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

Tobias Licha[a,*], Anne Niedbala[a], Elke Bozau[b], Tobias Geyer[a]

[a] Geoscience Centre, Applied Geology, University of Göttingen, Goldschmidtstr. 3, 37077 Göttingen, Germany
[b] Hydrogeology Group, Clausthal University of Technology, Leibnizstr. 10, 38678 Clausthal-Zellerfeld, Germany

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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.

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, mutanogenic 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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* Corresponding author. Tel.: +49 551 39 12861; fax: +49 551 39 9379.
E-mail address: tlicha@gwdg.de (T. Licha).
URL: http://www.uni-goettingen.de (T. Licha).

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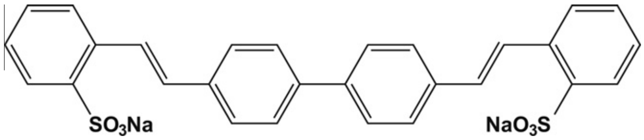
Table 1
Properties of tinopal.

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 separations 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 tinopalate (T^{2-}) and its respective salts tinopalates. The solubility products (K_{sp}) of four tinopalate salts (MgT, CaT, Al_2T_3, 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 (Na_2T, 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 ^{13}C 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 tinopalate salts (Me_xT_y)

In total, four tinopalate salts (MgT, CaT, Al_2T_3, 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 concentration of 1 mmol L^{-1} (pH = 3). Individual stock solutions with a concentration of 75 mmol L^{-1} were prepared from Tinopal CBS-X (Na_2T), calcium chloride ($CaCl_2 \cdot 2H_2O$), magnesium chloride ($MgCl_2 \cdot 6H_2O$), aluminum nitrate ($Al(NO_3)_3) \cdot 9H_2O$), ferric chloride ($FeCl_2 \cdot 4H_2O$), and ferrous nitrate ($Fe(NO_3)_3 \cdot 9H_2O$). After mixing 40 mL of the respective metal salt solution with 40 mL of the Tinopal CBS-X solution these were stored in sealed pre-cleaned glass bottles for 3 weeks at 80 °C for maturing in order to allow good crystallization. This procedure was done analogous to slow crystallization as described in Schwertmann and Cornell (2000). Each synthesis was done in duplicate. In order to avoid converting ferrous iron by oxidation to ferric iron, solutions were initially purged with argon and during maturing, sodium bisulfite was added to a final concentration of 100 mg L^{-1}. The absence of ferric iron was controlled photometrically with the rhodanide reaction. After a few days the amorphous precipitate started forming fine crystals. Thereafter, highest crystallization rates were seen in calcium followed in descending order, by aluminum, iron, and magnesium. Tinopalates produced in the laboratory could be visually distinguished by color and crystal forms (Table 2). After a few days of maturing in solution at 80 °C fine yellow and acicular crystals appeared in the solution of CaT while in the other three solutions platelet crystals were formed. The observed tinopalate colors range from pale yellow (MgT) and tan (Al_2T_3) to rust brown (Fe_3T_2). The stoichiometric ratio between cation and tinopalate is given in Table 2.

For the purification of the synthesized products they were transferred into a centrifuge tube and centrifuged for 15 min at 5000 rpm (Centrifuge 5804, Eppendorf AG, Hamburg, Germany). The crystalline residues were washed twice with 0.001 mol L^{-1} HCl (pH = 3) followed by washing with rising pH-values (0.0001 mol L^{-1}, 0.00001 mol L^{-1}). Finally, the products were washed twice with ultrapure water and the final washing solution checked for neutral conditions. The cleaned residues were put on a watch glass and dried at 80 °C until constant mass was observed.

