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Kinetics of S_N1 Reactions in Binary Liquid Mixtures near the Critical Point of Solution

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We have measured the rates of the S_N1 hydrolysis reactions of 2-chloro-2-methylbutane in isobutyric acid + water and 2-bromo-2-methylpropane in trietylamine + water near their respective consolute points. In the former mixture, two phases coexist *below* the critical solution temperature, while in the latter, two phases coexist *above* the critical solution temperature. Because each hydrolysis reaction produced a strong electrolyte among its products, we could follow the progress of the reaction by making measurements of the conductance. To interpret these measurements properly, however, we had to take into account the following phenomena: (1) the effect of the composition on the critical temperature, (2) the effect of the liquid−liquid-phase transition when it occurred during the course of the run, and (3) the competition between the effects of temperature and the effects of concentration on the response of the conductance probe. With these phenomena accounted for, however, we found in the case of both reactions that the specific rate of hydrolysis slowed at temperatures above the critical solution temperature and accelerated at temperatures below it. From the point of view of thermodynamics, the causative factor in slowing down is the derivative of the reaction Gibbs free energy with respect to the extent of reaction, which goes to zero at the critical point. In contrast, speeding up has no ready theoretical explanation. The experimental results imply, nevertheless, that *speeding up is not confined to the two-phase side of the phase diagram.*

I. Introduction

The consolute point is an extremum in the temperature vs mole fraction phase diagram of a constant pressure, binary liquid mixture where the homogeneous solution first begins to separate into two immiscible layers. The extreme value of the temperature along the boundary separating the two immiscible liquids is called the critical solution temperature, T_c^o. A binary mixture having a liquid−liquid-phase boundary that is concave down is said to have an upper critical solution temperature (UCST), while a mixture having a liquid−liquid-phase boundary that is concave up is said to have a lower critical solution temperature (LCST).

Often, one or both of the components of a binary liquid mixture with a consolute point is an acid, a base, or a nucleophile. Upon introduction of a reactant or a catalyst, a chemical reaction can be initiated. This permits liquid mixtures to be used to study the effect of a critical point on the net rate of reaction.[1−5]

The relationship between the net rate of reaction and the Gibbs free energy can be derived most easily by considering a reversible elementary reaction written in the form

$$\nu_1(\mathbf{1}) + \nu_2(\mathbf{2}) \rightarrow \nu_3(\mathbf{3}) + \nu_4(\mathbf{4}) \qquad (1)$$

in which reactants **1** and **2** are converted into products **3** and **4**. The respective stoichiometric coefficients are ν_1, ν_2, ν_3, and ν_4. We let $c_i(0)$ be the initial concentration of species i. The concentration, $c_i(t)$, at a later time, t, is $c_i(t) = c_i(0) \pm \nu_i\xi(t)$, where $\xi = \xi(t)$ is the extent of reaction (or reaction progress variable), and the upper sign applies to products while the lower sign applies to reactants.

Using conductivity to follow the extent of reaction, Snyder and Eckert[1] examined the disappearance of ethyl iodide on the one phase side of the LCST of triethylamine + water and reported an apparent slowing down in the rate near the consolute point. In a separate experiment in which they exploited gas chromatography to follow the progress of the reaction, they reported an enhanced rate in the Diels−Alder addition of isoprene to maleic anhydride near the UCST of two solvent pairs, hexane + nitrobenzene and hexane + nitroethane. Subsequently, Becker and collaborators[2] studied the trifluoroacetic acid-catalyzed reaction of acetic anhydride + 1,2-ethanediol to form the 1,2-ester of ethanediol and acetic acid. Following the reaction by calorimetry, Becker et al. reported that near the consolute point, there was a decrease in the rate of heat evolution, which they associated with the slowing down in the rate of reaction of the solvent pair.

Using conductivity as a measure of the extent of reaction, we have recently observed slowing down in the net rates of five different hydrolysis reactions near the equilibrium consolute points of three water-based binary liquid mixtures.[3−5] The reactants and their respective binary solvents were 2-chloro-2-methylbutane (*tert*-amyl chloride) in isobutyric acid + water (UCST), 2-chloro-2-methylpropane (*tert*-butyl chloride) in isobutyric acid + water, 2-bromo-2-methylpropane (*tert*-butyl bromide) in triethylamine + water (LCST), 3-chloro-3-methylpentane in 2-butoxyethanol + water (LCST), and 4-methylbenzyl bromide in 2-butoxyethanol + water. These reactions have the common feature that they all proceed by the S_N1 mechanism.[6] We regard the slowing down that we have observed in the net rates of these reactions, to be a reflection of the *Principle of Universality* that is assumed to govern all critical phenomena.[7−9]

In the theory of critical phenomena, an analogy is drawn between the *liquid−liquid* phase boundary of a mixture in the region of its consolute point and the *liquid−vapor* coexistence curve of a pure fluid in the vicinity of its critical point.[7] On the basis of this analogy, pure liquids and liquid mixtures are said

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to be in the same *universality* class.[7-9] Certain of the thermodynamic derivatives for a pure fluid go to zero at the liquid–vapor critical point. The *Principle of Universality* asserts that the critical behavior of the thermodynamic derivatives for a pure fluid can be used to predict the critical behavior of the analogous thermodynamic derivatives of any other system in the same universality class.[7-9] In the case of the rate of a chemical reaction, the appropriate thermodynamic derivative is $(\partial\Delta G/\partial\xi)_e$, where ΔG is the Gibbs free energy difference between products and reactants, and the subscript "e" stands for chemical equilibrium.[10,11] In mixtures supporting a chemical reaction, ξ serves as the order parameter that distinguishes one thermodynamic state of the fluid from another. In our experiments, we have encountered four critical phenomena that depend on the value of ξ.

