Density and Viscosity of Concentrated Aqueous Solutions of Lithium Hypochlorite

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This paper reports the densities and viscosities of aqueous solutions of lithium hypochlorite containing low concentrations of chloride and chlorate impurities. It also reports solubility results for the system LiOCl + H_2O in the essential absence of impurities.

Introduction

Hypochlorite salts are an industrially important class of oxidizers and bleaches. Lithium hypochlorite has also found extensive application as a swimming pool sanitizing agent. Commercial production of lithium hypochlorite has heretofore produced a complex mixture of lithium, sodium, and potassium cations and a mixture of hypochlorite, chloride, and sulfate anions. A second method of manufacture of lithium hypochlorite involves a double displacement reaction of lithium chloride with sodium hypochlorite and the selective precipitation of lithium hypochlorite monohydrate from the mixture (*1*). Subsequent advances in the technology of manufacture of hypochlorous acid have allowed the preparation of essentially pure solutions of metal hypochlorites including lithium hypochlorite (*2*, *3*). These solutions can be evaporatively concentrated to obtain essentially pure LiOCl·H_2O (*4*). Physical property data for aqueous solutions of lithium hypochlorite have not been previously reported, although the solubility system lithium hypochlorite + lithium chloride + water has been studied (*5*). In this paper, viscosity and density data for solutions containing up to 34 mass % (7.6 M) lithium hypochlorite are given over the temperature range 20–40 °C. The solubility of lithium hypochlorite as a function of temperature has been determined at concentrations between 5 and 38 mass % lithium hypochlorite.

Apparatus and Procedures

Temperature of Crystallization of LiOCl. Solutions of LiOCl in water were analyzed iodometrically for hypochlorite and chlorate ion concentrations and argentometrically for chloride ion concentration. The solutions were placed in a constant-temperature bath which was controlled to a temperature at least 20 °C below the anticipated freezing point. The temperatures of the solutions were measured as a function of time and cooling curves plotted to obtain the temperature for the initial crystallization. Determinations of the solubility were made for solutions on either side of the eutectic point, which was then determined graphically. Duplicate crystallizations were conducted on several solutions with a replication of temperatures of ±0.2 °C.

Densities. Density measurements were made by discharging a class A 25 mL pipet calibrated with deionized water into a weighed beaker. Temperatures were controlled to ±1 °C. All determinations were done in triplicate. The average standard deviation was 0.0005 g·cm^{-3}.

Viscosities. Viscosities were measured using a calibrated Cannon-Ebbelohde Semi-Micro dilution visometer immersed in a constant-temperature bath controlled to ±1 °C. All measurements were done in triplicate. Standard deviations for the individual measurements are given in Table 2.

Source of Materials. Aqueous solutions of LiOCl were prepared by the reaction of commercial grade LiOH with concentrated solutions of commercial HOCl. All solutions were analyzed as described above. Replicate analyses of solutions resulted in standard deviations of 0.04 mass % LiOCl and 0.02 mass % in all other components.

Table 1. Freezing Temperatures t for LiOCl + H_2O for Mass Fraction w of LiOCl (1), LiCl (2), $LiClO_3$ (3), and LiOH (4)

	solution phase				solid phase			
t/°C	$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
−5.0	5.83	0.38	0.31	0.02	3.61	0.82	0.37	nd[a]
−10.5	9.63	0.61	0.54	nd	5.24	0.62	0.91	nd
−16.0	12.45	0.80	0.56	0.19	10.09	1.90	1.14	1.08
−25.5	17.90	1.40	1.30	nd	25.58	1.39	1.07	nd
−24.0	18.40	1.17	0.94	0.07	22.51	1.12	0.57	0.03
−12.0	28.20	1.47	1.67	0.08	36.37	0.91	0.58	nd

[a] nd, none detected (less than 0.02%).

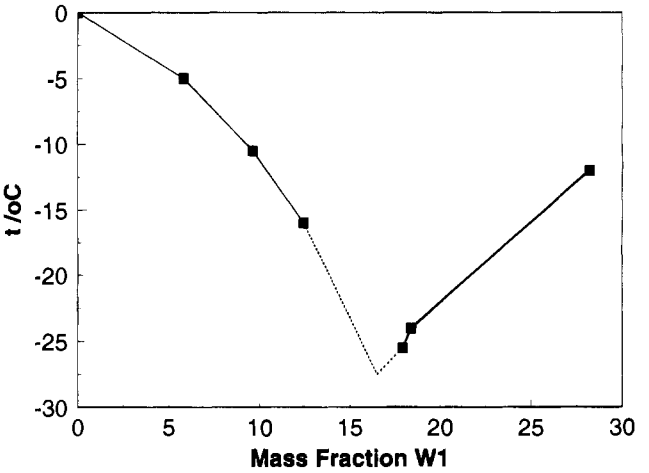

Figure 1. Freezing temperatures t/°C for LiOCl (1) + water (2) as a function of mass fraction w_1.

Results and Discussion

Table 1 lists the results of the cooling curve analyses for the LiOCl solutions from 5 to 38 mass % LiOCl. Mass concentrations of chloride, chlorate, and hydroxide ion in the solutions are also given. The solid phase formed from solutions of above 16.5 mass % lithium hypochlorite is assumed on the basis of other studies (*5*) to be LiOH·H_2O.

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Table 2. Densities and Visocosities of Aqueous Solutions of LiOCl (1) + LiCl (2) + LiOH (3) + $LiClO_3$ (4) + H_2O (5)

$100w_1$	$100w_2$	$100w_3$	$100w_4$	t/ °C	ϱ/ (g·cm^{-3})	$\sigma(\varrho)$ (g·cm^{-3})	η/ (mPa·s)	$\sigma(\eta)$/ (mPa·s)
34.73	0.75	nd[a]	0.88	20	1.2819	0.0006	19.08	0.29
30.32	0.73	0.04	0.34	20	1.2425	0.0002	10.81	0.22
20.31	0.76	nd	0.48	20	1.1540	0.0004	3.49	0.09
15.05	0.36	0.02	0.17	20	1.1117	0.0003	2.51	0.02
	0.36	0.02	0.17	30	1.1091	0.0012	1.90	0.01
	0.36	0.02	0.17	40	1.1065	0.0005	1.34	0.02
10.11	0.24	nd	0.11	20	1.0731	0.0003	1.79	0.01
	0.24	nd	0.11	30	1.0701	0.0002	1.38	0.01
	0.24	nd	0.11	40	1.0675	0.0007	0.95	0.01
5.02	0.12	nd	0.06	20	1.0331	0.0004	1.29	0.01
	0.12	nd	0.06	30	1.0297	0.0002	1.01	0.01
	0.12	nd	0.06	40	1.0286	0.0002	0.75	0.01

[a] nd, none detected (less than 0.02%).

The solubility as a function of temperature is given in Figure 1. The eutectic temperature and composition were estimated and are shown in Figure 1 by dotted lines.

Table 2 lists the measured densities. The experimental densities were regressed against temperature and mass fraction w of LiOCl, where w = mass % LiOCl/100. Equation 1 fits all densities over the temperature range 20–40 °C up to 35 mass % LiOCl.

$$d(\text{g·cm}^{-3}) = 0.9943 + 0.08327w - 0.00027t/°\text{C} \quad (1)$$

Experimentally measured viscosities are also given in Table 2. The average activation energy for viscous flow for concentrations of up to 15 mass % is 22 800 J/mol of LiOCl.

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