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Reaction Kinetics and Critical Phenomena: Iodination of Acetone in Isobutyric Acid + Water near the Consolute Point

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The rate of iodination of acetone has been measured as a function of temperature in the binary solvent isobutyric acid (IBA) + water near the upper consolute point. The reaction mixture was prepared by the addition of acetone, iodine, and potassium iodide to IBA + water at its critical composition of 38.8 mass % IBA. The value of the critical temperature determined immediately after mixing was 25.43 °C. Aliquots were extracted from the mixture at regular intervals in order to follow the time course of the reaction. After dilution of the aliquot with water to quench the reaction, the concentration of triiodide ion was determined by the measurement of the optical density at a wavelength of 565 nm. These measurements showed that the kinetics were zeroth order. When at the end of 24 h the reaction had come to equilibrium, the critical temperature was determined again and found to be 24.83 °C. An Arrhenius plot of the temperature dependence of the observed rate constant, k_{obs}, was linear over the temperature range 27.00−38.00 °C, but between 25.43 and 27.00 °C, the values of k_{obs} fell below the extrapolation of the Arrhenius line. This behavior is evidence in support of *critical slowing down*. Our experimental method and results are significant in three ways: (1) In contrast to in situ measurements of optical density, the determination of the optical density of diluted aliquots avoided any interference from critical opalescence. (2) The measured reaction rate exhibited critical slowing down. (3) The rate law was pseudo zeroth order both inside and outside the critical region, indicating that the reaction mechanism was unaffected by the presence of the critical point.

1. Introduction

For the case of a binary liquid mixture with a miscibility gap, the opposite sides of the coexistence curve in the temperature versus mole fraction phase diagram converge at the consolute point.[1] The temperature at the point of convergence is called the critical solution temperature. If the coexistence curve is concave *down*, the critical temperature is an *upper* critical solution temperature (UCST), while if it is concave *up*, the critical temperature is a *lower* critical solution temperature (LCST). The consolute point can be determined visually by observing the disappearance of the meniscus which separates the two liquid phases that correspond to the opposite sides of the coexistence curve.

The consolute point is a member of a class of critical points where certain analogous thermodynamic properties tend either to zero or to infinity as the temperature approaches the critical temperature.[2,3] This isomorphic behavior at critical points is predicted by the *principle of critical point universality*[2,4,5] and has been observed experimentally in phenomena as diverse as the liquid−vapor transition of pure liquids,[6−11] the Curie point transition in ferromagnetic materials,[6,7] the lambda line of liquid helium,[7] the normal conducting to superconducting transition in superconductors,[7] and the liquid−liquid transition in liquid mixtures.[2,3,8,11]

To determine the critical properties of a reaction taking place in a binary liquid mixture, we start by specifying the stoichiometry,

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D \tag{1}$$

which permits the Gibbs free energy of reaction

$$\Delta G = \nu_D \mu_D + \nu_C \mu_C - \nu_B \mu_B - \nu_A \mu_A \tag{2}$$

to be defined in terms of the stoichiometric coefficients, $\{\nu_i\}$, and chemical potentials, $\{\mu_i\}$, of the chemical components $i =$ A, B, C, D.[12,13] If we let $c_i(0)$ be the initial value of the concentration of one of the participants in the reaction, then the concentration at a later time, t, is $c_i(t) = c_i(0) \pm \nu_i \xi(t)$, where $\xi(t)$ is called the extent of reaction. The plus sign applies in the case of the products, $i =$ C, D, while the minus sign applies in the case of the reactants, $i =$ A, B. The rate of relaxation of $\xi(t)$ from its initial value $\xi(0)$ to its equilibrium value ξ^e is determined by the kinetic rate law.

To apply the *principle of critical point universality* to the rate law, the thermodynamic variables are first divided into two classes called: (1) *fields* and (2) *densities*. A *field* variable has a uniform value across all phases coexisting at equilibrium.[2] In the case of a chemically reacting liquid mixture, field variables include the kelvin temperature, T, the pressure, P, and the chemical potentials, $\{\mu_i\}$, $i =$ A, B, C, D. Being a linear combination of chemical potentials, ΔG is also a field variable. A *density* variable has a different value in each coexisting phase.[2] In the case of a chemically reacting liquid mixture, the relevant density variables include the mass fractions of the various chemical components and the extent of reaction variable, ξ.

