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Solution and Complexing Studies. I. Gas–Liquid Chromatographic Investigation of Supposed Complexing Systems

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Abstract: GLC measurement of the infinite dilution liquid-gas partition coefficients (K_R) of chloroform, 1,2-dichlorethane, benzene, toluene, ethylbenzene, and the three xylenes in each of the electron acceptor (A)/inert solvent (S) systems, di-*n*-octyl ether/*n*-heptadecane and di-*n*-butyl tetrachlorophthalate/squalane over the whole range $x_A = 0-1$ reveals that plots of K_R against molarity (C_A) or volume fraction (ϕ) of A are strictly linear. Thus $K_R = \phi_A K_{R(A)}{}^0 + \phi_S K_{R(S)}{}^0$ where a K^0 designates a liquid-gas partition coefficient for a solute at infinite dilution in either pure A or S. Since the conventional GLC equation for the stability constant (equilibrium quotient) of a 1:1 complex (K_1) is $K_R = K_{R(S)}{}^0(1 + K_1 C_A)$, it follows that $K_1 = \bar{V}_A(K_{R(A)}{}^0 - K_{R(S)}{}^0)/K_{R(S)}{}^0$ where $\bar{V}_A$ is the molar volume of A. It is possible through this equation to calculate nominal stability constants from data relating solely to pure A and S. The remarkable generality of this observation is demonstrated by comparison of calculated and published data for more than seventy charge-transfer or hydrogen-bonding systems described in the literature. The general equation described above can be derived on the basis of any model of solution in which A and S do not interact. Thus, for example, they can be immiscible, or ideal, or nonideal provided the interaction of a solute with A in S is the same as in pure A. Since there is spectroscopic evidence of interaction of the solutes used with both pure A components and, further, none of the solutes provide ideal solutions in either the A or S components used, it is suggested that in the solvent mixtures used there is a high degree of aggregation such that on dilution of A by S the local concentration of A is still that of the pure liquid. Whatever the explanation, it is clear that the conventional dilution approach to determination of stability constants, at least in systems such as these, does not provide a meaningful measurement of K_1. Further, the solvent systems used show such conformity of behavior, which we are unable to describe on the basis of existing theories, that a re-evaluation of theory is indicated.

Evidence for the existence of weak molecular complexes can be derived inferentially via studies based on a variety of techniques, but quantitative evaluation of the associated stability (formation) constants or, more correctly, equilibrium quotients, almost always involves the use of partition or spectroscopic (uv-visible or NMR) data deriving from experiments involving variation of component concentrations. More than 10 years ago the formal analogy between the classical partition method and an alternative GLC approach was pointed out and placed on a quantitative basis[1-3] and shortly afterwards[4] a general theory of the GLC approach to complexing studies was developed. These observations catalyzed interest in the GLC method since among its numerous practical advantages[4] it is ideally suited for nonaqueous systems, and weak complexing largely involves organic systems of very limited aqueous solubility.

With few exceptions, GLC studies have been concentrated on reactions of the type

$$\mathrm{D(g)} \xrightleftharpoons{K_{\mathrm{R(S)}}{}^0} \mathrm{D(l)}$$

$$\mathrm{D(l)} + \mathrm{A(l)} \xrightleftharpoons{K_1} \mathrm{AD(l)}$$

where D is a volatile solute, and A is an involatile additive dispersed in the column in an "inert" solvent S. The simplest equation describing the behavior of such a system is

$$K_R = K_{R(S)}^{0}(1 + K_1C_A) \qquad (1)$$

where K_R is the observed partition coefficient of D between a mixture of A and S of concentration C_A (mol $l.^{-1}$) and the gas phase, and $K_{R(S)}^0$ is the corresponding quantity at $C_A = 0$, i.e., pure S. The equation can, of course, be put in terms of corrected retention volumes with some consequent arithmetic simplification. Equation 1 is rigorously valid only for very dilute solutions of both D and A. D, of course, is almost always likely to meet this condition in GLC but rarely can C_A be kept trivial if K_1 is small (*ca.* <2 l. mol^{-1}) since measurements otherwise become highly inaccurate. Several authors have attempted to modify eq 1 to allow for this,[5,6] which has, in general, involved some attempt to introduce a theoretical dependence of K_R^0 upon C_A. However, some workers[7,8] have taken the view that the whole equation should be recast in terms of mole fraction defined quantities so as to meet some arbitrarily defined thermodynamic criterion.

