

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

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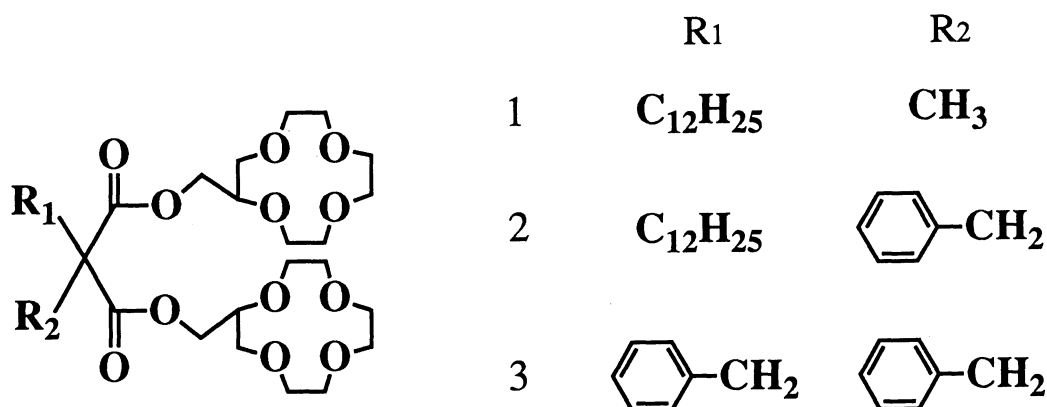
The complex formation of malonate-type bis(12-crown-4)s with sodium picrate was studied by ^{23}Na NMR. The dependence of the ^{23}Na NMR signals on the molar ratio $[\text{bis}(12\text{-crown-4})]/[\text{Na}^+]$ is quite different from that on a molar ratio $[\text{monocyclic } 12\text{-crown-4}]/[\text{Na}^+]$, 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.¹⁻⁴⁾ The Na^+ -selective electrode based on dodecylmethylmalonate of bis(12-crown-4), for instance, can be used for practical purposes such as the determination of Na^+ in serum, urine and seawater, because of its good reproducibility and short response time in addition to its high selectivity to Na^+ .⁵⁾

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.⁶⁾

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⁻³ 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^{-3} mol dm⁻³ in CH_3NO_2 containing 10% CD_3NO_2 for field locking. Bis(12-crown-4)s, 1, 2, and 3, were prepared by reaction of hydroxymethyl-12-crown-4⁷⁾ with corresponding dicarboxylic



chlorides.⁵⁾ Other chemicals were obtained from Wako or Aldrich.

²³Na 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]/[Na⁺] (ρ) at 26 °C in CH₃NO₂ (Fig. 1). Only one broad ²³Na signal was obtained in this case. The chemical shift to the downfield as ρ increased reached a limiting value at ρ larger than ca. 2. This suggests the formation of a 2:1 (12-crown-4:Na⁺) complex.

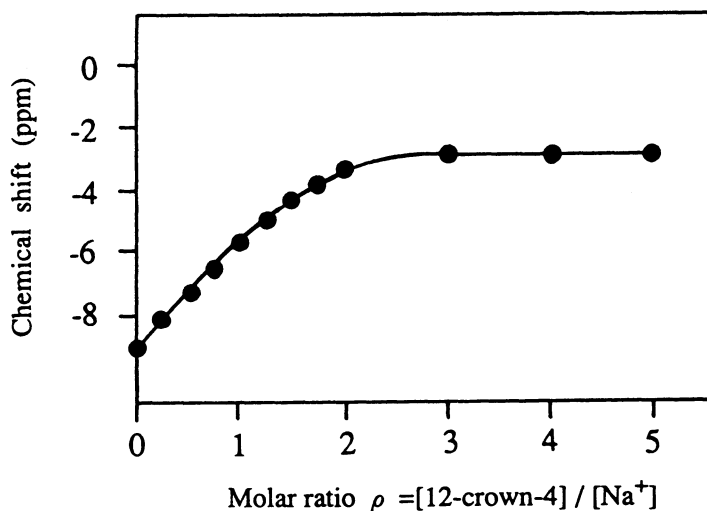


Fig. 1. ²³Na chemical shift vs. molar ratio ρ in CH₃NO₂ at 26 °C.

