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Solvent extraction of Gd(III) from perchlorate and nitrate media with mixtures of thenoyltrifluoroacetone and Benzo-15-Crown-5

Valeri Jordanov

Department of General and Inorganic Chemistry, University of Chemical Technology and Metallurgy, 8 Kliment Okhridski Blvd., 1756 Sofia, Bulgaria

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Abstract

The extraction of Gadolinium (Gd) from perchlorate and nitrate media in 1,2-dichloroethane ($C_2H_4Cl_2$), carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) by mixtures of 2-thenoyltrifluoroacetone (HTTA) and a crown ether benzo-15-crown-5 (B15C5) is investigated. The composition of the extracted species is determined as $Gd(TTA)_3.nB15C5$ (n=1 in nitrate medium and n=2 in perchlorate medium). The values of the equilibrium constant $K_{T,S}$ and $\beta_{T,S}$ are calculated. The influence of the water medium and the polarity of organic diluents on the extraction process are discussed.

Keywords: Lanthanoids; Thenoyltrifluoroacetone; Benzo-15-crown-5; Synergistic extraction.

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1. Introduction

The chelating extractant 2-thenoyltrifluoroacetone has been extensively studied in the extraction of trivalent lanthanoids (Ln^{3+}) in various organic diluents [1-4]. It has been found, that the extraction of lanthanoids significantly increases in the presence of different synergistic agents as organophosphorous compounds, 1,10-phenantroline, amines, and quaternary ammonium salts [5-12].

In the last 15-20 years, crown ethers (CE) have been often used as synergistic agents in the extraction and separation of trivalent lanthanoids [13-27], divalent transition and alkali metals [28, 29]. The crown ethers basicity and concentration, polarity of the organic diluents, as well as the ionic medium and ionic strength in the aqueous phase influence the complex formation type [14-16, 25]. Adduct complex formation-$Ln(TTA)_3.nCE$ (n=1 or 2) [13-16, 25] and ion-pair complexes-$[Ln(TTA)_2.CE]^+X^-$ ($X = NO_3^-$ or ClO_4^-) [17-20, 27] have been established. In the present study, synergistic extraction of Gd from perchlorate and nitrate media with mixtures of HTTA and B15C5 in 1,2-dichloroethane, carbon tetrachloride and chloroform is investigated.

2. Experimental

2.1. Reagents

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[*] Corresponding author. Tel.: +35 902 8163413.
E-mail address: val_bgm@abv.bg (V. Jordanov)

HTTA (Merck, p.a.) and B15C5 (Fluka, puriss.) were used as supplied without further purification. The stock solutions of the Gd were prepared from its oxide Gd_2O_3 (Fluka,puriss) dissolving it with 11.6 mol L^{-1} HNO_3 and 18 mol L^{-1} $HClO_4$, respectively. Arsenazo III (Fluka) was of analytical grade purity, just as were the other reagents used.

2.2. Procedure

The experiments were carried out using 10 cm^3 volumes of aqueous and organic phases. The samples were shaken mechanically for 60 min at room temperature which was sufficient to reach equilibrium. After phase separation, the concentration of Gd in the aqueous phase was determined photometrically using Arsenazo III [30].

The initial concentration of Gd was 2.5×10^{-4} mol dm^{-3} in all experiments. The acidity of the aqueous phase was measured by a pH-meter with an accuracy of 0.01 pH unit. The ionic strength was maintained at 0.1 mol dm^{-3} with $(K,H)ClO_4$ and $(K,H)NO_3$.

3. Results and Discussion

The solvent extraction of lanthanoids (Ln) with HTTA alone in C_6H_6 has been studied by Poskanzer and Foreman [1]. Later, the Ln extraction from perchlorate and nitrate media with HTTA alone in other organic diluents has been investigated, too [2-4]. The complexes $Ln(TTA)_3$ were obtained in all cases. The metal extraction can be expressed by

$$\mathrm{Ln}^{3+}_{(aq)} + 3\mathrm{HTTA}_{(O)} \leftrightarrows \mathrm{Ln(TTA)}_{3(O)} + 3\mathrm{H}^{+}_{(aq)} \qquad (1)$$