Between 1967 and 1972 the main aim was essentially to establish the validity of the GLC derived K_1 values. Broadly speaking, therefore, almost all the systems studied involved A/D components confidently expected on the basis of current theory to form charge-transfer or H-bond complexes of K_1 between about 0.2 and 2.0 l. mol^{-1}. Correspondingly, GLC studies were several times carried out[9-12] simultaneously with either or both the uv-visible and NMR methods. Although occasionally a closely similar value of K_1 was found by all three methods, in the majority of cases not only did the GLC and spectroscopically derived values disagree, but the respective spectroscopic values were also in conflict with each other. The common observation has been that GLC values are normally of a magnitude consistent with expectation and show interesting compatibilities and internal correlations, while the spectroscopic values have, in general, implied weaker complexing with frequent observation of negative formation constants. This last observation must clearly imply unreliability of the spectroscopic data, which in turn casts substantial doubt on the basis of the data processing equations involved. We do not propose to discuss this matter in detail here but will return to it elsewhere. In summary, we were led to the view[10] that the GLC data offered a better basis for interpretation than did the spectroscopic data, but that this in itself did not provide conclusive evidence that the GLC studies really involved a quantitative estimate of complexing.

This view led us to explore further the possible nature of the K_1 data evaluated from GLC results. For GLC purposes, the stability constant is defined in terms of molar concentrations

$$K_1 = C_{AD}/C_AC_D$$

while the true thermodynamic equilibrium constant is defined in terms of activities

$$K_1^{\text{th}} = a_{AD}/a_Aa_D$$

GLC studies have the advantage over other approaches of providing a value of the infinite dilution activity coefficient, γ_D^∞, so that some degree of conversion of the data toward an equilibrium constant is possible. It has been optimistically supposed that a_{AD}/a_A might be closely identifiable with C_{AD}/C_A, but our studies[9,10] have clearly shown that, using $\gamma_{D(x)}^\infty$, defined on a mole fraction scale, to make a partial transformation, this is certainly untrue for all the systems we have studied. Pursuing this, we then chose[10,19] to evaluate an alternative value of γ_D^∞, based on a molarity scale, defined via

$$p/p^0 = \gamma_{D(x)}x = \gamma_{D(C)}(C/C^0)$$

where C^0 is the concentration of pure liquid, D. Thus

$$\gamma_{D(x)}^\infty\bar{V}_S = \gamma_{D(C)}^\infty\bar{V}_D$$

where $\bar{V}$ defines a molar volume of pure liquid. We found that the numerical consistencies and internal correlations[9,10,19] noted in our GLC data were largely explicable as, essentially, reflecting consistencies in molar volumes. Furthermore, on applying this approach to our data for $K_{R(S)}^0$, i.e., the value for D in pure S, remarkable consistency was introduced such that for certain homologs in a given type of solvent, $\gamma_{D(C)}^\infty$ was reasonably constant and system independent.

The sum of the above findings led us to query once more the nature of our derived K_1, since the relative simplicity of our D/S data for $\gamma_{D(C)}^\infty$, over a wide range of solvents and solutes,[10,19] suggested that what was being identified as complexing might well be no more than a mixed solvency effect. This paper outlines our findings with respect to this possibility and, in order to give it generality, we include a summary of published work which is sufficiently comprehensive to allow the necessary recalculation of the data.

Experimental Section

The apparatus and methods adopted were as previously described[9,13] with the exception that a liquid bath column thermostat (Grant Instruments Ltd.) capable of operation within the range −30 to 70° and having temperature control of ±0.05° was used. Squalane, heptadecane, di-*n*-butyl tetrachlorophthalate (DNBT) and di-*n*-octyl ether (DNOE) were the best available gas chromatographic grades. The solutes, chloroform, 1,2-dichlorethane, benzene, toluene, ethylbenzene, and the three xylenes, were of spectrograde or Analar quality. The solid support used throughout the work was Sil-O-Cel C22 treated in the laboratory with hexamethyldisilazane. Nitrogen was of oxygen free grade and hydrogen, when used, was passed through a Deoxo unit; both gases were rigorously dried. Solvent support ratios were determined both by initial weighing and by Soxhlet extraction following experiments, no discrepancy being found between the results of the two sets of experiments. Comprehensive experimental tests also established that in no case was there either a sample size retention dependence or any contribution from solid or liquid surface adsorption. Liquid mixture densities were determined by standard methods. For all the mixed systems studied, the density was found to be a simple arithmetic average by volume of the values for the pure components. Thus, excess volumes of mixing were essentially zero.

