

Figure 7. Trajectory of the tricritical line in a quinary system in $T-\delta-\epsilon$ space, taken from ref 8 (schematic).

the ionic branch enters the 1-bar space from below the melting point at some higher value of δ .

Conclusion

A representation is suggested for the trajectories of the

three-phase bodies in quinary systems by arranging vertical sections through the pseudoternary phase prism at constant oil/brine ratio and constant brine concentration in $T-\gamma-\delta$ space, where γ is the weight percentage of the nonionic and the ionic detergent in the system, and δ is that of the ionic amphiphile in the mixture of the two amphiphiles. These trajectories vary strongly with the chemical nature of both amphiphiles as well as with the brine concentration. In the particular system chosen as a representative example, one finds a nonionic and an ionic branch of the trajectory which pass each other at an intermediate value of δ , thus dividing the phase behavior of the system into one part that is dominated by the nonionic, and one that is dominated by the ionic detergent. If, for a given oil, the temperature and the brine concentration are given, one may cut an isothermal section through the corresponding $T-\gamma-\delta$ space at that temperature in order to find the optimum ratio δ for this particular combination of detergents which yields the highest mutual solubility between brine and oil combined with the lowest interfacial tensions. Once a trajectory has been determined, it, furthermore, permits a study of the properties of the microemulsion as they change with δ . Last but not least, the trajectories may be used as guides for tracing the tricritical line.

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Experimental Observations of Complex Dynamics in a New Bromate Oscillator: The Bromate–Thiocyanate Reaction in a CSTR

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In a continuously stirred tank reactor (CSTR) the reaction between bromate and thiocyanate in acidic medium (HClO₄) exhibits sustained oscillations in the potential of a platinum redox over a wide range of flow rates and input concentrations. In closed system environments and in excess bromate concentrations the stoichiometry of the reaction is $6BrO_3^- + 5SCN^ + 2H_2O \rightarrow 3Br_2 + 5SO_4^{2-} + 5CN^- + 4H^+$. The production of bromine is preceded by a finite induction period. On varying the dynamical variable of the flow rate of reactants into the CSTR at fixed input concentrations, one observes various oscillatory states. The bifurcation sequence is highlighted by persistent quasi-periodic behavior.

Introduction

The number of chemical oscillators discovered in the past 5 years far outstrips the number of all the oscillators known before 1980^{1} This came directly on the heels of the discovery of a plausible algorithm for the systematic design of chemical oscillators.² The most significant discovery of this algorithm is the subset of chlorite-based oscillators.³ Among the chlorite oscillators were two-component, uncatalyzed oscillators such as the chlorite-iodide⁴ and chlorite-thiosulfate systems.⁵ Despite the apparent simplicity of the two-component oscillators, the chlorite-thiosulfate system displays a rich and varied dynamical behavior by altering only the dynamical variable of flow rate of reactants into the

reactor. Other interesting dynamical behavior has been observed in the chlorite-thiourea reaction in both batch and continuously stirred tank reactor (CSTR) conditions.6

Bromate-driven oscillators are by far the most thoroughly studied of all known oscillators,⁷ especially the Belousov-Zhabotinskii reaction and its variations.⁸ Until recently, however, uncatalyzed two-component bromate oscillators were unknown. A few two-component bromate oscillators have now been discovered, and they resemble chlorite-based oscillators more than the prototype Belousov-Zhabotinskii systems.9 Using the chlorite-iodide reaction¹⁰ and the bromate-iodide reaction⁹ as typical examples of these subclasses of chemical oscillators, one notices that in both cases (a) oscillations are only possible when the oxidant is in stoichiometric excess,¹¹ (b) more than one

⁽¹⁾ Epstein, I. R. J. Phys. Chem. 1984, 88, 187-198.

²⁾ Epstein, I. R. In Chemical Instabilities; Nicolis, G., Baras, F., Eds.; D. Reidel: Dordrecht, Holland, 1984; pp 3-18.

⁽³⁾ Orban, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. J. Am. Chem. Soc. 1982, 104, 5911-5918

⁽⁴⁾ Dateo, C.; Orbán, M.; De Kepper, P.; Epstein, I. R. J. Am. Chem. Soc. 1982, 104, 504-509.

