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A New Application of Rhodamine 200 B (Sulfo Rhodamine B)

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ABSTRACT

The laser dye Rhodamine 200 B (Sulfo Rhodamine B) (CI Acid Red 52) can be used as a fluorescent counterion for the transfer of various cationic species (e.g. cationic surfactants and crown-complexes of metal ions) into a chloroform phase. The extraction of ionic associates is found to be independent of the acidity of the aqueous phase within the range of pH 2–12. The extractability of the Rhodamine 200 B anion is compared with that of other dye anions.

1 INTRODUCTION

Ionic dyes are widely used as counterions during the extraction of various ions, specifically in analytical chemistry.[1,2] Of special interest is the use of fluorescent dyes, which allow the detection of small amounts of extracted ionic associates in the organic phase. For instance, to extract cations (cationic surfactants, complexes of metal ions with neutral ligands,

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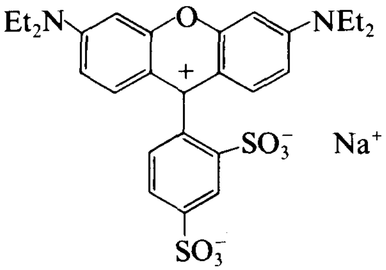
etc.) anionic oxyxanthene dyes of the eosin series have proved to be useful. Positively charged rhodamines and pyronines are traditionally used as transferers for various anions[1,2] and the aminoxanthene fluorophores are characterized by an intense fluorescence.[1,3] It was therefore of interest to also investigate the use of these dyes for the transfer of cationic species into the organic phase.

In the course of investigations of the extractability of ionic associates into chloroform, it was found Rhodamine that 200 B could be used as a fluorescent counterion in the ion pair extraction of various cations, especially cationic surfactants. The presence of two sulfonic acid groups in the dye ensures its existence in the form of monocharged anion R^- in aqueous solutions within the pH range 2 to 12:



Thus protolytical properties result in the extraction of ion pairs to be independent of pH within the commonly used acidic area. The dye (CI Acid Red 52, CI 45100),[4] also referred to as Sulfo Rhodamine B[3] or Lissamine Rhodamine RB 200,[5] has been shown to be useful as a luminophore,[3,5,6] laser material[7] and a dye for microscopy,[8] but as far as we know, it has not yet been used in solvent extraction.

The structurally similar triphenylmethane derivative, Disulfine Blue VN 150 (CI Acid Blue 1, CI 42045)[9] or Xylene Blue VS,[10] which does not contain a heterocyclic oxygen atom, has been used for the extractive-photometric determination of cationic surfactants.[9] However, it is not fluorescent and besides, extraction of the ion associates of the dye is pH-dependent ($pK_a = 2{\cdot}63$ in water).[9]

2 EXPERIMENTAL

Sulfo Rhodamine B (Rhodamine 200 B), $C_{27}H_{29}N_2NaO_7S_2$, was supplied by the Factory of Chemical Reactants, Shostka (Ukraine); it had $\lambda_{max} = 565$ nm, $\varepsilon_{max} = 110 \times 10^3$ cm^{-1} mol^{-1} dm^3 in water. The purity was checked by examining the excitation spectra. Some experiments were also carried out with various samples of Lissamine Rhodamine RB 200 (a dye for microscopy), donated by T. A. Shakhverdov (S.I. Vavilov State Optical Institute, St Petersburg, Russia); the results obtained were qualitatively analogous. Other reactants, including Methylene Blue, were of analytical grade (as a rule from Minkhimprom, USSR); 18-crown-6 was from the Institute of Organic Chemistry, USSR Academy of Sciences, Novosibirsk.

The IR spectrum of Rhodamine 200 B was used to characterize the dye sample used. Taking into account the results of previous studies,[11-15] the following assignment for the main bands in the spectrum (NaR, in KBr) can be made: 1590, 1558, 1530, 1510, 1490 and 1470 cm^{-1}, aromatic ring vibrations; 1340 cm^{-1}, C-aryl bond vibrations, polarized by the charge, as is usual for triphenylcarbonium ions;[11] 1120–1145 cm^{-1}, ν^{as} of SO_3^-; 1035 cm^{-1}, ν^{s} of SO_3^- (other investigations have reported:[13] 1026–1037 cm^{-1}); 668 cm^{-1} and 625 cm^{-1}, δ^{as} and δ^{s} of SO_3^-. In an earlier publication,[13] the band at 1199 cm^{-1} was assigned to ν^{as} of SO_3^-, but we have observed a band in this region not only for Rhodamine 200 B (1182 cm^{-1}), but also for other rhodamines which do not contain the SO_3^- group,[15] while the band at 1140 cm^{-1} appears on the spectrum of sulfone-Fluorescein.[14]

