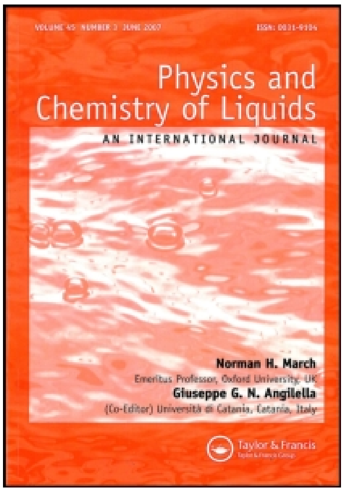

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Transfer and distribution of methylene blue through w/o-o/w and w/o-bicontinuous interface

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To cite this Article Chen, Yuan and Guo, Rong(2010) 'Transfer and distribution of methylene blue through w/o-o/w and w/o-bicontinuous interface', Physics and Chemistry of Liquids, 48: 3, 307 — 315
To link to this Article: DOI: 10.1080/00319100902822752
URL: http://dx.doi.org/10.1080/00319100902822752

Physics and Chemistry of Liquids
Vol. 48, No. 3, June 2010, 307–315

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(*Received 5 October 2008; final version received 15 February 2009*)

The distribution of methylene blue (MB) between the microemulsion phases with different structures of sodium dodecyl sulphate/*n*-pentanol/water (SDS/n-$C_5H_{11}OH/H_2O$) system was determined by UV-Vis spectroscopy, and the study of the effect of MB on the interphase electric properties studied by the method of AC impedance provides further evidence for it. The results show that MB transfers from the upper phase (W/O) to the lower phase (O/W or bicontinuous) with the increase of the total SDS content at the constant weight ratio of n-$C_5H_{11}OH/H_2O = 50/50$ and the total MB concentration of $1.2 \times 10^{-5}\,mol\,L^{-1}$, namely the distribution coefficient of MB decreases. The addition of MB results in the decrease of the distribution coefficient of SDS between the upper and lower phases. The changes of the electrochemical properties further prove the transfer and redistribution of SDS and MB.

Keywords: distribution coefficient; methylene blue; microemulsion; surfactant

1. Introduction

The liquid–liquid interfaces abound in the organism and nature. It has been well recognised that the liquid–liquid interface plays an essential role in many areas of physical chemistry such as electrochemistry, phase transfer catalysis, drug availability, ion separation by liquid–liquid extraction, biomedical engineering, pharmacology, food processing and liquid chromatography, as well as membranes mimics [1–6]. It also has implications in environmental processes or atmospheric pollution. In terms of usually studied oil–water interface, surfactant molecules arrange only at the interface, and in the bulk phases (in the oil phase and in the water phase) there does not exist the surfactant molecular aggregates. The properties of such liquid–liquid interfaces are far from that of the interfaces in the organism. Therefore, we choose the water in oil (W/O) to oil in water (O/W) and W/O to bicontinuous (BI) interface to carry on our study. During this interface, surfactant molecules are not only located at the liquid–liquid interface, but also assemble into micelles in the bulk solution to form W/O (in the upper

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ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100902822752
http://www.informaworld.com

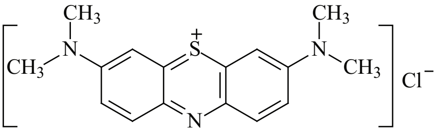

Figure 1. Molecular structure of MB.

phase), O/W or BI (in the lower phase) microemulsions. This interface takes on particular bionic.

Methylene blue (MB) is also named methylenum caeruleum, tetramethylthionine chloride or Swiss blue. Its structure, shown in Figure 1, is coplanar, polycyclic and aromatic. MB is a basic dye that belongs to the thiazine class. It has long been used as a tool to dissect intracellular redox metabolism [7–9], as well as for biological staining and diagnosis of diseases including carcinoma [10–11], and can be used as an effective antidote [12]. Moreover, some researchers have reported that it was potentially effective for the treatment of chloroquine-resistant malaria caused by *Plasmodium falciparum* and had a promising application in the photodynamic therapy for anticancer treatment [13–14]. It is widely accepted in the pharmaceutical industry that the overall distribution, metabolism and efficacy of many drugs can be altered based on their affinity to serum albumin.

