

Evaluation of Complex Formation of Bis(12-crown-4)s with Sodium  
Picrate in Solution by  $^{23}\text{Na}$  NMR Spectroscopy

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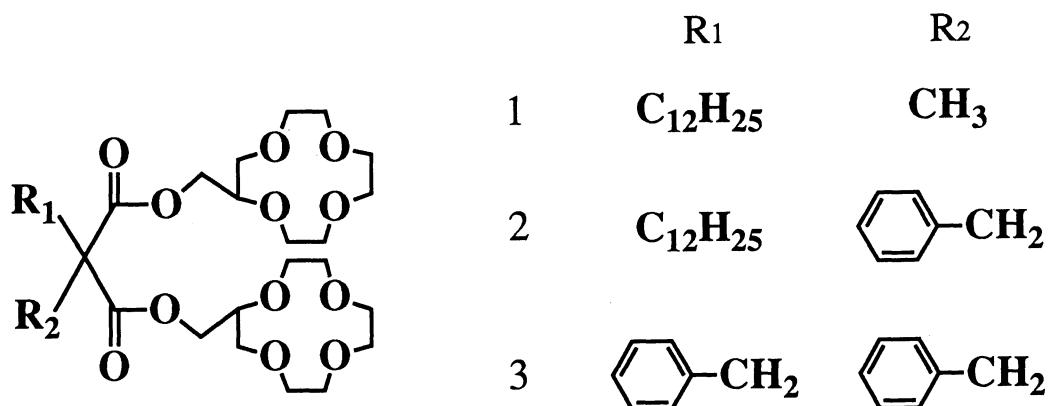
The complex formation of malonate-type bis(12-crown-4)s with sodium picrate was studied by  $^{23}\text{Na}$  NMR. The dependence of the  $^{23}\text{Na}$  NMR signals on the molar ratio [bis(12-crown-4)]/[Na<sup>+</sup>] is quite different from that on a molar ratio [monocyclic 12-crown-4]/[Na<sup>+</sup>], indicating the stable sandwich-type complex formation for the bis(12-crown-4)s.

Bis(crown ether)s have shown higher electrochemical selectivities for each alkali-metal cation than corresponding monocyclic analogs, when used as the neutral carriers for ion-selective electrodes.<sup>1-4)</sup> The Na<sup>+</sup>-selective electrode based on dodecylmethylmalonate of bis(12-crown-4), for instance, can be used for practical purposes such as the determination of Na<sup>+</sup> in serum, urine and seawater, because of its good reproducibility and short response time in addition to its high selectivity to Na<sup>+</sup>.<sup>5)</sup>

NMR of alkali-metal cations is a powerful tool for investigating their complexation with crown ethers in solution. To our knowledge, these NMR studies have focused on monocyclic crown ethers.<sup>6)</sup>

In this communication, we describe the complex formation between malonate-type bis(12-crown-4)s and sodium picrate in nitromethane.

NMR spectra were obtained at 105.6 MHz on a JEOL JNM-GSX-400 spectrometer (Osaka University) at 26 °C. A 0.1 mol dm<sup>-3</sup> aqueous NaCl solution was used as an external reference and the downfield shift from the reference is designated as positive. The concentration of sodium picrate was kept constant at 3.3 × 10<sup>-3</sup> mol dm<sup>-3</sup> in CH<sub>3</sub>NO<sub>2</sub> containing 10% CD<sub>3</sub>NO<sub>2</sub> for field locking. Bis(12-crown-4)s, 1, 2, and 3, were prepared by reaction of hydroxymethyl-12-crown-4<sup>7)</sup> with corresponding dicarboxylic



chlorides.<sup>5)</sup> Other chemicals were obtained from Wako or Aldrich.

$^{23}\text{Na}$  chemical shift of sodium picrate in the presence of monocyclic 12-crown-4 was measured as a function of the molar ratio [12-crown-4]/[ $\text{Na}^+$ ] ( $\rho$ ) at 26 °C in  $\text{CH}_3\text{NO}_2$  (Fig. 1). Only one broad  $^{23}\text{Na}$  signal was obtained in this case. The chemical shift to the downfield as  $\rho$  increased reached a limiting value at  $\rho$  larger than ca. 2. This suggests the formation of a 2:1 (12-crown-4: $\text{Na}^+$ ) complex.

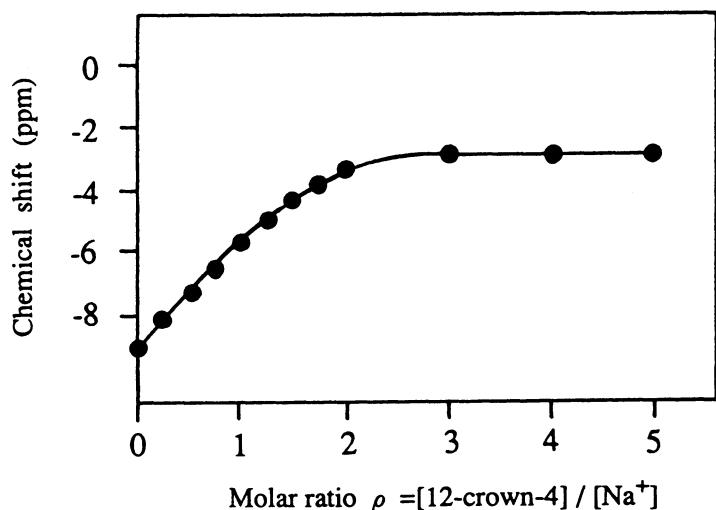


Fig. 1.  $^{23}\text{Na}$  chemical shift vs. molar ratio  $\rho$  in  $\text{CH}_3\text{NO}_2$  at 26 °C.

