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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.

Keywords: *N*-Methylformamide; Non-alcoholic KF reagent; Lithium bis(oxalato)borate; Water determination

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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 ($LiPF_6$) is the conductive salt typically used in lithium ion batteries. Even with water present at trace levels, the PF_6^- 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 $LiPF_6$, especially in relation to lithium manganese spinel ($LiMn_2O_4$) and lithium iron phosphate ($LiFePO_4$) 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]:

$$I_2 + CH_3SO_3^-{\cdot}BH^+ + H_2O + 2B \\ \rightarrow CH_3SO_4^-{\cdot}BH^+ + 2BH^+{\cdot}I^-$$

This reaction was originally proposed to be a two-step reaction [4] when taking place in standard pyridine (Py)-buffered KF media. Py·SO_3 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_3, 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_3, (and not Py·SO_3 which needs quite long time for its formation) is the reaction product of the first step in the

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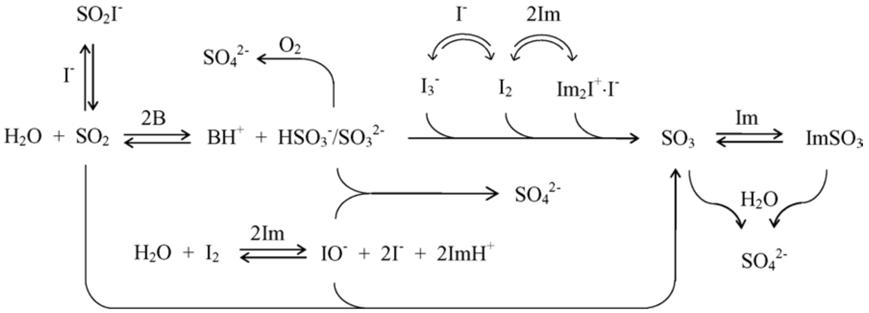

Fig. 1. Some possible reaction pathways in NMF reagents. B, base; Im, imidazole.

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 SO_3 and the reaction between 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 ($I_2 + SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2I^-$) increased from approximately 5% in 2-propanol to 12% in *tert*-butanol and nearly 100% in pure pyridine. Grünke [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 $PySO_3HNCOH$ 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 SO_3 (or formamide·SO_3 [11]) and water. For a pyridine-buffered reagent based on dimethylformamide, the stochiometric 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 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 ($\varepsilon_r = 192$) 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 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 irritating to eyes and respiratory system. Ethylene carbonate can cause serious damage to eyes. Ethyl methyl carbonate is flammable, harmful in contact with skin or if swallowed, and irritating to eyes and respiratory system. *N*-Methylformamide may cause harm to the unborn child and is also harmful in contact with skin. Lithium bis(oxalato)borate is harmful if swallowed.

1.3. Instrumentation

During preparation of samples, an AQUA 40.00 titrator from Analytik Jena was used. Otherwise, a Metrohm 756 KF Coulometer with diaphragm cell was used together with Vesuv 2.0 database software for determinations with both alcoholic and non-alcoholic reagents. An in-house constructed titrator [17], based on computer controlled continuous coulometry with a specially designed diaphragm-free cell [18], was used with commercial methanolic reagents for standardization of water standards. The sulfur dioxide content was determined coulometrically according to a previously described procedure [19], although with a cell of the same type as mentioned above [18].

1.4. Preparation of reagents

Appropriate amounts of imidazole and imidazolium iodide were dissolved in NMF, dried over 3 Å molecular sieves. The solution was placed on a balance and purged with sulfur dioxide until the desired amount was dissolved. After adding iodine (typically 50 mM) the volume was adjusted to 100 ml with a final portion of NMF. The reagents were typically allowed to stand with the excess iodine over night since there have been indications of oxidizable impurities in the NMF. After introduced in the titration vessel the reagent was decolored (iodine excess was consumed) by addition of water.

