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## PHYSICAL CHEMISTRY OF SOLUTIONS

# Effect of Methanol on the Dissolution of Neodymium Oxide in Hydrochloric Acid Solutions[1]

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**Abstract**—The effect of methanol on the solubility of $Nd_2O_3$ in HCl medium in the temperature range of 25–55°C were studied. $HCl–CH_3OH$ was observed to be a better solvent than $HCl–CH_3OH–H_2O$ and hydrochloric acid for the dissolution of $Nd_2O_3$ mainly due to prevention of neodymium hydroxide and dissolution increased with increase of HCl concentration even at high HCl concentrations. Presence of methanol in the medium was determined to cause corresponding decreases in conductivity, $E_{SCE}$, pH values with corresponding increase in $E_R$ values. Neodymium compounds formed in $HCl–CH_3OH$ medium at 25°C were isolated and identified using X-ray diffraction, thermal and chemical analysis methods and their thermal behaviour were investigated between 25–1100°C. $NdCl_3 \cdot x_1CH_3OH$ and $NdCl_3 \cdot x_2CH_3OH \cdot 4.14H_2O$ ($x_1 + x_2 = 2.8$) were formed in non-aqueous medium and these compounds were converted into $NdCl_3$, $NdCl_{2.37}$ and $NdCl_3 \cdot 0.47CH_3OH$ with complete and partial loss of water and methanol around 240°C respectively. Methanol was completely removed around 390°C with formation of $NdCl_{2.37}$ (77.5%) and NdOCl (22.5%) and NdOCl was detected as the major stable phase above 700°C.

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A continuous decrease in the solubilities of rare-earth chlorides in aqueous hydrochloric acid solutions are observed with increase of HCl concentration [1]. Solubility of rare-earth chlorides in alcohols and aqueous alcohols were studied and it was observed that the solubility increased markedly with temperature [2–4]. Also, complex formation of rare-earth elements with chloride ions in alcohols were investigated [2, 5, 6], alcoholates with the general formula $MCl_3 \cdot 3ROH$ and $MCl_3 \cdot 2ROH \cdot H_2O$ were isolated and some physico-chemical properties of the alcoholate derivatives were studied. The precipitation of lanthanum hydroxide at high HCl concentrations was prevented by use of mixed-aqueous ($HCl–CH_3OH–H_2O$) and preferably non-aqueous ($HCl–CH_3OH$) solvents, the solubility of $La_2O_3$ was improved, the composition of the crystal solvates were determined as $LaCl_3 \cdot x_1CH_3OH$ and $LaCl_3 \cdot x_2CH_3OH \cdot 3H_2O$ ($x_1 + x_2 = 2.35$) and their thermal behaviours were investigated [7].

This study is a complementary of an earlier investigation on the dissolution behaviour of $La_2O_3$ in $HCl–H_2O$, $HCl–CH_3OH–H_2O$ and $HCl–CH_3OH$ [7]. It was aimed to obtain comparative data for determining the effect of methanol on the solubility of $Nd_2O_3$ in HCl medium in the temperature range 25–55°C so as to be able to point out the differences with that of $La_2O_3$ that might be used in rare-earth technology.

## EXPERIMENTAL

$Nd_2O_3$ and $HCl–CH_3OH$ solution were prepared as described [7] by dissolving $Nd(NO_3)_3 \cdot 6H_2O$ (BDH, 99.9% pure) in Merck grade $HNO_3$ and by saturating methanol with HCl gas respectively. For the preparation of the $HCl–CH_3OH–H_2O$ solutions, the saturated $HCl–CH_3OH$ solution was diluted with water. Hydrochloric acid, sulphuric acid and absolute methanol were Merck reagents and absolute methanol was dried before use.

The leaching experiments were carried out in a 200 mL three–necked Pyrex reactor using the same experimental procedure, measurements and analyses as described in the previous work [7].

ICP and XRF techniques were used for Nd analysis at low concentrations and gravimetric analysis based on oxalate precipitation [8, 9] at high concentrations. The chloride content of the $HCl–CH_3OH$ solutions was analyzed by the Volhard method [10]. The products were identified using Rigaku Model 2-22E2 thermal and Leco Model 1000 elemental analyzers. Conductivity, $H^+$ potential and medium potential measurements were done using Tacusell CD6N Model conductivity meter with CM02/55 type electrode,

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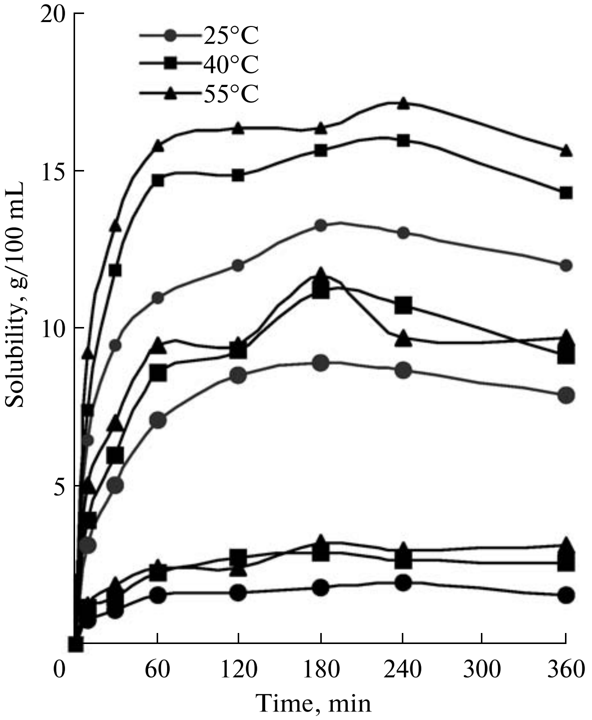

