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Effect of Crystallization Water and Nature of an Aluminum Alkyl on the Reduction of Eu^{3+} to Eu^{2+} in Interaction of $EuCl_3 \cdot 6H_2O$ with Bu^i_3Al and Et_3Al

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Abstract—Volumetric and photoluminescence analytical techniques were employed to study the effect of crystallization water and nature of an aluminum alkyl on the reduction of Eu^{3+} to Eu^{2+} in a heterophase interaction of $EuCl_3 \cdot 6H_2O$ in toluene with Bu^i_3Al and Et_3Al.

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Studying the fundamental aspects of the interaction of $LnCl_3 \cdot 6H_2O$ crystal hydrates with aluminum alkyls (R_3Al) is a topical task for the following reasons. First, these reactions are used to synthesize effective catalysts for polymerization of butadiene [1] and condensation of aniline with aldehydes and amino quinolines to give, respectively, polybutadiene, substituted quinolines, naphthyridines, and phenanthrolines [2, 3]. Second, interaction of a crystal hydrate (CH) $EuCl_3 \cdot 6H_2O$ has been used to obtain [4] a new complex $EuCl_2 \cdot 0.5H_2O \cdot 0.05(Bu^i_2Al)_2O$ exhibiting a bright blue photoluminescence (PL) at room temperature, whereas it is known [5, 6] that Eu^{2+} compounds exhibiting a PL (due to emission from the Eu^{2+} ion) are used in manufacture of luminescent lamps, lasers, X-ray dosimeters, and paper-bleaching agents. The use of the reaction of the CH with Bu^i_3Al to obtain a Eu^{2+} compound has a number of important advantages: simple glass reactor, room temperature, short synthesis duration (0.5 h), and comparatively inexpensive domestic starting reagents. At the same time, the reactions conventionally used for this purpose [7]: reduction of $EuCl_3$ with metallic Ln or H_2, thermal decomposition of $EuCl_3$, and interaction of metallic Eu with $HgCl_2$ have important shortcomings: need for special apparatus (autoclave), high temperatures (400–700°C), long synthesis durations (4–10 h), and corrosive medium (HCl).

Taking into account that (i) the reaction of CH with R_3Al is promising for development of a high-tech and economical method for synthesis of luminescent compounds of Eu^{2+} and (ii) aluminum alkyl can attack both the Eu^{3+} ion and crystallization water, we studied for the first time the influence exerted by crystallization water of a CH and by the nature of an aluminum alkyl on the reduction of Eu^{3+} to Eu^{2+} in heterophase interaction of the CH in toluene with Bu^i_3Al and Et_3Al.

EXPERIMENTAL

We used a CH (chemically pure grade), benzine solutions of R_3Al (purified by distillation [8]), and toluene distilled over metallic Na. Argon was passed through a PG (Gas absorber) device. The products formed in the interaction of the CH with R_3Al: alumoxane, alkanes, and $EuCl_2 \cdot 0.5H_2O \cdot 0.05(Bu^i_2Al)_2O$ complex, were analyzed by the procedure described in [2], and 2,5-methylhexane, by GLC (Chrom 5, column 3 m long and 4 mm in diameter, 5% SE-30 on Chromaton N-AW-HMDS as stationary phase). The processes of europium dehydration and reduction, which occur in the reaction of the CH with R_3Al, were monitored in parallel runs by measuring, respectively, the volume of the alkanes evolved with a gas burette [2] and the intensity of PL from europium. For this purpose, a weighed portion of the CH (0.54 g) was

placed in a quartz ampoule with a magnetic stirrer, toluene was added, and the Eu^{3+} PL intensity was measured in the solid phase at 612 nm (20°C). Then agitation was switched on and R_3Al was introduced using a syringe, with Al/Eu ratios of 12, 20, 30, 40. The total volume of the reaction solution was 10 ml. At certain intervals of time, the PL from the solid phase was recorded (with the stirrer switched off) at 612 nm for Eu^{3+} and 485 nm for Eu^{2+}. PL spectra were measured with a spectrofluorimeter based on an MDR-23 monochromator and a FEU-39 photomultiplier as a photodetector.

On addition of a Bu^i_3Al solution to a suspension of the CH in toluene, the red Eu^{3+} PL disappears ($\lambda_{max} = 612$ nm) and there appears a blue Eu^{2+} PL ($\lambda_{max} = 485$ nm), with its brightness gradually reaching the maximum value (by approximately 80th minute) (Fig. 1, curves *1* and *2*). By this instant of time, the whole amount of Eu^{3+} is reduced to Eu^{2+}. During and after the interaction of the CH with R_3Al, the whole amount of europium remains in the solid phase.