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Critical effects can be expected in the derivative of a *field* with respect to a *density*.[2] Such a derivative is $(\partial\Delta G/\partial\xi)_e$, where the subscript, e, indicates evaluation at chemical equilibrium. The existence and nature of the critical effect depend upon the number of *inert* components in the mixture.[13] A component is considered to be inert if its mass fraction is a constant independent of T and P. If the mixture contains *two* or *more* inert components, no critical effect is to be expected. If the mixture contains only *one* inert component, then for values of T near the critical temperature T_c $(\partial\Delta G/\partial\xi)_e$, is expected to be proportional to $|T - T_c|^x$, where x is the order of a tenth; this functional form is said to go to zero *weakly*.[2] In the case where the mixture contains *no* inert components, $(\partial\Delta G/\partial\xi)_e$ is expected to be proportional to $|T - T_c|^x$, where x is of the order of unity; this functional form is said to go to zero *strongly*.[2] Be it *weak* or *strong*, the value of x is independent of both chemical reaction and solvent.

The rate law, which determines the dependence of the net rate of reaction $\mathrm{d}\xi/\mathrm{d}t$ upon ξ, can be derived from the law of mass action.[12,13] Since the thermodynamic driving force for the law of mass action is $(-\Delta G/T)$, a Taylor series expansion of $\Delta G(\xi)$ about equilibrium suffices to introduce $(\partial\Delta G/\partial\xi)_e$ into the rate law. One finds that under critical conditions where $(\partial\Delta G/\partial\xi)_e$ disappears, so also does $\mathrm{d}\xi/\mathrm{d}t$.[12,13] This behavior of $\mathrm{d}\xi/\mathrm{d}t$ is called *critical slowing down*.

In previous experimental searches for critical slowing down involving reactions in multicomponent liquid mixtures, the time evolution of the extent of reaction variable was determined by an in situ measurement of some physical property, such as gas evolution,[13] heat evolution,[14] or electrical conductivity.[15−21] It is important to note, however, that an in situ measurement of the concentration of a component in a mixture in the critical region can suffer interference from competing critical effects; for example, critical opalescence can interfere with the measurement of optical density.[22] In contrast to these in situ methods of analysis, the sampling method[23] has the virtue that aliquots can be harvested from the fluid in its critical state and then be diluted out of the critical region prior to the determination of composition.

Below, we report our measurements of the rate of iodination of acetone by triiodide ion in isobutyric acid + water (UCST). *This acid-catalyzed reaction was selected not only because its mechanism has long been known*[24,25] *but also because the rate is slow enough to be easily followed using the sampling method.*

2. Theory

The goal of this section is to derive the rate law that links $\mathrm{d}\xi/\mathrm{d}t$ and ξ in the case of the iodination of acetone. Here, t is the time. One of the results of this derivation will be an equation that gives the functional dependence of the observed rate constant, k_{obs}, upon $(\partial\Delta G/\partial\xi)_e$. Before considering the details of the full mechanism, we first develop an expression for the rate of a concerted reaction that serves as a typical step in the mechanism.

In the vicinity of the consolute point, a reacting liquid mixture behaves as a nonideal solution. To include the effects of nonideality on the net rate of a concerted reaction taking place in such a mixture, the law of mass action must be written in terms of the thermodynamic activities; moreover, because every chemical transformation is to a certain extent reversible, both forward and reverse reactions must be taken into account.[12,13,26,27] Assuming the reaction in eq 1 to be concerted, we can incorporate these effects into the rate law by writing it in the form

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{k'}{\gamma^*}{a_A}^{\nu_A}{a_B}^{\nu_B} - \frac{k''}{\gamma^*}{a_C}^{\nu_C}{a_D}^{\nu_D} \tag{3}$$

where the $\{a_i\}$ are the thermodynamic activities of the substances i = A, B, C, D, γ^* is the activity coefficient of the transition state, and k' and k'' are rate coefficients for reaction in the forward and reverse directions, respectively.[13,26,27] Defined in this way, the rate coefficients, k' and k'', have the units of $\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$.

