Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **16:** 377–382, 1993.

Surface Tension Studies on the Complexation of Dodecylpyridinium Chloride by β-Cyclodextrin in Aqueous Electrolyte Solutions

JAN CZAPKIEWICZ* and BOŻENA TUTAJ
Faculty of Chemistry, Jagiellonian University, 30–060 Kraków, Ingardena 3, Poland.

(Received: 15 September 1993; in final form: 29 December 1993)

Abstract. Surface tension measurements have been performed at 25°C for aqueous mixtures of dodecylpyridinium chloride and β-cyclodextrin in 0.1 M NaCl. Data analyses assuming 1:1 stoichiometry were applied to estimate the complexation constant of the host-guest complex formation. The technique yields consistent results for solutions with a swamping, constant concentration of a simple inorganic electrolyte.

Key words: β-cyclodextrin, dodecylpyridinium chloride, complexation, surface tension.

1. Introduction

Cyclohexaamylose and its hepta- and octa-homologues constitute a group of the so-called cyclodextrins (denoted by α-, β- and γ-CD respectively), which are capable of forming inclusion complexes with a wide variety of chemical species [1–4]. The cyclodextrins are known to strongly complex cationic, anionic, zwitterionic and nonionic surfactant molecules in aqueous solutions. Inclusion of an ionic amphiphile in the cavity of the host decreases the mobility of the trapped ion. This effect has been broadly exploited in conductometric studies on the stoichiometry and formation constants of cyclodextrin-ionic surfactant complexes [5–22]. It has also been applied in developing electrophoretic techniques of separation of a variety of ionic compounds complexed by cyclodextrins [4].

It is generally accepted that the hydrophobic moiety of the surfactant penetrates the cavity of cyclodextrin. One may thus expect a decrease in surface activity of the surfactant upon complexation. In fact, Szejtli [2] has illustrated the anti-frothing effect of β-CD on a commercial detergent. To date, relatively few surface tension studies have been undertaken of the CD-surfactant systems in aqueous solutions. The available results indicate that the complexes do not exhibit surface activity since solutions containing cyclodextrins in large excess had a surface activity comparable to that of pure water [5, 12, 13, 16, 23, 25]. Loss of surface activity of the complexed amphiphile is accompanied by loss of tendency to form micellar

---

* Author for correspondence.

systems i.e. an apparent increase in the critical micelle concentration (cmc) is observed in the presence of cyclodextrins [5, 11, 13, 16, 24].

Surface tension measurements seem thus to be more suitable for studying complexation of surfactants by cyclodextrins than conductivity measurements where only small differences between equivalent conductances of the free and complexed ions are encountered. Okubo *et al.* initiated such studies for the β-cyclodextrin-cetyltrimethylammonium bromide system (CTABr) [5]. They pointed out that if the complexed electrolyte has no surface activity, the observed surface activity of the system is attributed to the free monomeric state electrolyte and the equilibrium constant for the formation of inclusion complexes, therefore, can be determined by using the surface tension vs CTABr concentration profiles in the presence and absence of CD. The authors, however, were not able to carry out such a determination because, as they stated, of the comparatively large experimental error particularly in the concentration region of CTABr where the surface tension decreases sharply. Such a finding appears to have discouraged workers in this field since in later reports on the surface tension of ionic amphiphiles in the presence of cyclodextrins, this approach has not been attempted. The situation seems more promising in the case of nonionics. Nelson and Warner [24] were able to derive from their surface tension data the values of binding constants for three different nonionics complexed by β-CD and quite recently Funasaki *et al.* [26] have shown that the surface tension data for aqueous solutions of dodecyl maltoside with cyclodextrins, reported by Saenger and Muller-Fahrnow [25], yield acceptable values for the binding constants when formation of ternary and/or quaternary complexes of the CD_2-S, CD-S_2 and CD_2-S_2 type, is taken into account (S indicates the surfactant). They concluded that the surface tension method can be used as a unique tool for the investigation of cyclodextrin-surfactant interactions. It should be pointed out, however, that estimation of the concentration of the uncomplexed surfactant made by referring to the dependence of surface tension on the concentration of the surfactant in the absence of CD may be valid for nonionics only, unless a swamping amount of inorganic electrolyte is added to the solution of ionic surfactants. Complexation of the latter generates a surface inactive electrolyte which has a co-ion common with the surfactant. The surface tension reflects the activity of the surface active ion and of its counter-ion. One should thus take into account the 'salting-out' effect due to the formation of the ions of the complexed surfactant or assure a constant activity of the counter-ion by using a sufficiently high concentration of a simple inorganic electrolyte. We decided to check the correctness of this reasoning by carrying out surface tension measurements for solutions of dodecylpyridinium chloride and β-CD in 0.1 M NaCl. The surface properties of solutions of this surfactant in the presence of swamping amounts of electrolytes have been thoroughly studied by Rosen *et al.* [27].

