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Liquid–liquid extractions using poly(propylene imine) dendrimers with an apolar periphery

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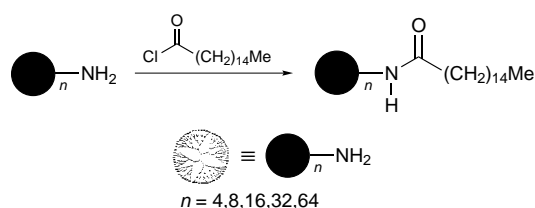
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The modification of poly(propylene imine) dendrimers with apolar endgroups yields effective and highly selective basic extractants of anionic dye molecules from water to solvents, like dichloromethane and toluene.

Liquid–liquid extraction is a well known technique in the field of (preparative) organic, inorganic and analytical chemistry.^{1a,b} The technique is based upon the transfer of a substance (solute) from one liquid (*e.g.* aqueous phase) to a second liquid (*e.g.* organic phase), the latter being reasonably immiscible with the first one. Extractants can influence the distribution of the solute molecules between the two phases to a large extent. It is well known that acidic extractants, like alkylphosphoric acids and alkylcarboxylic acids can extract positively charged (metal) ions^{1a,b} while basic extractants are capable of extracting anionic species from water to the organic phase. Primary, secondary and tertiary amines are interesting extractants because of their organophilic nature (high solubility in organic solvents) and their basicity.^{2a–c}

Recently, we have been investigating the endgroup modification of polar poly(propylene imine) ASTRAMOL™ dendrimers³ with apolar endgroups, *e.g.* linear alkyl chains and adamantane.⁴ These and other dendrimers are interesting molecules to study host–guest properties.^{5a–g} In this paper we describe generations 1–5 (number of endgroups $n = 4–64$) of the poly(propylene imine) dendrimers modified with palmitoyl chloride⁶ yielding ‘inverted unimolecular dendritic micellar’ structures with a polar interior of tertiary amines and an apolar periphery (Scheme 1). The extraction properties of the dendritic structures were investigated, using different anionic xanthenes dyes as solute molecules (**I** Fluorescein, **II** 4,5,6,7-tetrachloro-fluorescein, **III** Erythrosin B, **IV** Rose Bengal).

The extraction yield,[†] using a fifth-generation palmitoyl dendrimer as a function of the pH of the aqueous solution (Fig. 1) indicated that at low pH all four solute molecules, as a 1 : 1 mol ratio of dye and dendrimer could be transferred to the organic layer, whereas at higher pH no extraction is possible, except for Rose Bengal. The sensitive and abrupt pH-dependent extraction yield describes the distribution ratio of the solute between the two phases. Differences in pK_a and hydrophobicity of the solutes are likely to account for the different inflection points of the ‘titration’ curves. The (large) hydrophobicity of Rose Bengal seems a reasonable explanation for extraction of this probe by clathration even at high pH ($pH > 12$). From the fact that cationic probes, like Ethidium Bromide can not be extracted into the organic phase, we conclude that the



Scheme 1 Modification of poly(propylene imine) dendrimers

interaction between solute and dendritic structure is mainly determined by their acid–base properties and that the dendritic structures behave as basic extractants.

Under different pH conditions the relative absorption in UV–VIS of Rose Bengal in the aqueous layer was determined as a function of the dendrimer to dye ratio (Fig. 2). At $pH = 7$ the interaction between solute and dendrimer is much stronger than at $pH = 11$ and 14. From the inset in Fig. 2 ($pH = 7$) we can determine the dendrimer to dye ratio of the complex that is initially formed in the organic phase. It is concluded that approximately 50 (!) dye molecules ($M_{dye} = 1 \times 10^3$) are

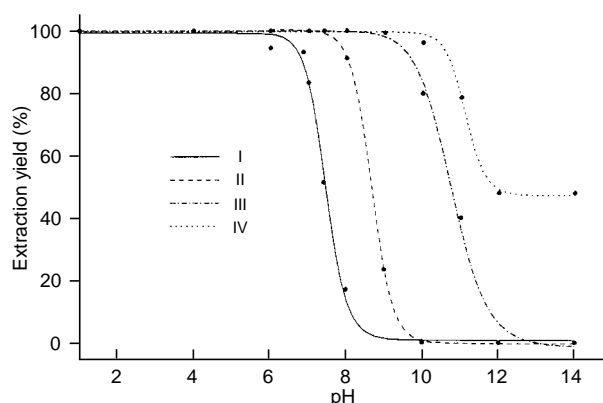


Fig. 1 Extraction yield of fifth-generation palmitoyl dendrimer as a function of pH for different dye molecules I–IV. Dendrimer : dye ratio is 1 : 1 (mol/mol); [dendrimer] = 2.5×10^{-5} M. Equal volumes of both phases are used.

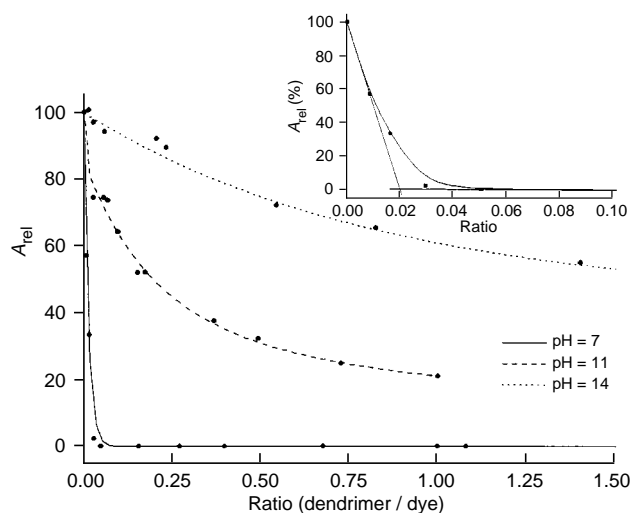


Fig. 2 Relative absorbance of Rose Bengal **IV** in the aqueous layer as a function of the dendrimer to dye ratio. Fifth-generation palmitoyl dendrimer was used as dendritic extractant. Dye concentration was kept constant during measurement (2.5×10^{-5} M). Inset shows cut-off at a ratio ≈ 0.020 , *i.e.* 50 dye molecules per dendrimer.

