



An assessment of selected properties of the fluorescent tracer, Tinopal CBS-X related to conservative behavior, and suggested improvements

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SUMMARY

A conservative or well known reactive behavior of water tracers is a prerequisite in the quantitative evaluation of their tracer breakthrough curves. The fluorescent dye, Tinopal CBS-X, is one of the few licensed fluorescent dyes for water tracing with safe use. Its main advantage is its blue fluorescence, which is barely visible to the human eye and thus can be used when coloring water must be avoided. However, scientists have described the recovery of this dye as poor to very poor in field tracer experiments. Hence, this study focuses on examining the interaction of the main water chemistry with Tinopal CBS-X by determining the solubility products of the dye with most common cations. The findings of this investigation reveal that the tracer forms precipitates of very low aqueous solubility with di- and trivalent cations (pK_{sp} 6.4–16.8). As a consequence, Tinopal CBS-X is not a conservative tracer and respective tracer breakthrough curves will exhibit strong tailings at least in part, as result of precipitations formed. The addition of a chemical modifier, EDTA, is suggested to enhance the solubility of Tinopal CBS-X in order to overcome its non-conservative behavior. Equations for estimating the amount of EDTA necessary are provided. In the light of these results, earlier reported tracer breakthrough curves are revisited and re-interpreted.

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1. Introduction

Fluorescent dyes are the most practical and widely used water tracers to date (Käss, 1998, pp. 19–100). Many of them are reasonably conservative (Behrens, 1986) meaning that they should not undergo any interaction with the water chemistry (e.g., precipitation) nor with the solid material (e.g., sorption on soil or aquifer material) nor should they suffer from degradation during their transport through the water body. This conservative behavior or a well known reactive behavior is a prerequisite in the evaluation of their tracer breakthrough curves from which quantitative information on the water body can be derived (Luhmann et al., 2012). This includes information such as connectivity, flow velocities, effective porosities, and mixing processes (Sabatini and Austin, 1991; Behrens, 1986). Any unknown or unnoticed deviation from this conservative behavior will consequently lead to inaccurate results of the aforementioned transport parameters (Field et al., 1995). Compared to other tracers like salts (e.g., LiBr) these dyes have the advantages of low purchase cost together with an easy application (injection, sampling, and analysis), and combine a

low detection limit with onsite and online determination in their chemical analysis.

Tinopal CBS-X, also known as distyryl biphenyl (DSBP), is one of the few licensed fluorescent dyes for water tracing and belongs to the group of fluorescent whitening agents (Field et al., 1995). Smart (1984) and Behrens et al. (2001) showed that Tinopal CBS-X possesses neither toxicological, cariogenic, mutagenic nor ecotoxicological characteristics and hence can be classified as a suitable water tracer even in sensitive areas like groundwater protection zones (Field, 2005). This is important, as any non-toxic compound with fluorescent properties is highly valued as a water tracer. In addition to its safe use, its main advantage is its blue fluorescence, which is barely visible to the human eye (Gaspar, 1987, p. 11). Therefore, Tinopal CBS-X is recommended when visible coloring of the water must be avoided, e.g. in the catchment of mineral springs (Goldscheider et al., 2003) or in public water-supply springs. Although Tinopal CBS-X is non-conservative, these benefits add value to its continued use as an artificial tracer in environmental applications.

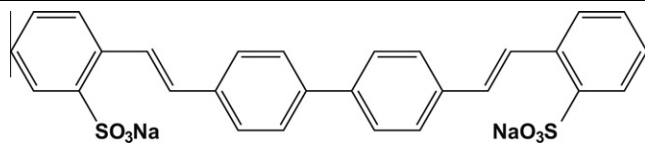
Despite being such a valuable water tracer, reports on Tinopal CBS-X's successful application are rare (Semeraro et al., 2007). The main disadvantage of Tinopal CBS-X is that it is frequently described as having poor to very poor recovery in field tracer experiments when compared with other tracers (Vincenzi et al., 2011; Geyer et al., 2007; Semeraro et al., 2007; Käss, 1998, p. 52, and

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Table 1
Properties of tinopal.

Structure	CAS-number	FW ^a	pK _a ^b	Log D ^{b,c,d}	Solubility ^{b,e}
	27344-41-8	562.58 g mol ⁻¹	-0.92	-3.61	1085.8 g L ⁻¹

^a Formular weight/molecular weight.

^b Sci Finder (<http://www.cas.org/products/scifinder>) predicted values.

^c n-Octanol water partitioning coefficient for anionic species.

^d at pH = 7.

^e at 20 °C.

Uggeri and Vigna, 1997). Tinopal CBS-X is frequently described as having a low practical solubility (e.g., Käss, 1998, p. 51; Uggeri and Vigna, 1997), although its theoretical solubility is in the range of 1 kg L⁻¹ (Table 1). Its low recovery together with its low solubility adds significant complexity to the design of quantitative tracer tests with Tinopal CBS-X. This also applies to qualitative tracer tests of high volume systems such as karst aquifers and mines adits (Goldscheider et al., 2007; White, 2007, and Käss, 1998, pp. 50–51). Its low solubility together with a high dilution leads to very low concentrations at observation points. Given the currently rising background concentrations of optical brighteners in the environment (e.g. Poiger et al., 1998, which estimate background concentrations in Swiss surface waters of up to 0.5 µg L⁻¹) it may become difficult and highly system and/or site specific to unambiguously assign the origin of the fluorescence signal at the observation point to the tracer experiment. Our own investigations in a small river in Germany showed a background fluorescence signal equivalent to a Tinopal CBS-X concentration of 1.47 µg L⁻¹ (Nödler et al., 2011, Fig. 1, L10).

