

An 8-sulfonamidoquinoline derivative with imidazolium unit as an extraction reagent for use in ionic liquid chelate extraction systems

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1 **An 8-sulfonamidoquinoline derivative having imidazolium unit as an extraction**
2 **reagent for use in ionic liquid chelate extraction system**

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15

16 **Abstract**

17 To evaluate the superiority of using a task-specific onium salt (TSOS), a novel
18 TSOS reagent 1-methyl-3-[2-(8-quinolinylaminosulfonyl)ethyl]imidazolium chloride
19 (HmimesqCl) was synthesized, and its performance in extraction of different divalent
20 metal cations was investigated. This TSOS reagent has both a cationic imidazolium
21 unit and an anionic (proton-dissociable) complexation unit for the extraction of metal
22 cations into an ionic liquid. In the use of HmimesqCl, relatively high extraction of
23 metals resulted in comparison with the use of its non-imidazolium analogs, without
24 changing the extraction selectivity.

25

26 *Keywords:* Ionic liquids; Chelate extraction, Divalent metal cations;

27 8-Sulfonamidoquinoline derivative; Task-specific onium salt.

28

29 **1. Introduction**

30 Ionic liquids (ILs) have attracted much interest as novel solvents [1-16]. They are
31 salts with low melting points ($< 100\text{ }^{\circ}\text{C}$ in general) and are hydrolytically stable.
32 Furthermore, several ILs, such as 1,3-dialkylimidazolium hexafluorophosphates and
33 bis(trifluoromethanesulfonyl)imides, are immiscible with water; therefore, they can be
34 used as extraction solvents for liquid-liquid extraction.

35 The use of ILs as an extraction phase in solvent extraction was reported for
36 organic materials by Huddleston et al. in 1998 [17] and for metal cations by Dai et al. in
37 1999 [18]. Many researchers have studied the use of ILs in extraction, and several
38 reviews have been published [19-28].

39 In metal extraction, the low solubility of extraction reagents into the ILs is a
40 serious disadvantage; low extraction capacity often results [19]. Reagents do not solvate
41 well because many ready-made extraction reagents are optimized for use in normal
42 solvent extraction and most have high solubility in low-polar organic solvents. In other
43 words, the development of novel extraction reagents with high affinity to ILs is an
44 important subject. Thus, several researchers have investigated the possible use of
45 several reagents as extraction reagents in an IL-extraction system [29-35]. These
46 reagents contain both a cationic imidazolium unit and a neutral complexation unit, and
47 they are classified as task-specific ionic liquids (TSILs) or task-specific onium salts
48 (TSOSs). Unfortunately, both the imidazolium units and the complexed parts of the
49 TSOSs have positive charges, which lower complexation stability with the metal cation
50 due to electrostatic repulsion [32]. Namely, these TSOSs often have lower extraction
51 ability than their imidazolium-free analogs that show no repulsion in complexation.

52 We have investigated the use of anionic (proton-dissociable) complexants,
53 including 8-quinolinol derivatives [36-38], β -diketones [38-44] and

54 8-sulfonamidoquinoline derivatives [38,45] such as
55 4-methyl-*N*-(8-quinolinyl)benzenesulfonamide (8-(*p*-toluenesulfonamido)quinoline,
56 Htsq), in the IL-extraction. In this system, named the “ionic liquid chelate extraction
57 system”, complexation of the reagents to the metals neutralizes the positive charge of
58 the metals, resulting in a lower positive, neutral or negative charge. Therefore, TSOSs
59 having both the imidazolium and proton-dissociable complexation units can result in
60 suppression of the electrostatic repulsion mentioned above and enhancement of the
61 extraction of the metal in the IL phase. However, the use of a proton-dissociable TSOS
62 has received limited study. To date, only Ouadi et al. [46] has reported on the nature of
63 1-butyl-3-[3-(2-hydroxybenzylamino)propyl]imidazolium salts as extraction reagents
64 for americium (III); unfortunately, the 2-hydroxybenzylamine unit had limited ability to
65 complex.

66 In this study, we performed a one-pot synthesis to form a proton-dissociable
67 TSOS containing an 8-sulfonamidoquinoline complexation unit,
68 1-methyl-3-[2-(8-quinolinylaminosulfonyl)ethyl]imidazolium chloride
69 (8-{2-[1-(3-methylimidazolio)]ethanesulfonamido}quinoline chloride, HmimesqCl; see
70 Fig. 1 (a)). We also displayed its possible use for the extraction of different divalent
71 metal cations into an IL, 1-butyl-3-methylimidazolium hexafluorophosphate
72 ([bmim][PF₆]). The 8-sulfonamidoquinoline unit was selected due to the high metal
73 extractability of various other known 8-sulfonamidoquinoline derivatives [38,45,47-57].
74 When compared to a simple derivative, 8-quinolinylaminosulfonylethane
75 (8-ethanesulfonamidoquinoline, Hesq; see Fig. 1 (b)), the HmimesqCl showed higher
76 extractability for these metals in the IL-extraction system.

77

78 2. Experimental

79 *2.1. Reagents*

80 The one-pot synthesis of HmimesqCl was performed as follows: To 100 cm³ of
81 CH₃CN solution containing 1.73 g (12 mmol) of 8-aminoquinoline and 2.9 cm³ (37
82 mmol) of 1-methylimidazole, 40 cm³ of CH₃CN solution containing 1.2 cm³ (11 mmol)
83 of 2-chloroethanesulfonyl chloride was added dropwise. The mixture was stirred at 50
84 °C for 5 h after which it was stirred at room temperature overnight. The resulted solid
85 was filtered and colorless needles were obtained after recrystallization from ethyl
86 acetate – methanol. Yield: 1.93 g (5.5 mmol, 50 %), Anal. calcd. for C₁₅H₁₇ClN₄O₂S: C
87 51.06, H 4.86, N 15.88. Found: C 50.58, H 4.90, N 15.86. ¹H NMR (DMSO-*d*₆): δ =
88 3.80 (s, 3H, CH₃-), 3.94 (t, 2H, -NHSO₂-CH₂CH₂-), 4.75 (t, 2H, -NHSO₂-CH₂CH₂-),
89 7.59–7.73 (m, 4H, Ar), 7.80–7.85 (m, 2H, Ar), 8.47 (d, 1H, Ar), 8.97–9.01 (m, 1H, Ar),
90 9.26 (s, 1H, Ar), 9.96 (br s, 1H, -NHSO₂-).

