Correlation of Stability Constants of Hydrocarbon Complexes with Silver Nitrate in Ethylene Glycol

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A correlation method suggested by a micropartition (MP) model of solution is applied to published g.l.c.-derived data for the stoicheiometric stability constants of a range of C_4—C_6 unsaturated hydrocarbons with Ag^+ in solution in ethylene glycol. The correlation is successful for 11 families of compounds, although the grouping within families is unexpected. On the basis of this correlation it is shown that true stability constants are almost certainly greater than the values customarily cited for Ag^+–unsaturated compound pairs and a route to quantitative evaluation of ' solvent effects ' is indicated.

We have shown recently [1-5] that for all non-interacting, charge-transfer, or hydrogen-bonding systems so far studied by the chromatographic method for which the necessary calculations may be performed, equation (1)

$$K_R = \phi_A K^{\circ}_{R(A)} + \phi_S K^{\circ}_{R(S)} \qquad (1)$$

is obeyed to, at worst, ±10%, and in most known instances to within experimental error. K_R is the g.l.c. infinite-dilution liquid–gas partition coefficient of a volatile solute, D, with a binary stationary-phase mixture composed of liquid A (presumed to be reactive towards D) and an ' inert ' solvent, S. $K^{\circ}_{R(A)}$ and $K^{\circ}_{R(S)}$ represent the corresponding solute partition coefficients with pure A and pure S, respectively, and ϕ defines a volume fraction. Since, for all systems quoted,[1-5] excess volumes of mixing were essentially trivial, equation (1) reduces to (2) where c_A is the molar concentration of A in the solvent mixture, $\bar{V}_A$ is the molar volume of pure A, and $\Delta K^{\circ}_R = K^{\circ}_{R(A)} - K^{\circ}_{R(S)}$.

$$K_R = K^{\circ}_{R(S)} + c_A \bar{V}_A \Delta K^{\circ}_R \qquad (2)$$

The conventional g.l.c. equation for evaluating stability constants, $K_1^{\text{expt.}}$, from the data for a 1 : 1 complexing reaction $A + D \rightleftharpoons AD$ is (3). Comparison

$$K_R = K^{\circ}_{R(S)} (1 + K_1^{\text{expt.}} c_A) \qquad (3)$$

of equations (2) and (3) then allows the identification (4). Since, as stated, we have also shown that all non-

$$K_1^{\text{expt.}} = \bar{V}_A \Delta K^{\circ}_R / K^{\circ}_{R(S)} \qquad (4)$$

complexing systems studied by g.l.c. *also* obey equations (1) and (2), there is clearly ambiguity as to the actual meaning of $K_1^{\text{expt.}}$.

To account for these phenomena, we have proposed a microscopic partition (MP) model of solutions and have

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[1] J. H. Purnell and J. M. Vargas de Andrade, *J. Amer. Chem. Soc.*, 1975, **97**, 3585.

[2] J. H. Purnell and J. M. Vargas de Andrade, *J. Amer. Chem. Soc.*, 1975, **97**, 3590.

[3] R. J. Laub and J. H. Purnell, *J. Amer. Chem. Soc.*, 1976, **98**, 30.

[4] R. J. Laub and J. H. Purnell, *J. Amer. Chem. Soc.*, 1976, **98**, 35.

[5] R. J. Laub, D. E. Martire, and J. H. Purnell, *J.C.S. Faraday II*, 1978, 213.

shown[3,4] that if complexing between A and D is regarded as occurring in a given system then, according to the foregoing, the true stability constant, K_1^t, is related to $K_1^{\text{expt.}}$ by (5). Here, $K^{\circ,t}_{\text{R(A)}}$ is the true partition coefficient for non-complexed (free) D between pure A and the gas phase, and $\Delta K^{\circ,t}_{\text{R}} = K^{\circ,t}_{\text{R(A)}} - K^{\circ,t}_{\text{R(S)}}$. For simplicity in this and subsequent discussions we set $K^{\circ,t}_{\text{R(S)}} = K^{\circ}_{\text{R(S)}}$ since we know of no systems for which complexing of a third component with two supposedly interacting liquids in admixture has been studied or implied by the results.