2.3. Determination of solubility products, K_{sp}, in dissolution experiments

For each precipitate 10 vessels (5 glass vials, 5 plastic vials) were prepared, each containing 100 mg of the respective pulverized precipitates and 10 mL of ultrapure water. In the case of FeT, oxygen free water was used to avoid an oxidation of ferrous iron in solution (Schwertmann and Cornell, 2000; Appelo and Postma, 2005). Blank vials were used as quality control in order to check the release of ions from vial materials. Only the results from the vials for which its manufacturing material showed the lowest release of respective cations from the blank samples were later used for interpretation. The vials were sealed and shaken in a horizontal shaker with 250 rpm (KS 501D, IKA, Germany) at the respective temperature (25 ± 1 °C or 10 ± 1 °C). After the equilibration time of 5 days, both phases were separated by centrifugation for 10 min at 4000 rpm (Centrifuge 5804, Eppendorf AG, Hamburg, Germany). The supernatant was removed and prepared for chemical analysis by filtering through an inorganic membrane filter (Anotop 10 IC, 0.2 μm; Whatman International Ltd., England).

2.4. Chemical analysis and tinopalate characterization

Multiple injections, regular standards and daily recalibration ensured good data quality. Tinopal CBS-X concentrations were analyzed on a fluorescence spectrometer (Carry Eclipse, Varian) using an excitation wavelength of 349 nm and an emission wave length of 428 nm with a slit width of 5 nm each at a temperature of 25 °C. The determination of calcium and magnesium was realized by using a DX-500 Ion Chromatography System with conductometric detection and electrochemical suppression (Dionex, Sunnyvale, CA). This isocratic system operates with 32.5 mmol L^{-1} methanesulfonic acid as the eluent at a flow rate of 0.38 mL min^{-1} and a temperature of 44 °C using an IonPac CS16 (3 × 250 mm, Dionex) column. Concentrations of aluminum and iron were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer Optima 3300, 1300 W). Aluminum was detected at a wavelength of 273.95 nm and iron at 396.14 nm.

The synthesized tinopalates were investigated for their crystallization degree by X-ray powder diffraction on a Philips wide-angle goniometer PW1800. The radiation used was Cu Kα operating at 40 kV and 30 mA. The samples were measured in stepscan mode between 4° and 70° 2θ with steps of 0.05° 2θ and a counting time of 3 s. The synthesized tinopalates proved to be x-ray amorphous. No clear crystalline structure was found under the XRD-experimental conditions. This is surprising because a slow crystal growth was applied, and defined stoichiometric ratios between cation and tinopalate were observed for each precipitate (Table 2).

3. Results and discussion

3.1. Solubility products, pK_{sp}, of tinopalates

The solubility products K_{sp} (Table 2), and pK_{sp} as the negative logarithm to base 10 from K_{sp}, were calculated from determined molar concentrations c of the dissolution experiments according to the following formula

$$\mathrm{MeT} \rightleftharpoons \mathrm{Me}^{2+} + \mathrm{T}^{2-} \quad K_{sp} = (c_{\mathrm{Me}^{2+}}\gamma^{2+})(c_{\mathrm{T}^{2-}}\ \gamma^{2-}) \tag{1}$$

$$\mathrm{Me_2T_3} \rightleftharpoons 2\mathrm{Me}^{2+} + 3\mathrm{T}^{2-} \quad K_{sp} = (c_{\mathrm{Me}^{3+}}\gamma^{3+})^2(c_{\mathrm{T}^{2-}}\ \gamma^{2-})^3 \tag{2}$$

with γ as the ion specific activity coefficient. Eq. (1) is used for MgT, CaT, and FeT and Eq. (2) for Al_2T_3 and Fe_2T_3. The respective activity coefficients for the dissolution experiments determining K_{sp} were derived from the Debye–Hückel theory

$$\lg \gamma_i = -Az_i^2\sqrt{0.5\sum(c_i z_i^2)} \tag{3}$$

with A as a tabulated factor (0.4960 for 10 °C, 0.5092 for 25 °C), z_i as the respective charge of the ion for which the activity coefficient is calculated, and the term under the square root is the ionic strength of the whole solution with c_i as the molar concentrations of each ion in solution, because observed ionic strengths were very low with 1.167 mmol L^{-1} for CaT (25 °C), 0.753 mmol L^{-1} for CaT (10 °C), 1.309 mmol L^{-1} for MgT (25 °C), 0.927 mmol L^{-1} for MgT (10 °C), 3.366 mmol L^{-1} for FeT (25 °C), 1.473 mmol L^{-1} for Al_2T_3 (25 °C), and 2.926 mmol L^{-1} for Fe_2T_3 (25 °C).

