Russian Journal of Applied Chemistry, Vol. 78, No. 4, 2005, pp. 541–545. Translated from Zhurnal Prikladnoi Khimii, Vol. 78, No. 4, 2005, pp. 548–552.

Spontaneous Decomposition of Industrially Manufactured Sodium Hypochlorite Solutions

I. P. Sizeneva, N. B. Kondrashova, and V. A. Val'tsifer

Institute of Technical Chemistry, Ural Division, Russian Academy of Sciences, Perm, Russia

Received December 16, 2004; in final form, November 2004

Abstract—Spontaneous decomposition of industrially manufactured aqueous solutions of sodium hypochlorite was studied. The rate constants of the decomposition reactions were calculated for different pH values.

In view of the exceedingly high toxicity and volatility of metallic mercury (MPC for habitats 0.0003 mg m^{-3}) [1] and its wide use, the problem of efficient salvation in tackling with possible mercury spillage events remains a matter of current interest. For this purpose, new demercurization methods are being developed and the already existing techniques are being improved. At present, the most widely used methods are those in which mercury is oxidized with strong oxidizing agents [2, 3]. In developing a demercurizer, with industrially manufactured sodium hypochlorite (HC) solutions as an oxidizing agent, it became necessary to assess the stability of solutions of this kind in storage and to study the oxidizing activity of these industrial solutions at various pH values.

HC solutions are nonequilibrium systems that undergo spontaneous decomposition. The problem of spontaneous decomposition of HC solutions has been extensively studied. The influence exerted by the concentration, temperature, and acidity on decomposition processes has been analyzed and the possible mechanisms and kinetic characteristics of decomposition have been reported [4–8]. In the known studies, solutions of both calcium and sodium HC were examined. Model solutions have been mostly studied, with the HC solutions having low concentrations: 0.01–0.20 M in terms of active chlorine.

The aim of this study was to assess the stability of industrially manufactured concentrated HC solutions in order to determine the maximum shelf life of solutions of this kind. Another goal was to determine the kinetic characteristics of real solutions used to prepare the demercurizing agent.

The choice in developing the demercurizer was made in favor of sodium HC, taking into account its availability as a solution, high content of active chlorine, and high stability against decomposition in an alkaline medium (compared with calcium HC) [9]. The behavior of the solutions was analyzed at two temperatures, 25 and 35°C, in view of the regional climatic conditions (the maximum summer temperature is not, as a rule, higher than 35°C).

EXPERIMENTAL

As object of study served industrially manufactured (Berezniki Soda Plant Open Joint-Stock Company) sodium HC solution with a concentration of 180–200 g l^{-1} in terms of active chlorine. Model solutions were prepared by passing at (0–5°C) Cl_2 obtained by reacting chemically pure hydrochloric acid with $KMnO_4$ through a NaOH solution containing no carbonates. The excess amount of the alkali was about 20 g l^{-1}. The reaction vessel was cooled with a mixture of NaCl and ice. The pH values of the solutions were measured with an EV-74 ionometer with glass and silver chloride electrodes.

In stability studies, the alkaline (pH 13.5) HC solutions under study were thermostated in hermetically sealed polyethylene jars for 3 months. The pH value of the solutions remained virtually constant, irrespective of the duration and temperature of experiments, because of the presence of an excess amount of NaOH in the HC solutions.

The dependence of the degree of HC decomposition on the pH value was studied at 25 and 30°C.

Table 1. Decomposition of industrially manufactured sodium HC in solutions of different concentrations at 25 and 35°C

