

## Evaluation of Zirconium(IV) Complex with *N*-Dodecyliminodiacetate as an Anionophore for Ion-Selective Electrodes

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The chemistry of anion recognition is now being uncovered and producing a variety of practical applications, including separation and sensing.<sup>1-3</sup> The use of Lewis acid-base interactions is a promising approach in this respect. We previously found that zirconium(IV) could be immobilized on a chelating polymer, having an iminodiacetate (IDA) group (-LH<sub>2</sub>), as a 1:1 complex of [(-L)Zr(OH)<sub>2</sub>].<sup>4,5</sup> This polymer complex shows both exchange and addition reactions with anions, which can be applied to the selective adsorption of fluoride and the chromatographic separation of anions.<sup>5,6</sup>

In this work, we studied whether such specificity of Zr(IV) could be utilized for potentiometric sensing of anions. A lipophilic derivative of IDA, *N*-dodecyliminodiacetic acid (H<sub>2</sub>dida), was adopted to introduce a Zr(IV) center in the membrane phase, and the performance of its Zr(IV) complex, Zr(dida)Cl<sub>2</sub>, was studied.

### Experimental

#### Reagents

A lipophilic chelating ligand of H<sub>2</sub>dida was synthesized by the controlled addition of NaOH to a mixture of dodecylamine with chloroacetic acid in an aqueous tetrahydrofuran solution. A crude precipitate obtained by acidification was recrystallized from a large volume of water. Yield: 87%; mp 132 - 133°C; <sup>1</sup>H NMR(D<sub>2</sub>O, KOD) δ = 0.7 - 1.0 (t, 3H, CH<sub>3</sub>), 1.0 - 1.5 (m, 20H, (CH<sub>2</sub>)<sub>10</sub>), 2.3 - 2.6 (b, 2H, CH<sub>2</sub>-CH<sub>2</sub>-N=), 3.0 - 3.2 (m, 4H, =N-CH<sub>2</sub>-COO<sup>-</sup>); MS (SIMS) *m/z* 301 (M<sup>+</sup>). Strong IR absorption at 1710, 1480, 1440, and 1200 cm<sup>-1</sup> indicated dimerization in a solid. This compound was not sufficiently soluble in any solvent, except for 1-butanol, which showed an appreciable solubility.

A 1:1 complex, [Zr(dida)Cl<sub>2</sub>] (**1**), was prepared by the reaction of zirconium tetrachloride (230 mg, 1.0 mmol) and H<sub>2</sub>dida (300 mg, 1.0 mmol) in dehydrated 1-butanol under reflux for 40 h; the evolution of HCl gas was confirmed. IR absorption characteristic of the dimeric acid disappeared by complexation, and only two bands at 1630 and 1400 cm<sup>-1</sup> remained. This complex could not be purified, because of the absence of a suitable solvent for recrystallization. Calcd. for ZrC<sub>16</sub>H<sub>29</sub>NO<sub>4</sub>Cl<sub>2</sub>·C<sub>4</sub>H<sub>9</sub>OH·2H<sub>2</sub>O: Zr, 16.0; C, 42.0; H, 7.6; N, 2.5; H<sub>2</sub>O, 6.3%. Found: Zr (ICP-AES), 16.3; C, 41.4; H, 7.7; N,

2.7; H<sub>2</sub>O (Karl-Fischer titration), 6.2%.

#### Measurement

A polymeric membrane consisting of 1% ionophore, 66% *o*-NPOE, and 33% PVC by weight was subjected to the measurement. Another membrane, containing 30 mol% sodium tetraphenylborate (NaTPB) relative to the ionophore in addition to these three components, was also used to examine the effects of an additive salt. The electromotive force of the cell, Ag/AgCl | KCl(satd) || test solution | membrane | internal solution | Ag/AgCl, was measured at 25 ± 0.1°C. The selectivity coefficients, with salicylate (Hsal<sup>-</sup>) as a primary species, were determined by a separate solution method at a fixed concentration of 10<sup>-2</sup> mol dm<sup>-3</sup> at pH 2. With regard to anions involved in acid-base equilibria, an apparent coefficient against the total concentration (*k'*<sub>sal,X</sub>) as well as a conventional coefficient against the concentration of the relevant species (*k*<sub>sal,X</sub>) was calculated from a practical point of view.

