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Spectrophotometric Detection for Flow Injection Analysis of Tertiary Alkylamines in Terms of the Intermolecular Charge-Transfer Interaction with Iodine

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Synopsis. Spectroscopic studies of the intermolecular charge-transfer interaction with iodine have been extended in order to develop a new spectrophotometric detection method for flow injection analysis (FIA). Tertiary alkylamines, as a model compound of spectroscopically inactive species, have been determined with high detection sensitivity by FIA using the present detection method.

Although both spectrophotometric and electrochemical detectors are generally used for flow injection analysis (FIA) or high-performance liquid chromatography (HPLC), it is necessary for compounds inactive to both detectors to be derivatized to active species.[1,2] Some compounds are, however, allowed to be derivatized by a few methods with experimental difficulties.[2,3] It is therefore very significant and important to develop a direct detection method for spectroscopically inactive species without derivatization. On the other hand, the intermolecular charge-transfer (CT) process of organic molecules has been investigated in various fields of chemistry, physics, and biophysics. However, analytical applications using this CT interaction have been quite limited in number. In this paper we have addressed ourselves to the development of a new spectrophotometric detection method for flow systems in terms of intermolecular CT spectra with iodine, adopting an FIA method in order to avoid problems concerning chromatographic separation. The present technique has been examined by the determination of tertiary alkylamines as a model compound possessing no bands in the ultraviolet—visible region, and being extremely difficult to be derivatized to spectroscopically active species.

Experimental

Spectral Measurements. Iodine molecular complexes with alkylamines were studied in heptane and dichloromethane. Their spectral measurements were performed using 1 or 10 cm matched quartz cells equipped with stoppers, regulated to 25 °C by circulating constant temperature water throughout the cell compartment by the use of a Taiyo thermoleader (Model EZL-80).

Flow Injection System. The FIA apparatus is shown schematically in Fig. 1; it comprises Shimadzu LC-6AD and LC-3A HPLC pumps to provide a flow of the dichloromethane carrier and to deliver a dichloromethane solution of iodine; a Rheodyne 7125 injector with a 20-μl loop is used to introduce the analyte. A Gasukuro Kogyo low-dead-volume mixing tee was used to mix the mobile phase carrying the analyte with the iodine solution. A Shimadzu SPD-6A spectrophotometric detector was set at 290 nm. These instruments were connected using a stainless-steel pipe with an inner diameter 0.3 mm (Fig. 1).

Chemicals and Solvents. The samples employed here were triethylamine, tripropylamine, and tributylamine, which were commercially available from Nacalai Tesque, Inc., and were purified by repeated distillation under reduced pressure. Solvents used for spectroscopic observations were heptane and dichloromethane of spectrograde purity, dried over CaH_2 and then carefully rectified. Dichloromethane of special guaranty grade was used as an FIA carrier without any further treatment. The carriers available for the present detection scheme were solvents inactive to iodine, that is, having no electron-donating character such as saturated hydrocarbons or alkyl chlorides. If heptane was used as a carrier, we failed to pump quantitatively throughout the apparatus because of its low viscosity.

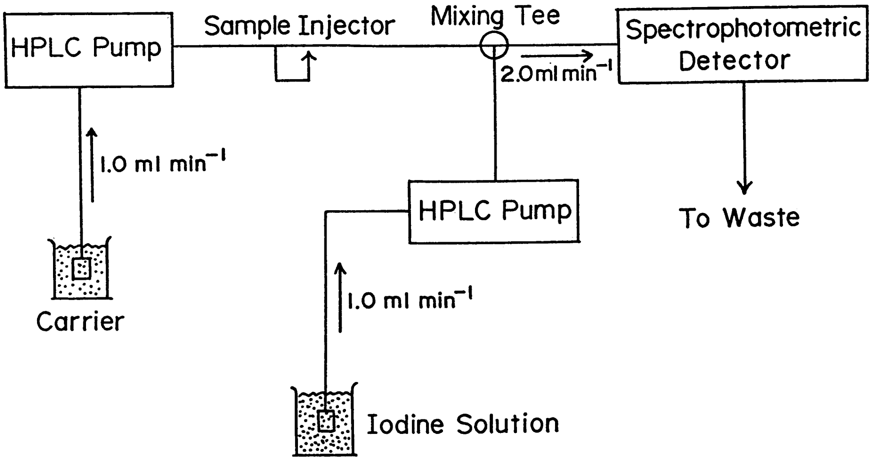

Fig. 1. Schematic diagram of the flow injection apparatus.