We have studied the distribution and transfer of L-phenylalanine [15], L-tryptophan [16], malachite green [17] and gatifloxacin [18] through the water-in-oil (W/O)–oil-in-water (O/W) interface and W/O–BI interface in sodium dodecyl sulphate/*n*-pentanol/water (SDS/n-$C_5H_{11}OH/H_2O$) system by means of UV-Vis spectroscopy and AC impedance. And the comprehensive information of the interfacial potential, capacitance, resistance and interfacial charge transfer current has been gained without any damage to the interface structure. In the present article, the distribution and transfer of MB between the two phases taking place at the W/O–O/W and W/O–BI interface have been studied. The study can provide some instructional information for the improved application of MB as a kind of clinical medicine.

2. Experimental

2.1. *Materials*

Sodium dodecyl sulphate (SDS, Sigma, $>98\%$) is an analytic reagent recrystallised twice in ethanol to ensure that its surface tension has no lowest point around the critical micelle concentration (cmc) by the platinum ring method. MB is an analytic reagent purchased from Sinopharm Chemical Reagent Co. Ltd; n-$C_5H_{11}OH$ (99%) was purchased from Aldrich. Water used was deionised and distilled.

2.2. *Measurement of UV-Vis spectra*

A series of SDS/n-$C_5H_{11}OH/H_2O$/MB solutions were prepared, kept at $25.0 \pm 0.1°C$ for 10 h to reach the phase equilibrium and then separated into two phases after the equilibrium. The absorption spectra of the upper and lower phases were obtained in the range of the wavelengths 800–200 nm using the blank reagent as reference. The absorption intensities of the characteristic peak were recorded with a UV-2550 spectrophotometer (Shimadzu, Japan).

2.3. *Determination of SDS content*

A PXD-12 model digital ion analyser in combination with 102 P^{Na} selective electrode were used to determine the concentration of Na^+ ion and accordingly, this is used to calculate the SDS content. Four-point calibration was carried out before the measurements. Determinations of sample and calibration solution were performed triplicate.

2.4. *Determination of electric properties*

Electrochemical measurements were performed using an Autolab PGSTAT 30 (Eco-Chemie, the Netherlands) connected with a personal computer. Two pairs of three-electrode systems were used in the electrochemical experiments. The size of the Pt–Pt electrode was 0.3 cm × 0.7 cm, and the distance between the two electrodes (working electrodes) was 0.3 cm. The reference electrodes were two saturated calomel electrodes (SCE). The potential applied was 0.6 V (*vs.* Hg_2Cl_2/Hg), the frequency range was 100,000 Hz–0.01 Hz, and the equilibrium time was 10 s. The pure resistance, capacitances and charge transfer resistance R_{ct} can be obtained from the complex plane impedance plots [19]. The determining system was rectified by the standard simulative electric circuit.

All experiments were carried out at $25.0 \pm 0.1°C$. In order to attain equilibrium, the samples were placed in a water thermostat at $25.0 \pm 0.1°C$ for 10 h before the experiments.

3. Results and discussion

3.1. *Distribution of SDS between the upper and lower phases*

As shown in the partial phase diagram of the SDS/n-$C_5H_{11}OH/H_2O$ system (Figure 2) prepared in our previous study [20], LL is the coexisting region of W/O and O/W or BI microemulsions, which is of great interest to us. In the LL region, the SDS/n-$C_5H_{11}OH/H_2O$ system separates into two phases (the upper phase and the lower phase) spontaneously. With the constant weight ratio of n-$C_5H_{11}OH/H_2O$ at 50/50 and rise in the total content of SDS in the system, the increase of SDS content in the upper phase is different from that in the lower phase (Figure 3a), so is the change of the structure in these two phases [15]. And the distribution constant (K_{SDS}) of SDS between the upper and lower phases in the system decreases (Figure 3b). As seen from the tie line in Figure 2, corresponding to the slow increase of the SDS content in the upper phase, the upper phase is always W/O microemulsion, and what increases is just the concentration of the reversed micelles, no structural change occurs. But for the lower phase, when the total content of SDS is less than 3.0%, the lower phase is O/W microemulsion (line a–a′, b–b′ in Figure 2). When the total content of SDS reaches 3.0%, the composition of the lower phase does not exist in the O/W microemulsion region any more; the lower phase changes to BI microemulsion (line c–c′, d–d′, e–e′ in Figure 2).

