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Kinetics of a Hydrolysis Reaction in an Oil/Water Microemulsion System Near the Critical Point

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Abstract We have constructed the pseudoternary phase diagram of surfynol465 + *n*-butanol + cyclohexane + H_2O with $k_m = 2$ (where k_m is the weight ratio of surfynol465 to *n*-butanol) by the water titration method. Electrical conductivity measurements were employed to investigate the microstructures of the single-phase region. In the oil/water microemulsion region, we have measured the hydrolysis reaction rate of 2-bromo-2-methylpropane near and far away from the critical point. It was found that the Arrhenius equation was valid for correlating experimental measurements far away from the critical point but a significant acceleration effect exists near the critical point, which is not consistent with thermodynamic interpretation of Griffiths and Wheeler.

Keywords Critical effect · Critical point · Microemulsion · Phase diagram

1 Introduction

During the last four decades there have been extensive theoretical and experimental studies of the critical behavior [1–6] and chemical reactions near the consolute point [7–11]. The consolute point is an extremum in the temperature versus mole fraction phase diagram of a constant pressure liquid–liquid mixture, where the homogeneous solution first begins to separate into two immiscible layers. Near a consolute point, large fluctuations of the order parameter dominate, resulting in behavior quite different from that far away from the consolute point. Upon introduction of a reactant to the liquid, a chemical reaction can often

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be initiated. This permits critical mixtures to be used to study the critical effect on the net rate of reaction.

The influence of the critical phenomena on chemical reactions has been reported by Wheeler et al. [7–11]. However, not all the experimental results are consistent with these theories, which support slowing down of chemical reactions near the critical point. Snyder and Eckert [12] reported clear evidence of speeding up of the reaction of isoprene with maleic anhydride near the liquid–liquid critical point. Kim and Baird [13–20] measured the rates of thirteen different chemical reactions in three different critical binary liquid mixtures; in six cases [13–16], slowing down was found and in four cases [1–19], speeding up was evident. In two cases [20], no effects were detected while in one case [20] the rate constant oscillated in magnitude by about 10 %. Recently, Shen and colleagues [21, 22] studied the kinetics of the oxidation of iodide ion by persulfate ion and the alkaline fading reaction of crystal violet in the critical water/oil microemulsion of water/bis(2-ethylhexyl) sodium sulfosuccinate/*n*-decane with the molar ratios of water to sodium bis(2-ethylhexyl) sulfosuccinate being 35.0 and 40.8 and to 2-butoxyethanol + water, respectively. It was found that Arrhenius equations were valid for correlating experimental measurements far away from their respective critical regions but there was significant slowing near their respective critical regions. Obviously, several kinds of critical effects were found in different critical mixtures and even in the same one.

It should be pointed out that the hydrolysis reaction rate of 2-bromo-2-methylpropane in the one-phase region of triethylamine + H_2O [17] at temperatures near its critical point is speeded up, which is different from six other hydrolysis reactions in liquid–liquid mixtures at temperatures near their respective consolute points [14, 15]. The structure of these reactants and reaction mechanism are similar; however, the critical effects are different. These differences may be related to the reactants or the critical mixtures. To explore whether the critical effects are related to the critical mixtures, recently we studied the hydrolysis reaction rate of 2-bromo-2-methylpropane in a similar mixture of triethylamine + D_2O [23]. It was found that the reaction rate in the one phase region at temperatures near the critical point slowed down, which is not consistent with the results of Kim et al. [17].

In order to further explore whether the critical effects are related to the critical mixtures, we have extended the studies of critical effect on the chemical reaction to more complicated microemulsion systems [24]. To the best of our knowledge, the critical effect of the oil/water (O/W) microemulsion on reaction rate is seldom explored. In this work, we have measured the hydrolysis reaction rate of 2-bromo-2-methylpropane in the O/W microemulsion region of surfynol465 + *n*-butanol + cyclohexane + H_2O with $k_m = 2$ (where k_m is weight ratio of surfynol465 to *n*-butanol), near and far away from its critical

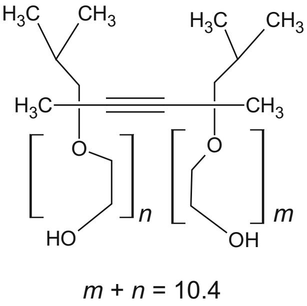


Fig. 1 Structure of surfynol465

point, by electrical conductivity and the experimental results are compared with those of the same reaction in triethylamine + H_2O and triethylamine + D_2O.