⁽⁵⁾ Orban, M.; De Kepper, P.; Epstein, I. R. J. Phys. Chem. 1982, 86, 431-433.

⁽⁶⁾ Alamgir, M.; Epstein, I. R. Int. J. Chem. Kinet. 1985, 17, 429-439.

⁽⁷⁾ Noyes, R. M. J. Am. Chem. Soc. 1980, 102, 4644–4649.
(8) (a) Belousov, B. P. Sb. Ref. Radiat. Med. 1958 1959, 145. (b) Zhabotinskii, A. M. Dokl. Akad. Nauk SSSR 1959, 157, 392.

⁽⁹⁾ Alamgir, M.; De Kepper, P.; Orbán, M.; Epstein, I. R. J. Am. Chem. Soc. 1983, 105, 2641-2643

⁽¹⁰⁾ Kern, D. M.; Kim, C-H. J. Am. Chem. Soc. 1965, 87, 5309-5313.

stoichiometry is possible depending upon the ratio of the initial concentrations of oxidant to reductant, and (c) more than one "drive" reaction is possible in the reaction mixture.¹²

The idea of chemical oscillations has now been widely accepted. With the emergence of so many new chemical oscillators, the main thrust of experimental work is now on the mechanism of the new oscillators and the unraveling of any dynamic phenomena associated with any oscillator. The chlorite-thiosulfate reaction has shown complex periodic and aperiodic oscillations and chemical chaos.¹³ The wide variety of oscillatory states observed in the chlorite-thiosulfate⁵ and chlorite-thiourea⁶ reactions is rivaled only by the venerable Belousov-Zhabotinskii (BZ) reaction.^{14,15} The BZ reaction was the first to show period doubling of oscillations,¹⁶⁻¹⁹ multiple-peak periodic oscillations, a bifurcation sequence (of oscillatory states) that can be modeled by the iterations of unimodal one-dimensional maps,16 and deterministic chemical chaos.^{21,22} Apart from the first two properties, the latter two properties of the BZ system have not been discovered in any other chemical system. It has also been difficult to accept that global behavior of a chemical oscillator which is influenced by many different chemical species can produce such coherence as onedimensional dynamics and even deterministic chaos.

We report in this paper the discovery of a new two-component bromate oscillator with thiocyanate as the reductant. This new oscillator displays very large amplitude oscillations in the redox potential of a platinum electrode in a CSTR. What sets this oscillator apart from the others is that it is the first two-component bromate oscillator which shows a remarkable variety of periodic and aperiodic oscillatory states by altering the dynamical variable of flow rate of reactants into the reactor. Our interest was initially roused in this system because thiocyanate rapidly decolorizes bromine, while bromate can be reduced by thiocyanate to give bromide according to the reaction²³

$$BrO_3^- + SCN^- + H_2O \rightarrow Br^- + SO_4^{2-} + CN^- + 2H^+$$
 (R1)

Thus in acidic medium, when bromate is in stoichiometric excess, the bromide from reaction R1 can react with bromate to give back bromine²⁴

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow Br_2 + 3H_2O \qquad (R2)$$

which will oxidize thiocyanate, and the cycle begins again.

We felt, then, that at the appropriate flow rate, in stoichiometric excess of acidic bromate solutions, the bromate-thiocyanate reaction could yield oscillatory behavior.

(11) Generally, nonlinearities in bromate oxidations are observed when the bromate concentrations are in stoichiometric excess over the reductant. See: Simoyi, R. H.; Masvikeni, P.; Sikosana, A. J. Phys. Chem. **1986**, 90, 4126. King, D. E. C.; Lister, M. W. Can. J. Chem. **1968**, 46, 279-286.

(12) A good example also is the recently discovered $BrO_3^--CS(NH_2)_2$ oscillator. In excess bromate concentrations the stoichiometry is 8BrO₃⁻ + CS(NH₂)₂ + 8H⁺ + 6H₂O \rightarrow 4Br₂ + 5(NH₄)₂SO₄ + 5CO₂, while in low bromate concentrations the stoichiometry is 4BrO₃⁻ + 3CS(NH₂)₂ + 3H₂O \rightarrow 3CO(NH₂)₂ + 6H⁺ + 3SO₄²⁻ + 4Br⁻. See: Simoyi, R. H. J. Phys. Chem. **1986**, 90, 2802-2804.

