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Solubilities of $LaCl_3$ in HCl Aqueous Solution at (25, 35, and 45) °C

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The solubility of $LaCl_3$ in pure water at (25.00, 35.00, and 45.00) °C was measured as 48.18 ± 0.01 wt %, 49.73 ± 0.02 wt %, and 51.27 ± 0.02 wt %, respectively. The solubility of $LaCl_3$ in the HCl aqueous solution under various concentrations below 30 wt % at the above temperatures was also measured. The isothermal solubility diagrams of the $LaCl_3-HCl-H_2O$ system at the above temperatures were constructed.

Introduction

$LaCl_3$ is an important compound in rare earth metallurgy. Its solubility in aqueous solution has been measured.[1–3] However, the data are not in agreement. For the solubility of $LaCl_3$ in water at 25 °C, Friend's datum was 49.27 wt %, whereas Powell's was 48.88 wt %. This is mainly due to a great change in the solubility of $LaCl_3$ with temperature.

Friend[1] prepared lanthanum chloride by dissolution of the pure oxide in diluted acid and concentration in a water bath. The crystal was thoroughly drained through a sintered glass funnel. In a previous paper,[4] Friend described in detail the apparatus employed and the method for determination. Friend thought the method developed was the most accurate because the salt undergoes little hydrolysis. However, the diluted solution was faintly opalescent, and error may have occurred in measuring the solubility.

Powell[3] employed a complex analysis process. Because the analytical process is long, error may have occurred in many processes, such as, for example, in two steps of fuming, because a small amount of sample may have been carried over by the fumes.

Neither Friend nor Powell controlled the temperature accurately. Friend controlled the temperature to ± 0.1 °C and Powell to ± 1 °C.

Because the solubilities of $LaCl_3$ in HCl aqueous solutions at various temperatures are important in rare earth metallurgy, it is necessary to obtain accurate data for this system. In this paper, the solid–liquid phase equilibrium method was adopted to obtain the solubilities of $LaCl_3$ in HCl aqueous solutions from (0 to 30) wt % concentration and at (25.00, 35.00, and 45.00) °C. The data were compared with those of Friend and Powell, and isothermal solubility diagrams of the $LaCl_3-HCl-H_2O$ system at the above-mentioned temperatures are obtained.

Experimental Section

Reagents and Preparation of Solution. Lanthanum chloride (formula $LaCl_3 \cdot 7H_2O$), GR grade, TREO % > 45 (TREO represents total rare earth oxide), La_2O_3/TREO % > 99.9, was produced by the LeShan AOPULE Rare Earth Application Technology Development Co. Ltd., China. Silver nitrate (formula $AgNO_3$) was primary reagent grade, with a purity of 99.99 %. Potassium hydrogen phthalate (formula $KHC_8H_4O_4$) was primary reagent grade, with a purity of 99.99 %. Sodium hydroxide, GR grade, had a purity of 97.0 %. Hydrochloric acid (37 %) was AR grade. Potassium chromate, AR grade, had a purity of 99.5 %. Silver nitrate, potassium hydrogen phthalate, sodium hydroxide, hydrochloric acid, and potassium chromate were all produced by the Guangzhou Chemical Reagent Factory (China).

After drying at 120 °C for two hours and then cooling to room temperature in a desiccator, the silver nitrate was dissolved into redistilled water to prepare a 0.100 $mol \cdot L^{-1}$ $AgNO_3$ solution. The potassium hydrogen phthalate, dried at 110 °C for two hours, was prepared into a solution and then was titrated by standard sodium hydroxide solution with phenolphthalein as an indicator. The concentration of this standard sodium hydrogen was calculated from the titration result. The hydrochloric acid solutions of various concentrations were titrated by the standard sodium hydroxide solution using methyl orange as an indicator. The concentrations of the hydrochloric acid solutions were calculated from the titration results.

