

Complexation Between Rare Earth Metals and 1, 5-di(2-hydroxy-5-sulfophenyl)-3-Cyanoformazan Occurring on Cetyltrimethylammonium Bromide Micelle

L-X. Zheng^a, H-W. Gao^{b,*} and R-Y. Xue^c

^aSchool of Occupation Training, Anhui University of Science and Technology, Huainan, 232007, P. R. China

^bSchool of Environmental Science and Engineering, Tongji University, Shanghai, 200092, P. R. China

^cShandong Dacheng Pesticide Co. Ltd, Zibo, 255000, P. R. China

(Received 27 April 2003, Accepted 9 October 2003)

The microsurface adsorption-spectral correction technique (MSASC) has been applied to investigation of the ternary interaction of 1,5-di(2-hydroxy-5-sulfophenyl)-3-cyanoformazan (DHSPCF) with cetyltrimethylammonium bromide (CTAB) and rare earths Y, Eu, Dy and Yb. The CTAB micelle enriched DHSPCF molecules on its microsurface in monolayers and then sensitized the complexation between rare earths and DHSPCF. The binary aggregate and the ternary complex both were characterized.

Keywords: MSASC Langmuir aggregation, 1,5-di(2-hydroxy-5-sulfophenyl)-3-cyanoformazan, Cetyltrimethylammonium bromide, Rare earths, Ternary complex

INTRODUCTION

Surfactant (S) is widely used in our life and work. Its basic and application studies in surface chemistry and organic chemistry are always very active, for example in the interaction with dyes [1,2], polymers [3,4] and biomacromolecules [5,6], and synthesis of new-type efficient surfactants [7-9]. Understanding the interaction of S with an organic molecules or an inorganic compound is helpful to investigate the synergistic mechanism of S in every aspects; *e.g.*, in separation, trace analysis and washing. The dye (L) is often selected as a spectral probe in study of the interaction. The micelle extraction [10], synergism perturbation [11], break point approach [12], hydrogen bond formation [13], micelle catalysis [14], asymmetric microenvironment [15] were ever established to explain the synergism of S, *e.g.*, solubilization, stabilization and sensitization. In the present work, the MSASC technique [16] as a combination of spectral correction technique [17] and Langmuir isothermal adsorption was applied to the

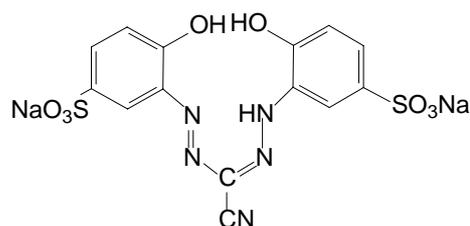


Fig. 1. Structural graph of DHSPCF

study of ternary complexation of 1,5-di(2-hydroxy-5-sulfophenyl)-3-cyanoformazan (DHSPCF, Fig. 1) with cetyltrimethylammonium bromide (CTAB) and four rare earth metals (REs: Y, Eu, Dy and Yb) at pH 9.74. Figure 1 shows that DHSPCF forms a bivalent anion in aqueous solution so as to bind on CTAB. Thus, REs can complex DHSPCF on CTAB. Both the CTAB-DHSPCF aggregation and the RE-DHSPCF complexation were characterized.