The instantaneous value of the Gibbs free energy of reaction is

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{{a_C}^{\nu_C}{a_D}^{\nu_D}}{{a_A}^{\nu_A}{a_B}^{\nu_B}}\right) \tag{4}$$

where ΔG° is the Gibbs free energy of reaction for reactants and products in their standard states. The equilibrium constant, K, is defined by

$$K = \frac{({a_C}^{e})^{\nu_C}({a_D}^{e})^{\nu_D}}{({a_A}^{e})^{\nu_A}({a_B}^{e})^{\nu_B}} \tag{5}$$

where $\{a_i^e\}$ are the equilibrium values of the activities. The equilibrium constant is related to ΔG° by the familiar equation

$$\Delta G^\circ = -RT\ln K \tag{6}$$

At chemical equilibrium,$\mathrm{d}\xi/\mathrm{d}t$ must be zero. This permits the right-hand side of eq 3 to be set to zero; then, if eqs 5 and 6 are incorporated into the result, one obtains

$$K = \frac{k'}{k''} = \exp(-\Delta G^\circ/RT) \tag{7}$$

By introduction of eqs 4 and 7, eq 3 can be rewritten in the form[13,27]

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{k'}{\gamma^*}{a_A}^{\nu_A}{a_B}^{\nu_B}[1 - e^{\Delta G/RT}] \tag{8}$$

Equation 8 serves as the basis for analyzing the effects of a critical point on the rate of a concerted reaction.

We now return to the iodination of acetone. In our experiments, molecular iodine was made soluble by reacting it with aqueous potassium iodide. Because of the association reaction

$$I_2 + I^- \rightleftarrows {I_3}^- \tag{9}$$

which has equilibrium constant[28] $K = 708$, the active iodine containing species in the reaction mixture was assumed to be ${I_3}^-$. Taking triiodide as the active species, the acetone iodination reaction mechamism[25] can then be written in the form

$$\mathrm{Ac} + \mathrm{HA} \overset{K_1}{\rightleftarrows} \mathrm{AcH}^+ + \mathrm{A}^- \qquad \text{(equilibrium)} \tag{10.1}$$

$$\mathrm{AcH^+ + A^- \underset{k_2''}{\overset{k_2'}{\rightleftarrows}} E + HA} \qquad \text{(slow)} \qquad (10.2)$$

$$\mathrm{E + I_3^- \underset{k_3''}{\overset{k_3'}{\rightleftarrows}} AcH^+ + 2I^-} \qquad \text{(fast)} \qquad (10.3)$$

$$\mathrm{AcHI^+ + A^- \overset{K_4}{\rightleftarrows} AcI + HA} \qquad \text{(equilibrium)} \qquad (10.4)$$

In this scheme, Ac stands for acetone, HA stands for isobutyric acid, A^- stands for the isobutyrate ion, and AcI stands for iodoacetone, $CH_3(CO)CH_2I$. The last of these is the principle product. The remaining symbols refer to the reaction intermediates, which include the acetone cation, $(CH_3)_2C{=}OH^+$, denoted by AcH^+; the iodine substituted cation, $(CH_3)(ICH_2)C{=}OH^+$, denoted by $AcHI^+$; and the enol, $(CH_3)(HO)C{=}CH_2$, denoted by E.

The reactions in eqs 10.1 and 10.4, are each assumed to be at instantaneous equilibrium. If K_1 is the equilibrium constant for the reaction in eq 10.1, the activities of the species involved satisfy the equation

$$K_1 = \frac{a_{\mathrm{AcH^+}} a_{\mathrm{A^-}}}{a_{\mathrm{Ac}} a_{\mathrm{HA}}} \qquad (11)$$

The formation of the enol is assumed to be rate controlling.[25] If we denote the rate constants for reaction in the forward and reverse directions in eq 10.2 by k_2' and k_2'', respectively, and the corresponding rate constants for reaction in the forward and reverse directions in eq 10.3 by k_3' and k_3'', then the net rate of change of the enol concentration, [E], is

$$\frac{d[\mathrm{E}]}{dt} = \frac{k_2'}{\gamma_2^*} a_{\mathrm{AcH^+}} a_{\mathrm{A^-}} - \frac{k_2''}{\gamma_2^*} a_{\mathrm{E}} a_{\mathrm{HA}} - \frac{k_3'}{\gamma_3^*} a_{\mathrm{E}} a_{\mathrm{I_3^-}} + \frac{k_3''}{\gamma_3^*} a_{\mathrm{AcHI^+}} a_{\mathrm{I^-}}^{2} \qquad (12)$$