Results and Discussion

Formation of the Iodine Complexes with Tertiary Alkylamines. The intermolecular n–σ type CT interaction of alkylamines with strongly electron-accepting iodine has been both theoretically and experimentally investigated in detail.[4–6] The spectral measurements and their analyses gave constants (K) of the iodine CT complex formations of triethylamine, tripropylamine and tributylamine in heptane at 25 °C as 4840, 807 and 1370 mol^{-1} dm, respectively, by the use of Kubota's and Benesi–Hildebrand's equations;[7–9] this value for triethylamine was in fair agreement with that determined by Nagakura.[5] A theoretical analysis using the above equations has made it possible to evaluate the absorption maximum (λ_{max}) and its molecular extinction coefficient (ε_{max}) of the intermolecular CT bands for tertiary alkylamines–iodine–heptane system as ca. 280 nm and 2.5×10^4, respectively. The CT spectra were also recorded in dichloromethane with the addition of alkylamines to an iodine solution, showing an isosbestic point resulting from the 1 : 1 complex formation. Since the concentration ratio of alkylamines to iodine was unsuitable for the above equations, accurate K values in dichloromethane could not be evaluated. However, the absorbance of the CT spectra observed is linearly dependent on the donor concentration, indicating that the CT complexes are considered to form quantitatively in dichloromethane in view of the large K values in heptane.[10] The apparent λ_{max} and ε_{max} of the CT transition were evaluated in dichloromethane as 288 nm and 1.54×10^4 for triethylamine, 291 nm and 1.10×10^4 for tripropylamine, and 291 nm and 1.93×10^4 for tributylamine, respectively. Therefore, these bands seem to be applicable to the determination of tertiary alkylamines with a spectrophotometric detector.

The amines are no sooner added to the iodine solution than the solution apparently changes color, indicating that the CT complexes are formed promptly. The temperature dependence on the K values of the iodine CT complexes were investigated;[5,7] it is thus concluded that the lower is the temperature the easier is formation, since the change in enthalpy is negative for complex formation. However, the 10^{-4} mol dm^{-3} level of iodine was sufficient to quantitatively form CT complexes with the amines under 10^{-5} mol dm^{-3} at room temperature, owing to their large K values.

FIA Determination of Tertiary Alkylamines. Optimum FIA conditions were established as follows on the basis of a series of preliminary investigations. A mode of post-injection was adopted to the present FIA determination, since direct injection to the carrier containing iodine did not give the expected increase in the FIA response. The FIA peak height was practically independent of the period from mixing to detection, indicating that the formation rate of the CT complexes is very fast. A commercial mixing tee without further improvement is capable of mixing the carrier with the iodine solution. The pumps were operated at a flow rate of 1.0 ml min^{-1}, which was adequate to obtain a sharp peak. With regard to the concentration of iodine, the 10^{-4} mol dm^{-3} level is sufficient for a quantitative formation of the CT complexes, as mentioned above. The use of a solution of more than 10^{-3} mol dm^{-3} gave an unstable base line. Detection at 290 nm was selected in consideration of the λ_{max} of the CT

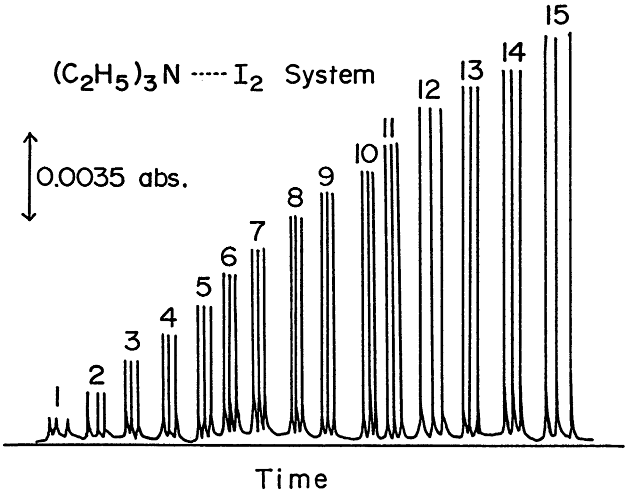

Fig. 2. Flow injection response of triethylamine. The time required for an appearance of the peak is 1.5 min after injection of a sample. Conditions: flow rate of carrier, 1.0 ml min^{-1}; flow rate of iodine solution, 1.0 ml min^{-1}; sample injection, 20 µl; detection wavelength, 290 nm. Concentration of iodine solution is 1.13×10^{-4} mol dm^{-3}. Concentrations of triethylamine are (1) 0.67, (2) 1.34, (3) 2.01, (4) 2.68, (5) 3.35, (6) 4.02, (7) 4.69, (8) 5.36, (9) 6.03, (10) 6.70, (11) 7.37, (12) 8.04, (13) 8.71, (14) 9.38, and (15) 10.1×10^{-6} mol dm^{-3}.

