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Effect of the Consolute Point of Isobutyric Acid + Water on the Rate of an S_N1 Hydrolysis Reaction[1]

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The rate constant for the S_N1 hydrolysis of 2-chloro-2-methylbutane was measured near the consolute point of the liquid mixture isobutyric acid + water. At temperatures far from the upper critical solution temperature, T_c, of this mixture, the rate constant obeyed the Arrhenius equation. In the one-phase region just above T_c, however, the rate constant decreased below the Arrhenius background, while in the two-phase region below T_c, it increased. This combination of slowing-down with speeding-up appears to be beyond the scope of explanation of the current theories of dynamic critical slowing-down.

KEY WORDS: critical slowing-down; hydrolysis of 2-chloro-2-methylbutane; isobutyric acid; water.

1. INTRODUCTION

The consolute point is an extremum in the temperature-vs-mole fraction phase diagram for a binary mixture where the homogeneous liquid solution first begins to separate into two immiscible liquid layers. A mixture of two components having a liquid–liquid phase boundary in this variable space that is concave down is said to have an upper critical solution temperature (UCST). The UCST is the minimum temperature above which the two liquids are miscible in all proportions. In contrast, a liquid–liquid phase boundary that is concave up is described as having a lower critical solution

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temperature (LCST). The LCST is the maximum temperature below which the liquids are miscible in all proportions.

Binary liquid mixtures can be used as solvents for chemical reactions. The consolute point of the liquid mixture at one atmosphere pressure and the liquid–vapor critical point of a pure fluid are members of the same universality class [1]. This implies that the consolute point can be exploited to study the effects of thermodynamic criticality on the rates of chemical reactions. Recently, we have reported the observation of a slowing-down in the rates of five S_N1 hydrolysis reactions at the consolute points of three liquid mixtures. The reactants and solvents were 2-chloro-2-methylbutane (*t*-amylchloride) in isobutyric acid + water (UCST), 2-chloro-2-methylpropane (*t*-butylchloride) in isobutyric acid + water, 2-bromo-2-methylpropane (*t*-butylbromide) in triethylamine + water (LCST), 3-chloro-3-methylpentane in 2-butoxyethanol + water (LCST), and 4-methylbenzyl bromide in 2-butoxyethanol + water [2]. In each case, the reaction kinetics were first-order.

In this paper, we revisit the hydrolysis of 2-chloro-2-methylbutane in isobutyric acid + water [3] by introducing very careful measurements of the specific rate of reaction in the well-stirred liquid in the two-phase region below the critical solution temperature, T_c. Above T_c, we observe slowing-down of the reaction rate, but below T_c we find speeding-up. These results are of interest when compared with the most recent theories [4, 5]. These theories relate the reaction rate to the values of thermodynamic derivatives and predict that the occurrence of slowing-down depends upon the Griffiths–Wheeler classification and enumeration of the thermodynamic variables determining the position of chemical equilibrium [6, 7].

2. EXPERIMENT

2.1. Experimental Method

The solvent was isobutyric acid (IBA) + water. The isobutyric acid was purchased from Aldrich, while the water was once-distilled from a glass system. The solvent mixture was prepared at the critical composition (38.8 wt% IBA) by weighing. Before addition of the reactant, the critical temperature was $T_c{}^\circ = 26.12°C$. The reaction mixture consisted of 7.75 μL of 2-chloro-2-methylbutane added to 125 ml of solvent. Both reactant and solvent were temperature equilibrated in a 10-L water bath before mixing. The reaction cell was a hand-made Pyrex tube with a height of 18 cm, a diameter of 3.5 cm, and a volume of 180 cm^3. The tube wall was made as thin as possible to facilitate rapid heat transfer.

If we let RCl represent 2-chloro-2-methylbutane, the overall reaction was

$$\mathrm{RCl} + \mathrm{HOH} \rightarrow \mathrm{ROH} + \mathrm{HCl} \tag{1}$$

where ROH is 2-methyl-2-butanol. Since HCl is a strong electrolyte, the rate of the reaction could be followed by observing the buildup of conductance. The conductance measurements were made using the immersion probe of a Hanna Instruments Model HI 9032 microcomputer-controlled conductivity meter. The temperature range of the meter was 0 to 50°C, with a conductance resolution of 0.1 μS. The cell and the probe were held at the desired temperature in the water bath, which was controlled by a Philadelphia Roto-Stat differential thermoregulator connected to a Cole Parmer, 115-V variable-output, Model G-02149-20 controller. The temperature was sensed with a Model S27929 L180 G(D) platinum resistance thermometer supplied by Minco Products, Inc. The resistance of the thermometer was read using a Hewlett–Packard Model H3458A, 8.5-digit multimeter. Over the length of a kinetics run, the temperature of the bath was stable to ± 0.3 mK.

