Suppression of the Rate of Hydrolysis of t-Amylchloride at the Consolute Composition of Isobutyric Acid + Water

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Abstract

We have measured the rate of hydrolysis of t-amylchloride in the solvent, isobutyric acid + water, prepared at its consolute composition. The consolute temperature of the mixture depends upon the initial amount of t-amylchloride, being 32.3 C when 100 μL are added to 25 mL of the solvent and 36.46 C when 150 μL are added. In both cases, however, we found that the specific rate of reaction is suppressed over a temperature range of about 0.2 C on either side of the local consolute temperature, T_C. These observations serve to demonstrate the concept of "critical slowing down" in chemical kinetics. The decrease in specific rate with temperature, T, could be fitted to $| T - T_C |^{-x}$ with $x = 0.63 \pm 0.28$. Within the experimental error, this value of the exponent is consistent with the value ($x = 0.80$) predicted theoretically on the basis of the principle of universality.

Keywords: critical state, chemical kinetics, mixture, t-amylchloride, isobutyric acid, water

I. Introduction

Because of the isomorphism that exists between the equilibrium thermodynamic surfaces for systems of one and two components, respectively, analogous thermodynamic derivatives diverge with the same exponents.[1] This is a consequence of the principle of universality, which depends upon the fact that the critical properties of one and two component fluids can be represented by the same Ising model in 3-dimensions. These properties recommend two-component liquid mixtures as solvents for chemical reactions. In contrast to pure fluids where the critical point ordinarily occurs at many atmospheres of pressure, liquid mixtures can be used at ordinary pressures. The theoretical concepts for exploiting critical point chemistry have been discussed by Wheeler,[2] Milner and Martin,[3] Greer,[4] and by Gitterman.[5]

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In 1973, Snyder and Eckert[6] examined experimentally the rate of the Menschutkin addition reaction of ethyl iodide on the one-phase side of the lower consolute temperature (LCST) of triethylamine + water. They reported an apparent slowing down in the reaction rate as the consolute point was approached. Subsequently, Becker and collaborators[7] examined the trifluoroacetic acid catalyzed reaction of acetic anhydride + 1,2 ethanediol. In this case, the reacting pair also served as its own solvent. Becker *et al*. reported that near the consolute point, there was a decrease in the rate of heat evolution, which they associated with a slowing down in the rate of reaction.

The observation "critical slowing down" has not been universal, however. Snyder and Eckert[6] have reported an accelerated rate in the Diels-Alder addition of isoprene to maleic anhydride near the upper consolute temperatures (UCST) of two solvent pairs, hexane + nitrobenzene and hexane + nitroethane.

A shift in the position of chemical equilibrium is also expected at the consolute point. In the case of the dimerization of NO_2 to N_2O_4 in perfluoromethylcyclohexane + carbon tetrachloride (UCST), Greer and collaborators reported that the equilibrium shifted by 4% toward the NO_2 side as the consolute point was approached.[8]

Below, we report our measurements of the rate of hydrolysis of t-amylchloride near the consolute point of isobutyric acid + water. We find a slowing down of the reaction rate, whose temperature dependence is consistent with the principle of universality.

II. Experiment

II 1. General

Isobutyric acid (2-methylpropionic acid) and water are miscible in all proportions at temperatures above an UCST of 26.12 C, which occurs at the composition 38.8 weight percent isobutyric acid. When t-amylchloride (2-chloro-2-methylbutane) is added, it reacts with the water in the solvent pair to produce as products primarily t-amylalcohol (2-methyl-2-butanol) and hydrochloric acid.

II 2. Materials

In making up the solvent, we used isobutyric acid purchased from Lancaster Synthesis Inc. This material and the water, which constituted the solvent pair, were each once distilled from a glass system. Our t-amylchloride was obtained from Aldrich Chemical Co.