$$K_\mathrm{T} = \frac{[\mathrm{Ln(TTA)_3}]_{(O)}.[\mathrm{H}^+]^3_{(aq)}}{[\mathrm{Ln}^{3+}]_{(aq)}.[\mathrm{HTTA}]^3_{(O)}} \qquad (2)$$

$$D_\mathrm{T} = \frac{[\mathrm{Ln(TTA)_3}]_{(O)}}{[\mathrm{Ln}^{3+}]_{(aq)}} \qquad (3)$$

where D_T denotes the distribution coefficient, Ln – lanthanoids, and “aq” and “o” denote the aqueous and organic phase, respectively. In the present study, the extraction of Gd with HTTA from perchlorate medium in 1,2-dichloroethane, carbon tetrachloride and chloroform is investigated. The experimental data about the distribution coefficient D_T vs. pH and [HTTA] in $C_2H_4Cl_2$ are shown in Figs.1 and 2.

The plots are linear, having slopes close to 3. Hence, the extraction of Gd with HTTA alone can be represented by the following equation

$$\mathrm{Gd}^{3+}{}_{(aq)} + 3\mathrm{HTTA}_{(o)} = \mathrm{Gd(TTA)}_{3(o)} + 3\mathrm{H}^{+}{}_{(aq)} \qquad (4)$$

The values of equilibrium constant K_T for Gd extraction with HTTA alone are presented in Table 1. The extraction of Gd with B15C5 alone is negligible under the experimental conditions of the present study. For determining the composition of the extracted species and calculating the values of the equilibrium constant, a traditional method called “slope analysis” has been used. It is based on an examination of the variation of $D_{T,S}$ (the distribution coefficient related to the synergistic effect) as a function of the relevant experimental variables. Double logarithmic plots of $D_{T,S}$ vs. one of the parameters (pH, [HTTA] and [B15C5]), one of them being a variable while keeping the other two constant, indicate the stoichiometry of the extractable complex. If the extractants’ concentration is constant, while the hydrolysis in the aqueous phase and the polymerization in the organic phase are negligible, then the plots will be straight lines with slopes giving the number of the ligands of adducts formation.

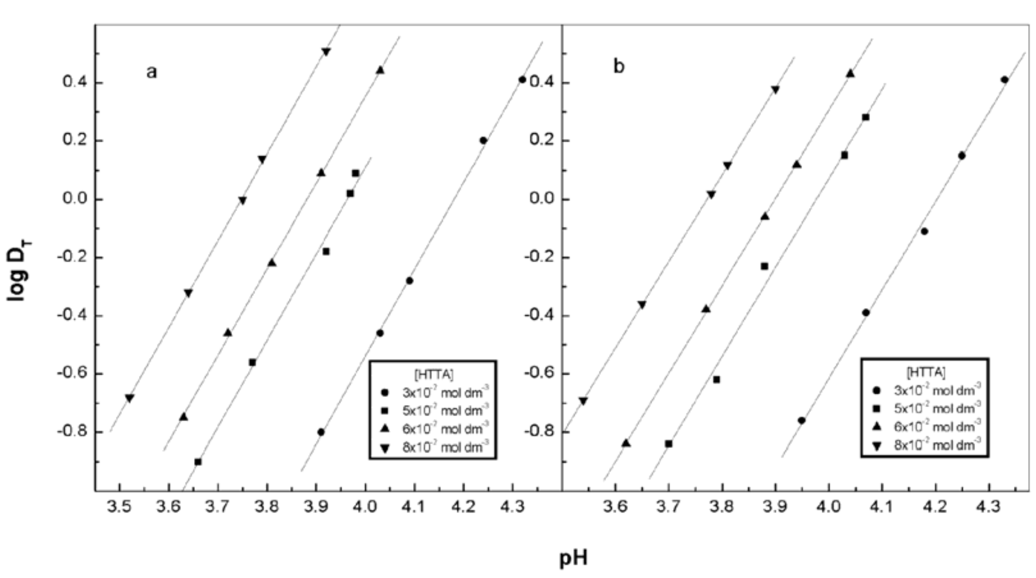

Fig. 1. Log D_T vs. pH for Gd extraction with HTTA in $C_2H_4Cl_2$; a – ClO_4^- medium; b – NO_3^- medium.