- (13) Orbán, M.; Epstein, I. R. J. Phys. Chem. 1982, 86, 3907-3910. (14) Hudson, J. L.; Mankin, J. C. J. Chem. Phys. 1981, 74, 6171-6177.
- (15) Turner, J. S.; Roux, J. C.; McCormick, W. D.; Swinney, H. L. Phys.
- Lett. A 1981, 85A, 9-13.
- (16) Simoyi, R. H.; Wolf, A.; Swinney, H. L. Phys. Rev. Lett. 1982, 49, 245-248.
- (17) Swinney, H. L.; Roux, J.-C. In Non-Equilibrium Dynamics in Chemical Systems; Vidal, C., Pacault, A., Eds.; Springer-Verlag: New York, 1984; pp 124-140.
- (18) Coffman, K.; McCormick, W. D.; Swinney, H. L. Phys. Rev. Lett. 1986, 56, 999-1002
- (19) For a model of the Belousov-Zhabotinskii oscillator with period doubling see: Turner, J. S. In Aspects of Chemical Evolution; Nicolis, G., Herschkowitz-Kaufman, Eds.; Wiley: New York, 1980.
- (20) Hudson, J. L.; Hart, M.; Marinko, D. J. Chem. Phys. 1979, 71,
- 1601-1606. (21) Roux, J.-C.; Simoyi, R. H.; Swinney, H. L. Physica D (Amsterdam)
- 1983, 8D, 257-266 (22) Schmitz, R. A.; Graziani, K. R.; Hudson, J. L. J. Chem. Phys. 1977, 67. 3040-3044.
- (23) Radhakrishnamurti, P. S.; Misra, S. A.; Panda, J. K. Indian J. Chem., Sect. A. 1981, 20A.
- (24) Vogel, A. I. Quantitative Inorgranic Analysis, 3rd ed.; Wiley: New York, 1961; p 383.



Figure 1. Redox potential traces for the batch reaction between bromate and thiocyanate at different initial bromate concentrations showing all the four stages. The arrows denote the point at which production of bromine commences. $[H^+]_0 = 0.06 \text{ M}, [SCN^-]_0 = 0.004 \text{ M}.$



Figure 2. Batch environment absorbance traces at $\lambda = 390 \text{ nm} (Br_2)$ at different initial bromate concentrations. $[H^+]_0 = 0.08 \text{ M}, [SCN^-]_0 =$ 0.004 M.

Experimental Section

The following analytical grade chemicals were used without further purification: potassium bromate (British Drug Houses), potassium thiocyanate (E. Merck), sodium perchlorate (Aldrich), and perchloric acid (70%, PAL Chemicals). The batch reactions were carried out in a 125-mL reactor with a thermostating jacket which maintained a temperature of 25 ± 0.1 °C. The reaction was followed by monitoring the redox potential of the system (platinum electrode with a calomel reference), the potential from a specific bromide electrode (Orion Research), and absorbance of the bromine produced in the reaction ($\lambda = 390$ nm). The spectrophotometric measurements were performed on a Pye Unicam SP1750 UV spectrophotometer equipped with thermostatable compartments. Ionic strength was maintained at 0.2 M (NaClO₄). All solutions were prepared with doubly distilled water.

Flow Experiments. The experiments were carried out in a Pyrex continuously stirred tank reactor of volume 23.5 mL.²⁵ The reactor was fed by a Gilson Miniplus II peristaltic pump with a HP4 pumping head. Three polyethylene tubes were used for input, and one tube was used for the outflow. Long polyethylene tubes of about 3 m each in length were used between the pump and the reactor so as to minimize the pulsating effect of the peristaltic pump in the reactor. Each of the polyethylene tubes ferried perchloric acid, potassium bromate, and potassium thiocyanate, respectively, into the reactor. Since cyanide is one of the products of the reaction, the effluent from the reactor was run into a chilled vat to discourage the escape of the rather volatile HCN. The cyanide was later disposed of as AgCN. The stock solutions were

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⁽²⁵⁾ Same reactor design has also been used in the chlorite-bromide system. See: Alamgir, M.; Epstein, I. R. J. Phys. Chem. 1985, 89, 3611-3614.



