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2,4,6-Trisubstituted Phenols as Cooperative Carriers in Crown-ether Mediated Extraction and Transport of Cations

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Trisubstituted phenols having two bulky groups at 2,6-position and pKa value below 7 proved to be good cooperative carriers in solvent extraction and liquid membrane transport of alkali-metal cations with crown ethers.

Cation transport through a bulk liquid membrane containing crown ethers has been extensively studied. The influence of the structure of crown ethers on the transport rate and selectivity has been reported in detail for the cation transport.[1,2] However, only a little attention has been given to the effect of the cooperative carriers: counter anions, although they were shown to be very important in these systems.[3,4] For inorganic anions, it was found that the anions with smaller Gibbs free energies of hydration allowed faster cation transport.[5] Anions of weak organic acids are considered to become promising cooperative carriers by adjusting their lipophilicity and acidity, as shown in the selective cation transport by the system composed of higher alkanoic acids and crown ethers,[6] but there is little study on the relationship between the structural factors of organic anions and their capability as a cooperative carrier. This paper deals with the interesting behavior of several 2,4,6-trisubstituted phenols as cooperative carriers, and presents the importance of the environment around the anion-center arisen from the 2,6-substituent to the cation extraction and transport in addition to their acidity and lipophilicity.

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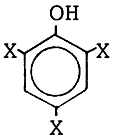
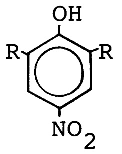
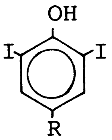


1a X = NO_2,
1b X = Cl,
1c X = Br,
1d X = I.



2a R = CH_3,
2b R = $CH(CH_3)_2$,
2c R = $C(CH_3)_3$.



3a R = CH_2CH_3,
3b R = $(CH_2)_6CH_3$,
3c R = $(CH_2)_{17}CH_3$.

Compounds **1a-1d** are commercially available. **2a-2c** were obtained by treating 2,6-dialkylphenols with $NaNO_3$ and HCl in an ether-water system in the presence of 0.1 equiv. of $La(NO_3)_3$.[7] **3a-3c** were prepared by iodination of 4-alkylphenols with iodine-morpholine complex in THF.[8] The products were purified by recrystallization from methanol and their structures were confirmed with ^{1}H-NMR, IR spectra, and elemental analysis. The acidic constant pKa was determined by spectrometric titration in 20% dioxane aqueous solution(w/w) at 25 °C.[9] The solvent extraction was carried out as published method,[10] CH_2Cl_2 = H_2O = 10 ml, 25 °C; Aqueous phase: [MOH] = 0.01 M (1 M = 1 mol dm^{-3}), [HA] = 7.0×10^{-5} M (HA: **1a-1d, 2a-2c,** and **3a-3c**); Organic phase: [Benzo-18-crown-6] = 3.5×10^{-4} M. After stirring for 40 min, [HA] and [A^-] in organic phase were determined from UV spectra. Liquid membrane transport experiments were conducted using a vessel reported previously[11] under following conditions: Source phase: [MOH] = 0.01 M aqueous solution 24 ml; Membrane phase: [B18C6] = 7.0×10^{-4} M and [HA] = 1.0×10^{-3} M in 50 ml dichloromathane; Receiving phase: [HCl] = 0.01 M aqueous solution 12 ml. The cation concentration in receiving phase was determined by atomic absorption spectrophotometry after stirring(400 rpm) for 6 h at 25 °C. In Table 1 the percentage of A^- in organic phase represents the extractability of cations. And the lipophilicity of the phenols can be shown as the percentage of HA in organic phase(HA% in parenthesis) which markedly changed among the phenols examined. A similar distribution result of the phenols between the two phases was obtained from the experiment in the absence of the crown ethers.

The cooperative carriers give a large effect on both extraction and cation transport, and the more the cation is extracted, the faster the cation is transported. Although the extractability with these new cooperative carriers

Table 1. Effects of Cooperative Carriers on Extraction and Cation Transport

HA	pKa	A^-(HA) in Organic phase(%)		Cation transported($\times 10^3 M^{-1}$)		
		Na^+	K^+	Na^+	K^+	K^+/Na^+
1a	1.7	3.3(0)[a]	54.1(0)[a]	1.5	7.3	4.9
1b	6.4	-[b]	0(2.1)	-[b]	0.6	-[b]
1c	6.5	-[b]	0.9(4.8)	0.2	1.7	8.5
1d	6.6	1.7(3.3)	25.9(7.1)	0.5	8.4	17
2a	7.2	0.1(0.4)	1.3(0.5)	0.1	0.3	3.0
2b	7.1	0.3(25.7)	11.9(24.6)	0.3	1.5	5.0
2c	6.9	2.2(82.8)	26.5(65.7)	0.7	6.1	8.7
3a	7.8	0(54.0)	0(57.2)	-[b]	1.6	-[b]
3b	9.1[c]	0(100)	0(100)	0.1	2.2	22
3c	-[b]	-[b]	0(100)	-[b]	1.6	-[b]

a) HA and A^- for picric acid could not be distinguished in UV spectra, but the extraction experiment in the absence of the crown ether showed no HA and A^- exist in organic phase under the conditions.

b) Not determined. c) In 50% dioxane aqueous solution(w/w).

(**1b**-**1d**, **2a**-**2c**, and **3a**-**3c**) is smaller than that with picric acid(**1a**) which is widely used in extraction and cation transport,[12,13] two of them(**1d** and **2c**) make the cation transport more selective with a comparable rate. Triiodophenol (**1d**) and 4-nitro-2,6-di(t-butyl)phenol(**2c**) give much larger extractability and transport rate of the cation than those having smaller 2,6-substituents, though their acidity(pKa value) are very close. The enhancement may be partially explained by the increase in lipophilicity of the phenols as shown by Kuwamura et al. with an alkanoic acid-crown ether system.[6] However the dramatic increase in the extraction and transport with **1d** as compared to **1c** suggests that large 2,6-substituents can also affect the extraction and transport through a steric hindrance. The bulkiness of 2,6-substituents could be considered to give a dehydration effect around the phenolate oxygen resulting in the enhancement of K^+/Na^+ selectivity in the transport. Examination of more lipophilic cooperative carrier(**3a**-**3c**) shows that the acidity of these phenols is so low that a stable complex could not form in organic phase, but interestingly they can transport K^+ with the rate comparable to **1c** and **2b**.

In this case the phenolate anions in organic phase can be observed only under stirring conditions and they disappeared in several seconds when the stirring stopped.[14] However we can not explain this phenomenon now.

In conclusion, suitable acidity (pKa< 7), high lipophilicity, and a large steric hindrance for dehydration effect in the complex seem to be important factors in the choice of a good cooperative carrier for crown-ether mediated extraction and cation transport.

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14) UV spectra under the stirring conditions were determined by a multichannel spectrophotometer(Otsuka Electronics, MCPD-100) equipped with an immersion type quartz fiber probe coupled for incident and receive of beams.

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