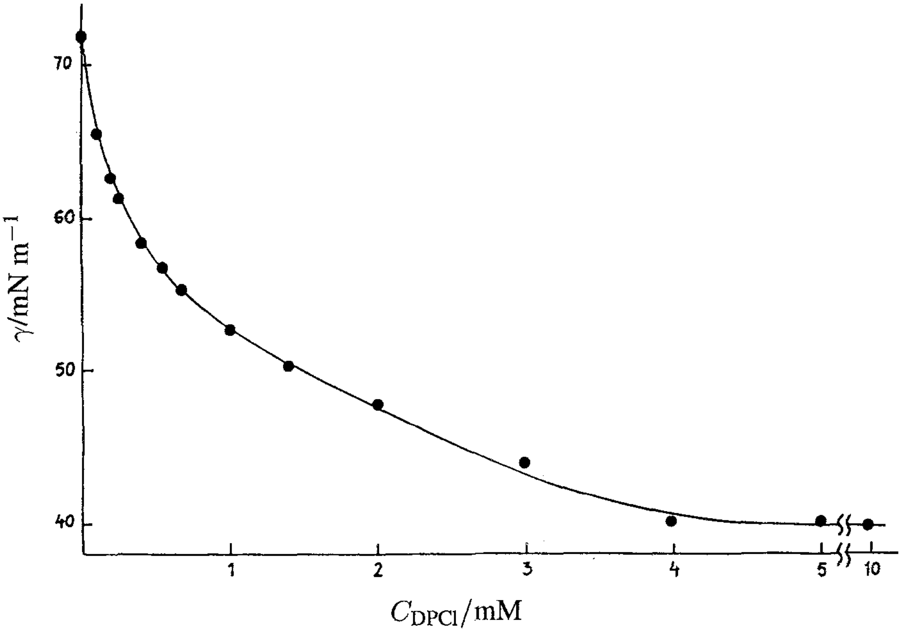

Fig. 1. Surface tension isotherm for dodecylpyridinium chloride in 0.1 NaCl.

2. Experimental

n-Dodecylpyridinium chloride monohydrate (DPCl) was synthesized and purified by the method described previously [28]. β-Cyclodextrin (Chinoin) was used without further purification. Thermogravimetric analysis and vacuum drying over phosphorus pentoxide indicated that the material contained eleven water molecules per molecule of β-CD. Sodium chloride of analytical grade was dried at 300°C. The solutions were prepared in doubly distilled water. Surface tension measurements were performed at 25 ± 0.1°C with the drop weight method.

3. Results and Discussion

3.1. SURFACE PROPERTIES OF DODECYLPYRIDINIUM CHLORIDE

The surface tension isotherm measured for DPCl in 0.1 M NaCl at 25°C is shown in Figure 1. The concentration range studied was from 0.1 to 10 mM i.e. it covered the cmc which, according to Rosen *et al.* [27], is 4.8 mM. In the premicellar concentration range of 0.2 to 2.5 mM the isotherm can be described by the relation

$$\gamma = [-6.48 \pm 0.10]\ \ln(Cf) + [6.05 \pm 0.77] \qquad (1)$$

where C is the molar concentration of DPCl and f is the activity coefficient of the surfactant cation, in 0.1 M NaCl, calculated from the extended Debye–Huckel equation:

$$\log f = \frac{-B\sqrt{I}}{[1 + 3.3\alpha\sqrt{I}]} \tag{2}$$

where I is the total ionic strength of the solution, B is 0.509 and α is taken as 0.6 for the surfactant ion [27]. In 0.1 M NaCl f is 0.7961.

The value of the slope of equation (1) represents the –RTΓ expression in the Gibb's adsorption equation. Hence, Γ, the maximum surface excess concentration of DPCl amounts to 2.6×10^{-6} mol m^{-2} which corresponds to the minimum area per surfactant molecule at the air-solution interface (63×10^{-20} m^2). Rosen *et al.* report a value of 55×10^{-20} m^2 for the same system [27]. Since the surface tension of the solutions of DPCl in 0.1 M NaCl attain, at the high concentration range, a constant value of 40 nNm^{-2}, we can calculate the cmc value by putting $\gamma = 40$ in Equation (1). Solving the equation for C yields a value of 5.3 mM for the cmc. The relevant literature data for this system are 4.8 mM [27] and 2.3 mM [29]. The latter value was determined for a commercial sample of DPCl (in 0.1 M KCl) which, presumably, was contaminated by higher homologues. Note that the corresponding value reported for solutions of the surfactant in pure water is also low (14 mM [29]) when compared with other literature data: 16.2 mM [27], conductometry; 16.3 mM [30], potentiometry; 16.5 mM [28], potentiometry and 17.8 mM [27], surface tension measurements.

