

Charge-transfer complexes of iodine and nonionic surfactants: interpretation and use in the Winkler method*

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Abstract: Formation constants (K_c) and molar absorption coefficients (ϵ_c) of complexes of iodine and various nonionic surfactants were determined, providing a basis for selection of a surfactant for use in a spectrophotometric modification of the Winkler method. The method of calculation of K_c and ϵ_c was extended to include absorption by triiodide at the wavelength of maximum absorbance of the complex. Because the molar absorption coefficients of polyoxyethylene 10 oleyl ether (oleth 10) and polyoxyethylene 23 oleyl ether were significantly greater than those of other surfactants, they are superior candidates for use in the Winkler method. Formation constants could not be correlated with molecular characteristics of the surfactants such as alkyl chain or polyoxyethylene chain length, nor with physical characteristics of iodine-surfactant solutions such as reduction of iodine loss due to volatilization.

Keywords: Iodine; oxygen; complexes; surfactants; Winkler method; spectroscopy.

Introduction

A spectrophotometric modification of the Winkler method for oxygen measurement has been developed which employs a nonionic surfactant to minimize loss of iodine during the assay and to exploit the amplified spectral characteristics of the iodine-surfactant complex [1]. Many nonionic surfactants can be used in this modification in which iodine, generated from iodide in proportion to dissolved oxygen, interacts with the surfactant to form a complex which is easily measured using UV spectroscopy [2]. In order to select the best surfactant for the method, we have investigated the interaction of iodine with various nonionic surfactants.

Figure 1 summarizes the principal interactions which can affect aqueous solutions of iodine, including solutions that contain nonionic surfactants. It has been proposed [3-7] that the formation of a charge-transfer complex (CTC) is the primary interaction between nonionic surfactants and iodine (Fig. 1, K_c).

In most instances, including when the Winkler method is performed, the solubility of

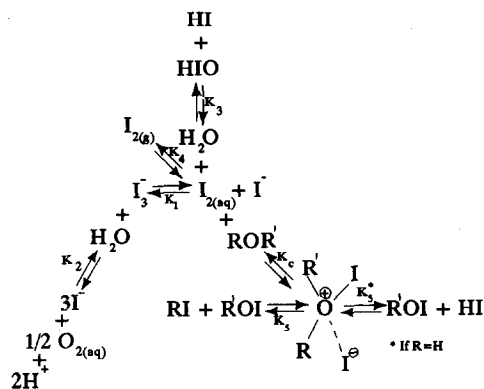


Figure 1
 Principal interactions affecting aqueous iodine solutions, including those with nonionic surfactants.

iodine is increased by the presence of iodide. Iodine and iodide form triiodide, a charge-transfer complex which has been studied extensively [8-10], and represented in Fig. 1 by K_1 . The formation constant and molar extinction coefficient of triiodide are well known at various temperatures.

The equilibrium represented by K_2 (Fig. 1) is sometimes known as the 'oxygen error re-

*Presented at the Seventh Annual Meeting and Exposition of the American Association of Pharmaceutical Scientists (Analysis & Pharmaceutical Quality Section), San Antonio, TX, USA, 15-19 November 1992.

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action' [11], in which iodide is oxidized to iodine in the presence of oxygen in an acidic solution. This reaction is responsible for the importance of proper iodide concentration in the Winkler method, as the assayed solution of triiodide is very acidic ($\text{pH} \approx 2$) and excess iodide is required [8, 10].

The equilibrium represented by K_3 (Fig. 1) is the hydrolysis of iodine, which has been well characterized ($K_3 = 2.58 \times 10^{-13}$ M at 25°C) [9], but seldom mentioned as a source of error in the Winkler method [12, 13]. Due to the acidity of the sample and the small magnitude of the equilibrium constant, this equilibrium probably does not significantly affect the iodine concentration of the sample.

