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STABILITY CONSTANTS OF HYDRACID–TRIBUTYL PHOSPHATE COMPLEXES IN ALKANE SOLUTION: HYDROCHLORIC ACID AND HYDROGEN CYANIDE

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SUMMARY

The gas chromatographic technique of elution by characteristic point (ECP) has been used to determine the stoichiometric stability constants (K_1) of complexes of both hydrochloric acid and hydrogen cyanide with tributylphosphate (TBP) in hexadecane solution. The study covered the temperature range 25–65°C and the concentration ranges in solution: TBP (0–1.1 *M*) and acids (0–0.3 *M*). Values of K_1 determined ranges between 20 and 120 l mol⁻¹ depending on conditions. An extension of gas–liquid chromatographic theory to take into account dilution of solvent and depletion of TBP (due to the large K_1 prevailing) at high acid levels is presented and its validity demonstrated. This will allow correction for purely formal effects to be made in future studies of this type.

The results are shown to be of high accuracy and, hence, both to provide a secure reference base for further studies and to establish ECP as a technique of wide applicability, and relative practical simplicity, for the investigation of systems of large K_1 at finite (practical) concentrations.

Measurements for the acids in hexadecane alone allow estimation of the enthalpy of vaporisation of hydrochloric acid around its critical temperature as 3.8 kcal mol⁻¹, and of monomeric hydrogen cyanide (25–65°C) as 2.4 kcal mol⁻¹. The latter figure implies an enthalpy associated with the hydrogen-bonding polymerisation of liquid hydrogen cyanide of 3.6 kcal mol⁻¹.

INTRODUCTION

The earliest quantitative study of a complexation reaction by a gas chromatographic technique appears to be that of Du Plessis and Spong¹ who determined the stoichiometry of a silver ammine complex via elution of ammonia from a silver nitrate column. Significant advance, however, came with the work of Gil-Av and Herling² who derived the equation, for 1:1 complex stoichiometry, linking the infinite dilution partition coefficient (K_R^∞) of a volatile complexer (A) with the stability constant (K_1) and the concentration (c_B°) of complexing agent (B) in the column solvent. Shortly thereafter, Purnell³, presented a general treatment allowing evaluation of stability

constants from retention data for complexes of any type and stoichiometry. These equations have formed the basis of the many studies since conducted. Reported work has been entirely confined to the condition of infinite dilution of the volatile ligand and, further, with only a few notable exceptions, such as the work of Schurig *et al.*⁴, to weak complexes (K_1 ca. 1 l mol^{-1}). There is no reason to be bounded by these constraints as we show later.

The construction of adsorption isotherms from gas–solid chromatographic (GSC) elution data is a process of long standing, having been pioneered by Glueckauf⁵, James and Phillips⁶ and Gregg and Stock⁷ in the 1940s and 1950s. Its more widespread use, however, followed the comprehensive investigations of Cremer⁸, Cremer and Huber^{9–10} and of Huber and Keulemans¹¹ who concentrated on the technique later designated “elution by characteristic point” (ECP) by Conder and Purnell^{12–15}. The latter developed a general theory of chromatographic retention applicable at all solute concentrations to all forms of chromatography and which took into account all the equilibrium and kinetic processes that contribute to band shape and retention. They characterised a number of variants of technique¹⁵ which could provide partition data and showed how these would be extracted from the raw data. The treatment also indicated the experimental requirements for elimination of some or other of the non-ideal processes that contribute to the elution process.

In the ECP technique, two such processes dominate. First, the compression of carrier gas. In practice, this is minimised, and the associated approximations validated, by use of very small pressure drops (short columns, coarse packing). Secondly, the sorption effect which arises because of changes of localised mobile phase velocity over the solute band and which leads to skewing in the direction of the band front. This process is minimised by working in conditions where the solute partial pressure in the carrier (p) is small (large K_R).

Given these conditions are met, the necessary data for the determination of partition coefficients as a function of sample size (concentration) can be evaluated directly from the chromatograms via the equations:

$$q = n_A S_A / V_L S_t \quad (1)$$

where q (mol. vol.⁻¹) is the amount of sample sorbed per unit volume of liquid, and n_A is the number of moles injected. S_A is the area of the chromatographic trace comprising the sum of (i) the rectangle of peak height (h) and length ($t - t_d$), the distance from the dead volume to peak maximum and (ii) the residual area of the trailing side. S_t is the area bounded by the peak itself. For the gas phase, the concentration c is given by

$$c = n_A s h / S_t F_c \quad (2)$$

where s is the chart speed and F_c is the fully corrected carrier flow-rate. Obviously consistent units must be used throughout. It is then found that

$$K_R = q/c = c_l/c_g$$

It is an elegant aspect of ECP that, provided n_A is known accurately, detector calibration is unnecessary.

We now turn to an important issue that does not seem to have been addressed previously. In GSC, V_L is replaced in eqn. 1 by adsorbent weight (w_s) which remains constant at all solute concentrations since adsorbent surface area is invariant. In gas-liquid chromatography (GLC), however, the liquid (solvent) volume increases as the amount of volatile sample rises. Thus, K_R will appear to change for reasons that have nothing to do with non-ideality of solution but because of the way in which we define K_R . This must, therefore, be allowed for.

