

## Bifurcation Phase Studies of Belousov-Zhabotinsky Reaction Containing Oxalic Acid and Acetone as a Mixed Organic Substrate in an Open System

C. Basavaraja, Do Sung Huh,\* Sung Hyun Park, Un Ji Jeon, R. Pierson, T. K. Vishnuvardhan,† and V. R. Kulkarni†

Department of Chemistry and Institute of Functional Materials, Inje University, Gimhae, Kyungnam 621-749, Korea

\*E-mail: chemhds@inje.ac.kr

†Department of Chemistry, Gulbarga University, Gulbarga 585-106, India

Received June 11, 2007

Belousov-Zhabotinsky (BZ) reaction containing oxalic acid and acetone as a mixed organic substrate catalyzed by Ce(IV) in a flow system has been investigated. The reaction system is analyzed by varying flow rate, inflow concentrations, and temperature. Interchangeable oscillating patterns are observed in a certain range of concentrations, and above or below the condition a steady state is obtained. The increase in temperature increases the frequency and decreases the amplitude of oscillations. The apparent activation energy for the system is calculated by using the Arrhenius equation, which means that temperature has a greater effect on the reaction. Bifurcation phase diagrams for the system show the region of oscillations or steady states along with a small region of multistability. Further the behavioral trend observed in this system is discussed by mechanistic character of the system.

**Key Words :** Oscillating reactions, Mixed system, Bifurcation diagrams, Multistability

### Introduction

Oscillating reaction systems far from equilibrium has most interesting property called excitability. Such a system behaves straightforwardly when well stirred but if unstirred develops a three-dimensional well defined structures in the form of periodic or concentric waves or patterns which appears as though a plain water surface is disturbed by a falling raindrop. After the discovery of these phenomena it has become more fascinating and can be observed in many physical, chemical, and biological systems at far from equilibrium condition. There are several reports on the classical BZ systems both under closed and open system conditions. This has become a prototype for investigating temporal and spatiotemporal nonlinear phenomena, such as oscillations, chaos and its control, traveling and spiral wave propagation, and excitability, etc. Despite its use in innumerable studies, some details of its reaction mechanism, especially those concerning the reactions involving the organic compounds, still remain to be elucidated. Particularly little is known about the mechanistic details of those BZ variants where the organic substrate cannot be brominated during the reaction. In studies of the BZ reaction a large number of organic reducing agents have been used.<sup>1,2</sup> One group of organic substrates can be brominated and therefore, macroscopically no bromine formation can be observed.<sup>3</sup> In this case, the organic substrate plays a dual role in the BZ mechanism: it reduces the metal ion catalyst and removes the bromine from the system, yielding brominated organic compounds. Among the organic substrates belonging to this group we find the classical substrates malonic acid and malic acid. During the oxidation of substrates of the second group, the oxidation produces elementary bromine which gets accumulated in the reaction mixture. Then, the bromine

acts as a final product inhibiting the oscillations.<sup>3,4</sup> Therefore, in the vast majority of studies relating with the BZ system, bromine has been removed from the reaction mixtures either by chemical or by physical methods. The simplest way of the chemical removal of bromine is the addition of acetone which leads to a mixed substrate system, as acetone itself was shown to be a suitable substrate of the BZ reaction.<sup>5</sup> Examples for the chemical bromine removal are the oxalic acid-acetone system,<sup>6,8</sup> the tartaric acid-acetone system,<sup>9</sup> and the aldoses-acetone systems showing dual frequency oscillations.<sup>10</sup> Noszticzius and Bodiss removed bromine with a nitrogen stream from the oxalic acid system to produce oscillations.<sup>11</sup> Later, oscillatory oxidation of various organic substrates such as hydroxyl acids<sup>12-14</sup> and sugars<sup>15</sup> were used in the Ce-catalyzed BZ reaction under continuous bubbling with nitrogen. The oxalic acid system was also studied under open conditions in a continuous-flow stirred tank reactor (CSTR), which represents a third type of bromine removal.<sup>16</sup> There is a lower critical limit of bromine concentration which must be maintained in the reaction medium in order to support oscillations. If bromine is removed completely with a high flow rate of nitrogen, the reactions show an aperiodic behavior and oscillations do not start at all.<sup>13,17</sup> The importance of the presence of bromine was also pointed out in several later studies.<sup>18-22</sup> Recently we have taken up to study the BZ system containing bromate-Ce(IV)-H<sub>2</sub>SO<sub>4</sub>-oxalic acid and acetone as a mixed organic substrate in a CSTR both by simulation as well as experiment.<sup>23-26</sup> By performing rudimentary experiments at various values of parameters such as initial temperature, inflow concentrations, and the flow rates, the values of the critical limits of other parameters are determined. The effect of temperature on the behavior is also obtained and the apparent activation energy