Partition coefficients (K_R) were calculated[9,10] from the fully corrected (net) retention volumes (V_N) via the standard equation

$$K_R = V_N/V_L$$

where V_L is the volume of solvent in the column. All other physical data required were taken from standard sources.[14]

Results

The solvent systems studied in this work were DNOE/heptadecane and DNBT/squalane. These were chosen on the basis that (a) complexing of the selected solutes with these electron acceptors would be expected on the basis of current theory, and had nominally been shown to occur,[7,17] and (b) the full range of solubility (mole fraction, x = 0–1) could be achieved. Both systems were studied at 30°; several columns at each of six different electron acceptor concentrations were used in each case. The partition coefficients quoted later are thus the average of at least three individual measurements with each of several columns.

Figures 1 and 2 illustrate the results for the DNOE/heptadecane (30°) and DNBT/squalane (30°) systems with all eight solutes, in the form of plots of K_R against volume fraction of either DNOE or DNBT. These data, which

Table I. Test of Equation 5[a]

	DNOE/*n*-heptadecane				DNBT/squalane			
	$K_{R(A)}^0$	$K_{R(S)}^0$	$[\bar{V}_A\Delta K_R/K_{R(S)}^0]$	K_1(exptl)	$K_{R(A)}^0$	$K_{R(S)}^0$	$[\bar{V}_A\Delta K_R/K_{R(S)}^0]$	K_1(exptl)
Chloroform	579	250	0.398	0.407	718	232	0.664	0.640
1,2-Dichloroethane	535	317	0.208	0.215	984	294	0.744	0.745
Benzene	663	509	0.092	0.093	1218	442	0.557	0.548
Toluene	2189	1718	0.083	0.083	4141	1446	0.591	0.572
Ethylbenzene	5787	4619	0.077	0.077	8805	3688	0.440	0.410
o-Xylene	8508	6816	0.075	0.075	18034	5405	0.741	0.698
m-Xylene	6930	5804	0.059	0.059	12118	4408	0.555	0.521
p-Xylene	6735	5595	0.062	0.062	12896	4379	0.609	0.580

[a] Data relate to 30° C. $\bar{V}_A$(DNOE) = 0.3025 l. mol^{-1} ; $\bar{V}_A$(DNBT) = 0.3171 l. mol^{-1}.

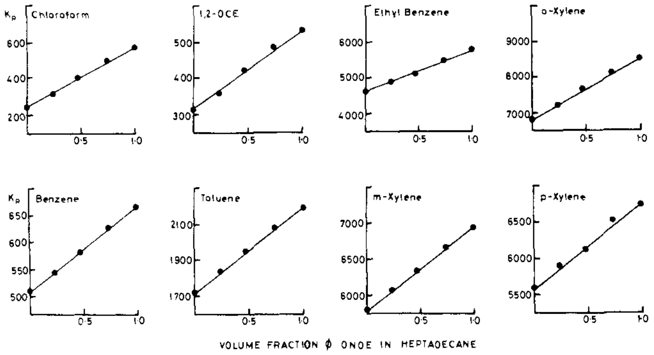

Figure 1. Plots of experimental K_R for named solutes against volume fraction (ϕ) of DNOE in *n*-heptadecane at 30°.

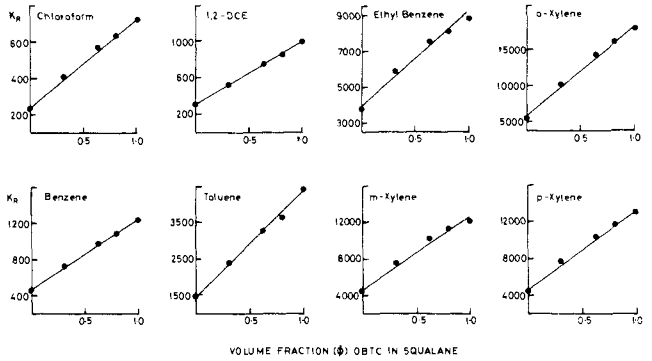

Figure 2. Plots of experimental K_R for named solutes against volume fraction (ϕ) of DNBT in squalane at 30°.

