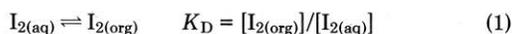


A Graphical Procedure for the Simultaneous Determination of the Distribution Constant of Iodine and the Stability Constants of Trihalide Anions

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When a solution of iodine in a water-insoluble organic solvent (e.g., trichloroethylene) is thoroughly shaken with an aqueous solution of a halide (X^- , $X = F, Cl, Br, I$), two equilibria are simultaneously established (aq = aqueous phase; org = trichloroethylene phase)



and



Hence the apparent distribution constant $K_{D'}$ of iodine between the organic phase and the aqueous phase is given by

$$K_{D'} = \frac{[I_{2(org)}]}{[I_{2(aq)}] + K_s[I_{2(aq)}][X_{(aq)}^-]} \quad (3)$$

which from eqn. (1) gives

$$\frac{1}{K_{D'}} = \frac{1}{K_D} + \frac{K_s}{K_D} [X_{(aq)}^-] \quad (4)$$

In the case of $X = F, Cl, Br$, the complex trihalide anions, I_2X^- , have low stabilities in water. Thus if a relatively large initial concentration of the halide ($[X_{(aq)}^-]_0$) is used, its concentration may be considered to be insignificantly changed at equilibrium hence giving

$$[X_{(aq)}^-]_0 \approx [X_{(aq)}^-]$$

Now (eqn. (4)) becomes

$$\frac{1}{K_{D'}} = \frac{1}{K_D} + \frac{K_s}{K_D} [X^-(aq)]_0 \quad (5)$$

A plot of $1/K_{D'}$ versus $[X_{(aq)}^-]_0$ should give a linear relation in the region in which the assumption that $[X_{(aq)}^-] = [X_{(aq)}^-]_0$ at equilibrium holds. The intercept on the y-axis gives $1/K_D$, while from the slope one obtains the value of K_s . The values so obtained may be checked by a least-squares calculation for reliability.

Further, from a suggestion by the reviewer, it was found that the results are improved if eqn. (5) is rearranged to give eqn. (6) as follows

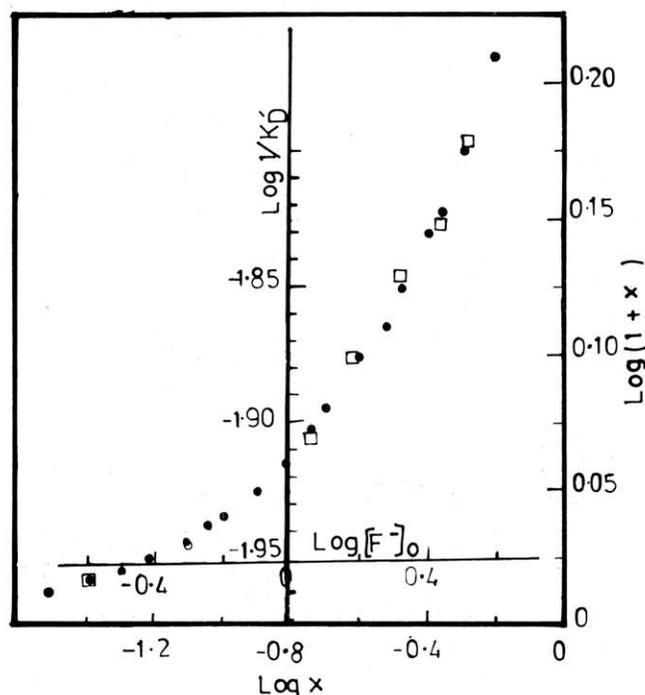


Figure 1. A plot of $\log(1/K_{D'})$ versus $\log [F_{(aq)}^-]_0$ best fitted on the master plot ($\log(1+x)$ versus $\log x$). Horizontal displacement is -0.8 hence $\log k_0 = -0.8$; the vertical displacement is $+0.02$, hence $\log K_D = 1.95 + 0.02 = 1.97$.

$$K_D/K_{D'} = 1 + K_s[X_{(aq)}^-]_0$$

hence

$$\log K_D + \log(1/K_{D'}) = \log(1 + K_s[X_{(aq)}^-]_0) \quad (6)$$

Now a plot of $\log(1/K_{D'})$ versus $\log [X_{(aq)}^-]_0$ (on transparent paper) is made on the same scale as that of the master plot of $\log(1+x)$ versus $\log k$ for $-2 \leq x \leq 0.5$. The plot of $\log(1/K_{D'})$ versus $\log [X_{(aq)}^-]_0$ is then translated horizontally and vertically on the master plot until the experimental data best fits on the master plot. From the vertical and horizontal displacements one obtains the values for $\log(K_D)$ and $\log K_s$, respectively, as shown in Figure 1.

