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メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/1670

Aqueous Solution Properties of Pyridinium-type Perfluorinated Surfactants and
Simulation of Mixture CMC.

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Solution Properties of Pyridinium-type Surfactants

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ABSTRACT: The critical micelle concentrations (CMC) of 1,1,2,2-tetrahydroperfluoroalkylpyridinium chloride have been determined by the measurements of surface tension and electrical conductivity etc. The CMC of perfluorinated surfactants were only about two hundredths times that of hydrocarbon one with same carbon number. Aqueous solutions of fluorocarbon surfactants gave low surface tensions in comparison with those of hydrocarbon surfactants. The area per surfactant molecule at air-water interface decreased with increasing the length of fluorocarbon chain. Electromotive force measurements were made with chloride-responsive electrodes on surfactants solutions. The micelle ionization degrees decreased with increasing the length of alkyl chain. The group contribution method simulated the mixture CMC of binary surfactants with various alkyl chain lengths. The group contribution method proved to be very useful to predict not only the mixture CMC but also the demixing regions of binary mixtures having great differences in CMC.

KEY WORDS: 1,1,2,2-tetrahydroperfluoroalkylpyridinium chloride, group contribution method, demixing region, micelle ionization degree, mixture CMC

Mixture CMC have been often simulated by assuming that the micelles regarded as a separated pseudo-phase in equilibrium with surfactant monomer.[1] The CMC of surfactant mixtures with the same head groups but differing alkyl chain lengths can be predicted by assuming that mixtures obey the law of ideal solution in the micelle phase. However, the mixture CMC of fluorocarbon and hydrocarbon surfactants can be much larger than that predicted by the method using the law of ideal solution.[2] Then regular solution model can be used to simulate the CMC of such a nonideal mixtures.[3] The variation of mixture CMC for many systems were simulated by the regular solution model using only the CMC of pure components and the interaction parameter. However, the method using the useful regular solution model cannot give the correct interaction parameter as well as a priori prediction of mixture CMC without experimental mixture CMC. To solve such problems, we have been reported that the group contribution method is useful to predict the mixture CMC of binary surfactants.[4,5] The group contribution method is a powerful tool for the series of surfactant mixtures containing the same functional groups but differing hydrophobic chain lengths. We can predict the mixture CMC of nonideal mixtures by using the CMC of pure components and the group interaction parameters without experimental mixture CMC.

Experimental Procedures

Materials. Cationic fluorocarbon surfactants were synthesized from corresponding 1,1,2,2-tetrahydroperfluoroalkyl iodide (PCR Inc., FL, USA) as reported previously.[5] The abbreviation of surfactant are as follows: HFOPC, $[\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{NC}_5\text{H}_5]^+\text{Cl}^-$; HFDePC, $[\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{NC}_5\text{H}_5]^+\text{Cl}^-$; HFDPC, $[\text{C}_{10}\text{F}_{21}\text{CH}_2\text{CH}_2\text{NC}_5\text{H}_5]^+\text{Cl}^-$. Dodecylpyridinium chloride (DPC) and cetylpyridinium chloride (CPC) were obtained Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and recrystallized three times from acetone-ethanol mixture. Tetradecylpyridinium chloride (TPC) was prepared by the same procedures reported previously. [5] The other reagents were of guaranteed grade.

Measurements. Conductivity measurements were carried out using conductivity meter, Model CM-20S (TOA Electronics Ltd., Tokyo, Japan). When the slopes of the conductivity vs concentration curve change, the mixture CMC is given by the inflection point. Surface tension of surfactant aqueous solution was measured by Wilhelmy technique (Kyowa-Kagaku surface tension meter Model A-3, Saitama, Japan). Electromotive force of aqueous surfactant solution was measured with Orion 701A digital ionanalyzer (Orion Research Inc., MA, USA) using a chloride ion selective electrode (Orion 96-17B). The electromotive force measurements showed a good Nernstian response (58mV) below the CMC of surfactant. The electromotive force is used for monitoring the concentration of free chloride counter ion. The micelle ionization degree was evaluated by Shirahama's method.[6] Steady-state fluorescence spectra of pyrene were measured as reported previously. [7] The decrease in fluorescence intensity at 384nm is used for the determination of CMC due to the significant quenching along with the micelle formation. All experiments were performed at 25°C.