is calculated by using Arrhenius equation. Further the bifurcation phase diagrams are constructed, which shows the regions of oscillations, steady states, and multistability.

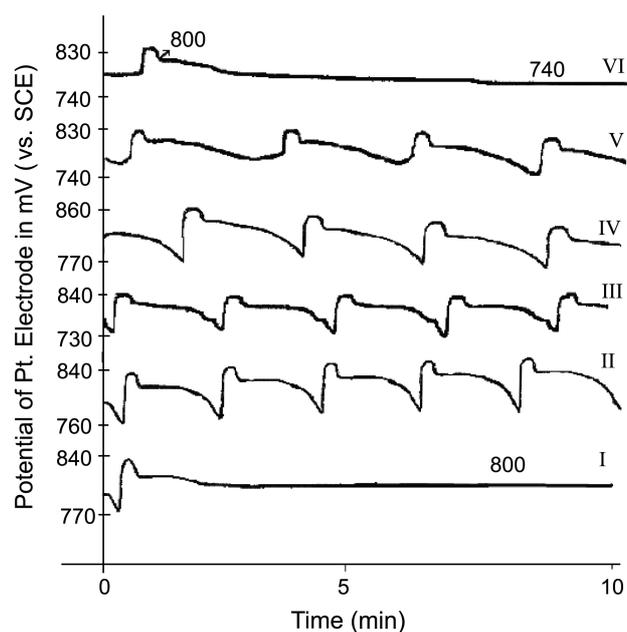
### Experimental

**Apparatus and method.** All reagents used in this experiment are of analytical grade and purchased from Sigma-Aldrich. Double distilled water is used to prepare solutions and the potassium bromate is recrystallized in water before using. A schematic diagram and the description of the CSTR experimental set up have been described elsewhere.<sup>25</sup> All the experiments were carried out at  $298 \pm 0.5$  K except the one to study the effect of temperature. When the temperature of the reservoir solutions became constant (within  $\pm 0.5$  °C), the experiments are started by pumping the reaction solutions into the empty reactor. The potential changes are observed using a Pt-electrode, and a reference electrode which is a double junction of Ag/AgCl saturated with KCl as an inner solution and 1 M sulfuric acid as an outer solution, respectively.

### Results and Discussion

**Effects of flow rate ( $k_0$ ) and inflow concentration.** At first, the  $k_0$  was varied at constant inflow concentrations chosen as standard where  $[\text{BrO}_3^-]_0 = 0.03$  M,  $[\text{oxalic acid}]_0 = 0.05$  M,  $[\text{H}^+]_0 = 1.5$  M,  $[\text{acetone}]_0 = 0.5$  M,  $[\text{Ce(IV)}]_0 = 0.001$  M. The typical potential behavior at different  $k_0$  is shown in Figure 1. The oscillatory region for  $k_0$  have been obtained between  $3.9 \times 10^{-4} \text{ s}^{-1}$  -  $1.6 \times 10^{-2} \text{ s}^{-1}$ , while steady states are observed at both extreme conditions such as high potential steady state at low  $k_0$  and low potential steady state at high  $k_0$  as shown in the figure. The oscillations are like hump-backed in nature which varied with the  $k_0$ . The amplitude of these oscillations increases in the middle ranges of value of  $k_0$ , after which decreases as  $k_0$  increased so as the frequency of these oscillations. The period of oscillations shows a definite trend of increasing as  $k_0$  is increased. When  $k_0$  decreases to about  $3.9 \times 10^{-4} \text{ s}^{-1}$  a slow decrease is followed by a rapid increase of potential which is followed by a slow decrease and later it attains a steady value. When  $k_0$  increases to about  $1.6 \times 10^{-2} \text{ s}^{-1}$  initially there is a slight increase in the potential followed by a single oscillation and again attains a steady potential which remains same. Thus, a high potential steady state at low  $k_0$  (the (I) in Fig. 1) and a low potential steady state at high  $k_0$  (the (VI) in Fig. 1) are observed.