The band at 1645 cm^{-1} may be attributed to vibrations of the carbon–nitrogen bond if the contribution of the 'ammonium' structure is large ($C{=}\overset{+}{N}$). However, it is more probable that this band, which is present in spectra of all rhodamines,[15] should be attributed to ν^{s} of the cationic heterocycle; in the case of the zwitterion of sulfone-Fluorescein (similar to Rhodamine 200 B, but containing OH groups instead of NEt_2, and a SO_3^- group only in the 2'-position), a similar narrow absorption (1627 cm^{-1}) is present.[14] For the latter dye, the band at 1525 cm^{-1} has been attributed to ν^{as} of the cationic heterocycle.[12] In the case of Rhodamine 200 B, these vibrations are the origin of the absorption at 1530 cm^{-1} (or presently 1558 cm^{-1}). In the case of the zwitterion of Fluorescein, ν^{as} is at 1536 cm^{-1},[12,14] but ν^{s} is merged with other absorptions.

The purity of cetyltrimethylammonium bromide (Serva, Heidelberg) and of other cationic surfactants (in the form of chloride salts) was checked using two-phase titration with a standard solution of sodium laurylsulfate (NPO Sintez PAV, Shebekino, Russia). The purified sample of tetraphenylarsonium chloride (monohydrate) showed spectral characteristics (λ_{max} 259 and 265 nm, ε_{max} 2550 and 2780) similar to those reported in the literature.[16] Chloroform (Minmedprom, USSR) was distilled and purified according to the standard technique and kept under the water layer. Absorption, fluorescence and excitation spectra were recorded using Specord UV-VIS, Specord M40 and Hitachi 850 instruments, respectively.

The extraction equilibria were studied spectrophotometrically, checking both the organic and the aqueous phases at 20°C. As a rule, the phase volumes were generally equal (10 cm^3). After shaking for 20 min and centrifuging, the phases were separated and aliquots withdrawn. The equilibrium time was determined in preliminary experiments.

3 RESULTS AND DISCUSSION

3.1 Electronic spectra of extracts

Quantitative results of investigations of the ion associates solvent extraction of R^- with various cations are described below

$$C_w^+ + R_w^- \rightleftharpoons \langle C^+ . R^- \rangle_o. \qquad (1)$$

The subscripts w and o denote the water phase and organic phase, respectively; chloroform was used as the organic phase. Various counterions, i.e. tetraphenylarsonium ($AsPh_4^+$), cetylpyridinium (CP^+), cetyltrimethylammonium (CTA^+) and ($K(18\text{-crown-}6)^+$) give coloured extracts. The reagent in the forms HR or NaR was practically unextractable. In acidic media, protonation of the N atoms occurs. The first step is characterized by a pK_a value of 0·08 ± 0·19 ($H_2O–H_2SO_4$; H_o-scale);[17] i.e. $H_2O–HClO_4$ system, pK_a is 0·4 ± 0·2.

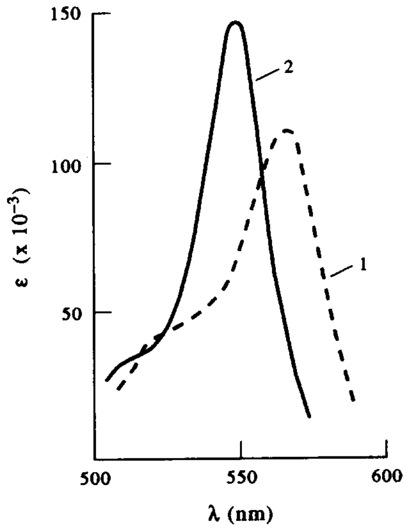


Fig. 1. Absorption spectra of Rhodamine 200 B: (1) in water (R^-); (2) in chloroform extract ($AsPh_4^+R^-$).