Results and Discussion

The surface tensions of aqueous surfactant solutions were measured in order to estimate the CMC and purity of the cationic fluorocarbon surfactants. Figure 1 shows the surface tensions of fluorocarbon and hydrocarbon surfactants against the logarithm of surfactant concentration. It is well known that small amounts of surface-active impurities can alter such as CMC and surface tensions. The presence of surface-active impurities can be detected by a minimum in the surface tension-concentration curve near CMC. The new fluorocarbon surfactants were more surface active than hydrocarbon surfactants and gave no indication of a minimum near their CMC. In spite of rather short fluorocarbon chain, the CMC of fluorocarbon surfactants were considerably low due to the high hydrophobicity of fluorocarbon chain. The CMC are in accord with those determined by other methods.

The surface tensions of HFOPC, HFDePC and HFDPC aqueous solutions significantly decreased up to 27.5, 26.1 and 25.6 mN/m, respectively. The minimum area per molecule at the solution-air interface was calculated from the equation of Gibbs adsorption isotherm. The values of HFOPC, HFDePC and HFDPC were 61.4, 54.2 and 39.8 Å²/molecule, respectively, which decreased with increasing the chain length in contrast to hydrocarbon surfactants. (Table 1) The fluorocarbon chains in the adsorbed film are rather packed together even if the cross section area of fluorocarbon chain would be about 1.5 times larger than that of hydrocarbon. The compactness of fluorocarbon chain in adsorbed film seems to be independent of the bulkiness of fluorocarbon chain.

The micelle ionization degree will depend on the chain length and size of ionic head group of surfactant. The measurement of electromotive force was used to estimate the micelle ionization degree. Figure 2 shows the plots of electromotive force of chloride ion against the logarithm of surfactant concentration for NaCl and surfactant aqueous solutions. The slope of NaCl calibration line was close to the theoretical value, 59.2 mV, and those of surfactants systems below their CMC. The deviation from the calibration line above CMC can be ascribed for the decrease in concentration of free chloride ion. Then the micelle ionization degree (α) was evaluated according to Shirahama's method.[6] The α values for pyridinium-type surfactant were summarized in Table 1 along with CMC values. The α values decreased with

increasing the chain length of surfactant. In addition, the α values of fluorocarbon surfactant were similar to those of hydrocarbon surfactants due to the same ionic head group.

The conductivity method was used to determine the CMC of single and binary surfactant systems. Figure 3 shows the conductivity curves of TPC and HFDePC, and their equimolar mixture at fixed composition. The CMC of TPC and HFDePC were 4.1 and 2.7 mM, respectively, which are good accordance with those determined other methods. The experimentally determined CMC were summarized in Table 1. The pyridinium-type surfactant is known to quench pyrene fluorescence. The Stern-Volmer plots gave the CMC precisely due to the sharp changes in fluorescence intensity as reported in reference 7.

The mixture CMC of equimolar HFDePC-TPC became higher than those of pure surfactant systems. This demonstrates the immiscibility of HFDePC and TPC in the micelles. The mixture CMC of various pairs of pyridinium-type surfactants were determined by the conductivity method. The CMC values of HFDePC-TPC, HFDePC-CPC and HFDPC-CPC were plotted against mole fraction of fluorocarbon surfactant as shown in Figure 4. The group contribution model can be used to simulate the mixture CMC curves in a similar procedure according to references 4 and 5. The group contribution method predicted that the demixing of micelle occurs when mole fraction of fluorocarbon surfactant were 0.40~0.65, 0.40~0.72, 0.12~0.90 for HFDePC-TPC, HFDePC-CPC and HFDPC-CPC mixtures, respectively. That is, the micelle demixing regions increase with increasing the chain length of surfactants. The hydrocarbon-rich micelles solubilize the fluorocarbon surfactant to some extent, while the fluorocarbon-rich micelles solubilize the hydrocarbon surfactant sparingly. The difference in solubilization power between two kinds of micelles suggests the differences in micelle size as well as micelle micropolarity.

