PROPERTIES OF METAL-CONTAINING ETHYLENE BISDITHIOCARBAMATE FUNGICIDES NABAM AND ZINEB IN ALKALINE SOLUTION

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ABSTRACT

Ethylene bisdithiocarbamate compounds (EBDCs) are difficult to study because they are normally used as divalent metallic complex that have low solubilities in water or organic solvents, such as zineb, maneb, mancozeb and propioneb. Since methods for the quantitative analysis of these compounds are limited, their residues in agricultural products as well as in the environment are difficult to monitor. In contrast to other compounds, the mono-valent metallic salt nabam is highly water-soluble. The present research was designed to study the metallic ion release from zineb (zinc ethylene bisdithiocarbamete, $C_4H_6N_2S_4Zn$) and nabam (disodium ethylene bisdithiocarbamate, $C_4H_6N_2S_4Na_2$), effect of NaOH concentration on zineb and nabam ionization, $EBDC^{2-}$ ion stability and $EBDC^{2-}$ detection at various pH settings. Also, A fast and simple method for high performance liquid chromatographic (HPLC) determination of nabam and zineb was developed using a Hypersil® strong anion exchanger (SAX) as column packing material. The SAX system uses quaternary ammonium NR_4^+ as the active ion exchange site. The column was used for the simultaneous purification and determination of the $EBDC^{2-}$ ion.

Key words: ethylene bisdithiocarbamate; HPLC; anion exchanger column

RESULTS AND DISCUSSION

Bisdithiocarbamate fungicides based on salts of divalent metal ions show different degrees of water solubility, while the mono-valent metallic salt nabam is highly water-soluble (Table 1). Mono-valent cations (i.e., in nabam and amobam) are connected to $EBDC^{2-}$ ion via an ionic bond; di-valent cations (i.e., in zineb and mancozeb) are connected to $EBDC^{2-}$ ion via a copolymerization bond. In the saturated solution of zineb, only a small amount of free Zn was measured in solution, but 86% Na of the dissolved nabam was measured in the nabam solution. Zineb dissolved in 0.1 M NaOH resulted in 80% Zn measurement in the aqueous solution (Fig 1).

Table 1. Water solubility of metal-containing ethylene bisdithiocarbamate fungicides

Fungicides	*Chemical name*	*Solubility*
Nabam	Disodium ethylenebisdithiocarbamate	200 g liter^{-1}
Amobam	Diammonium ethylenebisdithiocarbamate	(Soluble)
Maneb	Manganese ethylenebisdithiocarbamate	160 mg liter^{-1}
Mancozeb	Coordination product of zinc ion, manganese ethylenebisdithiocarbamate	6-20 mg liter^{-1}
Zineb	Zinc ethylenebisdithiocarbamate	10 mg liter^{-1}
Propineb	Zinc 1-methyl-ethylenebisdithiocarbamate	< 1 mg liter^{-1}

Source: The Pesticide Manual, 11th Edn, The British Corp Protection Council, 1997.

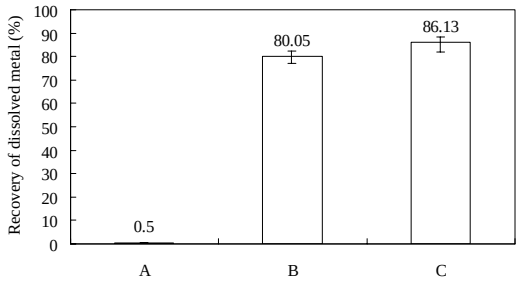

Figure 1. Percentage of dissolved metal in solutions containing: A, 2.5g liter^{-1} zineb in water; B, 2.5g liter^{-1} zineb in 0.1M NaOH and C, 0.25g liter^{-1} nabam in water.

The high water solubility of nabam allowed the direct injection of nabam solution (without NaOH) into the HPLC via the Hypersil SAX column for isolation and determination of the $EBDC^{2-}$ ion as previously described in section *2.2.5* . A retention time of 5.21 min and maximum UV absorption peak of 284 nm were measured for the $EBDC^{2-}$ ion. An HPLC analysis of dissolved zineb in 0.01 M NaOH solution showed that the isolated $EBDC^{2-}$ ion had a retention time and UV spectrum that were identical to those for nabam dissolved in water. Recovery of $EBDC^{2-}$ ion from the zineb alkaline solution revealed that: (a) peak areas were related to the NaOH concentration, and (b) the $EBDC^{2-}$ ion cannot be detected when zineb is not present in the alkaline solution (Fig 2). The highest peak (established as 100%) occurred at a 0.01 M NaOH concentration; peaks of approximately 9.1 % and 24.0% occurred at 0.001 and 0.005 M NaOH concentrations, respectively, at pH values of 6.18 and 10.45, also respectively. Below 0.01 M NaOH concentration was insufficiently alkaline to completely dissolve zineb. The largest peak for nabam was also noted at a 0.01 M NaOH concentration; however, its solubility allowed a peak of only 86% in the absence of alkali (Fig 3). Peaks for both nabam and zineb started to decrease when [OH^-] concentration exceeded 0.01M.