Further, in strongly complexing systems, where solubility is essentially determined by complexation, as the volatile reactant concentration increases at fixed concentration of the complexing solvent, there is progressively less free solvent to dissolve both complex and uncomplexed ligand. We show later how these effects can be allowed for.

Tributyl phosphate [TBP = (BuO₃)PO] is remarkable in that it complexes with a huge range of substances, sometimes very weakly but, more often, very strongly. It is also soluble in many organic liquids whilst also dissolving water via formation of a discrete complex or complexes. In consequence, it is very widely used as an extractant in counter-current and related purification processes. Since it does not have a dissociable proton it can act as a Bronsted base and form, as the ligand, very strong complexes with acids. In aqueous solutions, it is thought¹⁶ that hydrogen chloride, for instance, is bound in complexes of the type [(BuO)₃PO]HCl · (H₂O)₃ or [(BuO)₃PO]₂HCl · (H₂O)₆. In wet organic phases, however, the species present is thought¹⁷ to be the ion pair [H(H₂O)₄]⁺[X(TBP)_x]⁻, X typically being Cl, Br, etc. In anhydrous systems the evidence¹⁶ is clear that the TBP-acid stoichiometry is 1:1 which means that the complex may be represented as [(BuO)₃PO]HCl. Despite the widespread use and interest in TBP as an extractant, few measurements of the stability constants of its complexes have been reported. A notable exception¹⁸ is the GLC based study of TBP-alcohol complexes which yielded, effectively at infinite dilution, values for C₁-C₉ alcohols in the range 4.3-0.2 l mol⁻¹. These are, of course, quite small.

The aims of this work are thus threefold.

- (1) To illustrate how the GLC technique may be applied to complexing systems of very large K_1 .
- (2) To validate the use of the technique at finite volatile ligand concentrations.
- (3) To generate reliable values of K_1 for TBP-hydracid complexes as a basis for more extensive studies relating to systems of practical interest.

THEORY

Dilution effect on K_R

Let us take the simplest situation, that in which a solute (1) dissolves in solvent (2) with an activity coefficient (γ) that is concentration independent. Then we may write

$$p_1 = p_1^\circ \gamma_1 \frac{n_1}{n_1 + n_2}$$

where p_1 and p_1° represent the partial and saturation vapour pressures and n the number of moles.

Dividing top and bottom by $\Sigma V = V_1 + V_2$ gives, assuming ideal gas behaviour,

$$p_1 = p_1^\circ \gamma_1 c_1^l \frac{\Sigma V}{n_1 + n_2} = c_1^g RT$$

where c represents concentration in the indicated phase. Hence, the partition coefficient, K , is given by

$$K = c_1^l / c_1^g = \frac{n_1 + n_2}{\Sigma V} \frac{RT}{\gamma_1 p_1^\circ}$$

At infinite dilution of 1, as is well known,

$$K^\infty = \frac{RT}{\bar{V}_2 \gamma_1 p^\circ}$$

Hence, with γ_1 constant,

$$K = K^\infty \frac{n_1 + n_2}{\Sigma V} \bar{V}_2$$

Substituting throughout, $V/\bar{V} = n$, $V/\Sigma V = \phi$ and recognising that $\phi_1 + \phi_2 = 1$,

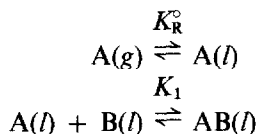
$$K = K^\infty \left[1 + \phi_1 \left(\frac{\bar{V}_2}{\bar{V}_1} - 1 \right) \right] \quad (3)$$

Thus, if $\bar{V}_2 > \bar{V}_1$, as will usually be the case in GLC, as ϕ_1 increases, K will appear progressively to exceed K^∞ . Thus, where γ values are constant, the variation of K will superficially imply concentration dependent non-ideal interaction where none exists. The factor in parentheses should therefore be used to correct K for this effect if the real effects of concentration on γ_1 (and/or γ_2) are to be isolated. Finally, we note that where, as in this work, the liquid complexer is dissolved in an unreactive solvent (diluent), \bar{V}_2 is the molar volume of the mixture, which can be directly measured.

Solvent depletion in complexation

Having already dealt with the dilution effect we can treat this problem initially as one in which the solvent system maintains constant volume.

Consider first the simple situation of a system of 1:1 stoichiometry described by



It is well known^{2,3} that at infinite dilution, the effective partition coefficient K_R is given by

$$K_R = K_R^{\circ} [1 + K_1 c_B^{\circ}] \quad (4)$$

where c_B° is the initial concentration of liquid-phase complexer. But, as the amount of A rises in the system, more and more of B is removed as AB, and since the model we are considering is one in which we vary the amount of A added and maintain c_B° at some fixed value, this must have an effect on K_R since the prevailing concentration, c_B , is not constant. At constant system volume

