Chemical Dynamics and Critical Phenomena: Electrical Conductivity and Reactivity of Benzyl Bromide in Triethylamine + Water Near its Consolute Point

Christopher D. Specker · Joel M. Ellis · James K. Baird

Abstract   The binary liquid mixture of triethylamine + water has a lower consolute point at a critical composition of 32.27 mass% triethylamine. Starting at a temperature within the one-phase region, the electrical conductivity of a sample of this mixture was measured and found to increase smoothly with increasing temperature before *falling sharply* at 291.24 K (18.09°C). Since opalescence was visible at this temperature, it was identified with the critical solution temperature of the binary mixture. A solution of 90 μL of benzyl bromide dissolved in 90 mL of 32.27 mass% triethylamine + water was prepared, and the resulting Menschutkin reaction between benzyl bromide and triethylamine was allowed to come to equilibrium. The electrical conductivity of this equilibrium mixture was measured in the one-phase region and was found to increase smoothly with increasing temperature before *rising sharply* at 291.55 K (18.40°C). This temperature was identified as the critical temperature of the ternary. The rate of approach of the ternary mixture to chemical equilibrium was also measured and shown to be governed by a first-order rate law. The temperature dependence of the rate coefficient followed the Arrhenius equation up to a temperature of about 290.74 K (17.59°C). Above this temperature, the rate coefficient fell by as much as 22% below the value predicted by extrapolation of the Arrhenius equation. This suppression in the rate reaction in the vicinity of the critical temperature can be interpreted as evidence for the existence of critical slowing down.

Keywords   Benzyl bromide · Critical slowing down · Electrical conductivity · Reaction rate · Triethylamine · Water

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1 Introduction

For the case of a binary liquid mixture with a miscibility gap, the point of convergence of the sides of the coexistence curve in the temperature versus mole fraction phase diagram is termed the *consolute point*. The extreme value of the temperature along the coexistence curve is called the *critical solution temperature*. If the coexistence curve is *concave down*, the maximum temperature along the curve corresponds to an *upper critical solution temperature* (UCST). If the curve is *concave up*, the minimum temperature along the curve corresponds to a *lower critical solution temperature* (LCST) [1]. Since the distinction between two coexisting liquid phases disappears at the consolute point, its thermodynamic properties are governed by the *principle of critical point universality* [2–7].

To explore the effect of this principle on the net rate of a chemical reaction, one can use as the solvent for the reaction the homogeneous liquid phase that exists near the consolute point of a binary mixture [8–15]. Consider the general chemical reaction

$$\nu_1(1) + \nu_2(2) \rightarrow \nu_3(3) + \nu_4(4) \tag{1}$$
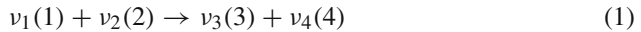
in which reactants (1) and (2) are converted into products (3) and (4). The respective stoichiometric coefficients are ν_1, ν_2, ν_3, and ν_4. If we let $c_i(0)$ be the initial concentration of species, i, then the concentration, $c_i(t)$, at a later time, t, is $c_i(t) = c_i(0) \pm \nu_i \xi(t)$, where $\xi(t)$ is the extent of reaction, and the upper sign applies to products while the lower sign applies to reactants [11–17]. At time $t = 0$, the extent of reaction has the value $\xi(0) = 0$, while at chemical equilibrium, it has the value $\xi = \xi_e$. If the kinetics are *first order*, the rate law is

$$\frac{d\xi}{dt} = -\frac{1}{\tau}(\xi - \xi_e) \tag{2}$$

where $1/\tau$ is the specific relaxation rate [13,15–18]. The Gibbs free energy difference separating reactants and products is

$$\Delta G = \nu_4 \mu_4 + \nu_3 \mu_3 - \nu_2 \mu_2 - \nu_1 \mu_1 \tag{3}$$

In terms of ΔG, the specific relaxation rate is given by

$$\frac{1}{\tau} = \frac{r'(\xi_e)}{RT} \left(\frac{\partial \Delta G}{\partial \xi}\right)_e \tag{4}$$

where R is the universal gas constant, T is the absolute temperature, $r'(\xi_e)$ is the rate of reaction in the forward direction, and the subscript, e, denotes evaluation at chemical equilibrium [13,15–18].