$$K_1^{\text{expt.}} = \frac{\bar{V}_{\text{A}}\Delta K^{\circ,t}_{\text{R}}}{K^{\circ}_{\text{R(S)}}} + \frac{K_1^t K^{\circ,t}_{\text{R(A)}}}{K^{\circ}_{\text{R(S)}}} \qquad (5)$$

$$K_1^{\text{expt.}} = \frac{\bar{V}_{\text{A}} K^{\circ,t}_{\text{R(A)}}\,(1 + K_1^t/\bar{V}_{\text{A}})}{K^{\circ}_{\text{R(S)}}} - \bar{V}_{\text{A}} \qquad (6)$$

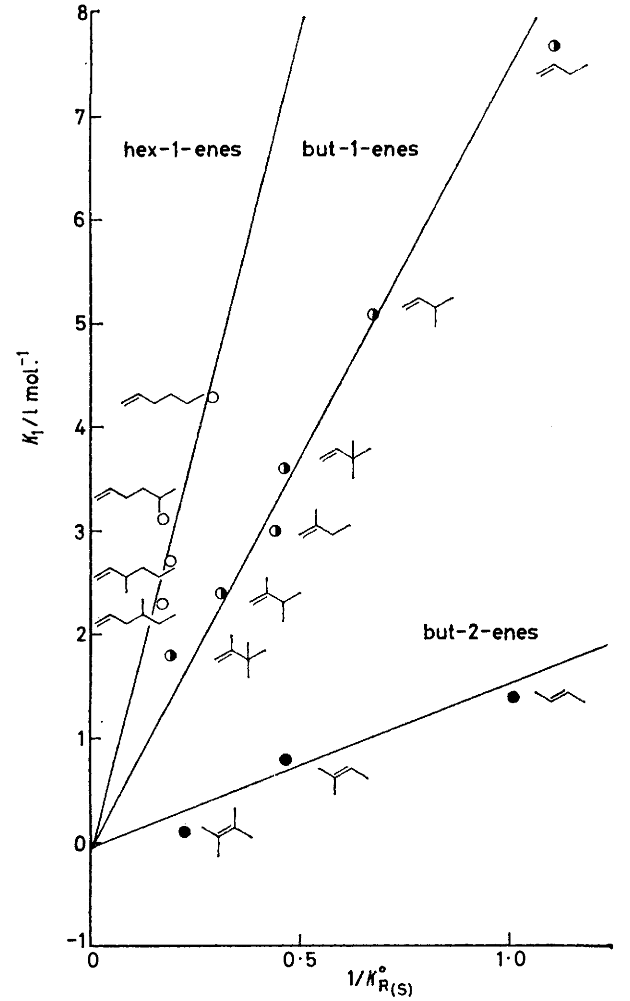

FIGURE 1 Plots of $K_1^{\text{expt.}}$ against $1/K^{\circ}_{\text{R(S)}}$ for but-1-enes, but-2-enes, and hex-1-enes with silver nitrate in ethylene glycol at 40 °C

Rearrangement of equation (5) yields (6) from which we see that the current hypothesis can be tested by plotting data in the form, $K_1^{\text{expt.}}$ against $1/K^{\circ}_{\text{R(S)}}$, since equation (6) predicts linearity and an intercept, $-\bar{V}_{\text{A}}$. Evidence for the applicability of equation (6) will, evidently, provide support for the MP theory but, in addition, will give us an initial approach to the quantitative assessment and identification of solvent effects in complexing systems. Unfortunately, the literature presently provides very few data suitable, and of sufficient accuracy, for this test. The literature does, however, contain several papers (*cf.* ref. 6) listing g.l.c.-measured values of $K_1^{\text{expt.}}$ for reaction of Ag^+ in ethylene glycol with a wide range of olefins, dienes, trienes, aromatic, and some cyclic unsaturated compounds. The two main sources[7,8] disagree somewhat in the quantitative values quoted for the same systems and there is also disagreement as to the consequences of salt effects. Thus, the majority of the data can be regarded as liable to some degree of error. Even so, consideration of equation (6) suggests that if there is any consistency in the data, *e.g.*, among homologues or otherwise related