### Results and Discussion

#### pH response

The anionophore **1** showed a sub-Nernstian response to the pH (42 mV/pH) over a pH range of 2 - 10 (○ in Fig. 1). It is well known that lipophilic organic amines as a neutral carrier

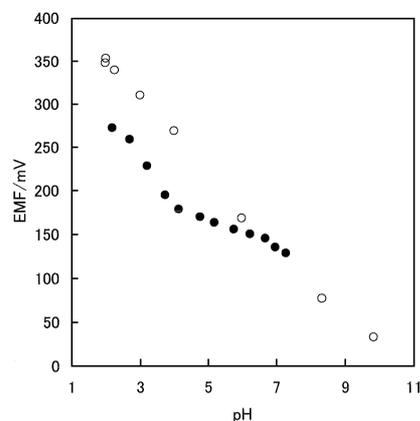


Fig. 1 Effects of pH on the potential response of ISE based on **1**. Total concentration of salicylate/mol dm<sup>-3</sup>: 0 (○), 10<sup>-3</sup> (●).

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Table 1 Potentiometric selectivity coefficients

Anion	[Zr(dida)Cl <sub>2</sub> ]		[Zr(dida)Cl <sub>2</sub> ], NaTPB (30 mol%)		TDDMACl	
	log $k'_{\text{sal},X}$	log $k_{\text{sal},X}$	log $k'_{\text{sal},X}$	log $k_{\text{sal},X}$	log $k'_{\text{sal},X}$	log $k_{\text{sal},X}$
Salicylate	0.00	0.00	0.00	0.00	0.00	0.00
Benzoate	-0.46	0.54	-2.25	-1.20	-1.07	-0.07
ClO <sub>4</sub> <sup>-</sup>	-1.24	-2.30	-3.73	-4.44	3.48	3.81
SCN <sup>-</sup>	-1.36	-2.42	-3.44	-4.16	2.64	1.97
F <sup>-</sup>	-2.40	-2.37	-3.64	-3.49	-1.43	-1.43
H <sub>2</sub> PO <sub>3</sub> <sup>-</sup>	-2.45	-3.44	-3.75	-4.39	-1.33	-2.02
Phthalate	-2.82	-2.84	-4.18	-4.26	1.74	1.70
Br <sup>-</sup>	-2.85	-3.90	-3.92	-4.63	0.38	-0.29
HSO <sub>3</sub> <sup>-</sup>	-2.87	-3.63	-3.50	-4.05	-1.67	-2.25
Malate	-3.02	-2.54	-3.73	-3.33	-1.67	-1.28
NO <sub>3</sub> <sup>-</sup>	-3.02	-4.08	-3.57	-4.28	1.57	0.90
Cl <sup>-</sup>	-3.07	-4.13	-4.20	-4.91	-0.34	-1.02
Acetate	-3.13	-1.45	-4.53	-2.88	-1.44	0.21
HSO <sub>4</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	-3.13	-3.92	-4.33	-4.92	-1.21	-1.80
Tartrate	-3.19	-3.15	-3.86	-3.84	-1.90	-1.90
Oxalate	-3.25	-4.17	-3.72	-4.35	-1.04	-1.70
Succinate	-3.50	-2.38	-3.60	-2.42	-1.29	-0.16
Citrate	-3.70	-3.67	-5.13	-5.08	-0.88	-0.78
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-3.71	-5.33	-4.71	-6.23	-2.11	-3.63
Fumarate	-3.75	-3.68	-3.34	-3.26	-0.65	-0.58

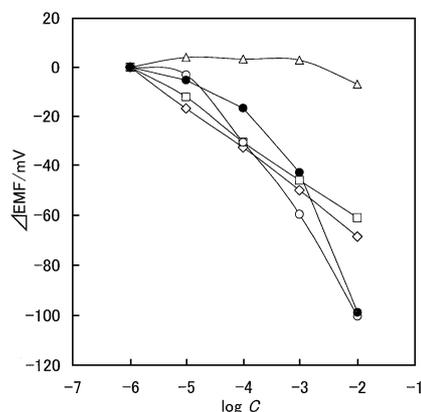


Fig. 2 Potential response of ISE based on **1** to selected anions. pH 4.0. Anion: salicylate (○, ●), ClO<sub>4</sub><sup>-</sup> (◇), SCN<sup>-</sup> (□), Cl<sup>-</sup> (△). NaTPB/mol%: 0 (○, ◇, □, △), 30 (●).

show a Nernstian pH response, which is ascribed to protonation to a nitrogen atom and coextraction of a counter anion.<sup>7</sup> Some metal-porphyrin complexes also show a sub-Nernstian response, which is ascribed to the substitution reaction of an anion on the metal center with hydroxide ion.<sup>8,9</sup> This might be the case in the present system.