$$\Sigma V = V_{A(l)} + V_{B(l)} + V_{AB(l)} + V_{dil.}$$

When complexing is strong $V_{A(l)}$ is, of course, very small. Now,

$$\Sigma n_{A(l)} = n_{A(l)} + n_{AB(l)}$$

whence, dividing through by ΣV ,

$$\Sigma c_{A(l)} = c_{A(l)} + c_{AB(l)}$$

But

$$c_{AB(l)} = K_1 c_{A(l)} c_{B(l)},$$

while,

$$c_{B(l)} = c_B^{\circ} - c_{AB(l)}$$

and correspondingly,

$$c_{AB(l)} \gg c_{A(l)}$$

so, with little approximation,

$$\Sigma c_{A(l)} = c_{A(l)} + K_1 c_{A(l)} [c_B^{\circ} - \Sigma c_{A(l)}]$$

Dividing now by $c_{A(l)}$ we have

$$K_R = K_R^{\circ} [1 + K_1 (c_B^{\circ} - \Sigma c_{A(l)})]$$

When $\Sigma c_{A(l)}$ is small, this reduces to eqn. 4. Otherwise, we have

$$K_R = K_R^{\circ} [1 + K_1 c_B^{\circ}] - K_R^{\circ} K_1 \Sigma c_{A(l)} \quad (5)$$

Thus, in the absence of a dilution effect, we would expect a linear plot (of negative slope) of K_R against $\Sigma c_{A(l)}$, the latter is, of course, the quantity directly measured in ECP. We note that in the circumstances prescribed, the intercept is the value of K_R at some value of c_B° at infinite dilution of A while the slope is the negative value of that of the corresponding plot also at infinite dilution, *viz.* $K_R^{\circ} K_1$ (eqn. 4).

The combined effects

We see immediately that, when $\bar{V}_2 > \bar{V}_1$, the dilution effect (eqn. 3) increases K_R whereas the depletion effect (eqn. 5) reduces it. When both effects occur, as must be the case, we would then anticipate that a plot according to eqn. 5 would deviate in an upward direction from its initial linearity, *i.e.* the equation would appear to fail for purely formal reasons. Only if there were dramatic changes in the various activity coefficients would the converse occur.

Within the constraints of the approximations stated earlier, it is evident that we can allow for this by combining eqns. 3 and 5 to give

$$K_R = K'_R [1 + \phi_1 \left(\frac{\bar{V}_2}{\bar{V}_1} - 1 \right)] \quad (6)$$

where K'_R is the value of K_R to be anticipated via eqn. 5, that is, when the dilution effect is neglected.

With this treatment we are now in a position to correct our data for the formal effects occurring at finite concentration of solute A in GLC when complexing is strong.

EXPERIMENTAL

GC measurements were made using a purpose-built high precision instrument. The system employed a Porter gas flow controller (Hatfield, PA, U.S.A.) in conjunction with a two-stage pressure regulator using helium as carrier gas. To reduce problems of potential reaction of the solutes within the detector, a dual thermister katharometer, operated at just above the column operating temperature, was employed.

The column of 1 m \times 4 mm I.D. stainless steel packed with 40–60 mesh coated particles allowed operation at a pressure drop across the column of no more than 150 Torr while providing an acceptable number of theoretical plates ($N > 500$). Pressure drops were measured with a mercury manometer and flow-rates with a soap-film meter making the appropriate corrections for the saturation vapour pressure of the water. The eluent was scrubbed of the hydracid by employing an alkali trap which was replaced at regular intervals.

The injector and column were immersed in a thermostatic water bath equipped with a Techne Tempette (Cambridge, U.K.) TE-8D thermoregulator which provided a temperature stability of $0 \pm 0.01^\circ\text{C}$ and temperatures measurement to within $\pm 0.1^\circ\text{C}$.

To minimise possible interfacial adsorption of the solutes at the solid support, the highly silanized support Chromosorb GAW-DMCS (Jones Chromatography, Llanbradach, U.K.) was used. Column packings containing from 2 to 7% (w/w) of liquid phase (TBP in hexadecane) were prepared by the rotary evaporator technique with dichloromethane as the slurry solvent. The dried, free-flowing powders were then packed into precoiled columns with the aid of aspiration and gentle tapping. The phase loadings were determined both by initial weighing and by replicate thermogravimetric analysis with no discrepancy seen between the two measurements.

The densities of the TBP and hexadecane over a range of temperatures are listed in the literature^{19,20}. Those of their mixtures were measured directly and found to be

a simple arithmetic volume average of the values for the individual components, indicating a negligible excess volume of mixing. The density equation used was

$$\rho = (0.9964 - 0.00807t)\varphi_{\text{TBP}} + (0.7879 - 0.00688t)\varphi_{\text{C}_{16}}$$

where t is in $^{\circ}\text{C}$ and φ is the volume fraction.

Solutes were injected through a PTFE coated silicone septum via a Hamilton 1000 series gas-tight syringe. Samples were injected either as headspace samples from aqueous solutions or as ether solutions, with sample sizes ranging from 1 to 100 μl .

RESULTS

Fig. 1 illustrates typical chromatograms obtained with different sample sizes of hydrogen cyanide eluted from a column of TBP-hexadecane (30:70 v/v) at 25°C . The peaks obtained are ideally suited to ECP analysis since at all levels the diffuse trailing edges of the peaks share a common envelope whilst at all but the lowest levels the leading edges are essentially vertical. This conformity establishes that the correct experimental conditions for ECP are operative. It implies also that liquid and solid surface effects are absent, a fact established by use of columns of different solvent loadings which showed no difference in values of K_{R} .