The most troublesome side reaction with respect to the Winkler method is the volatilization of iodine, represented by equilibrium K_4 (Fig. 1). Over the years, this has been the most highly recognized source of error associated with the Winkler method [8, 10, 14–18]. Several authors have reported improved accuracy and precision with specially designed titration apparatus or glassware [15–18].

Addition of a nonionic surfactant to the acidic triiodide solution results in the formation of an iodine–surfactant charge-transfer complex (K_c , Fig. 1). This formation shifts the equilibria away from iodine, which is subject to side reactions which alter the total iodine concentration. We attempted to relate changes in two of these side reactions, volatilization of iodine and production of iodine from iodide in acidic solution, to the formation constants of the charge-transfer complexes formed on addition of surfactant.

Formation constants and molar absorption coefficients of CTCs resulting from iodine and selected surface-active agents have been determined using a spectrophotometric method [19, 20], but no systematic study of surfactant–iodine CTCs has been reported. These parameters can provide a basis for selection of a surfactant for use in the spectrophotometric modification of the Winkler method; larger extinction coefficients are desirable to increase resolution, and complexes with larger formation constants would minimize the concentration of free iodine, which is subject to various side reactions that decrease the accuracy of the Winkler method [8–13, 21–24].

The formation constants and molar absorption coefficients of CTCs resulting from

the interaction of iodine and two series of commercially available nonionic surfactants, with varying alkyl chain length and number of ethylene-oxide units have been determined in order to facilitate the selection of a surfactant for the spectrophotometric modification of the Winkler method. The method of calculation of the formation constant and molar absorption coefficient has been extended to account for absorbing species not considered in previous work [19, 20, 25, 26].

Experimental

Iodine (resublimed, Fisher, Fair Lawn, NJ, USA) and all polyoxyethylene ethers (Sigma, St Louis, MO, USA) were used as received. For convenience, the nomenclature adopted by the Cosmetic, Toiletry and Fragrance Association, Inc. will be used for all polyoxyethylene ethers: steareth 10 denotes polyoxyethylene 10 stearyl ether; ceteth 10, polyoxyethylene 10 cetyl ether; trideceth 10, polyoxyethylene 10 tridecyl ether; oleth 10 and oleth 23, polyoxyethylene 10 and 23 oleyl ether, respectively; and laureth 6, 7, 8, 9, 10 and 23 represent polyoxyethylene 6, 7, 8, 9, 10 and 23 lauryl ether, respectively. All solutions were prepared with water purified with a Nanopure filter system (Barnstead, Dubuque, IA, USA).

Absorption spectra were obtained with a Lambda 6/PECSS system equipped with a thermostated cell holder (Perkin Elmer, Norwalk, CT, USA), and quartz cells with 1 cm optical path length. Iodine solutions were prepared daily.

Theoretical Derivation

Lang [25] has shown that the following equation allows for the calculation of the formation constant, K_c , and the molar absorption coefficient, ϵ_c for a 1:1 complex:

$$\frac{[A]_0[D]_0l}{A_c} = \frac{1}{\epsilon_c} \left\{ [A]_0 + [D]_0 - \frac{A_c}{\epsilon_c} \right\} - \frac{1}{K_c \epsilon_c}, \quad (1)$$

where $[A]_0$ and $[D]_0$ are the concentrations of electron acceptor (iodine) and donor (surfactant), respectively; A_c is the absorbance due to the complex, and l is the path length of the optical cell. If an initial estimate can be made for ϵ_c , the values of ϵ_c and K_c can be obtained from the slope and intercept of a plot of $([A]_0[D]_0l/A_c)$ vs $\{[A]_0 + [D]_0 - (A_c/\epsilon_c)\}$.

Successive iterations of the equation provide K_c and ϵ_c .