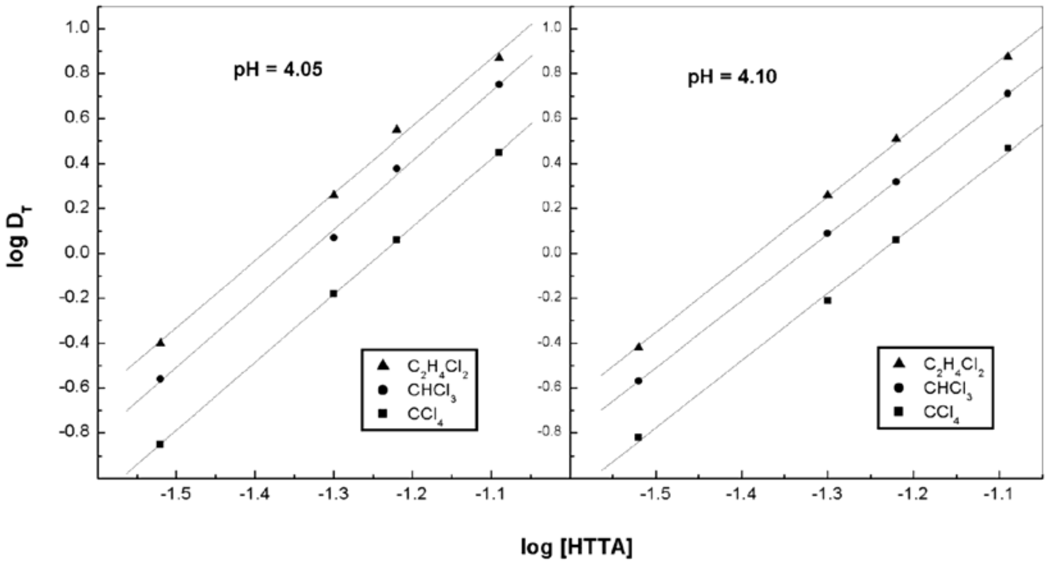

Fig. 2. Log D_T vs. log [HTTA] for Gd extraction. a – ClO_4^- medium; b – NO_3^- medium.

Table 1

Values of the equilibrium constant for Gd extraction with HTTA alone and with mixtures of HTTA and B15C5.

Medium	Diluent	logK_T	log$K_{T,S}$	log$\beta_{T,S}$
ClO_4^-	CCl_4	-8.48±0.03	-0.97±0,03	7.51±0.06
	$CHCl_3$	-8.15±0.04	-1.72±0.04	6.43±0.08
	$C_2H_4Cl_2$	-7.98±0.03	-2.37±0.03	5.61±0.06
NO_3^-	CCl_4	-8.55±0.01	-2.07±0,03	6.48±0.0
	$CHCl_3$	-8.32±0.04	-2.68±0.04	5.64±0.08
	$C_2H_4Cl_2$	-8.04±0.05	-3.06±0.02	4.98±0.07

The experimental data for the synergistic solvent extraction of Gd with mixtures of HTTA and B15C5 are shown on Figs 3-6. The plots of log $D_{T,S}$ vs. pH and log[HTTA] are linear, with slopes close to 3, and the plots of log $D_{T,S}$ vs. log[B15C5] show slopes close to 2 and 1 in perchlorate and nitrate media, respectively.