During the course of the reaction, the liquid in the conductance cell was vigorously stirred to homogenize the mixture and to guarantee mass transfer equilibrium across any phase boundaries in the case of experiments carried out in the two-phase region. The temperature compensation feature of the Hanna instrument was used to eliminate the effects of temperature fluctuations and also to remove the effect of background conductance from the measured values.

In general, the addition of a third component to a binary liquid mixture shifts the critical temperature [8, 9]. If the third component is more soluble in one of the original components than the members of that pair are in each other, the region of binary miscibility shrinks. This is reflected by an increase in an UCST and a decrease in an LCST [10].

After the reaction mixture had come to chemical equilibrium, the critical temperature was remeasured by observing the appearence of opalescence and was found to be $T_c = 26.32$°C. Since this represents an increase in the UCST, the combination of the equilibrium concentrations of RCl, ROH, and HCl had the effect of decreasing the miscibility of isobutyric acid + water mixture. For the purposes of illustration, we show in Fig. 1 how the value of T_c measured at chemical equilibrium depended upon the initial concentration of RCl. Nevertheless, because each kinetics run was started with the same initial amounts of solvent and reactant, and the reaction went essentially to completion, the equilibrium critical temperature of 26.32°C could be treated as a constant for the system.

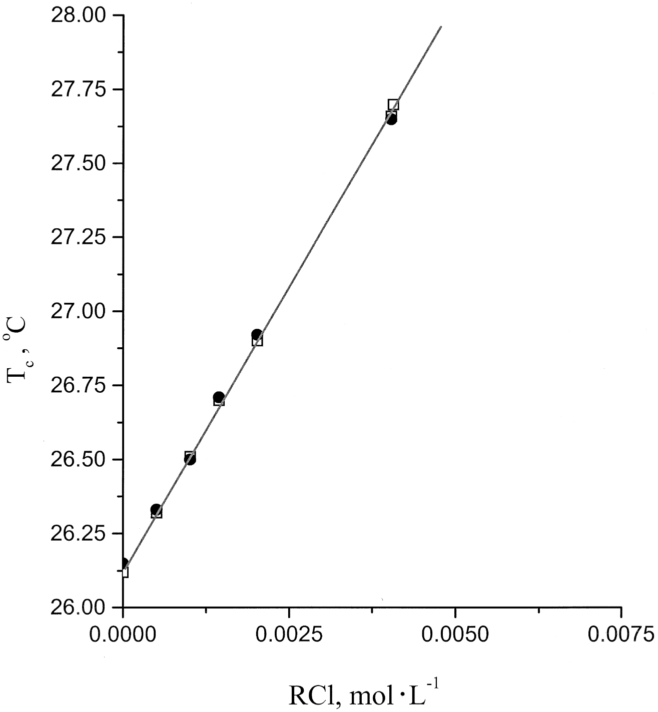

Fig. 1. Equilibrium critical temperature, T_c, for solutions of 2-chloro-2-methylbutane in 38.8 weight% isobutyric acid + water as a function of the initial concentration of 2-chloro-2-methylbutane (RCl). The two plotting symbols represent measurements made starting with different batches of isobutyric acid + water.