Secondly, the effect of the inflow concentrations are studied by varying  $[\text{BrO}_3^-]_0$ ,  $[\text{acetone}]_0$ ,  $[\text{oxalic acid}]_0$ , and  $[\text{H}^+]_0$  at fixed  $k_0$  as  $3.8 \times 10^{-3} \text{ s}^{-1}$  by keeping other parameters as same as in Figure 1.  $[\text{BrO}_3^-]_0$  is varied between 0.015-0.05 M. Steady states are observed at both higher and lower  $[\text{BrO}_3^-]_0$  which are considered as low and high potential steady states, respectively. At very low  $[\text{BrO}_3^-]_0$  the oscillatory patterns follows a hump-backed nature. Further increase in  $[\text{BrO}_3^-]_0$  leads to a steady potential. In a similar



**Figure 1.** Platinum electrode traces obtained by different  $k_0$  at  $[\text{BrO}_3^-]_0 = 0.03$  M,  $[\text{oxalic acid}]_0 = 0.05$  M,  $[\text{H}^+]_0 = 1.5$  M,  $[\text{acetone}]_0 = 0.5$  M,  $[\text{Ce(IV)}]_0 = 0.001$  M at  $25 \pm 0.5$  °C.  $k_0$  is  $3.9 \times 10^{-4} \text{ s}^{-1}$  for (I),  $9.7 \times 10^{-4} \text{ s}^{-1}$  for (II),  $3.8 \times 10^{-3} \text{ s}^{-1}$  for (III),  $8.2 \times 10^{-3} \text{ s}^{-1}$  for (IV),  $12.0 \times 10^{-3} \text{ s}^{-1}$  for (V), and  $16.0 \times 10^{-3} \text{ s}^{-1}$  for (VI).

fashion  $[\text{acetone}]_0$ ,  $[\text{oxalic acid}]_0$ , and  $[\text{H}^+]_0$  are varied in the ranges 0.3-1.5 M, 0.01-1.12 M, and 0.5-2.25 M, respectively. The results show that a high potential steady state is obtained at low  $[\text{acetone}]_0$  and a low steady state is obtained at high  $[\text{oxalic acid}]_0$ . Similarly, a low potential steady state is observed at low  $[\text{H}^+]_0$  while a high steady state is obtained at high  $[\text{H}^+]_0$ , respectively. The results indicate that the effect of both  $[\text{H}^+]_0$  and  $[\text{oxalic acid}]_0$  to the oscillation pattern is similar. That means that by increasing both  $[\text{H}^+]_0$  and  $[\text{oxalic acid}]_0$  from a lower to a higher value, the amplitudes of oscillations increases and at much higher values steady states are obtained. However, the results by  $[\text{BrO}_3^-]_0$  and  $[\text{acetone}]_0$  are not same. By the results, low  $[\text{BrO}_3^-]_0$  and  $[\text{acetone}]_0$  condition induces low and high steady states, respectively, while high  $[\text{BrO}_3^-]_0$  and  $[\text{acetone}]_0$  condition induces high and low steady states, respectively. Table 1 shows high and lower steady states along with approximate values platinum potential obtained upon varying individual concentrations. It is clear from the table that  $[\text{BrO}_3^-]_0$  and  $[\text{H}^+]_0$  have a similar role to the steady state behavior (low/high) of the system, and  $[\text{acetone}]_0$ ,  $[\text{oxalic acid}]_0$ , and  $k_0$  have also effected similarly to the behavior of steady state. However, the trend of steady states obtained by the variation of  $[\text{BrO}_3^-]_0$  and  $[\text{H}^+]_0$  is opposite to that obtained by the variation of  $[\text{acetone}]_0$ ,  $[\text{oxalic acid}]_0$ , and  $k_0$ .

