

The Use of Polyiodide Mixtures as Constant Activity Sources in Studies of Molecular Complexes of Iodine

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Methods are described for using tetramethylammonium polyiodides as sources of constant iodine activity in condensed phase and vapour phase studies of the formation of molecular complexes of iodine. The techniques are particularly useful in investigating the formation of weak molecular complexes for which it is difficult to determine reliable equilibrium constants by conventional spectral procedures.

Iodine has been the most widely used acceptor molecule in studies of charge transfer (CT) interactions, in solution and in the vapour phase.¹⁻³ However, serious problems are involved, both in obtaining sufficiently accurate spectral measurements and in interpreting spectral data in terms of parameters characteristic of molecular complexes of iodine. (For a discussion of some of these problems, see Ref. 1.) Therefore, the validity of many of the published thermodynamic and spectral constants, particularly those for weak donor-iodine complexes, has been questioned by numerous investigators.

One limiting feature in many spectral studies of donor-acceptor interactions is the difficulty of controlling the concentrations of the various complexing species. Previous reports from this Laboratory have described techniques for performing spectral and classical studies of liquid and vapour systems, in which the activity of water has been maintained at a desired level by utilizing constant humidity sources, such as aqueous salt solutions or crystalline hydrates.⁴ These methods have found wide application in solving the experimental problem of handling water at the low concentrations involved in studies of hydrogen-bonded complexes of water in organic solvent systems of interest.⁵ Physical measurements made on the water-solvent systems at constant water activity have been treated as blanks for measurements of properties of the ternary systems (water-polar solute-solvent) at the same water activity; changes in these properties are attributed entirely to the formation of discrete water-solute complexes.⁵ The similarities of problems encountered in studying iodine ad-

ducts and those arising in investigations of complexes of water led us to examine the possibility that methods utilizing a constant iodine activity source might possess advantages over conventional techniques for investigating weak donor-acceptor interactions. Earlier research by Kortüm and co-workers⁶ had shown the feasibility of using solid iodine to control the activity of iodine in ternary donor-iodine-organic solvent systems, although the methods described have not been widely applied in research on molecular complexes. We report here simple and accurate methods for maintaining constant (reduced) iodine activities in organic solvent and vapour systems. Polyiodides of organic and quaternary ammonium cations are employed as constant activity sources; these salts may be placed in direct contact with equilibrating vapour or organic solvent systems in both spectral and classical experiments designed to yield information about complex-formation reactions.

TETRAMETHYLAMMONIUM POLYIODIDES

Fig. 1 shows the solid-vapour phase diagram for the tetramethylammonium iodide (TMAI)-iodine system at 25°; the iodine activity, a_{I_2} , is plotted against the ratio of the number of moles of I to the number of moles of the tetramethylammonium cation (n_I/n_{TMA}). Iodine activities have been determined by using a solubility method similar to that employed by Foote and Fleischer.⁷ A weighed amount of pure TMAI was shaken for several days with a measured volume of a heptane or cyclohexane solution of known I_2 molarity; spectral

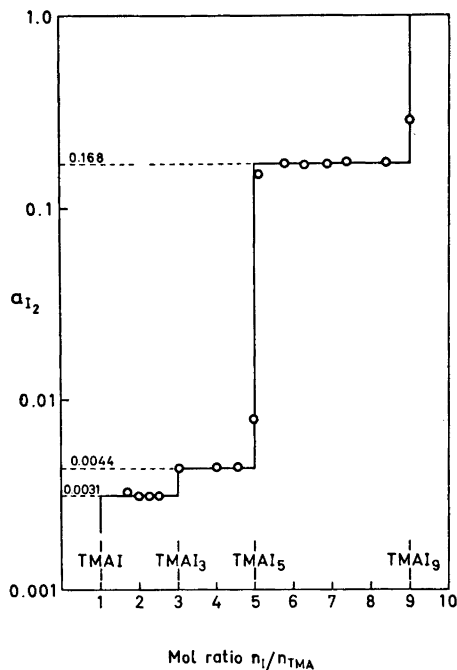


Fig. 1. The solid-vapour phase diagram for the tetramethylammonium iodide-iodine system at 25°. The iodine activity a_{I_2} is plotted against the ratio of the number of moles of I to the number of moles of the tetramethylammonium cation (n_I/n_{TMA}) in the solid mixtures.

determination of the iodine remaining in solution at equilibrium permitted calculation of the mole ratio of iodine to TMAI in the solid phase at a given solution concentration.* The results are in general agreement with those given earlier,⁷ although the previous report by Foote and Fleischer does not include corrections for non-ideality of iodine in the solvent they employed (toluene), and it includes data for polyiodides, TMAI_n , for which $n > 9$. At iodine activities at least as great as 0.28, in cyclohexane and heptane, we found no evidence for the formation of polyiodides richer in iodine than TMAI_9 . A microbalance technique has also been employed to determine the vapour pressure of iodine (p_{I_2}) in equilibrium with $\text{TMAI}_5/\text{TMAI}_9$ solid mixtures and the enthalpy (ΔH) for the reaction $\frac{1}{2}\text{TMAI}_9(\text{s}) = \frac{1}{2}\text{TMAI}_5(\text{s}) + \text{I}_2(\text{v})$. At 35° , $\Delta H = 15.2 \pm 0.3$ kcal, and $p_{\text{I}_2} = 0.116 \pm 0.004$ torr.⁸ Extrapolated to 25° , these results yield the value $a_{\text{I}_2} = 0.164$, in good agreement with the data obtained from the solubility experiments for the $\text{TMAI}_5/\text{TMAI}_9$ mixtures.