Apparatus. To control temperature accurately, a water tank was designed, and its internal dimensions were 41.5 cm long, 31.5 cm wide, and 29.5 cm high. It was wrapped with foaming plastics as heat-insulating material. The recycled water accessed the tank through the bottom side hole and flowed out from the opposite side of the top. The tank was connected to a constant temperature bath (type CH1015, with the water temperature controlled at a precision of 0.1 °C, temperature fluctuation ± 0.05 °C, pumping output 10 $L \cdot min^{-1}$, made by the Shenzhen Sanli Chemicals Co. Ltd., China). To detect the properties of this water tank, a Beckman thermometer was used and indicated that the water temperature in the tank had a ± 0.02 °C fluctuation. A WLB21 Series Second Standard Glass Hg thermometer with an uncertainty of ± 0.05 °C (produced by Nanking huaqing appearance machine electricity equipment center) was used to measure the temperature of the water. All equilibrium experiments were made in the tank. Electronic balances of Satorius BP190S (within the measure range from (0 to 200) g and an uncertainty of ± 0.0001 g) were used in our experiments. The balances were always calibrated before use every day. Each weighing was usually repeated at least three times, and the average was taken as the result. An A grade buret (GB12803-12808-1991) with an uncertainty of ± 0.05 mL was employed in the titrations.

Procedure. The solubility of $LaCl_3$ in HCl aqueous solution was measured employing the solid–liquid-phase equilibrium method.[5]

Glass test tubes (25 mL) with ground glass joints were used to determine the solubilities. The solid $LaCl_3 \cdot 7H_2O$, about 16 g,

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Table 1. Experimental Data of Solubilities of $LaCl_3$ in HCl Aqueous Solutions[a]

T		HCl	saturated solution (wt %)			solution-solid phase (wt %)		
(°C)	no.	$mol \cdot L^{-1}$	HCl	$LaCl_3$	H_2O	HCl	$LaCl_3$	H_2O
25.00	1	0.000	0.00	48.18 ± 0.01	51.82	–	–	–
	2	1.001	1.68 ± 0.01	42.29 ± 0.06	56.03	0.23 ± 0.01	62.86 ± 0.07	36.91
	3	1.490	2.41 ± 0.01	40.73 ± 0.04	56.86	0.44 ± 0.01	61.44 ± 0.09	38.12
	4	2.024	3.00 ± 0.02	39.52 ± 0.06	57.48	0.61 ± 0.02	60.62 ± 0.04	38.77
	5	2.796	5.33 ± 0.03	34.88 ± 0.05	59.79	0.91 ± 0.01	61.79 ± 0.05	37.30
	6	3.899	7.58 ± 0.03	30.75 ± 0.05	61.67	1.22 ± 0.02	60.46 ± 0.06	38.32
	7	4.939	7.89 ± 0.01	29.76 ± 0.02	62.35	1.39 ± 0.01	61.46 ± 0.03	37.15
	8	5.892	12.50 ± 0.03	21.70 ± 0.03	65.80	3.91 ± 0.03	54.69 ± 0.04	41.40
	9	7.857	17.31 ± 0.02	14.57 ± 0.03	68.12	4.50 ± 0.02	52.65 ± 0.05	42.85
	10	9.583	26.10 ± 0.01	4.34 ± 0.02	69.56	8.62 ± 0.02	45.67 ± 0.07	45.71
35.00	1	0.000	0.00	49.73 ± 0.02	50.27	–	–	–
	2	1.001	1.46 ± 0.02	44.51 ± 0.03	54.03	0.62 ± 0.01	56.45 ± 0.06	42.93
	3	2.024	2.53 ± 0.03	42.24 ± 0.04	55.23	0.66 ± 0.02	56.61 ± 0.08	42.73
	4	2.796	2.59 ± 0.03	35.09 ± 0.03	58.94	0.66 ± 0.01	62.66 ± 0.09	36.68
	5	3.899	7.35 ± 0.01	32.60 ± 0.02	60.05	1.23 ± 0.02	60.46 ± 0.05	38.31
	6	4.939	10.37 ± 0.03	26.95 ± 0.04	62.68	1.46 ± 0.03	60.61 ± 0.11	37.93
	7	5.892	15.94 ± 0.03	18.52 ± 0.03	65.54	3.23 ± 0.03	56.40 ± 0.08	40.37
	8	7.857	24.05 ± 0.05	8.02 ± 0.02	67.93	6.05 ± 0.04	51.46 ± 0.06	42.49
	9	9.583	29.73 ± 0.03	4.86 ± 0.03	65.41	11.31 ± 0.05	42.84 ± 0.14	45.85
45.00	1	0.000	0.00	51.27 ± 0.02	48.73	–	–	–
	2	1.490	1.55 ± 0.01	48.50 ± 0.04	49.95	0.44 ± 0.01	60.40 ± 0.15	39.16
	3	2.024	2.27 ± 0.02	47.63 ± 0.06	50.10	0.55 ± 0.01	61.59 ± 0.13	37.86
	4	2.796	4.00 ± 0.01	43.72 ± 0.08	52.28	1.63 ± 0.02	56.91 ± 0.07	41.46
	5	3.899	6.51 ± 0.03	37.87 ± 0.06	55.62	0.97 ± 0.01	62.22 ± 0.05	36.81
	6	4.939	9.33 ± 0.03	34.02 ± 0.04	56.65	1.83 ± 0.02	59.83 ± 0.12	38.34
	7	5.892	11.54 ± 0.02	30.42 ± 0.05	58.04	2.59 ± 0.03	58.06 ± 0.13	39.35
	8	7.857	21.23 ± 0.03	15.35 ± 0.05	63.42	4.76 ± 0.02	54.67 ± 0.09	40.57