Figure 3. (a) Bromate dependence of the induction period in Figure 2. $[H^+]_0 = 0.08 \text{ M}, [SCN^-]_0 = 0.004 \text{ M}.$ (b) Acid dependence of the induction period. $[BrO_3^-]_0 = 0.04 \text{ M}, [SCN^-]_0 = 0.004 \text{ M}.$

prepared in 5-L volumetric flasks. These reservoirs were always refilled when they were about half-full to minimize fluctuations in the concentrations of the stock solutions.

In a typical experiment the reactor was filled at the highest possible pump rate. The pumping rate was next reduced in steps. The pump speed was held at each step for a least three residence times to allow all transients to disappear. After the lowest pump speed was reached the pump speed was next increased back to its former value to probe for possible hysteresis. Our estimation gave reproducibility of flow rate of about $\pm 1\%$. This small fluctuation was mainly due to the degeneration of the polyethylene pump tubes with time. The stirring rate was held constant at about 1000 rpm by a magnetic stirrer.

Results

Batch Experiments. The reaction's behavior in batch appeared to be very similar to the behavior observed with the chlorite-thiourea⁶ and the bromate-thiourea¹² reactions. From the redox potential traces (Figure 1) the reaction proceeds in four stages: an induction period during which the potential remains constant, followed by a very rapid rise in potential to attain another induction period, and finally a slow increase in potential to attain the final value of about 930 mV. The absorbance traces ($\lambda = 390$ nm) were simpler (Figure 2). The production of bromine is preceded



Figure 4. (a) A section of the phase diagram of the bromate-thiocyanate system. [HClO₄]₀ = 0.133 M, $k_0 = 5.25 \times 10^{-4} \text{ s}^{-1}$. (b) Hysteresis and oscillations in the bromate-thiocyanate system. The dashed line denotes the limit of the oscillation amplitude of the platinum electrode potential in the oscillatory state. Symbols are as in (a).

by a finite induction period. There is an inverse relationship between the induction period and the initial concentrations of both acid and bromate (Figure 3, a and b), and these effects are identical. The bromine production commences during the fourth stage in the redox potential traces (Figure 1).

For stoichiometric purposes, a series of experiments had been performed at fixed initial acid and thiocyanate concentrations while the bromate concentrations were varied. At equimolar concentrations of bromate and thiocyanate the reaction followed the stoichiometry of reaction $R1.^{23}$ Molecular bromine was not produced until bromate was in stoichiometric excess as determined by (R1). The quantity of bromine was also proportional to the excess bromate concentration to a certain degree. These results showed that the final stoichiometry of the reaction in excess bromate concentrations was a combination of R1 and R2 (5R1 + R2) to give

$$6BrO_3^- + 5SCN^- + 2H_2O \rightarrow 3Br_2 + 5SO_4^{2-} + 5CN^- + 4H^+$$
(R3)

Flow Experiments. In all our experiments the acid concentration was held constant at 0.133 M and the only parameters varied were the concentrations of bromate and thiocyanate and the flow rate. The first phase diagram was obtained by maintaining a constant flow rate while using different combinations of bromate and thiocyanate concentrations (Figure 4a). Oscillations were possible when the $[BrO_3^-]_0/[SCN^-]_0$ ratio was at least 1.5, though lower ratios could be tolerated when both the $[BrO_3^-]_0$ and the $[SCN^-]_0$ were high. No attempt has been made in Figure 4a to label the type of oscillations observed in the oscillatory region, but generally, large-amplitude oscillations were observed in the center of the oscillatory region. At lower

 $[BrO_3^-]_0/[SCN^-]_0$ sections of the oscillatory region, the oscillations were of the small-amplitude type and confined to low potentials, while the upper reaches of the $[BrO_3^-]_0/[SCN^-]_0$ ratio gave single-peak, small-amplitude oscillations which were confined to high potentials. Figure 4a is only a part of the phase diagram because if the acid was held constant and the bromate and thiocyanate concentrations were reduced 10-fold, oscillations could still be observed, albeit with a longer period of oscillation. If these concentrations were reduced further, only steady state II is observed. High initial bromate and thiocyanate concentrations gave only steady state I as the oscillatory region gradually narrowed and then finally disappeared.

