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SHORT COMMUNICATION

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Influence of surfactant vesicles and their polymerization on the complex formation between indoleacetate and methylviologen

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Abstract The association constant K between methylviologen MV and indoleacetate IA was decreased by the addition of cationic vesicles, and the K increased at high vesicle concentrations. The influence of the polymerization of surfactants with different chain lengths on K was different. The concentration dependence of K was analyzed by a theory in terms of the partition coefficients of reactants between the bulk solvent phase and the local vesicle environment. The theoretical partition coefficients were determined graphically. The measured dependence of K on vesicle concentration was satisfactorily reproduced by the theory. When dimyrystyldiallylammonium bromide (DMAB) was added to the complex, the polymerization of the surfactant increased the partition coefficients of IA and the complex but decreased that of MV. However, the polymerization of dicetyldiallylammonium bromide (DCAB) showed the reverse tendency. The influence of polymerization on K or the partition coefficient was discussed in terms of the difference in the polymerization mechanism due to the differences in the distance between the neighboring nonpolymerized surfactant molecules and the polymerization induced change in that distance.

Key words Vesicle – methyl viologen – indoleacetate – association constant – partition coefficient

Introduction

Vesicles are known to catalyze certain reactions [1–4]. Alkaline hydrolysis or aminolysis of *p*-nitrophenyl esters were accelerated by cationic surfactant vesicles, and the polymerization of the surfactant suppressed the acceleration [1]. The change in the rate constant was analyzed by the theory of partition coefficients. A similar way of analyzing the association constant, instead of the rate constant, may be applicable to the vesicle system.

In the preceding papers [5, 6], we introduced an idea to understand the minimum or the maximum in the association constant K that appears when a polyelectrolyte is increasingly added to a system of complex formation between two substrates. The idea was the use of partition coefficients instead of activity coefficients for the association constant. This idea was based on the difficulty of applying the electrolyte theory to complex organic reactions. Incorporation of hydrophobicity and interaction forces other than electrostatic into the electrolyte theory is difficult. Furthermore, our theory also provided a method of determining the partition coefficient of each complexing reactant between the bulk solution and the polymer environment. These values were in good agreement with those determined independently from gel filtration [7]. For example, the partition coefficients of butylviologen and hexylviologen between sodium polystyrenesulfonate and bulk water were (theory) 2500, 3350 and (gel filtration) 2390, 3660, respectively. The determined coefficient

together with the theory successfully reproduced the curves for the dependence of association constants on the polymer concentration.

The partition coefficient of the reaction substrates between the bulk water and the vesicles can be influenced by the electrostatic and the hydrophobic forces between the substrates and the vesicles. The electrostatic force is sensitive to the surface charge density or the distance between the neighboring charges of the charged aggregates. The influence of polymerization of the surfactant vesicles on the association constant will be interesting if it is analyzed with the theory of the partition coefficient. Recently, Sackmann et al. [8, 9] reported that the polymerization of surfactant vesicles induced phase separation due to the decrease in the distance between the neighboring hydrophilic groups of the surfactants. Higashi et al. [10] also studied the polymerization of styrenesulfonate as the counterion of the surfactant bound on the surface of gold and obtained similar results. These results must be due to the shorter length of the vinyl group than the diameter of the domain occupied by a surfactant molecule in the membrane. We then used surfactants having two allyl groups as polymerizable groups at the hydrophilic head. With these surfactants, it is interesting to study if the distance between the neighboring surfactant molecules changes on polymerization. Our way of analysis of association constant in terms of partition coefficients may then provide a method to estimate the change in the charge density of the vesicle due to polymerization.

In this paper, therefore, we extended our way of analysis to the change in the association constant induced by cationic surfactant vesicles and studied the influence of the polymerization of the surfactants on the partition coefficients of complex-forming compounds, i.e., methylviologen (MV) and indoleacetate (IA).

Experimentals

Materials

Methylviologen (MV) was purchased from Nakarai Chemicals Co. and was used as received. Indoleacetate (IA) was guaranteed reagent grade and was purified by recrystallization before use.

Polymerizable surfactants with two alkyl chains used for the preparation of vesicles were dimyrystyldiallylammonium bromide (DMAB) and dicetyldiallylammonium bromide (DCAB). These surfactants were synthesized according to the method of E. Tsuchida et al. [11]. The structure of the surfactants was checked by H-NMR. Water used in preparation of the solutions was purified by deionization and subsequent distillation.

