

EFFECT OF PHENOL DERIVATIVE ON THE SELECTIVITY OF ORGANIC SULFONATE
SELECTIVE ELECTRODE

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The interference of inorganic anions such as perchlorate, thiocyanate, and iodide against p-toluenesulfonate selective electrode decreased remarkably by the addition of p-t-octylphenol in o-dichlorobenzene medium. After infrared investigations, this phenomenon was attributed to the presence of hydrogen bonding between p-t-octylphenol and p-toluenesulfonate.

In a previous paper, the authors developed a new type of electrode responsive to p-toluenesulfonate using organic compounds of high melting point solidified at room temperature as a solvent.¹⁾ Various electrodes responsive to such organic sulfonates have been reported.^{2,3,4)}

In the preparation of a liquid membrane electrode specific to an objective ion, usually is chosen a proper solvent which makes the interference of other ions as low as possible. However, the interference of the ions such as perchlorate, thiocyanate, and iodide whose hydration energy is small, is difficult to eliminate.

In the present work, it was shown that the interference was drastically decreased by the addition of phenol derivative in a solvent of liquid membrane.

In the experiment, ion exchanger was made of 0.05M trioctylmethyammonium p-toluenesulfonate salt prepared with Capriquat (trioctylmethyammonium chloride) in o-dichlorobenzene. The potential measurements were carried out by an Orion digital Ionalyzer (Model 601) connected to a National recorder (Model VP654A). The effect of the addition of 0.5M phenol derivative on the selectivity was examined.

Table 1
Selectivity coefficients
for p-toluenesulfonate
selective electrode

Ion	log K_{pTS-j}	
	A	B
ClO_4^-	2.3	-0.6
SCN^-	1.2	-0.3
$*C_{10}H_8SO_3^-$	1.1	0.8
BF_4^-	0.7	-1.5
I^-	0.6	-1.1
ClO_3^-	-0.2	-1.5
$C_6H_5SO_3^-$	-0.3	-0.5
NO_3^-	-0.4	-1.3
Br^-	-1.0	-1.5
BrO_3^-	-1.5	-2.0
Cl^-	-1.9	-1.8

*1-Naphthalenesulfonate
(A) without and (B) with
p-t-octylphenol

The selectivity coefficient, $\log K_{i-j}$ of interfering ions was obtained by the separate solution method; the electrode potential of 0.01M-objective ion and that of interfering ion were measured and the difference of these potentials was divided by the slope obtained from the calibration curve of objective ion. The results are shown in Table 1.

It is clear that by the addition of phenol derivative, the interference of inorganic ions such as perchlorate, thiocyanate, and iodide decreases extremely, as well as the order of selectivity coefficient varies among these inorganic ions.

In order to clarify the role of phenol in this phenomenon, the infrared spectra of p-t-octylphenol in o-dichlorobenzene were measured. The absorption band of OH group of the former at 3580 cm^{-1} shifted to 3180 cm^{-1} when trioctylmethylammonium p-toluenesulfonate was added. This shift can be attributed to the formation of hydrogen bonding between the phenol and sulfonate.⁵⁾ This interaction seems to make the electrode highly specific to organic sulfonate.

Further detailed investigations are now under way and will be presented elsewhere.

References

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