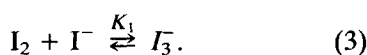
Rohatgi-Mukherjee *et al.* modified Lang's equation to account for absorbance of iodine [19], which also absorbs at the wavelength of maximum absorbance of the complex:

$$\frac{[D]_0 l}{\frac{A_T}{[I_2]_0} - \epsilon_0} = \frac{1}{\epsilon_c - \epsilon_0} \left\{ [A]_0 + [D]_0 - \frac{\left(\frac{A_T}{[I_2]_0} - \epsilon_0 \right) [A]_0}{(\epsilon_c - \epsilon_0)} \right\} - \frac{1}{K_c(\epsilon_c - \epsilon_0)}, \quad (2)$$

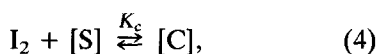
where A_T represents the total absorbance at the wavelength of maximum absorbance of the complex, $[I_2]_0$ represents the initial iodine concentration, and ϵ_0 refers to the molar absorption coefficient of uncomplexed iodine at this wavelength.

Rohatgi-Mukherjee *et al.* [19] assumed that all absorbance at the maximum for the complex is caused by either the complex or iodine, as no iodide was added to the dilute (0.2 mM iodine) iodine solution. This is not likely, as triiodide is always present due to the hydrolysis of iodine (K_3 , Fig. 1) and impurities in the iodine. Even small amounts of triiodide can contribute to the total absorbance at the wavelength of maximum absorbance for the complex, due to the large molar absorption coefficient at 294 nm ($35,388 \text{ M}^{-1} \text{ cm}^{-1}$) and at 380 nm ($14,195 \text{ M}^{-1} \text{ cm}^{-1}$) [9].

Upon dissolution of iodine, hydrolysis will take place until equilibria K_1 and K_3 (Fig. 1) are satisfied. K_2 is negligible due to its small magnitude and the large magnitude of K_1 , such that most iodide produced from hydrolysis will complex with iodine. This assumes that volatilization (K_4 , Fig. 1) is negligible due to the low concentration of iodine. Once equilibrium is established, it can be assumed that K_2 and K_3 are negligible with respect to K_1 such that the equilibrium concentrations of iodine, iodide, triiodide and complex should be a function of K_1 .



When surfactant is added, iodine is also involved in the following equilibrium:



where $[S]$ and $[C]$ represent the equilibrium concentration of free surfactant and complex, respectively.

Although iodide does not absorb appreciably at wavelengths above 260 nm, triiodide does, and should be considered in the calculation of K_c and ϵ_c for the CTC. Once both equilibria are satisfied, the equilibrium concentrations of complex, surfactant, iodine, iodide,

and triiodide are a function of K_c and K_1 . The following extension of the iterative methods of Rohatgi-Mukherjee and Lang accounts for the absorbance of triiodide in the calculation of K_c and ϵ_c .

At any wavelength

$$A_T = A_c + A_{I_3} + A_{I_2}, \quad (5)$$

where A_T refers to the total absorbance at the absorbance maximum of the complex, and A_c , A_{I_3} , and A_{I_2} refer to the absorbance due to the complex, triiodide, and iodine, respectively. It follows that, for a path length of 1 cm;

$$A_T = [C]\epsilon_c + [I_3^-]\epsilon_{I_3} + [I_2]\epsilon_{I_2}, \quad (6)$$

where $[C]$, $[I_3^-]$, and $[I_2]$ refer to the equilibrium concentrations of complex, triiodide, and iodine, respectively, and ϵ_{I_3} and ϵ_{I_2} refer to the molar absorption coefficients of triiodide and iodine, respectively, at the absorbance maximum of the complex. If y is defined as the amount of iodine generated by equilibrium K_1 in response to depletion of iodine by equilibrium K_c , then equation (6) can be expressed in terms of initial concentrations of triiodide, $[I_3^-]_0$, and iodine, $[I_2]_0$:

$$A_T = [C]\epsilon_c + ([I_3^-]_0 - y)\epsilon_{I_3} + ([I_2]_0 + y - [C])\epsilon_{I_2} \quad (7)$$