* Corresponding author. E-mail: hwgao@mail.tongji.edu.cn

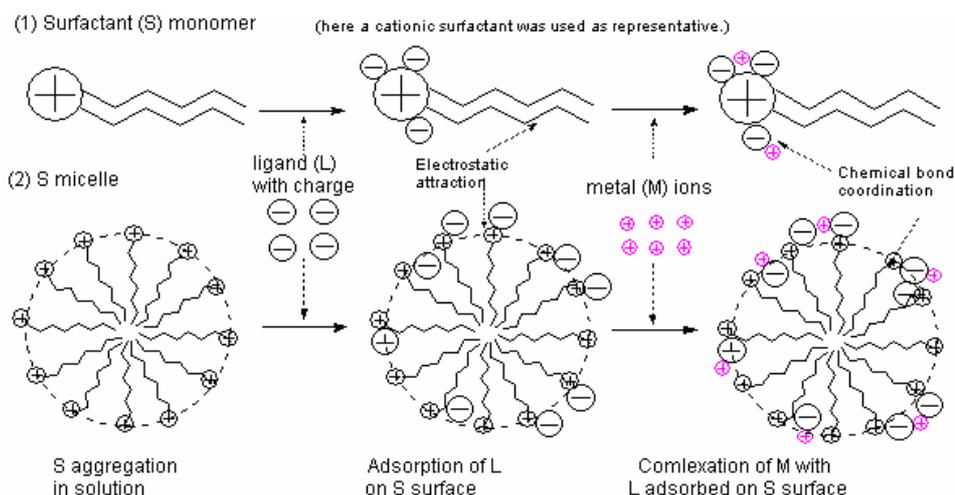


Fig. 2. The adsorption of dye ligand (L) on surfactant (S) monomer (1) and micelle (2) and the complexation of metal (M) with L.

PRINCIPLE

Figure 2 shows that the self-aggregation of S molecules forms a large electrostatic globe in aqueous solution when its concentration is more than the critical micellar concentration (CMC). The S monomer and micelle both attract the charged molecules, *e.g.* dye (L), to form an aggregate SL_N by non-covalent bonds. Thus, L molecules are enriched on S micelle. If a metal ion (M) is added into the solution, the complexation between M and L becomes rapid and sensitive. The aggregation of L on S obeys the Langmuir isothermal adsorption equation as followed [18].

$$1/\gamma = 1/N + 1/KNC_L \quad (1)$$

where the symbol K is the adsorption constant, C_L is the equilibrium molarity of L and γ is the molar ratio of L adsorbed to S. Within increase in L molarity, γ will approach to the maximal binding number, N . C_L and γ are calculated as follows [17, 19-20]:

$$\gamma = \eta \times C_{L0}/C_S \quad (2)$$

$$C_L = (1 - \eta)C_{L0} \quad (3)$$

where

$$\eta = (A_C - \Delta A)/A_0 \quad (4)$$

where C_S is the initial concentration of S and C_{L0} is that of L. η indicates the effective reaction fraction of L, A_C is the real absorbance of the S-L product, A_0 the absorbance of the L solution against water reference and ΔA indicates that of the S-L solution against a blank reference. All absorbances were measured at the peak wavelength (λ_2). A_C is calculated by means of [20]:

$$A_C = (\Delta A - \beta\Delta A')/(1 - \alpha\beta) \quad (5)$$

where $\Delta A'$ is the absorbance of the S-L solution measured at the valley wavelength (λ_1). Both α and β are the correction constants:

$$\alpha = \varepsilon_{SL}^{\lambda_1}/\varepsilon_{SL}^{\lambda_2} \quad (6)$$

and

$$\beta = \varepsilon_L^{\lambda_2}/\varepsilon_L^{\lambda_1} \quad (7)$$

The symbols $\varepsilon_{SL}^{\lambda_1}$, $\varepsilon_{SL}^{\lambda_2}$, $\varepsilon_L^{\lambda_1}$ and $\varepsilon_L^{\lambda_2}$ are the molar absorptivities of SL and L at λ_1 and λ_2 , respectively. Their ratio can be calculated by measuring the absorbances of known SL (no excess of L) and L solutions.

EXPERIMENTAL

Apparatus and Reagents

Absorption spectra were recorded on a TU1901 Spectrophotometer (PGeneral, Beijing) and independent absorbance measurements were carried out on a Model 722 Spectrophotometer. The pH of the solution was measured with a pHS-2C acidity meter (Leici Instruments, Shanghai, China). The temperature was adjusted and remained constant using a Model 116R electrically heated thermostatic bath (Changjiang Test Instruments of Tongjiang, China).

Stock standard solution of CTAB (1.00 mmol l^{-1}) was prepared by dissolving CTAB (Shanghai Chemical Reagents) in deionized water. Standard DHSPCF (1.00 mmol l^{-1}) solution was prepared by dissolving 250 mg of DHSPCF (provided by Changke Reagents Institute of Shanghai) in 500 ml deionized water. The CTAB-DHSPCF mixture was prepared by mixing 125 ml of 1.00 mmol l^{-1} DHSPCF, 100 ml of 10.0 mmol l^{-1} CTAB and 10 ml of pH 9.74 buffer solution and diluting to 500 ml, in which $0.025 \text{ mmol l}^{-1}$ $\text{DHSPCF}_{10}\text{CTAB}_{80}$ (80-micellar aggregation number of CTAB) was formed. Standard stock RE solutions (Y, Eu, Dy and Yb: all 10.0 mmol l^{-1}) were prepared by dissolving their oxide in 10 ml of HCl solution (1+1) and then diluting with deionized water. 1.00 mmol l^{-1} RE solutions were prepared daily. The acetic and ammonia buffer solutions between pH 5.05 and 11.55 were prepared to adjust the acidity of the solution. A 2.0 mol l^{-1} solution of NaCl was used to adjust the ionic strength of the aqueous solutions.