[a] Uncertainties (±) refer to one standard deviation (σ).

was dissolved in the test tubes with HCl solutions (4 mL) ranging from (0 to 9.583) $mol \cdot L^{-1}$ until excess solid was present in the solution. The solution was sealed with the joint to prevent volatilization of HCl and H_2O and then placed in the water tank and kept at 25.00 °C. The tubes were continually oscillated for a period of 48 h. After equilibrium, the solutions were kept in the tank at this temperature for 4 h. Three samples (each being about 0.5 g) of the clear saturated solution were taken out using a sucker and weighed accurately. The temperature of the sucker was slightly higher than that of the solution to prevent crystallization. Every solution was diluted to about 50 mL with redistilled water, according to the method of Khoo.[6] Every diluted solution was divided into two parts, each of them being 25 mL. One was titrated with a 0.0125 $mol \cdot L^{-1}$ NaOH solution using methyl orange as an indicator to determine the H^+ content, and the other was neutralized first by NaOH solution to a pH value of 4~6 and then was titrated with 0.100 $mol \cdot L^{-1}$ $AgNO_3$ solution using K_2CrO_4 as an indicator to determine the total content of chloride ions. The result of the H^+content was the average of three titriations. The result of the total Cl^- content was also from triplicate analyses. Three samples (each being about 1 g) of solid containing some saturated solution at its surface were withdrawn and weighed accurately. Its analysis was similar to the saturated solution.

The contents of HCl and $LaCl_3$ were calculated based on the H^+ content and the total contents of chloride ions and hydrogen ions, respectively.

The equations for calculation are

$$S_{\mathrm{HCl}}\,(\%) = \frac{C_1 V_1 \cdot 36.45}{W \cdot 1000} \cdot 100 \tag{1}$$

$$S_{\mathrm{LaCl_3}}\,(\%) = \frac{(C_2 V_2 - C_1 V_1) \cdot 245.256}{3W \cdot 1000} \cdot 100 \tag{2}$$

where S_{HCl} is the solubility of HCl and S_{LaCl3} is the solubility of $LaCl_3$; W is the weight of saturated solution or the solid–liquid phase; V_1 is the volume of NaOH for determination of H^+ (mL); C_1 is the concentration of NaOH ($mol \cdot L^{-1}$); V_2 is the volume of $AgNO_3$ for determination of the total content of Cl^- (mL); and C_2 is the concentration of $AgNO_3$ ($mol \cdot L^{-1}$).