By definition;

$$K_c = \frac{[C]}{[I_2][S]}, \quad (8)$$

so,

$$([S]_0 - [C])([I_2]_0 + y - [C]) = \frac{[C]}{K_c}, \quad (9)$$

where $[S]_0$ is the initial concentration of surfactant. Solving equation (7) for $[C]$ and

substituting into equation (9), the following expression can be found after rearrangement:

$$\frac{[S]_0([I_2]_0 + y)}{A_T - \epsilon_{I_2}([I_2]_0 + y) - \epsilon_{I_3}([I_3]_0 - y)} = \frac{1}{K_c(\epsilon_c - \epsilon_{I_2})} + \frac{1}{\epsilon_c - \epsilon_{I_2}}$$

$$\left\{ [S]_0 + [I_2]_0 + y - \frac{A_T - \epsilon_{I_2}([I_2]_0 + y) - \epsilon_{I_3}([I_3]_0 - y)}{\epsilon_c - \epsilon_{I_2}} \right\}. \quad (10)$$

Note that in order to use equation (10) to determine K_c and ϵ_c , y , $[I_2]_0$, and $[I_3]_0$ must be known.

Calculation of initial iodine and triiodide concentrations

By definition,

$$A_{460} = [I_3]_0 \epsilon_{1,460} + [I_2]_0 \epsilon_{1,460} \quad (11)$$

and

$$A_{287.5} = [I_3]_0 \epsilon_{1,287.5} + [I_2]_0 \epsilon_{1,287.5}. \quad (12)$$

Since the molar absorption coefficients of iodine and triiodide are known at 287.5 and 460 nm at 25°C, the initial concentrations of iodine and triiodide can be determined by simultaneously solving equations (11) and (12) using the absorbance of aqueous solutions in the absence of a surfactant at these wavelengths.

Calculation of y

By definition;

$$K_1 = \frac{[I_3]}{[I_2][I^-]}, \quad (13)$$

so;

$$K_1 = \frac{[I_3]_0 - y}{([I_2]_0 + y - [C])([I^-]_0 + y)}. \quad (14)$$

To solve for y , $[I^-]_0$ must be known. Due to experimental conditions the concentration of iodide is low, because it is formed through hydrolysis of iodine and complexes with iodine to form triiodide according to equilibrium K_1 . Once $[I_2]_0$ and $[I_3]_0$ are known, equation (13) can be used to determine $[I^-]_0$.

Solving equation (9) for y and substituting in

equation (14), a third degree polynomial is found of the form

$$\alpha[C]^3 + \beta[C]^2 + \chi[C] + \delta = 0, \quad (15)$$

where $\alpha = K_c^2 - K_1 K_c$

$$\beta = K_1 K_c ([S]_0 + [I_2]_0 - [I_3]_0) - K_c^2 ([I^-]_0 + 2[S]_0 + [I_2]_0) + K_1 - K_c$$

$$\chi = [S]_0 \{ K_1 K_c ([I^-]_0 - [I_2]_0) + K_c^2 (2[I_3]_0 + 2[I_2]_0 + [S]_0) + K_c \}$$

$$\delta = -K_c^2 [S]_0^2 ([I_3]_0 + [I_2]_0).$$

Since K_1 is known (714 M^{-1} at 25°C) [9], if an initial estimate can be made for ϵ_c , the Newton-Raphson method may be used to solve equation (15) for $[C]$. The most convenient method for obtaining an initial estimate of ϵ_c is to use data from two iodine-surfactant solutions and solve equation (1) simultaneously for ϵ_c and K_c [25]. With $[C]$, y can be calculated from equation (9).

Determination of ϵ_c and K_c : iteration procedure

A linear plot of equation (10) is then made, and better estimates for ϵ_c and K_c are calculated from the slope and intercept. A new value for y is calculated using the better estimate for K_c , and equation (10) is plotted again. This process is repeated until a consistent set of values for ϵ_c and K_c are obtained (less than 0.01% difference between two successive iterations). In most cases, convergence was achieved after three iterations, and never more than four.