cover the range pure inert solvent to pure acceptor, illustrate the remarkable finding of total linearity of the plots over the whole concentration range. This, thus, clearly establishes that the results are exactly described by the equation

$$K_R = \phi_A K_{R(A)}^0 + \phi_S K_{R(S)}^0 \qquad (2)$$

where $K_{R(A)}^0$ is the infinite dilution partition coefficient of any given solute between pure "reactant" A and the gas phase, and $K_{R(S)}^0$ is the corresponding quantity for pure inert solvent, S. The alternative formulation is

$$K_R = K_{R(S)}^0 + \phi_A[K_{R(A)}^0 - K_{R(S)}^0] \qquad (3)$$

which, since there is no excess volume of mixing, yields

$$K_R = K_{R(S)}^0 + \bar{V}_A C_A[K_{R(A)}^0 - K_{R(S)}^0] \qquad (4)$$

where $\bar{V}_A$ is the molar volume of pure A.

The formal GLC equation for evaluation of stability constants (equilibrium quotients) (K_1) on the basis that there is 1:l complexing of acceptor (A) and solute (D) is

$$K_R = K_{R(S)}^0 + K_{R(S)}^0 K_1 C_A \qquad (5)$$

for small values of C_A.

Obviously, eq 4 and 5 are formally identical and the present findings must cast substantial doubt upon the meaningfulness of eq 5 and the ideas which underlie it since, evidently, equating eq 4 and 5 yields

$$K_1 = \bar{V}_A \Delta K_R^0 / K_{R(S)}^0 \qquad (6)$$

where $\Delta K_R = K_{R(A)}^0 - K_{R(S)}^0$, i.e., the apparent stability constant is defined by quantities associated with pure solvent components. We may test eq 6 by comparing values of K_1 derived from the experimental data via eq 4 and values of $(\bar{V}_A \Delta K_R^0/K_{R(S)}^0)$ calculated directly. The relevant values are listed in Table I. In every instance the agreement is essentially perfect. This is a remarkable finding since it establishes that, for the systems under study at least, the apparent stability constants for 1:1 A/D complexes can be calculated precisely from solubility data for D in pure A and pure S, respectively.

We may extend this argument to the apparent activity coefficients for D in A + S mixtures. It is a matter of definition that

$$K_R = RT/p^0 \gamma_p^\infty \bar{V}_L$$

where p^0 is the saturation pressure of solute D, and γ_p^∞ is its infinite dilution activity coefficient (on the mole fraction scale) in solvent of molar volume $\bar{V}_L$. Using this definition, along with eq 4, we derive

$$\frac{1}{\gamma_p^\infty} = \frac{x_A}{\gamma_{p(A)}^\infty} + \frac{x_S}{\gamma_{p(S)}^\infty} \qquad (7)$$

where the subscripts denote pure A or S. Thus, a plot of $1/\gamma_p^\infty$ for D in a mixture of composition x_A, against x_A, should be a straight line of slope $[(1/\gamma_{p(A)}^\infty) - (1/\gamma_{p(S)}^\infty)]$ and intercept $(1/\gamma_{p(S)}^\infty)$. In every instance, this is observed to well within any reasonable estimate of experimental error.

Thus, the results presented here clearly present two substantially important problems. First, nominal stability constants can be calculated from simple solubility data, a totally unexpected result. Second, the mole fraction based activity coefficient of a third component at infinite dilution in a mixture of A and S appears to be simply the arithmetic average of the corresponding values for pure A and S, in contrast to the predictions of any current theory. It is clearly of the highest importance to test the generality of these findings, based as they are on the limited results of only 16 solvent/solute systems.

Discussion

Extensive testing of our findings is not as simple as it might seem, since first the literature contains few examples of complexing studies conducted over the whole range x_A = 0-1 and second, for the numerous systems of limited concentration range of A in S quoted, in only a handful of in-