**Fig. 1.** Solubility of $Nd_2O_3$ in $HCl–H_2O$.

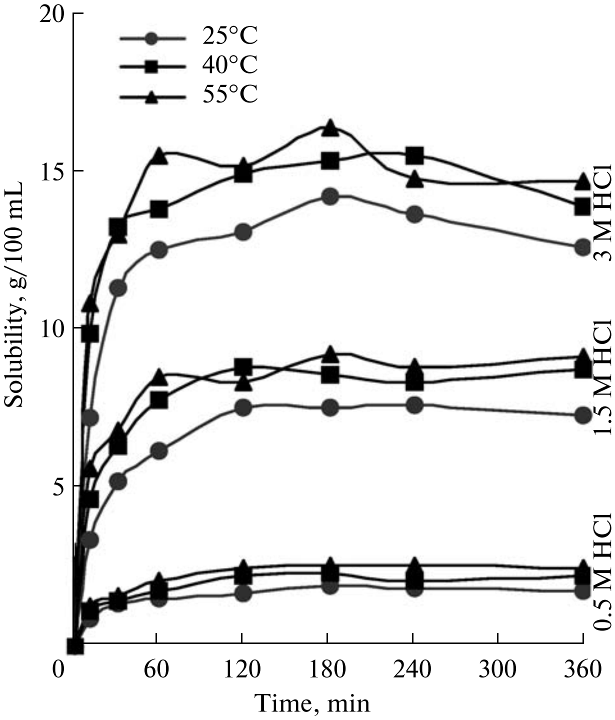

**Fig. 2.** Solubility of $Nd_2O_3$ in $HCl–CH_3OH–H_2O$ (25% $CH_3OH$).

glass electrode and Calomel reference electrode against platinum electrode, respectively.

## RESULTS AND DISCUSSION

The dissolution behaviour of $Nd_2O_3$ in $HCl–H_2O$, $HCl–CH_3OH–H_2O$ and $HCl–CH_3OH$ solutions at different HCl concentrations between 25–55°C for 6 h reaction time are given in Figs. 1–5. Dissolution of $Nd_2O_3$ is increased with increase of HCl concentration and temperature for all the experiments. Although a decrease in solubility in $HCl–H_2O$ system is observed at increasing reaction times, this tendency is gradually eliminated with decrease of water in the solvent systems and maximum dissolution values are reached in $HCl–CH_3OH$ solvent system.

Change of conductance, $E_{SCE}$, pH and $E_R$ with HCl concentration and temperature for the $HCl–H_2O$ solvent system for a reaction time of 6 hours are given in Figs. 6 and 7. The conductance and $E_{SCE}$ values of pure $HCl–H_2O$ solvent increase with HCl concentration. Similarly, the conductance and $E_{SCE}$ values of the leach solutions are also observed to increase with HCl concentration and temperature. But, for all temperatures and HCl concentrations, the values obtained for leach solutions are lower than that of pure solvents. This tendency can be explained by lowering of $H^+$ ion concentration in the medium due to basic property of neodymium and formation of higher valency neodymium complexes. The pH values of the leach solutions are very high compared to pure solvent and all decrease with increase of HCl concentration. $E_R$ values for leach solutions are much lower than that of pure solvent, all increase with HCl concentration and the most significant change for the leach solutions is observed at 25°C. Decrease in pH values and increase in $E_R$ values can be related to decrease in solubilities at higher HCl concentrations due to formation of $NdCl_3 \cdot 6H_2O$ as a solid phase [1] and possible hydroxide precipitation above pH 6.

Figures 8 to 13 show the change of conductance, $E_{SCE}$, pH and $E_R$ of $HCl–CH_3OH–H_2O$ solvent system for a reaction time of 6 hours. The conductance and $E_{SCE}$ values decrease (Figs. 8, 10, 12) in accordance with the decrease of water contents of the solvent systems. More pronounced decreases in pH and corresponding increases in $E_R$ (Figs. 9, 11, 13) can be related to the lowering of conductance of the medium due to increase of methanol in the solvents and the formation of $NdCl_3 \cdot xH_2O \cdot yCH_3OH$ type compounds.

Experimental data related with the non-aqueous solvent system and the leach solutions are given in Figs. 14 and 15. Change of conductance and $E_{SCE}$ with HCl concentration in non-aqueous medium is completely different than those of mixed-aqueous and aqueous mediums. Due to low conductance value of methanol, $HCl–CH_3OH$ solvent system has the lowest conductance values for all HCl concentrations. The conductance values of the leach solutions are lower than that of the pure solvent which can be explained by