Benischke et al. (2007) summarize the behavior of Tinopal CBS-X as being strongly sorbed by clay and based on experiments described in Käss (1998, p. 53) as not useful for acidic water tracing. Tinopal CBS-X is, however, always in its ionic form (doubly charged anion) when dissolved, as its pK_a (acid dissociation constant) is with -0.92 below the protonation capacity of water. It will therefore not exist in its protonated, neutral form for pH-values greater than 1. Therefore, its observed strong retardation in acidic medium (Käss, 1998, p. 53) cannot be caused by the adsorption of its protonated, neutral form. Its respective log D -3.61, as a measure for non-polar interactions of its anionic form (Table 1) and thus, for interaction with organic matter, can be seen as negligible (Schaffer et al., 2012). The low practical solubility of Tinopal CBS-X coupled with the aforementioned disadvantages may suggest a non-conservative transport behavior for Tinopal CBS-X. However, despite the now recognized drawbacks of Tinopal CBS-X as a hydrologic tracer agent, no systematic investigation has been initiated to quantify the disadvantages of using Tinopal CBS-X for hydrologic tracing studies.

It has long been established that cations, particularly calcium, aluminum, and iron, interact with the deprotonated anionic form of organic acids resulting in precipitates, for example calcium with oxalate (Jurinak et al., 1986) or multivalent cations with humic acids (Dudal and Gerard, 2004). This is used in wastewater treatment plants where iron and aluminum are applied in coagulation (Licskó, 1997). Consequently, Tinopal CBS-X as a divalent permanent organic anion with two sulfonic groups is prone to form low solubility salts with di- and trivalent cations. This may in turn explain the poor recovery and the observed poor water solubility when Tinopal CBS-X is used as a tracer for groundwater systems. Tracers with low solubilities are affected by the settling of their precipitates as tracer particles in the subsurface or by density sep-

arations during transport (Milanović, 1981, p. 269). This in turn greatly reduces the tracer recoveries by interfering with the quantitative interpretation of their tracer breakthrough curves.

In this paper, we quantify the interaction of Tinopal CBS-X with the most abundant di- and trivalent cations typically found in geothermal reservoirs, karst aquifers (i.e., calcium and magnesium), and acid mine drainage-influenced aquifers (i.e., aluminum and iron) by means of laboratory investigations. In order to be consistent with chemical nomenclature the anion of Tinopal CBS-X will be called tinoplate (T²⁻) and its respective salts tinopalates. The solubility products (K_{sp}) of four tinoplate salts (MgT, CaT, Al₂T₃, and Fe_xT_y) were determined at a temperature of 25 °C. Additionally the temperature dependency of the solubility products for MgT and CaT is investigated. Lastly, we suggest combining the complexing agent, EDTA, with Tinopal CBS-X prior to injection as a correction for the non-conservative behavior exhibited by Tinopal CBS-X.

2. Materials and methods

2.1. Chemicals

Tinopal CBS-X (Na₂T, physicochemical properties shown in Table 1) with a purity greater than 98% was purchased as a sodium salt from TCI (TCI Europe, Belgium) under the name of disodium 4,4'-bis(2-sulfonatostyryl)biphenyl. The structure of the compound suggests that it is prone to cis/trans isomerism on two double bonds leading to four different isomers (cis/cis, cis/trans, trans/cis, and trans/trans). Only the trans/trans isomer has good fluorescent properties (Poiger et al., 1996). In order to identify if the purchased compound is identical to the Tinopal CBS-X commonly used for water tracing and comprises only a single isomer, a ¹H NMR (proton nuclear magnetic resonance spectroscopy) and a ¹³C NMR (carbon nuclear magnetic resonance spectroscopy) spectrum were recorded. NMR confirmed that the compound investigated in this study was solely the trans/trans isomer and that it was identical to that which is commonly used for hydrologic tracing studies (also confirmed by NMR).

All other used chemicals were of high purity (>98%, analytical grade) and were purchased from either VWR (Darmstadt, Germany) or ThermoFisher (Schwerte, Germany). Ultrapure water for the preparation of all solutions was obtained from a combined water purification system consisting of Elix 5 and Milli-Q Gradient A10, both from Millipore (Schwalbach, Germany).

2.2. Synthesis of tinoplate salts (Me_xT_y)

In total, four tinoplate salts (MgT, CaT, Al₂T₃, and Fe_xT_y) were synthesized by slow precipitation from their respective aqueous solutions with subsequent slow maturing. In order to prevent coprecipitation of carbonates and/or hydroxides all solutions used in the synthesis were acidified with hydrochloric acid to a final

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