



Association of rhodamine cations with tetraphenylborate-anion in aqueous solution: structural properties of ions and stability of associates

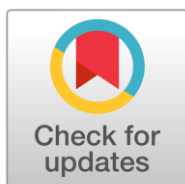
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Abstract: The ability of rhodamine cations to form cation-anionic associates with tetraphenylborate-anion in an aqueous solution has been studied. The thermodynamic values of the equilibrium association constants K_{as}^T were determined spectrophotometrically. The values of a number of properties of dye molecules (surface area, effective volume, hydrophobicity index $\log P$, standard enthalpy of hydration ΔH^0_{hydr}) were calculated using the QSAR model. The possibility of dependence of the value of K_{as}^T on these factors has been reviewed. It was shown that changes in $\lg K_{as}^T$ in the series of rhodamine associates are consistent with changes in the parameters $\log P$ and ΔH^0_{hydr} .

Keywords: Dyes, Rhodamines, Aqueous solution, Association, Hydrophobicity, Enthalpy of hydration

1. Introduction

The processes of association of molecular or ionic forms of dyes can significantly change the properties of the solution. Association as a result of the manifestation of intermolecular interactions is accompanied by an increase or decrease in light absorption and changes in spectral bands. For many years, the formation of stable stoichiometric associations between oppositely charged dye ions has been experimentally proven [1–9] even at low ($1 \cdot 10^{-6}$ – $1 \cdot 10^{-5}$ mol/L) concentrations. It is shown that “non-Coulomb” interactions are essential in the processes of cation-anion association of dyes or other polyatomic (organic) particles. Recently, the problems of the relationship between the structure of the dye and its ability to associate have become especially relevant. Of particular

interest is the development of theoretical propositions on the basis of which it would be possible to predict the structure of associates, their spectral-luminescent properties, based only on the peculiarities of the structure of dyes. To this end, the driving forces of the association are analyzing now. Spectral, thermodynamic, structural data, various theoretical approaches and computer modeling are involved in the consideration of associated compounds [10, 11]. The study of the association of dyes is also relevant in a practical sense due to the use of spectral and equilibrium properties of the associates. Regulation of the completeness of the association is considered as an effective factor in changing the spectral-luminescent characteristics of the medium [4, 9, 11].

Rhodamines attract special attention among other dyes. They have unique equilibrium and spectral properties, such as stability of cationic forms, high molar absorption coefficients, intense luminescence of solutions. The results of scientific research [4, 9] indicate that these dyes are significantly associated in aqueous solutions. This is due not only to the relatively large value of the relative dielectric constant of water, but also the ability of water to enhance the association of particles due to hydrophobic interactions. Rhodamine associates are used in the quantitative analysis of anionic surfactants and are very promising in terms of creating new methods for the quantitative determination of the content of chemical toxicants in aqueous media [9, 12]. The aim of this study is to analyze the relationship between the spectrophotometrically determined stability of rhodamine associates of the "rhodamine cation + organic anion" type and the calculated structural characteristics of rhodamines.

2. Experimental methods

2.1 Materials

Rhodamine 110 (R110), rhodamine B (RB), rhodamine 101 (R101), and also rhodamine 6G (R6G) in a number of experiments were used as rhodamines. Information about the dyes is given in Table 1. Spectral characteristics of dyes are given according to the works [13–18].

The hydrophobic anion of tetraphenylborate (TFB) was used as a counterion (the original preparation of TFB was in the form of sodium salt). It was previously used in the study of the association of organic dyes of different structure [2, 4, 5]. The dye formulations and the sodium salt of TFB were trademarks "Sigma" or "Apolda". The mass fraction of the main substance was at least 95 %. The acidity of aqueous solutions was monitored using a glass electrode.

2.2 Experimental conditions and equipment

The values of optical density (A), which were used in calculations of spectral and equilibrium characteristics, were checked for compliance with the basic law of light absorption.

When the concentration increases from 10^{-6} to 10^{-3} mol/L, there is a deviation of the optical density from the basic law of light absorption, which is explained by the combination of molecules (or cations) in the dimer [13-19]. Additions of salts (KCl, LiCl and others) also enhance self-association, which leads to "blurring" of isosbestic points in the spectral series [20]. This fact suggests the formation of particles of a higher degree of association and, as a consequence, to prevent the study of cation-anionic association in more concentrated solutions. So, we used aqueous solutions of rhodamines with concentrations of no more than $3 \cdot 10^{-5}$ mol/L, preventing dimerization of dyes.