First, the equilibrium value of ξ, which we call ξ_e, determines the concentrations of the products and any S_N1 reactant that remains at the end of the reaction. These equilibrium concentrations in combination usually cause a noticeable shift in the critical temperature. As a consequence, it becomes necessary to draw a distinction between the critical solution temperature, T_c^o, of a binary mixture and the equilibrium critical solution temperature, T_c, of a multicomponent reaction mixture in which the binary system plays the role of the solvent.[3-5] We have observed experimentally that

$$T_c = T_c^o + ac \tag{2}$$

where a is an empirical coefficient, which has a different value for each mixture, and c is the initial molar concentration of the S_N1 reactant.[12] Although T_c is a function of ξ_e, it can be connected to the *initial* concentration of the reactant as in eq 2, because of the stoichiometric relation that links reactant and products, and because all of the reactions, which we have studied so far, go essentially to completion. In cases where the presence of the reactant and its reaction products at equilibrium *enhances* the mutual solubility of the original solvent pair, an UCST is lowered ($a < 0$) while an LCST is raised ($a > 0$). On the other hand, when the presence of reactant and products *inhibits* the mutual solubility of the original pair, the effect on the phase diagram is to raise an UCST and to lower a LCST.[13,14]

Second, the extent of reaction, ξ, has a time dependence that is governed by a rate law involving an apparent rate constant which is sensitive to the difference between the thermostat temperature, T, and the equilibrium critical solution temperature, T_c.[3-5] At time $t = 0$, when the mixture contains only reactant and solvent, we take the value of ξ to be zero. As the time advances, $\xi(t)$ increases and approaches ξ_e asymptotically. The time derivative, $d\xi/dt$, equals the net rate of the forward reaction over its reverse. From the point of view of nonequilibrium thermodynamics, the generalized force driving the net rate is the instantaneous Gibbs free energy difference, ΔG separating the product from the reactants.[15] Sufficiently close to chemical equilibrium, ΔG can be expanded in a Taylor series

$$\Delta G(\xi) = \Delta G(\xi_e) + (\partial\Delta G/\partial\xi)_e(\xi - \xi_e) \tag{3}$$

Because $\Delta G(\xi_e) = 0$, the rate law for an *arbitrary* reaction *sufficiently close to equilibrium* is first order in $\xi - \xi_e$, and the rate constant is proportional to the thermodynamic derivative, $(\partial\Delta G/\partial\xi)_e$.[4,5,15] When the thermostat temperature, T, lies close to the equilibrium critical solution temperature, T_c, the Griffiths–Wheeler rules,[7] which are the thermodynamic expression of the *Principle of Universality*, govern the behavior of $(\partial\Delta G/\partial\xi)_e$. These rules predict that this derivative should go to zero in the case of a homogeneous reaction that takes place in a mixture that contains no more than one inert component. A component is considered to be inert if its mass fraction in the reaction mixture at equilibrium has a constant value independent of temperature and pressure.[5] When $(\partial\Delta G/\partial\xi)_e$ vanishes, the net rate of reaction is expected to be substantially reduced. This phenomenon is called *critical slowing-down*.[10,11]

Third, because the *equilibrium* value of the critical solution temperature, T_c, depends on concentration, it is plausible that the *instantaneous* value of the critical solution temperature during the course of the reaction has a value that depends on $\xi(t)$.[12] This raises the possibility that any in situ probe used to determine concentration can have a response that reflects the time dependence of the difference between the thermostat temperature and the instantaneous critical temperature. This response of the probe may be separate from its response to concentration. Devices for the measurement of conductivity[12] and optical density[16] are cases in point. Such probes need to be calibrated in critical mixtures having a steady, known composition in order to make sure that they maintain a response that is proportional to concentration as the thermostat temperature nears the equilibrium critical temperature, T_c.

Fourth, when the thermostat temperature happens to lie between T_c^o and T_c, a liquid–liquid phase transition will occur in the mixture as $\xi(t)$ advances.[5,12] The elapsed time, t, after the start of a run when the phase separation appears, is revealed by a change in slope of $d\xi/dt$ as function of t. Because of this change in slope, any ξ vs t data collected before the phase separation occurs will fail to extrapolate to the equilibrium value of the extent of reaction, ξ_e. As equilibrium is the reference point[10,11] for application of the Griffiths–Wheeler rules,[7] we have ignored in a given kinetic run any data collected prior to the occurrence of the phase transition. According to eq 2, however, if we keep c small, it is possible to restrict the range of thermostat temperatures over which a phase transition will occur during the course of a reaction.[12]

Since our earliest reports,[3,4] we have discovered that by measuring the conductivity of a *strongly stirred* reaction mixture with a Hanna Instruments, Inc. model HI 9032 conductivity meter, the precision of the determination of the rate of an S_N1 reaction in the critical region can be improved.[12] This observation has led us to repeat our measurements of the rate of hydrolysis of 2-chloro-2-methylbutane in isobutyric acid + water (UCST), which was the first reaction examined by us to show the effects of the critical point.[3] Our most recent experiment with this mixture, which we analyze below, included 33 new measurements of the reaction rate in the critical region as well as a new determination of the equilibrium critical temperature.[12] These new measurements revealed reaction rate *slowing-down* at temperatures in the one-phase region above T_c and *speeding-up* at temperatures in the two-phase region below T_c.

In contrast to reaction rate slowing-down, which can be given a thermodynamic interpretation,[4,5,15] speeding-up currently has no certain explanation. This difficulty has led us to pose the following question: Does speeding-up, which we have observed in the rate of hydrolysis of 2-chloro-2-methylbutane in isobutyric acid + water (UCST) at *T less than* T_c, occur because of the relationship between the two temperatures or simply because the mixture consists of two phases?

To answer this question, we report herein the results of new measurements of the rate of hydrolysis of 2-bromo-2-methylpropane at the consolute point of triethylamine + water, where by contrast because there is an LCST, the two liquid phases coexist when T is *greater than* T_c. In section II below, we describe the application of the Griffiths−Wheeler[7] rules that govern the critical behavior of thermodynamic derivatives. In section III, we provide the details of our experiments. As an extension of our previous work, we address special attention to the response of the conductivity probe to the instantaneous critical temperature. In section IV, we discuss our experimental observations and draw our conclusions.