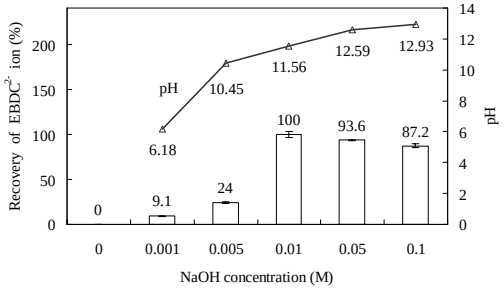

Figure 2. Recovery of $EBDC^{2-}$ ion from zineb solution at different NaOH concentrations.

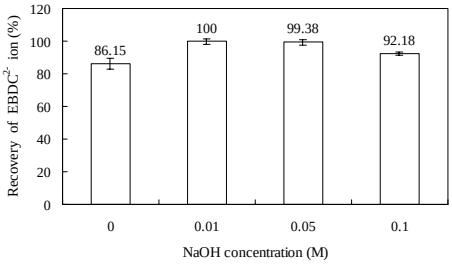

Figure 3. Recovery of $EBDC^{2-}$ ion from nabam solution at different NaOH concentrations.

Due to its tendency to immediately ionize to $EBDC^{2-}$ and Na^+ ion in water, nabam is considered to have low stability; the stability of the $EBDC^{2-}$ ion had to be taken into consideration when developing a method for HPLC determination of zineb. Data from our attempt to use nabam solution to determine $EBDC^{2-}$ ion stability are shown in Table 2. They show the $EBDC^{2-}$ ion concentration from nabam decreasing after 2 hrs, with only 85.4% of the original remaining at 8 hrs. Therefore, experiments that use nabam solution to prepare a calibration curve for zineb analysis must take no longer than 2 hrs. Greater stability occurs when zineb in 0.1 M NaOH solution is used in $EBDC^{2-}$ ion stability test with 98.5% of the original remaining after 24 hrs (Table 2). The difference may be attributed to pH: 9.2 for a nabam water solution and 12.9 for 0.1 M NaOH solution, suggesting that greater $EBDC^{2-}$ ion stability occurs with stronger alkaline solution. Marshall (1977) reported that lower pH results in the acceleration of CS_2 and ETU formation, causing nabam solution to become less stable.

Table 2. Stability of $EBDC^{2-}$ ion in nabam aqueous solution and in zineb 0.1 M NaOH solution at

$EBDC^{2-}$ ion	Incubation time (hr)							
	1	2	3	4	5	6	7	
	Recovery(%)							
A[a]	100	100.6	99.2	93	94	85.4	--	85.4
B[b]	100	101.4	101.9	101.7	102.4	102.4	98.5	98.5[c]

The linear relationship between peak area and nabam concentration (R^2=0.9999 within a range of 50 to 250 μg ml^{-1}) allows for the preparation of a calibration curve. When zineb was dissolved in 0.1 M NaOH containing 0.1%EDTA and the pH was adjusted with HCl, $EBDC^{2-}$ ion did not disappear from the lower pH solution (Fig. 4). As this suggests that dissociated $EBDC^{2-}$ ion does not form a precipitate, dissociated zineb may be treated with acid prior to HPLC injection to protect the column. The use of an anion exchange column in the HPLC analysis of zineb is limited by differences in optimum pH between column materials and the zineb alkali solution. In this study, the optimum pH for a SAX column containing the quaternary ammonium NR_4^+ as the active ion exchanger site was below 7.5. In order to protect the column while still obtaining satisfactory results and adequate retention times, the mobile phase used in our experiments consisted of a buffer solution of 0.03 M $NaClO_4$ and 0.01 M NaH_2PO_4 with a pH of 3.5. Unfortunately, this lower pH condition results in the soluble $Zn(OH)_4^{2-}$ precipitating as $Zn(OH)_2$, resulting in blocking of the column. Also noted, the production of a clear solution after the addition of zineb to a strong alkaline solution will re-precipitate as $Zn(OH)_2$ by adding acid. If more acid is added, the precipitate may be re-dissolved into Zn^{2+}, which then returns to its original form of insoluble zineb with $EBDC^{2-}$. These problems are resolvable by adding 0.1% EDTA to the 0.01 M NaOH solution, resulting in the formation of water soluble EDTA-Zn chelate, which can be used to resist the formation of $Zn(OH)_2$ precipitate and thus maintain solution clarity.

Gustafsson and Thompson (1981) first developed a method for HPLC determination of dithiocarbamate fungicides using a reverse phase column that required the dissolving of EBDCs in EDTA alkaline solution; their method required methylation. We believe the procedure described here is a fast, simple, and accurate alternative.

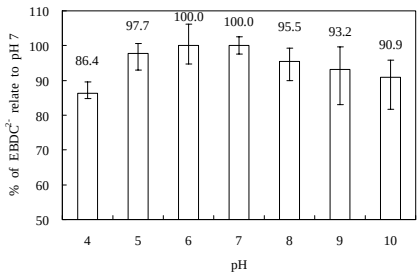

Figure 4. Effect of variation in pH on $EBDC^{2-}$ ion in the EDTA alkaline solution.