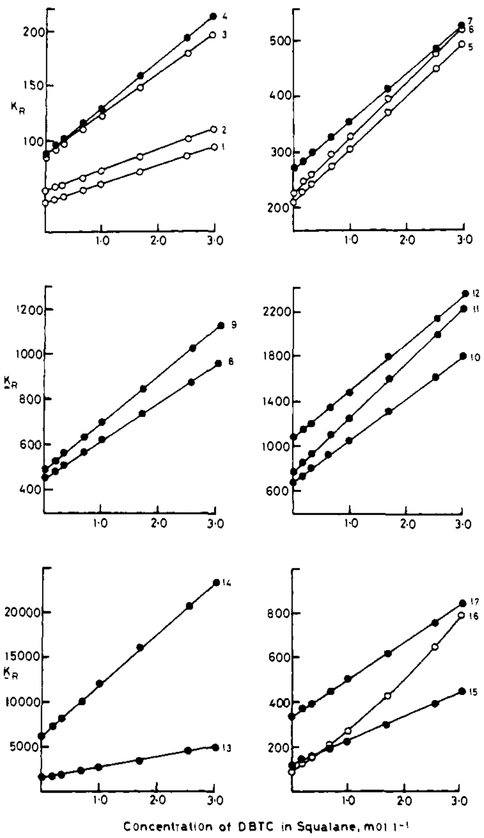

Figure 3. Plots of experimental K_R against molar concentration (mol $l.^{-1}$) of DNBT in squalane at 80.3°. Data of Eon, Pommier, and Guichon.[7] Solutes are: (1) 2-methylfuran; (2) 2,5-dihydrofuran; (3) benzene; (4) thiophene; (5) 2-methylthiophene; (6) 3-methylthiophene; (7) tetrahydrothiophene; (8) 2-ethylthiophene; (9) 2,5-dimethylthiophene; (10) 2-bromothiophene; (11) 3-bromothiophene; (12) 2,5-dichlorothiophene; (13) 2-iodothiophene; (14) 3,4-dibromothiophene; (15) 1-methylpyrrole; (16) pyrrole; (17) 2-chlorothiophene.

stances are data listed that allow both $K_{R(A)}{}^0$ and $K_{R(S)}{}^0$ to be calculated. In support of our findings we present here that selection of results for "complexing" studies which requires no recalculation, assumption, or additional measurement. We propose to deal with other work than this on another occasion.

First, the only fully comprehensive complexing study ($x_A = 0-1$) known to us is that of Eon, Pommier, and Guichon.[7] These workers studied the solvent DNBT/squalane at 80.3° with each of the solutes: 2-methylfuran, 2,5-dihydrofuran, benzene, thiophene, 2-methylthiophene, 3-methylthiophene, tetrahydrothiophene, 2-ethylthiophene, 2,5-dimethylthiophene, 2-chlorothiophene, 2-bromothiophene, 3-bromothiophene, 2,5-dichlorothiophene, 2-iodothiophene, 3,4-dibromothiophene, pyrrole, and 1-methylpyrrole. There is no doubt that current theory would predict substantial evidence of chemical complexing and Eon et al.[7] list values of K_1 evaluated from the data via eq 5. These authors, however, carried out their evaluations entirely in terms of mole fraction rather than molarity of A and assumed that the pronounced curvature of the plots of K_R against x_A derived from real properties of the system. Figure 3 shows their data replotted as K_R against C_A and we see remarkable confirmation of our own results in all but one instance (pyrrole). The curvature in the K_R/x_A plots, for which a substantial theoretical basis was developed by Eon et al., is, thus, no more than the arithmetic consequence of the concentration dependent interrelation of x with either C or ϕ. We may thus now add a further 17 systems compatible in behavior with our own.

Table II. Comparison of Experimental Values of K_1 (l. mol^{-1}) with Values Calculated via Equation 6[a]