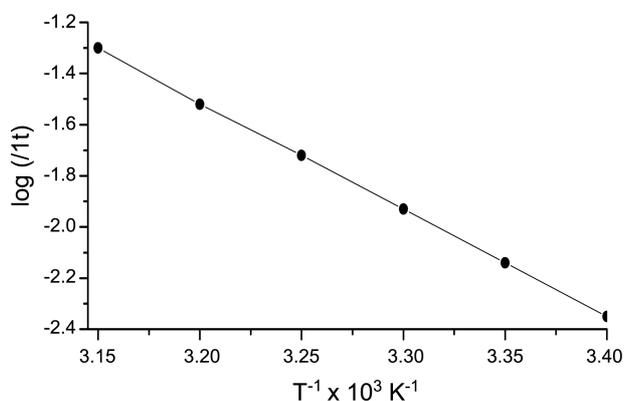
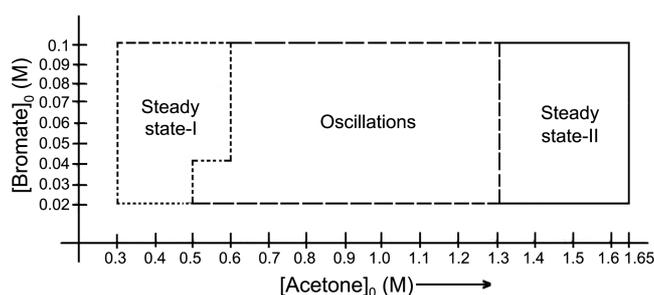
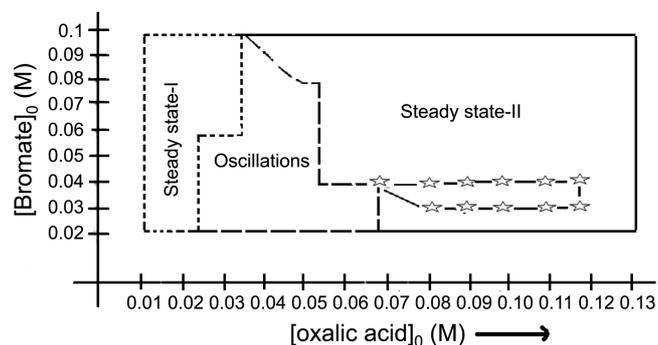
**The effect of temperature.** The temperature is one of the most important external factors which significantly control the kinetic behavior of self-oscillating systems. Earlier we have reported the effect of temperature on regular and irregular modes of the BZ reaction in a continuous-flow stirred-tank reactor (CSTR).<sup>23,25</sup> Körös *et al.* are the first to

**Table 1.** Higher and lower steady states along with approximate values platinum potential obtained upon varying individual concentrations

Parameter	Limits	Steady state potential (mV)	Steady state
Flow rate ( $k_0$ )	lower	800	high
	upper	740	low
$[\text{BrO}_3^-]_0$	lower	740	low
	upper	850	high
$[\text{Acetone}]_0$	lower	850	high
	upper	770	low
$[\text{oxalic acid}]_0$	lower	820	high
	upper	770	low
$[\text{H}^+]_0$	lower	750	low
	upper	870	high

