

Synthesis and Application of Hacddt Complex as A Neutral Carrier in Pvc Based ion Selective Electrodes for the Determination of Ions

Abstract

The use of Schiff base macrocyclic ligands and their metal complexes as carrier in ion-selective electrodes has been little known. The design of macrocyclic chemical structures capable of specific and effective molecular recognition of metal ions is of vital importance to broad areas of analytical chemistry and separation sciences. Selectivity of macrocyclic ligands in binding to metal ions can be finely tuned either by incorporating different soft and hard donor atoms in the chelating ring, or by modifying the flexibility properties of the macrocyclic structure. The 12-,14- and 16membered Schiff based macrocycles could prove to be a better option for the development of anionic/ cationic selective electrodes. Manganese complex of 1,2,5,6,8,11- hexaazacyclododeca- 7,12-dione-2,4,8,10-tetraene (HACDDT) used as an ion carrier in construction of acetate selective sensor exhibits high selectivity of acetate anion over other anions like nitrate and perchlorate ion. This electrode can be used for at least 9 months without any considerable divergence in its potential. It can be used as an indicator electrode in the potentiometric titration of silver ion.

Keywords: Hacddt, Glyoxal Bis Semicarbazone, Acetate Selective Sensor, Dibutyl Phthalate.

Introduction

Synthesis of Hacddt

(1,2,5,6,8,11-Hexaazacyclododeca-7,12-Dione-2,4,8,10-Tetraene)

In case of this ligand, first prepare intermediate product glyoxal-bis-semicarbazone, and the macrocycle is obtained when the intermediate product reacts with lithium hydroxide.

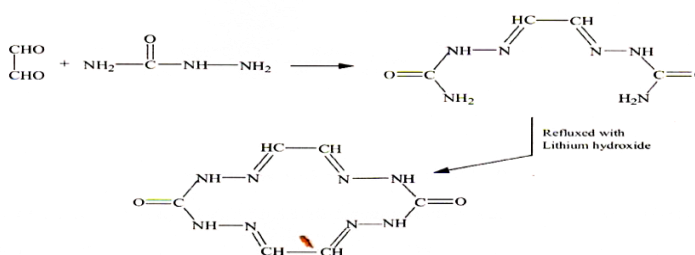
Synthesis of Intermediate Product (Glyoxal bis Semicarbazone)

An ethanolic (100 ml) solution of semicarbazide (0.04 mol, 4.44g) was added to an ethanolic (50 mL) solution of glyoxal (0.02 mol, 1.16g) in the presence of 2 mL of cone. HCl. All the reagents were added alternatively dropwise with stirring. The reaction mixture gives a homogeneous solution on reflux for about half an hour. After addition of all the reagents the mixture was refluxed for 5 hours along with mechanical stirring. On keeping it overnight, yellowish white coloured powdered solid was formed, which was filtered, washed with ethanol and dried in desiccator.

Yield: 60% ; Melting point: 255 °C. When ethanolic solution of this intermediate product glyoxal-bis-semicarbazone is reacted (refluxed) with equimolar solution LiOH, on cooling hexaazacyclo macrocyclic compound is obtained, which is filtered, washed with ethanol and dried in desiccator.

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Synthesis and Structure of HACDDT

Aim of the Study

acetate selective sensor constructed from manganese complex of HACDDT as an ion carrier represents high selectivity towards acetate ion over other ions.

Application of Hacddt

Manganese complex of 1,2,5,6,8,11-hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene (HACDDT) has been used as an ion-carrier in construction of ion-selective sensors for some common anions like nitrate, thiocyanate, iodide, salicylate, acetate, etc. The potential responses of these electrodes are shown in Figure 1. As can be seen, the membrane sensor displays selectivity for CH_3COO^- ions over other anions as a result of the selective interaction between the central metal ion and acetate ions. The preferential response towards CH_3COO^- is believed to be associated with the coordination of acetate with the central metal of the carrier resulting in an increase in size and axial coordination. It is well understood that the sensitivity and selectivity of the ion-selective electrode depend not only on the nature of the ion-carrier used, but also significantly on the membrane composition and the properties of solvent mediators and additive used. The potentiometric response curve of this acetate selective electrode exhibits stable potentiometric responses for acetate anions after conditioning for 2-3 days in 1.0×10^{-2} M NaCl solution.

The effect of the membrane composition, nature of solvent mediator and additive on the response characteristics of the acetate sensor are given in Table A. Since the nature of the plasticizers influences the dielectric property of the membrane phase and mobility of the ionophores in the PVC matrix, its selection is one of the most important tasks in designing a sensitive and

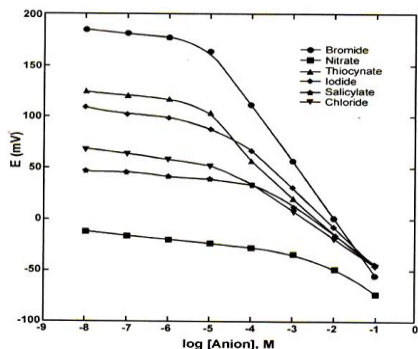
selective anion selective electrode. The responses of the acetate sensor based on HACDDT complex using three plasticizers having different polarities have been investigated. The plasticizers examined were DBP, DOS, BA and their nature significantly affected the sensor performance regarding slope, linear concentration range and detection limit (Figure 2). Among them DBP offered the best response to acetate anion with a slope of -55.0 mV/decade over a wide concentration range 2.5×10^{-5} to 1.0×10^{-1} M. the limit of detection was found to be 4.27×10^{-6} M. among the three different plasticizers used, the use of DBP (E 1) resulted in the best response characteristics, whereas the use of BA and DOS resulted in super-Nernstian slopes of the electrode response.