	30°C		40°C		50°C	
	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
	Di-*n*-octyl Ether/*n*-Heptadecane					
Methanol[15]	1.52	1.56	1.30	1.29	0.94	0.91
Ethanol	1.02	1.05	0.86	0.85	0.69	0.67
n-Propyl alcohol	0.98	1.00	0.81	0.81	0.67	0.65
Isopropyl alcohol	0.78	0.80	0.62	0.62	0.52	0.51
n-Butyl alcohol	0.99	1.02	0.77	0.77	0.61	0.60
2-Butanol	0.99	1.02	0.77	0.76	0.64	0.62
sec-Butyl alcohol	0.69	0.71	0.53	0.52	0.44	0.43
tert-Butyl alcohol	0.53	0.56	0.42	0.42	0.35	0.34
	Di-*n*-octyl Ether/*n*-Octadecane					
n-Propyl[16] alcohol	1.20	1.22	0.97	0.95	0.80	0.76
Isopropyl alcohol	0.90	0.92	0.75	0.74	0.64	0.60
n-Butyl alcohol	1.15	1.17	0.93	0.91	0.77	0.73
Isobutyl alcohol	1.15	1.17	0.93	0.91	0.76	0.72
sec-Butyl alcohol	0.77	0.79	0.64	0.63	0.54	0.51
tert-Butyl alcohol	0.62	0.64	0.52	0.51	0.44	0.42
CH_2Cl_2[17]	0.28	0.30	0.26	0.26	0.24	0.23
CH_2BrCl	0.29	0.31	0.26	0.26	0.24	0.23
CH_2Br_2	0.30	0.31	0.27	0.27	0.25	0.24
$CHCl_3$	0.39	0.41	0.35	0.35	0.31	0.29
$CHBrCl_2$	0.41	0.42	0.36	0.36	0.32	0.31
$CHBr_2Cl$	0.42	0.43	0.36	0.36	0.32	0.30
$CHBr_3$	0.41	0.43	0.37	0.37	0.33	0.31
CCl_4	0.07	0.08	0.06	0.07	0.06	0.06
$CBrCl_3$	0.11	0.12	0.09	0.10	0.08	0.08
CBr_4	0.12	0.14	0.11	0.12	0.09	0.09
1,1,1-$C_2H_3Cl_3$	0.10	0.12	0.10	0.10	0.09	0.09

[a] Experimental data of Martire et al.[15-17]

Second, Martire and his coworkers,[15-18] although working only over limited ranges of C_A, have fortunately, and consistently, recorded values of $K_{R(A)}{}^0$ as well as of $K_{R(S)}{}^0$ and $\bar{V}_A$, in their published works. We are thus able to calculate via eq 6 the values of K_1 they might have expected to find via their variant of eq 5, a variant incidentally that can be derived without assumption from eq 2. Tables II-IV list their published values and those that we calculate from their solubility data. It is clear that, to well within any reasonable estimate of experimental error, the calculated and published values are in excellent agreement. We are thus able to introduce a further 58 systems (and each at three temperatures, Tables II-IV) into agreement. Not only, therefore, have we now more than 90 cases of compatible and predictable behavior, the types of system involved range widely in that the data presented here include not only charge-transfer complexes of various types but hydrogen-bonding systems which, between them, cover the range of alleged K_1 between 0.05 and 3 l. mol^{-1}. It must be concluded that our findings are at least sufficiently general that they cover all GLC liquid systems (but one) in which a mixture of large inert molecules and large electron acceptor (donor) molecules dissolves small electron donor (acceptor) molecules.

We may now consider the more obvious implications of the conclusions. Perhaps the most unexpected feature of eq 2 is that it is precisely the result to be derived for the model

Table III. Comparison of Experimental Values of K_1 (l. mol^{-1}) with Values Calculated via Equation 6[a]

	30°C		40°C		50°C	
	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
			Di-*n*-octyl Thioether/*n*-Octadecane			
n-Propyl[16] alcohol	0.72	0.66	0.63	0.59	0.56	0.52
Isopropyl alcohol	0.60	0.55	0.53	0.49	0.48	0.44
n-Butyl alcohol	0.72	0.66	0.63	0.58	0.55	0.51
Isobutyl alcohol	0.74	0.68	0.62	0.57	0.53	0.49
sec-Butyl alcohol	0.54	0.50	0.49	0.45	0.43	0.40
tert-Butyl alcohol	0.48	0.44	0.42	0.39	0.38	0.35
CH_2Cl_2[17]	0.36	0.33	0.33	0.31	0.29	0.27
CH_2BrCl	0.41	0.37	0.38	0.35	0.33	0.30
CH_2Br_2	0.45	0.42	0.42	0.40	0.37	0.35
$CHCl_3$	0.42	0.38	0.38	0.35	0.31	0.29
$CHBrCl_2$	0.50	0.46	0.45	0.42	0.37	0.35
$CHBr_2Cl$	0.61	0.56	0.55	0.51	0.46	0.43
$CHBr_3$	0.73	0.67	0.65	0.60	0.52	0.49
CCl_4	0.14	0.12	0.13	0.12	0.11	0.10
$CBrCl_3$	0.29	0.27	0.27	0.25	0.23	0.21
CBr_4	0.93	0.85	0.80	0.74	0.59	0.55
1,1,1-$C_2H_3Cl_3$	0.16	0.15	0.15	0.14	0.13	0.12

