tetrachlorophthalate in squalane at 90°C. Numbers correspond to solutes listed in Table IIC.

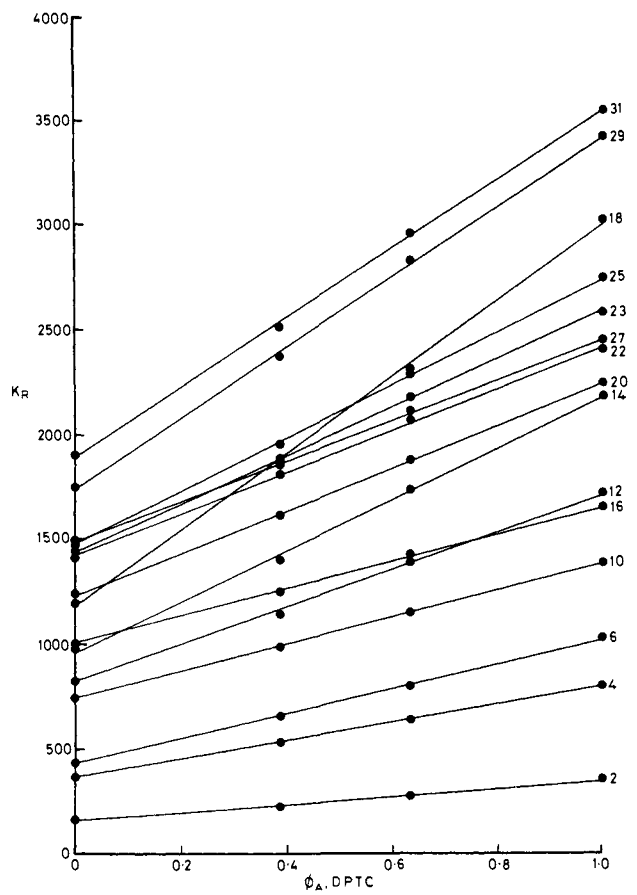

**Figure 4.** Same as Figure 3.

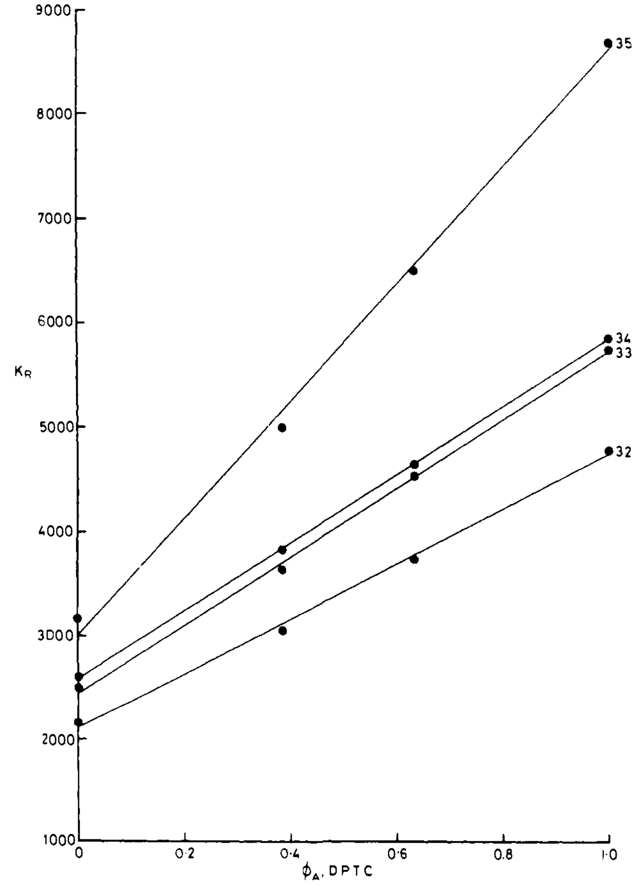

**Figure 5.** Same as Figure 3.

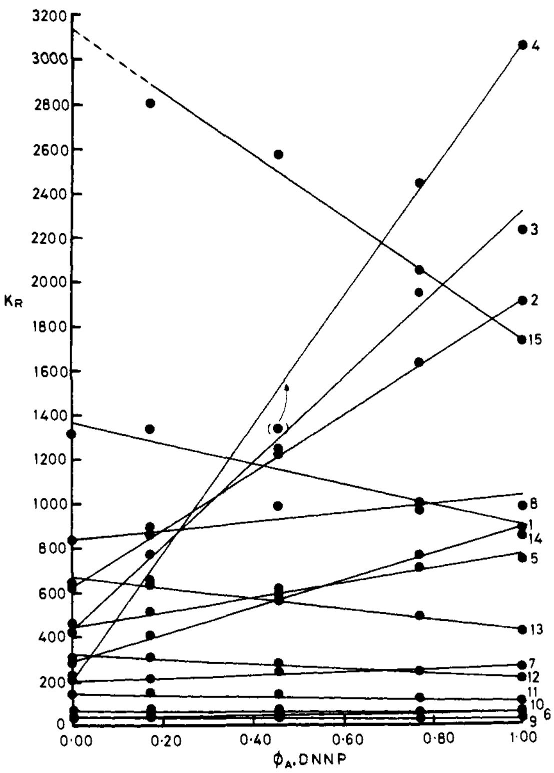

**Figure 6.** Plot of $K_R$ vs. $\phi_A$ for the system di-*n*-nonyl phthalate in squalane at 100°C. Numbers correspond to solutes listed in Table IID.

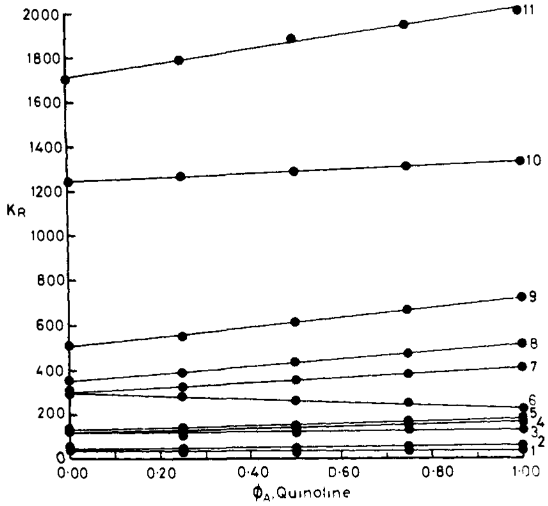

**Figure 7.** Plot of $K_R$ vs. $\phi_A$ for the system quinoline in diethyl maleate at 35°C. Numbers correspond to solutes listed in Table IIE.

where $w_A$ is the weight fraction of A. Hence, the volume fraction of A, in each case, is given by

$$\phi_A = (\rho_{mix} - \rho_S)/(\rho_A - \rho_S)$$

**Solubility Data.** For all five mixed solvent systems the published solubility data were listed in terms of quantities other than the partition coefficients. Thus, we were required to convert the data. For this reason we quote in Table II the recalculated values of $K_{R(A)}{}^0$ and $K_{R(S)}{}^0$.

Figures 1-7 illustrate the whole of the data, for the solutes and solvents specified in Table II, plotted in the form $K_R$ against $\phi_A$. In every instance, an excellent straight line is observed. Among the 400 experimental points plotted only ten or so lie any distance off the line drawn and, in most instances, no more than any one of these in its own set.

Thus, the 81 systems quoted may be taken, without exception, to obey eq 3 and, with the 98 systems listed in part I,[15] we now have recorded 179 systems of which only one,[15] and that only marginally, does not accord.

