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Analysis of Binary Mixtures of Tertiary Amines by Measurement of the Decomposition Rates of π-Complexes with Tetracyanoethylene

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A method has been developed for the determination of the fraction of a single species in a binary mixture of tertiary amines, by measurement of the pseudo first-order reaction rates for decomposition of the π-complexes with tetracyanoethylene. The initial absorbances at three wavelengths (u, v and w) and their sum in a simplified complementary tristimulus colorimetry were calculated by a numerical method. The color points of the reaction solution at the initial time were calculated, so that the fraction of as single species in a mixture of tertiary amines could be evaluated.

Keywords——fraction determination of a mixture; tertiary amine; tetracyanoethylene; decomposition of π-complex; pseudo first-order reaction rate; numerical method; simplified complementary tristimulus colorimetry

In the previous study,1) some tertiary amines were determined by a numerical method based on the decomposition rates of their π-complexes with tetracyanoethylene (TCNE). It was subsequently found that the π-complexes corresponding to some tertiary amines show large differences in decomposition rates with variation of the content of methanol in dichloromethane. For binary mixtures of the tertiary amines, if a single π-complex formed either has decomposed prior to the selected time or decomposes so slowly as not to interfere appreciably, it can be treated as a non-reactive absorbing species (I), and then the decomposition of the other π-complex can be followed independently. Several methods have been developed for such cases, but they are effective only at limited concentrations of each species, and tend to yield poor results.2) In this study the determination of the compositions of some binary tertiary amines was achieved by measurement of the rates of decomposition of their π-complexes. The method presented can be used for the determination of mixtures at any concentrations without prior knowledges of the initial concentrations of both tertiary amines, and gives good results by simple procedures.

In the simplified complementary tristimulus colorimetry (SCTS method),3) the absorbance of a reaction solution at any time t corresponding to wavelength u, A_{tu}, is given by

$$A_{tu} = \varepsilon_{\pi u}[\pi]_t + \varepsilon_{\sigma u}[\sigma]_t + \varepsilon_{\mathrm{I}u}[\mathrm{I}]_0 \tag{1}$$

where $[\pi]_t$, $[\sigma]_t$ and $[\mathrm{I}]_0$ are the concentrations of π-, σ-complex and I at the same time, and $\varepsilon_{\pi u}$, $\varepsilon_{\sigma u}$ and $\varepsilon_{\mathrm{I}u}$ are the molar absorption coefficients of the corresponding species at wavelength u, respectively. By substitution of q defined as

$$q = [\pi]_t/([\pi]_t+[\sigma]_t) \tag{2}$$

into Eq. (1), the following equation is obtained.

$$A_{tu}/([\pi]_t+[\sigma]_t) = q\varepsilon_{\pi u} + (1-q)\varepsilon_{\sigma u} + \varepsilon_{\mathrm{I}u}[\mathrm{I}]_0/([\pi]_t+[\sigma]_t) \tag{3}$$

The analogous equations for A_{tv} and A_{tw} at wavelengths v and w can be obtained. By considering that $J_t = A_{tu}+A_{tv}+A_{tw}$,

$$J_t/([\pi]_t+[\sigma]_t) = qE_\pi + (1-q)E_\sigma + E_\mathrm{I}[\mathrm{I}]_0/([\pi]_t+[\sigma]_t) \tag{4}$$

where E_π, E_σ and E_I are the overall absorptivities of π-, σ- complex and I corresponding to the three wavelengths, respectively. For each solution at the initial time and after completion of the reaction, Eqs. (5) and (6) hold:

$$J_0 = E_\pi[\pi]_0 + E_{\mathrm{I}}[\mathrm{I}]_0 \tag{5}$$

$$J_\infty = E_\sigma[\sigma]_\infty + E_{\mathrm{I}}[\mathrm{I}]_0 \tag{6}$$

where J_0 and J_∞ are the sums of three absorbances at the initial and final stages, and $[\pi]_0$ and $[\sigma]_\infty$ are the concentrations of π- and σ-complex. By considering that $[\pi]_0=[\sigma]_\infty=[\pi]_t+[\sigma]_t$, Eq. (4) can be rewritten by use of Eqs. (5) and (6) as

$$q = (J_t-J_\infty)/(J_0-J_\infty) \tag{7}$$

A first- or pseudo first-order rate equation can be given in terms of the mol fraction ($-\ln q=k_1t$),[3a] and so from Eq. (7):

$$\ln(J_0-J_\infty)/(J_t-J_\infty) = k_1t \tag{8}$$

The value of J_0 can be calculated from k_1 and J_t as a function of time by a numerical method based on Eq. (8).[1] The color point of the reaction solution at the initial time corresponding to wavelength u, Q_{0u}, is given by the following equation.