II. Theory

If the reaction in eq 1 is elementary, then the net rate of reaction, $d\xi/dt$, is given by

$$\frac{d\xi}{dt} = \frac{\kappa'}{y_*} a_1^{\nu_1} a_2^{\nu_2} - \frac{\kappa''}{y_*} a_3^{\nu_3} a_4^{\nu_4} \qquad (4)$$

where a_i ($i = 1, 2,3,4$) are the instantaneous thermodynamic activities of the reacting species, $y_*$is the activity coefficient of the transition state, and κ' and κ'' are the rate coefficients in the case of a dilute ideal solution for reaction in the forward and reverse directions, respectively.[4,15,17] At chemical equilibrium, $d\xi/dt = 0$, and the activities assume their equilibrium values, $a_i{}^e$. Setting the right-hand side of eq 4 to zero, we obtain

$$K = \frac{(a_3{}^e)^{\nu_3}(a_4{}^e)^{\nu_4}}{(a_1{}^e)^{\nu_3}(a_2{}^e)^{\nu_2}} = \exp(-\Delta G°/RT) = \frac{\kappa'}{\kappa''} \qquad (5)$$

where R is the gas law constant, T is the absolute temperature, and we have introduced the usual relation, $\Delta G° = - RT(\ln K)$, between the equilibrium constant, K, and the standard Gibbs free energy difference, $\Delta G°$, separating products from reactants. Away from equilibrium, the instantaneous Gibbs free energy difference, ΔG, is

$$\Delta G = \Delta G° + RT \ln \frac{a_3^{\nu_3}\ a_4^{\nu_4}}{a_1^{\nu_1}\ a_2^{\nu_2}} \qquad (6)$$

We next factor out the first term on the right-hand side of eq 4 to obtain

$$\frac{d\xi}{dt} = \frac{\kappa' a_1^{\nu_1} a_2^{\nu_2}}{y_*}\left[1 - \frac{\kappa''}{\kappa'}\frac{a_3^{\nu_3}\ a_4^{\nu_4}}{a_1^{\nu_1}\ a_2^{\nu_2}}\right] \qquad (7)$$

Using eqs 5 and 6, the right-hand of eq 7 becomes

$$\frac{d\xi}{dt} = \frac{\kappa' a_1^{\nu_1} a_2^{\nu_2}}{y_*}[1 - \exp(\Delta G/RT)] \qquad (8)$$

Note that when $\Delta G < 0$, the reaction is thermodynamically permitted, $d\xi/dt$ is positive, and the net reaction is in the forward direction, while when $\Delta G > 0$, the reaction is thermodynamically forbidden, $d\xi/dt$ is negative, and the net reaction is in the reverse direction. The factor

$$r' = \kappa' a_1^{\nu_1} a_2^{\nu_2}/y_* \qquad (9)$$

that multiplies the bracket in eq 8 is the rate of reaction in the forward direction.

The forward rate depends implicitly upon ξ and can be expanded in a Taylor series about ξ_e

$$r'(\xi) = r'(\xi_e) + \left(\frac{\partial r'}{\partial \xi}\right)_e (\xi - \xi_e) \qquad (10)$$

in analogy with eq 3. For a reaction which is kinetically first order in the forward direction, we set $\nu_1 = 1$ and $\nu_2 = 0$, and substitute eqs 3, 9, and 10 into eq 8. After noting that $\Delta G(\xi_e) = 0$ and collecting terms of first order in $(\xi - \xi_e)$, eq 8 becomes

$$\frac{d\xi}{dt} = -\frac{1}{\tau}(\xi - \xi_e) \qquad (11)$$

where

$$\frac{1}{\tau} = \frac{r'(\xi_e)}{RT}\left(\frac{\partial \Delta G}{\partial \xi}\right)_e \qquad (12)$$

and

$$r'(\xi_e) = \frac{\kappa' a_1(\xi_e)}{y_*(\xi_e)} \qquad (13)$$

For the case of a *reversible* reaction in which the kinetics are *first order* in both directions, the coefficients of terms of order $(\xi - \xi_e)^2$ and higher are zero in ideal solution where the activity coefficients are unity and independent of ξ. Equation 11 is then an exact expression for the net rate of reaction. Equation 11 also serves as an approximate rate expression for S_N1 reactions which are also *essentially irreversible*.[5] Since the reaction rate in the reverse direction is small in the case of an essentially irreversible reaction, $r'(\xi_e)$ must also be small in order to make the forward and reverse rates equal at equilibrium.

The Griffiths−Wheeler rules,[7] which govern the universal behavior of the thermodynamic derivatives near critical points, can be used to study the critical properties of the specific rate, $1/\tau$. According to Griffiths and Wheeler, the analysis should begin with a separation of the thermodynamic variables into two classes, *fields* and *densities.* A field is variable which at equilibrium has the same value in each coexisting phase. In liquid mixtures, the relevant fields are the temperature, the pressure and the chemical potential of each chemical component. A *density* is any variable that has different values in coexisting phases. Examples include entropy, enthalpy, and concentration variables such as mole fractions or mass fractions. Thus, ΔG is a field, because it is a linear combination of chemical potentials, while ξ is a density, because it is a concentration.

In the space of variables that includes only fields, the phase diagrams of pure fluids and binary liquid mixtures become analogous. Basing their arguments on this and other analogies involving phase transitions, Griffiths and Wheeler[7] concluded that, if the fixed variables in an experiment consisted of fields and no more than one density, then the derivative of a field with respect to a density, such as $(\partial\Delta G/\partial\xi)_e$, should go to zero as the power law, $|T - T_c|^x$, as T approaches T_c. The general order of magnitude of the exponent, x, depends on whether the number of densities held fixed is zero or one. In the case where no densities are held fixed, the value of x is expected to be of order unity, and the derivative is said to go to zero "strongly."[7] When one density is fixed, the value of x is expected to be of the order of $^1/_{10}$, and the derivative is said to go to zero "weakly."[7] In both cases, the exact value of x depends on the direction of approach to the critical point. When two or more densities are fixed, the value of the derivative is nonspecific. Because chemical reactions conserve mass, it is helpful to choose the mass fractions as the concentration variables when enumerating the densities. The principle of conservation of mass then makes it easy to determine which, if any, of the mass fractions are held fixed during the course of a reaction.[5] In a liquid-phase experiment, a density variable is considered to have a fixed value if that value is a constant independent of

TABLE 1: Solvents and Reactants[a]

solvent	wt(%), T_c^o(°C)	type	reactant	reactant/solvent volumes	a (°C/M)	T_c (°C)
isobutyric acid + water	38.8, 26.129	UCST	2-chloro-2-methylbutane	7.75 μL/125 mL	380	26.28
triethylamine + water	32.27, 17.93	LCST	2-bromo-2 methylpropane	7.0 μL/150 mL	−8.77	17.9