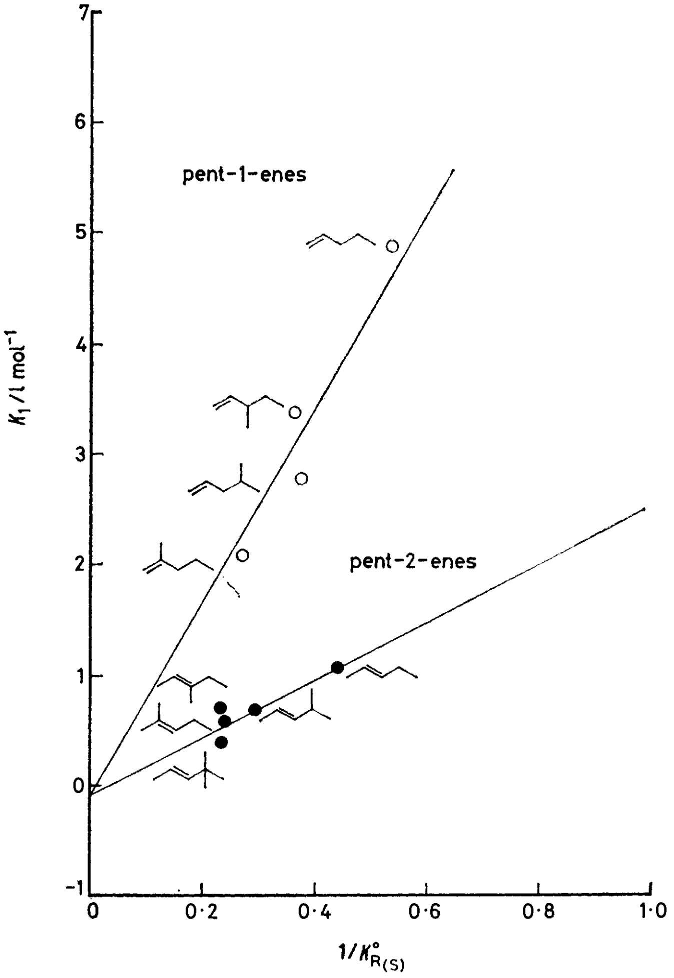

FIGURE 2 Plots of $K_1^{\text{expt.}}$ against $1/K^{\circ}_{\text{R(S)}}$ for pent-1- and -2-enes with silver nitrate in ethylene glycol at 40 °C

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[6] C. A. Wellington, *Adv. Analyt. Chem. Instrumen.*, 1973, **11**, 237.

[7] M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, 1962, **84**, 4697.

[8] R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Amer. Chem. Soc.*, 1965, **87**, 1827.

groups, it might be revealed by an appropriate plot. From the very large volume of available data we have identified a number of such relationships.

Family $K^{\circ}_{R(A)}$ values for Figures 1—4

	Family	$K^{\circ}_{R(A)}$
1	Prop-1-enes	1.6
2	But-1-enes	7.6
3	Pent-1-enes	8.8
4	Hex-1-enes	16
5	Pent-2-enes	2.6
6	Pent-2-yne	23
7	Hexynes	38
8	Heptynes	56
9	Octynes	60
10	Cyclopentene, methylenecyclopentane	43
11	Cyclopentenes, ethylidenecyclopentane	18
12	Cyclohexenes, ethylidenecyclohexane	56

Figures 1—4 show data for 12 distinct groups of compounds, where the lines have been drawn to intercept at the value of $-\bar{V}_A$, *i.e.*, the nominal molar volume of 'liquid' $AgNO_3$ that we deduced from measurements of the densities of $AgNO_3$–ethylene glycol mixtures at the relevant temperature. The Table lists the (hypothetical) $K^{\circ}_{R(A)}$ values for each family. There seems little doubt, given the uncertainties in the values of $K_1^{expt.}$ that the data lie close to, if not on, the lines drawn. Further, of course, the compounds associated with any line are very obviously related in structural terms.