General Procedures

Interaction of CTAB with DHSPCF. Into a 25 ml calibrated flask were added 1.00 ml of 1.00 mmol l^{-1} CTAB, 2.5 ml of pH 9.74 buffer solution and an appropriate volume of the DHSPCF solution. The mixture was diluted with deionized water to 25 ml and mixed thoroughly. After 5 min, the absorbances were measured at 486 and 568 nm against a reagent blank, treated in the same way without CTAB, and then A_c , η , γ and C_L were calculated.

Interaction of CTAB-DHSPCF aggregate with REs. $1.00 \mu\text{mol}$ of RE was added into a 25 ml flask. A 2.5 ml portion of a buffer solution of pH 9.74 and a known volume of the CTAB-DHSPCF aggregate solution were added. After 40 min, the absorbances were measured at 568 and 486 nm against a reagent blank, treated in the same way without RE,

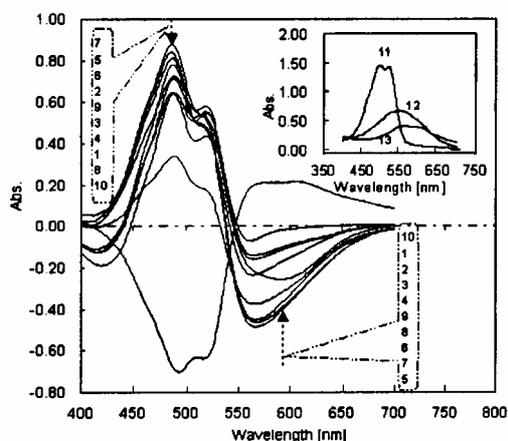


Fig. 3. Absorption spectra of DHSPCF, DHSPCF-CTAB and Dy-DHSPCF-CTAB solutions: Spectra 1 to 9 were recorded at pH 5.50, 5.89, 6.26, 7.10, 8.30, 8.70, 9.74, 10.35 and 11.55, respectively, where the solutions contained $0.0400 \text{ mmol l}^{-1}$ CTAB and $0.0400 \text{ mmol l}^{-1}$ DHSPCF. All spectra were measured against the reagent blanks without CTAB. Spectrum 10: $0.400 \text{ mmol l}^{-1}$ CTAB, $0.040 \text{ mmol l}^{-1}$ DHSPCF and $0.020 \text{ mmol l}^{-1}$ Dy at pH 9.74 against a reagent blank without Dy. Spectrum 11: $0.0400 \text{ mmol l}^{-1}$ DHSPCF, $0.400 \text{ mmol l}^{-1}$ CTAB and $12 \times 0.0400 \text{ mmol l}^{-1}$ DHSPCF. Spectrum 13: $0.160 \text{ mmol l}^{-1}$ CTAB, $0.020 \text{ mmol l}^{-1}$ DHSPCF and $0.200 \text{ mmol l}^{-1}$ Dy. The spectra 11-13 were measured against water at pH 9.74.

and then A_c , η and γ were calculated.

RESULTS AND DISCUSSION

Variation of Absorption Spectra with pH

The absorption spectra of the DHSPCF, DHSPCF-CTAB and Dy-DHSPCF-CTAB (Dy as a representative of REs) solutions are shown in Fig. 3. By comparing curves 1 to 9, the difference between peak and valley of curve 7 are the most, so that a buffer solution of pH 9.74 was selected in this work. Spectrum 12 shows that the peak of the DHSPCF solution is located at 545 nm, while from curve 11, it is seen that the absorption peak of the CTAB-DHSPCF aggregate is located at 478 nm. Thus, the spectral blue shift of the CTAB-DHSPCF aggregate is 67 nm. From curve 13, it is