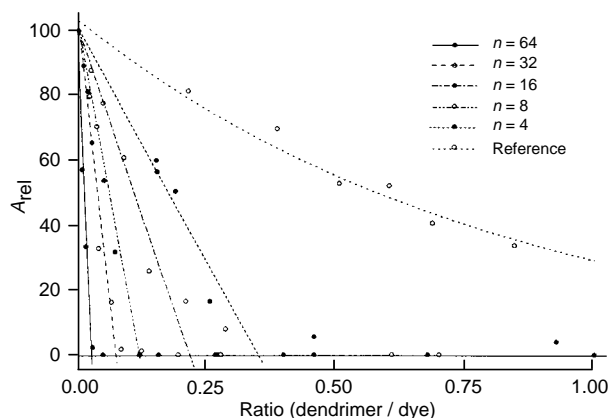


Fig. 3 Relative absorbance of Rose Bengal IV in the aqueous layer as a function of the dendrimer to dye ratio for different generations of palmitoyl dendrimers ($n = 4, 8, 16, 32, 64$). Tri-*n*-octylamine was used as reference compound. The concentration of extractant was kept constant [2.5×10^{-5} M] for all measurements.

extracted per fifth generation dendrimer ($M_{\text{dendr}} = 2.3 \times 10^4$). At pH = 7 all solute molecules can be extracted whereas at higher pH (pH > 10) there is an equilibrium and the dye is distributed over both layers. Even at higher ratios the extraction is not complete. The higher the extraction yield at a specific pH (Fig. 1), the faster is the (exponential) decrease in the absorption of the aqueous layer (Fig. 2).

Comparing all the generations of the palmitoyl dendrimers, we can conclude that the extraction is directly related to the number of tertiary amines in the dendritic interior (Fig. 3). The higher the generation of the dendrimer and the larger the number of tertiary amines in the interior, the more dye molecules can be extracted per dendrimer. Reference compound tri-*n*-octylamine (one tertiary amine) follows the same trend under these conditions as the dendritic extractants, but the extraction strength is less.

The dendritic extractant shows (almost) no difference in extraction yield of Fluorescein and Rose Bengal if the organic phase is changed from dichloromethane into toluene. Only in the case of Rose Bengal and high pH, is toluene less effective than dichloromethane. The extraction yield of tri-*n*-octylamine however deviates substantially when changing the organic phase; whereas in dichloromethane it is still possible to extract Fluorescein and Rose Bengal, Fluorescein can not be extracted into toluene using tri-*n*-octylamine. Rose Bengal still can be extracted, but the effectiveness is much smaller as is demonstrated by the inflection point that is several pH units lower. The results of tri-*n*-octylamine demonstrate that the strength of solvation decreases in the order dichloromethane > toluene, which is in full agreement with literature data.²⁶ Dendritic extractants, however, are not influenced by a change in solvent, probably due to their micellar character that shields the interior from the solvent.

The pH-dependent extraction behavior of the dendritic extractants (Fig. 1) enables us to perform back-extraction of the solute molecules. Fluorescein can be extracted into the organic phase at pH = 7 with a high extraction yield (ca. 90%). All Fluorescein in the organic phase can be recovered (extracted back) if an aqueous solution is used with pH = 10. In Fig. 1 it was already demonstrated that at pH = 10 no Fluorescein can be detected in the organic phase. Rose Bengal and Fluorescein show a pH region (pH ca. 8–10) in which there is maximum difference in extraction yield (Fig. 1). By adding Fluorescein

and Rose Bengal in different ratios in the aqueous layer and determining the absorption of both layers, it was demonstrated that even in a 10 000 : 1 ratio, Rose Bengal could be selectively extracted into the organic layer. This high selectivity is only possible due to the specific topology of the dendritic extractant in the liquid–liquid extraction process.

In summary, we conclude that the extraction of anionic solutes by modified poly(propylene imine) dendrimers is related to their tertiary amine interior. As a consequence the behaviour of these dendrimers is that of acting as long chain tertiary amines. The dendritic molecules, however, are solvent-independent extractants, while the high local concentration of tertiary amines in the dendritic interior, typical for the poly(propylene imine) dendrimers, creates a high selectivity in the extraction of solutes with different pK_a and hydrophobicity. As a consequence dendritic extractants might be very useful in the selective purification of anionic compounds.

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Footnotes and References

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† The extraction yield is defined as the relative extraction of the solute into the organic phase and is determined by measuring the decrease and increase in absorption of the aqueous and organic layer, respectively in UV–VIS. The absorption is determined at λ_{max} in both solvents for all dyes, where a small solvatochromic shift of λ_{max} in organic solvents is observed. In all cases a decrease in absorption of the aqueous layer simultaneously gives a complementary increase in absorption of the organic layer. If no extractant is dissolved in the organic layer, the solute (dye molecule) shows no detectable distribution into the organic layer.

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