2.2. Data Analysis

Consider a general chemical reaction

$$\nu_1(1) + \nu_2(2) + \nu_3(3) + \cdots \rightarrow 0 \tag{2}$$

involving the species (1), (2), etc., some of which may be ions. When species i is a reactant, the stoichiometric coefficient $\nu_i > 0$, while when i is a product, $\nu_i < 0$. If c_i^0 is the initial molar concentration of i, then its concentration at a later time is $c_i = c_i^0 - \nu_i \xi$, where ξ is the extent of reaction (reaction variable). Let Λ_i be the molar conductance of i, and let σ_s be the conductivity of the solvent. The instantaneous conductivity, σ, of the reaction mixture is then

$$\sigma = \sigma_s + \sum_i (c_i^0 - \nu_i \xi) \Lambda_i \tag{3}$$

At the start of the reaction, when $\xi = 0$, the conductivity is $\sigma^0 = \sigma_s + \sum_i c_i^0 \Lambda_i$. At reaction equilibrium, when $\xi = \xi_e$ and the c_i assume their equilibrium values, $c_i^e = c_i^0 - \nu_i \xi_e$, the conductivity is $\sigma^e = \sigma_s + \sum_i c_i^e \Lambda_i$. Since $\nu_i/(c_i^0 - c_i^e) = 1/\xi_e$ is the same for all i (the same for each species), Eq. (3) can be converted to

$$\sigma = \sigma^0 + \frac{(\sigma^e - \sigma^0)\, \nu_i \xi}{c_i^0 - c_i^e} \tag{4}$$

which is the basic result for the conductivity of reacting mixtures.

The kinetics of the reaction in Eq. (1) are first order in the concentration of RCl. Since equilibrium lies far to the right, the reaction goes essentially to completion and at time, t,

$$\xi = c_{\mathrm{RCl}}^0 (1 - e^{-t/\tau}) \tag{5}$$

where c_{RCl}^0 is the initial concentration of RCl, and the relaxation time, τ, is related to the first-order rate constant, k', by $k' = 1/\tau$.

To apply Eq. (4), we let $i = \mathrm{RCl}$. Since the reaction goes to completion, the equilibrium concentration is $c_{\mathrm{RCl}}^e = 0$. According to Eq. (1), $\nu_{\mathrm{RCl}} = 1$. The Hanna conductivity meter actually records the conductance, $L = \sigma A/s$, where A is the cross-sectional area of the measurement electrodes and s is their separation. The initial and equilibrium values of the conductance are $L^0 = \sigma^0 A/s$ and $L^e = \sigma^e A/s$, respectively. Substituting these results and Eq. (5) into Eq. (4), we obtain

$$L = L^0 + (L^e - L^0)(1 - e^{-1/\tau}) \tag{6}$$

The software of the Hanna meter compensated for L^0; hence, the difference, $L - L^0$, predicted by Eq. (6) was fit to the data from each run, with $L^e - L^0$ and $1/\tau$ taken as adjustable parameters.

During a few $(L - L^0)$-vs-t data collection runs, the thermostat temperature, T, was bracketed on one side by the critical temperature, T_c^0, of the binary liquid solvent and on the other by the critical temperature of the reaction mixture at chemical equilibrium, T_c, so that $T_c^0 < T < T_c$. In this circumstance, the reaction mixture made a transition from one phase to two phases during the course of the run. The observation of a phase change

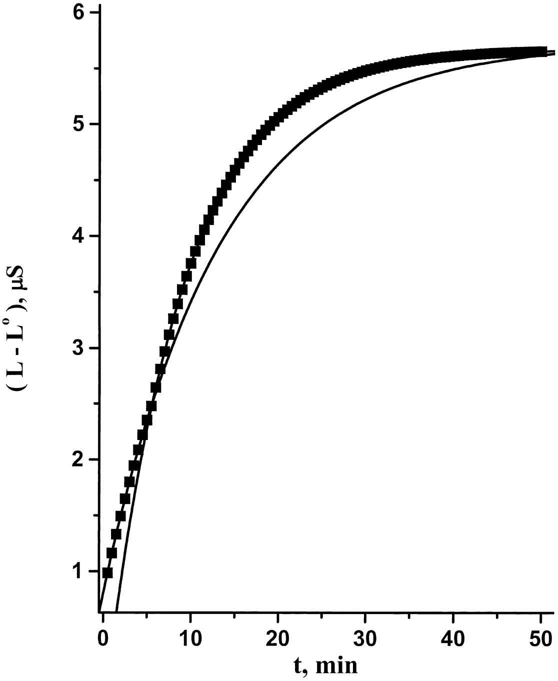

Fig. 2. Conductance, $L-L^0$, as a function of time, t, for the hydrolysis of 2-chloro-2-methylbutane in 38.8% isobutyric acid+water in a case where $T_c^0 < T < T_c$. The mixture underwent a transition from one liquid phase to two liquid phases about 6 min into the run.