$$Q_{0u} = A_{0u}/J_0 \tag{9}$$

where A_{0u} is the initial absorbance of the reaction solution, which was calculated by a numerical method based on Eq. (10) as described previously.

$$\ln(A_{0u}-A_{\infty u})/(A_{tu}-A_{\infty u}) = k_1t \tag{10}$$

Then the initial mol fraction of π-complex in a mixture of the complex and I, q_{0u}, was evaluated from Eq. (11) by use of Q_{0u}.

$$q_{0u} = E_{\mathrm{I}}(Q_{\mathrm{I}u}-Q_{0u})/[E_\pi(Q_{0u}-Q_{\pi u}) + E_{\mathrm{I}}(Q_{\mathrm{I}u}-Q_{0u})] \tag{11}$$

where $Q_{\pi u}$ and $Q_{\mathrm{I}u}$ are the color points of π-complex and I at wavelength u. Analogously, the color points corresponding to wavelengths v and w of the reaction solution at the initial time could be calculated and the mol fractions were then obtained.

As shown in Table I, the ratios of the observed k_1 for the decomposition of π-complex of 3-dimethylaminobenzoic acid (DBA) to that of *N*,*N*-dimethylaniline (DMA) varied from 25.8 to 3.15 with increasing content of methanol in dichloromethane, and the percentage methanol content which gave the most accurate result was 40% (v/v), which was in good agreement with the value expected from the following equation for the error in determination of DBA,[2a] since the concentrations of the π-complexes formed at the initial stage were equal to the initial concentrations of tertiary amines.[1]

$$\text{Error (\%) in } [\mathrm{DBA}]_0 = \{[\mathrm{DMA}]_0 \exp(-k_1t)/[\mathrm{DBA}]_0 \exp(-k_1't)\} \times 100 \tag{12}$$

where $[\mathrm{DBA}]_0$ and $[\mathrm{DMA}]_0$ are the initial concentrations, and k_1 and k_1' are the observed pseudo

TABLE I. Effect of Methanol Content in Dichloromethane on the Pseudo First-Order Rate Constants, k_1, for Decomposition of π-Complexes of DBA and DMA, and on the Determination of DBA in the Presence of DMA[a]

Methanol (v/v %)	DBA 10^2k_1 (min^{-1})[b]	DMA 10^2k_1 (min^{-1})	DBA amount present (%)	DBA amount found (%)[c]
5.0	0.096	2.48	80.4	129.8±0.54
10.0	0.301	4.67		117.8±0.05
20.0	0.675	5.87		111.8±0.05
30.0	1.050	6.53		81.5±0.30
40.0	2.370	7.46		80.3±0.19

a) Temperature: 20°C; *u* (650 nm), *v* (420 nm), *w* (380 nm).
b) It was assumed that k_1 for π-complex of DBA was affected by the change of electron density (the availability of electrons) on nitrogen resulting from the interaction between the carboxyl group in DBA and methanol.[4]
c) The values are the means ± S.D. of three determinations.

first-order rate constants. The optimal methanol contents for other mixture of tertiary amines were also studied by using Eq. (12) (as described in the legend to Table II). The results obtained are summarized in Table II. The average relative error based on the initial concentrations for all mixtures analyzed was 0.72%.