[a] The first column lists the components of the solvent mixture. The second column lists the consolute composition in terms of the weight percent of the nonaqueous component and gives the critical solution temperature, T_c^o, of the mixture before addition of the reactant. The third column indicates whether T_c^o is an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST). The fourth column identifies the reactant. The fifth column lists the volumes of reactant and solvent, respectively, employed to make up the reaction mixture. The sixth column gives the value of the constant, a, in eq 2, while the last column lists the value of the critical solution temperature, T_c, at reaction equilibrium.

temperature and pressure. For practical purposes, this assertion implies that in a liquid mixture consisting of a binary solvent, reactants, products, and catalysts, which are participating in a homogeneous chemical reaction, there can be no more than one component that is inert in the sense of not being included in any chemical equilibrium.

If one of the reactants or products is ionic, the progress of the reaction with time can be followed by measuring the conductance. The instantaneous value of the conductance, L, is given by

$$L = L^o + (L^e - L^o)(\xi/\xi_e) \qquad (14)$$

where L^o is the initial value, and L^e is the value at equilibrium.[5] Equation 14 is the basic expression for the conductance of reacting mixtures.

For the initial condition, $\xi = 0$ at $t = 0$, the integral of eq 11 is

$$\xi = \xi_e(1 - \exp(-t/\tau)) \qquad (15)$$

If we substitute this into eq 14, we obtain

$$L = L^o + (L^e - L^o)(1 - \exp(-t/\tau)) \qquad (16)$$

Equation 16 can be used to follow the course of an S_N1 reaction that involves a strong electrolyte as a product.

In the Experimental Section below, we explain how the above theory applies to the rates of each of the S_N1 reactions that we describe. In both cases, the progress of the reaction was followed by the conductance method.

III. Experimental Section

All reactants and organic solvents were purchased from Aldrich and used as received. Water was once distilled from a glass system. Table 1 summarizes the composition and the consolute point properties of the reaction mixtures. Column 2 of that table lists the critical composition and critical temperature, $T_c°$, for the binary mixtures, isobutyric acid + water,[18] and triethylamine + water.[19] In accord with eq 2, the critical temperature determined after addition of a small amount of the reactant and the establishment of chemical equilibrium was a linear function of the reactant concentration.[5,12,13] The appropriate value of the slope, a, is listed in column 6 of the table. Because the same concentration of reactant was used to start each run, however, the value of T_c listed in column 7 for each mixture at reaction equilibrium was a constant. In the case of each mixture, since the reaction went essentially to completion, the difference between $T_c°$ and T_c was due largely to the presence of the products.

The thermostat bath, temperature controller, the reaction cell, and the temperature measuring equipment were as previously described.[3−5] The reaction mixtures were well mixed with a magnetically driven stirring bar. Because a strong electrolyte was among the reaction products, the progress of the reaction could be followed by measuring the electrical conductance using a Hanna Instruments model HI 9032 microcomputer controlled conductivity meter. We found this device to be more convenient for recording data and also to have superior accuracy than the Radiometer CDM 83 meter, which we have used previously.[3,4] We now describe the experimental details that were peculiar to each of the reactions studied.

(1) Hydrolysis of 2-Chloro-2-methylbutane in Isobutyric Acid + Water. This reaction mixture, whose properties are summarized in the first line of Table 1, consisted of 7.75 μL of 2-chloro-2-methylbutane added to 125 mL of isobutyric acid + water at its critical composition. The overall stoichiometry of the reaction is

$$C_2H_5(CH_3)_2CCl + HOH \rightarrow C_2H_5(CH_3)_2COH + HCl \qquad (17)$$

Because the reaction mechanism is S_N1, the time dependence of L satisfied eq 16. The apparent first-order rate constant for this irreversible reaction is $1/\tau$. The software of the Hanna meter recorded the difference, $L - L^o$; hence, eq 16 was fitted to the data from each run with $L^e - L^o$ and $1/\tau$ taken as adjustable parameters.[12]

The critical temperature of our solvent mixture of isobutyric acid + water was $T_c^o = 26.129$ °C. The equilibration of the 2-chloro-2-methylbutane in this mixture decreased the mutual solubility of isobutyric acid + water and increased the critical temperature to $T_c = 26.28$ °C. In a few of our kinetic runs, the thermostat temperature was bracketed by the two critical temperatures, as $T_c^o < T < T_c$. In such case, the mixture crossed from the one-phase region into the two-phase region during the course of the run. As is illustrated in Figure 1, the occurrence of this phase transition could be detected by its effect on the curvature of a plot of the time dependence of $L - L^o$.[12] In the figure, the phase separation makes its appearance approximately 6 min into the run. In all such cases, we used only the $L - L^o$ data collected *after* to the appearance of the phase transition to determine the value of $1/\tau$, because only these data converged at long times to the actual equilibrium conductance value, L^e.

When a reaction mixture, which had reached chemical equilibrium, was subsequently warmed (or cooled) through the suspected critical region, direct measurements of the residual conductance, L^e, displayed a sharp minimum as a function of T. Opalescence could be observed in the liquid at this conductivity minimum, which demonstrated that the temperature of the minimum coincided with T_c. This minimum has its origin, we believe, in the conductivity critical slowing down phenomenon that has been reported in binary mixtures.[20,21] This effect can be amplified by the addition of small amounts of strong electrolyte.[20] If given sufficient time, a meniscus could be seen to form in the center of the cell. The position of the meniscus in the center indicated that the volumes of the coexisting liquid phases were equal and sufficed as a third means of establishing T_c. The volumes of the coexisting liquid phases further served