Solid TMAI_5 , prepared as described by Chattaway and Hoyle,⁹ is a convenient starting material for bringing systems to known I_2 activities, corresponding to either the $\text{TMAI}_3/\text{TMAI}_5$ or the $\text{TMAI}_5/\text{TMAI}_9$ plateau. In solution studies involving hydrocarbon solvents, the $\text{TMAI}_3/\text{TMAI}_5$ plateau is ideal for use in spectral experiments. For example, if solid TMAI_5 is shaken with heptane for about 8 h and left overnight in a constant temperature bath at 25° , the iodine concentration in solution reaches an equilibrium value of 1.97×10^{-4} M. This is an excellent starting concentration for spectral studies of donor-iodine interaction in heptane (*vide infra*). On the other hand, in vapour-phase equilibrations, it is generally desirable to employ a higher activity of iodine, which can be attained by allowing TMAI_5 to equilibrate with iodine vapours. At 35° , in an evacuated system, a 100 mg sample of pure, finely-ground TMAI_5 in contact with I_2 vapour at unit activity will react with the equivalent of at least 1 mole of I_2 per mole of TMAI_5 in just a few minutes. Equilibration to the final iodine activity ($a_{\text{I}_2} = 0.168$) is reached within a few hours in a several-liter evacuated system in contact with the TMAI_5 - TMAI_9 solid mixture. The rapidity of the equilibration seems remarkable, considering the difficulties generally encountered in attaining equilibrium in inorganic salt systems.

USE OF CONSTANT ACTIVITY SOURCES IN STUDIES OF DONOR-IODINE EQUILIBRIUM

1. Weak donor-acceptor complexes in solution. Usual spectral techniques for investigating the formation of weak molecular complexes involve maintaining a constant concentration of one of the components (usually the acceptor) and varying the concentration of the other over a wide range.¹⁻³ This is necessary, because in the dilute concentration region there is a near-linearity between the absorbance of the complex and the donor concentration; hence, only the product

* Iodine activities in solution are based on a standard state of pure solid iodine. To a first approximation, a_{I_2} equals the ratio of iodine concentration in solution to the limiting solubility of pure iodine in the hydrocarbon solvent at 25° . Activity coefficient corrections (amounting to a few per cent relative) have been made by employing solubility parameter theory (Hildebrand, J. H. and Scott, R. L. *Regular Solutions*, Prentice-Hall, Englewood Cliffs, 1962).

of the equilibrium constant (K) and the extinction coefficient (ϵ) can be inferred. In order to resolve the product $K\epsilon$ into separate values of K and ϵ , it is essential that absorbance measurements be made throughout a range of donor concentrations great enough, so that the curvature in a plot of absorbance *vs.* concentration can be determined with accuracy.¹⁰ Unfortunately, in the case of weak donor-acceptor interactions, the donor concentrations required are frequently considerably in excess of 1 M, so that, at the upper end of the range, the medium differs considerably from the pure solvent in its physical and chemical properties. Although one may hope for a fortunate cancellation of activity coefficient changes, it is not at all certain that the equilibrium constant will remain constant throughout the wide range of concentrations which has been employed in most studies of weak complexes.¹¹

We have developed a procedure which can be used to obtain separate values of K and ϵ , even in very dilute concentration regions, in which only a small per cent of the acceptor molecules are in the complexed form.¹² First, pure TMAI₅ is equilibrated with a solvent, such as heptane, and the spectrum of iodine in the equilibrium solution is measured. Then, a series of several solutions of donor in heptane in the dilute concentration region is similarly equilibrated with TMAI₅, and spectra are measured for all of these solutions. At the wavelength of the isosbestic point (which can be determined by conventional procedures¹⁻³) the absorbance of the solution is directly proportional to the total concentration of iodine — free plus complexed — and the increase in absorbance is attributed solely to formation of the complex. Since the extinction coefficient of the complex and of the uncomplexed iodine are equal at this wavelength, the concentration of the complex and K can be calculated directly.* The extinction coefficient of the complex at the CT-band maximum (ϵ_{CT}) can also be inferred directly from spectral measurements on the equilibrated solutions, provided the equilibration and spectrophotometer temperatures are the same. For a particular solution, simultaneous measurements may be made of the absorbance at the isosbestic wavelength and the wavelength corresponding to the maximum intensity of the CT-band (A_{iso} and A_{CT} , respectively). In the dilute concentration region, ΔA_{CT} (the change in A_{CT} , corrected for absorbance of free iodine and donor) varies linearly with ΔA_{iso} (the change in absorbance at λ_{iso}). The limiting slope of a plot of ΔA_{CT} against ΔA_{iso} equals the ratio $\epsilon_{CT}/\epsilon_{iso}$. Since ϵ_{iso} is simply equal to the known extinction coefficient of iodine in pure heptane at λ_{iso} , ϵ_{CT} can be calculated directly. A prime advantage of the present procedure over conventional spectral and solubility methods is that ϵ_{CT} can be determined independent of K from spectral measurements at two wavelengths.