Table 1. Spectral characteristics of dyes

Dye	λ_{\max} , nm	ϵ_{\max} , L/(mol·cm)
Rhodamine 110 (Ct ⁺), CAS Number: 13558-31-1	498	$9.8 \cdot 10^4$
Rhodamine B (Ct ⁺), CAS Number: 81-88-9	557	$10.8 \cdot 10^4$
Rhodamine 101, inner salt (Ct ⁺), CAS Number: 116450-56-7	554	$8.4 \cdot 10^4$
Rhodamine 6G (Ct ⁺), CAS Number: 989-38-8	526	$8.8 \cdot 10^4$

The ionic strength of the photometric solutions was 0.0004 – 0.001 mol/L. The acidity of the solutions was created in such a way as to provide an almost complete yield of the singly charged cationic form.

The association of rhodamines was studied at pH 1.5 – 1.8 (oxalate buffer solutions), taking into account the values of the dissociation constants of doubly and singly charged cations (for example, for RB, these values are 0.78 and 3.22 ± 0.01 , respectively [21]). In the absence of double-charged cations were confirmed by gradual acidification of the solution, which did not lead to a noticeable change in the absorption spectrum.

The absorption spectra were measured on upgraded spectrophotometer "Hitachi U3210" at room temperature. The error in determining the absorption wavelength was not less than $\pm 0,5$ nm. It is experimentally verified that temperature fluctuations within 2–3 degrees practically do not affect the spectral properties of the studied dyes.

3. Results and Discussion

An increase in the content of TFB at a constant concentration of rhodamine cation leads to a significant decrease in the intensity of light absorption, which reaches 45 – 55 %, and to a bathochromic shift of the absorption band of the dye. Changes in the spectra of aqueous solutions of dyes are presented in Figure 1; the absorption spectra of tetraphenylborate associates of rhodamine cations are shown in Figure 2.

This nature of the observed spectral changes indicates the formation of ionic associates in aqueous solution. By analogy with the systems "cyanine cation + TFB" [2, 4, 5], we can conclude that the association of the cation with the anion (An^-) occurs according to the scheme $Ct^+ + An^- \rightleftharpoons Ct^+ \cdot An^-$ with the equilibrium constant of the association:

$$K_{as} = \frac{[Ct^+ \cdot An^-] \times (C_{An} - [Ct^+ \cdot An^-])}{[Ct^+] \times (C_{Ct} - [Ct^+ \cdot An^-])^{-1}}$$

where C_{An} is the initial molar concentration of the anion, $[Ct^+ \cdot An^-]$ is the equilibrium concentration of the associate, C_{Ct} is the initial concentration of the cation. The content of the associate was calculated from spectral data by the equation:

$$[Ct^+ \cdot An^-] = \frac{(\epsilon_{Ct} \times C_{Ct} \times l - A) \times (\epsilon_{Ct} - \epsilon_{as})^{-1} \times l^{-1}}$$

where A is the optical density at the appropriate concentration of TFB (C_{An}) under λ_{max} of the absorption band of cation; l is the thickness of the absorbing layer; ϵ_{Ct} and ϵ_{as} are the molar absorption coefficients of the rhodamine and associate cations, respectively.

The concentration constant of the association practically does not differ from the thermodynamic one K_{as}^T , because ionic strength was no more 0,004 in experiments.

The characteristics of rhodamines and their associations with TFB are presented in Table 2.

The positive charge is delocalized on the xanthene fragment in rhodamine cations, Figure 3. However, the values of K_{as}^T differ statistically despite of the similarity of the structures of the dyes.

In addition to electrostatic factors, hydrophobic interactions play an essential role in the association of dyes in an aqueous medium. Associate of R101, which is formed by the most hydrophobic rhodamine (the structural properties of the dyes are discussed below), has the maximum K_{as}^T value. In aqueous solutions, the self-association (dimerization) of rhodamines is noticeable at concentrations of about 10^{-4} mol/L, and in other (organic) media it is noticeable at much higher concentrations. For example, in alcohol solutions it occurs at 10^{-2} mol/L [1, 5]. The dielectric constant (DC) of the medium does not play a fundamental role, in contrast to the hydrophobic component.