II 3. Measurement of the Reaction Rate Relaxation Time

The rate of hydrolysis of t-amylchloride in isobutyric acid + water was determined by measuring the time dependence of the increase in ionic conductivity of the reaction mixture caused by the build-up of HCl. Because HCl is a strong electrolyte, its conductivity easily dominates the solvent background conductivity due to the ionization of water and isobutyric acid, which are both weak electrolytes. The conductivity was measured using a Radiometer (Copenhagen) Model CDM 83 conductivity meter. The reaction mixture was contained in a test tube, which was large enough to accommodate the CDC immersion probe of this meter.

The test tube and the probe were held at the desired temperature by placing them in a water bath controlled by a Philadelphia Roto-Stat Differential Thermoregulator connected to a Cole Parmer, 115 V Variable Output, Model S27929 PA1 L180 G(D), Serial No. 1516, platinum resistance thermometer supplied by Minco Products, Inc. The resistance of the thermometer was read using a Hewlett-Packard Model H3458A, 8-1/2 digit multimeter. Over the period of two hours required to make each kinetics run, the temperature of the bath was stable to ± 0.3 mK.

To start a kinetics run, the solvent was prepared at its consolute composition by weighing. A 25 mL sample of the mixture was then transferred to the test tube, which was placed in the water bath and allowed to come to thermal equilibrium. To initiate the hydrolysis reaction, 150 μL of t-amylchloride were added to the test tube and mixed; this produced immediate turbidity. Upon settling for fifteen seconds, a liquid-liquid phase transition marked by a meniscus became apparent. The conductivity probe was inserted into the upper liquid layer. A sequence of conductivity readings equally spaced in time was begun. Between readings, the conductivity probe was used to stir the mixture in order to assure mass transfer equilibrium between the two layers. At the end of the sequence, there was a pause of length, Δ, equal to about 2.5 reaction half-lives after which additional readings were taken having equal spacing to the first.

Since the reaction is first order in the concentration of t-amylchloride, the two sets of conductivity measurements, $\sigma(t)$ and $\sigma(t+\Delta)$, could be combined in the Guggenheim equation,

$$\ln\left[\sigma(t+\Delta) - \sigma(t)\right] = \ln\left[\sigma_{HCl}\left(1 - e^{-\Delta/\tau}\right)\right] - t/\tau \qquad (1)$$

where σ_{HCl} is the conductivity of the HCl at chemical equilibrium and τ is the kinetic relaxation time for the reaction.[9] A plot of the left hand of Eq. (1) as a function of t formed a straight line with slope, $-1/\tau$.

II 4. Determination of the Critical Temperature

To determine the critical temperature at chemical equilibrium, the reaction mixture was held in a dilatometer for many half-lives. When the height, h, of the liquid in the capillary side-arm was measured as a function of temperature, there was a discernible change in slope at 36.46 C (309.61 K), which we took to be the critical temperature.

II 5. Analysis of the Relaxation Time

Except for eight temperatures near the consolute point lying between 309.45 K and 309.75 K, our measured values of $1/\tau$ fit the Arrhenius equation

$$\ln\left(1/\tau\right) = 33.23 - \frac{91{,}790}{RT} \qquad (2)$$

where R is the gas law constant in J mol^{-1} K^{-1}, and T is the absolute temperature. A graph of the data plotted according to Eq. (2) is shown in Fig. 1.

The Arrhenius line formed the "background" for the eight points in the critical region, which we assumed represented the effect of critical slowing down. For each of these eight points, the background value, $(1/\tau_b)$, of the reciprocal relaxation time was evaluated using Eq. (2). The difference, $\Delta(1/\tau) = \left|(1/\tau_b) - (1/\tau)\right|$, between the background value and the measured value, $1/\tau$, was computed. Taking $T_c = 309.61$ K, and $\varepsilon = \left|(T - T_c)/T_c\right|$. These differences were plotted logarithmically as shown in Fig.2. The magnitude of the slope gave the critical exponent x = 0.63 ± 0.28.