The observation of critical effects at the consolute point of a multicomponent mixture depends on a count of the number of inert components [15]. A component is considered to be inert if it is not involved in any chemical reaction. If the mixture contains *two or more inert components*, no critical effect is expected. If the mixture

contains *only one inert component*, then for T near the critical temperature, T_c, the thermodynamic derivative, $(\partial \Delta G / \partial \xi)_e$, 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* as T approaches T_c. 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* as T approaches T_c. In either circumstance, the value of x should be independent of the chemical nature of the fluid [2–7]. For a mixture that contains *no more than one inert component*, Eq. 4 implies that the net rate of reaction with *first-order* kinetics should *slow down* in the critical region.

When the reaction is irreversible and the kinetics are *second order*, the rate law involves both $(\xi - \xi_e)$ and $(\xi - \xi_e)^2$, and the thermodynamic derivatives, $(\partial \Delta G / \partial \xi)_e$ and $(\partial^2 \Delta G / \partial^2 \xi)_e$ [14]. Arguments can be marshaled to suggest that under conditions where there are *no inert components*, $(\partial \Delta G / \partial \xi)_e$ and $(\partial^2 \Delta G / \partial^2 \xi)_e$ should both go to zero as T approaches T_c [14]. The disappearance of these thermodynamic derivatives is sufficient to cause the net rate of reaction to *slow down* in second-order kinetics.

In search of kinetic critical phenomena, we have measured the rates of nine different chemical reactions in three different binary liquid mixtures [10–15]. The solvent pairs were isobutryric acid + water (UCST), 2-butoxyethanol + water (LCST), and triethylamine + water (LCST). In each case, the products included strong electrolytes [10–14] or gases [15] or both [15]. The nine reactions proceeded by various mechanisms and were governed by rate laws that were either first order [10–13, 15] or second order [14]. In seven cases, *slowing down* of the reaction rate was evident [10–15]. In three of these seven cases, the critical region was found to be subdivided into a temperature range over which the reaction *slowed down* and a contiguous temperature range over which the reaction *speeded up* [12, 13, 15]. In two cases, no critical effect was detected [15].

In each of our previous experiments [10–15], we have relied upon the known chemistries of the various reactants, products, catalysts, and solvents in order to enumerate the inert components. When identifying inert components by this method, we recognize, however, that although a reaction may be familiar in a pure solvent, it may fail to appear, or even be supplanted by another reaction when the solvent is a binary liquid mixture with a consolute point. As a replacement for this intuitive method, we have chosen to analyze our equilibrium reaction mixtures by GC/MS; this instrumental method permits us to identify the impurities present in the original materials and also to use the absence of suspected products to rule out the occurrence of potential side reactions. In our previous experiments [10–15], we have also relied upon the visual detection of critical opalescence to determine the critical temperature. To avoid the subjectivity associated with visual observations, we have chosen to associate the critical temperature with the temperature of onset of the sharp change in electrical conductivity that occurs when critical opalescence appears. In what follows, we apply these improvements in technique to the analysis of the critical slowing down which can be observed in the pseudo-first-order Menschutkin reaction [8] of benzyl bromide near the lower consolute point of triethylamine + water.

2 Experiment

Triethylamine and benzyl bromide were purchased from Aldrich and used without further purification. Water was once distilled from a glass system. The binary solvent mixture, triethylamine + water, was prepared at its critical composition (32.27 mass% triethylamine [13]) by weighing. A sample of the solvent mixture was equilibrated in a 14 L water bath, and the electrical conductivity was measured as a function of temperature using a Hanna Instruments Model HI 9032 conductivity meter. The data are summarized in Table 1. The critical temperature, T_c^0, of the binary mixture was identified with the temperature 291.24 K (18.09°C) at which the electrical conductivity begins its rapid descent. At this temperature, critical opalescence was well developed.