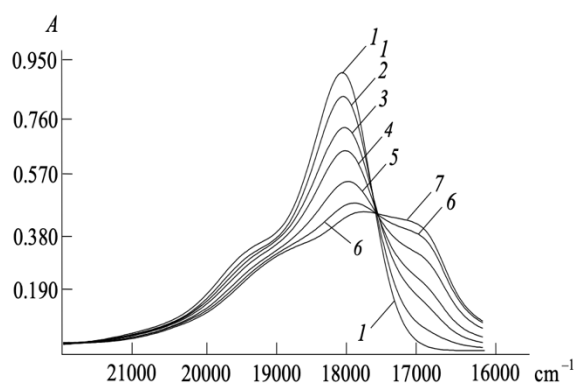


Figure 1. Absorption spectra in the system “RB + TFB”. Concentrations, mol/L, of RB: $1.07 \cdot 10^{-5}$ (1...7); of TFB: 0 (1), $1.01 \cdot 10^{-6}$ (2), $2.02 \cdot 10^{-6}$ (3), $5.04 \cdot 10^{-6}$ (4), $6.55 \cdot 10^{-6}$ (5), $8.06 \cdot 10^{-6}$ (6), $1.41 \cdot 10^{-5}$ (7). The comparison solution is water. The thickness of the absorbing layer is 1 cm

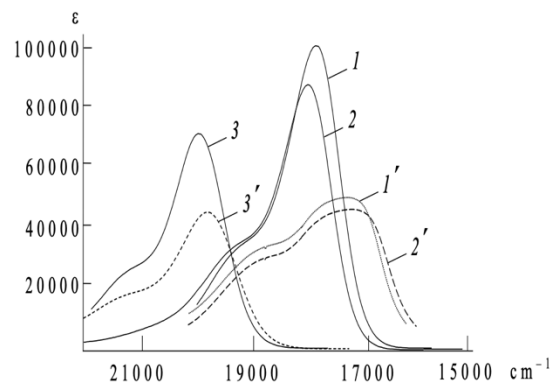


Figure 2. Absorption spectra of RB^+ (1), R101^+ (2), R110^+ (3) and their TFB^- associates (1'...3', respectively) in aqueous solutions

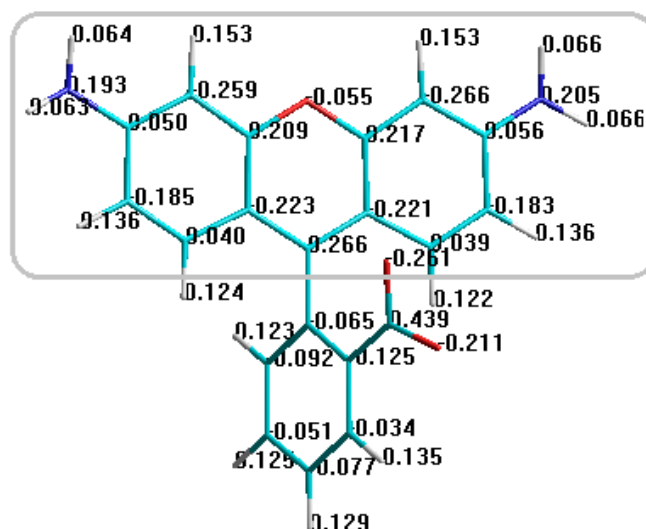


Figure 3. Distribution of electron density in the cation R110^+ (semi-empirical method PM3 , ground state; xanthene fragment shown in a frame)

Table 2. Characteristics of rhodamines and their associations with TFB^-

Characteristics	Катион (Ct^+)			
	R110^+	RB^+	R101^+	R6G^+
$\lambda_{\text{max}} (\text{Ct}^+ \cdot \text{TFB}^-)$, nm	501	575	580	540
ϵ_{max} , (an associate), $\text{L}/(\text{mol} \cdot \text{cm})$	$4.4 \cdot 10^4$	$4.8 \cdot 10^4$	$4.3 \cdot 10^4$	–
$\lg K_{\text{as}}^{\text{T}}$	4.30 ± 0.12	5.4 ± 0.2	6.6 ± 0.2	5.01 [22]
$\log P$ (a molecule)	2.92	6.39	6.76	5.63
ΔH_{hydr} , kJ/mol	–74.5	–22.5	–0.84	–19.7
Surface area, nm^2	3.62	6.30	7.10	7.64
Effective volume, nm^3	0.91	1.30	1.42	1.33