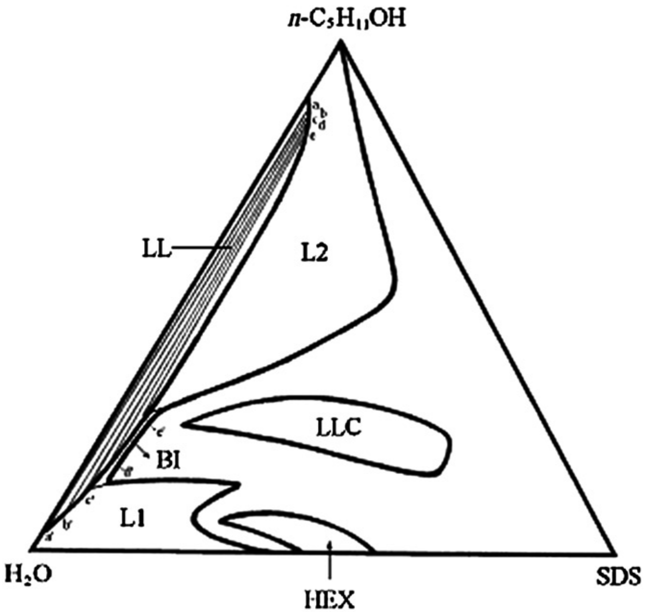

Figure 2. Partial phase diagram of the SDS/n-$C_5H_{11}OH$/H_2O system at 25°C. Total SDS content: a–a′: 1.0%; b–b′: 2.0%; c–c′: 3.0%; d–d′: 4.0%; e–e′: 5.0%.

The distribution constant (K_{SDS}) of SDS between the upper and lower phases in the SDS/n-$C_5H_{11}OH$/H_2O system can be expressed as follows:

$$K_{SDS} = \frac{w_{SDS\text{-up}}}{w_{SDS\text{-down}}}, \tag{1}$$

where $w_{SDS\text{-up}}$ and $w_{SDS\text{-down}}$ are qualitative percent of SDS in the upper and lower phases, respectively.

Methylene blue is positively charged, and SDS is an anionic surfactant. So the electrostatic force between SDS and MB is certain to bring the transfer of SDS between the two phases. As seen from Figure 4(a), the SDS content in the upper phase decreases and that in the lower phase increases with the increase of the total MB concentration whether the total SDS content is 1.0 or 4.0%, i.e. K_{SDS} decreases with the total MB concentration (Figure 4b), suggesting that SDS transfers from the upper phase to the lower phase with the addition of MB. In addition, from Figure 4(b) we can also see that the decrease extent of K_{SDS} at 4.0% total SDS content is slower than that at 1.0% total SDS content, which is related to the transformation of the lower phase from O/W to BI microemulsion.

3.2. *Distribution of MB between the upper and lower phases*

The distribution constant (K_{MB}) of MB between the upper and lower phases in the SDS/n-$C_5H_{11}OH$/H_2O system can be expressed as follows:

$$K_{MB} = \frac{[MB]_{up}}{[MB]_{down}}, \tag{2}$$

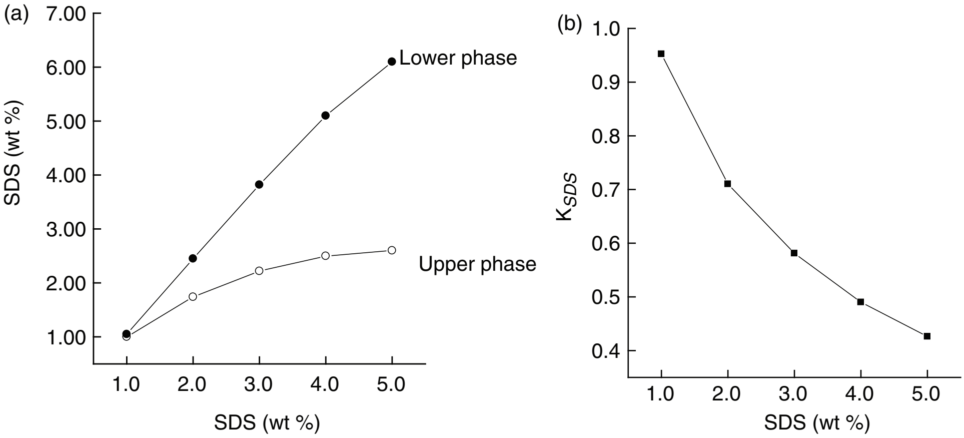

Figure 3. Effects of the total SDS content on (a) the distribution of SDS and (b) the distribution coefficient K_{SDS} between the upper and lower phases.

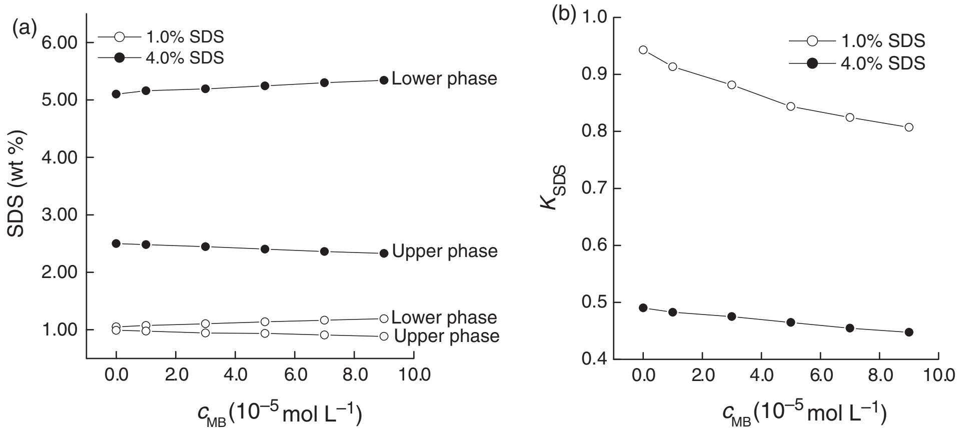

Figure 4. Effects of the total MB concentration on (a) the distribution of SDS and (b) the distribution coefficient K_{SDS} between the lower and upper phases at constant total content of SDS: (○) 1.0%, (●) 4.0%.

where $[MB]_{up}$ and $[MB]_{down}$ are molar concentrations of MB in the upper and lower phases, respectively.

According to the measured standard curves (figure not shown), the molar absorption coefficient of MB in O/W microemulsion is almost identical to that in W/O microemulsion and the absorbance of MB is linear to the concentration in the present study. So the concentration ratio of MB between the two phases can be replaced by the absorbance ratio of MB at 660 nm. Consequently, Equation (2) can be expressed as

$$K_{MB} = \frac{A_{up}}{A_{down}}. \tag{3}$$

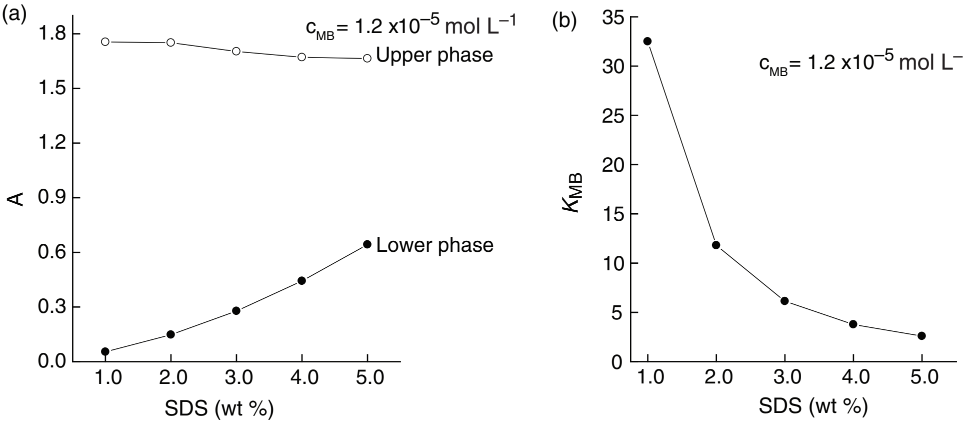

Figure 5. Effects of the total SDS content on (a) the distribution of MB and (b) the distribution coefficient K_{MB} between the upper and lower phases.