The reaction of the CH with Bu^i_3Al is also accompanied by vigorous evolution of gaseous Bu^iH, which points to dehydration of the europium ion (Fig. 1, curve *3*). By the instant of disappearance of the Eu^{3+} PL, about 33% Bu^iH is released, which corresponds, in terms of crystallization water that has entered into the reaction with Bu^i_3Al [in accordance with the stoichiometry of reaction (1)], to removal of two water molecules

$$H_2O + 2\,Bu^i_3Al \rightarrow (Bu_2^i\,Al)_2O + 2Bu^iH. \qquad (1)$$

It can be assumed that the observed decrease in the intensity of the Eu^{3+} PL is due to partial dehydration of the Eu^{3+} ion, which yields compounds characterized by a lower quantum efficiency of the Eu^{3+} PL because of the smaller number of water molecules coordinated with this ion, compared with the Eu^{3+} ion contained in the CH. A similar decrease in the PL intensity has been observed previously in the interaction of $TbCl_3 \cdot 6H_2O$ with R_3Al [2]. In addition, our measurements demonstrated that the PL intensity of anhydrous $EuCl_3$ (synthesized by the method described in [7]) is an order of magnitude lower than that for the CH. After 10–12 min of interaction between the CH and Bu^i_3Al, vigorous evolution of Bu^iH almost ceases (Fig. 1, curve *3*) and a steep rise in the Eu^{3+} PL intensity is observed (Fig. 1, curve *2*). By this time, the Eu/H_2O ratio is less than unity [found by calculating the amount of water reacted with Bu^i_3Al, using the kinetic curve of isobutane evolution (Fig. 1, curve *3*)].

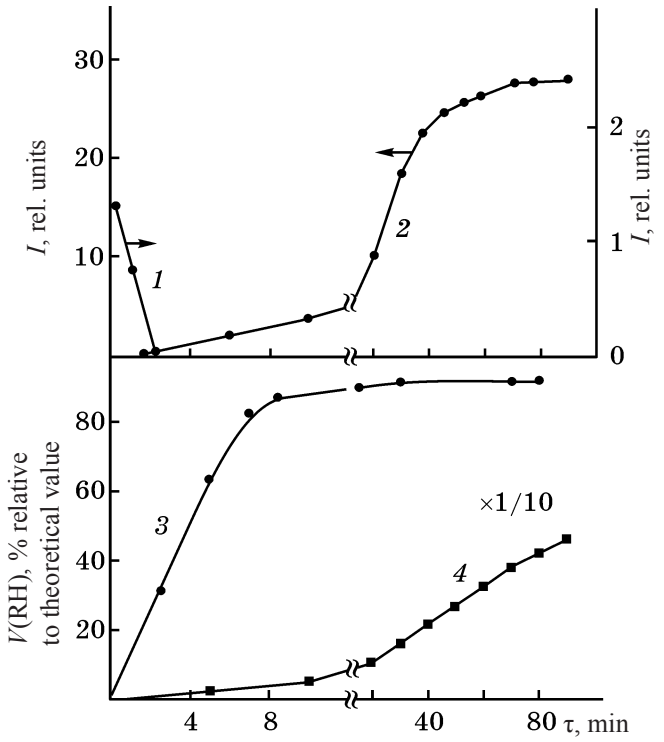

Fig. 1. Kinetics of variation of the PL intensity from (*1*) Eu^{3+} and (*2*) Eu^{2+} and for evolution of (*3*) Bu^iH and (*4*) EtH in the reaction of $EuCl_3 \cdot 6H_2O$ (0.54 mmol) in toluene with (*1–3*) Bu^i_3Al and (*4*) Et_3Al. $R_3Al/EuCl_3 \cdot 6H_2O = 30$, 20°C, λ_{ex} = 365 nm for Eu^{3+} and 280 nm for Eu^{2+}. (*I*) PL intensity, [*V*(RH)] alkane volume, and (τ) time.

The rate of Eu^{3+} reduction, estimated by the time in which the maximum PL intensity is reached, increases with the ratio between the starting reagents ($Bu^i_3Al/EuCl_3 \cdot 6H_2O$): 80 min (20), 65 min (30), 30 min (40). At $Bu^i_3Al/EuCl_3 \cdot 6H_2O \leq 12$, no Eu^{2+} PL is observed (monitoring time 1 h), because the whole amount of Bu^i_3Al is expended under these conditions in the reaction with water and europium is not reduced.

It was found that the nature of an aluminum alkyl strongly affects the time in which the blue Eu^{2+} PL appears. For example, in the interaction of the CH with Et_3Al, the PL is recorded much later (in 2 h), compared with the case of Bu^i_3Al (in 1.5–2 min). It was found that this effect is not due to different reactivities of Eu^{3+} toward aluminum alkyls of varied nature. This conclusion follows from an analysis of the results of the following experiments. Into a reactor containing a suspension of CH (0.54 mmol) in toluene, we introduced Bu^i_3Al (Al : Eu^{3+} = 12) in order to dehydrate the CH. After the evolution of the main amount of Bu^iH ceased (in ~10 min), the solution was decanted and the remaining solid product

(SP) was washed with toluene (3 × 30 ml). An analysis of the SP for the content of residual water (by Fischer) and europium (by chelatometry) demonstrated that it contains these components in an approximately 1 : 1 H_2O/Eu ratio. The solid product is characterized by a weak permanent Eu^{2+} PL (Fig. 2). Immediately after a toluene solution of Et_3Al or Bu^i_3Al (R_3Al/Eu = 18) is added to the SP, the Eu^{2+} PL intensity starts to increase, with the rates of this increase being about the same for these aluminum alkyls. If toluene is added instead of the aluminum alkanes, the Eu^{2+} PL intensity remains unchanged.