Notes. Thermodynamic values of $\lg K_{\text{as}}^{\text{T}}$ are calculated taking into account the correction for the ionic strength of the solution. Error of calculations of values: $\log P \pm 0.3$, $\Delta H_{\text{hydr}} \pm (0.8 - 1.0)$ kJ/mol, surface area $\pm (0.12 - 0.17)$ nm^2 , effective volume ± 0.02 nm^3 .

The strong influence of the hydrophobic component in the processes of self-association and cation-anionic association is confirmed by the experimental fact that some rhodamines do not form associates with organic anions in non-aqueous solvents at concentrations up to $3 \cdot 10^{-5}$ mol/L. For example, this concerns rhodamine R6G, which does not form cation-anionic associates with TFB in N-methylformamide (DC = 182), acetonitrile (DC = 37), and even in ethanol (DC = 24) [22]. Therefore, as can be seen from the data of $\lg K_{as}^T$ (Table 2), the cation-anionic associates of rhodamines $Ct^+ \cdot TFB^-$ are quite stable in water. For this reason, there is a need to explain the influence of the structural characteristics of rhodamines on the value of K_{as}^T .

We calculated some characteristics of dyes (Table 2; all data are QSAR model; geometric optimization of molecules has been performed by semi-empirical method *AM1*), among them: the effective surface area of the cation, its volume, the hydrophobicity parameter $\log P$, the standard enthalpy of hydration ΔH^0_{hydr} . Here we note that quantitative structure-activity relationship models (QSAR models) are regression or classification models used in the chemical sciences and engineering. Like other regression models, QSAR models relate a set of "predictor" variables to the potency of the response variable. The partition coefficient P is defined as a particular ratio of the concentrations of a solute between the two solvents (a biphasic of liquid phases); specifically for un-ionized solutes, and the decimal logarithm of the ratio is thus $\log P$ [23, 24]. Consistency analysis shows that not every dye characteristic can correlate with the stability of the associates. Among these characteristics, $\log P$ and ΔH^0_{hydr} deserve the most attention. Other characteristics largely depend on the approximations and convergence of successive iterations. They are difficult to predict in a particular solvent, because the problem of coordination of the models "particle in vacuum" and "particle in a solvent" in the theory of

solutions has not yet been solved. The changes in the values of $\lg K_{as}^T$ from $\log P$ (Figure 4) and $\lg K_{as}^T$ from ΔH^0_{hydr} (Figure 5) are similar.

In general, both the parameters $\log P$ and ΔH^0_{hydr} in some way reflect the hydrophobicity of the particle. However, the parameter $\log P$ depends only on the nature of the substituent and does not depend on its location in the molecule; hence, it is "indifferent" to particle geometry. The value of ΔH^0_{hydr} reflects the solvating properties of the dye, which depend on the steric factor. Therefore, the $\log P$ parameter should be used to search for the discussed correlations in the case when the molecules differ insignificantly in spatial factors. Many steric factors are similar in the case of the considered rhodamines. For example, the angle between the xanthene moiety and the 2-carboxyphenyl (or 2-ethoxyphenyl) substituent is 89° for R110 and 70° for other rhodamines (semi-empirical *AM1* method, ground state, vacuum).

Note that the parameters $\log P$ and ΔH^0_{hydr} of interacting counterions can explain the previously established [25] difference in the $\lg K_{as}^T$ values of the associate of rhodamine 3B ($R3B^+$) with TFB^- and the associate of $R3B^+$ with the anion of the oxyxanthene dye tetrabromophenylfluorone (TBFF). Since the hydrophobicity of TBFF is higher than that of TFB (the $\log P$ values are 7.9 and 7.3, respectively), the value of $\lg K_{as}^T$ for the associate $R3B^+ \cdot TBFF^-$ turns out to be greater (6.96 ± 0.12) than for $R3B^+ \cdot TFB^-$ (6.4 ± 0.1).