T, °C	t, h	Variation of c in storage, M	k, mol l^{-1} h^{-1}	Variation of c in storage, M	k, mol l^{-1} h^{-1}
25	0	c_{in} = 5.20 M		c_{in} = 2.10 M	
	144	5.10	0.2618×10^{-4}	2.09	0.2060×10^{-4}
	216	4.86	0.6229×10^{-4}	2.08	0.2120×10^{-4}
	312	4.50	0.9588×10^{-4}	2.07	0.4579×10^{-4}
	384	4.39	0.9240×10^{-4}	2.00	0.6200×10^{-4}
	480	4.19	0.9658×10^{-4}	1.97	0.6547×10^{-4}
	696	3.90	0.9210×10^{-4}	1.92	0.6414×10^{-4}
	1272	3.20	0.9449×10^{-4}	1.80	0.6239×10^{-4}
	2040	2.70	0.9078×10^{-4}	1.64	0.6253×10^{-4}
k_{av} (312–2040 h) = $(0.9371 \pm 0.0225) \times 10^{-4}$				k_{av} (384–2040 h) = $(0.6296 \pm 0.0155) \times 10^{-4}$	
35	0	c_{in} = 5.20 M		c_{in} = 2.10 M	
	144	4.50	0.2077×10^{-4}	2.00	0.1653×10^{-4}
	216	4.20	0.2119×10^{-3}	1.95	0.1695×10^{-3}
	312	3.65	0.2617×10^{-3}	1.89	0.1696×10^{-4}
	384	3.45	0.2540×10^{-3}	1.85	0.1676×10^{-3}
	480	3.23	0.2444×10^{-3}	1.80	0.1653×10^{-3}
	696	2.76	0.2443×10^{-3}	1.69	0.1660×10^{-3}
	960	2.12	0.2910×10^{-3}	1.58	0.1633×10^{-3}
	1272	1.84	0.2761×10^{-3}	1.46	0.1641×10^{-3}
	2136	1.30	0.2649×10^{-3}	1.20	0.1672×10^{-3}
k_{av} = $(0.2507 \pm 0.0266) \times 10^{-3}$				k_{av} (384–2040 h) = $(0.1668 \pm 0.021) \times 10^{-3}$	

The experiments were performed with solutions containing the same amounts of active chlorine (1.24, 1.29 M) at a virtually constant pH value, which was continuously monitored during the experiments. The acidity of the medium was adjusted by adding an H_2SO_4 solution. The degree of decomposition was determined after 10 min.

To study the kinetics of decomposition at different acidities, HC solutions were placed in hermetically sealable glass jars, with the required acidity adjusted by introduction of an HCl solution. Changes in the acidity of the medium and in the concentration were determined at regular intervals of time. In all the experiments, the variation of the HC concentration was monitored iodometrically.

The experiments in which the stability of sodium HC solutions was studied were carried out with industrial and model solutions of close concentrations. The data obtained were used to calculate the order of the reaction by which the alkaline solution of sodium HC decomposes, using the known Van't Hoff formula

$$n = \frac{w_1/w_2}{\log(c_1/c_2)}.$$

This formula makes it possible to determine the reaction order n from the initial rates w_1 and w_2, i.e., from the reaction rates at different initial concentrations c_1 and c_2 of the starting HC.

The calculations demonstrated that spontaneous decomposition of sodium HC in alkaline solutions occurs as a second-order reaction at both 25 and 35°C. The second reaction order was also obtained by graphical differentiation from the slope of the dependence of the rate of HC decomposition on the logarithm of the concentration, $\log(-\Delta c/\Delta t) - \log c$. The rate constants of the decomposition reaction were calculated using second-order kinetic equations

$$k = 1/t \, \frac{c_0 - c}{c_0 c}.$$

The results obtained are listed in Table 1.

The second order of the reactions and the formal rate constants of decomposition were obtained using the above-described procedures for a model HC solution with a concentration of 2.26 M at two temperatures: $k_{av} = 0.2060 \times 10^{-4}$ M at 25°C and $k_{av} = 0.1064 \times 10^{-3}$ M at 35°C.

The activation energies calculated using the Arrhenius equation

$$E = \frac{\log (k_2/k_1)}{(T_2 - T_1)/T_2T_1},$$

were 82.33 kJ mol^{-1} (19.67 kcal mol^{-1}) for a sodium HC solution with a concentration of 5.2 M and 79.53 kJ mol^{-1} (19.00 kcal mol^{-1}) for that with a concentration of 2.1 M. The results obtained are in an agreement with published data for alkaline HC solutions [10].