III. Theory

III 1. Reaction Rate and Affinity

For an elementary reaction in non-ideal solution among chemical species denoted as (1), (2), (3), and (4),

$$\nu_1(1) + \nu_2(2) = \nu_3(3) + \nu_4(4) \tag{3}$$

where ν_i (i = 1,2,...,4) are the stoichiometric coefficients, Haase[10] writes the net reaction rate, r,

$$r = \lambda \left[\kappa_f a_1^{\nu_1} a_2^{\nu_2} - \kappa_r a_3^{\nu_3} a_4^{\nu_4} \right] \tag{4}$$

In Eq. (4), a_i (i = 1,2,...,4) are the thermodynamic activities of the respective species, $1/\lambda$ is the activity coefficient of the transition state, while κ_f and κ_r are rate coefficients for reaction in the forward and reverse directions, respectively, in the case of ideal solution.

If we now let RCl represent the alkylhalide, the rate determining step in the hydrolysis of t-amylchloride is [9]

$$RCl \rightarrow R^+ + Cl^- \tag{5}$$

The second step,

$$R^+ + HOH \rightarrow ROH + H^+ \tag{6}$$

in the mechanism produces the alcohol, ROH, and can be assumed to be at equilibrium.

The overall reaction,

$$RCl + HOH \rightarrow ROH + HCl \tag{7}$$

is obtained by summing Eqs. (5) and (6).

The relaxation time is defined in terms of the observed reaction rate, $-d\xi/dt = (\xi - \xi_e)/\tau$, where ξ is the reaction variable (molar concentration of reacted RCl = concentration of HCl) at time, t, and ξ_e is its equilibrium value. Applying Eq. (4) to Eqs. (5) - (7), one obtains

$$\frac{1}{\tau} = \left(\frac{\kappa_f}{RT}\right)\left(\frac{y_{RCl}(\xi_e)}{y^*_{RCl}(\xi_e)}\right)\left(\frac{C_{RCl}(\xi_e)}{C_o}\right)\left(\frac{\partial A}{\partial \xi}\right)_e \tag{8}$$

where A is the affinity for Eq. (7) (negative of the Gibbs free energy of reaction), $y_{RCl}(\xi_e)$ and $y^*_{RCl}(\xi_e)$ are the activity coefficients of RCl and its transition state, respectively, both evaluated at

equilibrium, $C_{RCl}(\xi_e)$ is the equilibrium concentration of RCl , and C_o is the concentration in the thermodynamic standard state. The specific rate of ionization of RCl in ideal solution is κ_f . Eq. (8) relates $1/\tau$ to the equilibrium thermodynamic derivative $(\partial A/\partial\xi)_e$, whose behavior near the consolute point can be analyzed on the basis of the Griffiths-Wheeler rules.[1]

III. 2 Griffiths- Wheeler Analysis

The analysis of any critical phenomenon begins with the separation of the thermodynamic variables into two classes: (1) "fields," such as temperature, pressure, and component chemical potentials, which are the same in each co-existing phase, and (2) "densities," such as entropy, enthalpy, and component concentrations, which have different values in each co-existing phase. Being a difference in chemical potentials, A is a field, while ξ is a density; hence, the derivative $(\partial\xi/\partial A)_e$ is the derivative of a density with respect to a field. Arguing on the basis of the principle of universality, Griffiths and Wheeler assert that the divergence of such a derivative depends upon the number of densities which are required as independent variables.[1]

An evaluation of the critical properties of $(\partial\xi/\partial A)_e$ thus rests upon a determination of the number and character of the independent thermodynamic variables. For simplicity of argument, we shall consider for the moment the reaction taking place above the consolute temperature, where all components are miscible. Let X_{RCl}, $X_{HOH,}$, $X_{ROH,}$,$X_{HCl,}$and X_{IBA} be the mole fractions describing the composition, where X_{IBA} is the mole fraction of isobutyric acid. All of these are densities. The remaining variables are the temperature and pressure, both of which are fields. The total number of variables describing the system is thus seven.