Table 2
Properties of synthesized tinopalates; experimental data represent the mean of 20 individual solution experiments with duplicate analyses.

Cations	Molecular formula	Molecular weight (g/mol)	Color	Crystal form	pK_{sp} 25 °C (298.15 K)	pK_{sp} 10 °C (283.15 K)
Ca^{2+}	$Ca(C_{28}H_{20}O_6S_2)$	556.67	Yellow	Acicular	7.21 ± 0.009	7.56 ± 0.008
Mg^{2+}	$Mg(C_{28}H_{20}O_6S_2)$	540.89	Pale yellow	Platelet	7.12 ± 0.005	7.39 ± 0.007
Fe^{2+}	$Fe(C_{28}H_{20}O_6S_2)$	572.44	Light brown	Platelet	6.38 ± 0.007	
Al^{3+}	$Al_2(C_{28}H_{20}O_6S_2)_3$	1603.73	Tan	Platelet	16.78 ± 0.009	
Fe^{3+}	$Fe_2(C_{28}H_{20}O_6S_2)_3$	1661.46	Dark brown	Platelet	15.53 ± 0.012	

The calculated activity coefficients were as follows: 0.852 for Ca^{2+} and T^{2-} (25 °C), 0.880 for Ca^{2+} and T^{2-} (10 °C), 0.844 for Mg^{2+} and T^{2-} (25 °C), 0.867 for Mg^{2+} and T^{2-} (10 °C), 0.762 for Fe^{2+} and T^{2-} (25 °C), 0.667 for Al^{3+} and 0.835 for T^{2-} (25 °C), and 0.565 for Fe^{3+} and 0.776 for T^{2-} (25 °C).

As expected, the observed solubilities of tinopalates with di- and trivalent cations are rather low (Table 2). For calcium tinopalate the solubility is just about four times higher compared to the solubility of calcite. Furthermore, the solubility products for ions with the most impact on Tinopal solubility, Ca^{2+} and Mg^{2+} (Table 3), were determined at a typical groundwater temperature of 10 °C. This study shows an increase in solubility with increasing temperature (Table 2). By using the van't Hoff equation

$$\log(K_{sp}^{25\,^\circ C}/K_{sp}^{10\,^\circ C}) = \Delta_S H/(2.303\,R)/(1/283.15 - 1/298.15) \qquad (4)$$

with R as the ideal gas constant, the standard solvation enthalpy $\Delta_S H$ can be estimated from the solubility products K_{sp} at the different temperatures.

The observed standard solvation enthalpies $\Delta_S H$ are for CaT 37.7 ± 1.8 kJ mol^{-1} and for MgT 29.1 ± 1.3 kJ mol^{-1}. This endothermic solvation behavior together with the observed enthalpy values are in good agreement with literature data on other compounds with organic anions like calcium oxalate (Königsberger and Königsberger, 2001; Kustov et al., 2010). The determined solubility products now explain the discrepancy between the high solubility predicted by the web tool from the American Chemical Society *Scifinder* (Table 1), which applies to pure water, and the low solubility described by e.g. Käss (1998, p. 51). The maximum solubilities of Tinopal CBS-X in different water types of various aquifer systems are given for practical reasons in Table 3. To account for the complexity of the water chemistry in natural waters, the solubilities of Tinopal CBS-X were calculated by using the code PHREEQC (Parkhurst and Appelo, 1999) combined with the database *phreeqc*. Tinopalate was defined as a *solution master species* and the tinopalate salts with the newly investigated values (log k and delta h) were inserted as *phases* in the database. The tracer input was modeled by adding Na_2T into the *solution* of different groundwaters. Groundwater data were obtained from the literature (Geller et al., 2009; Hem, 1985; Henrickson and Jones, 1952, and White et al., 1963). It is interesting to note that the solubility of Tinopal CBS-X is largely controlled by the divalent cations, Ca^{2+} and Mg^{2+}, because the trivalent ions and Fe^{2+} are typically underrepresented in natural water.