study effect of temperature on the BZ system.<sup>27</sup> Initial temperature has a pronounced effect on the nature of oscillations and changing the temperature takes the system into a different oscillating mode. Here we have studied the behavior by varying the initial temperature from 293-318 K in steps of 5 K. At lower temperatures *i.e.* at 298 K and 303 K, the oscillation behavior showing a hump-backed nature is observed and this nature disappears as the temperature is increased and at higher temperatures, namely, at 308, 313, and 318 K the oscillations changed into the pattern of saw-tooth. The period (abbreviated as,  $t$ ) of oscillations decreases as the temperature is increased. The period was 225 sec at 293 K, 68 sec at 303 K and 20 sec at 318 K. Table 2 presents the period of oscillations at different temperature along with the values of apparent energy of activation calculated for two succeeding initial temperatures using Arrhenius equation. These values increase as the initial temperature is increasing, which indicates that the system is more sensitive to the initial temperature. Figure 2 shows the plot of  $\log(1/t)$  vs.  $1/T$  with least square fitting which is a linear. The average value of energy for activation ( $E_{av}$ ) is found to be 18.44 kcal/mol in the reaction system.

**Bifurcations study.** Figures 3 and 4 show  $[\text{acetone}]_0$  -

**Figure 2.** Plot of  $\log(1/t)$  vs.  $1/T$  for the period of oscillation. The initial composition of the solution is same with figure 1, and  $k_0 = 3.80 \times 10^{-3} \text{ s}^{-1}$ .**Figure 3.** Bifurcation phase plot for  $[\text{Acetone}]_0$ - $[\text{Bromate}]_0$  at  $[\text{Oxalic acid}]_0 = 0.05 \text{ M}$ ,  $[\text{Ce(IV)}]_0 = 0.001 \text{ M}$ ,  $[\text{H}^+]_0 = 1.5 \text{ M}$ , and  $k_0 = 2.0 \times 10^{-3} \text{ s}^{-1}$ .**Figure 4.** Bifurcation phase plot of  $[\text{Oxalic acid}]_0$ - $[\text{Bromate}]_0$  at  $[\text{Acetone}]_0 = 0.5 \text{ M}$ ,  $[\text{Ce(IV)}]_0 = 0.001 \text{ M}$ ,  $[\text{H}^+]_0 = 1.5 \text{ M}$ , and  $k_0 = 2.0 \times 10^{-3} \text{ s}^{-1}$ . A multistability is indicated by a symbol of star.

$[\text{BrO}_3^-]_0$  and  $[\text{oxalic acid}]_0$  -  $[\text{BrO}_3^-]_0$  bifurcation diagrams obtained at fixed values of  $k_0$  and at given initial concentrations as shown in respective figures. The experimental procedure for the diagrams are as follows:  $[\text{BrO}_3^-]_0$  is increased and decreased for a fixed values of  $[\text{oxalic acid}]_0$  and  $[\text{acetone}]_0$  which are taken from a lower to a higher values in respective diagrams.

Figure 3 shows the behavior of  $[\text{acetone}]_0$  -  $[\text{BrO}_3^-]_0$  plane. The range of  $[\text{acetone}]_0$  is 0.30-1.65 M. The system shows steady state at both high and low  $[\text{acetone}]_0$  at all  $[\text{BrO}_3^-]_0$  and it is showing oscillatory in the middle concentration condition which lies in the range 0.5-1.3 M. At lower  $[\text{acetone}]_0$  the system indicates oscillations at both lower and higher  $[\text{BrO}_3^-]_0$ , while at steady state exists at higher  $[\text{acetone}]_0$  regardless of  $[\text{BrO}_3^-]_0$ . The steady state at higher  $[\text{acetone}]_0$  is indicated as steady state-II and the other existing at lower  $[\text{acetone}]_0$  is indicated as steady state-I in the figure. The oscillations at low  $[\text{BrO}_3^-]_0$  are hump backed, and this nature changes to saw-tooth or remains same as  $[\text{BrO}_3^-]_0$  is increased. The frequency of oscillations increases by increasing  $[\text{BrO}_3^-]_0$  and decreases by decreasing  $[\text{BrO}_3^-]_0$  without any significant change in the behavior.