Not all of these are independent, however. Since Eq. (7) conserves moles, the mole fraction of isobutyric acid is constant throughout the reaction,

$$X^o_{IBA} = X_{IBA} \tag{9}$$

Also the mole fractions of the products are related to those of reactants by the equations:

$$X^o_{RCl} = X_{RCl} + X_{ROH} \tag{10}$$

$$X^o_{HOH} = X_{HOH} + X_{HCl} \tag{11}$$

$$X_{ROH} = X_{HCl} \tag{12}$$

The initial values for the mole fractions of isobutyric acid, t-amylchloride, and water, X^{o}_{IBA}, X^{o}_{RCl}, and X^{o}_{HOH}, respectively, are established when the system is prepared in the laboratory. These values, along with the pressure, locate the critical point along the critical line. In addition, at equilibrium,

$$A = 0 \tag{13}$$

Eqs. (9) - (13) constitute a total of five constraints on the seven variables describing the system. Hence, the number of thermodynamically independent variables is 7 - 5 = 2. These are P and T, which are both fields. The former equals one atmosphere, while the latter is specified by the thermostat. In the case where only fields are independent, $\left(\partial\xi / \partial A\right)_e$, which is the derivative of a density respect to a field, should diverge like the isothermal compressibility of a one-component fluid. According to Eq. (8), $1/\tau$ should go to zero. Since the critical point is approached along an isobar, the exponent is $1 - \left(1/\delta\right) = 1 - \left(1/4.9\right) = 0.80$.[11] This value of the exponent agrees within experimental error with our measured value, x = 0.63 ± 0.28.

IV. Discussion

Near the consolute point of a multi-component fluid, there are fluctuations in temperature, pressure, and composition. Where the rate of chemical reaction in such a system is slow as compared with the rates of dissipation of these fluctuations by transport, the reaction kinetics are homogeneous.[4] This is the assumption behind the analysis in Sect. III.1, where $1/\tau$ was found to be proportional to $\left(\partial A / \partial\xi\right)_e$. In considering the divergence of $\Delta\left(1/\tau\right)$, we have ignored in Eq. (8) any critical behavior in the rate coefficient κ_f, or in the ratio, $y_{RCl}\left(\xi_e\right)$ / $y^{*}_{RCl}\left(\xi_e\right)$. While little is known about the critical behavior of the former, the activity coefficients of third components, in the dilute solution near the critical point of a binary solvent, are not expected to diverge.[12]

When t-amylchloride is added to isobutyric acid + water, the critical point is raised. This is due to the fact that t-amylchloride is more soluble in one of the solvent pair (probably water) than in the other. Moreover, this effect depends upon the amount of t-amylchloride added. Indeed,

when only 100 μL of t-amylchloride are added to 25 mL of the solvent mixture, the critical point is 32.3 C. Suppression of the rate of reaction still occurs in this mixture, nevertheless, but as shown in Fig. 3, it is shifted to center on the new consolute temperature. This confirms the assumption of Griffiths and Wheeler,[1] that so far as the critical response of multi-component systems is concerned, any point along the critical line is the same as any other.

In enumerating the thermodynamic variables determining the critical behavior of $\left(\partial A / \partial \xi\right)_e$, we have considered reaction in the one-phase region above the consolute point. Most of our conductivity data were, however, collected below the consolute point by probing the top phase while it was in instantaneous equilibrium with the lower. Nevertheless, when two phases are present, our conclusions remain unchanged, since there are then 14 variables and 12 constraints; and the independent variables continue to be only temperature and pressure. One must also consider side reactions such as the loss of Cl^- by t-amylchloride to form 2-methylbutene-2 or 2-methylbutene-1, as well as sequential reactions, such as the esterification of t-amylalcohol by isobutyric acid. None of these can change the count of independent variables, however, since with the introduction of each new chemical component there comes an additional constraint equation associated with the reaction which forms it.

In the experiments described above, we have demonstrated that the rate of hydrolysis of t-amylchloride suffers critical slowing down along the critical isopleth of isobutyric acid + water. In the multicomponent space which includes t-amylchloride, we have shown that the effect probably occurs along a critical line, since the slowing down is centered on the local critical temperature as determined by the initial amount of t-amylchloride added to the mixture. Finally, the experimental value of the exponent governing the temperature dependence of the degree of slowing down appears to be consistent with that predicted on the basis of the principle of universality.