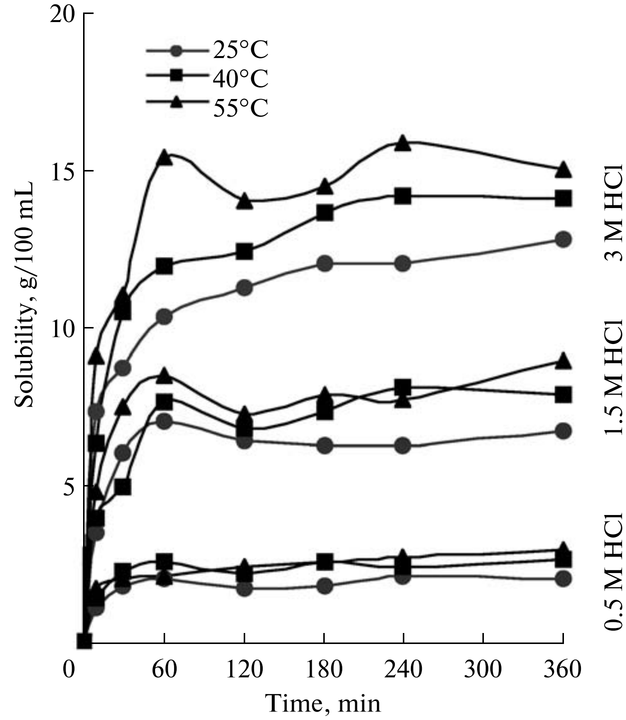

**Fig. 3.** Solubility of $Nd_2O_3$ in $HCl–CH_3OH–H_2O$ (50% $CH_3OH$).

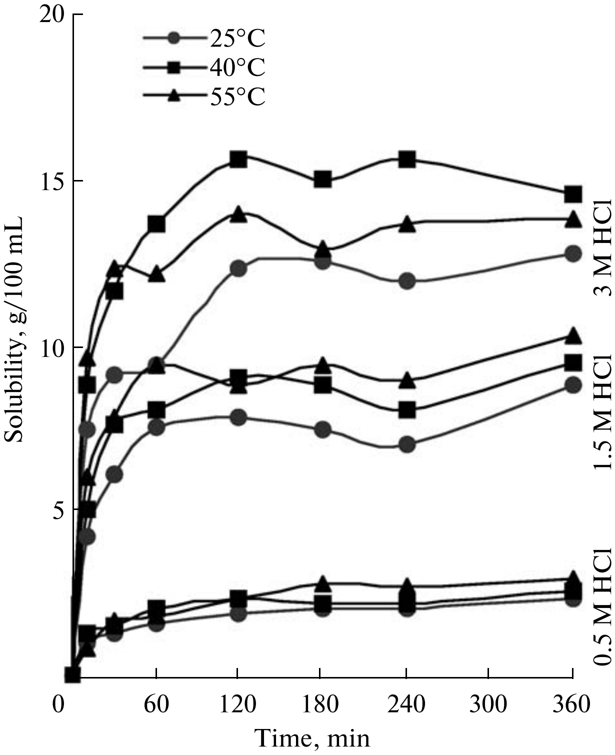

**Fig. 4.** Solubility of $Nd_2O_3$ in $HCl–CH_3OH–H_2O$ (75% $CH_3OH$).

formation of neutral neodymium–methanol compounds. $HCl–CH_3OH$ solvent system has the lowest $E_{SCE}$ value due to low ionization of methanol but the $E_{SCE}$ values of the leach solutions are higher than those of aqueous and mixed-aqueous leach solutions and even that of the $HCl–CH_3OH$ solvent system because of the higher $H^+$ ion concentration of the medium. The conductance values of the leach solutions in non-aqueous medium are much lower than those of aqueous and mixed-aqueous mediums due to low conductance of methanol and due to formation of neutral neodymium–methanol compounds. Low pH values of the leach solutions prevent neodymium hydroxide precipitation and provide better dissolution.

**Table 1.** TGA-DTA analysis results for neodymium compounds

| Temperature range, °C | Weight loss, % |
|---|---|
| 68.5–126.1 | 15.9 |
| 126.1–140 | |
| 140.0–201.6 | 3.9 |
| 201.6–250 | 4.4 |
| 348.7–505 | 10.0 |

25 g of $Nd_2O_3$ was reacted with 50 mL of $HCl–CH_3OH$ solvent at 7 M HCl concentration for 60 minutes and a highly hygroscopic jelly product was obtained. Reaction products were dried at 75°C for 2 h, kept in vacuum desiccator and were identified by TGA, DTA, XRD and chemical analyses.

The thermal decomposition curve of the neodymium compounds in $HCl–CH_3OH$ solvent system showed five endothermic peaks of which the temperature ranges and the weight losses are given in Table 1.

For the determination of the decomposition products, the neodymium compound formed in non-aqueous medium was heated separately considering the temperature ranges given in Table 1 and compounds formed were identified by XRD and chemical analyses. The chemical analysis results and the XRD patterns are given in Table 2 and Fig. 16, respectively.

Evaluation of the XRD results together with chemical analysis and weight loss values show the presence of the neodymium compounds given in Table 3 and that of lanthanum (Table 4) for comparison purposes.