2 Experimental

2.1 Materials

2-Bromo-2-methylpropane (≥99 %) was provided by Aladdin Chemistry Co., Ltd. Cyclohexane (≥99.5 %) and *n*-butanol (99.5 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. Gemini surfactant surfynol465 was provided by Yongli Co., Ltd. (≥ 98 %) and the structure is shown in Fig. 1. Twice distilled water was used throughout the study.

2.2 Construction of the Phase Diagram

The pseudoternary phase diagram was constructed to investigate the concentration ranges of components for identifying the existence of microemulsion regions by the water titration method. Cyclohexane was mixed with surfynol465/*n*-butanol mixture (2:1); water was then added dropwise using a micropipet until the transparent and homogeneous dispersion converted to a turbid mixture. The appearance of turbidity was considered as an indication of phase separation. The microemulsion regions were identified as optically transparent and isotropic mixtures. Finally, electrical conductivity measurements were employed to investigate the gradual changes occurring in the microstructure of the microemulsion system. The temperature was measured with a thermostat (SWQ-I_A, Sangli Electronic Instrument Company) in which the temperature was controlled within ±0.1 K.

2.3 Determination of the Critical Composition and the Critical Temperature of the System

The pseudoternary system has numerous double critical points; however, the critical composition and critical temperature of a double critical point can be obtained when the weight ratios of three components of a pseudoternary microemulsion system are determined. In this work, the critical composition was determined through the technique of "equal volume": adjusting the droplet concentration to achieve identical volumes of two separating liquid phases at the phase separation temperature, and the concentration and phase separation temperature were taken to be the critical ones [25]. Samples with the critical composition were prepared in a test tube. It was placed inside a low temperature thermostatic bath (GDH-0506, Ningbo Scientz Biotechnology Company) in which temperature was controlled within ±0.002 K. The temperature was measured with a platinum resistance thermometer (SWC-II_D, Sangli Electronic Instrument Company). For a critical reaction mixture, the critical composition and critical temperature always change slowly during the reaction. In other words, the critical composition and the critical temperature determined immediately after mixing are different from those of the reaction mixture that has come to equilibrium. For a dilute critical mixture, the reaction has usually no measurable effect on critical composition; however, it can cause a noticeable shift in the critical temperature.

2.4 Kinetics Measurement

The electrical conductivity was measured using a conductivity meter (Model DDS-11A) which had a repeatability of 0.001 mS·cm^{-1}.

The overall reaction is:

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

Because the hydrolysis reaction produced the strong electrolyte HBr, we could follow the progress of the reaction by making measurements of the electrical conductivity. The instantaneous value of the conductance L is given by:

$$L = L_0 + (L_e - L_0)(\xi/\xi_e) \tag{1}$$

where L_0 is the initial value and L_e is the value at equilibrium and ξ is the extent of reaction. At time $t = 0$, the extent of reaction has the value $\xi(0) = 0$, while at chemical equilibrium it has the value $\xi = \xi_e$.

If the reaction is first order, the rate law is [17]:

$$\frac{d\xi}{dt} = -k(\xi - \xi_e) \tag{2}$$

For the initial condition, $\xi = 0$ at $t = 0$, the integral of Eq. 1 is:

$$\xi = \xi_e(1 - \exp(-kt)) \tag{3}$$

where k is the rate constant.

If we substitute this into Eq. 1, we obtain:

$$L = L_0 + (L_e - L_0)(1 - \exp(-kt)) \tag{4}$$

By fitting the experimental value of $L - L_0$ to time t, the reaction rate constant k of the hydrolysis reaction of 2-bromo-2-methylpropane can be obtained.