After reaching the thermal equilibrium with the water bath, $90\,\mu L$ of benzyl bromide was added to 90 mL of the solvent mixture at a temperature where only one phase was present. The stoichiometry of the expected Menschutkin reaction [8] is

$$C_6H_5CH_2Br + (C_2H_5)_3N \rightarrow (C_6H_5CH_2)(C_2H_5)_3N^+ + Br^- \qquad (5)$$
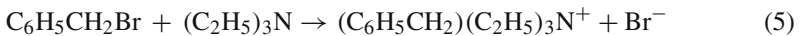
Since the product, benzyl triethylammonium bromide, is a strong electrolyte, the progress of the reaction could be followed by measuring the electrical conductivity as a function of time.

The reaction vessel was a 100 mL cylindrical glass flask with two necks, one of which was used to introduce the reactant, while the other was used to introduce the probe of the conductivity meter. In the case of all our measurements, the contents of the reaction vessel were vigorously stirred with a magnetic stirrer to guarantee the homogeneity of the mixture. The temperature controller and temperature measuring equipment were as previously described [11, 12].

At chemical equilibrium, an aliquot was extracted from the reaction mixture, and its composition was analyzed using an Agilent 6890 Series gas chromatograph feeding an Agilent 5973 mass selective detector. This GC/MS combination revealed the presence of unreacted benzyl bromide, triethylamine, water, and N-benzyl-N,N-diethylamine. The latter substance is thought to be a decomposition product of benzyl triethylammonium bromide, which was produced in the sample upon its entrance into the mass spectrometer section of the GC/MS. Benzyl triethylammonium bromide was missing

Table 1 Electrical conductivity as a function of temperature for a mixture of triethylamine + water at its consolute composition of 32.27 mass% triethylamine

T (°C)	$\sigma\ (\mu S \cdot cm^{-1})$	T (°C)	$\sigma\ (\mu S \cdot cm^{-1})$	T (°C)	$\sigma\ (\mu S \cdot cm^{-1})$
9.85	468	16.55	582	18.14	622
10.33	476	17.44	604	18.2	619
10.98	483	17.72	614	18.22	406
12.82	512	17.85	618	18.22	463
14.34	538	18	623	18.225	441
15.44	557	18.09	628	18.39	660

Table 2 Electrical conductivity as a function of temperature for an equilibrium mixture of $100\,\mu L$ of benzyl bromide in $100\,mL$ of triethylamine + water at its consolute composition of 32.27 mass% triethylamine

T (°C)	$\sigma\ (\mu S \cdot cm^{-1})$	T (°C)	$\sigma\ (\mu S \cdot cm^{-1})$	T (°C)	$\sigma\ (\mu S \cdot cm^{-1})$
8.99	603	16.091	740	18.35	797
9.36	610	16.678	754	18.37	802
9.99	622	17.131	766	18.373	814
10.56	631	17.53	778	18.379	797
11.07	640	17.85	787	18.395	807
11.5	647	18.154	797	18.401	833
12.4	665.2	18.2	798	18.417	850
13.192	681	18.213	799	18.427	856
14.353	705	18.277	799	18.459	892
15.03	718	18.30	799	18.559	905
15.548	728	18.34	800		

from the spectrum, because being an ionic compound, this quaternary ammonium salt should not have sufficient vapor pressure to be detected by mass spectrometry. The GC/MS spectrum also revealed traces of benzyl chloride and dibutyl ethylamine, which were likely impurities in benzyl bromide and triethylamine, respectively. In our reaction mixture, neither benzyl chloride nor dibutyl ethylamine is inert, however, because each can be expected to undergo Menschutkin reactions like their respective analogues, benzyl bromide and triethylamine. There was no evidence in the GC/MS spectrum for the presence of benzyl alcohol, which would otherwise be expected as the product of the side reaction of benzyl bromide with water.