Vesicles were prepared by ultrasonic dispersal of aqueous DMAB or DCAB using a Nippon-Seiki 150W Ultrasonicator (US-150). Polymerization of the vesicles was conducted by the irradiation of light using a Wacom 500W Xe-lamp (KXL-500F) on the vesicle solution in a quartz test tube under nitrogen for 6 h. The distance between the test tube and the lamp was fixed at 23 cm. The polymerization of surfactant was monitored and confirmed by following the disappearance of the allyl signal in the NMR spectrum. The 6 h irradiation was sufficient for the complete polymerization based on the independently determined time-conversion curves for the polymerization.

Measurements

A differential scanning calorimeter (MacScience DSC-3200) was used for the determination of T_c of the vesicles.

The stoichiometry of the complex produced from MV and IA was determined by the method of continuous variation [12]. The absorbance at 400 nm, which corresponds to the complex, was plotted against the fraction of IA concentration, i.e., [IA]/([IA] + [MV]).

The apparent association constant K was determined with Foster–Hammick–Wardley plots [13] from the slopes of the $(\varepsilon - \varepsilon_0)/N$ versus $(\varepsilon - \varepsilon_0)$ plot, where ε_0 is the sum of absorbances of MV and IA, ε is the absorbance of the mixture, and N is the concentration of IA. The concentration of MV was 4.0×10^{-4} mol·dm^{-3}, and that of IA was varied from 4.0×10^{-2} to 2.4×10^{-1} mol·dm^{-3}. A Shimadzu UV-3100 spectrophotometer equipped with electrically controlled thermostated cell holders and magnetic stirrers was used. The light path of the cell was 1.0 cm.

Results and discussion

The result of determination of the stoichiometry of the complex formation by the continuous-variation method is shown in Fig. 1. The curve had a maximum absorbance at [IA]/([IA] + [MV]) = 0.5, which implies that the composition of the complex is 1:1 and that the Foster–Hammick–Wardley plot is applicable to our system (Fig. 2).

The association constant K determined with the Foster–Hammick–Wardley plots was plotted against surfactant concentration. Figure 3 shows the influences of the nonpolymerized and polymerized DMAB and DCAB vesicles on the complex formation. K_0 is the association constant in the absence of vesicles. Increasing the concentration of the surfactant vesicles slightly decreased the K value at low concentrations but increased it at high

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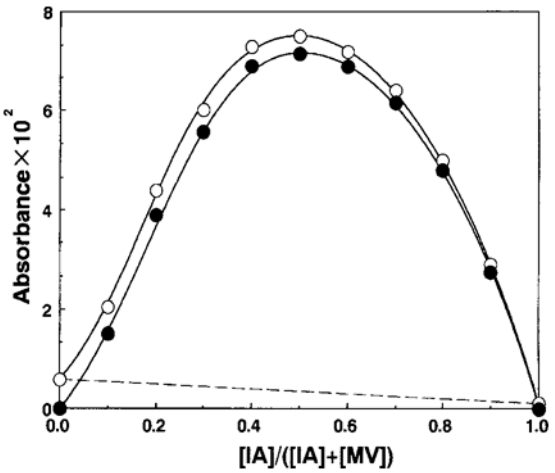

Fig. 1 Continuous variation method for the determination of the stoichiometry of complexation between indoleacetate (IA) and methylviologen (MV) at 25 °C. Absorbance of the complex (●) was calculated from the observed absorbance of the mixture solution (○) and the absorbance estimated for no complexation (---). The wavelength was 400 nm. $[IA] + [MV] = 4.13 \times 10^{-3}$ mol·dm^{-3}