Figure 4 shows the behavior of  $[\text{oxalic acid}]_0$  -  $[\text{BrO}_3^-]_0$  plane. The range of  $[\text{oxalic acid}]_0$  is 0.01-0.13 M. This diagram shows two different regions of steady states, oscillatory and a small portion a region of multistability. The system shows a steady state at both high and low  $[\text{oxalic acid}]_0$  at all  $[\text{BrO}_3^-]_0$  and it is showing oscillatory in the

**Table 2.** The period of oscillations at different temperature along with the values of apparent activation energy calculated using Arrhenius equation

Temp. (K)	1/T × 10 <sup>3</sup>	Period (t) in sec	log (1/t)	Energy of Activation (kcal/mol)
293	3.41	225	-2.35	16.28
298	3.35	140	-2.14	17.29
303	3.30	86	-1.93	17.76
308	3.25	53	-1.72	17.95
313	3.20	33	-1.52	19.60
Mean = 18.44				

Inflow Condition: [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.03 M, [oxalic acid]<sub>0</sub> = 0.05 M, [Ce(IV)]<sub>0</sub> = 0.001 M, [H<sup>+</sup>]<sub>0</sub> = 1.5 M, [acetone]<sub>0</sub> = 0.5 M, and k<sub>0</sub> = 3.80 × 10<sup>-3</sup> s<sup>-1</sup>

middle concentration condition which lies in the range 0.025-0.07 M of [oxalic acid]<sub>0</sub>. The system exhibits a steady state region at low and high [oxalic acid]<sub>0</sub>, which are considered as steady state-I and steady state-II, respectively. The system indicates a multistability for a particular region of [oxalic acid]<sub>0</sub> i.e. 0.07-0.12 M when [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> lies in the range 0.03-0.04 M as indicated in the figure, and a steady state-II is observed at larger [oxalic acid]<sub>0</sub>. The steady state-II remains while [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> is decreased. And the multistability is indicated by a symbol of star as shown in the figure. The appearance of the multistability is due to a hysteresis effect that is carried along the system during the variation of [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub>. The nature of oscillations are hump backed and this nature remains regardless of the change of [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub>, however, amplitude increases with the increase in [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> and decreases by decreasing the [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub>.

Variations in the input parameters lead to changes in the characteristic parameters of the time series, such as the oscillatory period, and the frequency and amplitude of the oscillations. These features change monotonically with the initial conditions. In the presence of bromine it seems plausible that radical species are dominant in the oscillatory mechanism even at usual concentration conditions. The role of radicals in the bromine-containing oscillators was also suggested by Rastogi<sup>22</sup> and by Adamcikova and Sevcik<sup>20,21</sup> for the special reactions of sugars; however, they preserved the bromide control by bromine hydrolysis in their mechanistic assumptions for the explanation of oscillations. The increase in temperature increases the frequency and decreases the amplitude of oscillation and the apparent activation energy increases with the temperature. The simple approaches of Körös<sup>27</sup> considering monomolecular treatment is too trivial and studies as indicated by our data as well as those indicated in the literature.<sup>28</sup> We have also obtained bifurcation diagrams in the range of parameter values showing an oscillatory and steady state behaviors; oscillations are observed in the middle ranges of input values.

### Conclusion

In this report a BZ reaction system with a mixed organic

substrate has been studied in a CSTR. It exhibits steady state behavior at both higher and lower values of concentrations which were accordingly regarded as lower and higher steady states. This system is also sensitive to temperature which showed increase in activation energy with increase in temperature. The [acetone]<sub>0</sub> - [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> diagram showed three states namely oscillatory, steady state-I, and steady state-II. The nature of oscillations changes accordingly from a hump-backed to a saw tooth and back upon increasing and decreasing [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub>. However, [oxalic acid]<sub>0</sub> - [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub> diagram exhibits a region of multistability along with steady state-I and steady state-II. There is no change in the oscillatory pattern other than amplitude, which increases and decreases upon increasing and decreasing the [BrO<sub>3</sub><sup>-</sup>]<sub>0</sub>, respectively.