obvious that the peak of the RE-CTAB-DHSPCF complex is located at 562 nm, and its spectral red shift is over 80 nm. This is attributed to the fact that the electrostatic attraction is often much weaker than the chemical bond. From spectrum 7, it is seen that the peak and valley of the CTAB-DHSPCF solution are located at 486 and 568 nm, respectively. Therefore, such two wavelengths were used in studying of the binary complex. From curves 11 and 12, the correction coefficients were calculated to be $\beta_{\text{DHSPCF}} = 0.716$ and $\alpha_{\text{CTAB-DHSPCF}} = 0.0611$. The real absorbance of the CTAB-DHSPCF aggregate at 486 nm is calculated by $A_c = 1.046 (\Delta A - 0.716 \Delta A')$. In addition, spectrum 10 seems to be an image of spectrum 7. In order to save the measurements, both 568 and 486 nm were used in study of the ternary complex as well. From spectra 12 and 13, the correction coefficients were calculated to be $\beta_{\text{CTAB-DHSPCF}} = 0.0611$ and $\alpha_{\text{RE-CTAB-DHSPCF}} = 0.470$. The real absorbance of the Dy-CTAB-DHSPCF complex at 628 nm is calculated by $A_c = 1.030 (\Delta A - 0.0611 \Delta A')$.

Effect of Ionic Strength and Temperature on Binary Complex

In order to investigate the effect of ionic strength of aqueous solution on the adsorption of DHSPCF on CTAB, 2.0 mol l⁻¹ NaCl was added and its effect is shown in Fig. 4. From curve 1, it is seen that, γ decreases with an increase in the ionic strength. This is attributed to the fact that a great deal of anions can be attracted on CTAB microsurface to screen CTAB from the binding of DHSPCF.

The effect of temperature on γ of DHSPCF to CTAB is also shown in Fig. 4. From curve 2, it is obvious that γ increases with temperature below 50 °C, while it shows a rapid decrease with temperature above 50 °C. This is attributed to the fact that a high temperature will accelerate the desorption of DHSPCF on CTAB. This obeys the common nature of a surface adsorption.

Effect of Time on Ternary Complex Formation

A Yb-DHSPCF-CTAB ternary solution was prepared at pH 9.74 and 20 °C and the effect of the reaction time on the corresponding γ is shown in Fig. 5. As seen, the ternary reaction is very slow at 20 °C and completes only after 30 min.

Characterization of Complexes

By varying the molar concentration of DHSPCF, the γ values of solutions containing 1.00 mmol l⁻¹ CTAB were

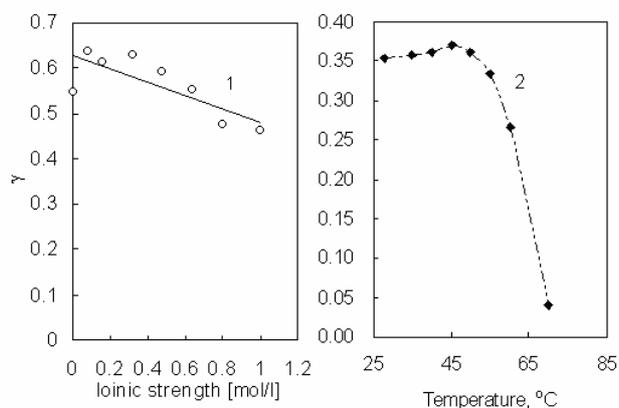


Fig. 4. Effect of ionic strength (1) and temperature (2) on γ of DHSPCF-CTAB where the solutions contained 0.040 mmol l⁻¹ CTAB and 0.040 mmol l⁻¹ DHSPCF at pH 9.74.

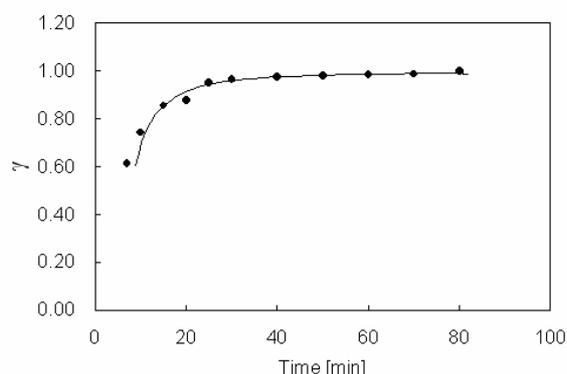


Fig. 5. Effect of time on the binding ratio of DHSPCF to Yb where the solutions contained 0.160 mmol l⁻¹ CTAB, 0.020 mmol l⁻¹ DHSPCF and 0.020 mmol l⁻¹ Yb at 20 °C.

measured at 20 and 40 °C, and the corresponding plots of γ^{-1} vs. C_L^{-1} are shown in Fig. 6.