As MB is positively charged in the SDS/n-$C_5H_{11}OH/H_2O$ system, the static interaction between MB cation and SDS anion will result in the transfer of MB between the two phases. In addition, MB can be solubilised in the SDS molecular organised assembly system, so the distribution of MB in the upper and lower phases of the SDS/n-$C_5H_{11}OH/H_2O$ system is related to the structure of the SDS molecular organised assembly in the system. In Figure 5(a) we can see that when MB is added to the system, there are much more MB molecules distributed in the upper phase than in the lower phase. When the total MB concentration is 1.2×10^{-5} mol L^{-1}, with the increase of the total SDS content, the absorbance of MB in the upper phase decreases slightly and that in the lower phase increases evidently, i.e. K_{MB} decreases with the total SDS content (Figure 5b), suggesting that some MB transfer from the upper phase to the lower phase with the addition of SDS. With the increase of the total SDS content, the SDS content in the lower phase increases greatly (Figure 3a), and the electrostatic attraction force between SDS and MB in the lower phase is much larger, which results in the transfer of MB from the upper phase to the lower phase. In addition, when the total content of SDS is greater than 3.0%, the network structure of the BI microemulsion in the lower phase enabled more MB to be solubilised in it, so MB molecules transferred from the upper phase to the lower phase through the interface, which increased the content of MB in the lower phase. Apparently, the increase of the MB content in the lower phase is closely related to the increase of the SDS content and the structure change in the lower phase.

In Figure 6(a), it is observed that the absorbance of MB in both the upper and lower phases increase with the total MB concentration and the increase in the upper phase is greater, so K_{MB} increases with the total MB concentration (Figure 6b). It is likely that the solubility of MB in the continuous phase n-$C_5H_{11}OH$ of the upper phase is much larger than that in the continuous water phase of the lower phase, so MB is inclined to distribute in the upper phase. From Figure 6(b) we can also see that the increase of K_{MB} at 4.0% total SDS content is slower than that at the 1.0% total SDS content, which is related to the change of the structure from O/W to BI microemulsion in the lower phase.

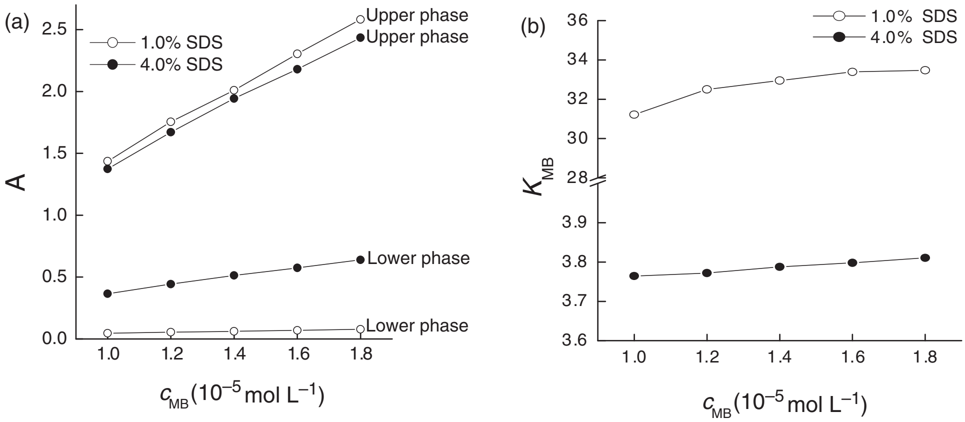

Figure 6. Effects of the total MB concentration on (a) the distribution of MB and (b) the distribution coefficient K_{MB} between the lower and upper phases at constant total content of SDS: (○) 1.0%, (●) 4.0%.

3.3. *Effect of MB on the interphase electric properties*

The interactions between MB and SDS molecules make some MB molecules to be located at the interface, and lead to the redistribution of SDS between the upper and lower phases, which affect the capacitance, resistance and interfacial charge transfer current of the system.