Suppose V_3 represents the volume of NaOH for neutralizing this system to pH 4~6. It can be found that V_3 almost equals V_1. Therefore, we substitute V_1 for V_3 to calculate $S_{\mathrm{LaCl_3}}$ in eq 2. The error introduced by this substitution can be ignored.

The solubilities of the $LaCl_3-HCl-H_2O$ system at (35.00 or 45.00) °C were determined in a similar fashion.

Results and Discussions

According to the phase equilibrium theory, the composition of the solid–liquid phase must be on a tie line which connects the composition of the pure solid with that of the saturated solution in the phase diagram. Extrapolating the line connecting the composition of the saturated solution in different HCl concentrations with that of the corresponding solid–liquid phase at this concentration, a point which presents the composition of pure solid, can be obtained by converging these lines at various concentrations.

Isothermal Solubility Diagrams of the $LaCl_3-HCl-H_2O$ System at (25.00, 35.00, and 45.00) °C. The experimental data at (25.00, 35.00, and 45.00) °C are shown in Table 1.

The isothermal solubility diagrams of the $LaCl_3-HCl-H_2O$ system at the measured temperatures are shown in Figure 1, Figure 2, and Figure 3, respectively, where it can be seen that the solubility of $LaCl_3$ in HCl aqueous solution decreases with an increase of HCl. The point representing the solid is considered as $LaCl_3 \cdot 7H_2O$ within experimental error. The isothermal solubility curves of $LaCl_3$ in the HCl solution at these temperatures are plotted in Figure 4, where it can be seen that the curve at 35 °C is up slightly when the concentration of HCl is more than 30 wt %. Perhaps, this is due to the formation of La^{3+} complexes in the concentrated HCl solution.

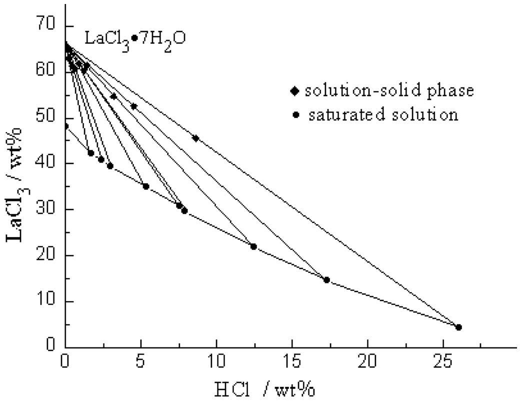

Figure 1. Isothermal solubility diagram of the $LaCl_3-HCl-H_2O$ system at 25 °C.

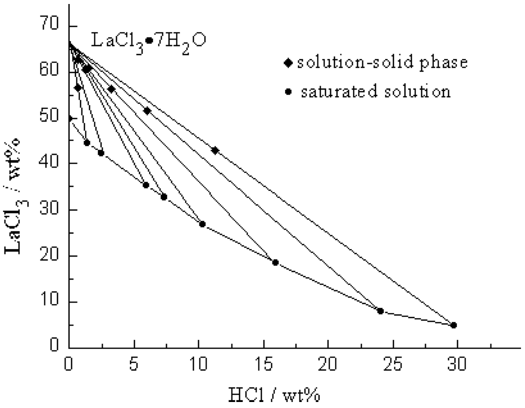

Figure 2. Isothermal solubility diagram of the $LaCl_3-HCl-H_2O$ system at 35 °C.