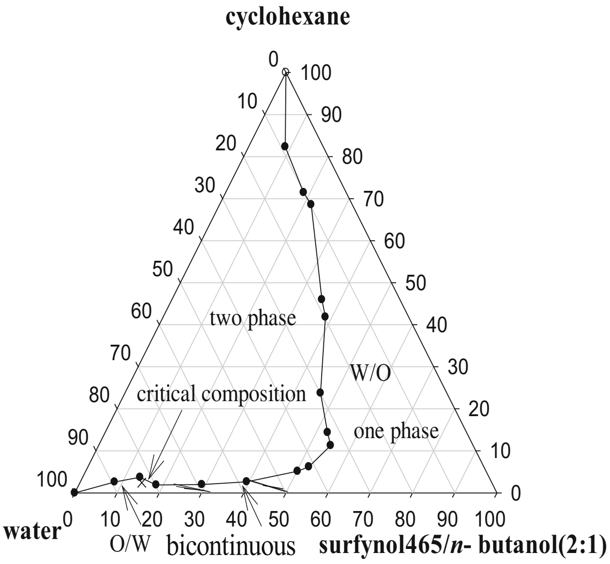


Fig. 2 Pseudoternary phase diagram of surfynol465 + n-butanol + cyclohexane + H_2O with $k_m = 2$ at 303.2 K

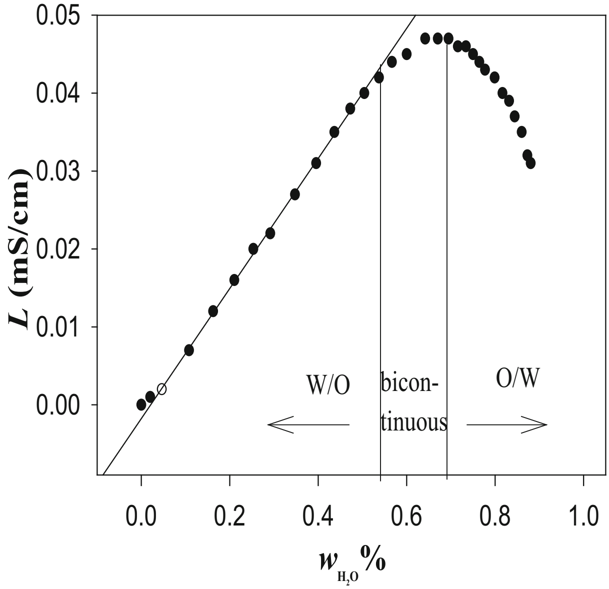
3 Result and Discussion

Figure 2 shows the pseudoternary phase diagram of surfynol465 + *n*-butanol + cyclohexane + H_2O with $k_m = 2$ at 303.2 K. A large single isotropic region extending from the water corner to the cyclohexane one is observed. The region marked "one phase" is the one phase microemulsion and the region marked "two phase" is a turbid region, that is, a microemulsion in equilibrium with an excess cyclohexane or water phase. The compositions are listed in Table 1. The large single phase microemulsion region has been differentiated into discrete reverse micelle (water/oil), bicontinuous, and normal micelle (O/W) regions according to the electrical conductivity measurements. The electrical conductivity measurement is the most widely used simple technique for examining the microstructures and their structural changes in surfactant based microemulsion systems. We have measured electrical conductivity as a function of water weight fraction $w_{H_2O}\%$ to identify the microstructure type of the microemulsion phase in the present investigation. Figure 3 is a representative electrical conductivity versus $w_{H_2O}\%$ profile at 303.2 K for the studied microemulsion system. The curve can be divided into four distinct segments. (1) The initial nonlinear part may be attributed to inverse microdroplet aggregation; (2) the next linear increase is due to the formation of aqueous microdomains, which results from the partial fusion of clustered inverse microdroplets, suggesting that a water/oil microemulsion is formed in this low water content region; (3) the third nonlinear increase of electrical conductivity indicates that the medium undergoes a gradual structural transition and a bicontinuous microstructure is formed due to the progressive growth and interconnection of the aqueous microdomains; (4) the final decrease of electrical conductivity with increase of water content corresponds to the appearance of water–continuous microemulsion. That is, an O/W microemulsion is formed at high water content, and the decrease of electrical conductivity results from the progressive decrease of the concentration of the O/W microemulsion droplets. These results are similar to the observations made in an earlier study on the electrical conductivity of microemulsions [26].