3.2. DETERMINATION OF THE BINDING CONSTANT OF β-CD WITH DPCL

In order to study the complexation of DPCl by β-CD, three series of their mixtures in 0.1 M NaCl were prepared and their surface tensions were measured. We made the assumption that β-CD and the complexed surfactant are surface inactive and that the two species do not influence the surface properties of free DPCl in the presence of the swamping, constant concentration of NaCl. The surface tension of the mixtures reflects then the equilibrium concentration of the uncomplexed surfactant. The total concentrations of the two reactants (C_{DPCl} and $C_{\beta\text{CD}}$) in the mixtures are given in Table I together with the equilibrium concentration of the free surfactant [DPCl] calculated from surface tension data by applying equation (1) cast in the form:

$$C = [\text{DPCl}] = 3.196\, e^{-0.1543\gamma}\,. \tag{3}$$

The equilibrium constant for the formation of the 1:1 complex is expressed by

$$K = \frac{[\text{DPCl} : \beta\text{-CD}]}{[\beta\text{-CD}]\,[\text{DPCl}]} \tag{4}$$

TABLE I. Total concentrations of the surfactant and of the complexing agent, C_{DPCl} and $C_{\beta\mathrm{CD}}$ respectively, and equilibrium concentrations of the uncomplexed surfactant [DPCl], in 0.1 M NaCl

C_{DPCl}/mM					
1.00		2.00		4.00	
$C_{\beta\mathrm{CD}}$/mM	[DPCl]/mM	$C_{\beta\mathrm{CD}}$/mM	[DPCl]/mM	$C_{\beta\mathrm{CD}}$/mM	[DPCl]/mM
0.25	0.80	1.6	0.55	3.6	0.7
0.50	0.55	2.4	0.20	4.0	0.46_5
0.75	0.36	3.2	0.09_5	5.6	0.14
1.00	0.22	4.0	0.06	6.0	0.12
1.25	0.14				
1.50	0.09_5				

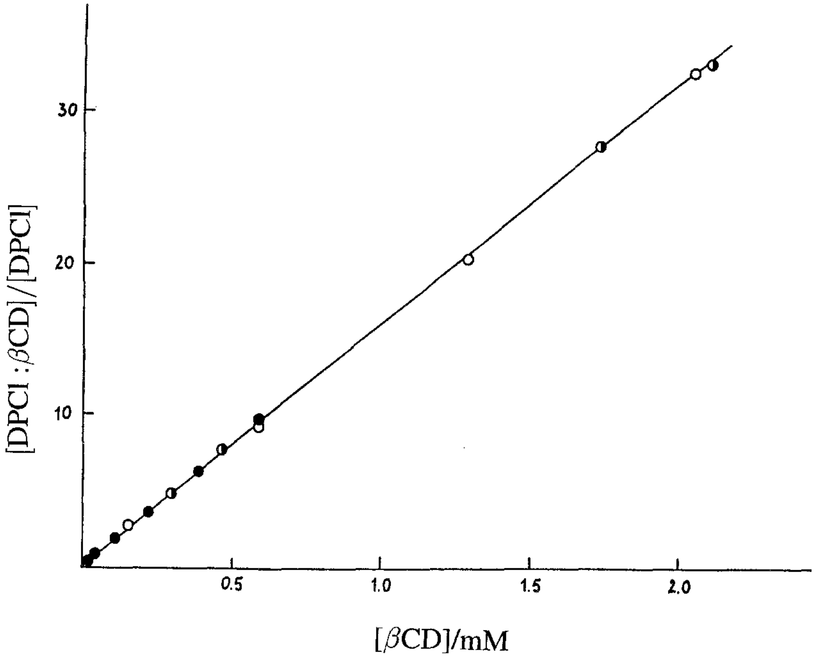

Fig. 2. Relation between the [CDPCl:β-CD]/[DPCl] ratio and [β-CD]; •, ○ and ◐ data points are for solutions for which CDPCl was 1, 2 and 4 mM respectively.

where [DPCl:β-CD] is the concentration of the inclusion complex and [β-CD] and [DPCl] are equilibrium concentrations of the reactants respectively. It follows that [DPCl:β-CD] = C_{DPCl} – [DPCl] and [β-CD] = $C_{\beta\mathrm{CD}}$ – [DPCl:β-CD] = $C_{\beta\mathrm{CD}} - C_{\mathrm{DPCl}}$ + [DPCl]. The 1:1 model predicts thus a linear increase of the [DPCl:βCD]/[DPCl] ratio. Figure 2 illustrates the fit of our data to this model.