Curves 1 and 2 are linear indicating that the aggregation of DHSPCF on CTAB obeys the Langmuir isothermal adsorption. From the intercepts, the maximal binding number of DHSPCF is calculated as $N = 0.5 \pm 0.05$ at 20 °C and $N = 0.69 \pm 0.06$ at 40 °C. The break point approach [12] was used to examine the aggregation of DHSPCF on CTAB by measuring the variation of surface force of the solutions. The binding numbers above have been confirmed. Therefore, the monomer aggregates DHSPCF-CTAB₂ at 20 °C and DHSPCF₂CTAB₃ at 40 °C were formed. The variation of the

Complexation of Rare Earths with DHSPCF and CTAB

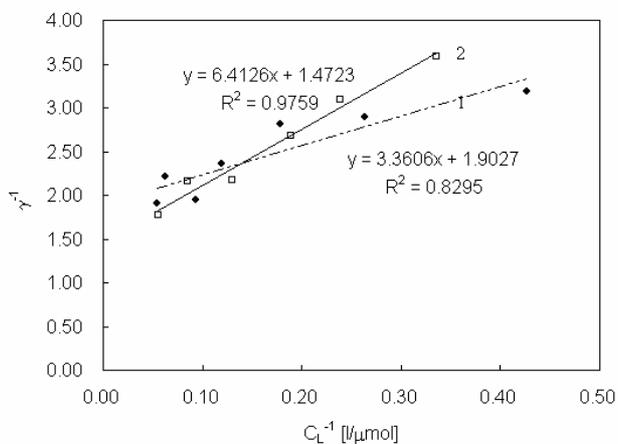


Fig. 6. Plots of γ^{-1} vs. C_L^{-1} where the solution contains $0.040 \text{ mmol l}^{-1}$ CTAB: (1) 20°C and (2) 40°C .

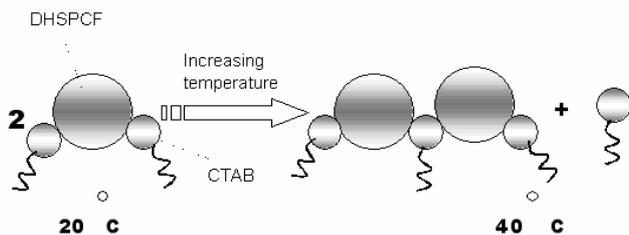


Fig. 7. Graphical sketch for variation of the CTAB-DHSPCF aggregate at 20°C and 40°C .

DHSPCF-CTAB aggregate with temperature is sketched in Fig. 7. The large micellar aggregate, $\text{DHSPCF}_{35-45}\text{CTAB}_{80}$ will be formed at 20°C only when the solution contains both CTAB over 0.25 mmol l^{-1} and enough DHSPCF. From the line slopes, the binding constants of the aggregates were calculated to be $K = (2.24 \pm 0.31) \times 10^5$ at 20°C and $(9.69 \pm 0.82) \times 10^4$ at 40°C .

By varying the addition of $0.025 \text{ mmol l}^{-1}$ $\text{DHSPCF}_{10}\text{CTAB}_{80}$, the DHSPCF-CTAB-RE solutions were measured. Plots γ vs. $C_{\text{SL}0}$ are shown in Fig. 8. From the regression equations, the maximal composition ratios were calculated as follows: DHSPCF: Y = 4:1, DHSPCF: Eu = 4:1, DHSPCF: Dy = 5:1 and DHSPCF: Yb = 5:1 at 20°C . Therefore, the ternary products $\text{Y}_{2.5}\text{DHSPCF}_{10}\text{CTAB}_{80}$, $\text{Eu}_{2.5}\text{DHSPCF}_{10}\text{CTAB}_{80}$, $\text{Dy}_2\text{DHSPCF}_{10}\text{CTAB}_{80}$ and