An attempt was initially made to evaluate the molar absorptivities of the ionic associates $(C^+R^-)_o$. In this respect, complete extraction of the dye under conditions of excess cations, or application of the equilibrium concentration in the aqueous phase ($[R^-]_w = A_w/\varepsilon_w \cdot 1$) were used. A poor relationship between the absorptivities of the ionic associates and the nature of the counterions was apparent. The absorption characteristics of the dyes in the extracts were as follows: λ_{max} $(C^+R^-)_o$ 548–550 nm; ε_{max} $(145 \pm 8) \times 10^3$ and $(143 \pm 8) \times 10^3$ with $AsPh_4^+$ and CP^+, respectively.

The absorption spectra are shown in Fig. 1. The spectrum in chloroform is similar to that of the Rhodamine B cation HR^+, which possesses an analogous chromophore (in $CHCl_3$ λ_{max} $((HR^+Cl^-)_o)$ is 550 nm, $\varepsilon_{max} = 158 \times 10^3$). Compared to that in aqueous solution, the spectrum of R^- of Rhodamine 200 B displays a hypsochromic shift (15–17 nm), similar to that of the Rhodamine B zwitterion ($R^\pm$; λ_{max} in H_2O and $CHCl_3$: 553 nm and 535 nm, respectively).[18]

The ε_{max} values of R^- in the associates, determined in systems containing crown ethers, vary within the range $137–144 \times 10^3$.

Extraction of the ionic associate formed by the dye under study and the cationic dye Methylene Blue, semiquantitatively demonstrated the monoanionic nature of Rhodamine 200 B in the extract (Fig. 2). Assuming that the Methylene Blue chromophore in the ionic associate maintains its own ε_{max} value at 655 nm (85×10^3), then the ε value of the R^- ion at 548 nm is 140×10^3 (by subtracting the Methylene Blue absorption in this region). If, as is usual in ionic pairs of dyes, the intensity of the long wavelengths band decreases,[19] then the ε_{max} value of the R^- ion can be expected to be somewhat lower.

The λ_{max} of the R^- emission in the extracts is 568–571 nm (small differences depending on the cation); λ_{max} of excitation ~550–554 nm (Fig. 3).

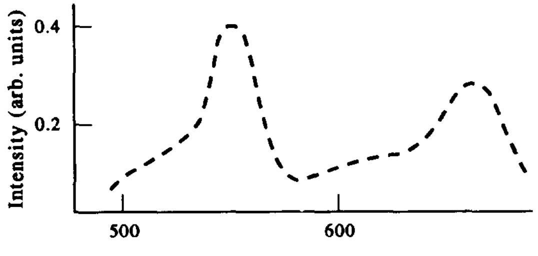


Fig. 2. Absorption spectrum of chloroform extract of the ion pair: Rhodamine 200 B (R^-) + Methylene Blue (C^+).

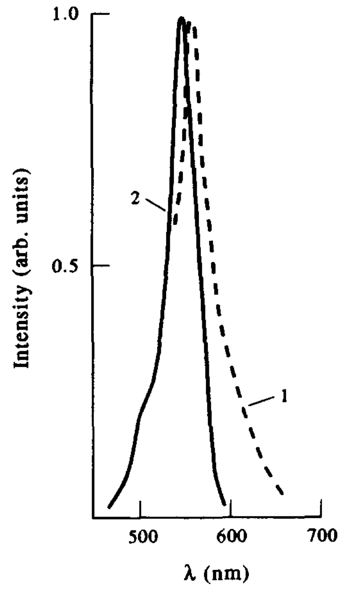


Fig. 3. Emission (1) and excitation (2) spectra of Rhodamine 200 B (R^-) associated with (K 18-crown-6)$^+$, extracted into chloroform.