Fig. 2 shows a comparable set for hydrochloric acid eluted from TBP-hexadecane at 45°C . Here we see a high degree of conformity down to some lower sample level beyond which retention increases. As was said earlier, in the presence of water, hydrochloric acid may complex in more than one way and the indications in the literature are that water-HCl-TBP complexes are stronger than are those of HCl-TBP. Appropriate experiments established that this was the case, at sufficiently

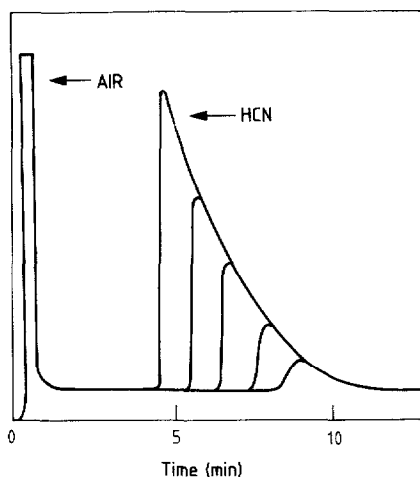


Fig. 1. Elution chromatograms of 0–10 ml samples of headspace gas over aqueous HCN solutions. Column: 1 m \times 4 mm I.D. stainless steel packed with 7% (w/w) of 30% (v/v) TBP in hexadecane on 40–60 mesh (ASTM) Chromosorb-G (AW-DMCS). Fully corrected flow-rate of He, 40.4 ml min^{-1} ; elution temperature, 25°C .

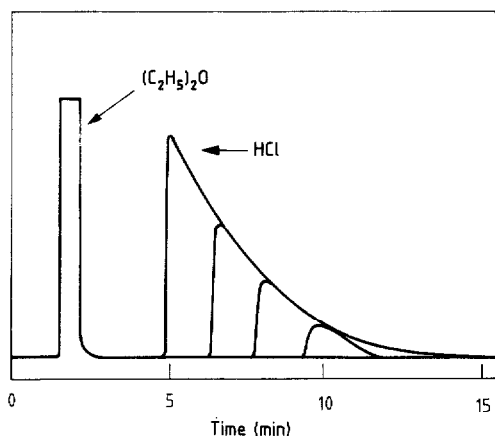


Fig. 2. Elution chromatograms of 0–100 μ l of 0.1 M solution of HCl in $(C_2H_5)_2O$. Column: 1 m \times 4 mm I.D. stainless steel with packing as in Fig. 1. Fully corrected flow-rate of He, 40.2 ml min^{-1} ; elution temperature, 35°C.

high water levels the hydrochloric acid peak was followed by a near-plateau extending to long retention times. Intensive drying failed, as is seen, to eliminate the tail completely, although it diminished further with increasing temperature. Where necessary, the extrapolated trailing side of the curve was used to evaluate K_R at low levels of hydrochloric acid and, as seen later, this provided highly compatible data.

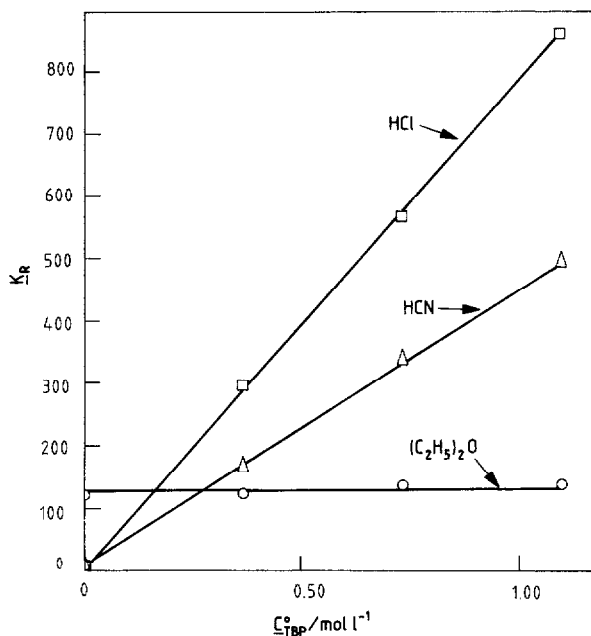


Fig. 3. Plots of infinite dilution partition coefficients between TBP–hexadecane and the gas phase, as a function of TBP concentration, for HCl, HCN and $(C_2H_5)_2O$. Elution temperature, 25°C.

Infinite dilution studies

In situations where small samples provided adequate peak size for direct measurement, K_R could be evaluated via the basic equation, $K_R = V_N/V_1$, where V_N is the fully corrected net retention volume and V_1 is the solvent volume. For skewed peaks, an adequate estimate of V_N is derived, following Littlewood²⁰, from

$$t_R = t_T + t_F - t_{\max}$$

where t_T is the time of intersection at the baseline of a tangent to the leading edge, t_F that for the trailing edge and t_{\max} is the peak maximum retention time. In many experiments, particularly at higher TBP concentration, retention was so great that peak broadening precluded this approach. Then, the trailing edge envelope for both hydrogen cyanide and hydrochloric acid was extrapolated to the base line.