This procedure allows the distribution constant to be determined simultaneously with the trihalide anion stability

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Experimental Results and Calculated Values of the Distribution and Stability Constants for Halogen Systems

System $X_{(aq)}^-/I_{2(org)}$	$X_{(aq)}^-$ mol/dm ³	Log $[X_{(aq)}^-]_0$	$1/K_D$	Log $1/K_D'$	K_D^a			K_s^a			ΔH_{aq} kJ/Mol
					eqn. (5)	eqn. (6)	LSC	eqn. (5)	eqn. (6)	LSC	
X = F	0.250	-0.602	0.0113	-1.95	91	93	93	0.15	0.16	0.16	-505
	1.15	0.0607	0.0125	-1.90							
	1.50	0.176	0.0134	-1.87							
	2.11	0.324	0.0146	-1.84							
	2.75	0.439	0.0154	-1.81							
	3.20	0.505	0.0163	-1.79							
X = Cl	0.0318	-1.50	0.0111	-1.96	90	93	92	0.86	0.96	0.92	-363
	0.250	-0.602	0.0135	-1.87							
	0.512	-0.291	0.0166	-1.78							
	1.03	0.0124	0.0205	-1.69							
	1.62	0.211	0.0275	-1.56							
X = Br	0.0307	-1.51	0.0142	-1.96	89	89	82	9.1	8.7	8.3	-336
	0.050	-1.30	0.0161	-1.79							
	0.150	-0.824	0.0284	-1.55							
	0.250	-0.602	0.0382	-1.42							
X = I	794 ^b	-295

^a Eqn. (5) or eqn. (6) = data obtained using eqn. (5), or eqn. (6), LSC = data obtained by linear least-squares calculation.

^b Theoretical value from Ref. (1).

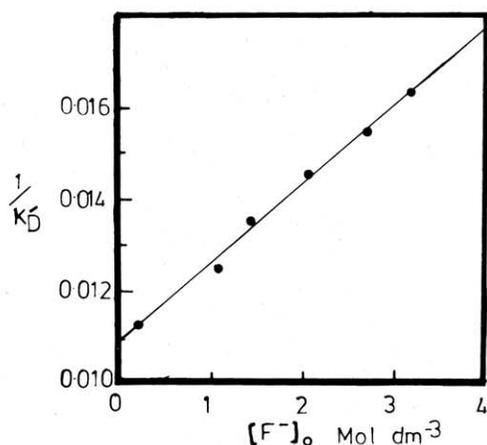


Figure 2. $1/K_D'$ versus $[F_{(aq)}^-]_0$ for the $F_{(aq)}^- - I_{2(org)}$ system.

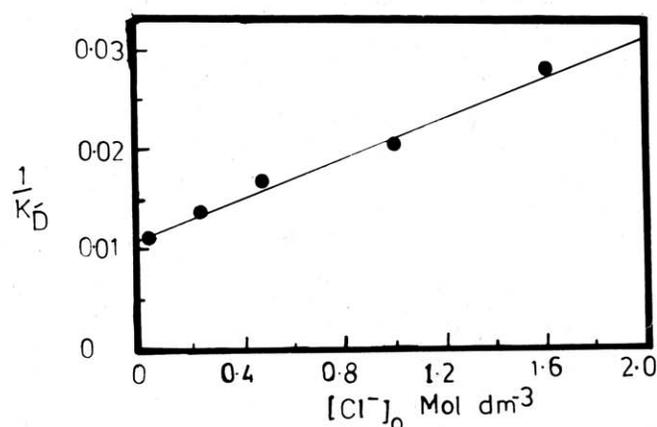


Figure 3. $1/K_D'$ versus $[Cl_{(aq)}^-]_0$ for the $Cl_{(aq)}^- - I_{2(org)}$ system.

constant. For this reason more chemistry than just that of the distribution equilibria may be incorporated in the experiment since, using the K_s values and other physico-chemical data, studies of the properties of the complex trihalide anions may then be made, thereby increasing the instructional value of distribution equilibria experiments.

Experimental

Twenty milliliters of a saturated solution of iodine in trichloroethylene is transferred into a stopper bottle and then diluted with 10 ml of trichloroethylene. Then, 30–50 ml of an aqueous solution of the potassium halide, whose concentration is known accurately, is added. The stoppered bottle and the contents are thoroughly shaken and then placed in a water bath thermostated at 29 °C. The shaking is repeated at 5-min intervals for half an hour after which the bottles are left undisturbed. After the phases are separated the concentrations of iodine in the aqueous and organic phases are determined by standard iodometric procedures. Worth noting is the fact that determination of K_D' simply requires the ratio of the volumes of the thiosulfate solution reacting with iodine present in 1 ml of the liquid phases. It is not necessary to determine the actual concentration of iodine in each phase.