The value of the binding constant for the complexation of DPCl by β-CD in 0.1 M NaCl, estimated from the slope of the plot, amounts to $K = 15600\,\mathrm{M}^{-1}$. This value is ca three times higher than that evaluated from conductometric measurements in pure water by Satake *et al.* [9]. We assume that the difference accounts for the 'salting out' effect due to the presence of high electrolyte concentration used in the surface tension measurements. The present technique is complementary in respect to conductometry which cannot be applied to cyclodextrin-surfactant-electrolyte systems.

References

1. W. Saenger: *Angew. Chem., Int. Ed. Engl.* **19**, 344 (1980).
2. J. Szejtli: *Cyclodextrins and their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982.
3. J.L. Atwood, J.E.D. Davies, and D. MacNicol: *Inclusion Compounds*, Vols. 1–3; Academic Press, London, 1984.
4. S. Li and W.C. Purdy: *Chem. Rev.* **92**, 1457 (1992).
5. T. Okubo, H. Kitano, and N. Ise: *J. Phys. Chem.* **80**, 2661 (1976).
6. K. Fujita, T. Ueda, T. Imoto, I. Tabushi, K. Hayakawa, and T. Maeda: *Bioorg. Chem.* **11**, 108 (1982).
7. I. Satake, T. Ikenoue, T. Takeshita, K. Hayakawa, and T. Maeda: *Bull. Chem. Soc. Jpn.* **58**, 2746 (1985).
8. K. Králova, L. Mitterhauszerová, and J. Szejtli: *Tenside Detergents* **20**, 37 (1983).
9. I. Satake, S. Yoshida, K. Hayakawa, T. Maeda, and Y. Kusumoto: *Bull. Chem. Soc. Jpn.* **59**, 3991 (1986).
10. A. Hersey, B.H. Robinson, and H.C. Kelly: *J. Chem. Soc. Faraday Trans.* **82**, 1271 (1986).
11. J. Georges and S. Desmettre: *J. Coll. Interface Sci.* **118**, 192 (1987).
12. X.-K. Jiang, J.-H. Gu, X.-E. Cheng, and Y.-Z. Hui: *Acta Chim. Sin.* **45**, 159 (1987).
13. A. Diaz, P.A. Quintela, J.M. Schuette, and A.E. Kaifer: *J. Phys. Chem.* **92**, 3537 (1988).
14. R. Palepu and V.C. Reinsborough: *Can. J. Chem.* **66**, 325 (1988).
15. D.J. Jobe, R.E. Verall, R. Palepu, and V.C. Reinsborough: *J. Phys. Chem.* **92**, 3582 (1988).
16. K. Králova and L. Mitterhauszerová: *Tenside Detergents* **26**, 18 (1988).
17. R. Palepu, J.E. Richardson, and V.C. Reinsborough: *Langmuir* **5**, 218 (1989).
18. T. Okubo, Y. Maeda, and H. Kitano: *J. Phys. Chem.* **93**, 3721 (1989).
19. R. Palepu and V.C. Reinsborough: *Can. J. Chem.* **67**, 1550 (1989).
20. E.S. Aman and D. Serve: *J. Coll. Interface Sci.* **138**, 365 (1990).
21. C.D. Lavandier, M.P. Pelletier, and V.C. Reinsborough: *Aust. J. Chem.* **44**, 457 (1991).
22. D.J. Jobe, R.E. Verrall, E. Junquera, and E. Aicart: *J. Phys. Chem.* **97**, 1243 (1993).
23. A.E. Kaifer, P.A. Quintela, and J.M. Schuette: *J. Incl. Phenom.* **7**, 107 (1989).
24. G. Nelson and I.M. Warner: *Carbohydr. Res.* **192**, 305 (1989).
25. W. Saenger and A. Muller-Fahrnow: *Angew. Chem., Int. Ed. Engl.* **27**, 393 (1988).
26. N. Funasaki, H. Yodo, S. Hada, and S. Neya: *Bull. Chem. Soc. Jpn.* **65**, 1323 (1992).
27. M.J. Rosen, M. Dahanayake, and A.W. Cohen: *Colloid. Surf.* **5**, 159 (1982).
28. J. Czapkiewicz and B. Tutaj: *Colloid Polym. Sci.* **268**, 484 (1990).
29. N.D. Weiner and G. Zografi: *J. Pharm. Sci.* **54**, 436 (1965).
30. T. Maeda and I. Satake: *Bull. Chem. Soc. Jpn.* **57**, 2396 (1984).