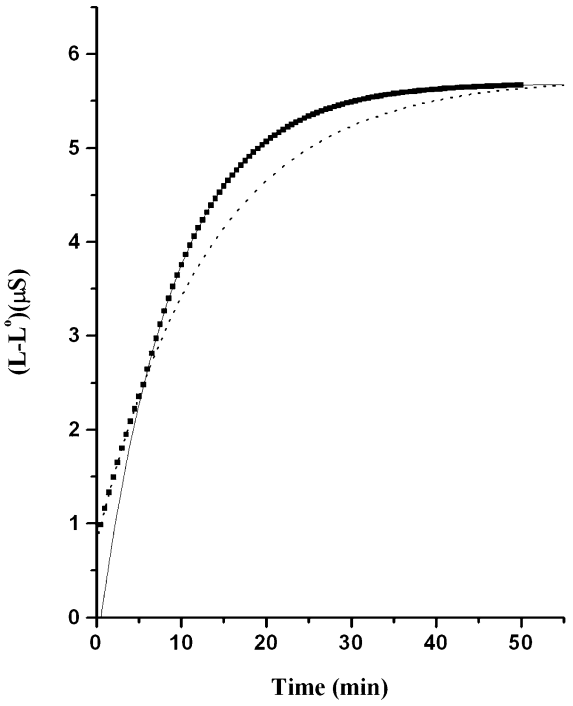

Figure 1. Conductance, $L - L^o$, is a function of time, t, for the hydrolysis of 2-chloro-2-methylbutane in 38.8 wt % isobutyric acid + water in a case where $T_c^o < T < T_c$.

to demonstrate that the reaction products were so dilute as to have no measurable effect on the critical composition[23,24] of the mixture.

When T was close enough to T_c, the possibility existed that conductivity critical slowing down might distort the concentration response of our probe during the course of a kinetics run. We studied this effect by measuring the temperature dependence of the conductance of a series of critical mixtures of isobutyric acid + water containing increasing concentrations of hydrochloric acid.[12] The results of these measurements are summarized in Figure 2. At each HCl concentration in the figure, the conductance passed through a minimum as a function of temperature. The minimum we identified with the critical temperature, which itself increased with additions of HCl. The vertical dashed line on the *left* in the figure represents an isotherm. To use this figure to understand the effect of conductivity slowing down during the course of a kinetics run, we imagine the temperature of the thermostat fixed at the temperature of this isotherm. As the hydrolysis run proceeds, the concentration of HCl increases with time. Following the progress of the reaction, the conductance measurements will pass along the isotherm from bottom to top in the figure. Each successive intersection of the isotherm with a conductance vs T curve represents a separate measurement of the conductance during the course of the run. To be useful as a measure of the extent of reaction, the conductance values measured at these intersections should remain proportional to the HCl concentration. Figure 3 demonstrates that the required linear relationship does exist. Indeed, we have noted that in well stirred mixtures, conductance measurements remain proportional to concentration along isotherms on either side of the critical temperature.

We point out that Figure 2 can also be used to illustrate the mechanism behind the change in slope shown by the curve in Figure 1. The vertical dashed line on the *right* in Figure 2 represents an isotherm at a temperature that is initially above T_C^o. As the kinetics run passes along this isotherm from bottom to top, the intersections with the conductance vs T curves occur first to the right of the critical minimum and then to the left. Between, a phase transition occurs, which affects the rate of hydrolysis, as is illustrated by the change in slope in Figure 1.

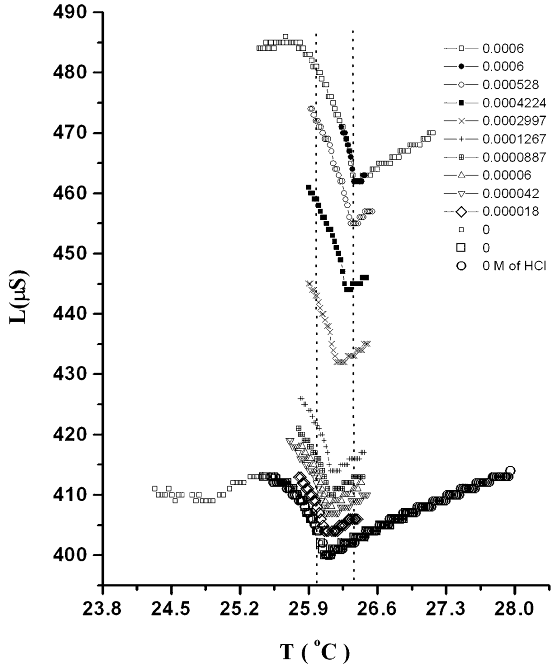

Figure 2. Conductance of 38.8 wt % isobutyric acid + water with added molar concentrations of hydrochloric acid. The Celsius temperature of the mixture is T. The minimum in each curve, which occurs at the critical solution temperature is due to the conductivity slowing down effect. The dashed line at the left of the figure represents an isotherm below the UCST of the mixture. Intersections of this isotherm with the conductance vs T curves correspond to conductance values in the well-stirred two-phase mixture. The isotherm on the right corresponds to a temperature which is above the UCST for low values of the HCl concentration and below the UCST for high values of the HCl concentration.

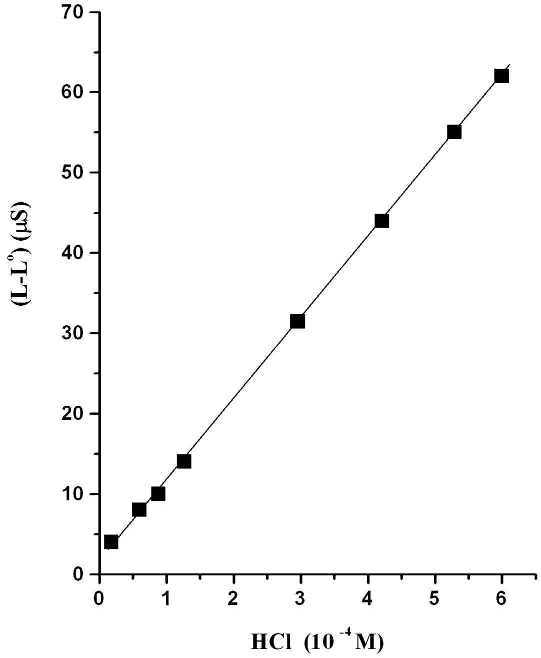

Figure 3. Conductance as a function of HCl concentration along the left-hand isotherm in Figure 2.