We have applied the technique described above to investigate several complexes of iodine, including those with pyridine, diethyl ether, benzene, and

* It is worth noting that in studies of the variation of properties of the complex with temperature, it is possible to equilibrate donor-iodine-solvent systems at any required constant temperature, withdraw samples of the liquid above the polyiodide mixture from the equilibrators, and determine the total iodine concentration of these solutions in a spectrophotometer thermostatted at a temperature near room temperature. Thus, equilibrations may be performed at temperatures far removed from ambient, and the samples analyzed at a temperature more convenient for spectral work.

several alkyl-substituted benzenes in heptane; these complexes range from moderately strong to weak with respect to the energy and free energy of donor-acceptor interactions.¹² In the case of the pyridine-I₂ complex, the value of K obtained with the new method agrees well with results from the recent literature. However, the value determined here for K for the ether complex is somewhat larger than values obtained by usual spectral procedures, and the values of K for the aromatic donors are considerably larger than those obtained with the conventional spectral method. The values of ϵ for the aromatic systems are correspondingly smaller than those reported previously. These initial results encourage us to believe that the new method will be valuable in assessing the reliability of previously reported values of K and ϵ for weak complexes and in yielding new spectral and thermodynamic results for complexes which are so weak that therefore it has been impossible to resolve the product $K\epsilon$ into its components.

It should be noted that values of K for donor-iodine complexes can be obtained by employing non-spectral analytical methods to determine iodine concentrations in solutions equilibrated with either TMAI₅ or TMAI₉. The total or analytical concentration of iodine is equal to that of free plus complexed iodine, and since the concentration of free iodine is determined for a blank in which no donor is present, the concentration of the complex is determined directly by difference. The assumption is made, as is usual in dilute solution studies of complex-formation, that each solute species individually obeys Henry's law and that non-specific effects do not operate to increase the iodine solubility.

2. Gas-phase complexes. Analytical difficulties, problems of chemical instability and narrowness of accessible ranges of donor concentration have limited the number and reliability of values of K and ϵ for gas-phase complexes of iodine.¹⁻³ By using a procedure entirely analogous to that described for the condensed-phase studies, it is possible to maintain the activity of I₂ in a gas-phase system at a fixed value by allowing it to equilibrate in direct contact with TMAI₅/TMAI₉ mixtures. Introduction of a gaseous species increases the amount of iodine in the gas phase; the increase in concentration of iodine is again attributed to formation of the complex. Spectral or other analytical procedures may be used to determine the increase in iodine concentration.

One promising technique for determining the small changes in iodine concentration which occur when a weak donor-iodine complex forms in the vapour phase is based on the use of a sensitive microbalance.⁸ Initially, a sample of TMAI₅/TMAI₉, suspended from one arm of the balance, is allowed to equilibrate in an evacuated, thermostatted several-liter system until a constant activity of iodine is attained, as indicated by the constancy of the weight of the polyiodide (equilibrium is reached within a few hours). Next, a sample of donor vapour is introduced into the system and after equilibrium is again attained, the decrease in weight of the polyiodide sample is determined and equated to the increase in the amount of iodine present in the gas phase. In studies of diethyl ether·I₂ and hexane·I₂ at 35°, donor pressures in the range 20 to 200 torr, have been employed.⁸ In these systems, diffusional mixing of gaseous iodine and

donor seems to be the limiting factor; equilibrium is reached, however, within about 8 to 24 h.*

We are currently applying polyiodides of tetramethylammonium, ammonium, and cesium as constant activity sources in several studies of gas-phase and condensed-phase complexes of iodine. The $\text{TMAI}_3/\text{TMAI}_5$ mixture is also being employed as a source of iodine in determinations of limiting values of Henry's law constants of iodine in various nonpolar and slightly polar solvents; these constants are useful in predicting the effects of solvents on equilibrium constants and enthalpies of formation of molecular complexes.⁵ The simplicity, directness and rapidity of the techniques described here should make them applicable in numerous studies of donor-acceptor interactions involving iodine.

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* The method described here for determining gas-phase equilibrium constants from measurements of changes in iodine concentration resembles the solute isopiestic technique,^{4,5} both in operation and in interpretation of results. We propose calling it the vapour-phase isopiestic method.