91 The synthesis of Hesq was performed from 8-aminoquinoline and
92 1-ethanesulfonyl chloride using the reported procedure for the preparation of Htsq [58].
93 ¹H NMR (DMSO-*d*₆): δ = 1.21 (t, 3H, CH₃-), 3.25 (q, 2H, -CH₂-), 7.54–7.77 (m, 4H,
94 Ar), 8.42–8.46 (m, 1H, Ar), 8.93–8.96 (m, 1H, Ar), 9.30 (br s, 1H, -NHSO₂-).

95 The IL [bmim][PF₆] was synthesized from 1-chlorobutane, 1-methylimidazole
96 and hexafluorophosphoric acid according to reported procedure [17]. Metal standard
97 solutions for atomic absorption spectrometry (1,000 μg cm⁻³ dissolved in dil. nitric
98 acid) were used as metal standards. Other chemicals included reagent-grade materials,
99 which were used without further purification. Distilled deionized water was used
100 throughout.

101

102 *2.2. Apparatus*

103 A Hitachi model Z-6100 polarized Zeeman atomic absorption spectrophotometer

104 was used for the determination of the concentration of the metals in the aqueous phase.
105 A Horiba model F-52 pH meter equipped with a Horiba 9678-10D combined glass
106 electrode was used to determine the pH values. The absorption spectra of solutions were
107 recorded on a JASCO V-570 UV/visible/near-infrared spectrophotometer using 1 cm
108 matched quartz cells.

109

110 *2.3. Distribution of the extraction reagents*

111 Distribution of the extraction reagents between the [bmim][PF₆] and aqueous
112 phases was measured as follows: In a centrifuge tube, an aliquot (10 cm³) of aqueous
113 solution containing 5×10⁻⁴ mol dm⁻³ of each reagent, 1×10⁻¹ mol dm⁻³ of sodium
114 chloride, 1×10⁻² mol dm⁻³ of buffer (chloroacetic acid, acetic acid,
115 2-(*N*-morpholino)ethanesulfonic acid, 3-(*N*-morpholino)propanesulfonic acid,
116 *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid or *N*-cyclohexyl-
117 2-aminoethanesulfonic acid) and an appropriate amount of NaOH and 1 cm³ of
118 [bmim][PF₆] were shaken at 25±1 °C to be equilibrated. After the two phases were
119 separated by centrifugation, the pH in the aqueous phase was determined, and the
120 measured pH was used as the equilibrated pH. To the aqueous phase, a small amount of
121 concentrated hydrochloric acid was added to acidify to ca. 1 mol dm⁻³ HCl. From the
122 [bmim][PF₆] phase, a small amount was dissolved into 1 mol dm⁻³ HCl. Absorbance of
123 each the solution at 315 nm (maximum absorption wavelength for H₂mimesq²⁺; see
124 below) was measured, and the distribution ratio was calculated.

125

126 *2.4. Distribution of the metals*

127 In a centrifuge tube, an aliquot (1 cm³) of [bmim][PF₆] containing 1×10⁻³ mol
128 dm⁻³ of HmimesqCl or Hesq and 5 cm³ of an aqueous phase containing 1×10⁻⁵ – 1×10⁻⁴

129 mol dm⁻³ of M²⁺ (M = Co, Cu, Zn or Cd), 1×10⁻¹ mol dm⁻³ of potassium nitrate, 1×10⁻²
 130 mol dm⁻³ of buffer (chloroacetic acid, acetic acid, 2-(*N*-morpholino)ethanesulfonic acid,
 131 3-(*N*-morpholino)propanesulfonic acid, *N*-tris(hydroxymethyl)methyl-
 132 3-aminopropanesulfonic acid or *N*-cyclohexyl-2-aminoethanesulfonic acid) and an
 133 appropriate amount of NaOH were shaken at 25±1 °C for 45 min. After the two phases
 134 were separated by centrifugation, the pH and the metal concentration in the aqueous
 135 phase were determined. The measured pH was used for numerical analysis as
 136 equilibrated pH. The metal concentration in the extraction phase ([bmim][PF₆]) was
 137 determined after back-extraction into a 10-fold volume of 1 mol dm⁻³ nitric acid. The
 138 extraction ratio (%*E*) of the metal was calculated as 100 × (extracted amount of the
 139 metal) / (initial amount of the metal in the aqueous phase), and the distribution ratio (*D*)
 140 was calculated as (total metal concentration in the extraction phase) / (total metal
 141 concentration in the aqueous phase).

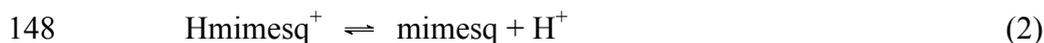
142

143 **3. Results and discussion**

144 *3.1. Acid dissociation equilibria of the reagents*

145 The reagent HmimesqCl dissociates in aqueous solution to Hmimesq⁺ and Cl⁻.

146 The Hmimesq⁺ can show the following acid dissociation equilibria:



149 where Eq. (1) corresponds to the acid dissociation of the quinolinium–NH⁺ and Eq. (2)
 150 corresponds to that of the sulfonamide–NH. To evaluate these equilibria and to
 151 determine respective acid dissociation constants, absorption spectra of 1.0×10⁻⁴ mol
 152 dm⁻³ HmimesqCl aqueous solutions containing 1.0×10⁻¹ mol dm⁻³ sodium chloride
 153 were measured at different pHs. Some of the spectra are shown in Fig. 2. The two