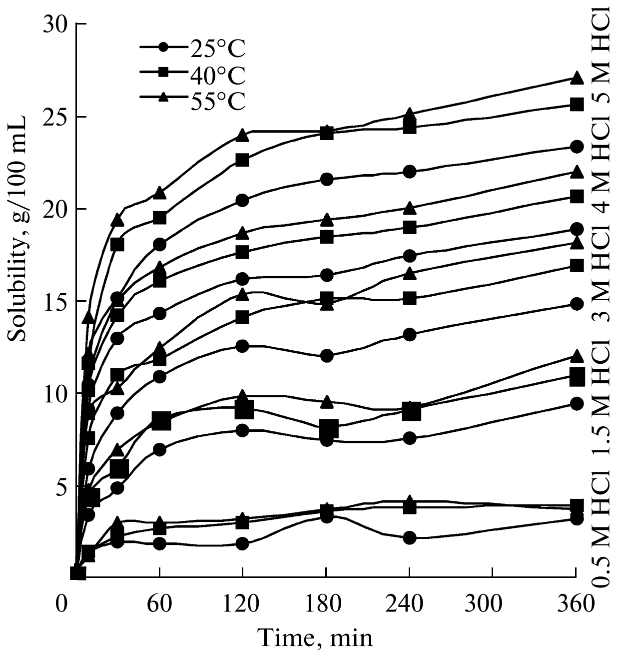

**Fig. 5.** Solubility of $Nd_2O_3$ in $HCl–CH_3OH$.

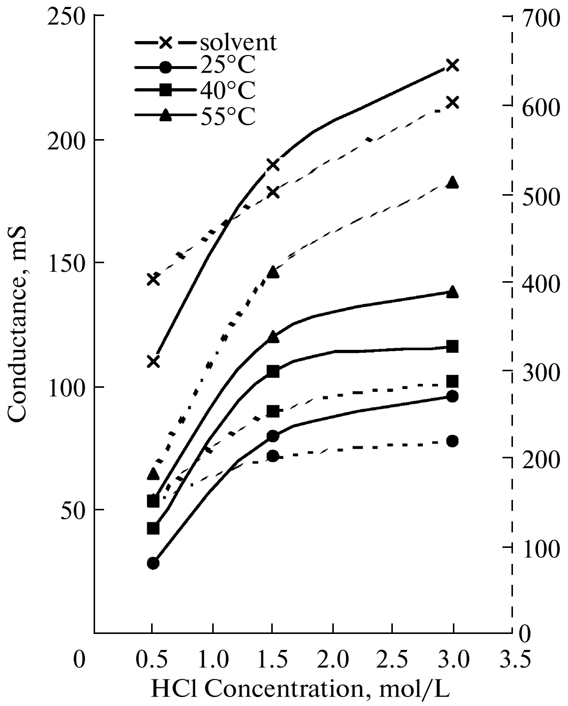

**Fig. 6.** Change of conductance and $E_{SCE}$ in $Nd–HCl–H_2O$ system with HCl concentration and temperature.

## CONCLUSIONS

$HCl–CH_3OH$ is a better solvent than $HCl–CH_3OH–H_2O$ and hydrochloric acid for the dissolution of $Nd_2O_3$. The main advantages of this non-aqueous solvent system is that neodymium hydroxide is not precipitated and dissolution increases with increase of HCl concentration even at high HCl concentrations. The dissolution behaviour of $Nd_2O_3$ in the solvent systems tested is similar to that of $La_2O_3$ but the solubility of $Nd_2O_3$ is lower. A solubility difference of 1.22 times between lanthanum and neodymium in aqueous medium was observed to increase to 1.40 times in non-aqueous medium.

Although $NdCl_3 \cdot nH_2O$ type compounds are formed in aqueous media at 25°C, $NdCl_3 \cdot x_1CH_3OH$ and $NdCl_3 \cdot x_2CH_3OH \cdot 4.14H_2O$ ($x_1 + x_2 = 2.8$) are formed in non-aqueous media. Water and methanol losses are observed up to 165°C and $NdCl_3$ is formed as a new phase. With increase of temperature to 240°C, water is completely removed and besides $NdCl_3$ as the major phase, $NdCl_{2.37}$ and $NdCl_3 \cdot 0.47CH_3OH$ are formed. Further increase of temperature to 390°C leads to decomposition of $NdCl_3$ and NdOCl starts to be formed besides the major phase $NdCl_{2.37}$. At 700°C, NdOCl becomes the stable phase (96%) with 4% of $NdCl_{2.37}$.

The thermal behaviours of the neodymium and lanthanum compounds formed in $HCl–CH_3OH$ solvent system are slightly different. For example, complete loss of water in neodymium and lanthanum compounds are at 240 and 165°C, respectively. Similarly, complete removal of methanol from neodymium compounds at 390°C takes place at 200°C for lanthanum compounds.

As can be seen, there are differences in the temperatures of water and methanol losses, in the types of chloride compound formations ($LaCl_3$, $NdCl_3$,

**Table 2.** Chemical analysis results of the thermal decomposition products

| Temperature, °C | Nd, % | Cl, % | C, % | H, % | Weight loss, % |
|---|---|---|---|---|---|
| 25 | 34.20 | 28.94 | 8.12 | 4.77 | — |
| 125 | 38.26 | 27.20 | 6.24 | 3.57 | 12.00 |
| 150 | 43.80 | 30.74 | 5.85 | 3.14 | 6.00 |
| 165 | 46.86 | 32.27 | 3.98 | 1.72 | 2.00 |
| 240 | 56.26 | 35.47 | 2.20 | 0.91 | 4.50 |
| 390 | 64.46 | 32.14 | – | – | 5.00 |
| 700 | 72.29 | 17.13 | – | – | 6.00 |