In Fig. 3 we show the results for 25°C at infinite dilution of hydrochloric acid, hydrogen cyanide and the reference solute $(C_2H_5)_2O$ as the concentration of TBP in hexadecane is varied. The latter was chosen since ethereal solutions of the acids were commonly used in the work. It is important to note that for the hydrochloric acid case large injection volumes were used and extrapolation of the curves excluded the small tail which was seen in the chromatograms. The magnitude of the tail, as already stated, is moisture sensitive but is reduced at high hydrochloric acid concentrations and

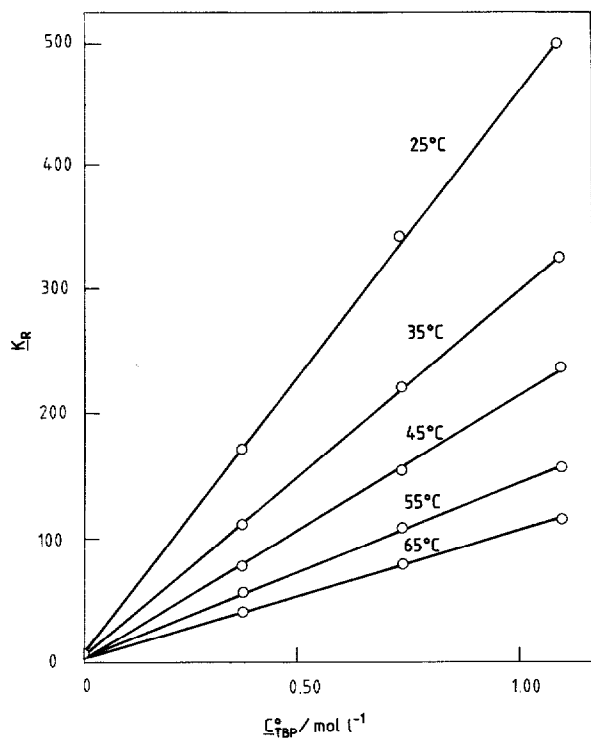


Fig. 4. Plots for HCN as in Fig. 3 for elution at temperatures in the range 25–65°C.

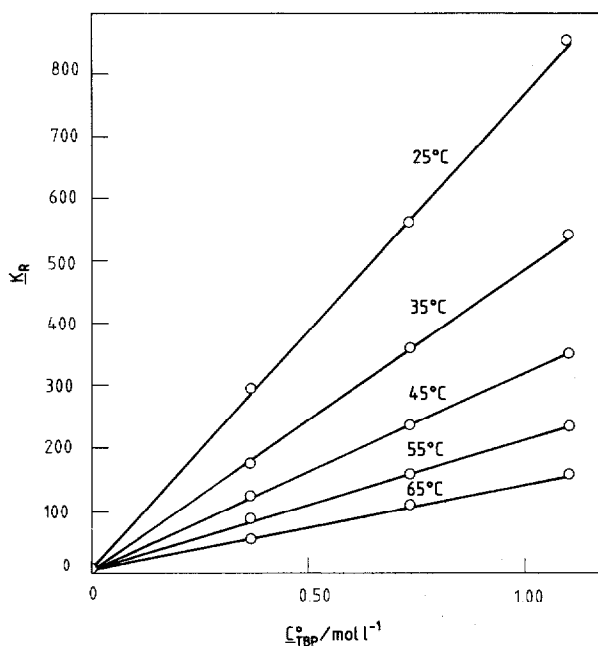


Fig. 5. Plots for HCl as in Fig. 3 for elution at temperatures in the range 25–65°C.

TABLE I

VALUES OF INTERCEPTS (K_R°) AND SLOPES ($K_R^\circ K_1$) FROM PLOTS ACCORDING TO EQN. 4 (FIGS. 4 AND 5) OF DATA FOR ELUTION OF HCl, HCN AND $(C_2H_5)_2O$ FROM TBP-HEXADECANE MIXTURES OF COMPOSITION $c_{TBP}^\circ = 0-1.1 \text{ mol l}^{-1}$ AND DERIVED VALUES OF STABILITY CONSTANTS (K_1) AND ASSOCIATED THERMOCHEMICAL QUANTITIES, ΔH_1° AND ΔS_1°

Data for K_R° yield enthalpies and entropies of solution of uncomplexed acids: HCl; $\Delta H^\circ = -8800 \text{ kcal mol}^{-1}$, $\Delta S^\circ = -9.1 \text{ cal mol}^{-1}K^{-1}$; HCN; $\Delta H^\circ = -2430 \text{ kcal mol}^{-1}$, $\Delta S^\circ = -3.9 \text{ cal mol}^{-1}K^{-1}$.

Solute	$t(^{\circ}C)$	K_R°	$K_R^\circ K_1$ ($l \text{ mol}^{-1}$)	K_1 ($l \text{ mol}^{-1}$)	$-\Delta H_1^\circ$ (kcal mol^{-1})	$-\Delta S_1^\circ$ ($\text{cal mol}^{-1}K^{-1}$)
HCl	25.0	6.4	773.8	120.9	4.44	5.4
	35.0	5.2	481.4	92.6		
	45.0	4.3	329.9	76.7		
	55.0	3.6	214.3	61.3		
	65.0	3.0	149.4	48.2		
HCN	25.0	8.3	447.0	53.9	4.87	8.5
	35.0	7.3	288.5	39.5		
	45.0	6.4	201.1	31.4		
	55.0	5.7	141.4	24.8		
	65.0	5.1	103.1	20.2		
$(C_2H_5)_2O$	25.0	117.9				
	35.0	88.5				
	45.0	65.3				
	55.0	52.4				
	65.0	41.5				