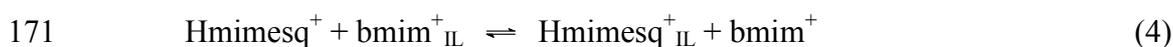
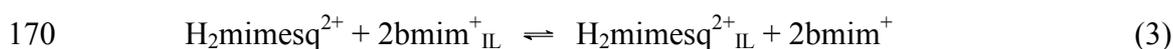
154 isosbestic points at 294 nm and 319 nm correspond to Eqs. (1) and (2), respectively.
 155 Maximum absorption wavelengths and molar absorptivities for $\text{H}_2\text{mimesq}^{2+}$, Hmimesq^+
 156 and mimesq were estimated to be 315 nm for $6.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, 304 nm for
 157 $3.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and 342 nm for $3.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively.
 158 Furthermore, the acid dissociation constants were obtained as $K_{a1} = 10^{-2.82 \pm 0.01}$ and $K_{a2} =$
 159 $10^{-7.60 \pm 0.01}$ from the non-linear least-squares fitting of absorbance (at 315 and 342 nm)
 160 versus pH. These constants were also determined for Hesq were obtained through the
 161 same technique ($K_{a1} = 10^{-3.41 \pm 0.01}$ and $K_{a2} = 10^{-9.01 \pm 0.01}$).

162

163 3.2. Distribution of the extraction reagents

164 It is well known that not only neutral species but also charged species are
 165 extractable into a hydrophobic IL phase from an aqueous phase [17]. Consequently,
 166 IL/water distribution behavior of extraction reagents can be complicated. Fig. 3 shows
 167 aqueous phase pH dependency of the distribution ratio (D_R) between the $[\text{bmim}][\text{PF}_6]$
 168 phase and the aqueous phase for HmimesqCl and Hesq .

169 The three plateaus in Fig. 3 (a) correspond to the following equilibria:



173 where subscript IL denotes the $[\text{bmim}][\text{PF}_6]$ phase. The cation-exchange distribution
 174 equilibrium constants (K_{CED}) for Eqs. (3) and (4) can be expressed as follows:

$$175 \quad K_{\text{CED}}(\text{H}_2\text{mimesq}^{2+}) = [\text{H}_2\text{mimesq}^{2+}]_{\text{IL}} [\text{bmim}^+]^2 / [\text{H}_2\text{mimesq}^{2+}] [\text{bmim}^+]_{\text{IL}}^2 \quad (6)$$

$$176 \quad K_{\text{CED}}(\text{Hmimesq}^+) = [\text{Hmimesq}^+]_{\text{IL}} [\text{bmim}^+] / [\text{Hmimesq}^+] [\text{bmim}^+]_{\text{IL}} \quad (7)$$

177 In these cases, the $[\text{bmim}^+]_{\text{IL}}$ and $[\text{bmim}^+]$ values are regarded as constant (the aqueous
 178 phase is saturated with $[\text{bmim}][\text{PF}_6]$ salt), and the following values (e.g. apparent

179 distribution coefficients, K_D) are also considered constant:

$$180 \quad K_D'(\text{H}_2\text{mimesq}^{2+}) = [\text{H}_2\text{mimesq}^{2+}]_{\text{IL}} / [\text{H}_2\text{mimesq}^{2+}]$$

$$181 \quad = K_{\text{CED}}(\text{H}_2\text{mimesq}^{2+})[\text{bmim}^+]_{\text{IL}}^2 / [\text{bmim}^+]^2 \quad (8)$$

$$182 \quad K_D'(\text{Hmimesq}^+) = [\text{Hmimesq}^+]_{\text{IL}} / [\text{Hmimesq}^+]$$

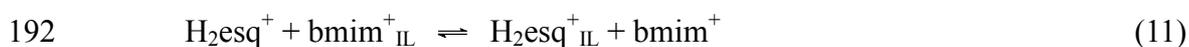
$$183 \quad = K_{\text{CED}}(\text{Hmimesq}^+)[\text{bmim}^+]_{\text{IL}} / [\text{bmim}^+] \quad (9)$$

184 Furthermore, the distribution constant (K_D) for neutral mimesq (Eq. (5)) can be
185 expressed as follows:

$$186 \quad K_D(\text{mimesq}) = [\text{mimesq}]_{\text{IL}} / [\text{mimesq}] \quad (10)$$

187 By using a non-linear least-squares fitting, the values of $\log K_D'(\text{H}_2\text{mimesq}^{2+})$, \log
188 $K_D'(\text{Hmimesq}^+)$ and $\log K_D(\text{mimesq})$ were determined as 0.71 ± 0.07 , 2.82 ± 0.06 and
189 0.04 ± 0.01 , respectively.

190 In the same manner, the two plateaus in Fig. 3 (b) corresponds to the following
191 two equilibria and constants:



$$193 \quad K_{\text{CED}}(\text{H}_2\text{esq}^+) = [\text{H}_2\text{esq}^+]_{\text{IL}}[\text{bmim}^+] / [\text{H}_2\text{esq}^+][\text{bmim}^+]_{\text{IL}} \quad (12)$$

$$194 \quad K_D'(\text{H}_2\text{esq}^+) = [\text{H}_2\text{esq}^+]_{\text{IL}} / [\text{H}_2\text{esq}^+]$$

$$195 \quad = K_{\text{CED}}(\text{H}_2\text{esq}^+)[\text{bmim}^+]_{\text{IL}} / [\text{bmim}^+] \quad (13)$$



$$197 \quad K_D(\text{Hesq}) = [\text{Hesq}]_{\text{IL}} / [\text{Hesq}] \quad (15)$$

198 The values of $\log K_D'(\text{H}_2\text{esq}^+)$ and $\log K_D(\text{Hesq})$ were determined as 0.43 ± 0.04 and
199 2.84 ± 0.01 , respectively. (The distribution of esq^- into the IL phase was not observed.)

200 It is interesting to note that the values of $K_D'(\text{Hmimesq}^+)$ and $K_D(\text{Hesq})$ are
201 similar to one another regardless of their different electric charges. This fact suggests
202 that introduction of the cationic imidazolium unit to Hesq not only enhanced the
203 hydrophilicity through its positive charge but also maintained IL-philicity because of its

204 structural similarity to Hesq.