The data in Table 3 clearly demonstrate that the fluorescent dye Tinopal CBS-X does not behave conservatively in the presence of di- or trivalent cations. Under these circumstances it is difficult to understand why this tracer is especially recommended for tracing high volume systems such as karst and mines (Goldscheider et al., 2007; White, 2007, and Käss, 1998, p. 50). These systems are especially rich in Ca^{2+} and Mg^{2+} (carbonate or dolomite karst) and waters in mining systems are often rich in Fe^{2+}/Fe^{3+} and low in pH resulting from pyrite oxidation (Nordstrom, 2011). However, as geochemical modeling shows, even in acid mine drainage the solubility of Tinopal CBS-X is controlled by Ca^{2+} and Mg^{2+} (Table 3).

3.2. Application of EDTA to enhance performance of Tinopal CBS-X as conservative tracer

Selective removal of Tinopal CBS-X precipitating cations in the tracer pulse may be a way of improving its performance as a conservative tracer. This may be accomplished by creating a more effective reaction than the tinopalate precipitation. This can be found in the complexation of the cations with the chelating agent ethylenediaminetetraacetic acid (EDTA). EDTA is suggested as a chemical modifier as it is a harmless compound used as food preservative (Brul and Coote, 1999). Other complexing agents may also be used as long as their concentrations are low and they are recognized as harmless compounds (Hillebrand et al., 2012b).

The introduced solubility products can be used to estimate the minimum amounts of EDTA required for preventing tracer precipitation during injection. In order to estimate minimum amounts of EDTA necessary, the concentration of Tinopal CBS-X solubility controlling cations must be known. The coupled equilibrium is represented by two individual equilibria with their respective mass action laws

$$Me^{2+} + EDTA^{4-} \rightleftharpoons MeEDTA^{2-} \quad K_f = \frac{[MeEDTA^{2-}]}{[Me^{2+}]\alpha_{EDTA^{4-}}[EDTA]} \qquad (5)$$

$$MeT \rightleftharpoons Me^{2+} + T^{2-} \quad K_{sp} = [Me^{2+}][T^{2-}] \qquad (6)$$

where K_f is the formation constant of the respective EDTA complex, K_{sp} is the solubility product of the respective tinopalate, $[Me^{2+}]$ is molar activity of the divalent cation, $[T^{2-}]$ is molar activity of Tinopal CBS-X, and $[MeEDTA^{2-}]$ is the molar activity of EDTA complexed divalent cation at chemical equilibrium. Activity coefficients for natural water may be calculated using the Davies equation (Davies, 1962, pp. 37–53):

$$\log \gamma_i = -Az_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \qquad (7)$$

with I being the ionic strength of the whole solution, A a temperature dependent parameter (0.496 for 10 °C) and z_i is the charge of the ion for which the activity coefficient is calculated.

It should be noted, that the charge of the EDTA ion and thus its complexing ability strongly depends on the pH and can vary with the EDTA pK_a values between +2 and −4. Thus, the complex stability with EDTA is controlled by its acid base properties and is strictly pH dependent, so the total molar EDTA concentration must be corrected by the factor $\alpha_{EDTA^{4-}}$ to yield the freely available molar $EDTA^{4-}$ activity complexing the cation. The value for $\alpha_{EDTA^{4-}}$ is available from tables but can also be estimated in the groundwater relevant pH range (2–9) by the simple correlation $\log \alpha_{EDTA^{4-}} = 8.815 \ln(pH) - 20.668$. For a precise correlation see e.g., Harris (2010).

Table 3
Geochemically modeled solubilities of tinopal in natural waters using PHREEQC, calculated solubilities refer to Tinopal CBS-X with a purity >98%.

Water/aquifer material; data taken from	Temp. °C	pH	Ca^a mg L^{-1}	Mg^a mg L^{-1}	Fe^a mg L^{-1}	Solubility dependency	Solubility of Tinopal CBS-X mg L^{-1}
Acidic mine lake; Geller et al. (2009)	25.0	2.6	225	27	146	Ca^{2+}	34.4
Spring/limestone; see Section 3.3, this paper	8.9	7.5	109	9	–	Ca^{2+}	11.8
Groundwater/gypsum; Henrickson and Jones (1952)	10.0	–	636	43	–	Ca^{2+}	6.18
Groundwater/serpentine; Hem (1985)	52.5	6.5	34	242	–	Mg^{2+}	51.3
Groundwater/dolomite; White et al. (1963)	16.7	7.5	34	14	0.12	Ca^{2+}	47.5

[a] Total concentration, speciation was done by PHREEQC.