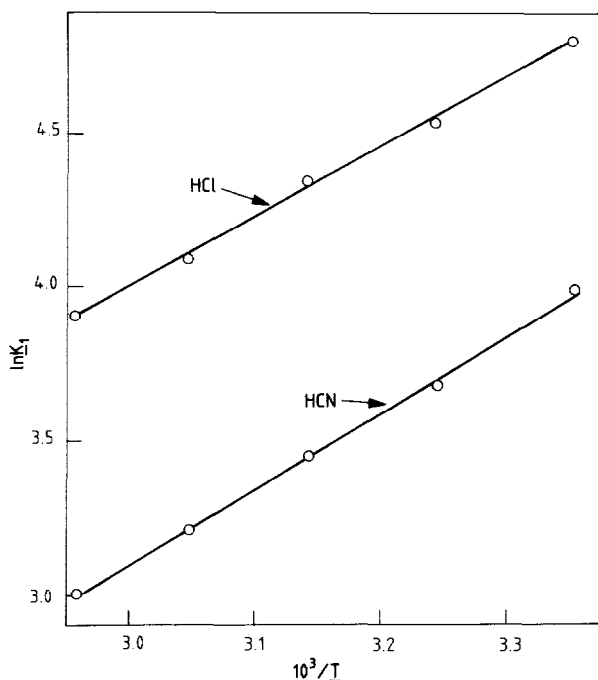


Fig. 6. Van't Hoff plots of $\ln K_1$ against T^{-1} for HCl and HCN complexes with TBP (1:1) in hexadecane.

elevated temperatures. At very high water concentrations, the tail becomes excessive so that study of hydrochloric acid elution in water saturated systems is precluded by the present method. No such problems were seen with hydrogen cyanide and every effort was made to exclude water from our system in studying hydrochloric acid.

The acid data clearly fall on excellent straight lines in accord with expectation for 1:1 complexes. The data for the ether show little change, perhaps rising a little with increasing c_{TBP}° , and confirm the absence of complexing in this case. Data for both acids over a wide range of temperature and c_{TBP}° are illustrated in Figs. 4 and 5. There is clearly excellent linearity in every instance. From the value of $(K_{\text{R}}^\circ K_1)$, having measured K_{R}° , we evaluate K_1 ; these data are listed in Table I along with the enthalpies and entropies associated with the acid-TBP-complex equilibrium, the corresponding Van't Hoff plots being shown in Fig. 6.

Eqn. 4 may be rewritten as

$$K_{\text{R}} = K_{\text{R}}^\circ + K_{\text{R}}^\circ K_1 c_{\text{B}}^\circ$$

and since $\Delta G^\circ = -RT \ln K$, this may be represented alternatively as

$$K_{\text{R}} = \exp(X) + c_{\text{B}}^\circ \exp(Y) \quad (7)$$

where $(X) = -\Delta G^\circ/RT$ for the equilibrium involving solution of uncomplexed acid and (Y) is the sum of this quantity for both processes, solution and complexing. We

TABLE II
COMPARISON OF EXPERIMENTAL AND CALCULATED (EQN. 9) PARTITION COEFFICIENTS (K_R) FOR HCN ELUTED FROM TBP-HEXADECANE MIXTURES OF INDICATED COMPOSITIONS

c_{TBP} (mol l^{-1})	t ($^{\circ}\text{C}$)	K_R^{exp}	K_R^{calc}	Relative deviation (%)
0.000	25.0	8.6	8.3	+3.5
0.000	35.0	7.1	7.3	-2.8
0.000	45.0	6.4	6.4	0.0
0.000	55.0	5.6	5.7	-1.8
0.000	65.0	5.3	5.1	+3.8
0.367	25.0	170.4	169.3	+0.7
0.363	35.0	111.0	113.9	-2.6
0.360	45.0	77.0	79.0	-2.6
0.357	55.0	56.6	55.9	+1.2
0.354	65.0	40.4	41.1	-1.7
0.733	25.0	341.7	329.8	+3.5
0.727	35.0	220.4	220.9	-0.2
0.720	45.0	154.6	151.7	+1.9
0.714	55.0	107.3	106.9	+0.4
0.707	65.0	79.8	77.0	+3.5
1.100	25.0	497.7	490.4	+1.4
1.090	35.0	320.1	327.5	-2.3
1.080	45.0	222.1	224.3	-1.0
1.071	55.0	157.0	157.6	-0.4
1.061	65.0	113.7	113.1	+0.5

