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A method for the determination of extraction capacity and its application to *N*,*N*,*N*′,*N*′-tetraalkylderivatives of diglycolamide-monoamide/n-dodecane media

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Abstract

The detailed study on the extraction capacity of *N*,*N*,*N*′,*N*′-tetraalkylderivatives of diglycolamide (DGA) was performed by using the novel analytical method, which determines the limit of metal concentration in the organic phase (LOC). The analytical results suggest that LOC of Nd(III) by *N*,*N*,*N*′,*N*′-tetraoctyl-diglycolamide (TODGA) depends on HNO_3 concentration and temperature. In order to increase LOC and suppress the third liquid phase, the modifier, *N*,*N*-dihexyl-octanamide (DHOA) of the aliphatic diluent was employed and its effect was investigated. The modifier can raise the LOC value, and it is noteworthy that LOC corresponds to the stoichiometric value, which is obtained by the extraction reaction, by using the extraction solvent of 0.1 M TODGA—(0.5–1 M) DHOA in n-dodecane. This condition suppresses the third liquid phase. In the absence of modifier, the relation of several DGA based compounds with LOC was investigated. It is confirmed that LOC using *N*,*N*,*N*′,*N*′-tetradodecyl-diglycolamide (TDdDGA), whose extractant has the longest alkyl chain in this work and forms hardly the third liquid phase, reaches to the stoichiometric value.
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Keywords: Diglycolamide; *N*,*N*′,*N*′-tetraoctyl-diglycolamide; Extraction; Capacity; Nd; Am

1. Introduction

Diglycolamide (RR–NCO–CH_2)$_2$–O, which is a kind of diamide derivatives, was introduced initially by Stephan et al. [1,2], they reported the extraction of divalent and trivalent metals, e.g., Ca(II), Sr(II), Hg(II) and lanthanides (Ln)(III), by *N*,*N*′-dimethyl-*N*,*N*′-dihexyl-diglycolamide. From 1995 to 2000, Choppin et al. and Sasaki et al. studied the synergistic extraction and the separation of Eu(III) and Am(III) by using the same diglycolamide as that of Stephan's, accompanying with the acidic extractant like beta-diketone [3–8]. Moreover, it was revealed that diglycolamide has the high extractability with actinide (An) in the absence of beta-diketone [9,10], and diglycolamide attached with four octyl functional groups (*N*,*N*,*N*′,*N*′-tetraoctyl-diglycolamide, TODGA) has the high solubility in aliphatic diluent and the high *D* values (more than 1000) of An(III) and An(IV) from nitric acid [11,12]. TODGA, which shows the advantages of the easy organic synthesis and the incineration by combustion, has two carbamoyl groups connected by the alkyl chain including ether oxygen. The ether oxygen and the two amidic oxygen may chelate with metal ions, then TODGA exhibits the tridentate feature [13]. Because of the high extractability for An(III) and An(IV), TODGA has been investigated to employ into the partitioning of the high level radioactive liquid waste [14,15].

In order to apply the extractant into the partitioning process, the extraction of the large quantity of the metal is so important that the representative extractants, e.g., tributylphosphate (TBP), octyl(phenyl)-*N*,*N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) and dimethy-

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ldibutyltetradecylmalonamide (MA), were used to study about the loading capacity and the third phase formation. These extractants have been requested to recover the concentrated metal ions of lanthanides, uranium, plutonium, americium in the spent nuclear fuel (SF) dissolved solution. The loading capacity and the formation of the third liquid phase for these extractants with various metal ions were studied extensively [16–22]. Kolarik and Horwitz [16] determined the maximum metal concentration in the organic phase after observing the disappearance of the third liquid phase as the extraction capacity. However, it is difficult to detect the small volume of the third liquid phase by observation, and it is considered that this method allows the somewhat large error.

The precise and the simple analytical determination method for the maximum metal concentration in the organic phase has been developed and employed. Using the DGA based extractants, the correlation of the extraction capacity with the extractant and the acid concentrations, temperature, the modifier concentration and structure of extractant is investigated. The conditions to exhibit the stoichiometric extraction of Nd(III) by DGA based extractants are also discussed in this paper.