[a] Experimental data of Martire et al.[16,17]

Table IV. Comparison of Experimental Values of K_1 (l. mol^{-1}) with Values Calculated via Equation 6[a]

	30°C		40°C		50°C	
	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
			Di-*n*-octylmethylamine/*n*-Octadecane			
n-Propyl[16] alcohol	2.47	2.51	1.91	1.92	1.48	1.47
Isopropyl alcohol	1.53	1.55	1.23	1.23	0.98	0.97
n-Butyl alcohol	2.41	2.45	1.85	1.86	1.43	1.41
Isobutyl alcohol	2.53	2.57	1.92	1.93	1.46	1.44
sec-Butyl alcohol	1.34	1.37	1.07	1.07	0.84	0.84
tert-Butyl alcohol	0.89	0.91	0.73	0.74	0.60	0.59
CH_2Cl_2[18]	0.21	0.21	0.18	0.18	0.16	0.16
CH_2BrCl	0.22	0.23	0.20	0.20	0.18	0.17
CH_2Br_2	0.25	0.26	0.22	0.23	0.20	0.20
$CHCl_3$	0.47	0.48	0.39	0.40	0.33	0.33
$CHBrCl_2$	0.51	0.53	0.43	0.43	0.36	0.35
$CHBr_2Cl$	0.58	0.60	0.50	0.49	0.43	0.41
$CHBr_3$	0.64	0.66	0.54	0.55	0.46	0.45
CCl_4	0.06	0.07	0.06	0.06	0.06	0.05
$CBrCl_3$	0.21	0.22	0.18	0.18	0.15	0.15
1,1,1-$C_2H_3Cl_3$	0.07	0.08	0.06	0.06	0.06	0.06

[a] Experimental data of Martire et al.[16,18]

wherein solute D is partitioned between the gas phase and a liquid mixture of two totally immiscible liquids. Following this analogy through, it is obviously also the equation derivable if A and S form an ideal solution since, in such a solution, there is no specific interaction of A and S. Finally, the equation can be derived for a nonideal solution of A and S provided that we assume that the activity coefficient of D with respect to either A or S in a mixture is exactly that pertaining to pure A or pure S. This latter situation is clearly the more realistic since our values of $K_{R(A)}{}^0$ and $K_{R(S)}{}^0$ yield solute activity coefficients ranging over nearly an order of magnitude around unity. We thus indicate only this derivation.

Starting with the simplest version of the solution equation

$$p/p^0 = \gamma x$$

we can write

$$p_D/p_D{}^0 = \gamma_{DA}x_{DA} = \gamma_{DS}x_{DS} = \gamma_{DAS}x_{DAS}$$

where the subscripts refer to parameters for D alone or in pure A, pure S, or A + S mixtures, respectively. Following this we may write

$$x_{DA} = n_{DA}/n_A \text{ and } x_{DS} = n_{DS}/n_S$$

while

$$x_{DAS} = (n_{DA} + n_{DS})/(n_A + n_S)$$

where *n* designates moles. Since

$$1/\gamma_{DAS} = (p_1{}^0/p_1)[(n_{DA}/n_A + n_S) + (n_{DS}/n_A + n_S)]$$

substitution for n_{DA} and n_{DS} immediately yields eq 7 and, hence of course, eq 2.

We thus see that the foregoing model, or that of total immiscibility of A and S, offers an account of our findings. We have failed completely to derive any equation remotely like, or as simple as, eq 2, on the basis of any current theory.

The above now poses a problem of substantial dimensions. Since our simple solution model provides a perfect quantitative description of a large number of complexing systems over the whole range of mixture composition, is there in fact any complexing (in the conventional definition) occurring at all? We cannot ignore the fact that for a number of the systems quoted here there is either uv-visible or infrared spectroscopic evidence for complexing. On the other hand, we must recognize that the overwhelming mass of evidence in the area of weak complexing is inferential, being based almost entirely on behavior in accord with eq 5 or its spectroscopic analog, i.e., on the characteristics of the system as a function only of dilution of reactants. Two alternatives are thus open to us. If we regard complexing, in the conventional sense, as occurring, then the degree of complexing is apparently not altered by dilution of A by S; hence, conventional partition and spectroscopic equations cannot then provide a basis for evaluation of a meaningful K_1. This view, it seems, must lead us to conclude that there is not random mixing in A + S mixtures, but rather a high degree of aggregation such that the *local* concentration of A is always that corresponding to pure A. In contrast, we may choose to regard solution interactions in a much broader way than has heretofore been the case, and complexing then only as the more energetic end of a spectrum of solution interactions. The associated spectroscopic phenomena would then require to be reinterpreted since, in this view, they normally would be associated with, presumably, spurious values of K_1.