Here, γ_2^* and γ_3^* are the activity coefficients of the transition states appropriate to eqs 10.2 and 10.3, respectively. Using eq 8 as our model, we can factor eq 12 into the form

$$\frac{d[\mathrm{E}]}{dt} = \frac{k_2'}{\gamma_2^*} a_{\mathrm{AcH^+}} a_{\mathrm{A^-}} [1 - e^{\Delta G_2/RT}] - \frac{k_3'}{\gamma_3^*} a_{\mathrm{E}} a_{\mathrm{I_3^-}} [1 - e^{\Delta G_3/RT}] \qquad (13)$$

where ΔG_2 and ΔG_3 are the respective Gibbs free energies of reaction. When the reaction mechanism is at *steady state*, the right-hand side of eq 13 is zero.[29] Under these circumstances, we can solve for $a_{\mathrm{E}} a_{\mathrm{I_3^-}}$ to obtain

$$a_{\mathrm{E}} a_{\mathrm{I_3^-}} = \frac{(k_2'/\gamma_2^*)[1 - e^{\Delta G_2/RT}]}{(k_3'/\gamma_3^*)[1 - e^{\Delta G_3/RT}]} a_{\mathrm{AcH^+}} a_{\mathrm{A^-}} \qquad (14)$$

Again employing eq 8 as our model, the net rate of disappearance of triiodide through the reaction in eq 10.3 can be written in the form

$$\frac{d[\mathrm{I_3^-}]}{dt} = -\frac{k_3'}{\gamma_3^*} a_{\mathrm{E}} a_{\mathrm{I_3^-}} [1 - e^{\Delta G_3/RT}] \qquad (15)$$

If we use eq 11 to replace $a_{\mathrm{AcH^+}} a_{\mathrm{A^-}}$ in eq 14 and substitute the result into eq 15, we arrive at the rate law

$$\frac{d[\mathrm{I_3^-}]}{dt} = -\frac{K_1 k_2'}{\gamma_2^*} a_{\mathrm{Ac}} a_{\mathrm{HA}} [1 - e^{\Delta G_2/RT}] \qquad (16)$$

Eq 16 gives the explicit dependence of $d[\mathrm{I_3^-}]/dt$ upon the thermodynamic force $(-\Delta G_2/T)$ that drives the rate-controlling step in the mechanism. We can now expand $\Delta G_2 = \Delta G_2(\xi_2)$ in a Taylor series about $\xi_2 = \xi_2^{\mathrm{e}}$, where ξ_2 is the extent of reaction variable that applies in the case of the reaction in eq 10.2, and ξ_2^{e} is its equilibrium value. To first order in $(\xi_2 - \xi_2^{e})$, this Taylor series is

$$\Delta G_2(\xi_2) = \Delta G_2(\xi_2^{\mathrm{e}}) + \left(\frac{\partial \Delta G_2}{\partial \xi_2}\right)_{\mathrm{e}} (\xi_2 - \xi_2^{\mathrm{e}}) \qquad (17)$$

Noting that the condition for equilibrium in eq 10.2 is $\Delta G_2(\xi_2^{\mathrm{e}}) = 0$, only the second term on the right-hand side of eq 17 survives. Upon substitution of eq 17 into eq 16, we obtain for the rate of disappearance of triiodide ion

$$-\frac{d[\mathrm{I_3^-}]}{dt} = k_{\mathrm{obs}} \qquad (18)$$

where

$$k_{\mathrm{obs}} = \frac{K_1 k_2'}{\gamma_2^*} a_{\mathrm{Ac}} a_{\mathrm{HA}} \left[1 - \exp\left(-\frac{1}{RT}\left(\frac{\partial \Delta G_2}{\partial \xi_2}\right)_{\mathrm{e}} (\xi_2^{\mathrm{e}} - \xi_2)\right)\right] \qquad (19)$$

Experiment has shown that early in the course of the reaction when $0 \le \xi_2 \ll \xi_2^{\mathrm{e}}$, zeroth-order kinetics prevail, and $[\mathrm{I_3^-}]$ decays linearly with time.[25] Equation 19 defines the pseudo-zeroth-order rate constant, k_{obs}. According to eq 19, the critical properties of k_{obs} depend upon the critical properties of $(\partial \Delta G_2/\partial \xi_2)_{\mathrm{e}}$.