## Discussion

The remarkably catholic nature of eq 3 is demonstrated by the very considerable diversity of binary mixture type, and solute type for each, which are listed. Thus, for example, squalane-1-dodecanol mixtures with alcohols, where hydrogen bonding might be anticipated, behave in exactly the same way as do mixtures of squalane-di-*n*-propyl tetrachlorophthalate and aromatics, where charge transfer has been postulated, as well as in the same manner as do mixtures of diethyl maleate-quinoline with alkanes and heterocyclics where little, if any, specific interaction can be visualized. Perhaps even more telling is the fact that the overall behavior of squalane-di-*n*-nonyl phthalate mixtures is the same with an aldehyde, a ketone, an alcohol, a phenol, an ether, aromatic hydrocarbons, and *n*-alkanes.

Furthermore, in several instances, the plots show a negative slope which, if interpreted in terms of complexing or other specific interaction, would imply a physically meaningless, negative equilibrium constant.

It is clear that the data presented here and elsewhere establish that eq 3 represents a considerable generalization of solution behavior in a very wide range of systems. Before proceeding farther it seems worthwhile, therefore, to review earlier work which can now also be interpreted to support the present view.

First, we turn to the method of solvent characterization for GLC use proposed, in terms of polarity, by Rohrschneider,[22] which is widely used. In effect, this method is merely an application of eq 3 since it relies on the idea of comparison of (retention) solution behavior of a given solvent with some solute with that of some standard solvent mixture with the same solute.