At sufficiently high flow rates, only steady state II is obtained (low Br_2). Upon gradual reduction of the flow rate, a point is reached where oscillations arise as the low potential steady state becomes unstable, leading to a supercritical Hopf bifurcation. These oscillations gradually increased in amplitude until at low enough flow rates they attain their maximum amplitude. Further reduction of flow rate will result in steady state I (high Br_2), and the solution remains permanently yellow. This sequence is shown in Figure 4b.

Bifurcation Sequence. As in the Belousov-Zhabotinskii reactions, the bromate-thiocyanate reaction in a CSTR displays single-peak limit cycle oscillations (Figure 5a) at appropriate flow rate.^{15,17} As the flow rate is increased, a complex bifurcation sequence is observed. Most of the periodic states observed were not very stable, and thus the system drifted intermittently between a periodic state and its chaotic equivalent while the flow rate was being held constant. This drift in reactor behavior is mostly due to incomplete mixing since only a magnetic stirrer was used for mixing. Our reactor also has no baffles, thus making it much more difficult to ensure thorough mixing. While locked onto a periodic oscillatory state, the system occasionally drifted into a state with the same period, but with an unpredictable ordering of the peaks (Figure 5b). After a short while, the system locked back onto the periodic state. We thus could never observe a periodic state continuously for more than an hour. An exception was the limit cycle periodic state (Figure 5a) which was stable for very long periods of time. Of the periodic states observed, the five-, four-, three, and two-cycle oscillations were found to be most stable. The five-cycle periodic oscillations in particular were stable over wide ranges in flow rate although the relative heights of the peaks varied in this range. At higher flow rates (after the five-cycle oscillations) the amplitude of oscillations began to vary in an undulating wave from (Figure 5c). This wave form applies to all the peaks of an oscillatory state. This coherence persists for long periods of time and flow rate.

Discussion

Since the bromate-thiourea and bromate-thiocyanate oscillators appear to be quite similar, the oscillation mechanisms in both cases could be the same. As in the bromate-thiocyanate reaction (R1), bromate can also oxidize thiourea to give bromide:¹²

$$3CS(NH_2)_2 + 4BrO_3^- + 3H_2O \rightarrow 3CO(NH_2)_2 + 3SO_4^{2-} + 6H^+ + 4Br^- (R4)$$

The bromide can produce bromine through reaction R2.

We have not conducted any stoichiometric determinations on the reaction between bromine and thiocyanate, but the following stoichiometry can be deduced from reactions R1 and R3:

$$3Br_2 + SCN^- + 4H_2O \rightarrow 6Br^- + CN^- + 8H^+ + SO_4^{2-}$$
 (R5)

Our preliminary investigations on the Br_2 -SCN⁻ reaction show that it is a very fast reaction and requires stopped-flow techniques for proper study (as in the case of the Br_2 -CS(NH₂)₂ reaction).

Our experiments did confirm an earlier conjecture that oscillatory behavior is only possible in two-component bromate oscillators when bromate is in stoichiometric excess over the reductant.¹² Excess bromate is necessary to make reaction R2, which is needed for both reactions R3 and R4, viable. The "drive" reaction for the bromate-thiocyanate oscillator is reaction R1 (R3 + R5). What allows this chemical system to oscillate and not



Figure 5. Redox potential time series plots with $[\text{HClO}_4]_0 = 0.133 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.0167 \text{ M}$, and $[\text{SCN}^-]_0 = 0.0067 \text{ M}$. Different oscillatory states are observed by altering the flow rate. (a) Limit cycle oscillations observed at very low flow rates. (b) Combination of periodic and chaotic five-cycle oscillations; $k_0 = 5.25 \times 10^{-4} \text{ s}^{-1}$. The system at this flow rate gives five-cycle periodic oscillations separated by intermittent bursts of chaotic five-cycle oscillations. (c) Complex quasi-periodic oscillations at $k_0 = 6.09 \times 10^{-4} \text{ s}^{-1}$. Just as the large-amplitude peaks can be connected by an undulating wave form, the shorter peaks also seem to be related to each other by the same wave form. (d) Alternating two-cycle and three-cycle oscillations when $k_0 = 7.52 \times 10^{-4} \text{ s}^{-1}$. (e) Small peak oscillations at high flow rates before the system goes on to the flow branch of the phase diagram. $k_0 = 9.50 \times 10^{-4} \text{ s}^{-1}$.