205

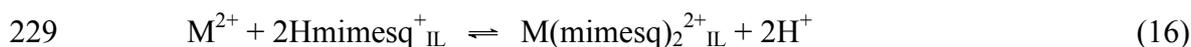
206 3.3. Extraction behavior of M^{2+}

207 The %*E* values of M^{2+} into the [bmim][PF₆] extraction phase were plotted as a
208 function of aqueous phase pH (equilibrated pH). The results are shown in Fig. 4. When
209 using HmimesqCl as the extraction reagent, > 95 % of the reagent existed as Hmimesq⁺
210 in the [bmim][PF₆] phase at pH > ca. 2.8 as shown in Section 3.2 and “Hmimesq⁺” will
211 replace the use of “HmimesqCl” hereafter. Alternatively, > 95 % of Hesq existed as the
212 neutral form in the IL phase at pH > ca. 3.0. The %*E* values, calculated from each metal
213 concentration in the back-extracted solution, were compatible with the metal
214 concentration remaining in the equilibrated aqueous phase. Thus, it was confirmed that
215 the back-extraction using 1 mol dm⁻³ nitric acid was effective not only with the Hesq
216 system but also with the Hmimesq⁺ system.

217 For all of the M^{2+} s, Hmimesq⁺ showed higher extractability than its
218 imidazolium-free analog Hesq. On the other hand, these two systems showed similar
219 extraction selectivity ($Cu^{2+} > Zn^{2+} > Cd^{2+} \approx Co^{2+}$) as shown in Fig. 4. Namely, the
220 introduction of the imidazolium unit to the Hesq resulted in the enhancement of its
221 extraction performance.

222 On a side note, Mn^{2+} was not able to be extracted in the examined extraction
223 conditions, and the extraction of Ni^{2+} needed more time to reach equilibration as was
224 reported previously in the use of other 8-sulfonamidoquinoline derivatives [45,54].

225 When most 8-sulfonamidoquinoline derivatives extract M^{2+} into the [bmim][PF₆]
226 phase, as neutral 1:2 complex has been reported to result [45]. Therefore, by using
227 Hmimesq⁺, the extraction equilibrium and the extraction constant (K_{ex}) can be expressed
228 as follows:



230 $K_{ex} = [M(mimesq)_2^{2+}]_{IL} [H^+]^2 / [M^{2+}] [Hmimesq^+]_{IL}^2$ (17)

231 In these cases, the D for M^{2+} is expressed as follows:

232 $D = [M(mimesq)_2]_{IL} / ([M^{2+}] + [M(OH)^+] + [M(OH)_2])$
 233 $= ([M(mimesq)_2]_{IL} / [M^{2+}]) (1 + \beta_1[OH^-] + \beta_2[OH^-]^2)^{-1}$
 234 $= (K_{ex}[Hmimesq^+]_{IL}^2 / [H^+]^2) (1 + \beta_1[OH^-] + \beta_2[OH^-]^2)^{-1}$ (18)

235 where β_1 and β_2 are stability constants for hydroxo complexes of $M(OH)^+$ and $M(OH)_2$,
 236 respectively. Assumingly, the following approximate relationship can be true:

237 $\log D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$
 238 $= \log K_{ex} + 2 \log C(HmimesqCl)_{IL} + 2pH$ (19)

239 where $C(HmimesqCl)_{IL}$ is the initial concentration of $HmimesqCl$ in the $[bmim][PF_6]$
 240 phase.

241 To confirm the extracted species and the extraction equilibria, the relationships
 242 between $\log D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$ of M^{2+} and aqueous phase pH at a fixed
 243 $C(HmimesqCl)_{IL}$ and between the $\log D(1 + \beta_1[OH^-] + \beta_2[OH^-]^2)$ and \log
 244 $C(HmimesqCl)_{IL}$ at fixed pH (equilibrated pH) were determined. The following β_i
 245 values for Co^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} were used for the calculation: $\log \beta_1 = 4.35, 6.30,$
 246 5.04 and 3.92 , and $\log \beta_2 = 9.19, 10.70, 11.09$ and 7.64 , respectively [59]. The obtained
 247 plots are shown in Figs. 5 and 6, respectively. In all cases, the plots formed straight lines
 248 with slopes close to 2. Based on these plots, the extraction mechanism for M^{2+} must be
 249 expressed as Eq. (16) for the $Hmimesq^+$ system.

250 The $\log K_{ex}$ values in the $Hmimesq^+$ system were calculated from experimental
 251 data ($pH > 2.8$) using Eq. (19). The obtained values are shown in Table 1 alongside
 252 those of the $Hesq$ and $Htsq$ [45] systems. The $\log K_{ex}$ values in the $Hmimesq^+$ system
 253 were 1.3 – 2.3 higher than those in the $Hesq$ system, which correspond to 0.7 – 1.2 pH

254 units in the %*E* vs. pH plots. Furthermore, these values were higher than those of the
255 more hydrophobic Htsq. From these facts, it can be deduced that the use of a TSOS,
256 which has a proton-dissociable complexation (chelation) group, as an extraction reagent
257 in the IL-extraction system is effective for the high-performance extraction of metal
258 cations in the IL phase.

259 While the solubility of Hesq in [bmim][PF₆] was ca. 10⁻² mol dm⁻³, HmimesqCl
260 dissolved in [bmim][PF₆] at more than 1 mol dm⁻³. Because of this higher value, this
261 TSOS possesses a much higher extraction capacity. Furthermore, by adding aqueous
262 sodium hexafluorophosphate to an aqueous solution of HmimesqCl, a phase separation
263 was brought about. The newly formed viscous lower phase, probably [Hmimesq][PF₆],
264 may be a hydrophobic IL, but further detailed investigation concerning the species is
265 required.

266

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363

364 **Figure/Table legends**

365

366 Fig. 1 Chemical structures of HmimesqCl (a) and Hesq (b).

367

368 Fig. 2 Absorption spectra of the 1.0×10^{-4} mol dm⁻³ HmimesqCl aqueous solutions
369 containing 1.0×10^{-1} mol dm⁻³ sodium chloride at different pH conditions (0.93, 2.26,
370 2.66, 3.05, 3.81, 4.69, 6.95, 7.44, 7.96, 8.63 and 11.29).