In general, the addition of a third component to a binary liquid mixture with a consolute point shifts the critical temperature [11–15]. As a consequence of this effect, it becomes necessary to draw a distinction between the critical temperature, T_c^0, of the binary solvent mixture and the critical temperature, T_c, of the multicomponent reaction mixture at chemical equilibrium. We have found in general that

$$T_c = T_c^0 + ac \qquad (6)$$

where a is an empirical constant and c is the initial concentration of the reactant [13–15].

To establish a value for T_c, the electrical conductivity of the equilibrium reaction mixture was measured as a function of temperature. These measurements are summarized in Table 2. We chose to identify T_c with the temperature 291.55 K (18.40°C) at which the conductivity begins its rapid ascent. At this temperature, critical opalescence was also well developed. On the basis of $T_c^0 = 291.24\,K$ and $T_c = 291.55\,K$, and the initial concentration of benzyl bromide, which was $c = 8.41 \times 10^{-3}\,M$, we used Eq. 6 to calculate $a = 36.9\,K/M$.

By virtue of the stoichiometry of the reaction in Eq. 5, the extent of reaction, $\xi(t)$, could be identified with the concentration of the reaction product, benzyl

Fig. 1 Guggenheim plot of the electrical conductivity versus time for a solution of $90\,\mu$L of benzyl bromide in 90 mL of the binary solvent, triethylamine + water, at its critical composition of 32.27 mass% triethylamine. The temperature was 287.95 K (14.80°C) and the value of the Guggenheim time delay was $\theta = 38.33$ min
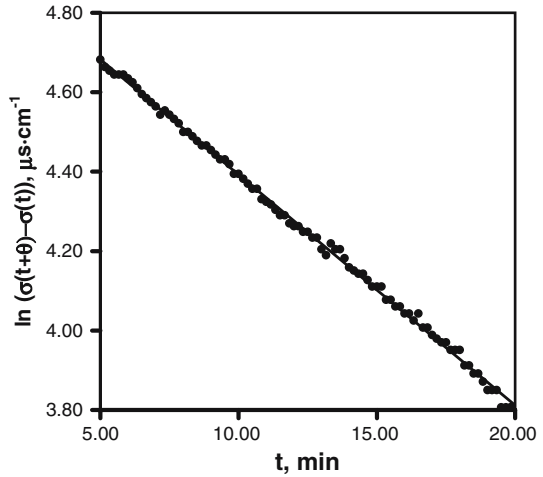
triethylammonium bromide. According to the Kohlrausch law of independent migration of ions [19], the electrical conductivity, $\sigma(t)$, of the reaction mixture at a time, t, during the course of the reaction can be represented by

$$\sigma(t) = \sigma^0 + \Lambda\xi(t) \tag{7}$$

The leading term, σ^0, in Eq. 7 is the electrical conductivity of the binary solvent mixture, while Λ is is the molar conductance of the product.

Since triethylamine is in vast excess in the reaction mixture, the rate law is pseudo-first order, and Eq. 2 applies. The integral of Eq. 2 is

$$\xi(t) = \xi_e(1 - e^{-t/\tau}) \tag{8}$$

Upon substitution of Eq. 8 into Eq. 7, we obtain

$$\sigma(t) = \sigma^0 + \Lambda\xi_e(1 - e^{-t/\tau}) \tag{9}$$

The Guggenheim method [20] can be used in Eq. 9 to determine the value of $1/\tau$ from the experimental measurements of $\sigma(t)$ versus t. For a fixed value of the time delay, θ, separating two sequences of electrical conductivity measurements, Eq. 9 can be rewritten in the form,

$$\sigma(t + \theta) - \sigma(t) = \Lambda\xi_e(1 - e^{-\theta/\tau})e^{-t/\tau} \tag{10}$$

Figure 1 shows a semilogarithmic plot of Eq. 10 for a run where the temperature of the reaction mixture was significantly below the critical temperature. The data form a good straight line, which proves that the kinetics are first order. The slope of the line is equal to $-1/\tau$. For comparison, Fig. 2 shows a semilogarithmic plot of Eq. 10 for a set of data where the temperature lay within the critical region of the reaction mixture.