just decay to a position of lowest free energy is the $[Br^{-}]/[Br_2]$ ratio. High bromide concentrations favor production of bromine (reaction R3) and vice versa for high bromine concentrations (reaction R5). The switch from one reaction to the other occurs when a critical $[Br^{-}]/[Br_2]$ ratio is reached. This critical ratio has also been invoked to explain establishment of oscillations in the chlorite-bromide system^{26,27} and the bromate-thiourea system.¹² More studies are needed in order to deduce conclusively

⁽²⁶⁾ Simoyi, R. H. J. Phys. Chem. 1985, 89, 3570-3574.

⁽²⁷⁾ Valdes-Aguilera, O.; Kustin, K.; Epstein, I. R. J. Phys. Chem., in press.

the mechanism of this new oscillator. This can be effectively done by using computer simulation techniques if the computing power is available.

We have mentioned that the oxidation of thiocyanate by bromate to give bromide (R1), the conversion of the bromide to give bromine (R2), and the oxidation of thiocyanate by bromine to give bromide (R5) are the major reactions involved in the mechanism. There is no experimental evidence that the reactions are going all the way according to the stoichiometries of reactions R1, R2, and R5. The oscillations may involve different processes than the total behavior of reactions R1, R2, and R5. Intermediates may hold the key to the oscillatory behavior. For example, sulfur goes from the 0 oxidation state (SCN⁻) to +6 (SO₄²⁻). This cannot occur in a single step. The stoichiometry of (R5) has been determined on a bulk system where the reaction was allowed to proceed for hours before the stoichiometric determinations were performed. It is conceivable that lower oxiation states of sulfur (e.g., +2 and +4) could be involved in the mechanism. The other well-known bromine species which are involved in the B-Z system (HBrO₂, HOBr, BrO₂) could prove to be very important in the mechanism.

The global behavior of the bromine-thiocyanate oscillator is also very fascinating. The bifurcation sequence obtained has not been observed in any other chemical oscillator. The quasi-periodicity and rampant intermittency observed suggest that the system may be subscribing to a dynamics of higher dimensionality than the one-dimensional dynamics observed in the B-Z.¹⁶ There are very few chemical oscillators which show different oscillatory states, and those that do should have their dynamics characterized to probe for any universality in their bifurcations.²⁸ We not only

need more detailed mechanistic studies on this oscillator, but more controlled experimental studies on the bifurcation sequence as has been done on the B-Z system.¹⁶ Particularly disturbing are recent studies which confirm that, second only to flow rate, stirring has the most profound effect on the behavior of a chemical oscillator.²⁹ Any further dynamical studies should involve higher rpm stirring rates in a reactor with baffles. These studies should be able to confirm whether plots b and c of Figure 5 really show intermittency and quasi-periodic behavior, respectively. In this oscillator, standard techniques like phase diagrams³⁰ and calculation of lyapunov characteristic exponents²¹ should be used on the chaotic regions of the bifurcation sequence to better understand the dynamics of this fascinating oscillator.

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Registry No. BrO₃⁻, 15541-45-4; SCN⁻, 302-04-5.

 (29) Kumpinsky, E.; Epstein, I. R. J. Chem. Phys. 1984, 82, 53-57.
 (30) Roux, J. C.; Turner, J. S.; McCormick, W. D.; Swinney, H. L. In Nonlinear Problems: Present and Future; Bishop, A. R., Campbell, D. K., Nicolaenko, B., Eds.; North-Holland: Amsterdam, 1982; p 409.