371

372 Fig. 3 Relationship between logarithmic distribution ratio ($\log D_R$) for extraction
373 reagents and aqueous phase pH. Initial reagent concentration in the aqueous phase was
374 5.0×10^{-4} mol dm⁻³. The solid curves were obtained by a non-linear least squares fitting.
375 Reagent: (a) HmimesqCl, (b) Hesq.

376

377 Fig. 4 Plots of the extracted ratios (% E) for some divalent metals as a function of the
378 aqueous phase pH equilibrated with extraction phase in the Hmimesq⁺ (a) and Hesq (b)
379 systems. Initial reagent concentration in the [bmim][PF₆] phase was 1×10^{-3} mol dm⁻³.
380 Sample: (\blacklozenge) Co²⁺, (\blacksquare) Cu²⁺, (\bullet) Zn²⁺, (\blacktriangle) Cd²⁺.

381

382 Fig. 5 Plots of the $\log D(1 + \beta_1[\text{OH}^-] + \beta_2[\text{OH}^-]^2)$ for some divalent metals as a
383 function of the aqueous phase pH in the Hmimesq⁺ system. Initial HmimesqCl
384 concentration in the [bmim][PF₆] phase was 1×10^{-3} mol dm⁻³. The broken line, with a
385 slope of 2, was obtained by a least squares fitting. Sample; (\blacklozenge) Co²⁺, (\blacksquare) Cu²⁺, (\bullet)
386 Zn²⁺, (\blacktriangle) Cd²⁺.

387

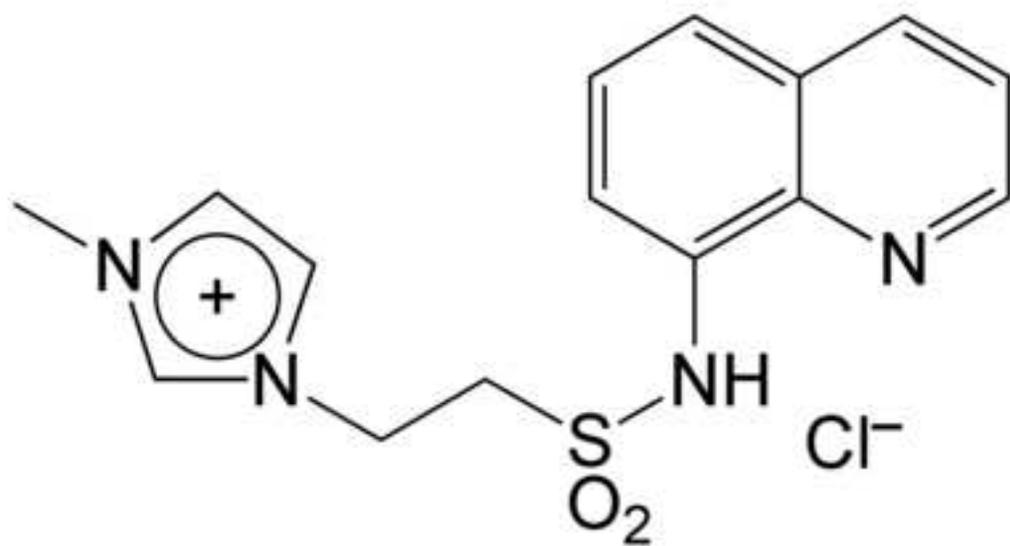
388 Fig. 6 Plots of the $\log D(1 + \beta_1[\text{OH}^-] + \beta_2[\text{OH}^-]^2)$ for some divalent metals as a

389 function of logarithmic initial concentration of HmimesqCl in the extraction phase.
390 Equilibrated aqueous phase pH was 4.1 (Co^{2+}), 2.6 (Cu^{2+}), 5.0 (Zn^{2+}) and 6.2 (Cd^{2+}).
391 The broken line, with a slope of 2, was obtained by a least squares fitting. Sample: (a)
392 Co^{2+} , (b) Cu^{2+} , (c) Zn^{2+} , (d) Cd^{2+} .
393
394 Table 1 Determined $\log K_{\text{ex}}$ values for the divalent metal cations in the [bmim][PF₆]
395 phase for each of the Hmimesq⁺, Hesq and Htsq systems (25±1 °C)

Table 1 Determined $\log K_{\text{ex}}$ values for the divalent metal cations in the [bmim][PF₆] phase for each of the Hmimesq⁺, Hesq and Htsq systems (25±1 °C)

Cation	Extraction reagent		
	Hmimesq ⁺	Hesq	Htsq [45]
Co ²⁺	-6.12±0.11	-7.95±0.26	-7.54±0.18
Cu ²⁺	1.33±0.13	-0.07±0.12	0.83±0.14
Zn ²⁺	-3.81±0.04	-5.12±0.13	-4.35±0.12
Cd ²⁺	-6.07±0.02	-8.34±0.02	-6.84±0.03

(a)



(b)