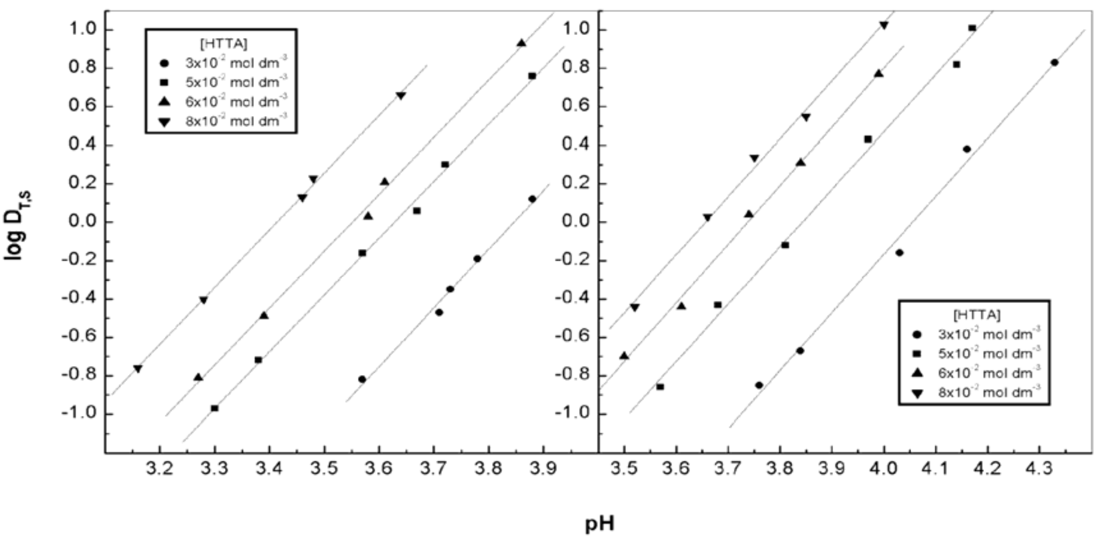

Fig. 3. Log $D_{T,S}$ vs. pH for Gd extraction with HTTA and B15C5 at [B15C5] = 5.10^{-3} mol.dm^{-3}. a – ClO_4^- medium; b – NO_3^- medium.

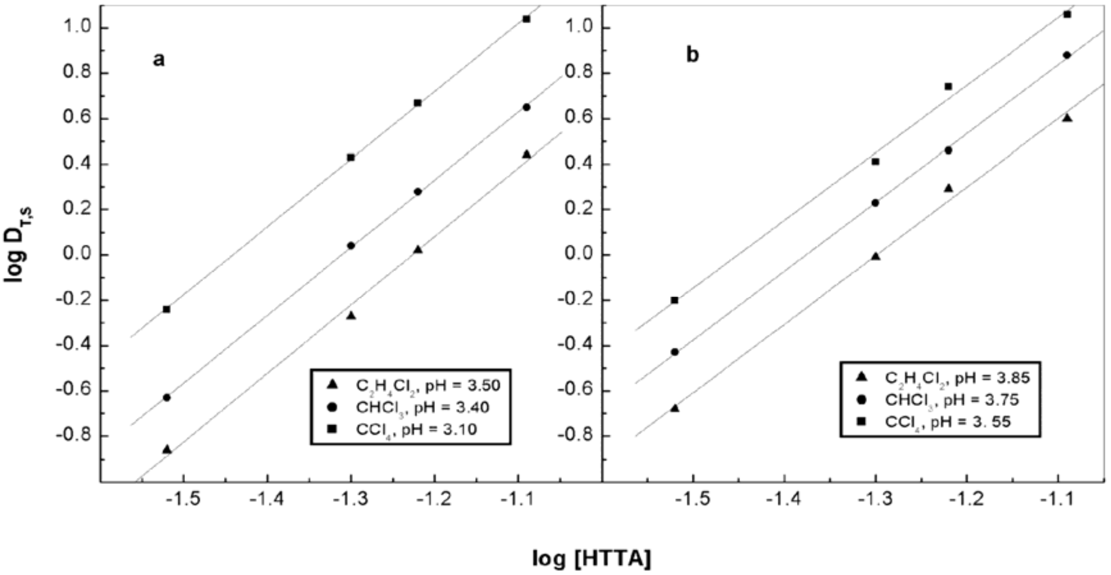

Fig. 4. Log $D_{T,S}$ vs. log [HTTA] for Gd extraction at [B15C5] = 5.10^{-3} mol.dm^{-3}. a – ClO_4^- medium; b – NO_3^- medium.