In Table 2, we have summarized our measurements of the relaxation rate, $1/\tau$, as a function of the Celsius temperature for the reaction in eq 17. Figure 4 is an Arrhenius plot of the

TABLE 2: Specific Relaxation Rate, 1/*τ*, vs Temperature for the Hydrolysis of 2-Chloro-2-methylbutane in Isobutyric Acid + Water[a]

temp (°C)	1/ τ (min^{-1})	temp (°C)	1/τ (min^{-1})
25.19	0.02264	26.35	0.0256
25.35	0.02392	26.36	0.02593
25.42	0.02355	26.41	0.02546
25.45	0.02366	26.45	0.02576
25.56	0.02443	26.47	0.02734
25.62	0.02516	26.52	0.02701
25.65	0.02499	26.53	0.02827
25.74	0.02518	26.58	0.02743
25.75	0.02492	26.58	0.02714
25.81	0.02558	26.59	0.02811
25.83	0.0258	26.60	0.02799
25.87	0.02586	26.62	0.02815
25.87	0.02662	26.65	0.02817
25.90	0.02625	26.68	0.02831
25.91	0.02758	26.75	0.02885
25.92	0.02756	26.86	0.02945
26.00	0.02736	26.93	0.02958
26.00	0.02803	27.13	0.03103
26.01	0.02762	27.28	0.03181
26.08	0.02811	27.41	0.03202
26.10	0.02846	27.56	0.03342
26.12	0.02862	27.76	0.03386
26.17	0.02868	27.93	0.03517
26.19	0.02822	28.15	0.03572
26.19	0.02854	28.31	0.03686
26.26	0.02748	28.50	0.03762
26.26	0.02662	28.66	0.03929
26.30	0.02679	28.84	0.04005
26.33	0.02609	29.02	0.04162

[a] The equilibrium critical temperature was $T_c = 26.28$ °C.

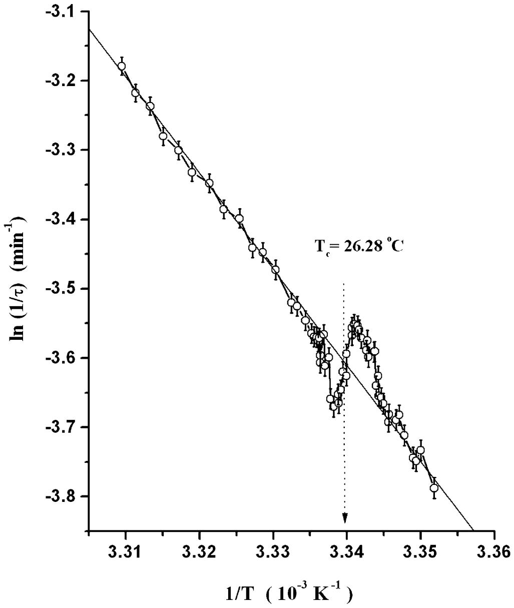

Figure 4. Arrhenius plot of the specific rate, $1/\tau$, for hydrolysis of 7.75 μL of 2-chloro-2-methylbutane in 125 mL of isobutyric acid + water at the consolute composition. The thermostat temperature is T and the equilibrium critical solution temperature is T_c.

temperature dependence of $1/\tau$. The straight line is given by the equation

$$\ln(1/\tau) = 42.2 - 114045/RT \tag{18}$$

which was computed by fitting data obtained in the one-phase region of the mixture at temperatures far above T_c. The units of τ are min, R is the universal gas constant, T is the absolute temperature, while the units of the coefficient of $1/RT$ are J/mol. The constant term on the right in eq 18 had a standard deviation of ± 1.2, while the activation energy had a standard deviation of ±3109 J/mol. Being fitted to 12 points above the critical region, eq 18 forms the "background" against which the size of the critical effect can be judged. Upon comparing the 33 measured values of ln($1/\tau$) in the critical region of the figure with this line, it is apparent that the specific rate of reaction *slows down* in the one-phase region above T_c and *speeds up* in the two-phase region below T_c.

The *slowing down* effect can be given a thermodynamic interpretation. In the S_N1 hydrolysis of an alkylhalide, RX, the first step in the mechanism involves the ionization of RX to form the carbocation, R^+, and the halide ion, X^-.[6] This rate-controlling step is followed by the rapid reaction between the carbocation and water to form the alcohol, ROH, and the strong acid, HX. We have shown that the relaxation rate for an S_N1 reaction is given by eqs 11 and 12 with $r'(\xi_e)$ being interpreted as the rate of formation of the carbocation at equilibrium.[4] As explained in the theory section above, the behavior of the derivative, $(\partial\Delta G/\partial\xi)_e$ as T approaches T_c, depends on the nature of the thermodynamic variables held fixed during the course of the reaction.[25-27] For a reaction in a thermostat open to the atmosphere, two of these are presumably the temperature, T, and the pressure, P. As composition variables describing the reaction, we take the mass fractions, w_{HA}, w_{HOH}, w_{RCl}, w_{ROH}, and w_{HCl} where HA is isobutyric acid, RCl is 2-chloro-2-methylbutane, and ROH is the corresponding alcohol. If we can assume that isobutyric acid is inert, then w_{HA}, T, and P are held fixed. Because of the chemical reaction connecting them, the mass fractions of RCl, HOH, ROH, and HCl depend on T, P, and, possibly, also w_{HA}. With one composition variable, w_{HA}, held fixed, $(\partial\Delta G/\partial\xi)_e$ should go to zero "weakly."

On the other hand, isobutyric acid is known to react with alcohols in acid solution to form esters.[28] This side reaction would introduce the mass fraction of the ester as a new composition variable and would at equilibrium make both this variable and the mass fraction of isobutyric acid a function of T and P. In such case, no composition variable would be held fixed. The derivative $(\partial\Delta G/\partial\xi)_e$ would then go to zero "strongly," and we should expect "slowing-down" in the rate of hydrolysis as $T \rightarrow T_c$.

The combination of "slowing-down" and "speeding-up" disposed symmetrically about T_c, as shown in Figure 4, would seem to be inconsistent with a temperature dependence of the form $|T - T_c|^x$. Nonetheless, we believe that we have observed "slowing-down" as otherwise predicted, at least for $T > T_c$.