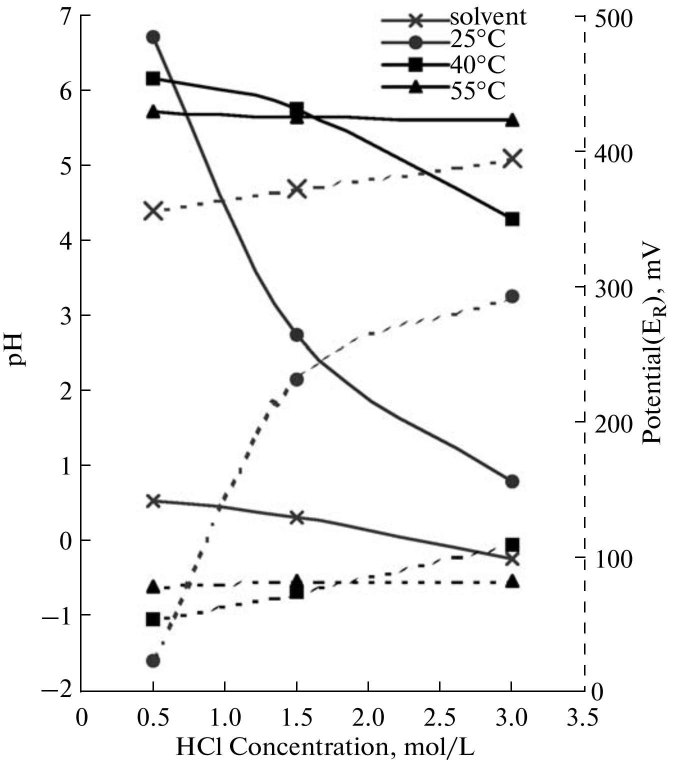

**Fig. 7.** Change of pH and $E_R$ in Nd–HCl–$H_2O$ system with HCl concentration and temperature.

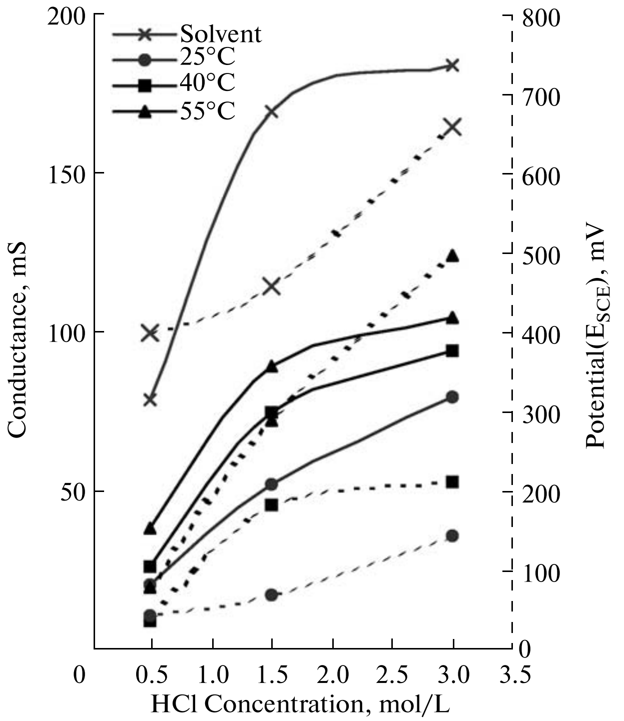

**Fig. 8.** Change of conductance and $E_{SCE}$ of Nd–HCl–$CH_3OH$–$H_2O$ system (25% $CH_3OH$) with HCl concentration and temperature.

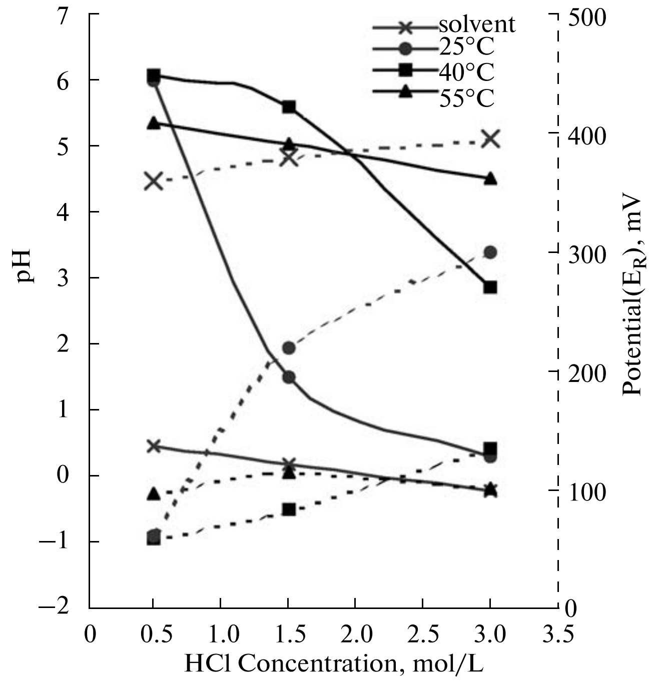

**Fig. 9.** Change of pH and $E_R$ of Nd–HCl–$CH_3OH$–$H_2O$ system (25% $CH_3OH$) with HCl concentration and temperature.