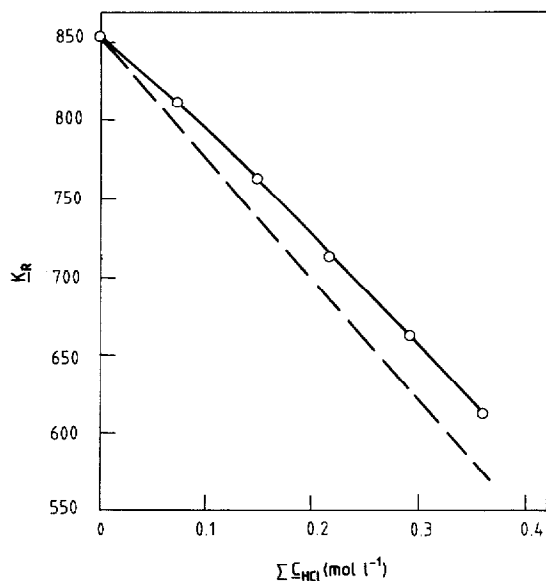


Fig. 7. Typical plot of K_R against total HCl in solution (complexed and uncomplexed) for elution of HCl from column as described in Fig. 1. Elution temperature: 25°C . Broken line corresponds to values of K' (eqn. 5) for these conditions.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED (EQN. 8) PARTITION COEFFICIENTS (K_R) FOR HCl ELUTED FROM TBP-HEXADECANE MIXTURES OF INDICATED COMPOSITION

c_{TBP} (mol l ⁻¹)	t (°C)	K_R^{exp}	K_R^{calc}	Relative deviation (%)
0.000	25.0	6.4	6.4	0.0
0.000	35.0	5.3	5.2	+1.2
0.000	45.0	4.2	4.3	-2.4
0.000	55.0	3.4	3.6	-5.9
0.000	65.0	3.1	3.0	+3.2
0.367	25.0	296.2	289.1	+2.4
0.363	35.0	177.4	183.5	-3.4
0.360	45.0	125.4	120.2	+4.1
0.357	55.0	78.3	81.0	-3.4
0.354	65.0	55.0	55.8	-1.5
0.733	25.0	561.9	571.0	-1.6
0.727	35.0	360.1	362.2	-0.6
0.720	45.0	237.3	236.2	+0.5
0.714	55.0	160.4	158.3	+1.3
0.707	65.0	111.0	108.5	+2.3
1.100	25.0	863.4	853.7	+1.1
1.090	35.0	527.5	540.5	-2.5
1.080	45.0	362.8	352.1	+2.9
1.071	55.0	231.0	235.7	-2.0
1.061	65.0	160.5	161.4	-0.6

can, thus, represent both the temperature and c_B^0 dependence of K_R in a single equation. The terms (X) and (Y) may be calculated either via the estimated values of the enthalpies and entropies of the competing processes or by statistically processing all of the data. Following this latter route we find:

$$\text{HCl} : K_R = c_{TBP}^0 \exp[(4132/T) - 7.219] + \exp[(1913/T) - 4.565] \quad (8)$$

$$\text{HCN} : K_R = c_{TBP}^0 \exp[(3679/T) - 6.262] + \exp[(1221/T) - 1.977] \quad (9)$$

In Tables II and III we present the data underlying Figs. 4 and 5, along with the values computed via the above equation. The agreement between the computed and experimental values is clearly excellent.

Studies at finite concentration

Fig. 7 shows a representative plot of the values of K_R measured for elution of hydrochloric acid at 25°C from a column of TBP-hexadecane (30:70 v/v) at acid sample sizes rising high enough to provide an acid concentration in solution of *ca.* 0.4 *M*.

The plot lies above the line for K' and bows upwards exactly as the theory presented earlier demands. In Table III we list the experimental values of K_R for three

temperatures along with those calculated via eqn. 6; the appropriate value of \bar{V}_1 for liquid hydrochloric acid being available in the literature²¹. The agreement is, in every case, remarkable in the light of the approximations made. The implications of this finding, that the stoichiometric stability constant is concentration independent, are discussed below.

DISCUSSION

We turn first to the results relating to the infinite dilution work. It is clear from the comparisons illustrated in Tables II and III that there is an excellent internal consistency in the data as expressed by the empirical eqns. 8 and 9. We can, now check the quality of the thermochemical data derived for K_1 since the coefficients within the quantities $\exp(X)$ and $\exp(Y)$ of eqn. 7 can be calculated from the thermochemical quantities evaluated and cited in Table I. The term $\exp(X)$ is given by

$$\exp(X) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

where the thermochemical quantities relate to the solution of uncomplexed acid, while

$$\exp(Y) = -\frac{\Delta H^\circ + \Delta H_1^\circ}{RT} + \frac{\Delta S^\circ + \Delta S_1^\circ}{R}$$

where now they comprise the sums for both the solution and complexing processes.

Thus, we would predict

$$\text{HCl} : K_R = c_{\text{TBP}}^\circ \exp[(4140/T) - 7.250] + \exp[(1910/T) - 4.573] \quad (8')$$

$$\text{HCN} : K_R = c_{\text{TBP}}^\circ \exp[(3668/T) - 6.246] + \exp[(1221/T) - 1.975] \quad (9')$$

The correspondence between the coefficients of eqns. 8 and 8' and of eqns. 9 and 9' is essentially perfect. This finally confirms the quality of both the retention data and the procedures adopted for their extraction from the chromatograms. More importantly, it provides a high degree of confidence in the values of K_1 , and of ΔH_1° and ΔS_1° , extracted therefrom.