Fig. 2 Guggenheim plot of the electrical conductivity versus time for a solution of 90 μL of benzyl bromide in 90 mL of the binary solvent, triethylamine + water, at its critical composition of 32.27 mass% triethylamine. The temperature was 291.35 K (18.20°C) and the value of the Guggenheim time delay was $\theta = 40.00$ min

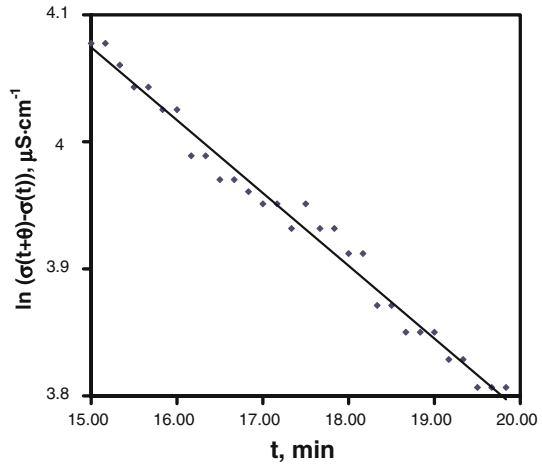**Table 3** Specific relaxation rate, $1/\tau$, as a function of temperature, T, for the Menschutkin reaction of 90 μL of benzyl bromide in 90 mL of triethylamine + water at its consolute composition of 32.27 mass% triethyalamine

T (°C)	$1/\tau$ (10^{-2} min^{-1})	T (°C)	$1/\tau$ (10^{-2} min^{-1})
18.40	7.35	16.66	6.33
18.30	11.9	16.00	6.10
18.27	8.01	15.40	5.95
18.20	5.73	15.13	5.83
18.18	6.15	14.80	5.82
18.17	5.34	14.52	5.69
18.12	5.80	14.00	5.65
18.08	6.00	13.50	5.47
18.05	6.07	13.00	5.28
17.91	6.06	12.00	5.03
17.68	6.23	11.00	4.76
17.58	6.37	10.52	4.65
17.00	6.21		

The data in Fig. 2 are a bit more scattered than those in Fig. 1. This contrast persisted generally in the case of benzyl bromide in triethylamine + water, when Guggenheim plots made inside and outside the critical region were compared.

Table 3 lists values of $1/\tau$ determined with the Celsius temperature decreasing. After conversion of the Celsius temperature to absolute temperature by the addition of 273.15, these data were plotted in the form, $\ln(1/\tau)$ versus $1/T$, as shown in Fig. 3. The data collected at temperatures that are far below the critical temperature at $T_c = 291.55$ K could be fitted to the Arrhenius line,

$$\ln(1/\tau) = \ln A - E/RT \qquad (11)$$

where $A = 11.4 \pm 0.3$ min^{-1}, $E = 34,100 \pm 800$ J·mol^{-1}, and $R = 8.314$ J·K^{-1}·mol^{-1}.