Table 1 Experimentally determined composition along the phase boundary of surfynol465 + *n*-butanol + cyclohexane + H_2O with $k_m = 2$ (where k_m is the weight ratio of surfynol465 to *n*-butanol) at 303.2 K

Surfynol465/*n*–butanol (2:1) (wt%)	Cyclohexane (wt%)	Water (wt%)
8.68	82.34	8.98
18.48	71.44	10.08
21.69	68.59	9.72
35.54	45.98	18.47
38.47	41.82	19.71
46.36	23.73	29.92
52.71	14.37	32.92
54.98	11.28	33.76
52.34	6.20	41.46
50.18	5.15	44.67
39.40	2.65	57.95
29.09	1.97	68.93
18.33	1.88	79.79
13.61	3.71	82.68

Fig. 3 Conductivity as a function of water concentration with weight ratio of surfynol465 + *n*- butanol (2:1) to cyclohexane being 27.62 at *T* 303.2 K



Using electrical conductivity as a measure of the extent of reaction in the critical microemulsion system, the critical composition should be located in the O/W or bicontinuous microemulsion region. It was found that the critical composition could not be located in the bicontinuous microemulsion region for surfynol465 + *n*-butanol + cyclohexane + H_2O, so we only studied the hydrolysis reaction of 2-bromo-2-methylpropane in the O/W microemulsion region. It is known that 2-bromo-2-methylpropane is insoluble in water, so the hydrolysis reaction may take place at the outer interface of the O/W microemulsion structure. The microemulsion system can provide a high interfacial area of contact for the reaction and the products of H^+ and Br^- will go into the continuous aqueous phase. So, in the O/W microemulsion region, this reaction can be followed by making measurements of the electrical conductivity. The concept of the hydrolysis reaction in the O/W microemulsion region is shown in the inset of Fig. 4.

The critical mass fraction of surfynol465 for the mixture of surfynol465 + *n*-butanol + cyclohexane + H_2O with $k_m = 2$ and $k_n = 4$ (where k_n is weight ratio of surfynol465 to cyclohexane) was found to be 0.0976, which is located in the O/W microemulsion region shown in Fig. 2. 2-Bromo-2-methylpropane was then added to the critical mixture using a micropipette with stirring. After about 60 s, the stirrer was stopped and the experimental data were recorded at the same time. The initial concentration of 2-bromo-2-methylpropane is 0.0045 mol·kg^{-1}. The critical temperatures determined immediately after mixing is 303.92 ± 0.05 K. Because the mixture has a lower critical solution temperature, it can be maintained in the one phase region during the entire course of the reaction simply by holding the thermostat at a temperature of 303.92 K or lower. The electrical conductivity of the critical reaction mixture of surfynol465 + *n*-butanol + cyclohexane + H_2O + 2-bromo-2-methylpropane (initial concentration $m = 0.0045$ mol·kg^{-1}) with $k_m = 2$ and $k_n = 4$ was measured as a function of time at different temperatures. Figure 4 shows a plot of Eq. 4 for a run at 303.375 K. By fitting the experimental value of $L - L_0$ at 303.375 K to time *t*, the rate constant *k* can be obtained.

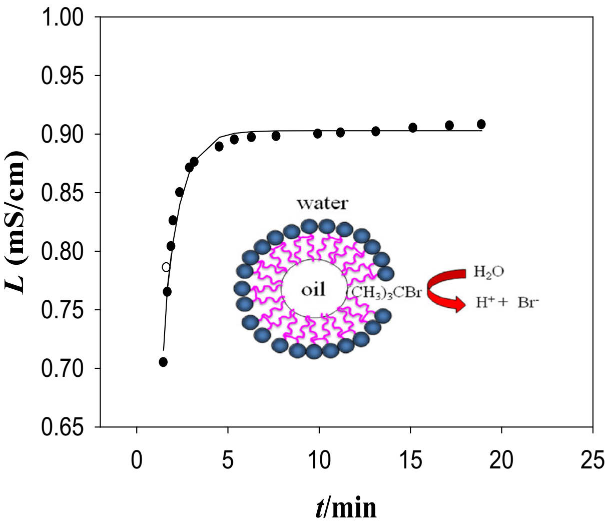


Fig. 4 Plot of instantaneous value of the electrical conductance L versus time t at 303.375 K for hydrolysis reaction of 2-bromo-2-methylpropane in surfynol465 + n-butanol + cyclohexane + H_2O with $k_m = 2$ and $k_n = 4$ at its critical composition. The *points* are the experimental data and the *solid line* is the fitting curve of the experimental value according to Eq. 1. The *inset* shows the concept of the hydrolysis reaction in the O/W microemulsion region