A lower pH is preferable for examining the response to anions, due to less interference from OH<sup>-</sup>.

#### Response to anions

Potential responses of the ISE based on **1** to selected anions at pH 4 (0.1 mol dm<sup>-3</sup> CH<sub>3</sub>COOH/CH<sub>3</sub>COONa) are shown by the open symbols in Fig. 2. The ISE showed practically no response to common inorganic anions, such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, and only weak response to lipophilic anions, such as SCN<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> (15 mV/decade at a concentration >10<sup>-6</sup> mol dm<sup>-3</sup>). In contrast, a more pronounced response was found for salicylate (43 mV/decade at a concentration >10<sup>-5</sup> mol dm<sup>-3</sup>).

With salicylate as a primary species, the selectivity coefficients of ISEs based on **1** and tridodecylmethylammonium chloride (TDDMACl) against some interfering anions (X) at pH 2 (0.1 mol dm<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>) are summarized in Table 1. The ISE based on **1** has an appreciable selectivity to salicylate against inorganic anions, aliphatic carboxylate and even benzoate.

The reaction of salicylate with **1** in 1-butanol was spectrophotometrically studied; the absorption maxima of salicylate, 230 and 297 nm, were shifted to 235 and 305 nm, respectively (Fig. 3a). The molar-ratio method indicated a reaction stoichiometry of **1**:sal<sup>-</sup> = 1:1 (Fig. 3b). High affinities of Zr(IV) to *o*-OH carboxylates, which have also been observed in the chromatographic systems,<sup>6</sup> is responsible for this selectivity. Although the precise structure of the resulting complex is useful for a further development of this type of ISEs, it is beyond the scope of this study.

The effects of pH on the response to salicylate at 10<sup>-3</sup> mol dm<sup>-3</sup> are shown by the closed symbols in Fig. 1. A higher pH increased a fraction of the responsive species of Hsal<sup>-</sup> and a negative potential response by salicylate, while increasing the interference by OH<sup>-</sup>. Thus, the largest potential difference from the blank was obtained at pH 4.

#### Effects of NaTPB

The addition of 30 mol% NaTPB deteriorated the detection limit (from 10<sup>-6</sup> to 10<sup>-5</sup> mol dm<sup>-3</sup>), while improving the potential slope to salicylate (from 43 to 55 mV/decade), as shown by the closed symbols in Fig. 2. The selectivity to salicylate, on the other hand, was enhanced against all interfering anions; especially by more than two orders of magnitude for SCN<sup>-</sup> and ClO<sub>4</sub><sup>-</sup>. These are ascribed to the exclusion of an ion-pair extraction mechanism, which, together with a Lewis acid-base reaction mechanism, contributes to the potential response of the additive-free electrode based on **1**.

Although zirconium(IV) was found to be an attractive recognition site for anions, the response was not large enough to use H<sub>2</sub>dida as a derivatizing reagent. The complexes with

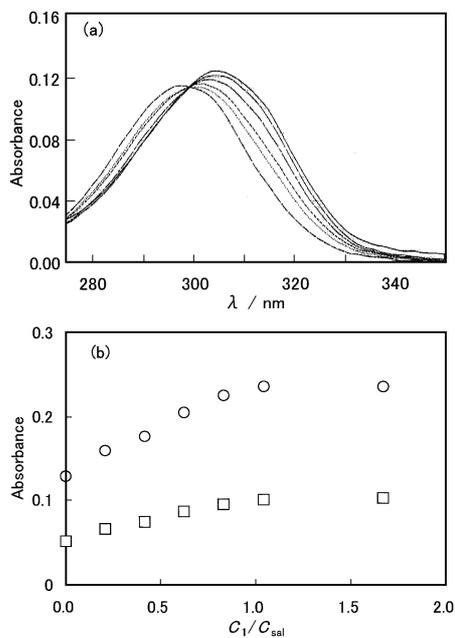


Fig. 3 UV spectral change by the reaction of salicylate with **1** (a) and a molar-ratio plot (b).  $C_1 = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Molar ratio: 0, 0.21, 0.42, 0.63, 0.83, 1.04, 1.67. Wavelength/nm:  $\circ$ , 240;  $\square$ , 315.

alternative ligands of porphyrins are now under systematic investigation in this laboratory.

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