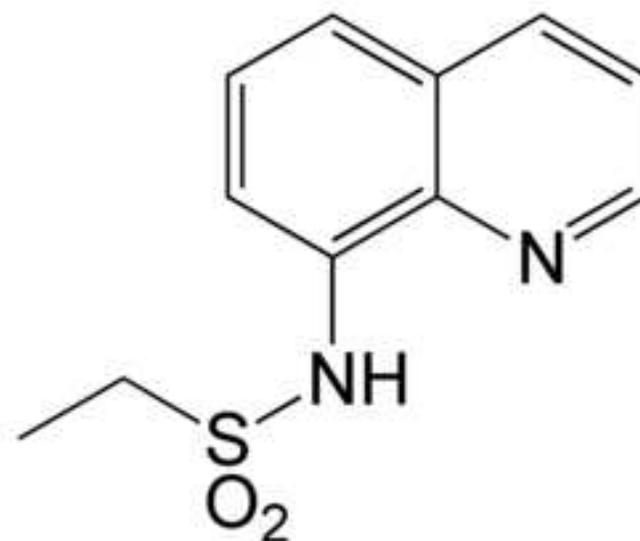


Figure 2
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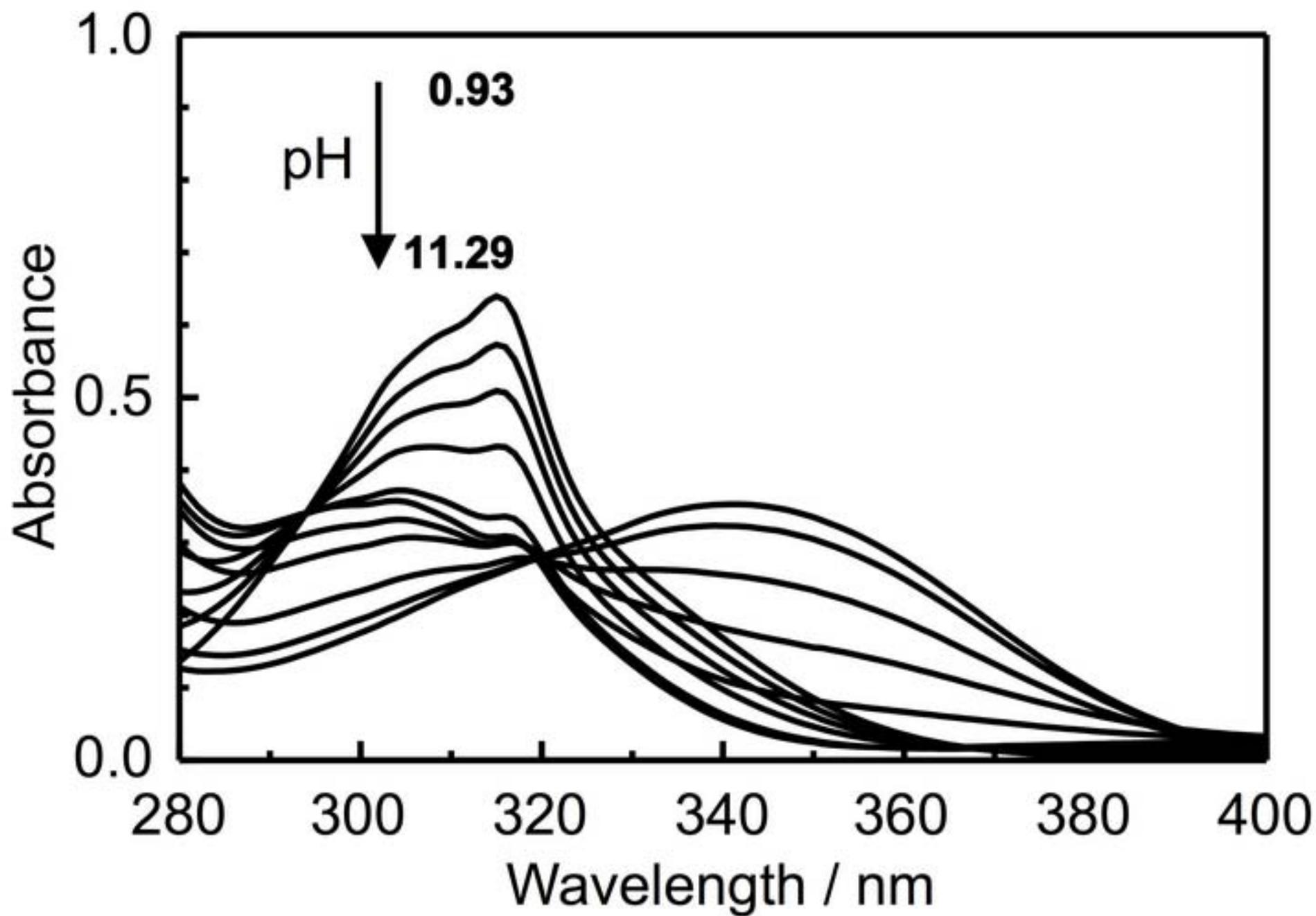