Having said this it is worthwhile in passing to comment on the values found for the enthalpy of solution of the uncomplexed acids which comprises the sum of the enthalpy of condensation and the excess enthalpy. For hydrochloric acid, the quoted enthalpies of vaporisation are (kcal mol⁻¹): 4.68(115.3 - 173.3 K); 4.19(122.5 - 309.5 K)²²; 3.87(189 K = normal boiling point)²³. It is clear that the value diminishes rapidly with increasing temperature up to the boiling point and may be expected to fall somewhat further as we move towards the critical temperature (324.8 K) which is roughly the centre of our experimental range. Our value of 3.8 kcal mol⁻¹ is thus very close to the anticipated value, which implies a very small, possibly zero, excess enthalpy of solution. Our result, therefore, provides a reasonable estimate of the enthalpy of vaporisation of hydrochloric acid around its critical temperature. For hydrogen cyanide however, the situation is quite different. The quoted value²⁴ for

TABLE IV

COMPARISON OF CALCULATED (VIA K' AND EQN. 6) AND EXPERIMENTAL PARTITION COEFFICIENTS (K_R) FOR HCl ELUTED AT FINITE CONCENTRATIONS IN THE LIQUID, FROM TBP-HEXADECANE (30:70)

t (°C)	c_{HCl} (mol l ⁻¹)	K_R^{calc}	K_R^{exp}	Relative deviation (%)
25.0	0.073	809.4	810.7	-0.2
	0.149	761.5	762.7	-0.2
	0.218	716.5	714.3	+0.3
	0.292	666.5	662.0	+0.7
	0.361	618.2	613.1	+0.8
35.0	0.062	516.4	517.0	-0.1
	0.129	489.4	488.2	+0.2
	0.196	461.5	454.9	+1.4
	0.273	428.4	417.0	+2.7
	0.334	401.4	382.4	+4.7
45.0	0.071	333.7	336.2	-0.7
	0.147	313.4	317.9	-1.4
	0.219	293.4	296.8	-1.2
	0.306	268.4	275.0	-2.5
	0.375	247.9	258.1	-4.1

293.3 K is 6.0 kcal mol⁻¹ compared with our value for the enthalpy of solution of -2.43. This would imply an excess enthalpy of about -3.6 kcal mol⁻¹. In the liquid, hydrogen cyanide is, in fact, polymerised via hydrogen-bonding and so the enthalpy of vaporisation must include the enthalpic contribution arising from the conversion to monomer in the gas phase. In our system hydrogen cyanide, in the uncomplexed form, exists only at very high dilution due to the large K_1 (see below) and so the equilibria involved in the polymerisation process must favour the monomer. We therefore may suggest that the value 2.4 kcal mol⁻¹ represents the enthalpy of vaporisation of the liquid monomer. If this is true, the hypothetical boiling point of monomeric liquid hydrogen cyanide is close to 120 K. Correspondingly, the enthalpy associated with hydrogen-bonding is -3.6 kcal mol⁻¹, a very reasonable figure.

Turning to the results at finite concentration of hydrochloric acid we note the remarkable applicability (Table IV) of the dilution-depletion theory advanced earlier. This is an important finding in that it allows a corrective basis for studies at high concentration and K_1 into the future. There are, however, implications of our findings with respect to activities in the system since the theory as presented assumed, for simplicity, no changes in activity coefficients as concentrations varied. Even at the highest concentrations of total acid (Σc_A) in solution there is little uncomplexed acid present on account of the very high values of K_1 . For example, when $K_1 = 50 \text{ l mol}^{-1}$ and $c_B^0 = 1 \text{ M}$, the ratio c_A/c_{AB} is only 0.02. Hence, we might well expect the activity coefficient of hydrochloric acid to remain constant in all the conditions employed here. The concentration of complex, however, rises from zero to as high as 0.3 M or so over the experimental range while that of TBP is correspondingly reduced. It thus appears that neither component exhibits a concentration dependence of the activity coefficient.

There is other evidence on this score too. The infinite dilution data plotted in Figs. 4 and 5 (eqn. 4) are certainly linear and while the acid and complex are present in only trace amounts in these experiments, the concentration of TBP ranges from zero to more than 1 *M*. Linearity of the plots would not be observed if the activity coefficient of TBP were more than trivially concentration dependent. It may be pointed out that, among the many examples of plots according to eqn. 4 in the literature, for a variety of complex types, there are few cases where curvature of such plots is seen. So too is the case in the spectroscopic (UV-VIS) and NMR approaches to K_1 evaluation wherein the data are processed via the Benesi-Hildebrand equation which is closely analogous to eqn. 4. The situation may thus be considered very common, if not general.

Finally, we turn to the results for K_1 . The values derived are of the anticipated magnitude and are associated with thermochemical quantities typical of complexation reactions, particularly of the acid-base type involved in formation of the 1:1 complexes which presumably arise via $\text{H} \cdots \text{O} \cdots \text{P}$ interaction. Given such a high quality data base it becomes possible either to calculate liquid-liquid extraction coefficients for these acids by combination with similar data for other solvents, or to calculate such data by use of extraction coefficients where these are known. Further, it should also be feasible to determine K_1 values for non-volatile acids such as nitric acid via competitive experiments. More generally, the demonstrated success of both the technique and the theoretical extension offered means that a wide variety of strongly complexing reactions can be studied with some confidence of success. In summary, the opportunity is available to place a large number of extraction processes of importance on a more quantitative and intelligible basis.

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