On the other hand, in the case of bis(12-crown-4), 1, two broad signals were observed in the range of [1]/[ $\text{Na}^+$ ] molar ratio  $\rho=0.23-0.93$  at 26 °C. The high-field signal decreased with increase of  $\rho$  and disappeared at  $\rho$  above 1, as shown in Fig. 2. The high- and low-field signals are assigned to the solvated (free) and complexed  $\text{Na}^+$ , respectively. At 26

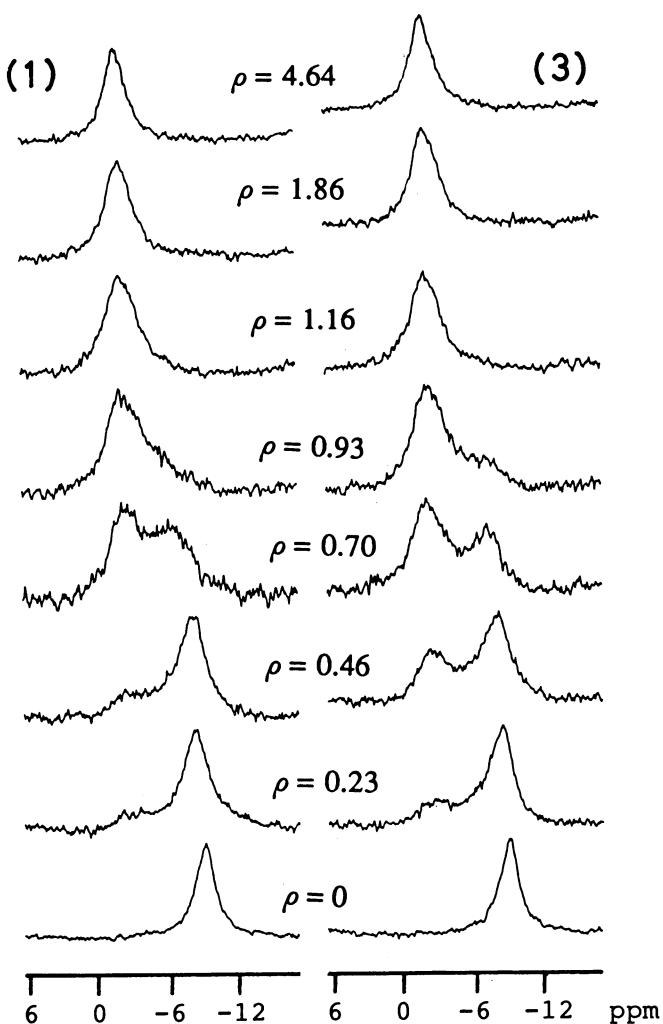


Fig. 2.  $^{23}\text{Na}$  NMR spectra of sodium picrate in the presence of bis(12-crown-4), (1) 1 and (3) 3, at different  $\rho$  values in  $\text{CH}_3\text{NO}_2$  at  $26^\circ\text{C}$ .

$^\circ\text{C}$ , the exchange between the two  $\text{Na}^+$  sites is slow by the NMR time scale. This situation is quite different from that of monocyclic 12-crown-4. This is convincingly interpreted as follows. The bis(12-crown-4), 1, can form a three-dimensional, rigid cavity consisting of the two crown units in its molecule.  $\text{Na}^+$  is strongly included into the cavity, and the stable intramolecular sandwich-type complex is formed. Consequently, the exchange is slow, and the two signals are obtained.

In the case of bis(12-crown-4), 3, the distinction of two  $^{23}\text{Na}$  signals is clearer, compared with that for 1. This may be attributed to the rigidity difference between 1 and 3, i.e., CPK molecular model considerations suggested that 1 is more flexible than 3 having the bulkier

benzyl substituents. Therefore,  $\text{Na}^+$  is complexed more strongly with 3.

The effect of the substituent bulkiness is also reflected in selectivity coefficients,  $K_{\text{NaM}}^{\text{Pot}}$ , for alkali metal ions measured with PVC membrane electrodes based on the bis(12-crown-4)s, i.e., carrier, 5 mg; PVC, 50 mg; o-nitrophenyl octyl ether, 125 mg; sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate, 1 mg. As shown in Fig. 3, the introduction of a bulky benzyl group brought about decrease in the selectivity coefficients (increase in selectivity). The compound 3 gave the most  $\text{Na}^+$ -selective electrode among the three bis(12-crown-4)s. This is ascribed to the enhanced tight fit of  $\text{Na}^+$  into the cavity of 3 due to its rigidity mentioned above.

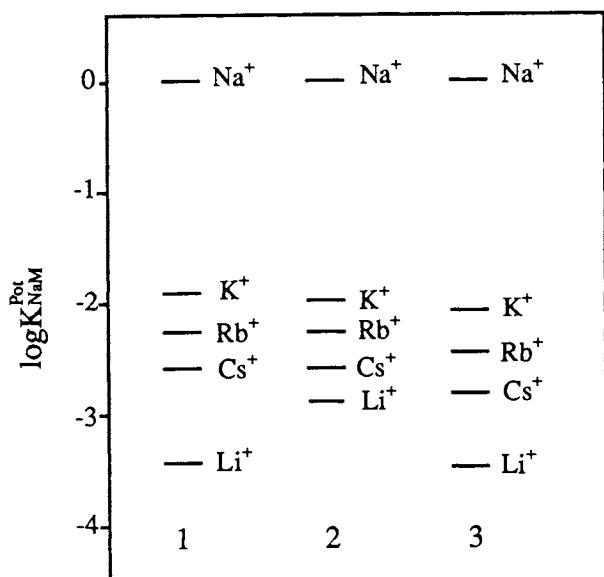


Fig. 3. Selectivity coefficients for alkali metal ions of electrodes based on bis-(12-crown-4)s.

#### References

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