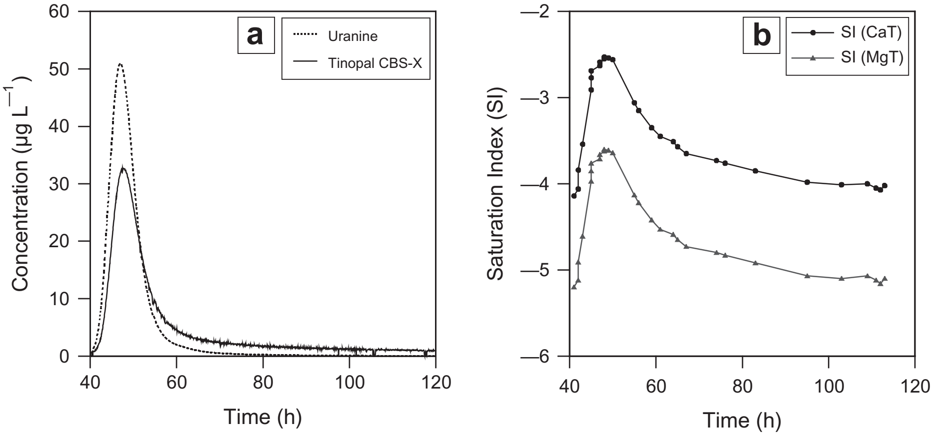


Fig. 1. (a) Observed concentrations of uranine and Tinopal CBS-X during the tracer breakthrough at the spring from the multitracer test described in Geyer et al. (2007), (b) respective saturation indices for CaT and MgT observed during that tracer breakthrough.

At chemical equilibrium the molar free metal ion activity from Eq. (6) can be substituted in Eq. (5), and assuming that $[\mathrm{MeEDTA}^{2-}]$ is equivalent to the initial molar Me^{2+} activity a simple equation is obtained for estimating the minimum EDTA concentration c_{EDTA} ($\mathrm{g\,L^{-1}}$) required per divalent ion to prevent Tinopal CBS-X precipitation during tracer injection

$$c_{\mathrm{EDTA}} = \frac{[\mathrm{T}^{2-}][\mathrm{Me}^{2+}]M_{\mathrm{EDTA}}}{K_{\mathrm{f}}\alpha_{\mathrm{EDTA}^{4-}}K_{\mathrm{sp}}\,\gamma_{\mathrm{EDTA}}} \tag{8}$$

with γ_{EDTA} as the activity coefficient of EDTA (valance of EDTA depends on water pH, for most natural waters its valence is -3) and M_{EDTA} as the molar mass of the respective EDTA form used. For practical reasons we suggest the use of easily soluble disodium EDTA dihydrate ($\mathrm{Na_2H_2EDTA{\cdot}2H_2O}$, CAS 6381-92-6, $M_{\mathrm{EDTA}} = 372.24\ \mathrm{g\,mol^{-1}}$). The required EDTA concentration ($\mathrm{g\,L^{-1}}$) can be also estimated for trivalent cations by using the following equation

$$c_{\mathrm{EDTA}} = \frac{\sqrt{[\mathrm{T}^{2-}]^3}[\mathrm{Me}^{3+}]M_{\mathrm{EDTA}}}{K_{\mathrm{f}}\alpha_{\mathrm{EDTA}^{4-}}\sqrt{K_{\mathrm{sp}}}\,\gamma_{\mathrm{EDTA}}} \tag{9}$$

For water containing all of the above counterions, the amount of EDTA required per ion is added and the total amount of EDTA can be calculated by combining Eqs. (8) and (9).

$$c_{\mathrm{EDTA}} = \sum \frac{[\mathrm{T}^{2-}][Me^{2+}]M_{\mathrm{EDTA}}}{K_{\mathrm{f}}\alpha_{\mathrm{EDTA}}K_{\mathrm{sp}}\,\gamma_{\mathrm{EDTA}}} + \sum \frac{\sqrt{[\mathrm{T}^{2-}]^3}[\mathrm{Me}^{3+}]M_{\mathrm{EDTA}}}{K_{\mathrm{f}}\alpha_{\mathrm{EDTA}}\sqrt{K_{\mathrm{sp}}}\,\gamma_{\mathrm{EDTA}}} \tag{10}$$

The validity of the Eq. (10) was evaluated by a small laboratory experiment. For this, solutions at various concentration ratios of counterions, Tinopal CBS-X and EDTA addition were prepared and precipitation controlled by photometric turbidity measurements.