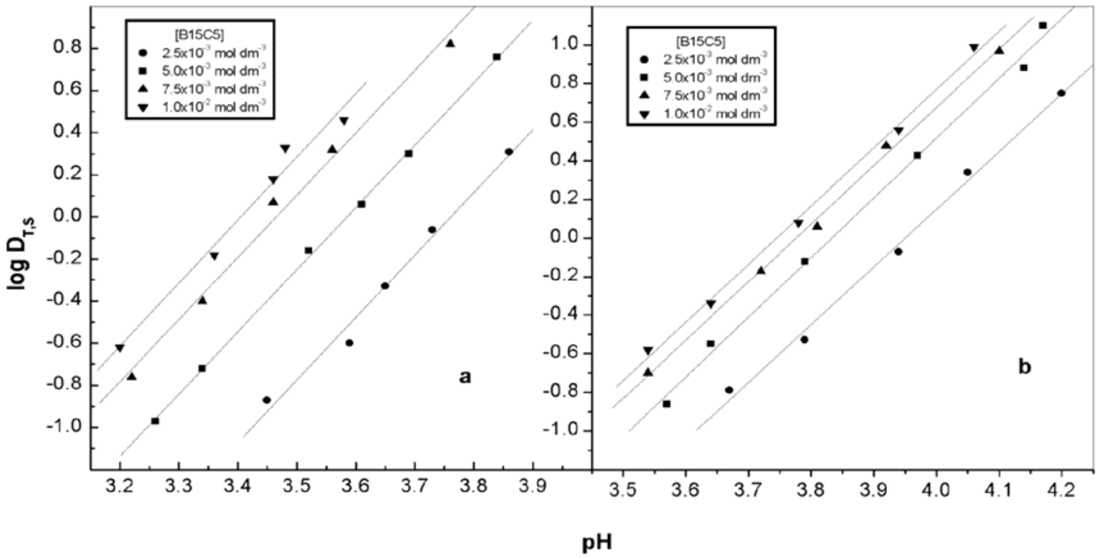

Fig. 5. Log $D_{T,S}$ vs. pH for Gd extraction with HTTA and B15C5 at [HTTA] = 5.10^{-2} mol.dm^{-3}. a – ClO_4^- medium; b – NO_3^- medium.

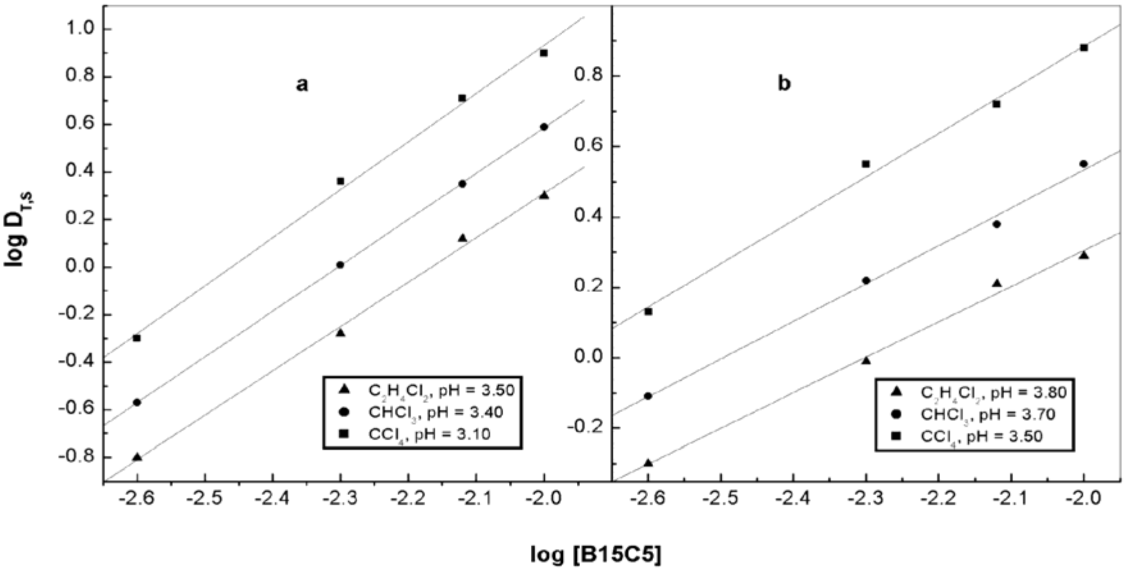

Fig. 6. Log $D_{T,S}$ vs. log [B15C5] for Gd extraction at [HTTA] = 5.10^{-2} mol.dm^{-3}. a – ClO_4^- medium; b – NO_3^- medium.