Results and Discussion

A series of polyoxyethylene (POE) lauryl ethers (laureth 6, laureth 7, laureth 8, laureth 9, laureth 10 and laureth 23) was selected to

examine the effect of the number of polyoxyethylene groups per surfactant monomer on the formation constant of the complex, K_c , and the absorption coefficient, ϵ_c . Trideceth 10, ceteth 10, and steareth 10 were selected to examine the effect of alkyl chain length on K_c and ϵ_c . Oleth 10 and oleth 23 were also included to compare the effect of the number of POE groups on the formation constant and absorption coefficient when the surfactant contains an unsaturated alkyl chain.

The spectra of iodine solutions containing varying concentrations of surfactant above the CMC were obtained at 25°C, and the absorbances of the absorption maxima used to calculate the formation constant K_c and the molar absorption coefficient ϵ_c for the complex. One set of visible and UV spectra obtained for POE laurel ether solutions is illustrated in Fig. 2. The amount of surfactant is varied, while all solutions contain the same amount of iodine. Note the presence of two distinct peaks; the charge-transfer peak at 294 nm from the $n-\sigma^*$ electron transfer, and the 'blue shifted' iodine peak at about 380 nm [27]. Mulliken [27] has proposed that the swollen size of the excited σ^* orbital increases the repulsion energy between the complex and the donor, and the repulsion energy is added to the energy of the excited iodine molecule. This repulsion energy, hence the observed blue shift, increases with increasing overlap of the surfactant (donor) and iodine (acceptor) orbitals in the ground state. The wavelength of maximum absorbance for each iodine-surfactant complex is listed in Tables 1 and 2.

Formation constants and absorption coefficients of the complexes formed between

iodine and each surfactant were calculated at the charge-transfer peak and the 'blue-shifted' peak using equation (2), and again with equation (10). The formation constants are listed in Table 1, and the molar absorption coefficients are listed in Table 2.

Nandy and Bhowmik [20] reported formation constants which were averages of constants calculated at the charge-transfer peak (293 nm) and at the 'blue-shifted' iodine peak (370 nm). They reported a mean deviation of 5% for their data. Because the formation constants from the charge-transfer peak and the 'blue shifted' iodine peak reported here are generally significantly different (Student's t -test, 95% level), we did not report an average value. Both equations (2) and (10) provided linear plots of the data. The goodness of fit was evaluated by comparison of the sample standard deviation from regression, s_{yx} . The use of equation (10) resulted in values of s_{yx} which were significantly smaller than those resulting from the use of equation (2) (t -test, 95% level) when the charge-transfer peak (294 nm) was used. There was no significant difference in s_{yx} when the 'blue-shifted' iodine peak was used. As a result, equation (10) is preferable to equation (2) for the calculation of K_c and ϵ_c .

The increased absorption coefficient of the blue shifted peak has been attributed to mixing of upper level bands of the charge-transfer band and the iodine band [25], and there seems to be a correlation between the blue shift and the absorption coefficient [27]. This correlation seems to be supported by our results. The complexes formed with iodine and oleth 10 or oleth 23 display the largest blue shift of surfactants examined, and they exhibit molar absorption coefficients significantly greater than the other surfactants.

One of the drawbacks of the Winkler method for oxygen measurement is the instability of iodine concentration due to various side reactions [8-18]. We studied the two most frequently cited side reactions, iodine loss due to volatilization (K_4 , Fig. 1), and acid-catalysed iodine generation from iodide (K_2 , Fig. 1), and the effect of surfactant on these reactions. We expected that surfactants which formed complexes with iodine with higher formation constants would reduce these side reactions by shifting the equilibrium away from iodine and triiodide.