Table A shows that the optimum amount of ionophore HACDDT is 1.7 %. It is well known that the cationic additives improve the EMF response of the anion-selective electrode. The presence of HTAB in the membrane composition increases the sensitivity of the sensor. The electrode E1 with an optimum ratio of HTAB/ HACDDT of about 0.35 % revealed a Nernstian response to the concentration of acetate. By addition of more HTAB to the membrane composition, the selectivity of the electrode for the high lipophilic anions such as perchlorate and salicylate will increase by co-extraction of ion-pair formation between perchlorate or salicylate anions and hexacycltrimethyl -ammonium cation. Table 12 shows that the PVC membrane electrode with PVC: DBP: HACDDT: HTAB percent ratio of 31.4: 66.3: 1.7: 0.6 results in the near-Nernstian behaviour of the membrane electrode over a very wide concentration range.

COMPOSITION AND ELECTRODE CHARACTERISTICS OF ACETATE ION-SELECTIVE USING HACDDT AS AN IONOPHORE

ISEs No.	PVC ^z	Plasticizer ^z	Ionoph. ^z	Add ^z (HTAB)	Linear_range (M)	Slope (mV/dec)	Detection limit (M)
E1	31.4	66.3 (DBP)	1.7	0.6	1.0×10^{-1} – 2.5×10^{-5}	-55.02	4.26×10^{-6}
E2	32.4	65.3(DOS)	1.7	0.6	1.0×10^{-1} – 2.5×10^{-5}	-34.89	1.31×10^{-5}
E3	32.5	65.2 (BA)	1.7	0.6	1.0×10^{-1} – 1.0×10^{-4}	-25.30	4.07×10^{-5}
E4	32.8	65.6 (DBP)	1.0	0.6	1.0×10^{-1} – 2.5×10^{-5}	-36.31	1.04×10^{-4}
E5	32.6	65.4 (DBP)	1.4	0.6	1.0×10^{-1} – 2.5×10^{-5}	-46.14	3.38×10^{-5}
E6	32.4	65.1 (DBP)	2.0	0.6	1.0×10^{-1} – 2.5×10^{-5}	-69.69	2.51×10^{-5}
E7	33.1	65.4 (DBP)	1.5	—	1.0×10^{-2} – 2.5×10^{-5}	-29.40	1.38×10^{-5}
E8	32.7	65.4 (DBP)	1.6	0.3	1.0×10^{-1} – 1.0×10^{-5}	-35.90	8.51×10^{-6}
E9	32.5	65.0 (DBP)	1.6	0.9	1.0×10^{-1} – 1.0×10^{-4}	-82.11	4.78×10^{-5}

DBP: Dibutyl phthalate, DOS: Dioctyl sebacate, BA: Benzyl acetate; HACDDT: 1,2,5,6,8,11-hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene; HTAB: Hexadecyltri -methylammonium; Z: compositions % (w/w)



Potentiometric response curves for different anions with Mn^{2+} complex of HACDDT (HACDDT = ,2,5,6,8,11-Hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene) as an ionophore in CH_3COO^- selective electrode

Table-A & Fig.1

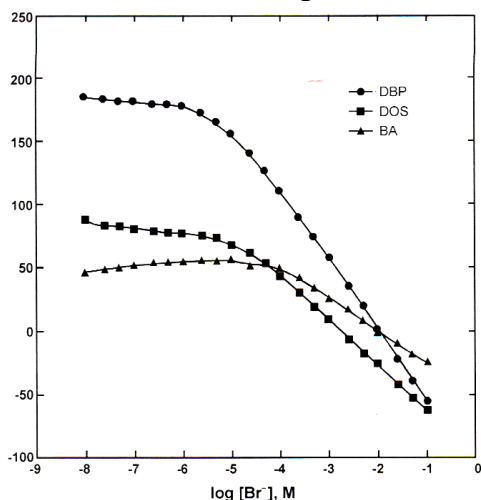


Figure 2 The curves showing the effect of different plasticizers
Potentiometric Selectivity Data for CH_3COO^- ISE (E1) Shown In Table B.

POTENTIOMETRIC SELECTIVITY DATA FOR CH_3COO^- ISE (E1)

Diverse ions	$K_{Cl,B}^{pot}$ (E1)	$\log K_{Cl,B}^{pot}$ (E1)
Chloride	3.16×10^{-3}	-2.50
Carbonate	4.57×10^{-4}	-3.34
Bicarbonate	2.63×10^{-3}	-2.58
Nitrite	6.02×10^{-3}	-2.22
Perchlorate	3.09×10^{-3}	-2.51
Nitrate	2.69×10^{-3}	-2.57
Salicylate	3.98×10^{-3}	-2.40
Sulphate	4.67×10^{-4}	-3.33
Fluoride	6.76×10^{-3}	-2.17
Bromide	7.76×10^{-1}	-0.11
Iodide	6.91×10^{-1}	-0.16
Thiocyanate	7.94×10^{-1}	-0.10

Conclusion

The proposed membrane acetate electrode was successfully used as an indicator electrode in potentiometric titration of acetate ion solution (20 mL, 0.01 M) with 0.01 M Mn^{2+} ion. Experiments were also conducted to measure the acetate anion concentration of the water sample containing a known concentration of acetate anion. Although the amount of acetate anion recovered was somewhat less than the added amount, the sensor electrode was confirmed to detect acetate anion very efficiently with 99 % recovery.

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