Figure 5 shows the CMC values of HFDPC-DPC and HFOPC-CPC mixtures having great differences in pure CMC. The demixing of micelle occurs when mole fraction of HFDPC was 0.09~0.83 for HFDPC-DPC mixture. On the other hand, the demixing of micelle will not occur for HFOPC-CPC mixture. The fluorocarbon chain length of 6 for HFOPC was not enough to cause demixing at 25 °C. The important features of group contribution method are its applicability to surfactant mixtures having great differences in CMC. We can easily evaluate the

demixing region for the series of mixed systems containing the same functional groups. In contrast, the regular solution method cannot give a prior prediction of interaction parameter, i.e., the demixing region without experimental CMC data. Moreover, the interaction parameter of regular solution was not very sensitive to simulate the mixture CMC curves if the CMC of two surfactants were significantly different. No one evaluate the micelle demixing regions of binary surfactants mixtures having great differences in CMC using such a regular solution model.

The low affinity between fluorocarbon and hydrocarbon chains leads to a strong deviation from ideal behavior. Even if the CMC of one surfactant were significantly different from the other in binary mixtures, we can deduced the nonideality from the group contribution method for the series of mixed systems containing same functional groups. If the mixing energy of surfactant in the micelles increase with increasing the chain length of hydrophobic groups, two surfactants will only partially mix in the micelle phase. The micelle demixing regions, i.e., the existence of two kinds of mixed micelles, can be evaluated by the group contribution method.

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Table 1. Experimental CMC, minimum surface tension, surface area per surfactant molecule and micelle ionization degree (α) for pyridinium-type surfactants.

Surfactant	CMC/mM				γ_{cmc} /mNm ⁻¹	A /Å ²	α
	a	b	c	d			
[C ₆ F ₁₃ CH ₂ CH ₂ NC ₅ H ₅] ⁺ Cl ⁻ (HFOPC)	21.7	18.0	21.1	20.5	27.5	61.4	0.39
[C ₈ F ₁₇ CH ₂ CH ₂ NC ₅ H ₅] ⁺ Cl ⁻ (HFDePC)	2.7	2.8	2.5	2.5	26.1	54.2	0.31
[C ₁₀ F ₂₁ CH ₂ CH ₂ NC ₅ H ₅] ⁺ Cl ⁻ (HFDPC)	0.33	0.32	0.30	0.32	25.6	39.8	0.30
[C ₁₂ H ₂₅ NC ₅ H ₅] ⁺ Cl ⁻ (DPC)	15.0	14.8	14.5	16.0	44.6	65.2	0.35
[C ₁₄ H ₂₉ NC ₅ H ₅] ⁺ Cl ⁻ (TPC)	4.1	4.1	4.2	4.0	42.2	69.6	0.31
[C ₁₆ H ₃₃ NC ₅ H ₅] ⁺ Cl ⁻ (CPC)	1.0	1.1	0.74	0.90	42.5	61.3	0.25

^a conductivity measurement, ^b surface tension measurement,

^c electromotive force measurement, ^d pyrene fluorescence measurement [7]

Figure 1. Plots of surface tension of surfactant aqueous solutions vs. the logarithm of concentration.

(○) DPC, (△) TPC, (□) CPC, (●) HFOPC, (▲) HFDePC, (■) HFDPC.

Figure 2. Plots of the electromotive force (E) of aqueous surfactant solution vs. the logarithm of concentration.

(◇) NaCl, (○) DPC, (△) TPC, (□) CPC,
(●) HFOPC, (▲) HFDePC, (■) HFDPC.

Figure 3. Plots of specific conductivity of aqueous surfactant solution vs. concentration.

(○) TPC, (●) HFDePC, (△) equimolar HFDePC-TPC mixture .

Figure 4. Mixture CMC of fluorocarbon and hydrocarbon surfactants with differing hydrophobic chain lengths. The solid lines and dot-dashed lines are the CMC curves and the micelle composition curves predicted by the group contribution method, respectively.

(○) HFDePC-TPC, (△) HFDePC-CPC, (□) HFDPC-CPC.

Figure 5. Mixture CMC of fluorocarbon and hydrocarbon surfactants with most different CMC of single surfactants. The solid lines and dot-dashed lines are the CMC curves and the micelle composition curves predicted by the group contribution method, respectively.

(○) HFOPC-CPC, (△) HFDPC-DPC.