The criterion for thermodynamic stability when the reaction mechanism is at equilibrium is $(\partial \Delta G_2/\partial \xi_2)_{\mathrm{e}} > 0$;[23] hence, because $\xi_2 \ll \xi_2^{\mathrm{e}}$, the argument of the exponential function on the right-hand side of eq 19 is negative definite. This makes $k_{\mathrm{obs}} > 0$, so that $d[\mathrm{I_3^-}]/dt < 0$ in eq 18. The latter condition persists until equilibrium is reached, when $d[\mathrm{I_3^-}]/dt$ approaches zero. The slow time decay of $[\mathrm{I_3^-}]$ can be followed by extracting aliquots from the reaction mixture, diluting them with water, and measuring the optical density.

3. Experimental Methods

Isobutyric acid, acetone, potassium iodide, and iodine were all obtained from Fischer and used without further purification. Water was once distilled from a glass system. A solution nominally 0.136 M in potassium triodide was prepared by stirring 0.068 mol of iodine into 500 cm^3 of water containing 0.2 mol of dissolved potassium iodide. The binary solvent mixture of isobutyric acid + water was prepared at the critical composition[30] of 38.8 mass % isobutyric acid by weighing.

In order to maintain a constant temperature in our experiments, we employed a 14 dm^3 water bath heated by a submerged

60 W light bulb. Power to the bulb was controlled by a Cole Parmer, 115 V variable output, model G-02149-20 controller connected to a Philadelphia Roto-Stat differential thermoregulator. The temperature of the bath was determined with a precision of 0.01 K by using a magnifying glass to read the gradations on a long mercury-in-glass thermometer.

Visual observation of critical opalescence and the disappearance of the meniscus in our sample of 38.8 mass % isobutyric acid + water showed that the critical temperature was 26.10 °C. Since the addition of a solute, even in a small amount, ordinarily produces a noticeable shift in the critical temperature of a binary liquid mixture,[31−33] preliminary experiments were required to find appropriate values for the concentrations of acetone and potassium triiodide. These concentrations could not be so high as to shift the critical temperature outside the easy operating range of our water bath nor could they be so low as to cause the value of k_{obs} to be immeasurably small.

The addition of acetone to our solvent mixture *lowered* the critical temperature, while the addition of potassium triiodide *raised* it. By exploiting these compensating effects, we settled on a recipe in which 0.3 cm^3 of acetone and 0.8 cm^3 of 0.136 M aqueous potassium triiodide were added to 30 cm^3 of 38.8 mass % isobutryric acid + water. The critical temperature of this mixture measured immediately after preparation was 25.43 °C. Depending upon the thermostat temperature, the triiodide concentration in the mixture decreased by 10−30% over the next 2.5 h. At the end of 24 h, when the disappearance of the brown color of dissolved iodine indicated that the reaction was at equilibrium, the critical temperature was measured and found to be 24.83 °C. This final value of the critical temperature served to define the critical end point of the phase transition.[34] Because the maximum instantaneous value of the critical temperature occurred at the *start* of the reaction, the mixture could be maintained in the single phase region during the entire course of the reaction simply by holding the thermostat at a temperature of 25.43 °C or higher.

To begin each kinetics run, 30 cm^3 of the reaction mixture was prepared according to the above recipe and added to a 3 cm i.d. × 25 cm long flat bottom, Pyrex test tube. A magnetic stirring bar was inserted, the test tube was closed with a stopper, and the contents were stirred continuously. After the elapse of 5 min, the first of a series of six 3 cm^3 aliquots was extracted using a seriological pipet. The remaining five aliquots were harvested at 30, 60, 90, 120, and 150 min after the start of the run. After extraction, each 3 cm^3 aliquot was diluted by the addition of 1 cm^3 of distilled water. The dilution served not only to quench the reaction but also to shift the aliquot out of the critical region.

To follow the progress of the reaction, the concentration of triiodide ion in each diluted aliquot was determined by measuring its optical density at a wavelength of 565 nm, using a Milton Roy Spectronic 21 DUV spectrophotometer. An extinction coefficient value of 86.86 dm^3·mol^{-1}·cm^{-1}, was used to convert the optical density measurements to concentrations. The values of the triiodide concentration versus time for two separate runs are shown in Figures 1 and 2. From each figure, the value of the observed zeroth-order rate constant was determined by calculating the slope and setting $k_{obs} = -d[I_3^-]/dt$.