Roman Symbols:		**Greek Symbols**		**Subscripts**	
A	reaction affinity	δ	critical exponent	b	background
C	molar concentration	Δ	time delay	c	critical

P	pressure	ε	$\left(= \left\lvert \left(T - T_c\right) / T_c \right\rvert\right)$	e	equilibrium
R	gas law constant	κ	specific reaction rate	f	forward
T	temperature	ξ	reaction variable	IBA	isobutyric acid
t	time	σ	ionic conductivity	o	standard state
X	mole fraction	τ	relaxation time	**Superscripts**	
x	reaction critical exponent			o	initial
y	activity coefficient			*	transition state

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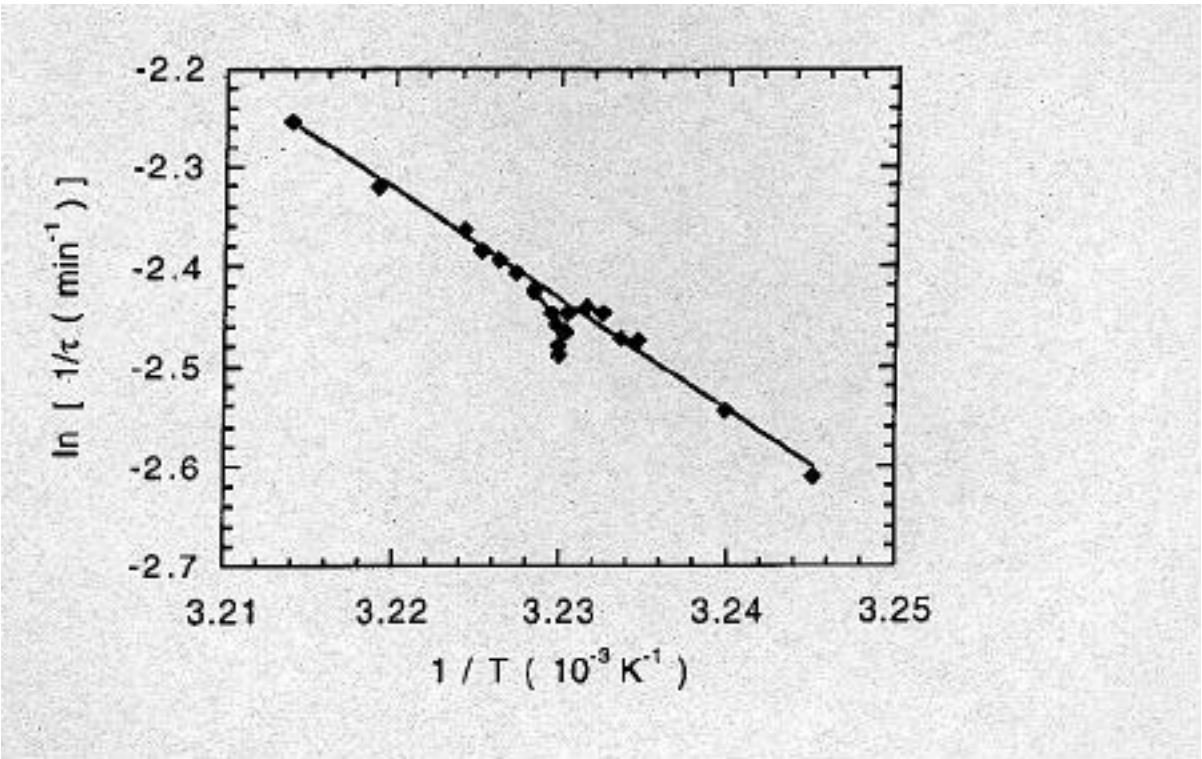
Captions

Fig. 1. Arrhenius Plot of the Specific Rate of Hydrolysis of 100 μl of t-Amylchloride in 25 mL of Isobutyric Acid + Water at its Consolute Composition. The least squares line, not including the eight points in the vicinity of the critical temperature $\left(1 / T_c = 3.230 \times 10^{-3} K^{-1}\right)$, is given by Eq. (2).