The decomposition of HC consists of two concurrent processes, oxygen and chlorate decompositions, which can be expressed by the following reactions

$$ClO^- + ClO^- = 2Cl^- + O_2, \quad (I)$$

$$ClO^- + ClO^- = ClO_2^- + Cl^-, \quad (II)$$

$$ClO_2^- + ClO^- = ClO_3^- + Cl^-. \quad (III)$$

The rate-determining reactions are (I) and (II), whereas reaction (III) is considerably faster than the first two [11].

As can be seen in Table 1, a certain deviation from the average kinetic parameters (reaction orders, reaction rate constants) is observed in the initial stage of the process (~216 h) at 25°C, which can be attributed to predominance of the oxygen decomposition [11]. At 35°C, the process is considerably faster: the chlorate decomposition predominates. The model solutions decompose in a similar way.

The experimental data were used to compare the decomposition rates of sodium HC in industrially manufactured and model solutions at 25 and 35°C. Figures 1 and 2 show kinetic curves that describe the self-decomposition of alkaline solutions of sodium HC. It can be seen that that the processes of spontaneous decomposition are autocatalytic at 25°C, with the process rates dependent on the initial concentration. The calculated rate constants of HC decomposition were used to compare the decomposition rates of HC in solutions with different concentrations at this temperature.

For example, sodium HC decomposes at 25°C in the solution with a concentration of 5.2 M approximately 1.5 times faster than in that with a concentration of 2.1 M. The temperature dependence of the decomposition rate is particularly strong. The decomposition is approximately 2.8 times faster at 35°C, compared with 25°C, for the solution with a sodium HC concentration of 5.2 M, and 2.65 times faster at a concentration of 2.1 M.

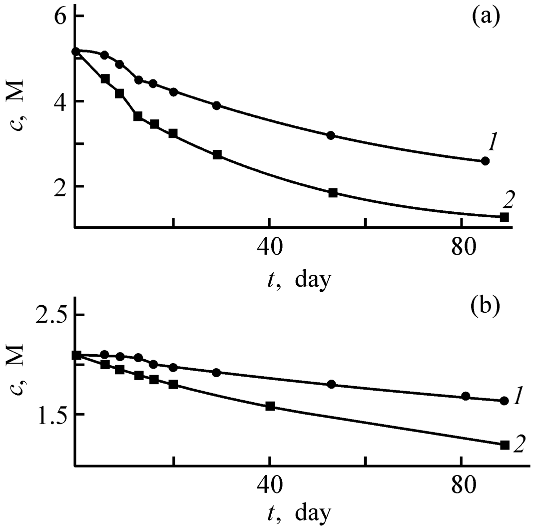

Fig. 1. Stability of industrially manufactured sodium hypochlorite solutions with a concentration of (a) 5.2 and (b) 2.1 M. (*c*) Concentration and (*t*) time; the same for Fig. 2. Temperature (°C): (*1*) 25 and (*2*) 35.

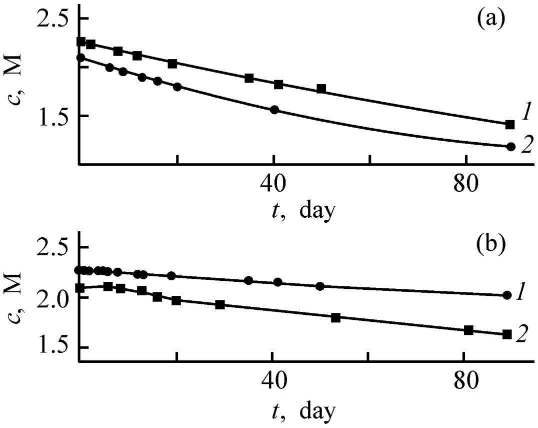

Fig. 2. Stability of (*1*) model sodium hypochlorite solutions with a concentration of 2.26 M and (*2*) industrially manufactured sodium hypochlorite solutions with a concentration of 2.1 M at (a) 35 and (b) 25°C.