On the basis of slope analysis data, the synergistic extraction of Gd can be described by the equations

$$Gd^{3+}_{(aq)} + 3HTTA_{(O)} + S_{(O)} \rightleftarrows Gd(TTA)_3 \cdot S_{(O)} + 3H^{+}_{(aq)} \qquad (5)$$

$$Gd^{3+}_{(aq)} + 3HTTA_{(O)} + 2S_{(O)} \rightleftarrows Gd(TTA)_3 \cdot 2S_{(O)} + 3H^{+}_{(aq)} \qquad (6)$$

where S denotes B15C5.

The equilibrium constant $K_{T,S}$ for the synergistic complex formation can be shown as follows

$$\log K_{T,S_1} = \log D_{T,S} - 3\log[\text{HTTA}] - \log[\text{S}] - 3\text{pH} \qquad (7)$$

$$\log K_{T,S_2} = \log D_{T,S} - 3\log[\text{HTTA}] - 2\log[\text{S}] - 3\text{pH} \qquad (8)$$

The formation of adducts in the organic phase can be expressed by the equations

$$\text{Gd(TTA)}_{3(\text{O})} + \text{S}_{(\text{O})} \leftrightarrows \text{Gd(TTA)}_3 \cdot \text{S}_{(\text{O})} \qquad (9)$$

$$\text{Gd(TTA)}_3 \cdot \text{S}_{(\text{O})} + \text{S}_{(\text{O})} \leftrightarrows \text{Gd(TTA)}_3 \cdot 2\text{S}_{(\text{O})} \qquad (10)$$

The equilibrium constant $\beta_{T,S}$ for the synergistic reaction in the organic phase can be determined as

$$\log\beta_{T,S} = \log K_{T,S} - \log K_T \qquad (11)$$

The values of log $K_{T,S}$ and $\beta_{T,S}$ are given in Table. The equilibrium constants are based on the assumption that the activity coefficients of the species do not change significantly under experimental conditions, i.e. they are concentration constants.

The experimental data show that, in the Gd extraction from nitrate and perchlorate medium, the synergistic complex contain one or two molecules of the synergist, Gd(TTA)_3.S and Gd(TTA)_3.2S, respectively. The adduct formation can be realized by two manners. In the first of them, the crown ethers accommodate the Ln^{3+} ion inside their cavity, and the TTA^{-} ions coordinate additionally to the metal. These structures are proposed by Gagabe et al. in the lanthanoids extraction with mixtures of HTTA and a crown ether (CE:18-crown-6, cyclochexano-18-crown-6 and benzo-18-crown-6) [4]. In the second manner, a coordination of chelating extractant with Ln^{3+} ions is realized and they are arranged in a single plane. Then, one or two molecules of crown ethers are coordinated as well. This type of coordination is established in the Ln extraction with mixtures of chelating extractants and different crown ethers [16, 25].

If the crown ether accommodates Gd^{3+} ion inside its cavity, the coordination of only two TTA^{-} ions is not difficult. The coordination of the third TTA^{-} ion, and especially the second molecule of crown ether, is sterically hindered. Then the values of adduct formation constant for Gd(TTA)_3.2S must be smaller than the one for Gd(TTA)_3.S. On the contrary, the experimental data show that the values are higher for adducts with two molecules of crown ether, therefore the Gd^{3+} is probably coordinated with all three TTA^{-} ions in a single plane.

Mathur and Khopkar have suggested that not all oxygen atoms of the crown ether are coordinated to the metal [31]. A sandwich type complex – LnP_3.2B15C5 in the extraction of lanthanoids with 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one has been found out [32]. Probably, the Gd(TTA)_3.2S is the same type of complex in which one B15C5 molecule is disposed on either side of the metal chelate.