during the reaction implied that the mixture possessed a time-dependent critical temperature, which was determined by its instantaneous composition. As illustrated in Fig. 2, the occurrence of a phase transition produced a distinct change in the curvature in the graph of $(L-L^0)$ vs t. In such cases, the pretransition data were excluded from the determination of the value of $1/\tau$, because only the post transition data could be expected to converge at long times to the appropriate equilibrium conductance value, (L^e-L^0)

In Fig. 3, we show an Arrhenius plot of the temperature dependence of $1/\tau$. The straight line is given by the equation

$$\ln(1/\tau) = 43.0 - 116{,}100/(RT) \tag{7}$$

The units of τ are min, R is the universal gas constant, T is the absolute temperature, and the units of the coefficient of $1/(RT)$ are $\mathrm{J \cdot mol^{-1}}$. The

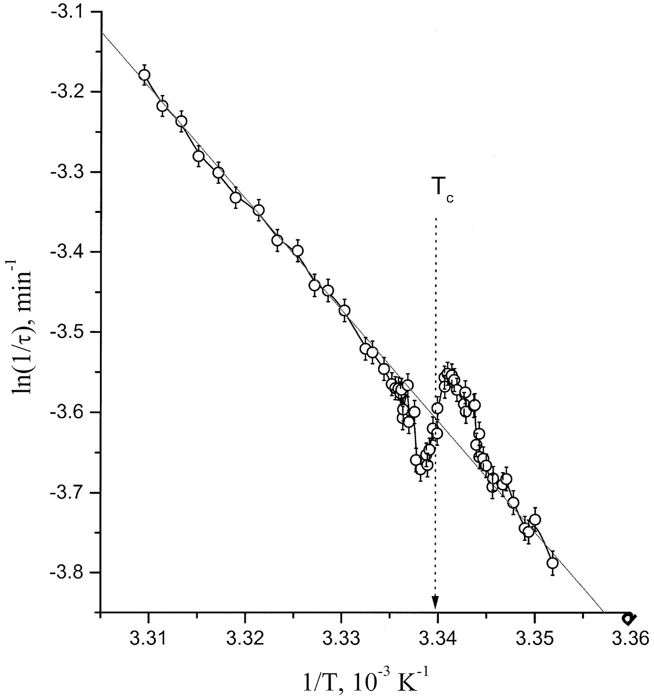

Fig. 3. Arrhenius plot of the relaxation rate, $1/\tau$, for the hydrolysis of 7.75 μl of 2-chloro-2-methylbutane in 125 ml of the mixture 38.8% isobutyric acid + water. The reciprocal of the absolute temperature is $1/T$, while the reciprocal of the equilibrium critical temperature is labeled T_c. This temperature corresponds to 26.32°C.

values of the coefficients in Eq. (7) were obtained by fitting the Arrhenius equation to data obtained in the one-phase region of the mixture at temperatures far above T_c. The constant term on the right in Eq. (7) had an estimated error of ± 0.02, while the activation energy (116.1 ± 1.7 kJ $\cdot$ mol^{-1}) was somewhat higher than that found previously for this system [3]. Equation (7) forms the "background" against which the size of critical effects can be judged. It is apparent from Fig. 3 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 it.

In our previous study of this reaction [3], we did not have enough data to distinguish the region of speeding-up from the background, and we located the critical temperature, T_c, near the minimum of the slowing-down region. Because we also used a high initial concentration of RCl, T_c was many degrees above T_c^0. By contrast, in the experiments we have just described, so little RCl was required that T_c and T_c^0 differed by less than the width of the critical region (about 1°C).

Snyder and Eckert measured the rate of reaction of isoprene with maleic anhydride near the UCSTs of hexane + nitrobenzene and hexane + nitroethane and, in both cases, observed only speeding-up [11]. This is the only other case of speeding-up of reaction rates in liquid mixtures that has come to our attention.

3. THEORY

3.1. Kinetics

As an S_N1 reaction, the hydrolysis of 2-chloro-2-methylbutane can be represented by the simple mechanism

$$\mathrm{RCl} \rightarrow \mathrm{R}^+ + \mathrm{Cl}^- \tag{8}$$

$$\mathrm{R}^+ + \mathrm{HOH} \rightarrow \mathrm{ROH} + \mathrm{H}^+ \tag{9}$$

where the first step is rate controlling. Equation (8) goes essentially to completion; nevertheless, since our object is to reference the kinetics to the value of ξ_e, we should consider this first step as reversible and express the rate of reaction in terms of $\xi - \xi_e$.