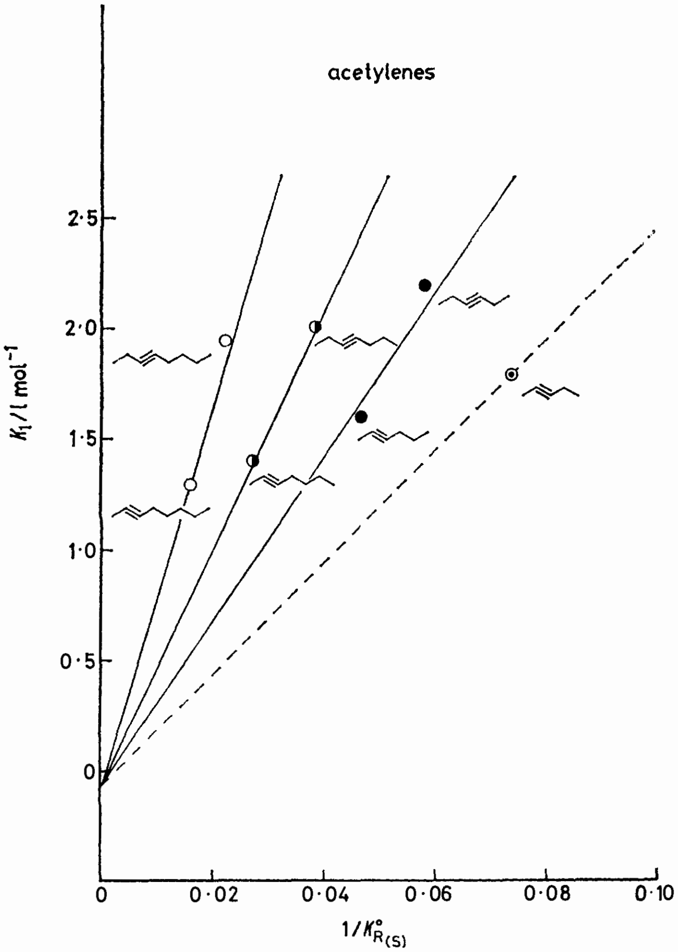

FIGURE 3 Plots of $K_1^{expt.}$ against $1/K^{\circ}_{R(S)}$ for acetylenes with silver nitrate in ethylene glycol at 40 °C

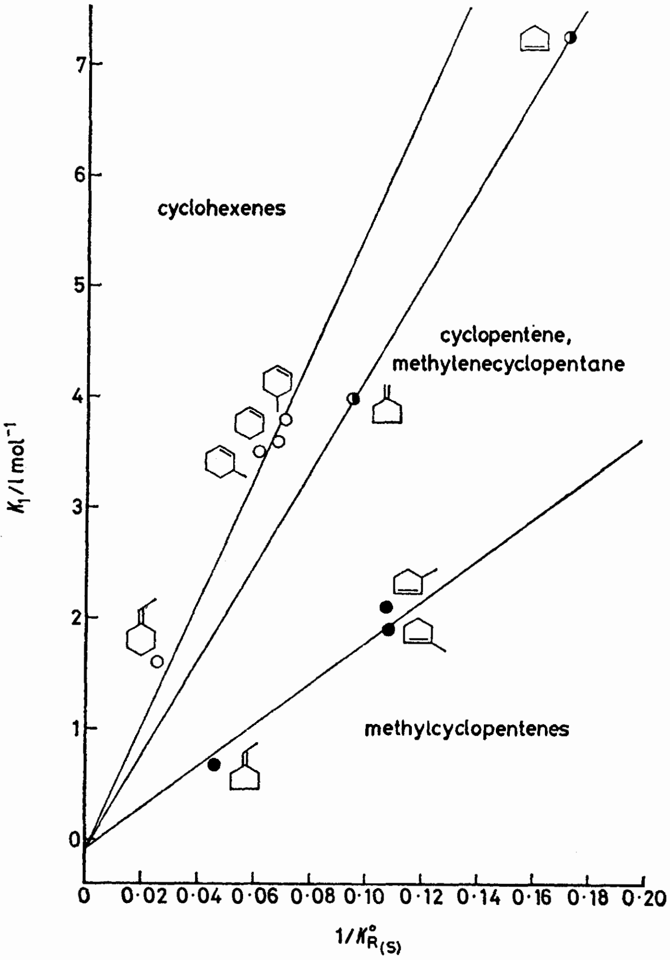

FIGURE 4 Plots of $K_1^{expt.}$ against $1/K^{\circ}_{R(S)}$ for cyclohexenes, cyclopentenes, and methylenecyclopentane with silver nitrate in ethylene glycol at 40 °C