Acid-catalysed iodine generation did not contribute significant error to the Winkler

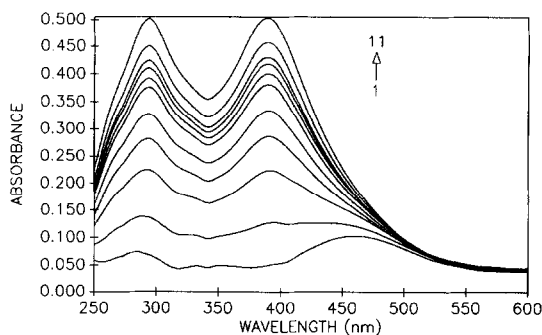


Figure 2

Visible and UV spectra of iodine and laureth 10 in water at 25°C. [1.36×10^{-4} M and [laureth 10] = (1) 0.0, (2) 1.0×10^{-4} M, (3) 2.0×10^{-4} M, (4) 3.0×10^{-4} M, (5) 4.0×10^{-4} M, (6) 5.0×10^{-4} M, (7) 6.0×10^{-4} M, (8) 7.0×10^{-4} M, (9) 8.0×10^{-4} M, (10) 1.0×10^{-3} M, (11) 1.5×10^{-3} M].

Table 1
Summary of formation constants of charge-transfer complexes of iodine and selected surfactants

Surfactant	I ₂ peak (nm)	Formation constant (M ⁻¹)			
		Equation (2)		Equation (10)	
		294 nm	I ₂ peak	294 nm	I ₂ peak
Laureth 6	390	2660 (530)*	2990 (440)	2960 (540)	3670 (140)
Laureth 7	389	3260 (890)	3710 (950)	3850 (1410)	4930 (1220)
Laureth 8	389	2460 (790)	2990 (1060)	2670 (790)	3540 (990)
Laureth 9	387	1320 (270)	1620 (200)	1440 (320)	2040 (390)
Laureth 10	388	2550 (290)	3140 (370)	2880 (400)	3980 (550)
Laureth 23	388	730 (200)	1130 (330)	810 (230)	1470 (540)
Trideceth 10	388	850 (160)	1150 (180)	910 (190)	1370 (260)
Ceteth 10	391	†	4830 (2380)	†	6700 (3530)
Steareth 10	390	1640 (440)	1920 (370)	1750 (430)	2280 (400)
Oleth 10	373	1620 (250)	3100 (500)	1700 (370)	3390 (880)
Oleth 23	374	2190 (90)	4340 (570)	2250 (90)	4680 (620)

*95% confidence interval in parentheses.

†The peak at 294 nm could not be used to calculate K_c due to nonlinear behaviour and excessive variability in the data.

Table 2
Summary of molar absorption coefficients of charge-transfer complexes of iodine and selected surfactants

Surfactant	I ₂ peak (nm)	Molar absorption coefficient (M ⁻¹ cm ⁻¹)			
		Equation (2)		Equation (10)	
		294 nm	I ₂ peak	294 nm	I ₂ peak
Laureth 6	390	4330 (1090)*	4350 (1110)	3680 (600)	3670 (660)
Laureth 7	389	4930 (870)	4790 (780)	4010 (900)	3880 (850)
Laureth 8	389	5130 (1290)	4870 (1050)	4380 (970)	4140 (810)
Laureth 9	387	6600 (870)	6000 (1750)	5100 (1730)	4550 (1380)
Laureth 10	388	5970 (370)	5540 (190)	4570 (370)	4310 (260)
Laureth 23	388	8080 (4980)	6400 (3670)	6016 (3633)	4709 (2658)
Trideceth 10	388	7954 (1462)	6748 (989)	6260 (1240)	5320 (1020)
Ceteth 10	391	†	4400 (2120)	†	3560 (920)
Steareth 10	390	6330 (1290)	6280 (1410)	5110 (360)	5150 (750)
Oleth 10	373	15300 (1790)	9210 (1060)	11600 (3170)	7200 (1920)
Oleth 23	374	14500 (810)	8990 (470)	10800 (420)	6890 (250)

*95% confidence interval in parentheses.

†The peak at 294 nm could not be used to calculate ϵ_c due to nonlinear behaviour and excessive variability in the data.

method if recommended [28] iodide concentrations are used. The amount of iodine produced from iodide was negligible in solutions up to 0.13 M in iodide and pH 2. Because the iodide concentration after acidification of a sample is approximately 15 mM, oxidation of iodide to iodine is not a significant source of error in the Winkler method.