Comparison with model solutions shows that decomposition of a diluted industrially manufactured sodium HC solution with a concentration of 2.1 M at 25°C is approximately 3 times faster than that of a model solution with a close concentration (c = 2.26 M). This can be attributed to presence in the industrial solution of mostly colloid particles of iron

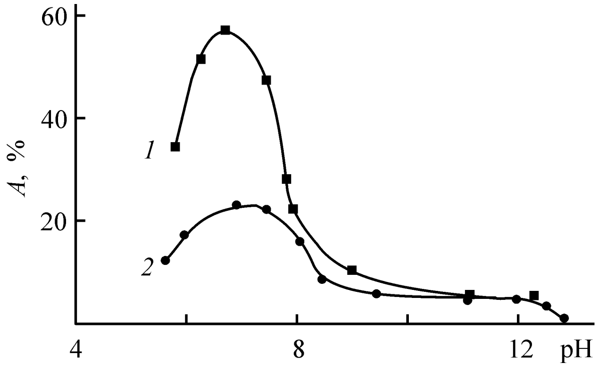

Fig. 3. Degree of sodium hypochlorite decomposition, *A*, vs. the pH value. (*A*) Ratio of the number of decomposed moles of HClO + ClO^- to their initial number. c_0 (M): (*1*) 1.24 and (*2*) 1.29. Temperature (°C): (*1*) 30 and (*2*) 25.

hydroxide $Fe(OH)_3$. These particles have an excess energy and accelerate the decomposition of HC, with the catalytic action of $Fe(OH)_3$ becoming less pronounced in the course of time, which is commonly accounted for by a decrease in dispersity, named "aging" [12]. At 35°C, the decomposition rate of the industrial solution exceeds that of the model solution only by approximately a factor of 1.5, because the accelerating effect of temperature equally tells upon the decomposition of both HC solutions. At the same time, the catalytic action of $Fe(OH)_3$ on the decomposition of the industrial becomes less pronounced as temperature increases, because a higher temperature favors coagulation, i.e., leads to coarsening of colloid particles and, consequently, to a decrease in their total surface area and excess energy.

The stability and oxidizing power of sodium HC solutions are strongly dependent on the activity of hydrogen ions in solution. Figure 3 shows how the degree of HC decomposition depends on the pH value at 25 and 30°C. It can be seen that the maximum degree of HC decomposition is observed at pH close to 7.

Table 2. Dynamics of variation of the pH value and concentration of sodium HC solutions

Solution no.	*t*, h	*c*, M	pH
1	0	1.188	8.06
	0.5	0.689	7.84
	1.0	0.437	7.52
	2.0	0.255	6.09
	3.0	0.207	6.05
	4.0	0.185	6.45
2	0	0.941	4.83
	96	0.323	5.01
	168	0.182	5.30
	384	0.132	5.25
	528	0.105	5.22

It is known that not only the mechanisms of HC decomposition in alkaline, neutral, and acid media, but also the rates of this process are different: the decomposition rate is at a minimum in a strongly acidic medium (pH < 1), increases with the pH value to reach a maximum in a nearly neutral medium, and then again decreases in an alkaline medium. Thus, the activity of hydrogen ions is one of the key factors affecting the composition and stability of HC solutions and, consequently, their oxidizing power [13–15].

The decomposition kinetics of industrial sodium HC solutions was studied at pH 6.5–8.0 (solution no. 1, c_0 = 1.188 M) and pH 4.8 (solution no. 2, c_0 = 0.941 M) at room temperature (21–22°C). A fast change in both the pH of the medium and the HC concentration was observed at pH 6.5–8.0. The experimental data obtained are listed in Table 2.

The order of the reaction of HC decomposition was determined from the variation of the HC concentration with time, and the rate constants of the reaction were calculated. The reaction order was found using the graphical variety of the method of substitution of experimental data (HC concentrations at different instants of time in the course of the reaction) into first-, second-, and third-order kinetic equations. For this purpose, time dependences of various functions of concentration were constructed. Each kinetic equation gives a straight line only in the appropriate coordinates [16]. Both for pH 6.5–8.0 and for pH 4.8, a linear plot was obtained for the $1/c$–t dependence, i.e., for a second-order kinetic equation. The reaction order was confirmed, as in the case of an alkaline medium, by graphical differentiation. The rate constants were calculated for a second-order kinetic equation:

pH	*k*, l^{-1} mol^{-1} h^{-1}
4.80	$(2.12 \pm 0.60) \times 10^{-2}$
8.0–6.5	1.34 ± 0.20
13.5	$(0.63 \pm 0.02) \times 10^{-4}$

It was noted in [8] that the reaction at pH 6.0–8.0 is so fast that the rate of self-decomposition increases by several orders of magnitude to become comparable with that of fast reactions.