Primavesi,[23] in a comparison of mixed bed and separate column GLC, found a simple (and the same) additivity of retention volume of several substances with weight composition of the solvent mixture in the two experimental situations. Similar observations have, more recently, been reported by Singliar, Bobak, Brida, and Lukacovic[24] and, interestingly, even for paper chromatography by Soczewinski.[25] The most significant work of this type, however, is that of Hildebrand and Reilley[26] who not only showed that pressure-corrected capacity factors (proportional to partition coefficients) were the same for each of several solutes with Carbowax/Silicone oil mixtures in a single column as with the pure materials in separate series columns but also presented their data in the form of an equation which is, essentially, a version of our eq 3.

Finally, we refer to the work of Keller and Stewart[27] and Young.[28] The former, in a consideration of the performance of mixed GLC solvents, derived an equation for the activity coefficient of a solute in terms of its activity coefficients in the pure liquids on the assumption of independent action of the two liquids. The equation is identical with that established experimentally and theoretically by us in part I.[15] Interestingly, Young,[28] contemplating this equation, concluded that it could not possibly be relevant in practice since it could not be derived on the basis of regular solution theory. An interesting review of possibilities in mixed solvent GLC has been given very recently by Pilgrim and Keller[29] but no theoretical development is offered.

During recent months Muanda, Nagy, and Nagy[30] have published a brief account of their results for two nominally charge transfer systems and shown that they too behave according to eq 3. These authors propose, as have we, a microscopic partition theory and indicate its application to NMR and uv-visible data. However, they introduce undefined quantities into their equations and little can thus be deduced in detailed terms.

In conclusion, a number of workers[31-41] have studied and reported on mixed solvent systems for GLC but, unfortunately have not provided sufficient information for us to convert the data; indeed, it would be necessary completely to repeat the work. Further, in a number of these cases, the systems were clearly subject to strong liquid surface adsorption effects and in one instance[39] we have established that the mixed solvent components only show limited miscibility. In the cases of all the systems not subject to the above criticisms, it is noteworthy that plots of relative retention volume (i.e., relative partition coefficients) were linear in weight percent composition of the mixed solvent, which, of course, is proportional to volume fraction if there is no excess volume of mixing such as we have established for the systems reported on here and earlier, and is a common feature of these systems. Notable among this group are the papers by Touchstone and coworkers[40,41] where linearity, as described, was exhibited for 91 steroids eluted from mixed silicone polymer liquid phases.

The foregoing, clearly, provides very substantial further support for our general viewpoint. Indeed, we are unaware of any unqualified evidence to the contrary.

In this, and the foregoing publication, we have presented quantitative evidence for 180 systems which included 11 separate solvent pairs. Admittedly, in all but one case, one component of the solvent pair is an alkane, but the other component has ranged widely in chemical type, including an amine, an ether, a thioether, aromatic esters, and haloaromatic esters. Combined with the wide range of chemical type of solute used, the evidence of compatibility with one theory is remarkable. It is to be noted also that we have adduced evidence for a number of other types of solvent mixture as well as for polymer-polymer mixtures. We have stated elsewhere that regular and athermal solution theories cannot lead to eq 3, as confirmed by Young.[28] The contrast in level of success self-evidently favors the MP approach.

Since we have shown earlier that the model of an ideal solution yields eq 3 it is, of course, a possibility that all the binary systems discussed form ideal solutions with each other. This is highly unlikely since, as stated elsewhere,[15] none of the solutions of D in A or S was ideal, and further we would require to accept that mixtures as diverse as a very strong electron acceptor and an alkane, the one perhaps cyclic and the other linear, were ideal. Since this possibility seems, therefore, so remote we discount it from further consideration.

In the matter of specific interactions in solution it is clear that, since current methods rely entirely upon dilution effects, the MP theory must lead us to the conclusion that, as they stand, these methods cannot provide meaningful values of $K_1$ whatever the nature of the interaction. This arises because, of course, in MP theory there is no effective dilution of component A by S. We shall develop this matter theoretically later in conjunction with an extension of the theory to account for NMR and uv-visible data pertaining to reputed complexing systems. The implications of this, in other areas of chemistry, will clearly need evaluation.

In conclusion, it is worth pointing out that the GLC technique can now be seen as providing a new approach to binary solution studies in that the volatile third component, D, being effectively at infinite dilution, acts as a molecular probe within the binary solvent mixture. The possible criticism that liquid distribution within a GLC column is atypical and so is responsible for our findings can be immediately discounted in the light of the exceptional degree of correlation 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 ($\phi$) 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:

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

where $\phi$ 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