Loss of iodine to volatilization was a very serious problem, and addition of a non-ionic surfactant nearly eliminated this error. Addition of 25 mM surfactant to a solution 5 mM in triiodide reduced iodine loss to volatilization to the point where it was no longer detectable by the method reported by Rammell and Splite [22]. However, no correlation was observed between iodine vapour pressure reduction and complex formation. All surfactants reduced loss of iodine to volatiliz-

ation beyond the detection limits of the method.

Maximization of the molar absorption coefficient of the iodine-surfactant complex is desirable for increased sensitivity of the spectrophotometric modification of the Winkler method. The molar absorption coefficients of oleyl-ether surfactants, oleth 10 and oleth 23, were found to be significantly different at the 95% level from the other surfactants by analysis of variance and Scheffe's multiple range test. The molar absorption coefficients of oleth 10 and oleth 23 were found to be not significantly different at the 95% level (Student's *t*-test).

Because the molar absorption coefficients of iodine complexes formed with oleth 10 and oleth 23 were significantly greater than those of other surfactants, either surfactant would be a

good choice for the spectrophotometric modification.

Trideceth 10, ceteth 10 and steareth 10 would not be an acceptable choice for the spectrophotometric modification because they are slightly turbid at low concentrations, and opaque or pearlescent at concentrations sufficient to solubilize the amount of iodine generated by the Winkler method. They were included in this study to examine the effect of alkyl chain length on formation and molar absorption coefficient of the complex. Due to excessive variability in the data, we were unable to determine the formation constant and molar absorption coefficient for the complex of ceteth 10 and iodine at 294 nm. No trend is evident for either formation constant or molar absorption coefficient with respect to alkyl chain length.

Laureth 6, laureth 7, laureth 8, laureth 9, laureth 10 and laureth 23 were included in this study to examine the effect of the number of POE groups per monomer on complex formation constants and molar absorption coefficient. The formation constant generally decreases with increasing POE units per monomer, laureth 7 being significantly larger than laureth 9 and laureth 23. The absorption coefficient increases with increasing POE units per monomer, but no two absorption coefficients are significantly different (anova, 95% level).

Conclusions

The formation constants and molar absorption coefficients for charge-transfer complexes formed from iodine and various nonionic surfactants were determined spectrophotometrically. Rohatgi-Mukherjee's equation was modified to include the absorbance of triiodide at the wavelength of maximum absorbance of the complex, and used to calculate the constants. The modified equation provided a better linear fit to the experimental data.

The effect of the number of POE groups and the effect of alkyl chain length on the formation constant and molar absorption coefficient of the complex were examined by selection of a variety of commercially available nonionic surfactants. The molar absorption coefficients of complexes formed from iodine and oleth 10 or oleth 23 were significantly greater than those of iodine and other surfactants. Our precision was not sufficient to

identify any significant relationships between the number of POE groups or alkyl chain length with molar absorption coefficient or formation constant. A thermodynamic treatment similar to those reported by others [19, 20] is suggested to identify possible relationships between surfactant structure and complex formation and spectral characteristics. In such a study the formation constant K_c is determined at at least three temperatures (T), and the standard enthalpy change (ΔH°) can be calculated from the van't Hoff equation (assuming that ΔH° does not change with temperature). The standard free energy change (ΔG°) can be calculated from the dependence of K_c on T , and once ΔG° and ΔH° are known, the standard enthalpy change (ΔS°) can be calculated (assuming ΔS° does not change with temperature).

Because of the significantly greater molar absorption coefficients of complexes formed by oleth 10 and oleth 23 with iodine, and because we were unable to identify differences between them with respect to vapour pressure reduction, either of these surfactants would be a good choice for the spectrophotometric modification of the Winkler method.

Acknowledgements — We thank Dr Edwin T. Sugita for helpful comments on the manuscript. This work has been supported by a predoctoral fellowship from the Pharmaceutical Manufacturers Association.

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[Received for review 17 October 1992]