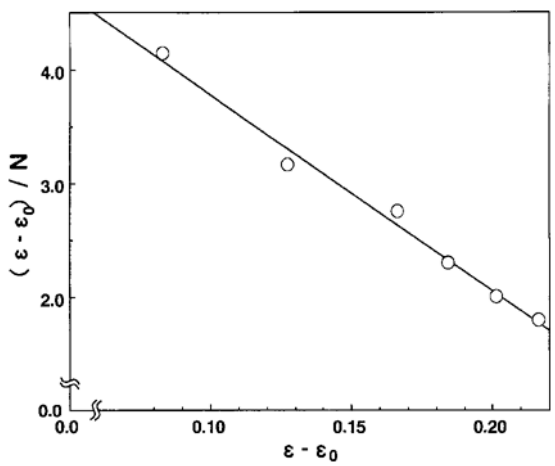

Fig. 2 Foster–Hammick–Wardley plot for complex formation between IA and MV at 25 °C. $[MV] = 2.0 \times 10^{-4}$ mol·dm^{-3}; $[IA] = 2.0 \times 10^{-2} \sim 1.2 \times 10^{-1}$ mol·dm^{-3}

concentrations; the curve then had a minimum. It is apparent that the polymerization of DMAB vesicles increased the K value, and the minimum slightly shifted to a lower concentration (a). On the other hand, in the case of the addition of the DCAB vesicles (b), polymerization increased the K value at low concentrations but decreased at high concentrations; the minimum then shifted to a higher concentration. The difference between the influences of the DMAB vesicles and the DCAB vesicles on the complex formation is interesting. The data in Fig. 3 were replotted in Fig. 4 to show the difference between the surfactants. In the previous paper [5, 6], we showed that the shape of the

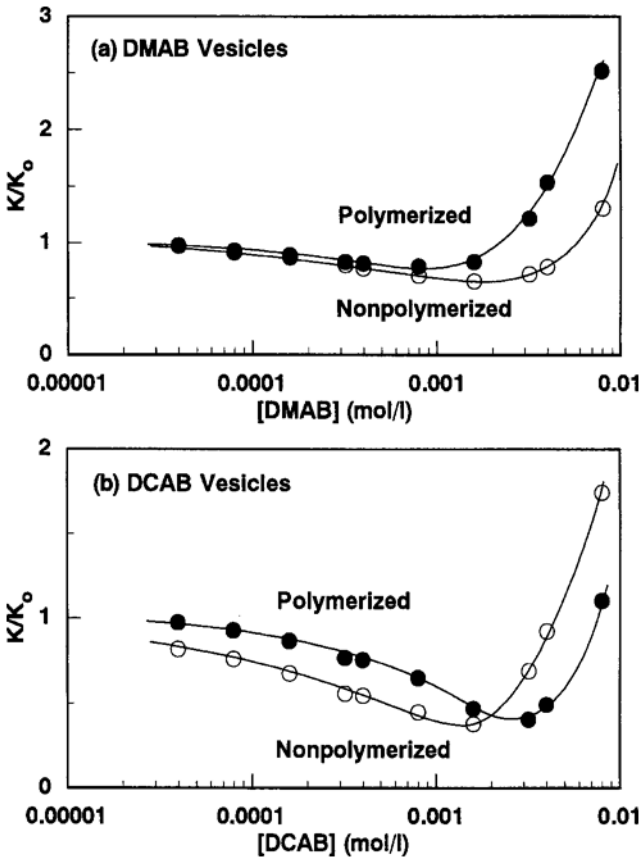

Fig. 3 Influence of DMAB (a) and DCAB (b) vesicles on complex formation between IA and MV at 25 °C. $[MV] = 8.0 \times 10^{-4}$ mol·dm^{-3}; $[IA] = 4.0 \times 10^{-2}$ mol·dm^{-3}

curve is dependent on the combination of the partition coefficients of reactants and product. The details of the theory have been described there. Only a few essential equations in the theory are shown here.

The ratio K/K_0 for the reaction $A + B = AB$ can be written in a simple fractional equation as

$$y = \frac{K}{K_0} = \frac{1 + Q_{AB}x}{(1 + Q_A x)(1 + Q_B x)} \tag{1}$$

where Q_A, Q_B, and Q_{AB} are defined as follows using the partition coefficients P_A, P_B and P_{AB} of the reactants A, B and the complex AB, respectively. The x is defined as CV, where C and V denote the concentration of the surfactant and the molar volume of the surfactant, respectively.

$$Q_A = P_A - 1, \qquad Q_B = P_B - 1,$$

$$Q_{AB} = P_{AB} - 1, \qquad x = CV\ .$$

The y versus x curves can be grouped into 14 classes by the combination of the conditions, i.e., the relative values of QV and a subcondition. In our case, where a minimum