2. Experimental

The structures of six DGA based extractants, *N*,*N*,*N*′,*N*′-tetrahexyldiglycolamide (THDGA), *N*,*N*′-dihexyl-*N*,*N*′-dioctyldiglycolamide (DHeDODGA), *N*,*N*′-diheptyl-*N*,*N*′-dioctyldiglycolamide (DHpDODGA), *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA), *N*,*N*,*N*′,*N*′-tetradecyldiglycolamide (TDDGA), and *N*,*N*,*N*′,*N*′-tetradodecyldiglycolamide (TDdDGA), and the modifier, *N*,*N*-dihexyloctamide (DHOA), were shown in Fig. 1. The purities of these extractants were over 98% and used without any additional purification. Other chemicals employed in these experiments were in analytical grade.

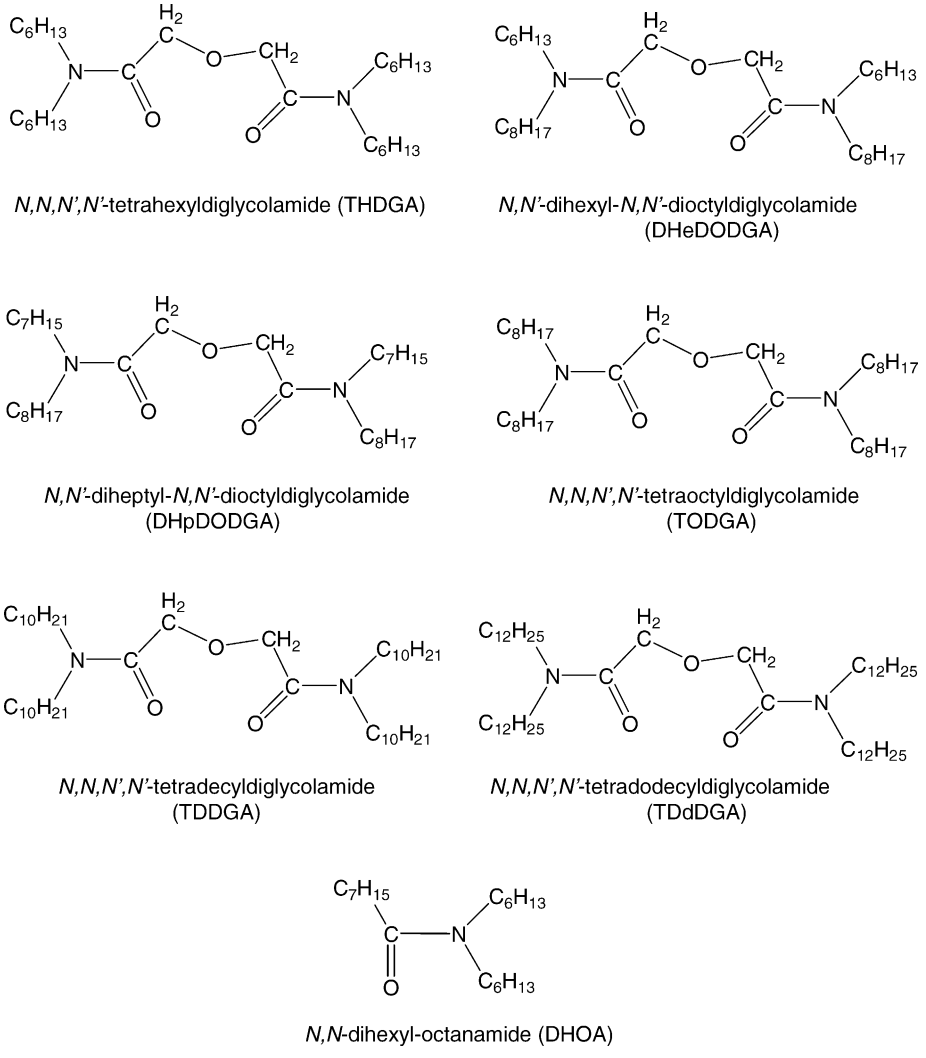

Fig. 1. Structures of DGA compounds and DHOA.

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