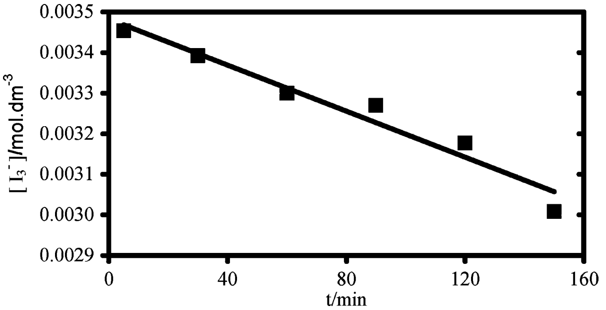

Figure 1. Time decay of the concentration of I_3^- at 25.43 °C. The slope of the line is $k_{obs} = 2.83 \times 10^{-6}$ mol·dm^{-3}·min^{-1}.

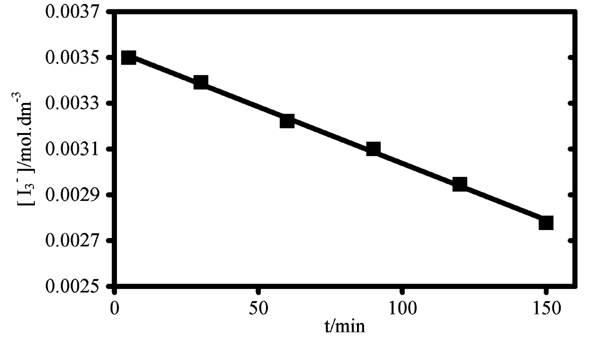

Figure 2. Time decay of the concentration of I_3^- at 27.00 °C. The slope of the line is $k_{obs} = 4.94 \times 10^{-6}$ mol·dm^{-3}·min^{-1}.

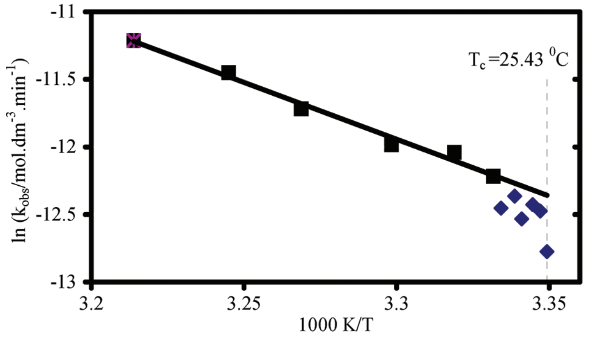

Figure 3. Arrhenius plot of the observed zeroth-order rate constant, k_{obs}, for the iodination of acetone in 38.8 mass % isobutyric acid + water.

TABLE 1: Observed Rate Constant, k_{obs}, as a Function of Temperature for the Iodination of Acetone in 38.8 Mass % Isobutyric Acid + Water

T/°C	$k_{obs}/10^{-6}$ mol·dm^{-3}·min^{-1}	T/°C	$k_{obs}/10^{-6}$ mol·dm^{-3}·min^{-1}
25.43	2.83	27.00	4.94
25.62	3.82	28.15	5.91
25.84	4.01	30.03	6.24
26.17	3.60	32.77	8.14
26.37	4.27	35.01	10.6
26.77	3.90	38.00	13.5

4. Results and Discussion

Figures 1 and 2 demonstrate that the concentration of triiodide ion decays linearly with time, and the kinetic rate law is zeroth order. Figure 3 shows an Arrhenius plot of the temperature dependence of k_{obs}. Table 1 lists the same data as a function of the celsius temperature. The six *highest* temperature points in Table 1, represented by the squares in Figure 3, lie on the Arrhenius line which has the equation

$$\ln k_{obs} = \ln A - E/RT \tag{20}$$

where $\ln A = 15.9 \pm 1.6$ and $E = 70.1 \pm 4.0$ kJ·mol^{-1}. In eq 20, both k_{obs} and A have the units mol·dm^{-3}·min^{-1}. Extrapolated into the low temperature region, this line serves as the "background" for judging the existence of a critical slowing down effect. The six *lowest* temperature points, which are plotted as diamonds in Figure 3, illustrate the magnitude of the critical effect. According to Table 1, these low temperature points define a critical region extending about 1.3 °C above the *initial* critical temperature at 25.43 °C or about 1.9 °C above the critical *end point* temperature at 24.83 °C. Because the temperature in Figure 1 is 25.43 °C, which is just 0.60 °C above the temperature of the critical end point, it is clear that the zeroth-order kinetic rate law is preserved well into the critical region.