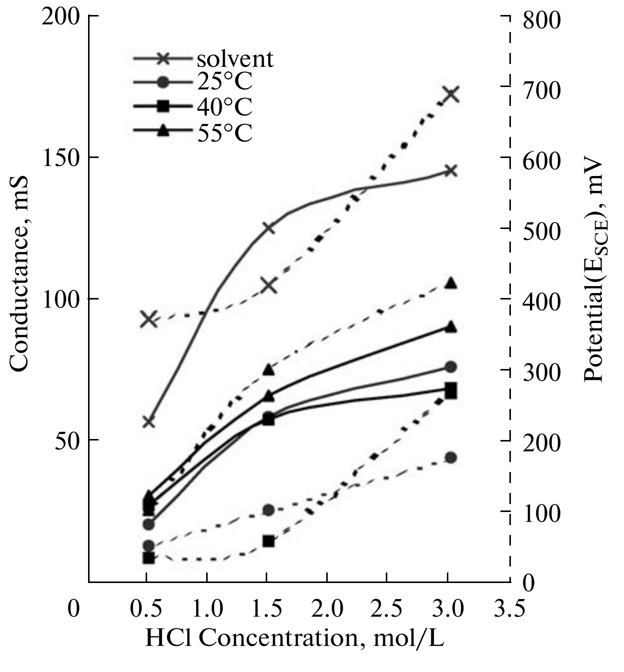

**Fig. 10.** Change of conductance and $E_{SCE}$ of Nd–HCl–$CH_3OH$–$H_2O$ system (50% $CH_3OH$) with HCl concentration and temperature.

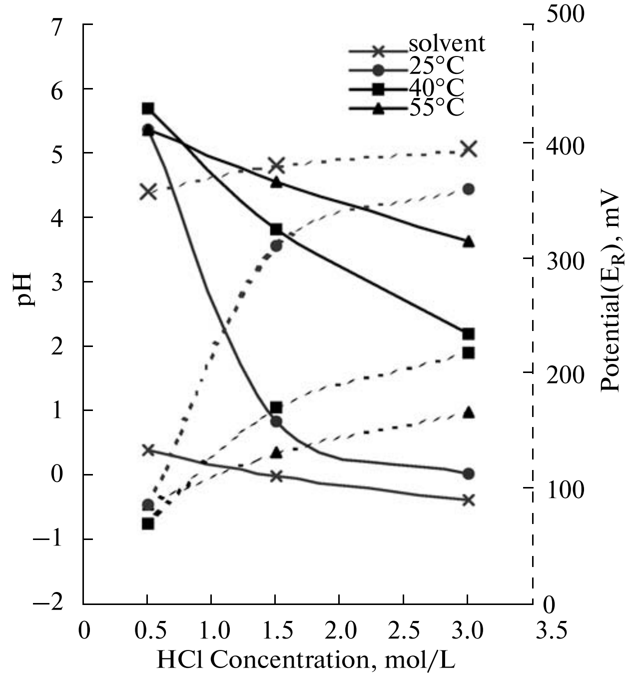

**Fig. 11.** Change of pH and $E_R$ of Nd–HCl–$CH_3OH$–$H_2O$ system (50% $CH_3OH$) with HCl concentration and temperature.

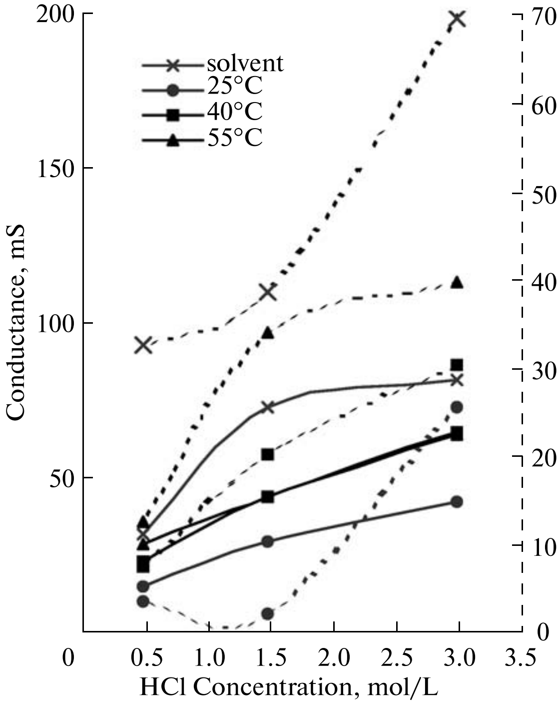

**Fig. 12.** Change of conductance and $E_{SCE}$ of Nd–HCl–$CH_3OH$–$H_2O$ system (75% $CH_3OH$) with HCl concentration and temperature.

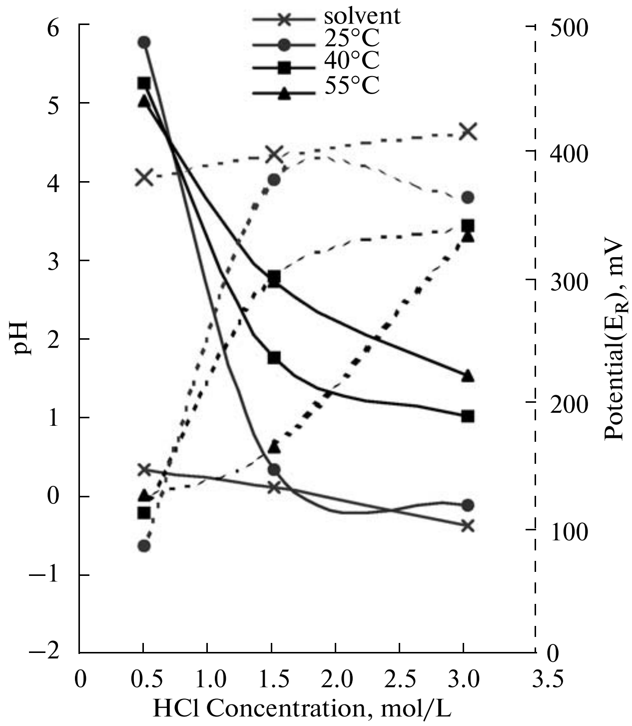

**Fig. 13.** Change of pH and $E_R$ of Nd–HCl–$CH_3OH$–$H_2O$ system (75% $CH_3OH$) with HCl concentration and temperature.