Effect of Solvent Structure on Electron Reactivity: 1-Butanol/Water Mixtures

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The solvent dependence of e_{s}^{-} reaction rate constants k_{2} and their Arrhenius parameters differ for efficient (nitrobenzene, acetone) and inefficient (phenol, toluene) scavengers. The n-butyl group is so large that 1-butanol is not completely miscible with water. The complex changes of physical properties of 1-propanol/water mixtures produced four different zones of es behavior on going from 0 to 1.00 mole fraction water. Zone c, 0.75-0.97 mole fraction water, which displays Stokes-Smoluchowski behavior of k_2 , is inaccessible in 1-butanol/water solvents because it is in the immiscible region. In zone a the viscosity normalized rate constant ηk_2 for inefficient scavengers decreases in spite of the decrease of the electron optical absorption energy E_r . Hydrogen-bonded structures, for example H₂O(ROH)₈, apparently make the positive hydrogens on the OH groups less accessible to solvate the electrons and less accessible to protonate S⁻.

Introduction

Rate constants of solvated electron reactions with an efficient scavenger in 1-propanol/water mixed solvents were classified into four zones by their viscosity dependence.¹ (a) Mole fraction x_{H_2O} < 0.15: Isolated water molecules apparently hydrogen bond with surrounding alcohol molecules and increase the orderliness of the local structure of the liquid.² The rate constant k_2 decreases with increasing water concentration,¹ as the liquid viscosity³ and dielectric relaxation time4-9 increase; the optical absorption energy

 $E_{A,max}$ of the solvated electrons decreases.² (b) 0.15 < x_{H_2O} < 0.75: k_2 increases in spite of the increasing viscosity, contrary to the Stokes-Smoluchowski relation.¹⁰ (c) 0.75 < $x_{H_2O} \lesssim 0.98$: $k_2 \propto \eta^{-1.0}$ as expected from the Stokes-Smoluchowski relation; $E_{A,max} \approx \text{constant.}^2$ (d) $x_{H_2O} > 0.97$: The dynamic parameters of the liquid change appreciably (dielectric relaxation,⁴⁻⁹ nuclear relaxation,¹¹ diffusion¹²), but k_2 changes less than expected from the Stokes-Smoluchowski relation; $^{1}E_{A,max}$ changes.²

⁽²⁸⁾ A number of unrelated physical systems like the nonlinear electrical circuits, the Rayleigh-Benard convection, the Couette-Taylor hydrodynamical system, and the Belousov-Zhabotinskii system as well appear to subscribe to the same dynamics. For a summary, see: Swinney, H. L. Physica D (Amsterdam) 1983, 7D, 3-15.

Maham, Y.; Freeman, G. R. J. Phys. Chem. 1985, 89, 4347.
 Leu, A. D.; Jha, K. N.; Freeman, G. R. Can. J. Chem. 1982, 60, 2342.

⁽³⁾ Timmermans, J. Physicochemical Constants of Binary Mixtures; In-terscience: New York, 1960; Vol. 4.

 ⁽⁴⁾ Jhon, M. S.; Eyring, H. J. Am. Chem., Soc. 1968, 90, 3071.
 (5) Hassion, F. X.; Cole, R. H. J. Chem. Phys. 1955, 23, 1756.

⁽⁶⁾ Hasted, J. B. In Water, a Comprehensive Treatise; Franks, F., Ed.; Plenum: New York, 1973; Vol. 2, p 405

⁽⁷⁾ Bertolini, D.; Cassettari, M.; Salvetti, G. J. Chem. Phys. 1983, 78, 365.

⁽⁸⁾ Gestblom, B.; Sjöblum, J. Acta Chem. Scand., Ser. A 1984, A38, 575.

⁽⁹⁾ Perl, J. P.; Wasan, D. T.; Winsor, P.; Cole, R. H. J. Mol. Liq. 1984, 28, 103.

⁽¹⁰⁾ Noggle, J. H. Physical Chemistry; Little and Brown: Toronto, 1985; pp 448, 551

^{(11) (}a) Goldammer, E. V.; Zeidler, M. D. Ber. Bunsenges. Phys. Chem. 1969, 73, 4. (b) Goldammer, E. V.; Hertz, H. G. J. Phys. Chem. 1970, 74, 3734

⁽¹²⁾ Franks, F.; Ravenhill, Egelstaff, P. A.; Page, D. I. Proc. R. Soc. London, A 1970, 319, 189.