(2) Hydrolysis of 2-Bromo-2-methylpropane in Triethylamine + Water. Since, as reported above, we have observed "speeding-up" in the rate of hydrolysis of 2-chloro-2-methylbutane in isobutyric acid + water (UCST) in the two-phase region, where $T < T_c$, we searched for a reaction mixture which might be used to ascertain whether this effect could be demonstrated when $T > T_c$. Any S_N1 reaction in a binary solvent with a LCST (a single phase below T_c and two phases above T_c) could presumably serve as an adequate test. We selected 2-bromo-2-methylpropane, which we found to react at a convenient rate in triethylamine + water (LCST). The overall stoichiometry of this hydrolysis reaction is

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr \tag{19}$$

In contrast to 2-chloro-2-methylbutane in isobutyric acid + water, where the value of T_c was determined by eq 2 with $a > 0$, the value of a in the case of 2-bromo-2-methylpropane in triethylamine + water had the opposite sign.

TABLE 3: Specific Relaxation Rate, 1/τ, vs Temperature for the Hydrolysis of 2-Bromo-2-methylpropane in Triethyamine + Water[a]

temp (°C)	1/τ (min^{-1})	temp (°C)	1/τ (min^{-1})
17.68	0.04244	18.17	0.04897
17.73	0.04327	18.20	0.04757
17.77	0.04465	18.21	0.04858
17.83	0.04388	18.23	0.05017
17.90	0.04195	18.27	0.05275
17.92	0.03854	18.31	0.05166
17.94	0.03758	18.32	0.05375
17.96	0.04107	18.39	0.05481
17.97	0.03924	18.59	0.05896
17.98	0.04001	18.62	0.06152
18.00	0.04326	18.71	0.06293
18.02	0.04144	18.84	0.06757
18.05	0.04334	18.91	0.06945
18.06	0.04376	18.99	0.07214
18.07	0.04453	19.02	0.07448
18.10	0.04517	19.13	0.07698
18.11	0.04801	19.21	0.08021
18.14	0.04718		

[a] The equilibrium critical temperature was $T_c = 17.90$ °C.

The reaction mixture, whose properties are summarized in Table 1, consisted of 7 μL of 2-bromo-2-methylpropane dissolved in 150 mL of triethylamine + water at its critical composition. Observing all the precautions discussed above concerning the response of the probe to phase transitions and the effect of conductivity "slowing down," we followed the progress of this first-order reaction using the conductance method. The conductance measurements were fitted to eq 16 in order to determine the value of 1/τ. Also using the conductance method, the critical temperature of the reaction mixture at chemical equilibrium was found to be $T_c = 17.9$ °C. The effect of the dissolution of the reaction products was to decrease the miscibility of isobutyric acid + water and lower the critical solution temperature. Because the mixture was so dilute in 2-bromo-2-methylpropane, the value of T_c was only slightly lower than the critical temperature, $T_c° = 17.93$ °C, of the binary mixture. Again, the meniscus appeared in the center of the cell.

Table 3 lists the measurements of 1/τ vs the Celsius temperature for the reaction in eq 19. In Figure 5, we show an Arrhenius plot of the temperature dependence of 1/τ. The two-phase region corresponds to $T > T_c$, while the one-phase region corresponds to $T < T_c$. The straight line is given by the equation

$$\ln(1/\tau) = 130 - 321477/RT \tag{20}$$

The units of τ are min. The constant term on the right in eq 20 has a standard deviation of ±−3.2, while the activation energy has a standard deviation of ±7865 J/mol. The data in the figure show "slowing-down" for $T > T_c$ and "speeding up" for $T < T_c$. In this regard, the temperature dependence of 1/τ is the same as that seen in the hydrolysis of 2-chloro-2-methylbutane + water, which has an UCST. This observation thus suggests that in critical mixtures, reaction rate "slowing-down" occurs when $T > T_c$, while "speeding-up" occurs when $T < T_c$, regardless of the number of phases coexisting.

Before enumerating the fixed densities and analyzing this experiment according to the Griffiths−Wheeler rules,[7] we should first note that triethylamine is not inert with respect to 2-bromo-2-methylpropane. The two can combine by way of a Menschutkin reaction[1] to form the quatenary ammonium bromide. Since the concentration of triethylamine is in vast excess over the concentration of 2-bromo-2-methylpropane in our mixture, however, the kinetics of their mutual Menschutkin reaction should be pseudo first order in the concentration of 2-bromo-2-methylpropane. Consequently, since both solvent components combine with the reactant via first order kinetics, the overall kinetics should also be first order. Since there are no chemically inert substances in the mixture, the rules of Griffiths and Wheeler[7] predict that the net rates of both the hydrolysis and Menschutkin reactions should decrease near the critical point. This is consistent with what we report in Figure 5 for at least for $T > T_c$.

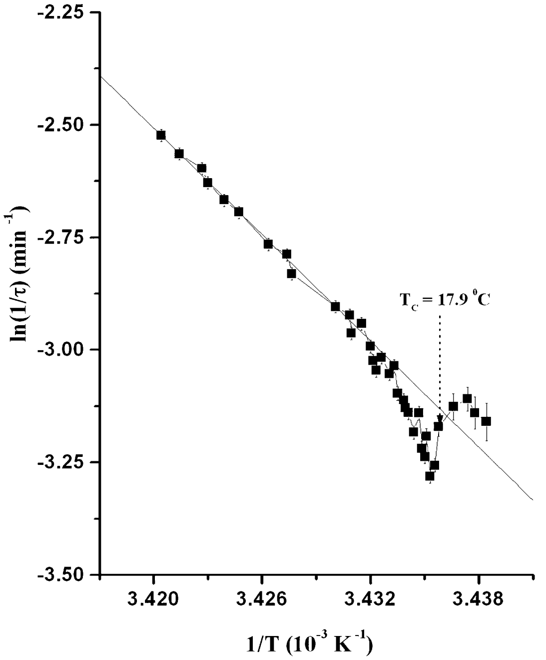

Figure 5. Arrhenius plot of the specific rate, 1/τ, for hydrolysis of 7.0 μL of 2-bromo-2-methylpropane in 150 mL of triethylamine + water at the consolute composition. The thermostat temperature is T and the equilibrium critical solution temperature is T_c.