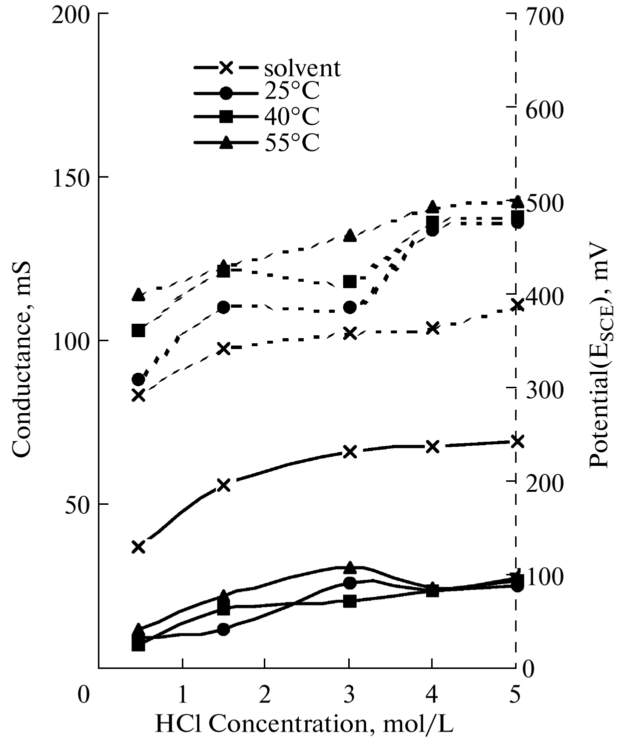

**Fig. 14.** Change of conductance and $E_{SCE}$ of Nd–HCl–$CH_3OH$ system with HCl concentration and temperature.

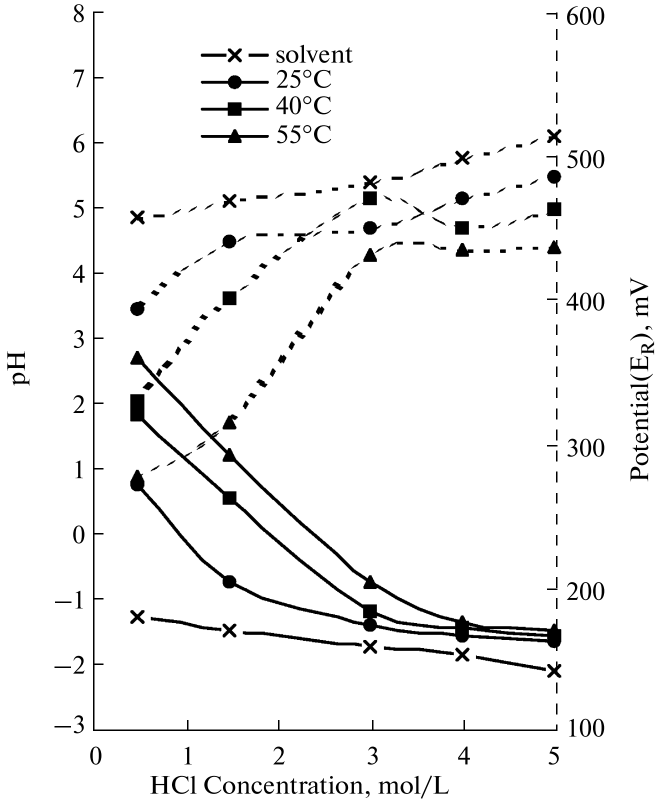

**Fig. 15.** Change of pH and $E_R$ of Nd–HCl–$CH_3OH$ system with HCl concentration and temperature.

**Table 3.** Neodymium compounds formed in HCl–$CH_3OH$ solvent system and the decomposition products between 25–1100°C

| Temperature, °C | Chemical Composition | |
|---|---|---|
| 25 | $NdCl_3 \cdot x_1CH_3OH$<br>$NdCl_3 \cdot x_2CH_3OH \cdot 4.14H_2O$ | $x_1 + x_2 = 2.8$ |
| 125 | $NdCl_3 \cdot x_1CH_3OH$<br>$NdCl_3 \cdot x_2CH_3OH \cdot 2.8H_2O$ | $x_1 + x_2 = 1.96$ |
| 150 | $NdCl_3 \cdot x_1CH_3OH$<br>$NdCl_3 \cdot x_2CH_3OH \cdot 1.96H_2O$ | $x_1 + x_2 = 1.6$ |
| 165 | $NdCl_3$<br>$NdCl_3 \cdot x_1CH_3OH$<br>$NdCl_3 \cdot x_2CH_3OH \cdot 0.6H_2O$ | $x_1 + x_2 = 1.02$ |
| 240 | 94.2% $NdCl_3$ + 6.8% $NdCl_{2.37}$<br>$NdCl_3 \cdot 0.47CH_3OH$ | |
| 390 | 77.5% $NdCl_{2.37}$ + 22.5% NdOCl | |
| 700 | 4.34% $NdCl_{2.37}$ + 94.36% NdOCl | |