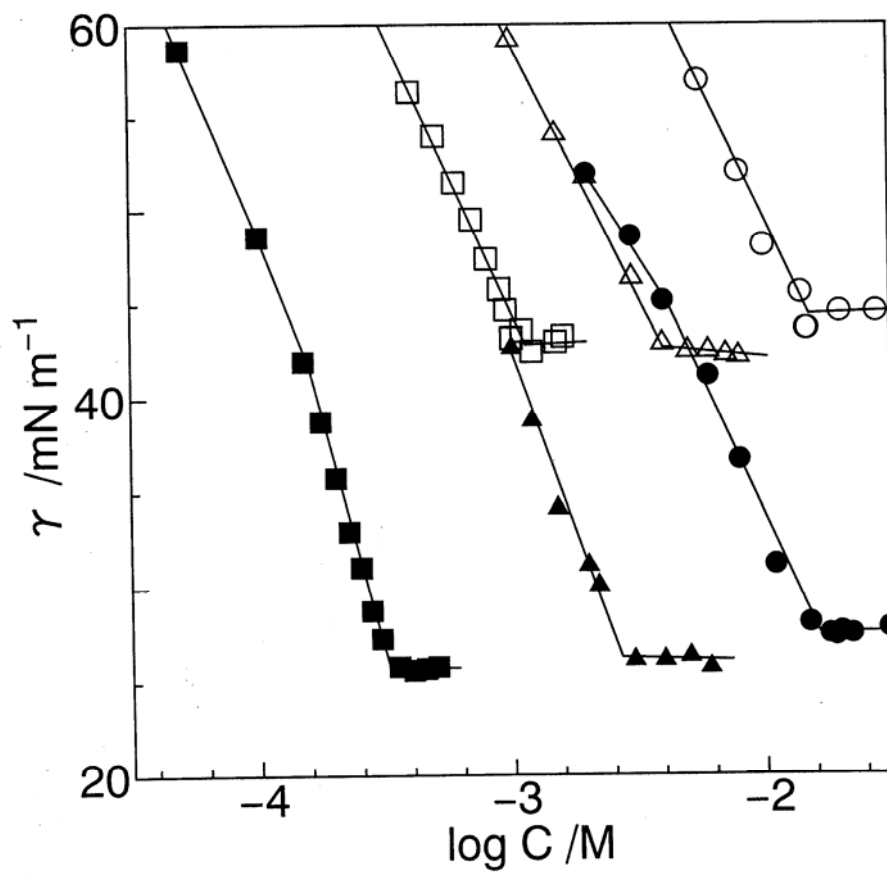


Fig 1

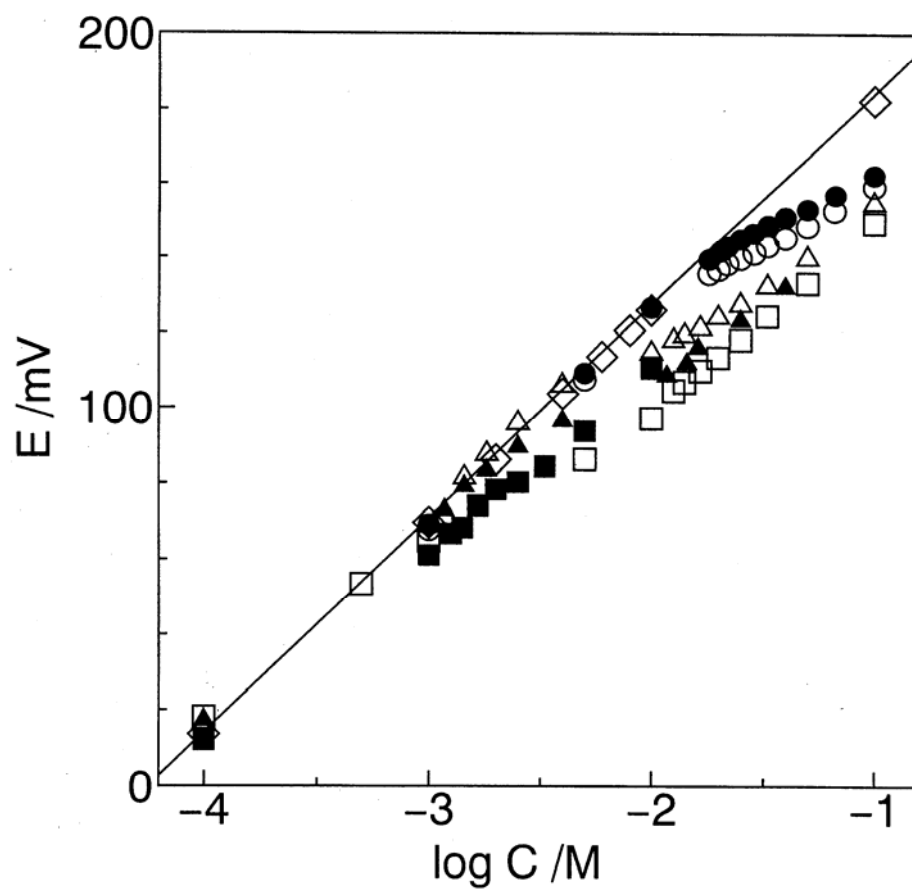