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

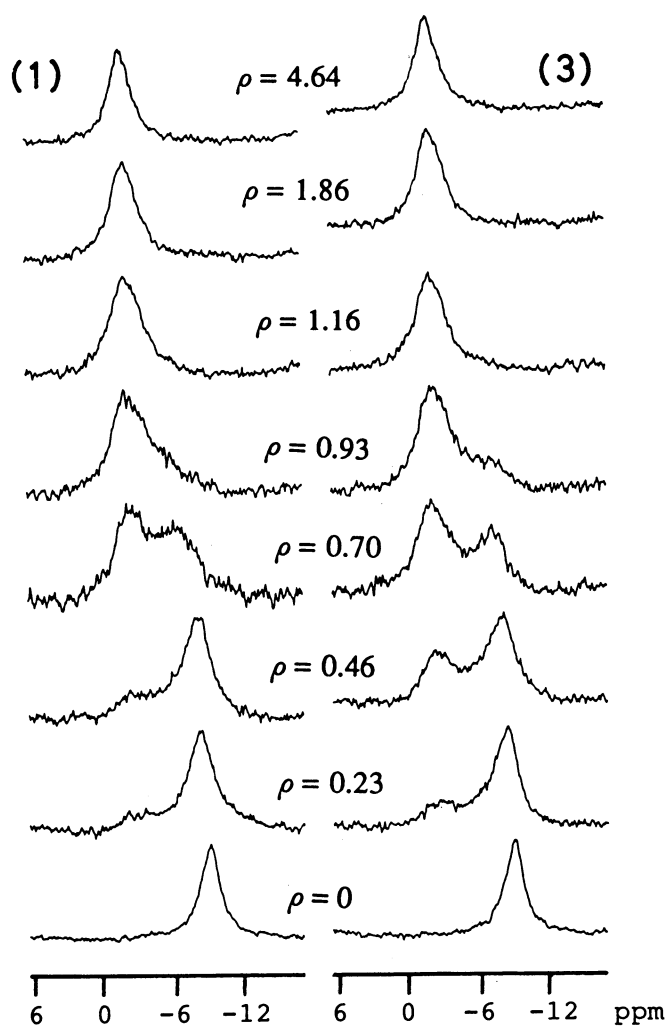


Fig. 2. ^{23}Na NMR spectra of sodium picrate in the presence of bis(12-crown-4), (1) **1** and (3) **3**, at different ρ values in CH_3NO_2 at 26 $^\circ\text{C}$.

$^\circ\text{C}$, the exchange between the two 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. 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}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, 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 Na^+ -selective electrode among the three bis(12-crown-4)s. This is ascribed to the enhanced tight fit of Na^+ into the cavity of 3 due to its rigidity mentioned above.

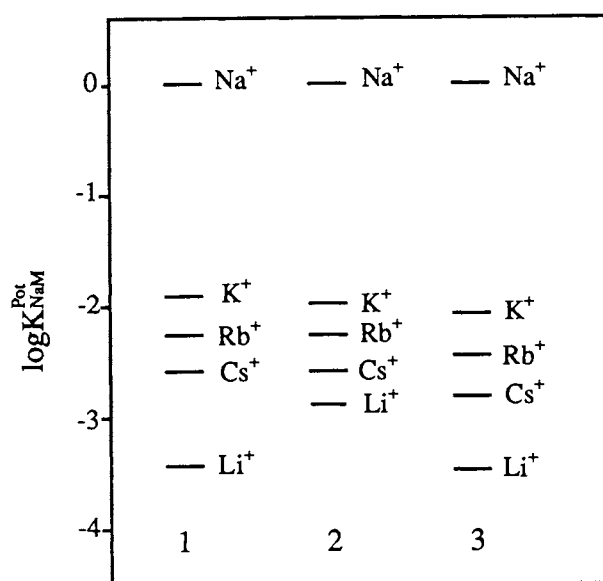


Fig. 3. Selectivity coefficients for alkali metal ions of electrodes based on bis-(12-crown-4)s.

References

- 1) H. Tamura, K. Kumami, K. Kimura, and T. Shono, *Mikrochim. Acta*, **1983**, 287.
- 2) K. Kimura, A. Ishikawa, H. Tamura, T. Shono, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 447.
- 3) K. Kimura, H. Oishi, H. Sakamoto, and T. Shono, *Nippon Kagaku Kaishi*, **1987**, 277.
- 4) G. J. Moody, B. B. Saad, and J. D. R. Thomas, *Analyst*, **114**, 15 (1989).
- 5) T. Shono, M. Okahara, I. Ikeda, K. Kimura, and H. Tamura, *J. Electroanal. Chem.*, **132**, 99 (1982).
- 6) H. P. Graves and C. Detellier, *J. Am. Chem. Soc.*, **110**, 6019 (1988), and references cited therein.
- 7) I. Ikeda, S. Yamamura, Y. Nakatsuji, and M. Okahara, *J. Org. Chem.*, **45**, 5355 (1980).

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