We have reviewed in this paper the readily available data for GLC studies and our findings therefore may be thought to relate to systems of a rather specific nature. Even so, we have uncovered a very large number of solvent systems showing remarkable simplicity of solution behavior, and it seems likely that, when the requisite data become available, the residue of published GLC data may well also be found to conform.

Irrespective of any eventual detailed interpretation of this work, it seems clear that the findings illuminate important and entirely novel aspects of the theories both of nonelectrolyte solutions and of weak molecular complexing.

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Solution and Complexing Studies. II. Comparison and Correlation of Nuclear Magnetic Resonance and Gas–Liquid Chromatographic Data

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Abstract: An NMR study of the effects of adding chloroform, 1,2-dichloroethane, benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene to both di-*n*-octyl ether (DNOE)/*n*-heptadecane and di-*n*-butyl tetrachlorophthalate (DNBT)/squalane mixtures at 30° has been carried out. Both solvent systems are miscible over the whole concentration range. Conventionally evaluated complexing stability constants (equilibrium quotients) are shown to be relatively inconsistent and to correlate poorly with corresponding GLC based data. A model based on partitioning of the voltatile electron donors between notionally immiscible electron acceptor and inert solvent mixture components leads to an equation relating chemical shifts with the relevant partition coefficients. This, in turn, leads to an equation connecting chemical shifts with GLC determined partition coefficients which provides a remarkable correlation of the data. This correlation provides a means to predict chemical shifts quantitatively from solution data. The evidence raises serious questions as to the meaning of NMR evaluated stability constants and indicates a need to reconsider theories of both nonelectrolyte solutions and of weak molecular complexes.

The measurement of stability (formation) constants, or more correctly equilibrium quotients, of chemical complexes by the NMR method is now well established and widespread. In essence, the method consists in measuring chemical shifts as a function of concentration of one or the other of the reactants A and D in an inert solvent S. If, for arguments sake, we consider the situation wherein the concentration of D in S is held constant then, for a 1:1 complex, the stability constant (K_1) for formation of AD is related to the chemical shifts via

$$1/\Delta = (1/K_1\Delta^0 C_A) + (1/\Delta^0) \tag{1}$$

where Δ^0 is the chemical shift difference ($\delta_S{}^0 - \delta_{AD}$), Δ is the difference ($\delta^0{}_S - \delta$) where δ is the measured shift, and C_A is the molar concentration of A. This equation is formally identical with the Benesi–Hildebrand equation which is used to process conventional spectroscopic data and, like the latter, may be reorganized into one or another of several forms for the purpose of graphical or numerical evaluation of K_1 from the data.

Several studies of weak molecular complexing involving concurrent use of both GLC and spectroscopic methods have been reported.[1-4] Only rarely have the quantitative data agreed even approximately and there are numerous examples of negative values of K_1 derived from the spectroscopic data; in general, GLC and NMR data are in serious conflict and there is only poor correlation between NMR and uv-visible data as well. On account of this we have elsewhere[2] suggested that GLC data are, on the whole, more likely to be reliable but that this, in itself, does not establish the validity even of these data. The findings with respect to GLC measured values of K_1 reported in part I[5] must add further to our concern regarding the above discrepancies. We have, thus, undertaken an NMR study of most of the GLC systems discussed in part I.

Experimental Section

Measurements were made with a Varian HA100D spectrometer operating at 100 MHz for ^{1}H. Sweep width calibration was carried out with a signal generator and a Varian V4315 frequency counter. The variable temperature controller was calibrated by following the separation of the two major peaks of the glycol spectrum.

Chemical shifts were measured via the reciprocals in order to improve precision. Water-free acetone was used as an external reference.

Results

Data were processed, via least-squares computer programs, to evaluate K_1 via eq 1 and its commonly preferred alternative formulations due to Scott[6] and Foster.[7] The latter two procedures yielded essentially the same result in most instances but a substantial difference from this was commonly noted in the value derived via eq 1. The reasons for this have been discussed on many occasions and need no repetition.