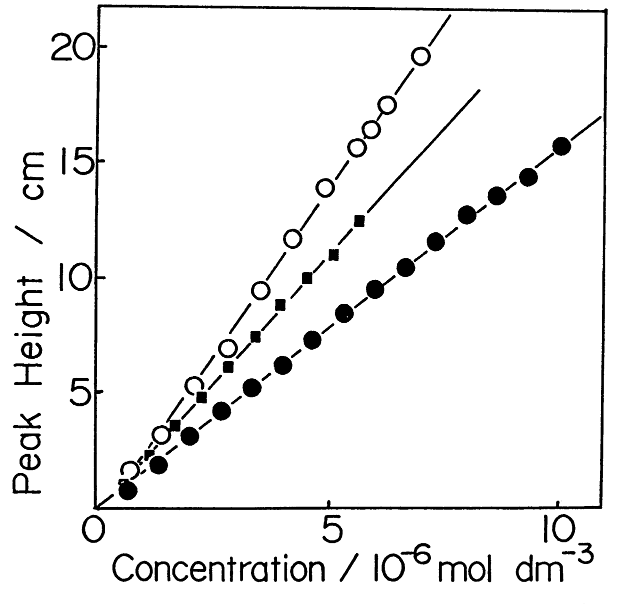

Fig. 3. Concentration (C) dependence of FIA peak height (PH) for triethylamine (●), tripropylamine (■), and tributylamine (○). The regression equations are PH=1.57C−0.137 (sample number (n)=15, standard deviation (s)=0.103, regression coefficient (r)=0.9995) for triethylamine, PH=2.24C−0.320 (n=10, s=0.103, r=0.9997) for tripropylamine, and PH=2.89C+0.867 (n=11, s=0.319, r=0.9988) for tributylamine.

Table 1. Detection Limit for Tertiary Alkylamines by the Present FIA method

Compounds	Detection limit[a)		
	mol dm^{-3}	10^{-9} g	10^{-12} mol
Triethylamine	6.71×10^{-7}	1.36	13.4
Tripropylamine	5.70×10^{-7}	1.63	11.4
Tributylamine	7.11×10^{-7}	2.63	14.2

a) The detection limit was examined with a 20-μl injection.

spectra for iodine–tertiary alkylamines–dichloromethane systems.

A typical response of FIA for the determination of triethylamine is shown in Fig. 2. The FIA response was very good for all of the samples, and the peak height was linearly dependent on the sample concentration (Fig. 3). The detection limit collected in Table 1 was determined as the lower linear range of the calibration lines, since an unavoidable background signal appears with sample injection to an FIA apparatus equipped with a spectrophotometric detector set at high sensitivity. Therefore, good linearity was obtained down to the detection limit determined here, as shown in Fig. 3. It may be allowed to detect more sensitively by adopting the present method to HPLC analysis. However, the detection limit obtained is far superior to the 4×10^{-5} mol dm^{-3} of triethylamine determined by the use of the derivatization method to chemiluminescence based on the oxidation of tertiary amines by benzoyl peroxide.[3)] The other methods concerning the derivatization of tertiary amines permit the detection of these analytes at only 2—10×10^{-6} g.[2)] Recently, Danielson et al. reported a generation of the chemiluminescent metal complexes of aliphatic amines with tris(2,2′-bipyridine)ruthenium(III).[11)] This method can be considered to be very superior and efficient for the determination of aliphatic amines with respect to the detection limits, permitting the limit of these analytes at the 0.04—2×10^{-9} g level. However, the chemiluminescent method upon reaction with tris(2,2′-bipyridine)ruthenium(III) seems to require the high technique in terms of treating unstable reagents and the construction of a spectroscopic cell to detect the emission of the short lifetime chemiluminescence. Therefore, our CT interaction method can be regarded being both profitable and useful as a simple determination of aliphatic amines in many respects.

As a conclusion, we may safely say that intermolecular CT interactions are applicable for the detection of tertiary alkylamines by FIA with a spectrophotometric detector. The present method appears to be very promising as a HPLC postcolumn detector. Further, since iodine forms CT complexes with many organic substances as a strong σ-electron acceptor, particularly with those having nonbonding electrons,[4—8)] this detection scheme might well be adopted for the determination of these compounds possessing no good chromophore.

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