Although the method described here could not be applied to mixtures whose components have small reaction rate differences, it should be possible to find conditions suitable for the measurement of many tertiary amine mixtures by changing some experimental conditions, *e.g.*, the reaction temperature, the concentrations of reagent and solvent, the addition of a catalyst, *etc.*

TABLE II. Determination of Binary Mixtures of Tertiary Amines

Mixtures[a]	Amount present		Amount found[b] % of A	Error (%)
	μg/ml	% of A		
A. DMA[c]	36.4	13.4	13.6±0.27	+1.49
B. EC	234.3			
	60.6	23.7	24.6±0.26	+3.80
	195.3			
A. DMA[d]	90.9	35.4	35.5±0.57	+0.28
B. DNA	166.2			
	133.3	44.5	44.6±0.38	+0.45
	166.2			
A. PY[e]	39.6	24.6	24.8±0.36	+0.81
B. CL	121.2			
	158.2	56.6	56.2±0.93	−0.71
	121.2			
A. AN[f]	188.2	68.5	68.8±0.21	+0.44
B. DNA	86.4			
	244.7	73.9	74.1±0.06	+0.27
	86.4			
A. DBA[g]	495.6	80.4	80.3±0.19	−0.12
B. DMA	121.2			
A. DBA[h]	330.4	93.2	93.2±0.31	0
B. CL	24.2			
	495.6	97.6	97.6±0.27	0
	12.1			
A. PY[i]	158.2	46.0	46.0±0.43	0
B. TBA	185.3			
A. AN[j]	56.5	24.0	24.2±0.69	+0.83
B. AT	179.4			
A. PP[k]	101.7	22.1	22.3±0.24	+0.90
B. DP	357.9			
	203.3	39.9	40.7±2.61	+2.01
	306.8			
A. AN[l]	75.3	19.7	19.7±0.03	0
B. DP	306.8			
	56.5	12.1	12.1±0.24	0
	409.1			
A. PP[m]	135.4	39.3	39.0±0.21	−0.76
B. AT	209.1			
	169.4	53.1	53.5±2.79	+0.75
	149.4			

[a] See experimental section. [b] Values are the means ± S.D. of three determinations. [c] 1.0% (v/v) CH_3OH, 25.5°C, *u* (675 nm), *v* (590 nm), *w* (400 nm). [d] 5.0% (v/v) CH_3OH, 25.5°C, *u* (675 nm), *v* (520 nm), *w* (420 nm). [e] 5.0% (v/v) CH_3OH, 20°C, *u* (650 nm), *v* (430 nm), *w* (380 nm). [f] 2.0% (v/v) CH_3OH, 25.5°C, *u* (530 nm), *v* (410 nm), *w* (390 nm). [g] 40.0% (v/v) CH_3OH, 20°C, *u* (650 nm), *v* (420 nm), *w* (380 nm). [h] 10.0% (v/v) CH_3OH, 25.5°C, *u* (650 nm), *v* (550 nm), *w* (450 nm). [i] 5.0% (v/v) CH_3OH, 25.5°C, *u* (650 nm), *v* (550 nm), *w* (450 nm). [j] 10.0% (v/v) CH_3OH, 25.5°C, *u* (580 nm), *v* (510 nm), *w* (420 nm). [k] 10.0% (v/v) CH_3OH, 25.5°C, *u* (580 nm), *v* (500 nm), *w* (480 nm). [l] 5.0% (v/v) CH_3OH, 25.5°C, *u* (590 nm), *v* (510 nm), *w* (490 nm). [m] 10.0% (v/v) CH_3OH, 25.5°C, *u* (580 nm), *v* (420 nm), *w* (380 nm). All methanol content are percentages in a mixture with dichloromethane.

Experimental

Materials——Antipyrine (AN), alimemazine tartrate (AT) and papaverine hydrochloride (PP) were of Japanese Pharmacopoeia (JP) X grades, and stock solutions were prepared according to the methods given in JP X. Dipyridamole (DP) was obtained as ampules for injection from Tanabe Seiyaku Co., Ltd. (Persantin®).⁵⁾ *N*-Ethylcarbazole (EC), *N*,*N*-dimethyl-3-nitroaniline (DNA), pyridine (PY), 2,4,6-collidine (CL), DMA and DBA were purified by the usual techniques. TCNE was purified as described previously¹⁾ and was freshly dissolved daily in 1% (v/v) methanol–dichloromethane mixture. Dichloromethane and methanol were distilled by the usual techniques.

Apparatus——Measurements of the absorption spectra and calculations of the color points were performed with the same instruments as described previously.⁶⁾

Procedure——The pseudo first-order kinetics for the decompositions of the π-complexes were obtained at a TCNE concentration of 20 times the total concentration of both tertiary amines, and the rate constants were calculated from the decreases of absorbance at regular intervals ($t=1.5$ min).

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