Equation 19 indicates that the critical behavior of k_{obs} depends upon the temperature dependence of the thermodynamic derivative $(\partial \Delta G_2/\partial \xi_2)_{\mathrm{e}}$ evaluated at the critical end point, which is reached at chemical equilibrium. The critical behavior of $(\partial \Delta G_2/\partial \xi_2)_{\mathrm{e}}$ is determined by a count of the number of fixed density variables. We begin this enumeration by adding eqs 10 to obtain the stoichiometry of the overall reaction

$$\mathrm{Ac} + \mathrm{A}^- + \mathrm{I}_3^- \rightarrow \mathrm{AcI} + \mathrm{HA} + 2\mathrm{I}^- \qquad (21)$$

Equations 9 and 21 include all of the starting materials with the exception of water. Although water is not part of either eqs 9 and 21, it participates with isobutyric acid in the Bronsted−Lowry acid/base equilibrium

$$\mathrm{HA} + \mathrm{H_2O} \rightarrow \mathrm{H_3O^+} + \mathrm{A}^- \qquad (22)$$

Wheeler[35] has pointed out that the total mass of water represented by the sum of $\mathrm{H_3O^+}$ and $\mathrm{H_2O}$ is conserved by eq 22. As a consequence, the composition of the mixture of isobutyric acid + water is uniquely determined by specifying the mass fraction, w, of water; hence, one density variable is held fixed. This view is consistent with the experimental behavior of the isobaric heat capacity, $C_{P,\mathrm{w}} = T(\partial S/\partial T)_{P,\mathrm{w}}$, which in the case of both acidic[36] and basic[37] binary liquid mixtures has been observed to diverge *weakly* as a function of temperature in the critical region. Here, S is the entropy, which is a *density*.

Applying Wheeler's criterion[35] to the case of the iodination of acetone in isobutyric acid + water, the amount of water in the mixture should be considered fixed, making water an inert component. The state of the system is then described by one fixed density variable, and $(\partial \Delta G_2/\partial \xi_2)_{\mathrm{e}}$ should go to zero *weakly* as $T \rightarrow T_{\mathrm{c}}$, where T_{c} is the temperature of the critical end point. In this view, the slowing down effect shown in Figure 3 can be considered to be a *weak* critical effect.

In deriving eq 19, we have adopted the point of view of homogeneous kinetics in the sense that the concentrations of reactants, products, and intermediates are not considered to vary in space.[38−40] Spatially nonuniform concentrations appear in the theory of dynamic critical phenomena when the couplings among reaction,[41−43] diffusion,[41−43] heat conduction,[41−43] and sound propagation[41,42] are taken into account. These so-called mode couplings contain the possibility of slowing down as well as speeding up.[42]

5. Conclusions

The iodination of acetone in isobutyric acid + water is the first *pseudo-zeroth*-order reaction to exhibit critical slowing down. The use of the aliquot method in the analysis of the triiodide concentration would seem to remove the possibility[22] that the cause of this slowing down effect is anything other than the influence of the critical point on the rate of the chemical reaction.

A comparison of Figures 1 and 2 reveals that the familiar zeroth-order rate law[25] persists both *inside* and *outside* the critical region. This preservation of kinetic order was noted previously in the case of the pseudo-first-order Menschutkin reaction of benzylbromide with triethylamine near the LCST of triethylamine + water.[21] Taken together, the Menschutkin reaction and the iodination of acetone reaction suggest that reaction mechanisms are unaffected by the presence of the critical point. This observation confirms the frequently made assumption[38−43] that those factors in the rate law which depend explicitly upon the details of the mechanism such as the combination, $(K_1k_2'/\gamma_2^*)a_{\mathrm{Ac}}a_{\mathrm{HA}}$, in eq 19, are unaffected by criticality and remain smooth functions of the temperature through the critical region.

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