In Fig. 4 the points are the experimental data and the solid line is the fitting curve of the experimental value according to Eq. 4. It can be seen that the fitting curve is in agreement with the experimental data, which suggests that the progress of the hydrolysis reaction of 2-bromo-2-methylpropane in the O/W microemulsion region can be followed by making measurements of the conductance and the concept of the hydrolysis reaction in the O/W microemulsion region shown in the inset of Fig. 4 is reasonable. With the same method, the rate constants at other temperatures were obtained and are listed in Table 2. In Fig. 5, we show an Arrhenius plot of the temperature dependence of k. The straight line, which was fitted to the data collected at temperatures outside the critical region, has the equation

$$\ln(k) = (35.05 \pm 1.07) - (98{,}440 \pm 2671)/RT \tag{5}$$

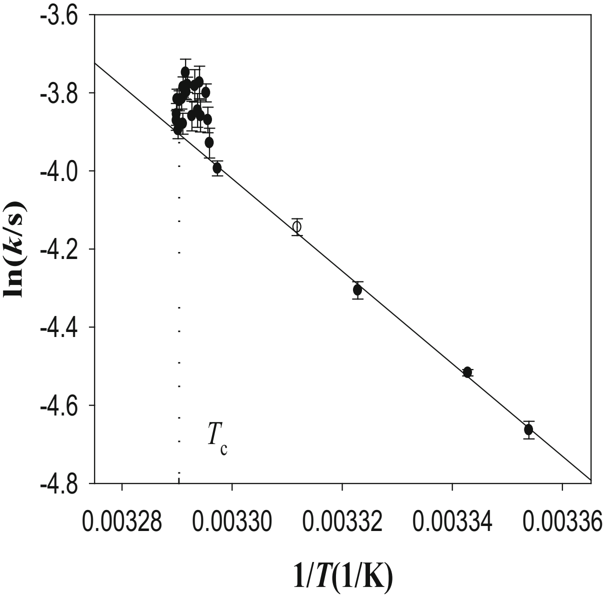
where the uncertainty is the standard error. This line can serve as the "background" for determining the existence of a critical effect. As mentioned by Griffiths and Wheeler [27], the observation of critical effects at the consolute point of a multicomponent mixture

Table 2 Rate constant k versus temperature T for the hydrolysis of 2-bromo-2-methylpropane in surfynol465 + n-butanol + cyclohexane + H_2O with $k_m = 2$ and $k_n = 4$ (where $k_m = w_{\text{surfynol465}}/w_{n\text{-butanol}}$ and $k_n = w_{\text{surfynol465}}/w_{\text{cyclohexane}}$) at its critical composition

T (K)	k (s^{-1})	T (K)	k (s^{-1})	T (K)	k (s^{-1})	T (K)	k (s^{-1})
298.159	0.00943	299.15	0.0109	300.948	0.0135	301.949	0.0159
303.275	0.0184	303.435	0.0209	303.408	0.0197	303.608	0.0214
303.466	0.02237	303.559	0.0210	303.575	0.0230	303.702	0.0211
303.655	0.0228	303.815	0.0225	303.796	0.0224	303.779	0.0228
303.809	0.0236	303.850	0.0227	303.875	0.0220	303.855	0.0207
303.915	0.02192	303.935	0.0203	303.951	0.0220	303.963	0.0208
303.961	0.0212						

The initial concentration of 2-bromo-2-methylpropane is 0.0045 mol·kg^{-1}. The critical temperature T_c is 303.92 ± 0.05 K