3.2 Evaluation of extraction constants

The extraction constants of ion pairs of Rhodamine 200 B with various colourless cations (C^+), K_{ex}, were spectrophotometrically determined using eqn (2):

$$K_{ex} = \frac{[C^+R^-]_o}{[R^-]_w[C^+]_w} \tag{2}$$

The equilibrium concentrations $[C^+R^-]_o$ and $[R^-]_w$ were obtained from direct spectrophotometric measurements in both phases, using λ_{max} as analytical positions. The total dye concentration agrees, within acceptable limits, with the analytical concentration. The $[C^+]_w$ values were calculated from differences between the analytical concentrations of the cations and the $[C^+R^-]_o$ values. The ion pairs were assumed to be practically completely dissociated in the aqueous phase and undissociated in chloroform. Attempts to calculate two parameters, viz. the dissociation constants of C^+R^- in water and the partition constants of C^+R^- between the phases, instead of K_{ex} were unsuccessful, as is usual for such systems.[20,21] The composition of the associates was established using the traditional methods;[1,18] polymerization in the organic phase[22] was not evident. The values of the overall constants, K_{ex}, calculated as described above, remained stable with variations in the total concentration of R^- (8·93 ×

TABLE 1

Log K_{ex} Values for Ionic Associates of Rhodamine 200 B with Various Cations in the System H_2O–$CHCl_3$

Cation	*Log K_{ex}*	*Log K_{C^+}*
$As(C_6H_5)_4^+$	4·76 ± 0·03	2·9[25]
$C_{16}H_{33}N(CH_3)_3^+$	5·48 ± 0·09	3·6
$C_{12}H_{25}NC_5H_5^+$	5·54 ± 0·16	3·6
$C_{16}H_{33}NC_5H_5^+$	6·43 ± 0·12	4·5

The log K_{ex} values for ion pairs of R^- with metal–crown ether complexes are: 3·22 (K 18-crown-6$^+$), 2·36 (Na 18-crown-6$^+$), 3·92 (Na dibenzo-18-crown-6$^+$) and 2·08 (Na 15-crown-5$^+$).[18,24]

10^{-6}–5·36 × 10^{-5} M); the analytical concentration of $AsPh_4^+$ was usually 5 × 10^{-5} M. Competition between the extraction of $AsPh_4^+R^-$ and of $AsPh_4^+Cl^-$ was insignificant, as was shown in the preliminary experiments (in the absence of R^- from two-phase system, the $AsPh_4^+Cl^-$ concentrations in $CHCl_3$ were determined from measurements in the UV region). This observation is in accord with the data for the extractability of $AsPh_4^+Cl^-$.[22,23] The buffers used for maintaining various pH values did not influence the C^+R^- extractability over a wide pH region; only in the case of phthalate buffers (pH ~ 4) was competition between the corresponding anion and R^- evident. Most of the final experiments were carried out with unbuffered systems. For the ion pair Na^+R^-, an approximate value for log K_{ex} ~ −2 was found; in this case, the dye content in $CHCl_3$ was checked fluorimetrically.

The same procedure was used in the case of ion pairs of R^- with cetylpyridinium and other cationic surfactants; total C^+ concentrations varied from 4 × 10^{-6} to 4 × 10^{-3} M and the total R^- concentration was between 3·67 × 10^{-5} and 8·93 × 10^{-6} M. Thermodynamic log K_{ex} values (average of ~12 determinations) are shown in Table 1; the Debye-Hückel equation was used to calculate the activity coefficients of the ions in the aqueous phase (the ionic strength was ≤0·01 M). Also given are the log K_{ex} values of the ion pairs of R^- with crown ether complexes of metal ions; in this case, C^+ denotes KL^+ or NaL^+ (where L is the macrocyclic ligand).

3.3 Quantitative characteristics of individual extractability

It is desirable to compare the extractability of the anion of Rhodamine 200 B with that of other dyes used for this purpose. Two principal approaches are known.

The individual extraction constants of the ions (K_{C^+}, K_{A^-}) may be calculated according to the assumption about the additivity of cation, anion and solvent contributions to log K_{ex} values:[25]

$$\log K_{ex}(C^+A^-) = \log K_{C^+} + \log K_{A^-} + \log K_{solvent} \quad (3)$$

The log K values for $AsPh_4^+$ and BPh_4^- are assumed to be equal and log $K_{solvent}$ for benzene is 0.[25] In this scale, at 25°C log K_{C^+} for $AsPh_4^+$ is 2·9, log K_{Br^-} is $-5{\cdot}6$ and log $K_{solvent}$ for $CHCl_3$ is 3·8 (the average of the extreme values 3·4 and 4·2).[25] Thus, for R^- of Rhodamine 200 B log K_{A^-} is $-1{\cdot}9$. This approach can be considered valid in the absence of specific interactions, in particular between the cation and the anion (such interactions can be expected for the pair: dye anion–crown complex of metal ion).[24]

Another approach to the K_{ex} interpretation involves the use of eqn (4), based on LFER (linear free-energy relationships):[26,27]

$$\begin{aligned} \log K_Y^X &= \log K_{ex}(C^+X^-) - \log K_{ex}(C^+Y^-) \\ &= \kappa(\Delta G_{hydr}^X - \Delta G_{hydr}^Y) \end{aligned} \quad (4)$$

where K_Y^X is the ion exchange constant in the solvent extraction system with a fixed cation (C^+) and ΔG_{hydr}^A denotes the hydration parameter, close to the free energy of hydration of the anions.