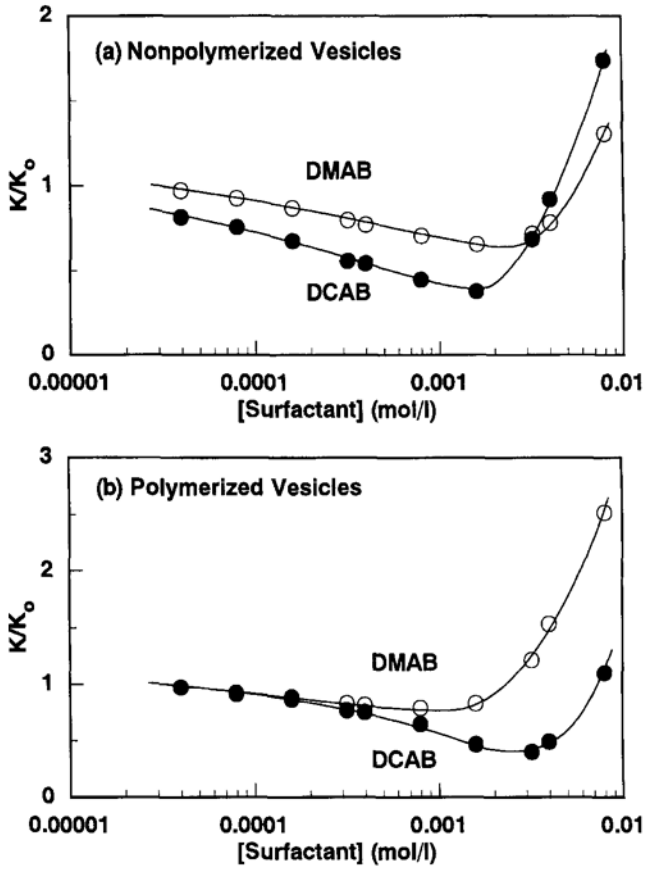

Fig. 4 Influence of nonpolymerized (a) and polymerized (b) vesicles on complex formation between IA and MV at 25 °C. [MV] = 8.0×10^{-4} mol·dm^{-3}; [IA] = 4.0×10^{-2} mol·dm^{-3}

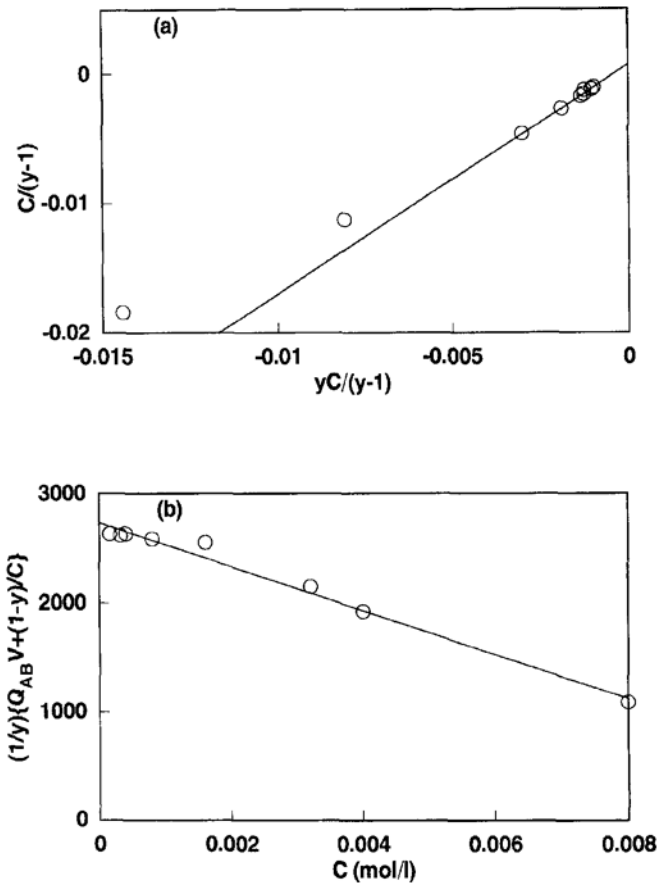

Fig. 5 Graphical treatment of the data on complexation of MV with IA in the presence of nonpolymerized DMAB vesicles according to Eq. [2](a) and [3](b)

appeared in the curve, the reactant A and the complex AB are likely to be attracted and another reactant B is repelled by the vesicle. The conditions $Q_A > Q_{AB} > 0 > Q_B$ or $Q_{AB} > Q_A > 0 > Q_B$ are then expected to hold in our case.