4. Conclusion

Based on spectrophotometric measurements, it was found that single-charged cations of rhodamines are able to form stable cation-anionic associations with a single-charged anion of TFB. It was found that the stability of the associates depends on the structural features that determine the hydrophobicity of the particles. The values of a number of structural factors of dye molecules (surface area, effective volume, hydrophobicity

log P, standard enthalpy of hydration $\Delta H^{\circ}_{\text{hydr}}$) have been analyzed within the QSAR model. The value of log P, in contrast to $\Delta H^{\circ}_{\text{hydr}}$, formally does not take into account differences in the relative position of the constituent fragments of molecules. Nevertheless the values of $\lg K_{\text{as}}^{\text{T}}$ tetraphenylborate associates correlate with the values of log P, as well as $\Delta H^{\circ}_{\text{hydr}}$ of dyes.

The above examples show that hydrophobic components acquire a significant role in the cation-anionic interactions of polyatomic organic dye ions. The obtained facts contribute to the further development of ideas about the processes of association of dyes as polyatomic particles in solutions.

References

- [1] E.D. Owen, Q. Sultana, A study of some intermolecular interactions between organic dye molecules in aqueous solution by fluorescence quenching and difference absorption spectrophotometry, *J. Appl. Chem. Biotechnol.*, 22(10) (1972) 1043–1052. <https://doi.org/10.1002/jctb.5020221003>.
- [2] Beom-Gyu Lee, Rae-Seok Jungv, Kang-Jin Kim, Aggregation of crystal violet with tetraphenylborate anions in aqueous solutions, *Bull. Korean Chem. Soc.*, 10(2) (1989) 148–151.
- [3] B. Armitage, J. Retterer, D. O'Brien, Dimerization of cyanine dyes in water driven by association with hydrophobic borate anions, *J. Amer. Chem. Soc.*, 115(23) (1993) 10786–10790. <https://doi.org/10.1021/ja00076a040>.
- [4] A.A. Ishchenko, S.A. Shapovalov, Heterogeneous association of the ions of dyes in solutions (review). *J. Appl. Spectrosc.*, 1(5) (2004) 605–629. <https://doi.org/10.1023/B:JAPS.0000049618.42857.0a>.
- [5] S.A. Shapovalov, V.L. Koval, T.A. Chernaya, A.Yu. Pereversev, N.A. Derevyanko, A.A. Ishchenko, N.O. Mchedlov-Petrosyan, Association of indopolycarbocyanine cations with anions of sulfphonephthalein and xanthene dyes, *J. Braz. Chem. Soc.*, 16(2) (2005) 232–240. <https://doi.org/10.1590/S0103-50532005000200017>.
- [6] S.A. Shapovalov, Cation-anionic association of organic dyes in aqueous solutions: structure and properties of associates, *Modern Org. Chem. Res.*, 2(4) (2017) 195–203. <https://dx.doi.org/10.22606/mocr.2017.24006>.
- [7] S.A. Shapovalov, V.K. Ponomarov, O.V. Mosharenkova, S.V. Butenko, Studies of the association of dyes with surfactants in aqueous solutions: spectrophotometry and computer simulation, *French-Ukr. J. Chem.*, 7(2) (2019) 9–19. <https://doi.org/10.17721/fujcV7I2P9-19>.
- [8] S. Shapovalov, V. Ponomariov, Interaction of dyes with cationic surfactants in solutions: determination of critical micelle concentration, *Int. Lett. Chem. Phys. Astronomy*, 81 (2019) 27–34. <https://doi.org/10.18052/www.scipress.com/ILCPA.81.27>.
- [9] S.A. Shapovalov, (2020) Association Processes with the Participation of Dyes in Solutions: Thermodynamic and Equilibrium Characteristics of Nanosystems. Riga: Academic Publishing of European Union, OmniScriptum Publishing group, Latvia, ISBN 978-620-2-92204-3.