The calculations of the latter values were performed using values of $\kappa = 0{\cdot}055$ and $\Delta G_{hydr}^A = -170$ kJ mol^{-1} for the monoanion (HR^-) of Bromothymol Blue.[27] For this dye log $K_{ex}(AsPh_4^+\ HR^-)$ was found to be 5·65; then, for Rhodamine 200 B ΔG_{hydr}^R is -186 kJ mol^{-1}.

The values obtained allow comparison to be made of extractability of R^- (Rhodamine 200B) with those of other ions. In the sequence of anions, R^- must be placed near the picrate and before Methyl Orange ($\Delta G_{hydr}^A = -193$ and -227 kJ mol^{-1}, respectively).[27] The ions ClO_4^-, I^- and Br^- are more hydrophilic ($\Delta G_{hydr}^A = -242$, -268 and -304 kJ mol^{-1}, respectively).[27] However, in the log K_{A^-} scale[25] the R^- ion lies between ClO_4^- and I^- (log $K_{A^-} = -1{\cdot}5$ and $-3{\cdot}1$, respectively)[25] and near to BF_4^- ($-2{\cdot}0$).[25]

Being less extractable than the monoanions (HR^-) of the structurally similar and widely used Eosin and Bromothymol Blue (log $K_{A^-} = -0{\cdot}5$ and $-1{\cdot}05$; $\Delta G_{hydr}^A = -160$ and -170 kJ mol^{-1}, respectively),[24,27] the R^- ion of Rhodamine 200 B exceeds the HR^- ions of the unsubstituted sulfonated xanthene and triphenylmethane dyes sulfone-Fluorescein and Phenol Red (log $K_A- = -2{\cdot}8$ and $-3{\cdot}0$; $\Delta G_{hydr}^A = -201$ and -205 kJ mol^{-1} respectively.)[24]

The log K_{C^+} values can be calculated using eqn (3). The value for CTA^+ is lower than the published value[25] of 3·9 for tetradecyltrimethylammonium; the log K_{A^-} value for Thymol Blue, obtained by us $(-1{\cdot}7)$,[24] also deviates from the data of the cited paper $(-0{\cdot}8)$.[25] Each methylene group is known to increase the log K_{ex} value, usually by 0·5–0·6 units.[20,21] From this point of view, the difference between log K_{C^+} values for CP^+ and dodecylpyridinium (0·9) is relatively small; some specific interactions in the ionic pairs may possibly be the reason.

The same conclusion follows from analysis of the data on the influence of inorganic salts on the extraction into chloroform of the ionic pair formed by Disulfine Blue VN 150 (D^-) and CTA^+.[28] We tried to compare the log K_{ex} values for ion pairs CTA^+A^- ($A^- = Cl^-, NO_3^-, Br^-, I^-, ClO_4^-$) obtained by Biswas and Mandal[28] with the scales of Kasahara *et al.*[25] and Shmidt *et al.*[27] The differences between the values log $K_{ex}(C^+X^-)$ and log $K_{ex}(C^+Y^-)$ for several pairs of anions (X^-, Y^-) deviated significantly from those calculated using eqn (3) (i.e. $= \log K_{X^-} - \log K_{Y^-}$), the discrepancies varying from 1·3 to $-1{\cdot}5$. Calculations using eqn (4)[27] lead to values also essentially deviating (to ±0·5 log units) from the experimental differences in log K_{ex} for chosen anion pairs (X^-, Y^-), although the value $\kappa = 0{\cdot}032$ for the system (H_2O–$CHCl_3$, CTA^+A^-) was obtained from data with the same set of anions ($A^- = Cl^-, Br^-, NO_3^-, ClO_4^-$).[27] Moreover, if a fixed K_Y^X value is calculated by using different approaches,[25,26] the discrepancy can reach one order of magnitude. It is evident that the interpretation of the data on the solvent extraction of ion pairs requires further improvement. Taking into account that for the ion pairs formed by CTA^+ with Disulfine Blue (D^-)[28] and Rhodamine 200 B (R^-) the log K_{ex} values (6·22 and 5·48, respectively) are estimated under similar conditions, the corresponding data may be used as a measure of their relative extractability.