Fig 2

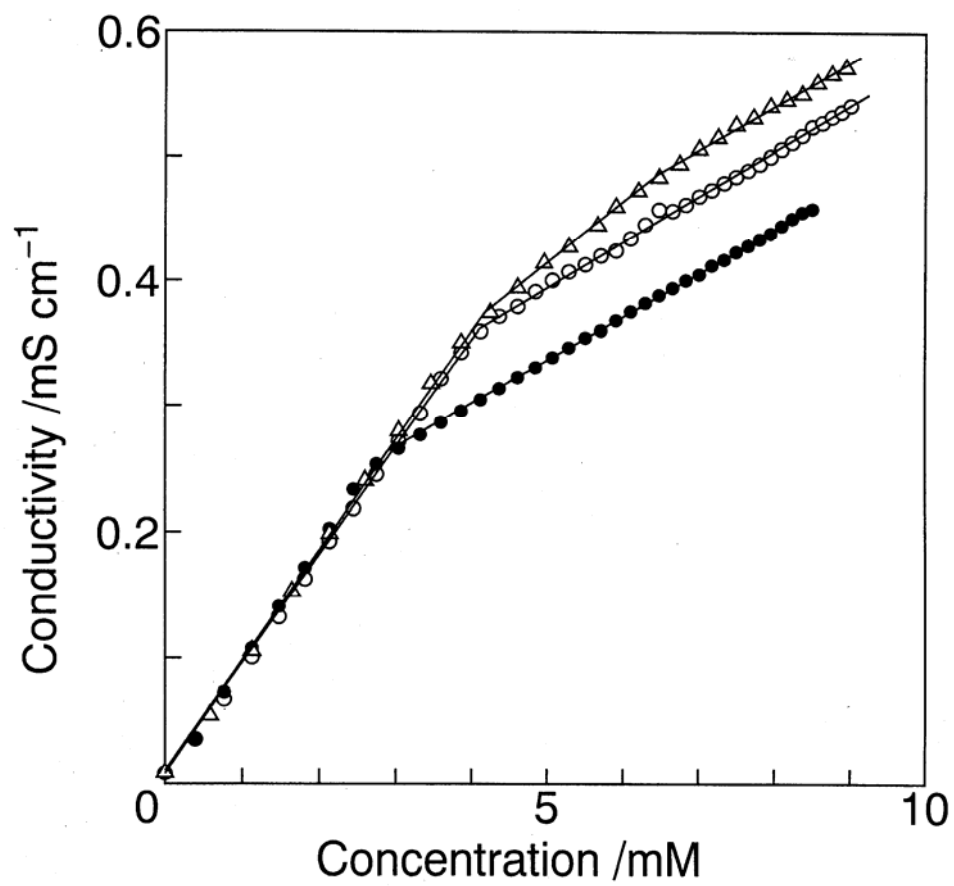


Fig 3