The same dependence was observed in the present study.

The decomposition of sodium HC solutions at pH < 4.8 was not considered because preparation of solutions of this kind is accompanied by vigorous evolution of Cl_2, which leads to its waste and inefficient use of HC.

CONCLUSIONS

(1) An assessment of the stability of industrially manufactured sodium hypochlorite solutions revealed that dilute sodium hypochlorite solutions are the most stable in storage at temperatures not exceeding 25°C. It was shown that model hypochlorite solutions prepared with distilled water are more stable in storage than the industrially manufactured solutions.

(2) It was demonstrated that the spontaneous decomposition of industrial sodium hypochlorite solutions in a wide range of pH values (4.8–13.5) is a second-order reaction. The rate constants of the decomposition process, calculated at different pH values, confirmed the extremal type of the dependence of the decomposition rate on the pH value. It was shown that the decomposition pattern of dilute hypochlorite solutions is also valid for concentrated solutions.

REFERENCES

1. Trakhtenberg, I.M. and Korshun, M.N., *Rtut' i ee soedineniya v okruzhayushchei srede* (Gigienicheskie i ekologicheskie aspekty) [Mercury and Its Compounds in the Environment (Hygienic and Ecological Aspects)], Kiev: Vysshaya Shkola, 1990.
2. Mel'nikov, S.M., *Tekhnika bezopasnosti v metallurgii rtuti* (Safety Measures in Metallurgy of Mercury), Moscow: Metallurgiya, 1974.
3. Zakharov, L.N., *Tekhnika bezopasnosti v khimicheskikh laboratoriyakh* (Sfety Measures in Chemical Laboratories), Leningrad: Khimiya, 1985.
4. Flis, I.E. and Bynyaeva, M.K., *Zh. Prikl. Khim.*, 1957, vol. 30, no. 3, pp. 339–345.
5. Flis, I.E., *Zh. Prikl. Khim.*, 1963, vol. 36, no. 8, pp. 1669–1675.
6. Grigor, T.T., Tumanova, T.A., Mishchenko, K.P., and Shalanki, L., *Zh. Prikl. Khim.*, 1967, vol. 40, no. 9, pp. 2039–2044.
7. Nikol'skii, B.P., Krunchak, V.G., L'vova, T.V., *et al.*, *Dokl. Akad. Nauk SSSR*, 1970, vol. 191, no. 6, pp. 1324–1326.
8. Nikol'skii, B.P., Krunchak, V.G., Pal'chevskii, V.V., and Sosnovskii, R.I., *Dokl. Akad. Nauk SSSR*, 1971, vol. 197, no. 1, pp. 140–142.
9. Krunchak, V.G., *Zh. Prikl. Khim.*, 1974, vol. 47, no. 9, pp. 2112–2113.
10. Perel'man, F.M. and Zvorykin, A.Ya., *Zh. Fiz. Khim.*, 1955, vol. 29, no. 6, pp. 980–982.
11. Prokopchik, A.Yu., *Zh. Fiz. Khim.*, 1955, vol. 29, no. 6, pp. 1020–1026.
12. Prokopchik, A.Yu. and Yanitskii, I.V., *Zh. Fiz. Khim.*, 1954, vol. 28, no. 11, pp. 1999–2005.
13. Nikol'skii, B.P. and Flis, I.E., *Trudy Len. Tekhnol. Inst.*, 1949, no. 1, pp. 61–90.
14. Nikol'skii, B.P. and Flis, I.E., *Zh. Obshch. Khim.*, 1952, vol. 22, no. 8, pp. 1298–1307.
15. Flis, I.E., *Zh. Prikl. Khim.*, 1958, vol. 31, no. 8, pp. 1194–1201.
16. Stromberg, A.G. and Semchenko, D.P., *Fizicheskaya khimiya* (Physical Chemistry), Moscow: Vysshaya Shkola, 1973.