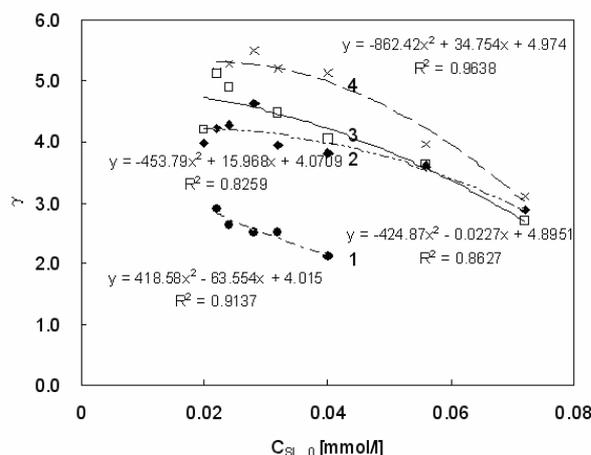


Fig. 8. Plots of γ vs. $C_{\text{SL}0}$ for (1) Y-DHSPCF-CTAB, (2) Eu-DHSPCF-CTAB, (3) Dy-DHSPCF-CTAB and (4) Yb-DHSPCF-CTAB

$\text{Yb}_2\text{DHSPCF}_{10}\text{CTAB}_{80}$ are formed in solution.

CONCLUSION

The investigation of the interaction of CTAB with DHSPCF confirms the Langmuir isothermal adsorption of small molecules on ionic surfactant by non-covalent bonds' co-interaction. The micelle enriching a great deal of ligand molecules provides the coordination reaction between metal and ligand with a catalyst carrier. It makes the determination of the binding ratio simpler than the classical methods, *e.g.* continuous variations [21]. The electrostatic attraction between S and L is always weaker than chemical bond connection, the binding number of L on S often trends to drop down with increasing temperature and ionic strength.

REFERENCES

- [1] B. Simon, J. Span, Dyes and Pigments 36 (1998) 1.
- [2] J.C. Russell, U.P. Wild, D.G. Whitten, J. Phys. Chem. 90 (1986) 1319.
- [3] C.L. Mesa, Colloids Surf. A 160 (1999) 37.
- [4] O. Anthony, R. Zana, Langmuir 12 (1996) 3590.
- [5] B. Lebreton, J. Huddleston, A. Lyddiatt, J. Chromatography B 711 (1998) 69.
- [6] R.C. Carlisle, M.L. Read, M.A. Wolfert, L.W. Seymour, Colloids Surf. B 16 (1999) 261.
- [7] D. Danino, Y. Talmon, H. Levy, G. Beinert, R. Zana, Science 269 (1995) 1420.

- [8] D. Danino, Y. Talmon, R. Zana, *Langmuir* 11 (1995) 1448.
- [9] R. Zana, Y. Talmon, *Nature* 362 (1993) 228.
- [10] H. Nishida, *Bunseki* 26 (1977) 271.
- [11] Y.X. Ci, M.M. Yang, *Chin. Sci. Bull.* 16 (1983) 980.
- [12] H.W. Gao, Z.J. Hu, J.F. Zhao, *Chem. Phys. Lett.* 376 (2003) 251.
- [13] Y.X. Zheng, L.D. Li, S.Q. Sun, *Chin. J. Chem. Reagents* 6 (1984) 273.
- [14] B. Savvins, P.K. Chernova, I.L.M. Kudpatseva, *Zh. Anal. Khim.* 33 (1978) 2127.
- [15] W.B. Qi, L.Z. Zhu, *Chem. J. Chin. Univ.* 7 (1986) 407.
- [16] H.W. Gao, J.X. Yang, J. Jiang, L.Q. Yu, *Supramol. Chem.* 14 (2002) 215.
- [17] H.W. Gao, Y.S. Chen, Y.C. Li, *Mikrochim. Acta* 137 (2001) 141.
- [18] I. Langmuir, *J. Am. Chem. Soc.* 40 (1918) 1361.
- [19] H.W. Gao, J.F. Zhao, *Aust. J. Chem.* 55 (2002) 767.
- [20] H.W. Gao, W.Q. Xu, *Anal. Chim. Acta* 458 (2002) 417.
- [21] W. Likussar, *Anal. Chem.* 45 (1973) 192.