

## Interference-free coulometric titration of water in lithium bis(oxalato)borate using Karl Fischer reagents based on *N*-methylformamide

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### Abstract

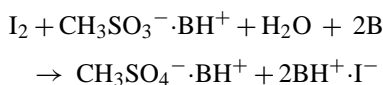
A non-alcoholic coulometric reagent based on *N*-methylformamide (NMF) was shown to eliminate the severe interference effect caused by the alcohol component of the conventional Karl Fischer (KF) reagent on the battery electrolyte lithium bis(oxalato)borate (LiBOB). For sample amounts up to 240 µg of water, the stoichiometry of the KF reaction deviated only slightly from the ideal 1:1 ratio for the best reagent composition. Both solid and dissolved (in acetonitrile, tetrahydrofuran (THF), and ethylene carbonate/ethyl methyl carbonate) LiBOB were titrated successfully using a Metrohm 756 KF Coulometer with a diaphragm cell. The detection limit was estimated to be 0.5–1 µg of water using 100 ml of reagent in this system.

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Water determination by Karl Fischer (KF) titration is an established tool for quality control of electrolyte solutions used in lithium ion batteries. Lithium hexafluorophosphate (LiPF<sub>6</sub>) is the conductive salt typically used in lithium ion batteries. Even with water present at trace levels, the PF<sub>6</sub><sup>-</sup> anions tend to react [1], thus forming HF, which may cause corrosion of the functional materials within the battery. In order to address the corrosive nature of LiPF<sub>6</sub>, especially in relation to lithium manganese spinel (LiMn<sub>2</sub>O<sub>4</sub>) and lithium iron phosphate (LiFePO<sub>4</sub>) cathode materials, alternative conductive salts have recently been introduced. One example is lithium bis(oxalato)borate (LiBOB) which is the first halogen-free conductive salt suitable for lithium ion batteries [2]. Water determination in LiBOB or LiBOB-based solutions using the standard Karl Fischer technique does, however, lead to erroneously high results due to a side reaction of the alcohol component with the BOB anion. Thus, a method is desired that allows for trace water determination in LiBOB and liquid electrolyte solutions based on LiBOB.

Successful Karl Fischer titrations necessitate the maintenance of a 1:1 stoichiometric ratio between iodine and water. Considering ‘normal’ titrations of milligram water or less carried out in methanolic reagents buffered with bases (B) like pyridine, imidazole, diethanolamine or acetate, deviations from the ideal 1:1 stoichiometry are not expected [3]. For such titrations, the overall KF reaction proceeds according to the following reaction [3]:



This reaction was originally proposed to be a two-step reaction [4] when taking place in standard pyridine (Py)-buffered KF media. Py·SO<sub>3</sub> was assumed to be formed in the first step followed by either reaction with water, forming sulfuric acid, or with methanol producing methyl sulfate. The formation of this intermediate, Py·SO<sub>3</sub>, has been questioned [3] based on experimental evidence for a very slow reaction with water as well as with methanol. Later on, Fischer et al. [5,6] showed, convincingly, that SO<sub>3</sub>, (and not Py·SO<sub>3</sub> which needs quite long time for its formation) is the reaction product of the first step in the

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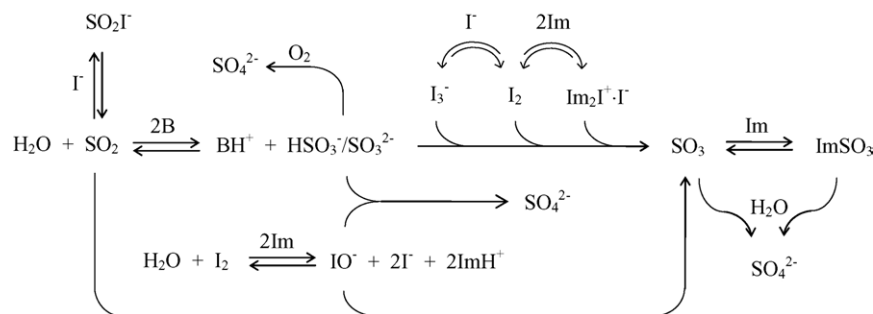


Fig. 1. Some possible reaction pathways in NMF reagents. B, base; Im, imidazole.

KF reaction and that this compound reacts rapidly with both methanol and water. This means that the stoichiometric ratio is governed by the difference in reaction rates between the hydrolysis of  $\text{SO}_3$  and the reaction between  $\text{SO}_3$  and the alcohol.