Equilibrium in the second step is reached quickly and lies far to the right. The molar concentrations, c_{R^+}, c_{ROH}, and c_{H^+}, of the species R^+, ROH, and H^+, respectively, are related by

$$K_{\mathrm{R}} = \frac{c_{\mathrm{ROH}} c_{\mathrm{H}^+}}{c_{\mathrm{R}^+}} \tag{10}$$

where, since the activity coefficients are included implicitly on the left of the equation, K_{R} is not an equilibrium constant but is an equilibrium concentration ratio. The extent of reaction, ξ, may be set equal to c_{Cl^-}, and because the concentration of R^+ is very low, we also have $\xi \simeq c_{\mathrm{ROH}} = c_{\mathrm{H}^+}$. These results permit Eq. (10) to be solved for

$$c_{\mathrm{R}^+} = \xi^2 / K_{\mathrm{R}} \tag{11}$$

We next let k' and k'' be the rate coefficients for reaction in the forward and reverse directions in Eq. (8). Since Eq. (8) is rate controlling, the rate law is

$$\frac{dc_{\mathrm{RCl}}}{dt} = -k' c_{\mathrm{RCl}} + k'' c_{\mathrm{R}^+} c_{\mathrm{Cl}^-} \tag{12}$$

If we introduce $c_{\mathrm{RCl}} = c^0_{\mathrm{RCl}} - \xi$ and use Eq. (11), then Eq. (12) becomes

$$\frac{d\xi}{dt} = k'(c^0_{\mathrm{RCl}} - \xi) - \frac{k''\xi^3}{K_{\mathrm{R}}} \tag{13}$$

The equilibrium value, ξ_{e}, of the reaction variable is obtained by setting the right-hand side of Eq. (13) to zero. Since the equilibria in both Eq. (8) and Eq. (9) lie far to the right, and $k''(c^0_{\mathrm{RCl}})^2/(k'K_{\mathrm{R}}) \ll 1$, we can then solve the resulting cubic equation to lowest order using perturbation theory [12] to obtain

$$\xi_{\mathrm{e}} = c^0_{\mathrm{RCl}}(1 - k''(c^0_{\mathrm{RCl}})^2/(k'K_{\mathrm{R}})) \tag{14}$$

Being a function of ξ, the right-hand side of Eq. (13) can be expanded in a Taylor series about $\xi = \xi_{\mathrm{e}}$; because the higher derivatives are zero, this series has only three terms:

$$\frac{d\xi}{dt} = -k'\left(1 + \frac{3k''\xi_{\mathrm{e}}^2}{k'K_{\mathrm{R}}}\right)(\xi - \xi_{\mathrm{e}}) - \frac{3k''\xi_{\mathrm{e}}}{K_{\mathrm{R}}}(\xi - \xi_{\mathrm{e}})^2 - \frac{k''}{K_{\mathrm{R}}}(\xi - \xi_{\mathrm{e}})^3 \tag{15}$$

Substituting Eq. (14) into Eq. (15) and collecting terms of lowest (actually zeroth) order in $k''(c^0_{\mathrm{RCl}})^2/(k'K_{\mathrm{R}})$, we obtain

$$\frac{d\xi}{dt} = -k'(\xi - \xi_{\mathrm{e}}) \tag{16}$$

Because of Eq. (14), we also have to lowest order $\xi_{\mathrm{e}} = c^0_{\mathrm{RCl}}$. Equation (16) is the rate law for a reaction which is essentially irreversible. With $k' = 1/\tau$, its integral is Eq. (5).