**Table 4.** Lanthanum compounds formed in HCl–$CH_3OH$ solvent system and the decomposition products between 25–1100°C [7]

| Temperature, °C | Chemical Composition | |
|---|---|---|
| 25 | $LaCl_3 \cdot x_1CH_3OH$<br>$LaCl_3 \cdot x_2CH_3OH \cdot 3H_2O$ | $x_1 + x_2 = 2.35$ |
| 120 | $LaCl_3 \cdot x_1CH_3OH$<br>$LaCl_3 \cdot x_2CH_3OH \cdot 0.5H_2O$ | $x_1 + x_2 = 1.90$ |
| 165 | $LaCl_3 \cdot 1.14CH_3OH$ | |
| 200 | 77.3% $LaCl_3$ + 22.7% LaOCl | |
| 560 | 33.14% $LaCl_3$ + 66.86% LaOCl | |
| 700 | 5.52% $LaCl_3$ + 94.47% LaOCl | |

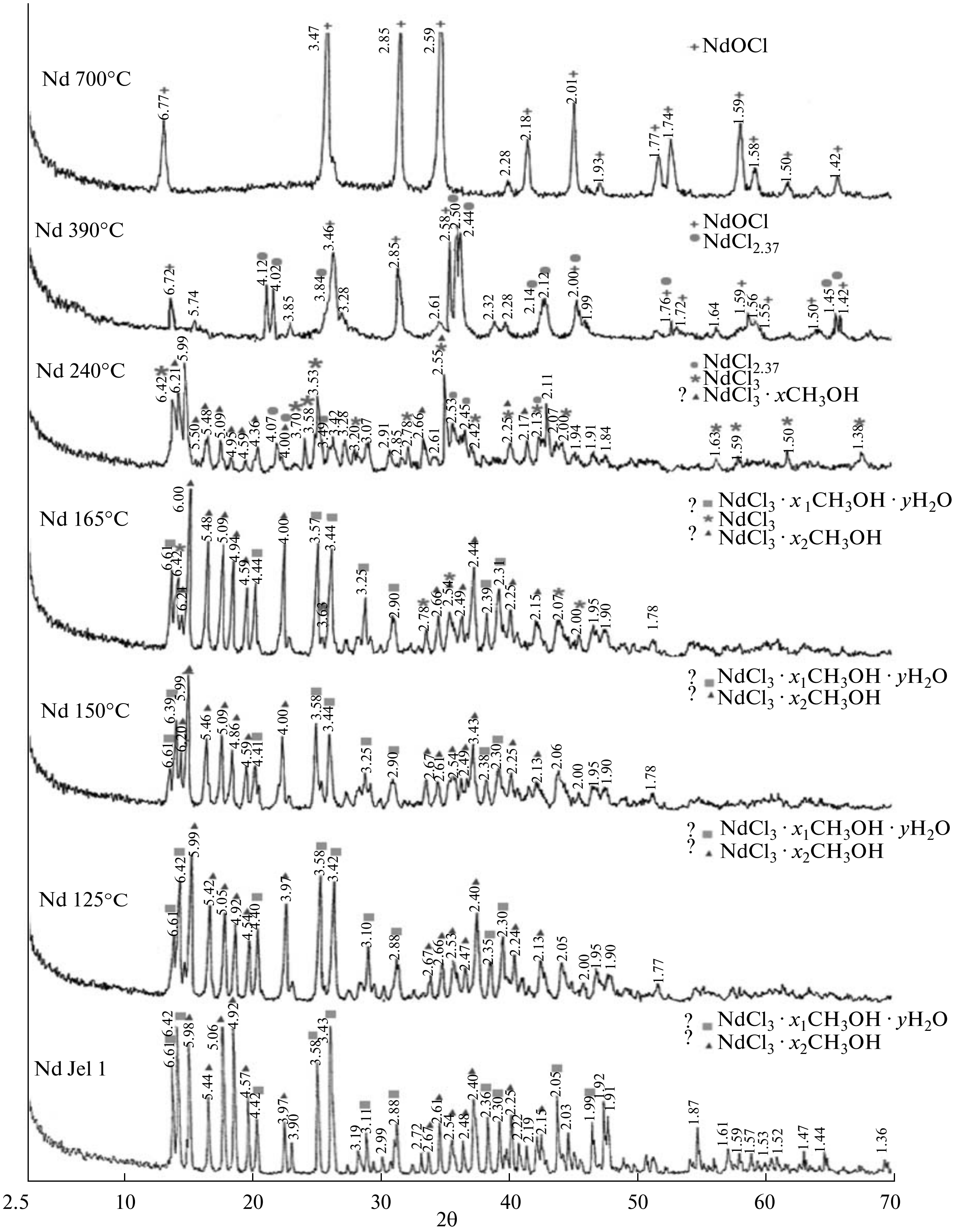

**Fig. 16.** Comparative XRD patterns of the decomposition products.

$NdCl_{2.37}$) and in the oxychloride conversion temperatures for $La_2O_3$ and $Nd_2O_3$. All these differences seem to have potential use areas for the processing (separation) of rare-earth elements that show very similar chemical properties.

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