The implications of Figures 1—4 seem clear since there can be little doubt that 1 : 1 complexing occurs. Hence, all members of a family have the same value of $K^{\circ}_{R(A)} = [K^{\circ,t}_{R(A)}(1 + K_1^{t})]$, *i.e.* they have identical solubility in the uncomplexed form in 'liquid' $AgNO_3$, irrespective of differences in saturation vapour pressure. Since we would expect $K^{\circ,t}_{R(A)}$ to be defined by an equation such as that normally used in g.l.c., *viz.*, (7) it would not be

$$K^{\circ}_{R(A)} = \frac{RT}{P_1^{\circ}\gamma_1^{\infty}\bar{V}_A} \tag{7}$$

expected that $K^{\circ,t}_{R(A)}$ would be constant within families. Thus, the family constancy of $K^{\circ}_{R(A)}$ values implies that $K^{\circ}_{R(A)} \simeq K^{\circ,t}_{R(A)}\ K_1$. Since $K^{\circ,t}_{R(A)}$ must be very small, K_1^{t} must be very much larger than the evaluated $K_1^{expt.}$. This obviously makes sense since the few available $K_1^{expt.}$ values measured in aqueous solution are, indeed, substantially larger than are those found in ethylene glycol solution. The interesting feature, then, is the implied relationship of $K^{\circ,t}_{R(A)}$ and K_1. These quantities are, respectively, defined by (8) and (9) where the subscript soln refers to ' liquid ' $AgNO_3$.

$$K_1{}^t = \frac{(\text{Complex})_{\text{soln}}}{(\text{Ag}^+)_{\text{soln}}(\text{Hydrocarbon})_{\text{soln}}} \qquad (8)$$

$$K^{\circ,t}_{\text{R(A)}} = \frac{(\text{Hydrocarbon})_{\text{soln}}}{(\text{Hydrocarbon})_{\text{gas}}} \qquad (9)$$

Thus, in the present context equation (10) is implied which demands that the concentration quotient is constant for all members of a family. In effect, this is a form of buffering action.

$$K^{\circ}_{\text{R(A)}} \simeq K_1{}^t K^{\circ,t}_{\text{R(A)}} = \frac{(\text{Complex})_{\text{soln}}}{(\text{Ag}^+)_{\text{soln}}(\text{Hydrocarbon})_{\text{gas}}} \qquad (10)$$

Conclusions.—We have shown in this paper, insofar as the data allow, that where complexation is universally accepted to be occurring, *i.e.* olefins with $AgNO_3$ dissolved in ethylene glycol, structurally related olefins, acetylenes, and cyclic unsaturated hydrocarbons show family behaviour for a given solvent with Ag^+. We are not aware of any previous demonstration of a coherent relationship for such systems. Furthermore, the families are of a totally unexpected nature in that they are not homologous series. For olefins, the position of the double bond and the number of carbon atoms in the parent compound skeleton defines a family, methyl substitution at any point therein seemingly forming daughter compounds of the series. For acetylenes, the length of the carbon skeleton determines a family, the position of the triple bond within a given skeleton determining members of that family. A family of cyclic olefins is defined by the number of carbon atoms in the ring and a double bond within or adjacent to that ring. In the case of cyclohexenes, methyl-substituted compounds are included in the family sired by cyclohexene. In contrast, methyl-substituted cyclopentenes form a separate family from cyclopentene and ethylidenecyclopentane.

The above finding of coherent behaviour according to equation (6) offers support of the microscopic partition model of diachoric solutions which we have recently proposed. In addition, new information concerning complexation with ionic salts has been presented which indicates that a re-evaluation of the heretofore offered explanation of such phenomena is in order. Preliminary work by us, for example, indicates that the curvature of K_{R} *versus* c_{A} plots for olefins with silver nitrate in either ethylene glycol or water may well be attributable to an excess mixing volume of solution of $AgNO_3$ rather than the ' salting out ' or ' ionic strength ' effects previously supposed to account wholly for the observations.

The inability to separate the terms, $K_1{}^t$ and $K^{\circ,t}_{\text{R(A)}}$ in equation (5) remains as a major difficulty in the identification of the strength of true charge transfer interactions, but if such a separation of terms *was* feasible, it would immediately be possible to explain quantitatively, among other things, the enormous variation of $K_1{}^{\text{expt.}}$ from one solvent to the next and from one technique to the other. What certainly appears to emerge from this analysis is that the true stability constants are very much larger than is currently supposed, *i.e.*, complexing is stronger. That this may also be true of many supposed ' weak ' molecular complexes must, on the same basis, be seriously considered.

We thank the Foxboro Co., Foxboro, Massachussetts and the S.R.C. for financial support for R. J. L.

[7/1839 *Received*, 19*th October*, 1977]