Figure 3
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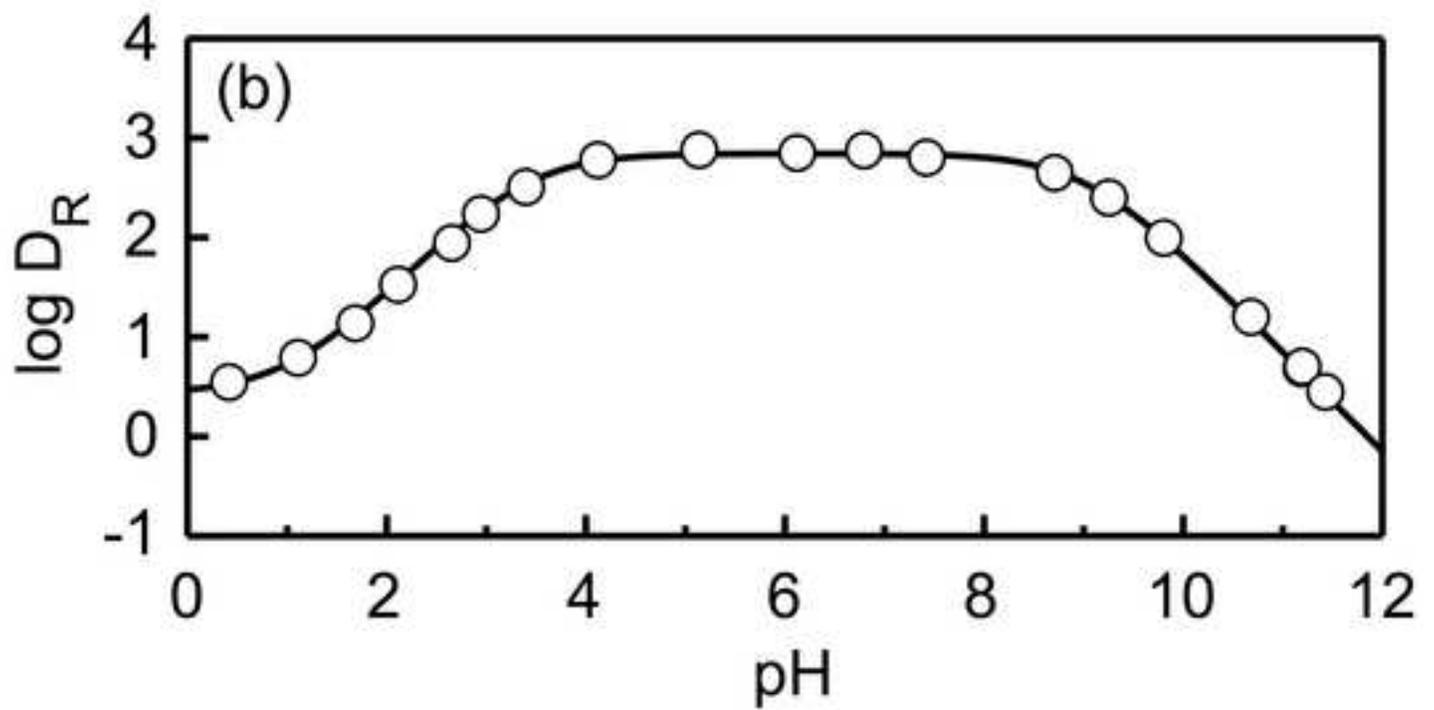
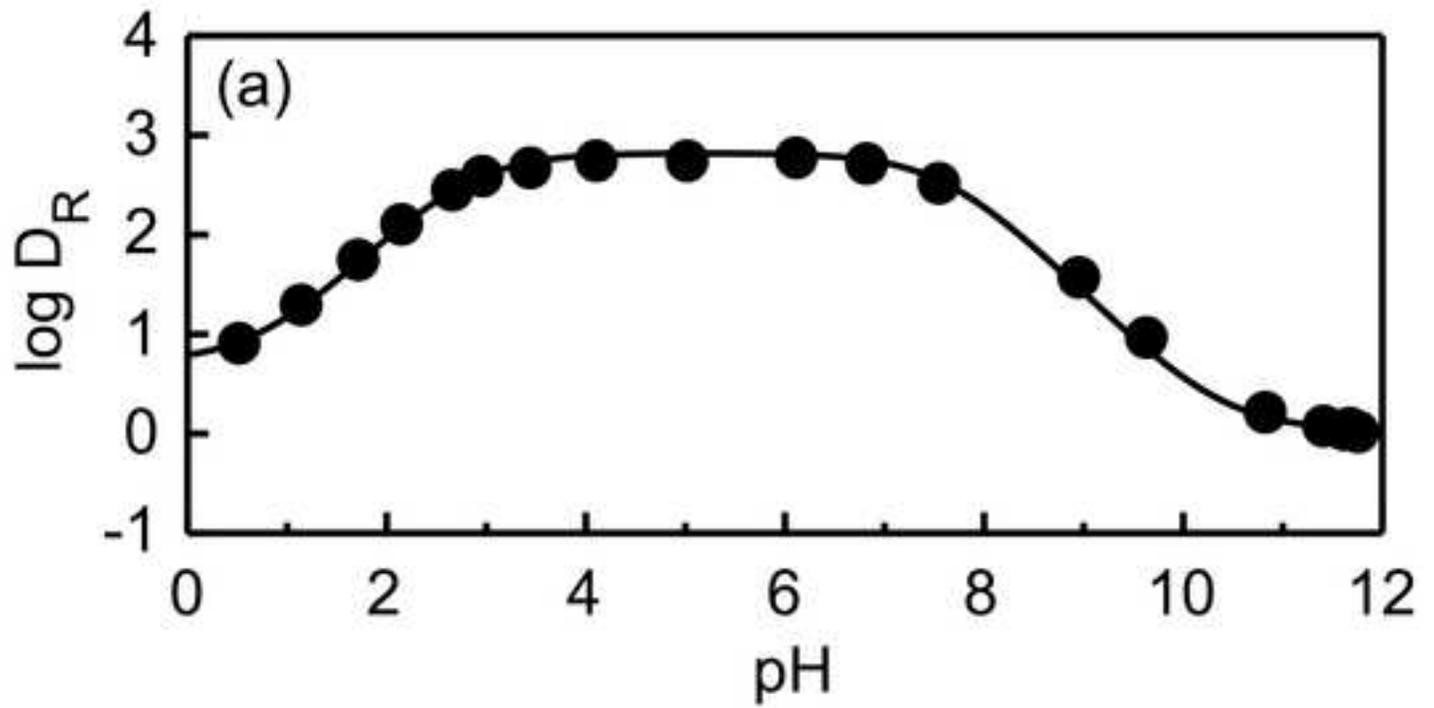