3.4 Determination of cationic surfactants

Due to the intense fluorescence of Rhodamine 200 B, use of it allows an extension of the range of determinable concentrations of cationic surfactants[29,30] compared with an extractive fluorimetric method employing Eosin.[31] The method has more than double the sensitivity, and more than a 10-fold increase in detection limit (3σ criteria). The determination of up to 1×10^{-8} M is possible[29,30] (Fig. 4).

The method was applied by us to determine several cationic surfactants (benzyldimethylalkylammonium, C_{10-14}, octylammonium and cetylammonium) in various technical products and aqueous media. Both fluorimetric and photometric detections were used. In the case of $C_8H_{17}NH_3^+$ and $C_{16}H_{33}NH_3^+$ ions, addition of 18-crown-6 increases the extraction, probably due to crown-complex formation of L with the $-NH_3^+$ group.

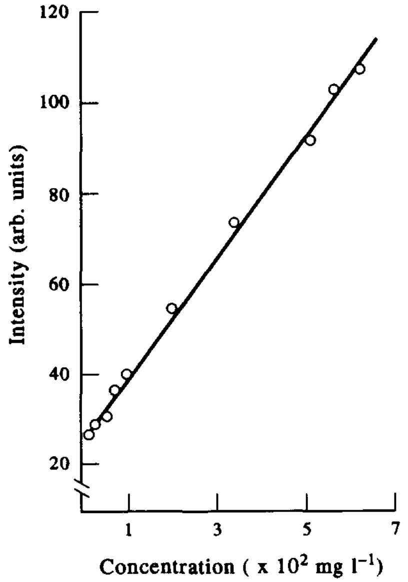


Fig. 4. Relationship between the emission intensity (corrected values) of the CP^+R^- associate in chloroform extracts at 570 nm with the cetylpyridinium chloride initial concentration in the aqueous phase; the volumes of the phases are equal. The correlation coefficient is 0·998.

3.5 Extraction of protonized crown ethers using Rhodamine 200 B

Crown ethers (for instance 18-crown-6) are known to be protonized in acidic media,[32,33] forming (H_3O^+. L) or (H^+. L). Some information is available on the extraction of such particles into the organic layer in the form of ion pairs;[34] it would be of interest to use not only picrates, but more complicated dyes as counter ions for them. Rhodamine 200 B is suitable for this purpose as the R^- ion is difficult to protonate. Detailed investigations of the extraction with 18-crown-6 and R^- were undertaken at pH 1·3 (HCl, HNO_3 or $HClO_4$). The colour intensity of the organic phase was highest in the experiments with hydrochloric acid and lowest with perchloric acid. This effect can be considered as reflecting the competition between R^- and the inorganic anion ($Cl^- < NO_3^- < ClO_4^-$), but the reasons may be more complicated when taking into account the peculiarities of the extraction of crown ethers in the presence of mineral acids.[35]

CONCLUSIONS

The dye Rhodamine 200 B forms extractable, in the chloroform phase, intensely fluorescing, ionic associates with hydrophobic enough cations such as cationic surfactants, crown-complexes of metal ions and ammonium ions, and protonated forms of crown ether 18-crown-6, with the tetraphenylarsonium ion. The extraction of the latter ion pair, $\mathrm{As(Ph)_4^+R^-}$, in a $\mathrm{H_2O}$–$\mathrm{CHCl_3}$ system, is characterized by the value $\log K_{ex} = 4{\cdot}76$. This allows determination of the individual extractability of the dye anion, $\mathrm{R^-}$: the Goto parameter ($\log K_{\mathrm{R}^-} = -1{\cdot}9$) and the Shmidt hydration parameter ($\Delta G^{\mathrm{R}}_{\mathrm{hydr}} = -186$ kJ mol^{-1}), and also enables a quantitative comparison with the extractability of other anions to be made.

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