3.2. Thermodynamics

A nonequilibrium thermodynamic analysis [13, 14] of the rate gives to the same degree in $(\xi - \xi_{\mathrm{e}})$,

$$\frac{d\xi}{dt} = \frac{-\kappa' a_{\mathrm{RCl}}(\xi_{\mathrm{e}})}{y^*(\xi_{\mathrm{e}})\,RT}\left(\frac{\partial \Delta G}{\partial \xi}\right)_{\mathrm{e}}(\xi - \xi_{\mathrm{e}}) \tag{17}$$

where κ' is the rate coefficient for the reaction in Eq. (8) in the forward direction in a dilute ideal solution, $a_{\mathrm{RCl}}(\xi_{\mathrm{e}})$ is the thermodynamic activity of RCl evaluated at equilibrium, $y^*(\xi_e)$ is the equilibrium value of the activity coefficient of the transition state, and $(\partial \Delta G/\partial \xi)_e$ is the equilibrium value of the reaction variable derivative of the instantaneous Gibbs free energy difference between products and reactants in Eq. (1) [2]. The factor, $\kappa' a_{\mathrm{RCl}}(\xi_e)/y^*(\xi_e)$, can be interpreted as the forward rate of the reaction in Eq. (8) at equilibrium. Since Eqs. (16) and (17) are each representations of the leading terms in Taylor series expansions of the net rate, we can set the coefficients of $(\xi-\xi_e)$ equal; thus we obtain

$$k' = \frac{\kappa' a_{\mathrm{RCl}}(\xi_e)}{y^*(\xi_e)\, RT}\left(\frac{\partial \Delta G}{\partial \xi}\right)_e \tag{18}$$

3.3. Summary

Equation (17) was derived by relaxation methods, where it was assumed that the value of ξ was always sufficiently close to ξ_e that powers of $(\xi-\xi_e)$ greater than the first could be ignored [2]. The derivation of Eq. (16) not only confirms that terms of order $(\xi-\xi_e)^2$ and higher can be omitted but also proves that this is true regardless of the value of $(\xi-\xi_e)$, as long as the reactions in Eqs. (8) and (9) are sufficiently irreversible to make $k''(c^0_{\mathrm{RCl}})^2/(k'K_{\mathrm{R}}) \ll 1$.

4. DISCUSSION AND CONCLUSIONS

If in Eq. (18), we can assume that, as $T \to T_c$, there are no critical point effects in the coefficient, $\kappa' a_{\mathrm{RCl}}(\xi_e)/y^*(\xi_e)$ [4, 5], then the behavior of k' near T_c is determined by the thermodynamic derivative, $(\partial \Delta G/\partial \xi)_e$.

According to Griffiths and Wheeler [15], the analysis of the critical behavior of $(\partial \Delta G/\partial \xi)_e$ begins with the separation of the thermodynamic variables into two classes. In the first class are the “fields,” such as temperature, pressure, and component chemical potentials. A field has the same value in each phase coexisting in equilibrium. In the second class are the “densities,” such as entropy and the concentrations of chemical components, which have different values in each coexisting phase.

Griffiths and Wheeler argue that if the experimental conditions are such that the fixed variables consist of fields and two or more densities, then the derivative of a field with respect to a density, such as $(\partial \Delta G/\partial \xi)_e$, will not go to zero as the temperature, T, approaches T_c. If fewer than two densities are held fixed, however, then $(\partial \Delta G/\partial \xi)_e \sim (|T-T_c|/T_c)^x$ for T near T_c. If one density is held fixed, $(\partial \Delta G/\partial \xi)_e$ is said to go to zero “weakly” in the sense that x involves one of the small critical exponents, either $\alpha = 0.11$ [16] (α determines the temperature dependence of the constant volume specific heat of a pure fluid) or $\beta = 0.332$ [16] (β determines the shape of the liquid–vapor coexistence curve of a pure fluid). If no densities are held fixed, $(\partial \Delta G/\partial \xi)_e$ is said to go to zero "strongly" in the sense that x involves one of the large critical exponents, either $\gamma = 1.24$ [16] (γ determines the temperature dependence of the isothermal compressibility of a pure fluid) or $\delta = 4.9$ [16] (δ determines the shape of the critical isotherm of a pure fluid).