The influence of water on the stoichiometry is more pronounced for reagents in which methanol is replaced by less reactive alcohols [3]. Scholz [3] found that the contribution from the Bunsen reaction ( $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{I}^-$ ) increased from approximately 5% in 2-propanol to 12% in *tert*-butanol and nearly 100% in pure pyridine. Grönke [7] reported an extensive study of higher alcohols and found, for example, a 4% deviation from the ideal stoichiometry using 1-propanol as the solvent for the KF reagent.

For a non-alcoholic KF reagent based on formamide/pyridine 1/4 [8,9] coulometric titrations of small amounts gave results corresponding to a stoichiometric KF reaction. Swensen and Keyworth [8] suggested the formation of a compound  $\text{PySO}_3\text{HNCOH}$  which hinders the Bunsen reaction from taking place. It should be emphasized that Scholz [3] recommended the use of at least 40% methanol in order to attain 100% recovery in volumetric titrations using formamide. In a study of the stoichiometry in mixtures of formamide and 2-methoxyethanol, Nordin-Andersson and Cedergren [10] found that for small amounts of water the ideal 1:1 ratio was attained relatively independent of the concentration of 2-methoxyethanol. For larger amounts of water, 80% (v/v) of 2-methoxyethanol was required for a stoichiometric reaction.

The rate of reaction is known to be very high in formamide [8,9] and the relatively small change in stoichiometry seen in the results of these authors can be explained by a kinetic discrimination of the probable side reaction between  $\text{SO}_3$  (or formamide- $\text{SO}_3$  [11]) and water. For a pyridine-buffered reagent based on dimethylformamide, the stoichiometric ratio found experimentally [11] could be predicted theoretically in the range 1:1 to 1:8 by taking into consideration the kinetics for both the KF reaction and the reaction between  $\text{SO}_3$  and water.

Water determination according to the standard KF method suffer in many situations from interference effects caused by the presence of an alcohol in the KF medium. Well-known examples are active carbonyl compounds like aldehydes and ketones [3], which produce water through the acetal- and ketal reactions. In the case of LiBOB water is also formed due to reaction with methanol, and therefore attempts to achieve 1:1 stoichiometry were made with the promising organic solvent

*N*-methylformamide (NMF). Owing to its very high dielectric constant ( $\epsilon_r = 192$ ) it is an efficient solvent for polar compounds, and previous unpublished investigations on coulometric titrations in this medium indicate a very rapid KF reaction. The use of *N*-methylformamide in both volumetric and coulometric KF titrations has been patented by Scholz [12] but no results have been presented so far.

As illustrated in Fig. 1, the complexity of a coulometric KF system based on *N*-methylformamide is very high, involving several possible reactions for which neither the reactants nor the kinetic data are known. The hydrolysis of iodine has been proposed to take place via a highly reactive  $\text{I}^+$  species [13,14] known to form readily in the presence of secondary and tertiary amines [15]. Reaction of the formed hypoiodite with sulfite or bisulfite would then lead to a deviation from the ideal 1:1 stoichiometry, and so would also oxidation of sulfite and hydrolysis of sulfur trioxide. Sulfur trioxide has on the other hand been shown to form a complex with imidazole [16] that reacts only slowly with water.

## 1. Experimental

### 1.1. Chemicals

Sulfur dioxide (puriss) and tetrahydrofuran (THF) (HPLC quality) were from Fluka, imidazole was from J.T. Baker, imidazolium iodide, Hydranal Coulomat AG, and AG-H were from Riedel-de Haën, iodine (reagent grade) was from Scharlau, acetonitrile (biotech grade) and *N*-methylformamide (99%) were from Aldrich, ethylene carbonate and ethyl methyl carbonate were from Tomiyama, and propyl acetate (zur Synthese) was from Merck. A solution of 1 M imidazolium iodide in dried NMF was used as catholyte in the coulometric cell.

### 1.2. Safety considerations

Methanol is highly flammable and toxic by inhalation, in contact with skin and if swallowed. Imidazole is harmful by inhalation, in contact with skin and if swallowed. Sulfur dioxide is intensely irritating to eyes and the respiratory tract. Iodine is a poison and may be fatal if swallowed. Acetonitrile is highly flammable, harmful by inhalation, in contact with skin and if swallowed, as well as irritating to eyes. Tetrahydrofuran is highly flammable, may form explosive peroxides, and is irritat-

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