- [10] A.V. Shestopalova, The investigation of the association of caffeine and actinocin derivatives in aqueous solution: a molecular dynamics simulation, *J. Molec. Liq.*, 127(1–3) (2006) 113–117. <https://doi.org/10.1016/j.molliq.2006.03.045>.
- [11] L. Kurunczi, S. Funar-Timofei, A. Bora, E. Seclaman, Application of the MTD-PLS method to heterocyclic dye-cellulose interactions, *Int. J. Quantum Chem.*, 107(11) (2007) 2057–2065. <https://doi.org/10.1002/qua.21384>.
- [12] S.A. Shapovalov, Russian Patent 1749786 (1993).
- [13] R.W. Ramette, E.B. Sandell, Rhodamine B equilibria, *J. Amer. Chem. Soc.*, 78(19) (1956) 4872–4878. <https://doi.org/10.1021/ja01600a017>.
- [14] T. Karstens, K. Kobs, Rhodamine B and Rhodamine 101 as reference substances for fluorescence quantum yield measurements, *J. Phys. Chem.*, 84(11) (1980) 1871–1872. <https://doi.org/10.1021/j100451a030>.
- [15] R.F. Kubin, A.N. Fletcher, Fluorescence quantum yields of some rhodamine dyes, *J. Luminescence*, 27(3) (1982) 455–462. [https://doi.org/10.1016/0022-2313\(82\)90045-X](https://doi.org/10.1016/0022-2313(82)90045-X).
- [16] D.A. Hinckley, P.G. Seybold, A spectroscopic/thermodynamic study of the rhodamine B lactone \rightleftharpoons zwitterion equilibrium, *Spectrochim. Acta. Part A*, 44(10) (1988) 1053–1060. [https://doi.org/10.1016/0584-8539\(88\)80227-7](https://doi.org/10.1016/0584-8539(88)80227-7)
- [17] L. Shaopu, L. Zhongfang, Studies on the resonant luminescence spectra of rhodamine dyes and their ion–association complexes, *Spectrochim. Acta. Part A*, 51(9) (1995) 1497–1500. [https://doi.org/10.1016/0584-8539\(94\)01325-B](https://doi.org/10.1016/0584-8539(94)01325-B).
- [18] A.G. Gilani, R. Sariri, K. Bahrpaima, Aggregate formation of Rhodamine 6G in anisotropic solvents, *Spectrochim. Acta. Part A*, 57(1) (2001) 155–162. [https://doi.org/10.1016/S1386-1425\(00\)00344-9](https://doi.org/10.1016/S1386-1425(00)00344-9).
- [19] D.A. Hinckley, P.G. Seybold, D.P. Borris, Solvatochromism and thermochromism of rhodamine solutions, *Spectrochim. Acta*, 42A(6) (1986) 747–754. [https://doi.org/10.1016/0584-8539\(86\)80095-2](https://doi.org/10.1016/0584-8539(86)80095-2).
- [20] S. Hamai, Complex formation in cationic dye-organic anion systems in aqueous solution, *Bull. Chem. Soc. Jpn.*, 58(7) (1985) 2099–2106. <https://doi.org/10.1246/bcsj.58.2099>.
- [21] N.O. Mchedlov-Petrosyan, Y.V. Kholin, Aggregation of rhodamine B in water. *Russ. J. Appl. Chem.*, 77(3) (2004) 414–422 <https://doi.org/10.1023/B:RJAC.0000031281.69081.d0>.
- [22] K. Hirano, Tokuhara M. Interionic transfer enhanced by hydrophobic interaction, *Bull. Chem. Soc. Jpn.*, 57(7) (1984) 2031–2032.
- [23] A.K. Ghose, G.M. Crippen, Atomic physicochemical parameters for three-dimensional structure-directed quantitative structure–activity relationships I. Partition coefficients as a measure of hydrophobicity, *J. Computat. Chem.*, 7(4) (1986) 565–577. <https://doi.org/10.1002/jcc.540070419>.
- [24] T. Cheng, Y. Zhao, X. Li, F. Lin, Y. Xu, X. Zhang, Y. Li, R. Wang, L. Lai,. Computation of octanol-water partition coefficients by guiding an additive model with knowledge, *J. Chem. Inform. Modeling*, 47(6) (2007) 2140–2148. <https://doi.org/10.1021/ci700257y>.
- [25] S.A. Shapovalov, T.A. Chernaya, E.A. Samoilov, Interaction of tetrabromophenylfluorone anion with organic counterions in aqueous solutions, *V.N. Karazin Kharkiv National University Bulletin. Chemical series*, 495(29) (2000) 110–112.

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Conflict of interest

None of the authors have any conflicts of interest to declare.

Does the Article Screened for Similarity?

Yes.

Data Availability

No additional data are available.

Ethics Approval

Ethics approval doesn't require for this study

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