Results and Discussion

The original concentration of the potassium halides ($[X_{(aq)}^-]_0$) and the corresponding values of $\log [X_{(aq)}^-]_0$ and $\log (1/K_D')$ and values of K_s and K_D obtained by the procedure employing eqns. (5) and (6) are given in the table. The values

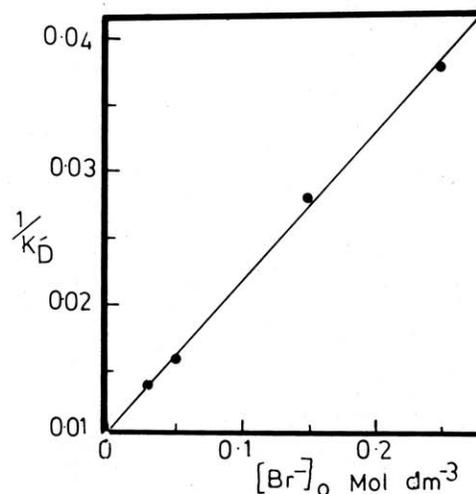


Figure 4. $1/K_D'$ versus $[Br_{(aq)}^-]_0$ for the $Br_{(aq)}^- - I_{2(org)}$ system.

of K_s and K_D obtained by the equal-weighted, linear least-squares calculations are also included. The plots of $1/K_D'$ versus $[X_{(aq)}^-]_0$ are given in Figures 2–4, the plot showing how K_s and K_D are obtained by fitting the plot of $\log (1/K_D')$ versus $\log [X_{(aq)}^-]_0$ on to the master plot, is shown in Figure 2. As

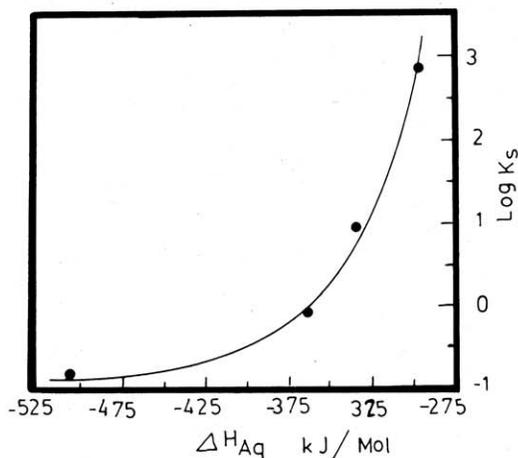


Figure 5. Log K_s versus the hydration energy of the halide anion X^- .

stated earlier the best values for K_D are obtained from the systems $I_{2(org)}/X_{(aq)}^-$, $X = F, Cl$. The values so obtained are consistent and are in good agreement with the values obtained by the linear least-squares calculation. K_D is, under these considerations, 93. The values of the stability constant K_s for I_2Br^- and I_2Cl^- (8.7 and 0.96, respectively) are reasonable when compared with those obtained by Benoit and Guay at 22 °C (12.6 and 1.58, respectively) (1). The stability constant of the complex anion I_2F^- , previously unknown, was found to be 0.16.

In general the reliability and consistency of the procedure have been demonstrated. As expected, attempts to apply the procedure to the $I_2/I_{(aq)}^-$ system have been unsuccessful since large deviations from the linear least-squares calculations were observed, showing clearly that the assumption that $I_3^- \ll I_{(aq)}^-$ does not hold.

Pedagogically this graphical procedure has several attractive features. It is very convenient for students because it requires accurate knowledge of only one parameter, i.e., $[I_{(aq)}^-]_0$ to obtain simultaneously K_D and K_s while errors and inaccuracies in the assumptions leading to eqn. (5) and (6) are indicated by obvious deviations on the respective plots. Further, if the class is divided into three groups each working on a different system, data on the three $I_2/X^-(aq)$ systems may be collected in a single session of about 4 h. The students may then compare their K_D values and use their K_s values to in-

vestigate important physico-chemical characteristics of the trihalide anions which emanate from the nature of the interhalogen bond. For instance, to students who have been successfully introduced to thermodynamics, a curious feature of the trend adopted by the K_s values is its incompatibility with the trend shown by the I-X bond energies which are 280, 211, 178, and 151 kJ/mol for $X = F, Cl, Br, I$, respectively (2). Nuclear quadrupole resonance data for several trihalide anions (3, 4) indicates that interaction of X^- with I_2 is greatest when the electronegativity of X is large. Accordingly one would have expected I_2F^- to be the most stable anion of the I_2X^- series. However, if the stability constants of the trihalide anions I_2X^- , X_3^- , and IX_2^- in protic and aprotic solvents (1, 5) are considered the critical influence on solvation, then the situation is clarified. Actually a plot of K_s 's versus the hydration energy of X^- (6) (Fig. 5) indicates that solvation of X^- contributes significantly to the energy barrier to be surmounted when I_2X^- is formed according to eqn. (2). In the absence of this factor, e.g., when the anion is formed in aprotic solvents such as nitromethane, the stability order reverses (1, 5) reflecting the intrinsic trend. The high susceptibility of F^- to solvation by water molecules is largely responsible for the observed low stability of I_2F^- .

Conclusion

In general a graphical approach to student experiments where possible is to be preferred because errors and limitations of the procedure are readily checked by established statistical methods. And, of course, experimental results presented graphically are usually more exciting, convincing and instructive than those presented otherwise. These advantages and the fact that K_D and K_s are obtained simultaneously make this procedure versatile for teaching programs on the distribution law. The procedure extends the experimental chemistry from distribution equilibria to important thermodynamic and bonding features.

Acknowledgment

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