3.3. Karst multitracer test revisited

Geyer et al. (2007) conducted a large scale multitracer test in a karst aquifer with the intention of determining specific karst features. In this instance, the tracers uranine, sulforhodamine G, and Tinopal CBS-X were simultaneously injected into a sinkhole and their breakthrough curves were determined 3 km away in the draining karst spring by means of an online fluorescence spectrometer. Immediately before the injection, 750 g uranine, 750 g sulforhodamine G, and 1500 g Tinopal CBS-X (>60% purity[1]) were mixed in a 1 $\mathrm{m^3}$ barrel. The final tracer solution was cloudy, clearly indicating a precipitation. After tracer injection, flushing with water was continued with approximately 77 $\mathrm{m^3}$ of water to force the multitracer solution into the saturated conduit system.

The Tinopal CBS-X breakthrough curve in the tracer test (Fig. 1a) exhibited in contrast to uranine, a significant tailing. Observed noise and tailing cannot be explained by a coincidental, additional optical brightener breakthrough from other sources, such as wastewater. The fluorescence detector monitored the spring for an entire hydrologic year and no further signals were recorded. Additionally, caffeine was used as an indicator at this spring to estimate the wastewater burden (Hillebrand et al., 2012a,b). Untreated wastewater is a negligible source for optical brighteners at this spring.

It led to the hypothesis that this behavior was caused by initial precipitation with subsequent re-dissolution of the precipitates. This hypothesis is now supported by the solubility product details provided in this paper. Considering the base water chemistry ($\mathrm{Ca^{2+}}$: 109.4 $\mathrm{mg\,L^{-1}}$, $\mathrm{Mg^{2+}}$: 8.8 $\mathrm{mg\,L^{-1}}$, $\mathrm{Na^{+}}$: 5.4 $\mathrm{mg\,L^{-1}}$, $\mathrm{K^{+}}$: 0.5 $\mathrm{mg\,L^{-1}}$, $\mathrm{HCO_3^{-}}$: 341.6 $\mathrm{mg\,L^{-1}}$, $\mathrm{NO_3^{-}}$: 15.6 $\mathrm{mg\,L^{-1}}$, $\mathrm{Cl^{-}}$: 13.7 $\mathrm{mg\,L^{-1}}$, and $\mathrm{SO_4^{2-}}$: 10.0 $\mathrm{mg\,L^{-1}}$) of the water used to prepare the tracer solution and all tracers added to it allows for the calculation of the amount of dissolved Tinopal CBS-X directly recharging the aquifer from Eq. (1) and the data provided in Table 2. When using the Davies equation (Eq. (7)) to estimate activity coefficients, a solubility of 26.5 mg in that 1 $\mathrm{m^3}$ of tracer solution is obtained. This means, that only 3% of Tinopal CBS-X were injected into the sinkhole as completely dissolved tracer. Although the flushing with additional 77 $\mathrm{m^3}$ of water would have theoretically been sufficient to dissolve the remaining 97% of tinopalates, it is practically impossible to achieve that. Under laboratory conditions, equilibrium at 10 °C was only reached after 5 days of intensive shaking. This may have been the reason why Tinopal CBS-X exhibited in contrast to uranine, a poor recovery because some of the precipitate remained trapped in the unsaturated zone (Milanović, 1981, p. 269). The calculation of the saturation indices for Ca and Mg tinopalates at the spring indicate strongly negative saturation index values and thus undersaturated conditions for CaT and MgT (Fig. 1b). This further

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[1] Although BASF/CIBA certifies it with >60%, random tests with NMR and fluorescence comparison yield purities always >90%, with one batch even >95%. Impurities were identified as NaCl and $\mathrm{Na_2SO_4}$. NMR confirmed that only the fluorescent trans/trans isomer is present. Thus, for estimating practical EDTA concentrations for field tracer experiments it is suggested to base calculations on a Tinopal CBS-X purity of 100%.

suggests that the precipitation of the respective tinopalates has occurred nearer to the point of injection than to the point of tracer breakthrough curves measurements.