For a reaction in a thermostat open to the atmosphere, the appropriate field variables are presumably the pressure, P, and the temperature, T. As composition variables (densities), we choose mass fractions as opposed to mole fractions [2, 3], because chemical reactions conserve mass but not moles. Use of mass fractions and mass conservation makes it easy to determine which, if any, of the composition variables are held fixed during the course of a reaction. In the case of our experiment, the appropriate composition variables are the mass fractions w_{IBA}, w_{HOH}, w_{RCl}, w_{ROH}, and w_{HCl} of the components, isobutyric acid (IBA), water, RCl, ROH, and HCl, respectively. If we can assume that isobutyric acid is inert, then w_{IBA}, T, and P are held fixed. Because of the chemical reaction connecting them, the mass fractions of the other components at equilibrium depend upon T and P and possibly also w_{IBA}. With one density, w_{IBA}, fixed, we conclude that $(\partial \Delta G/\partial \xi)_e$ should go to zero "weakly," and the kinetics of the reaction should slow down as $T \to T_c$. On the other hand, isobutyric acid is known to react with alcohols, such as ROH, to form esters. This event would introduce the mass fraction of the ester as a new composition variable and at equilibrium would make both this variable and w_{IBA} functions of T and P. Under these conditions, no density would then be held fixed, and we would expect $(\partial \Delta G/\partial \xi)_e$ to go to zero "strongly" and the kinetics of the hydrolysis reaction again to slow down as $T \to T_c$. Thus, whether or not IBA is inert, the application of Griffiths and Wheeler rules to Eq. (18) implies that the rate of hydrolysis of RCl should be slowed as is illustrated by the data in Fig. 2, at least for temperatures $T > T_c$.

In contrast, Milner and Martin [5] argue that the model of homogeneous kinetics implied by Eqs. (16)–(18) is unsatisfactory, because it ignores the coupling between the fluctuations in the thermodynamic variables that take place near a critical point. Because these fluctuations are long range as $T \to T_c$, Milner and Martin suggest that the kinetics can be represented by the equations of linearized hydrodynamics. This system of equations includes three sound modes (two transverse and one longitudinal), a heat relaxation mode, and a chemical relaxation mode. Since the modes with the slowest rate of decay will determine the critical slowing-down, Milner and Martin reject the three rapidly decaying sound modes in favor of the thermal and chemical modes. The decay of these two modes occurs by the interplay of chemical reaction with the diffusion of entropy and concentration. These effects can be represented in time and space by a pair of partial differential equations coupling the concentration and temperature fluctuations. The partial differential equations can be integrated to obtain the spatial normal modes and the temporal decay constants. Exactly which spatial normal modes are encountered in practice depends upon the boundary values and initial conditions satisfied by the entropy and the composition variable.

Because there are two coupled equations, each spatial normal mode is associated with two temporal decay constants. In analyzing the critical behavior of these constants, we assume that the mixture contains no inert chemical components. This makes the arguments appropriate to the case where we have taken into account the separate reaction between ROH and IBA to form an ester. 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:* For normal modes of long wavelength, the two decay constants are proportional to (in our notation) $(\partial T/\partial S)_{\Delta G}$ and $(\partial \Delta G/\partial \xi)_S$, respectively. Since ΔG is a field, and the entropy, S, is a density, the first of these derivatives should go to zero "strongly," while the second should go to zero "weakly." *Regime II:* For normal modes of short wavelength, the decay constants are proportional to $(\partial \Delta G/\partial \xi)_T$ and $(\partial T/\partial S)_\xi$, respectively. The first of these should go to zero "strongly." The second should go to zero "weakly," since ξ is a density. Because every decay constant is predicted to go to zero, both of these wavelength regimes are qualitatively consistent with the slowing-down observed in Fig. 3 for $T > T_c$.

Strictly speaking, Milner and Martin analyze in detail only a binary fluid with an isomerization reaction linking the components. Their conclusions appear to be general, however, so we have applied their picture to our more complex case.

Neither the model of homogeneous kinetics represented by Eq. (18) nor the hydrodynamic model of Milner and Martin would seem to be consistent with the speeding-up in reaction rate evident in Fig. 3 for $T < T_c$, since both theories rely upon thermodynamic derivatives which approach zero as $T \to T_c$. Below T_c, two phases coexist, and because of the strong stirring, the measured reaction rate may in fact be some composite of the individual rates prevailing in each phase. Indeed, all three chemical factors, κ', $a_{\mathrm{RCl}}(\xi_e)$, and $y^*(\xi_e)$, in Eq. (18) are likely to have different values in each phase, which implies that so also must k'. This holds out the possibility that the rate observed in the region $T < T_c$ may be only incidently related to the critical point.

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