Fig. 2. Log-Log Plot of the Suppression, $\Delta\left(1 / \tau\right)$, of the Specific Rate of Reaction as a Function of $\varepsilon = \left|T - T_c\right| / T_c$, where T is the Temperature and T_C is the Critical Temperature. The slope gives the critical exponent, x = 0.63 ± 0.28.

Fig. 3. Temperature Dependence of the Specific Rate, $1 / \tau$, of Hydrolysis of 100 μl of t-Amylchloride in 25 mL of Isobutyric Acid + Water at its consolute Composition. The critical temperature is 32.3 C.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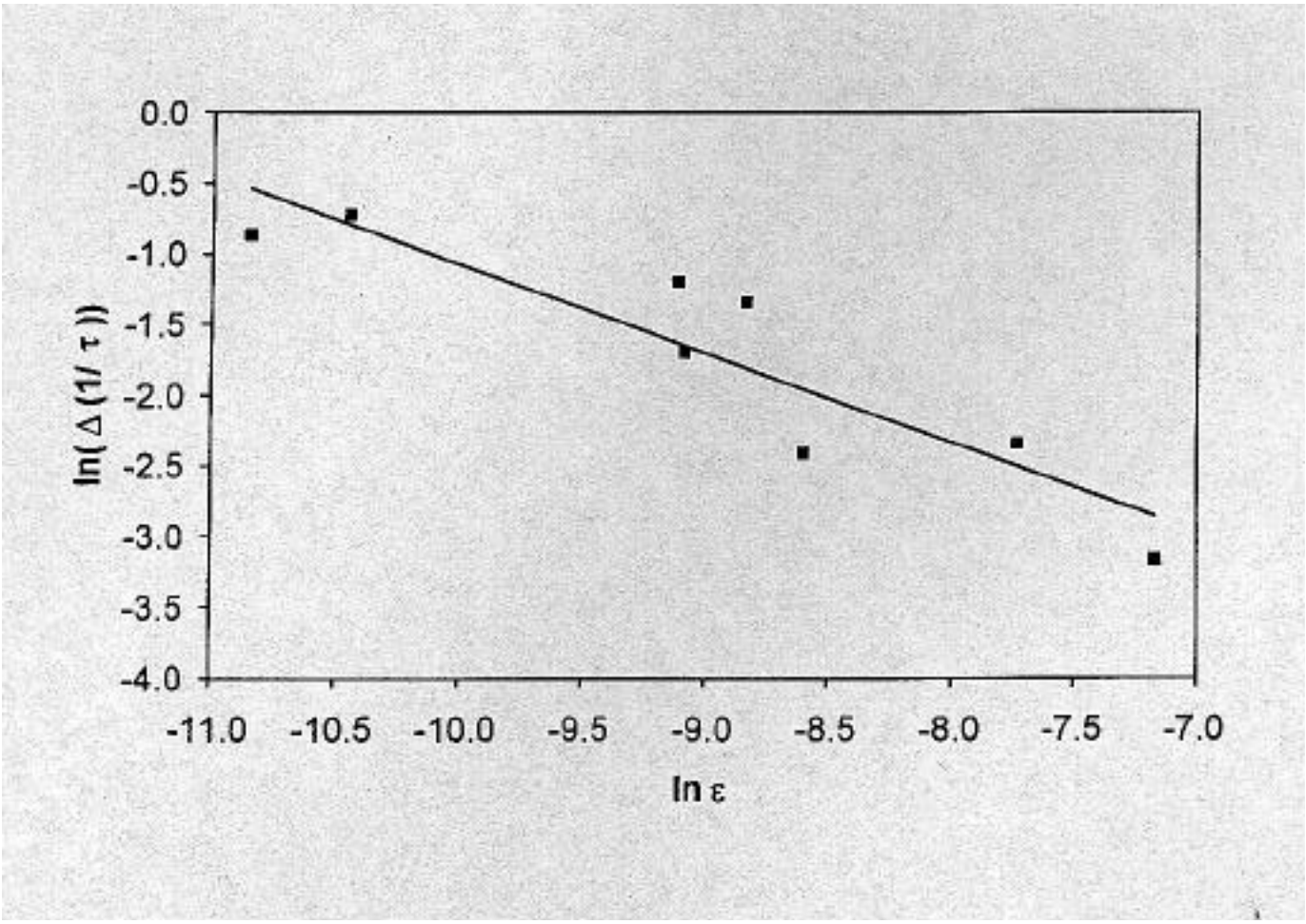
-2.3
-2.4
-2.5
-2.6
-2.7
ln [1/τ (min⁻¹)]
3.21
3.22
3.23
3.24
3.25
1 / T (10⁻³ K⁻¹)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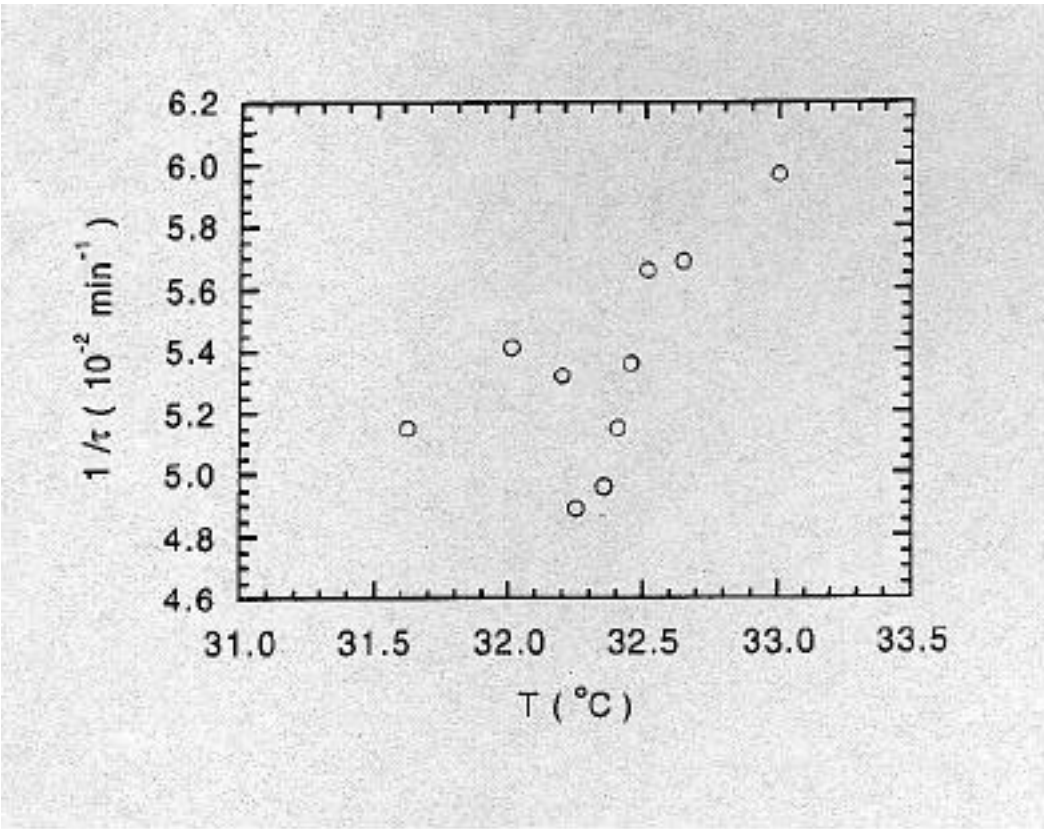
ln ε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5.2
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1 /τ (10^-2 min^-1)
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31.5
32.0
32.5
33.0
33.5
T (°C)