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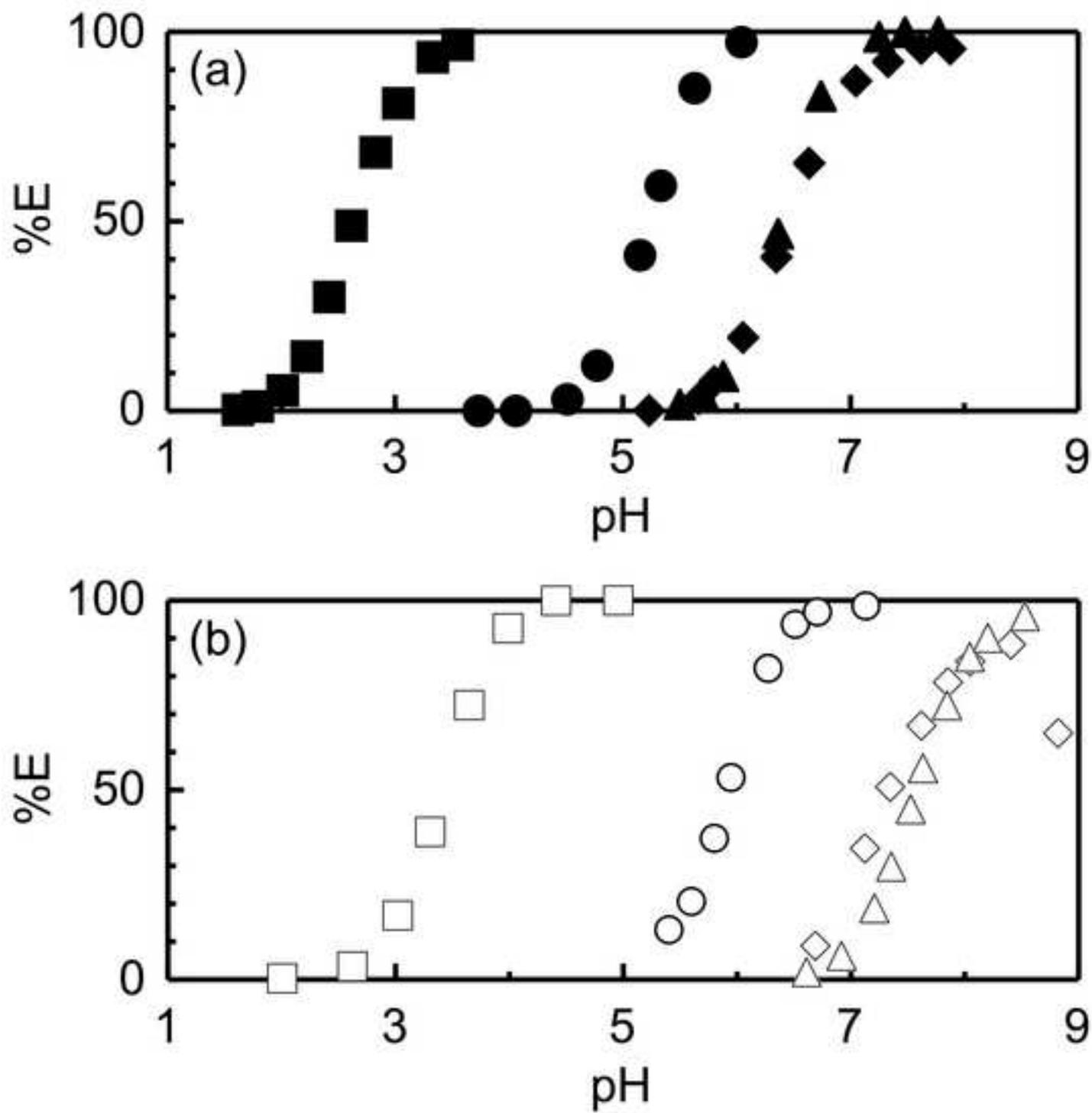


Figure 5
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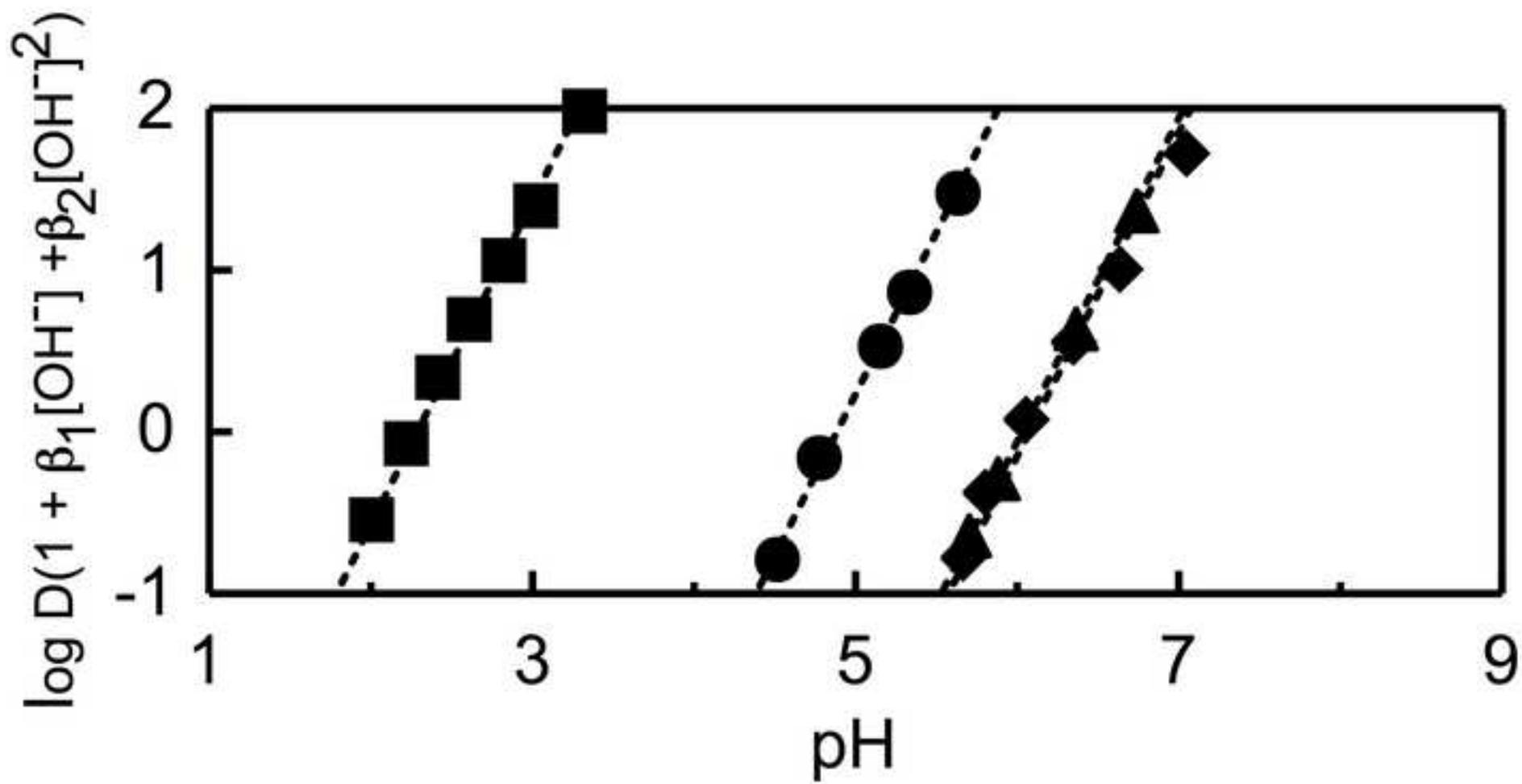


Figure 6
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