The $Q_{AB}V$ value for the complex was estimated using a transformation of Eq. (1):

$$\frac{C}{y-1} = \frac{1}{Q_{AB}V} + \frac{Q_A + Q_B}{Q_{AB}} \cdot \frac{y}{y-1} C + \frac{Q_A Q_B}{Q_{AB}} \cdot \frac{y}{y-1} \cdot VC^2 . \quad (2)$$

The values of Q_AV and Q_BV were further determined by Eq. (3) using the value of $Q_{AB}V$ evaluated from the intercept of Eq. (2).

$$\frac{1}{y}\left(Q_{AB}V + \frac{1-y}{C}\right) = (Q_A + Q_B)V + Q_A Q_B V^2 C \cdot \quad (3)$$

An example of the graphical determination of QV values from Eqs. (2) and (3) is shown in Fig. 5. Good linear plots were obtained. From the intercept and the slope of the plots of the left side of Eq. (3) vs C, Q_AV and Q_BV could be obtained. The values thus calculated are summarized in Table 1. The standard deviation in the table was obtained by the curve fitting procedure using a computer. The theoretical curves calculated from the QV values thus obtained are shown with the experimental data in Fig. 6. The agreement of the curves with the experimental points confirms our way of treating the data. Based on the table, we can say the following. When the DMAB vesicles were used, the absolute values of QV of reactant IA and the complex, both of which are adsorbed by the vesicle, increased due to the polymerization. The absolute value of MV (Q_BV) did not change very much on polymerization. When the DCAB vesicles were used, the values showed the reverse tendency due to the polymerization. When the influence of the nonpolymerized vesicles is compared, the DCAB vesicles resulted in a larger absolute value of Q_AV than the DMAB vesicles. However, the polymerized vesicles showed the reverse tendency. Because the electrostatic force between the cationic vesicles and the anionic IA or the cationic MV is important in our case, the effect of

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Table 1 QV values determined by graphical treatment and curve fitting treatment of the data for the complexation between MV and IA in the presence of surfactant vesicles at 25 °C

Surfactant	Nonpolymerized vesicle			Polymerized vesicle		
	Q_AV $\times 10^{-3}$	Q_BV $\times 10^{-1}$	$Q_{AB}V$ $\times 10^{-3}$	Q_AV $\times 10^{-3}$	Q_BV $\times 10^{-1}$	$Q_{AB}V$ $\times 10^{-3}$
DMAB	2.4 ± 0.2	-7.6 ± 0.1	1.2 ± 0.1	27 ± 74	-8.4 ± 0.4	23 ± 63
DCAB	11 ± 6	-9.3 ± 0.4	5.0 ± 3.2	1.2 ± 0.1	-10 ± 0	0.14 ± 0.05

The standard deviation was determined by the curve fitting treatment of the data.