It can be estimated the addition of at least 6.9 g of $Na_2H_2EDTA \cdot 2\,H_2O$ to the 1 m^3 tracer solution prior to the tracer injection would have been sufficient to prevent Tinopal CBS-X precipitation. This amount of EDTA is too low to lead to significant subsequent geochemical reactions with EDTA in the subsurface. The calculation was based on the water chemistry used to prepare the tracer solution (see above). Applying Eq. (9) to estimate c_{EDTA} the following parameter were used: $C_{Na_2T} = 1.5\ g\ L^{-1}$ (purity 60%), $\log \alpha_{EDTA^{4-}} = -2.88$ (pH 7.5, T 10 °C), $\log K_f = 11.03$ ($CaEDTA^{2-}$, 10 °C, data from Arena et al., 1983), $pK_{sp} = 7.56$ (CaT, 10 °C), $\log K_f = 8.86$ ($MgEDTA^{2-}$, 10 °C, data from Arena et al., 1983), $pK_{sp} = 7.39$ (MgT, 10 °C), $I = 17.9\ mmol\ L^{-1}$ (including Na_2T) and $\gamma_{EDTA} = 0.314$ with charge -3 at observed pH 7.5. Activity coefficients were calculated using the Davies equation (Eq. (7)).

As the complex formation constant for $MgEDTA^{2-}$ almost outweighs the solubility product of MgT, even small concentrations of magnesium need to be considered. In this example here, the EDTA contribution for calcium was 0.5 g m^{-3} while magnesium demands 6.4 g m^{-3}.

4. Conclusions

The findings of this study demonstrate that the fluorescent water tracer Tinopal CBS-X does not behave conservatively in the presence of higher valent cations. It will readily precipitate with the in surface and groundwater abundant cations Ca^{2+} and Mg^{2+}, but also with the in acid mine drainage abundant cations Al^{3+} and Fe^{2+}/Fe^{3+}. Therefore, the most important parameters for using this tracer are the corresponding solubility products under the consideration of the respective cation concentrations in the water. The provided solubility products allow the calculation of the maximum input concentration of Tinopal CBS-X as completely dissolved compound under various water chemistries. The maximum solubility of the tracer therefore depends on the tinopalate with the lowest solubility.

In order to use Tinopal CBS-X as a conservative tracer or enhance its performance as a qualitative tracer either the precipitation with subsequent re-dissolution of the tracer has to be considered in the analysis of its breakthrough curves within applied numerical models or a chemical modifier needs to be introduced to the tracer preparation solution in order to prevent precipitation. EDTA is suggested as a chemical modifier. However, the application of a more efficient complexing agent as modifier may result in a smaller mass to be added to Tinopal CBS-X than does EDTA. This is especially significant for waters with a pH < 7.5 because EDTA becomes extremely ineffective at lower pH values.

The tendency of tinopalate to interact with di- and trivalent cations may not only be limited to reactions in solution, but may also extent to mineral surfaces. As such, anion exchange processes for Tinopal CBS-X as retardation process and thus non-conservative behavior should be subjected to further investigations. It may however be difficult to separate ion exchange from precipitation in a practical sense.

It has long been established that higher valent cations interact with the deprotonated anionic form of organic acids resulting in precipitates. This especially applies to organic anions of higher valency with a pK_a 2 units below the water pH of the system to be investigated. Most effected are compounds with sulfonic groups ($-SO_3^-$) exhibiting pK_a values below 1. Great care should be taken if additionally other functional groups exist in the molecule, such as amides which can be protonated and thus positively charged. This can compensate the negative charge from the acid groups and the tracer behavior becomes more difficult to predict. As a practical rule, tracer solubility should always be established with the natural water of the system under investigation. If turbidity is observed, a complexing agent (e.g., EDTA) should be added.

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