IV. Discussion and Conclusions

The experiments described above illustrate the role of the extent of reaction, in specifying the critical properties of reacting mixtures. The determination of ξ necessarily rests on a chemical or physical measurement of the concentration of some one species that takes part in the reaction. In the case of a chemically reacting mixture near its critical point, an in situ measuring device may, as we have pointed out, suffer a response to the critical temperature that is separate from its response to the concentration of the reacting species. A case in point was analyzed by Morrison.[16] He has criticized the use of optical density measurements to detect the position of equilibrium in the dimerization of NO_2 to form N_2O_4 at the liquid−vapor critical point of carbon dioxide.[29] Morrison concluded that most of the decrease in transmitted light intensity observed when T was near T_c in these experiments was due not to the formation of colored NO_2 but rather to the critical opalescence in the fluid. In another case, the time dependence of the critical temperature was used to follow the rate of recombination of photodissociated chlorine atoms in supercritical Cl_2.[30] In subsequent work, Greer[31] showed that the use of thermal conductivity as a measure of concentration in this experiment suffered from a critical slowing down response near the liquid−vapor critical point that was independent of the extent of reaction. She concluded that the critical effects observed in her measurements of the atomic recombination rate were due to the slowing-down of the conductivity as opposed to the slowing-down of the recombination rate.

The competition between the response of a probe to $T - T_c$ per se and its separate response to concentration need not always invalidate the use of in situ probes in chemical reaction studies, however. In addition to our own work described above, we cite the measurements of dielectric constant that were used to determine the position of equilibrium in the dimerization of NO_2 at the UCST of perfluoromethylcyclohexane + carbon tetrachloride.[32] The dielectric constant depends on the number average molecular polarizability. As in the case of our conductance measurements, the response of this probe remained proportional to concentration even as the difference, $T - T_c$, changed.

We believe, nevertheless, that where possible, the simplest way to cope with competing critical effects may be to avoid the use of in situ probes, altogether. In the case of sufficiently slow reactions, where only one phase is present in the reaction mixture, it is feasible to extract representative aliquots from the well-stirred fluid near T_c. By rapid dilution or a temperature change, the reaction can be stopped in the aliquot and the mixture can be shifted to a noncritical condition, where standard methods of analytical chemistry can be reliably performed without concern for competing effects.

We now return to the question posed in the Introduction and give its answer: *Does speeding-up depend on the coexistence of two phases?* On the basis of our experiments, which are limited to S_N1 reactions, the answer would seem to be no, because speeding-up was observed in the two-phase region in the case of the hydrolysis of 2-chloro-2-methylbutane in isobutyric acid + water, while it was observed in the one-phase region in the case of the hydrolysis of 2-bromo-2-methylpropane in triethylamine + water.

The analysis of critical slowing down, which we have presented in the theory section, assumes that the kinetics are homogeneous.[4,5,10,11,33] The net rate of a first-order reaction in such case is determined by the first derivative of the Gibbs free energy with respect to ξ.

The assumption of homogeneous kinetics[4,5,33] has been challenged by Milner and Martin.[34] Their ideas have been reviewed by Greer.[35] Milner and Martin have stressed that spatial variations in composition near the critical point link sound propagation, thermal diffusion, and concentration diffusion to the rate of chemical reaction. They represent this coupling using the equations of linearized hydrodynamics.[36] Because these equations include both space and time derivatives, the kinetics can be said to be inhomogeneous. After noting that the longitudinal sound mode and the two transverse sound modes must decay rapidly on the time scale of most chemically reacting systems, they reduce the problem to the solution of a pair of partial differential equations, which couple thermal diffusion, concentration diffusion, and chemical reaction. Milner and Martin solve their equations in terms of spatial normal modes. Each normal mode is associated with two time decay constants. Which of the normal modes is encountered in practice depends on the boundary values and the initial conditions satisfied by the entropy and the extent of reaction. As in the theory of homogeneous kinetics, which we have described in the theory section above, thermodynamic derivatives appear. The behavior of these derivatives can be determined by applying the rules of Griffiths and Wheeler.[7] Although Milner and Martin analyze in detail only a binary fluid with an isomerization reaction connecting the two components, their conclusions appear to be general, so we apply them to our multicomponent reacting mixture.

In analyzing our experiments from the point of view of Milner and Martin,[34] we shall confine our attention to the case where there are no inert components. This is the criterion for “strong” slowing-down. According to Milner and Martin, the values assumed by the two decay constants fall into two regimes of behavior depending upon the wavelength of the normal mode. Regime I consists of normal modes of long wavelength. In this regime, the two decay constants (in our notation) are proportional to $(\partial T/\partial S)_{\Delta G}$ and $(\partial \Delta G/\partial \xi)_S$, respectively. Since ΔG is a field, while the entropy, S, and the extent of reaction, ξ, are densities, both of these derivative should go to zero as $T \rightarrow T_c$. Regime II consists of normal modes of short wavelength. In this regime, the decay constants are proportional to $(\partial \Delta G/\partial \xi)_T$ and $(\partial T/\partial S)_\xi$, respectively. Both of these derivatives should go to zero as $T \rightarrow T_c$.

Thus in both wavelength regimes, the theory of inhomogeneous kinetics as proposed by Milner and Martin[34] predicts a slowing-down in the net rate of reaction when the mixture contains no inert components. In this respect, the predictions of homogeneous kinetics[4,5,10,11,33] and inhomogeneous kinetics[34] are the same. Nevertheless, we have observed both slowing-down and speeding-up in the reaction rates in the critical region for the mixtures, 2-chloro-2-methylbutane in isobutyric acid + water, 2-bromo-2-methylpropane in triethylamine + water, both of which contain no inert components. Speeding-up has also been reported in the case of ethyl iodide in triethylamine + water, another reaction mixture that contains no inert components.[1] There has been a report of the experimental observation of speeding-up in the rate of dielectric relaxation in the nonreacting mixture, ethanol + dodecane near its consolute point.[37] This is in contrast to measurements of diffusion[38,39] and Newtonian viscous flow[39] in nonreacting mixtures which exhibit only slowing down. In addition, there have been reports of calculations[40,41] predicting an enhancement in the rate of thermal relaxation in pure fluids near the liquid−vapor critical point. Nevertheless, 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 point of solution.

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