Analysis of the results obtained shows that the reduction of Eu^{3+} by an aluminum alkyl to Eu^{2+} is a slower process than the dehydration of the Eu^{3+} ion, and the removal of water molecules from the coordination environment of Eu^{3+} accelerates its conversion to Eu^{2+}. Thus, crystallization water coordinated to the Eu^{3+} ion has a shielding effect on its reduction by an aluminum alkyl. The reactivities of the aluminum alkyls Bu^i_3Al and Et_3Al toward the Eu^{3+} ion are rather close. The shorter interval of time after which the blue Eu^{2+} PL appears in the reaction of the CH with Bu^i_3Al is due to the higher rate of its interaction with crystallization water. The most probable reason is that, in solution, Bu^i_3Al is in the form of a monomer, and Et_3Al, in the form of dimers [8]. It was found in this study that the products of interaction between the CH and Bu^i_3Al contain, in addition to the previously identified complex $EuCl_2 \cdot 0.5H_2O \cdot 0.05(Bu^i_2Al)_2O$, alkane, and alumoxane, also 2,5-dimethyl hexane (product of recombination of $Bu^i\bullet$ radicals) and Bu^i_2AlCl (identified by ^{13}C NMR).

On the basis of the results obtained, the reaction of the CH with aluminum alkyls can be described by the scheme

$$EuCl_3 \cdot 6H_2O + R_3Al \rightleftharpoons \begin{cases} EuCl_3\, x(H_2O)\, y(R_2Al)_2O + (R_2Al)_2O + RH & (2) \\ EuCl_2 \cdot 0.5(H_2O) \cdot 0.5(R_2Al)_2O + R_2AlCl + R{-}R & (3) \end{cases}$$

where $0.5 \le x < 6$ and $0 \le y \le 0.05$.

According to this scheme, the aluminum alkyl attacks two fragments of the CH, crystallization water and the lanthanide ion at an excess of R_3Al ($R_3Al/EuCl_3 \cdot 6H_2O > 12$). The existence of an auto-acceleration portion in the kinetic curve describing the variation of the Eu^{2+} PL intensity (Fig. 1) suggests the following. In the range $1 < H_2O/Eu^{3+} < 6$, the main interaction direction is the reaction of R_3Al with crystallization water (2) to give $(R_2Al)_2O$, RH, and $EuCl_3 \cdot x(H_2O) \cdot y(R_2Al)_2O$ compound containing a smaller amount of water than the CH. Under these conditions, the attack of the aluminum alkyl on CH, with reduction of the Eu^{3+} ion to Eu^{2+} and formation of R_2AlCl and R–R by (3), is a minority channel. As water molecules are removed from the coordination environment of Eu^{3+} (at $H_2O/Eu < 1$), Eu^{2+} starts to be intensely formed by scheme (3).

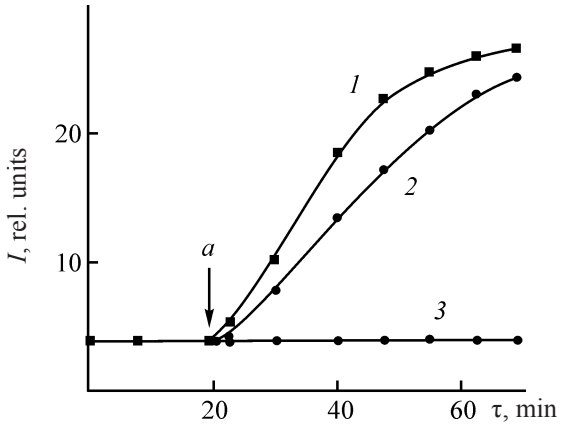

Fig. 2. Kinetics of variation of the PL intensity from Eu^{2+} (λ_{PL} = 485 nm) at 20°C. λ_{ex} = 280 nm; portion from zero to instant of time a is for the SP formed in the interaction (10 min) of $EuCl_3 \cdot 6H_2O$ (0.54 mmol) with Bu^i_3Al in toluene ($Bu^i_3Al/EuCl_3 \cdot 6H_2O = 20$) and washed with toluene. (*1, 2, 3*) Curves obtained upon addition of, respectively, Bu^i_3Al (0.54 mmol), Et_3Al (0.64 mmol), and toluene (5 ml) at the instant of time *a*. (*I*) PL intensity and (τ) time.

CONCLUSIONS

(1) In a heterophase interaction of $EuCl_3 \cdot 6H_2O$ with aluminum alkyls, molecules of crystallization water shield the Eu^{3+} ion and thereby hinder its effective reduction to Eu^{2+}.

(2) The aluminum alkyls Bu^i_3Al and Et_3Al have the same reactivity in the reduction of Eu^{3+}. However, use of Bu^i_3Al, which reacts with molecules of crystallization water faster than Et_3Al, is more effective for obtaining a brightly luminescent compound of Eu(II): $EuCl_2 \cdot 0.5H_2O \cdot 0.05(R_2Al)_2O$.

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