3 Discussion and Conclusions

In a mixture of triethylamine + water, the carriers of electric current are the triethyl ammonium ion and the hydroxide ion, which are the products of the Bronsted–Lowry acid/base reaction of triethylamine with water. For the case of a ternary mixture of benzyl bromide in triethylamine + water, the principle current carriers are the benzyl triethylammonium ion and the bromide ion, which are the products of the Menschutkin reaction summarized in Eq. 5. Procaccia and Gitterman [21] have suggested that measurements of transport coefficients as a function of temperature in the critical region of a fluid supporting a chemical equilibrium can differ sharply from similar measurements collected far from the critical point. In our Table 2, the electrical-conductivity data for temperatures in the two-phase region above the critical temperature at 291.55 K (18.40°C) would seem to bear this out. For comparison with these measurements, we should mention the work of Gopal et al. [22] and Ramakrishnan et al. [23], who measured the electrical resistances of the individual phases that coexist in the two-phase region below the UCST of several nonreacting, polar + nonpolar mixtures. They reported that one phase had a resistance rather much higher, while the other phase had a resistance rather much lower than the resistance determined for the homogeneous fluid in the single-phase region at temperatures above the UCST.

For some of the temperatures just below the critical temperature at 291.55 K (18.40°C) the value of $1/\tau$ in Fig. 3 reaches only about 78% of the value that would be expected on the basis of the Arrhenius line. This decrease in specific reaction rate is an example of critical *slowing down*. The absence of benzyl alcohol in the GC/MS spectrum indicates that water does not react significantly with benzyl bromide. As mentioned above, however, water reacts with triethylamine to produce triethylammonium hydroxide. Since triethylammonium hydroxide cannot be isolated from the mixture, however, it should perhaps be regarded as a "species" rather than as a "component." To the extent that the formation of triethylammonium hydroxide can be ignored, water can be considered to be inert. With water identified as the sole inert component, the *slowing down* apparent in Fig. 3 should be considered to be an example of a *weak* critical effect.

Fig. 3 Arrhenius plot of the specific relaxation rate, $1/\tau$, as a function of the reciprocal of the absolute temperature, $1/T$, for the Menschutkin reaction of $90\,\mu L$ of benzyl bromide in 90 mL of triethylamine + water at its consolute composition of 32.27 mass% triethylamine. The critical solution temperature of the reaction mixture at equilibrium was $T_c = 291.55$ K (18.40°C)
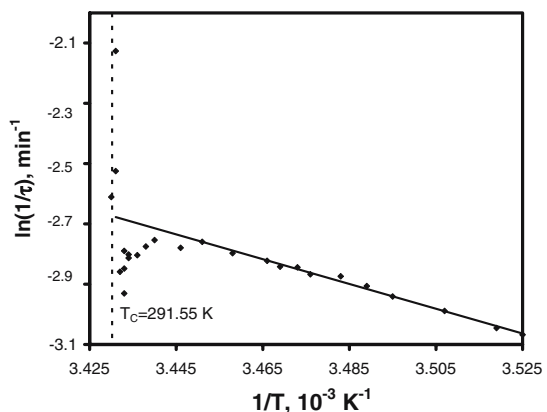
The two points in Fig. 3, corresponding to the two temperatures closest to the critical point, are scattered and provide only a hint of what might be considered to be *speeding up*. This contrasts with the firm evidence in support of *speeding up* that exists in the case of the reaction of 2-chloro-2-methylbutane in isobutyric acid + water (UCST) [12,13], the reaction of 2-bromo-2-methylpropane in triethylamine + water (LCST) [13], and the decomposition of acetone dicarboxylic acid in isobutyric acid + water (UCST) [15]. *Speeding up* also has been observed, for example, in the rate of dielectric relaxation in ethanol + dodecane (UCST) [24] and perhaps also in the rate of spinodal decomposition in triethylamine + water (UCST) [25].

Finally, it should be mentioned that critical *slowing down* is predicted by most theories of chemical reactions taking place near a critical point [16–18,26–29]. Except for the suggestion by Procaccia and Gitterman [18] that the thermodynamic criterion for the stability of coexisting phases permits $(\partial \Delta G/\partial \xi)_e$ to increase before it ultimately goes to zero as $T \to T_c$, we do not have an explanation for *speeding up*.

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