The relationships of the electric properties to the total concentration of MB in the system are shown in Figures 7(a–c). As discussed earlier [15], capacitance has relevance to the size, concentration and effective charge of the particle, the dielectric constant of the media, etc. The resistivity of the solution is related to the properties of the media and the concentration of the charged particles. As seen in Figure 7(a), with the increase of the total MB concentration, the capacitance in the lower phase (C_w), the capacitance in the upper phase (C_o) and the interphase capacitance (C_i) increase due to the increase of the concentrations of the charged particles. From Figure 7(b), it can be seen that in contrast to the capacitance, the resistivity in the lower phase (ρ_w), the resistivity in the upper phase (ρ_o) and the interphase resistivity ρ_i decrease with the increase of the total MB concentration. Corresponding to the decrease of the interfacial resistance, the resistance impeding the SDS from getting through the interface reduces too, so the interphase charge-transfer current i_0 increases accordingly (Figure 7c).

4. Conclusions

When the weight ratio of n-$C_5H_{11}OH/H_2O$ was 50/50 and the total concentration of MB was 1.2×10^{-5} mol L^{-1}, with the increase of the total content of SDS in the system, partial MB transfers from the upper to the lower phase and so the distribution constant K between the upper and lower phases of MB decreases. The electrostatic forces between MB and SDS make SDS molecules transfer from the upper to the lower phase. In addition, the addition of MB increases the

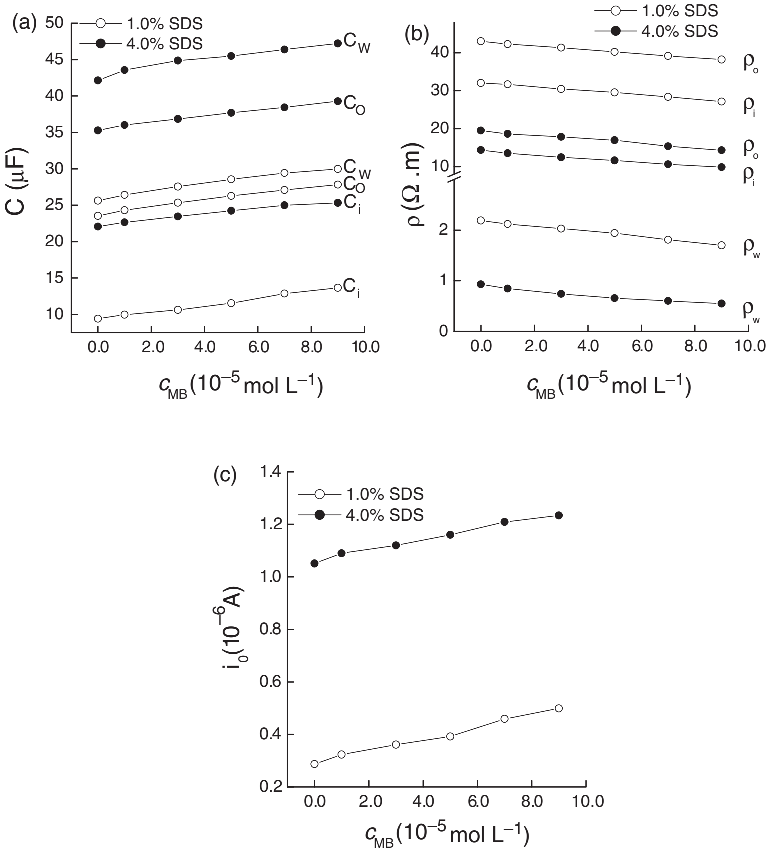

Figure 7. Dependence of (a) capacitance, (b) resistivity and (c) interphase charge-transfer current on the total MB concentration at constant total contents of SDS: (○) 1.0%, (●) 4.0%. C_o – capacitance in the upper phase; C_w – capacitance in the lower phase; C_i – interphase capacitance. ρ_o – resistivity in the upper phase; ρ_w – resistivity in the lower phase; ρ_i – interphase resistivity.

interphase capacitance and the interphase charge transfer current of the system and reduces the interphase resistivity of the system.

Acknowledgement

This work was supported by the National Nature Science Foundation of China (Nos. 20633010 and 20773106).

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