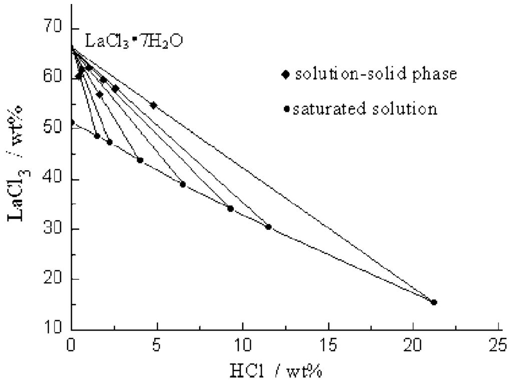

Figure 3. Isothermal solubility diagram of the $LaCl_3-HCl-H_2O$ system at 45 °C.

Solubility of $LaCl_3$ in the Aqueous Solution System. Fischer et al.[2] have measured the solubility of $LaCl_3 \cdot 7H_2O$ in HCl solution at 0 °C. They found that the solubility decreased with increasing concentration of HCl at < 30 wt %, obeying Engel's law at low HCl concentrations.

The solubilities of $LaCl_3$ in pure water were measured as 48.18 wt % at 25 °C, 49.73 wt % at 35 °C, and 51.27 wt % at 45 °C, in the present experiments. A plot for solubility of $LaCl_3$ in water is shown in Figure 5, where a difference is indicated between the data given by Friend[1] and those by Powell.[3] The present measured data agree with Friend's data at (35 and 45) °C well; however, 49.27 wt % was obtained by Friend at 25 °C and 48.88 wt % by Powell, whereas a value of 48.18 wt % was found in the present study.

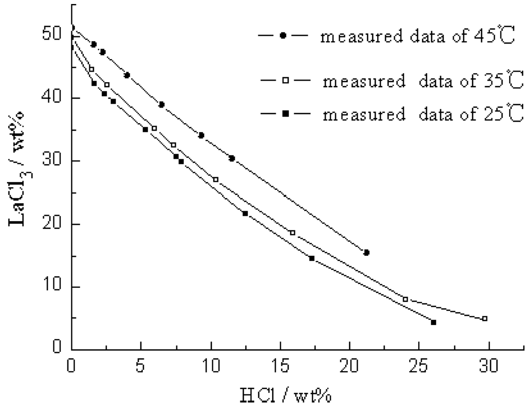

Figure 4. Plot of $LaCl_3$ isothermal solubility against HCl concentration at (25, 35, and 45) °C.

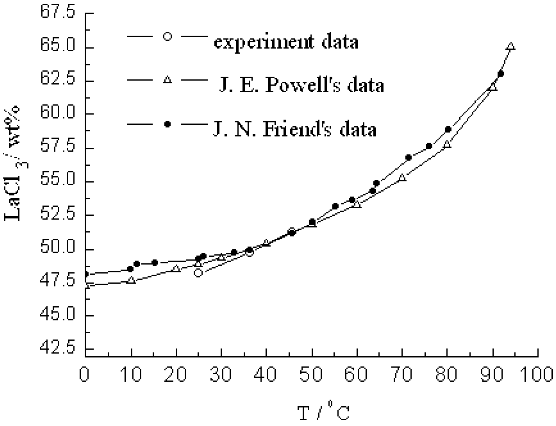

Figure 5. Plot of $LaCl_3$ solubility against temperature.

The data of this experiment have higher precision than those of Friend or Powell because of the more accurate analysis and temperature control.

Conclusions

The solubility of $LaCl_3$ in pure water at (25, 35, and 45) °C was measured as 48.18 ± 0.01 wt %, 49.73 ± 0.02 wt %, and 51.27 ± 0.02 wt %, respectively. The solubility of $LaCl_3$ in the HCl aqueous solution under the various concentrations at (25, 35, and 45) °C was also measured. The isothermal solubility diagrams of the $LaCl_3-HCl-H_2O$ system at those temperatures were obtained.

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