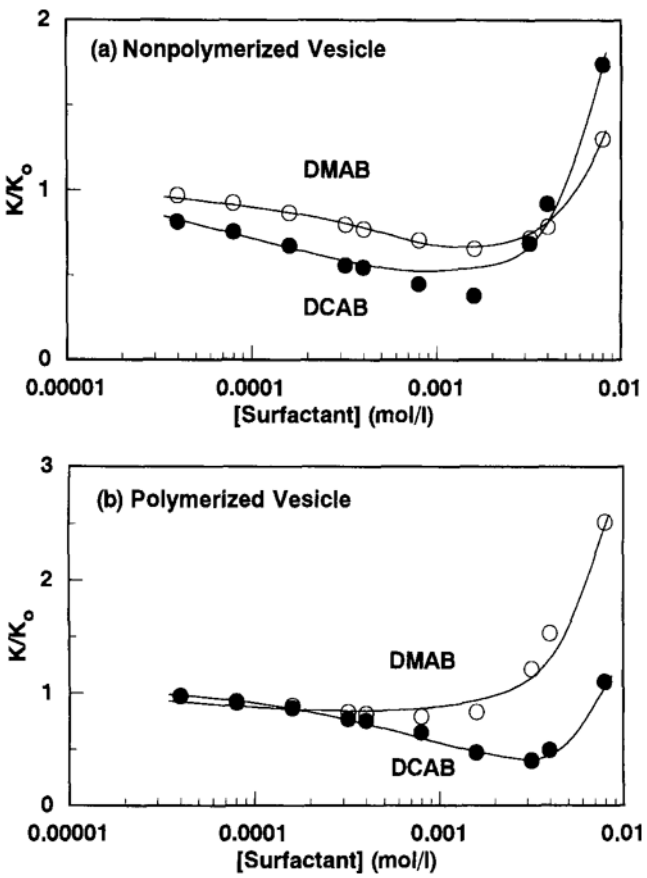

Fig. 6 Comparison of data with the theoretical curves based on the QV values determined from graphical analysis of the data. The lines indicate the theoretical curves

polymerization of the surfactant on the electrostatic force must be considered first. The former two results above mean that the electrostatic force increased due to the polymerization when DMAB, which has a shorter alkyl chain than DCAB, was used, but that force decreased due to the polymerization when DCAB was used. Similarly, the latter two results mean that the electrostatic force together with the hydrophobic force increases with the alkyl chain length of the nonpolymerized surfactant vesicles, but that force decreases with the increase in the chain length when the polymerized surfactant vesicles are used.

The possible influences of the increase in alkyl chain length are the increase in hydrophobic interaction between the reactants and the vesicles or among the surfactant molecules in the vesicular membrane, and the increase in the thickness of the vesicular membrane. Because the QV value of the produced cationic complex has a positive sign, the hydrophobic force played an important role. However, the polymerization will not significantly change the hydrophobic force. It is well-known that the increase in the alkyl chain length of phospholipids decreases the distance between the neighboring surfactant molecules in the membrane due to the increased hydrophobic interaction between the neighboring alkyl chains [14, 15]. Moreover, it must be noted that the reaction temperature (25 °C) was higher than the phase transition temperature (T_c) of DMAB (22 °C) and lower than that of DCAB (31 °C). It is known that the distance above the T_c is longer than that below the T_c [13]. The decrease in that distance will result in an increase in the charge density of the membrane and therefore the increase in the electrostatic force between the membrane and other ionic substrates [16]. Therefore, in the nonpolymerized state, the DCAB surfactant vesicles had a higher charge density and higher Q_AV and $Q_{AB}V$ values than the DMAB vesicles. However, why did the polymerization of the surfactant reverse the tendency? From the electrostatic point of view, the polymerization must have increased the charge density of the DMAB vesicles and decreased that of the DCAB vesicles. Because the charge density depends on the distance between the neighboring surfactant molecules, the polymerization must have decreased the distance in the DMAB vesicles and increased that in the DCAB vesicles. The results obtained above provide strong indirect evidence for the existence of more than two competing polymerization mechanisms, because the same structure of the polymer must have the same QV value. The main mechanism of the polymerization of a monomer containing a diallylamine group is well-known as a cyclopolymerization which produces a linear polymer [17]. However, the formation of a cross-linked network by the polymerization of the

individual allyl groups cannot be excluded [18, 19]. It can then be supposed that the two mechanisms are simultaneously competing in the polymerization of the vesicles, and their ratio changed with the distance between the neighboring nonpolymerized surfactant molecules. The long distance prefers the cyclopolymerization rather than the polymerization of individual allyl groups. The polymerization of the DMAB vesicles, which have a long distance, then drew the surfactant molecules together and increased the charge density. On the other hand, the polymerization of the DCAB vesicles is expected to result in the formation of many irregular and porous networks on the membrane, the formation of the many defects in the packing of the surfactant in the membrane, and thus the decrease in the apparent charge density or the increase in the mean distance between the neighboring surfactant molecules in the membrane.

In conclusion: A) The association constant K between MV and IA is decreased by the addition of cationic vesicles, and K increased at high vesicle concentrations. B) The influence of polymerization of surfactants with different chain lengths on K is different. C) The concentration dependence of K is analyzed by a theory in terms of partition coefficients of the reactants between the bulk solvent phase and the local vesicle environment. The theoretical partition coefficients are determined graphically. D) The measured dependence of K on vesicle concentration is satisfactorily reproduced by the theory. E) The influence of polymerization on K or QV is discussed in terms of the difference in the polymerization mechanism due to the difference in the distance between the neighboring surfactant molecules in the vesicular membrane.

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