The formation of lipophilic adduct complex is connected with displacement of residual water molecules coordinated to the chelate complex [5]. It has been found that the adduct formation is a stepwise process [33]. Firstly, one crown ether molecule removes these residual water molecules and depending on the experimental conditions the second crown ether molecule could bind to the metal chelate (equations 9 and 10). Since the perchlorate ion is more hydrophobic than nitrate ion, it is clear that in perchlorate medium there are more favorable conditions of reaching the second step of process and adduct formation of Gd(TTA)_3.2S. The ionic type complexes $[\text{Ln(TTA)}_2\text{CE}]^{+}\text{ClO}_4^{-}$ (CE= dicyclohexano-18-crown-6) are established in the extraction of lighter Ln from perchlorate medium into 1,2-dichloroethene [17]. The same type of complex $(KCE)^+M(PMBP)_3^-$ has been obtained by Lakkis at al. in the extraction of Co(II) and Ni(II) with mixtures of 1-phenyl-3 methyl-4-benzoyl-pyrazol-5-one and 18-crown-6 or dicyclohexano-18-crown-6 [28]. In our investigation, ion-pair complex formation is not established.

The data in Table and Fig. 7 shows that the values of log.$\beta_{T,S}$ decrease with increasing the dielectric constant of organic diluents. This can be explained by the increasing ability to solvate the extractants in polar diluents and the possibility of hydrogen-bonding formation between extractants and diluents.

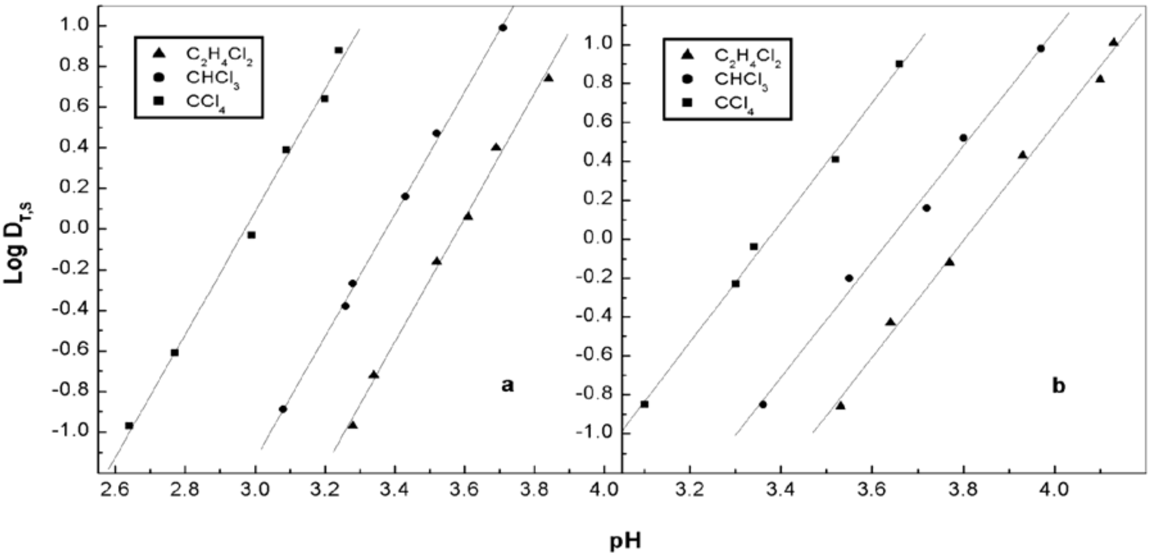

Fig. 7. Log $D_{T,S}$ vs. pH for Gd extraction at [HTTA] = 5.10^{-2} mol.dm^{-3} and [B15C5] = 5.10^{-3} mol.dm^{-3}. a – ClO_4^- medium; b – NO_3^- medium.

4. Conclusions

Gd is synergistically extracted with HTTA–B15C5 mixtures as adducts: Gd(TTA)$_3$.B15C5 from nitrate medium and Gd(TTA)$_3$.2B15C5 from perchlorate medium. The values of distribution ratio $D_{T,S}$ decrease in the order $CCl_4 > CHCl_3 > C_2H_4Cl_2$, i.e. the synergistic extraction is greatest in the least polar diluent. Polarity of organic diluents causes a considerable influence on the metal extraction but not on the stoichiometry of the extracted complexes.

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