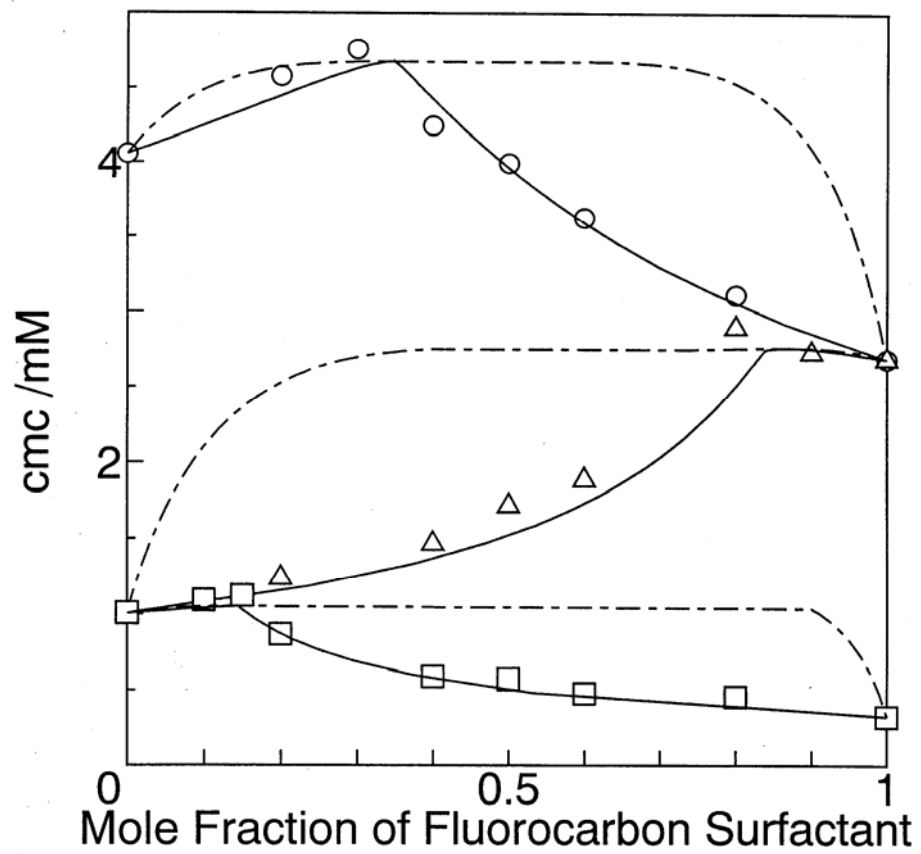


Fig 4

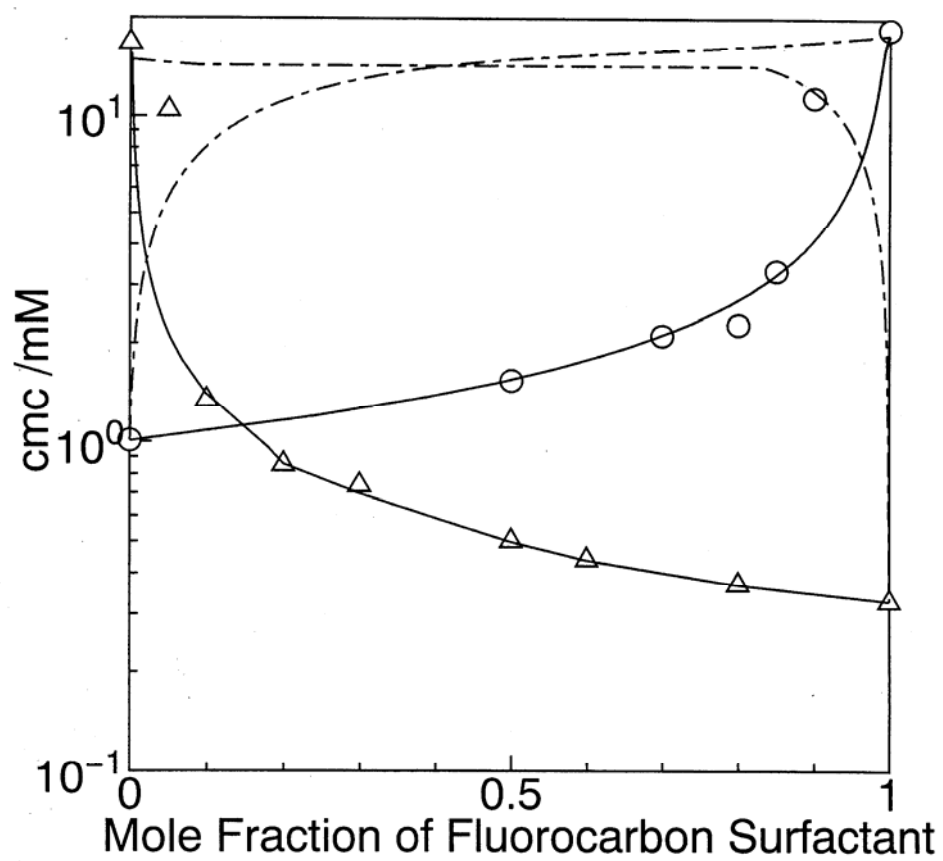


Fig 5