**Acknowledgements.** This work was supported by the 2007 FIRST project of Inje University.

### References

- Horvath, J.; Nagy-Ungvárai, Z. S.; Muller, S. C. *Phys. Chem. Chem. Phys.* **2001**, 3, 218.
- Pelle, K.; Wittmann, M.; Noszticzius, Z.; Lombardo, R.; Sbriziolo, C.; Turco-Liveri, M. L. *J. Phys. Chem. A* **2003**, 107, 2039.
- Scott, S. K. *Oscillations, Waves and Chaos in Chemical Kinetics*; Oxford University Press: Oxford, 1994.
- Field, R. J.; Koros, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, 94, 8649.
- Field, R. J.; Forsterling, H. D. *J. Phys. Chem.* **1986**, 90, 5400.
- Stroot, P. H.; Janjic, D. *Helv. Chim. Acta.* **1975**, 58, 116.
- Noszticzius, Z.; Magy, S. *Kém. Foly.* **1979**, 85, 330.
- Weigt, H. R. *Z. Chem.* **1990**, 30, 260.
- Guedes, M. C.; Faria, R. B. *J. Phys. Chem. A* **1998**, 102, 1973.
- Rastogi, R. P.; Singh, H. J.; Singh, A. K. *Discussion Meeting of Deutsche Bunsengesellschaft für Physikalische Chemie, Aachen, Germany, preprints, 1979*, 1, p 98.
- Li, H. X.; Jin, R.; Dai, W.; Deng, J. F. *Chem. Phys. Lett.* **1997**, 274, 41.
- Huh, D. S.; Choe, Y. M.; Park, D. Y.; Park, S. H.; Zhao, Y. S.; Choe, S. J. *Bull. Korean Chem. Soc.* **2005**, 26(11), 1682.
- Adamcikova, L.; Sevcik, P. *Coll. Czech. Chem. Commun.* **1982**, 47, 2333.
- Adamcikova, L.; Sevcik, P. *Z. Phys. Chem (Munich)*. **1982**, 132, 251.
- Adamcikova, L.; Halinárova, I. *Coll. Czech. Chem. Commun.* **1985**, 50, 1588.
- Sevcik, P.; Adamcikova, L. *J. Phys. Chem.* **1985**, 89, 5178.
- Gaspar, V.; Galambosi, P. *J. Phys. Chem.* **1986**, 90, 2222.
- Huh, D. S.; Choe, Y. M.; Park, D. Y.; Park, S. H.; Zhao, Y. S.; Choe, S. J. *Bull. Korean Chem. Soc.* **2005**, 26(2), 219.
- Blume, R.; Bader, H. J. *Z. Naturforsch.* **1984**, 39b, 1795.
- Adamcikova, L.; Sevcik, P. *Coll. Czech. Chem. Commun.* **1986**, 51, 2685.
- Sevcik, P.; Adamcikova, L. *React. Kinet. Catal. Lett.* **1987**, 33, 47.
- Rastogi, R. P.; Husain, M. M.; Chand, P.; Das, M. *Ind. J. Chem.* **2000**, 39A, 679.
- Basavaraja, C.; Kulkarni, V. R.; Vishnuvardhan, T. K.; Mohan, S.; Iyer, Y. M.; Subba Rao, G. V. *Ind. J. Chem.* **2005**, 44, 1894.
- Basavaraja, C.; Kulkarni, V. R.; Vishnuvardhan, T. K.; Mohan, S.; Iyer, Y. M.; Subba Rao, G. V. *Ind. J. Chem.* **2004**, 43A, 739.
- Basavaraja, C.; Kulkarni, V. R. *J. Ind. Chem. Soc.* **2004**, 81, 427.
- Basavaraja, C.; Kulkarni, V. R. *J. Ind. Chem. Soc.* **2003**, 80, 100.
- Koros, E. *Nature* **1974**, 251, 703.
- Kumpinsky, E.; Epstein, I. R. *J. Phys. Chem.* **1985**, 89, 688.