Fig. 5 Arrhenius plot of the rate constant for hydrolysis reaction of 2-bromo-2-methylpropane in surfynol465 + n-butanol + cyclohexane + H_2O with $k_m = 2$ and $k_n = 4$ (where $k_m = w_{\text{surfynol465}}/w_{n\text{-butanol}}$ and $k_n = w_{\text{surfynol465}}/w_{\text{cyclohexane}}$) at its critical composition. The initial concentration of 2-bromo-2-methylpropane is 0.0045 mol·kg^{-1}. The critical temperature T_c is 303.92 ± 0.05 K



depends on a count of the number of inert components. A component can be considered to be inert if it is not involved in any chemical reaction. If the mixture contains only one inert component, critical slowing down will be found. If the mixture contains two or more inert components, no critical effect is expected. In our reaction mixture, neither the reactants, 2-bromo-2-methylpropane and water, nor the products, hydrogen bromide and *tert*-butanol, can be considered to be inert because they are involved in the main reaction. However, surfynol465, n-butanol and cyclohexane can be assumed to be three inert components whose mass fractions are constant independent of T and p, and thus, no critical effect is expected in the mixture according to Griffiths and Wheeler. However, the net rate of the reaction in the one phase region at temperatures near the critical point shown in Fig. 5 speeds up, which is not consistent with thermodynamic interpretation of Griffiths and Wheeler. As mentioned above, the structure and mechanism of these hydrolysis reactions [14, 15, 17, 23] are similar; however the critical effects are different. It seems that the critical effects depend on the critical mixtures or reactants. Therefore it is worth comparing the critical effect of the same hydrolysis reactant of 2-bromo-2-methylpropane in our system with that in different critical mixtures of triethylamine + H_2O and triethylamine + D_2O. In triethylamine + D_2O, the net reaction rate is slowed down. However, critical speeding up is found in our mixture and triethylamine + H_2O, which is not consistent with thermodynamic interpretation of Griffiths and Wheeler. These phenomena indicate that critical effect on the net rate of the hydrolysis reaction of 2-bromo-2-methylpropane may depend on the specific property of the critical mixture.

It should be pointed out that Shen and colleagues [28] recently repeated the experiment of the hydrolysis reaction of 2-bromo-2-methylpropane in the critical mixture of triethylamine + H_2O. However, a critical slowing down rather than a speeding up was observed both in one phase region and the two phase region. These disagreements were attributed to improper use of the background Arrhenius equation according to Shen. Obviously, the critical effect on the hydrolysis reaction rate of 2-bromo-2-methylpropane is controversial, even in the same critical mixture. We consider that the controversy needs more experimental and theoretical studies. For our critical mixture, the critical speeding up may be related to the specific property normal micelle (O/W). As mentioned above, the hydrolysis reaction of 2-bromo-2-methylpropane may take place at the outer interface of the O/W microemulsion structure. Near the critical point, the products of H^+ and Br^- may go into the continuous aqueous phase more easily due to the critical concentration fluctuation [29, 30], which will promote the equilibrium process in favor of the products side and accelerate the hydrolysis reaction. Although specific properties of the critical mixture of solid–solvent clustering mechanism [31] and aggregates of ionic compounds [32] have been used to explain the critical speeding up, up to now there is no satisfactory universal theory for critical speeding. In other words, the contrast between the theory of critical slowing down and the experimental observation of speeding-up still remains one of the central puzzles in understanding the kinetics of chemical reactions at the critical solution point.

4 Conclusion

We have extended the studies of the critical effect on the chemical reaction to more complicated O/W microemulsion media, which is seldom explored. Using the water titration method, we have constructed the pseudoternary phase diagram of surfynol465 + *n*-butanol + cyclohexane + H_2O with $k_m = 2$. Electrical conductivity measurements were employed to investigate the microstructures of the single-phase region. In the O/W microemulsion region, we have measured the rate of hydrolysis reaction of 2-bromo-2-methylpropane near and far away from the critical point. It was found that the hydrolysis reaction rate of 2-bromo-2-methylpropane speeded at temperatures near the critical point, which is not consistent with thermodynamic interpretation of Griffiths and Wheeler. Moreover, the experimental results were compared with those of the same reaction in different critical mixtures, which indicated the critical effect on the hydrolysis reaction rate of 2-bromo-2-methylpropane might depend on the specific property of the critical mixture.

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