1.5. Preparation of samples

Preparation of LiBOB-based solutions was carried out at Chemetall GmbH in an argon-filled glove box (M. Braun, MB200). All glassware and other equipments used were dried in an oven antechamber at 120 °C and $<10^{-2}$ mbar base pressure for 16 h prior to introduction into the glove box. Initial test samples were prepared by dissolving 30 wt.% LiBOB in tetrahydrofuran and 20 wt.% in acetonitrile.

For the standard addition determination, a solvent mixture of ethylene carbonate and ethyl methyl carbonate in a ratio of 1:1 (w/w) was prepared, and the water content was found to be lower than 5 ppm when determined with a methanol-based reagent (Hydranal Coulomat AG). LiBOB was dissolved in the solvent mixture, with LiBOB concentration of 12 wt.% (solution A). The density of the solutions was 1.21 g/cm^3 at 25 °C. One part of this solution was used to prepare a second solution to which 500 ppm of water was added. By mixing proper amounts of the two solutions LiBOB-based electrolyte with 0 ppm, 100 ppm, 200 ppm, and 500 ppm added water were prepared. The test solutions were weighed into chromatography vials, sealed with a PTFE coated septum, and shipped to Umeå University. Possibly due to exposure to low temperature during transport, a crystalline precipitate was observed in some of the electrolyte solutions. This precipitate consists of the solvate between LiBOB and ethylene carbonate, which was dissolved by exposure to slightly elevated temperature.

1.6. Procedures

Unless otherwise stated the fixed settings of the coulometric titrator were 400 mA maximum current, 15 μg/min minimum titration rate, 2000 μg/min maximum titration rate, 10 μA polarization current, and an extraction time (fixed titration time without any other stop criteria) of 600–900 s. The dynamics setting (range for proportional regulation of current) was chosen to give fast titrations without overshooting the end point, and was typically 30 mV. Multiple injections were often performed during each run and the results were calculated manually from the raw report stored in Vesuv. Before the titrations were started, the system was conditioned by shaking the cell carefully to dry the internal surfaces, whereupon the cell was allowed to equilibrate until a stable background in the range of 0–3 μg/min was achieved. In some cases, the reagent was purged for 30 min with helium that was dried by passage through a column containing magnesium perchlorate. Samples were added using a 50-μL Hamilton syringe, calibrated to 50.4 μL and equipped with an 80 mm long needle. Two propyl acetate solutions, spiked with approximately 80 and 250 ppm water, were standardized by titration with Hydranal Coulomat AG-H and used for recovery studies.

2. Results and discussion

2.1. Initial investigation and comparison

Based on recipes from previous investigations, a non-alcoholic reagent was prepared by dissolving 2.5 M imidazole, 0.20 M imidazolium iodide, 0.24 M sulfur dioxide, and 0.10 M iodine in NMF. Samples of LiBOB in tetrahydrofuran and in acetonitrile were titrated, both with a commercial imidazole-buffered methanolic reagent (Hydranal Coulomat AG-H), and with the NMF reagent. The two samples produced similar titration courses, and the curves of a tetrahydrofuran sample in Fig. 2 clearly illustrate the incompatibility with methanol, as well as a promising titration with rapid kinetics in the NMF reagent. The result of 1500 μg water, obtained with the methanolic reagent, corresponds well to a possible reaction between methanol and one of the oxalate groups, producing equimolar amounts of dimethyl oxalate and water:

$$\begin{aligned}&\mathrm{Li(C_4O_8B)} + \mathrm{2CH_3OH}\\&\quad\rightarrow \mathrm{(C_2O_4)BOLi} + \mathrm{(H_3COOC)_2} + \mathrm{H_2O}\end{aligned} \tag{1}$$

In the case of the depicted tetrahydrofuran sample, a theoretical amount of 1400 μg water would be produced. Solid LiBOB samples also showed about the same titration course in the non-methanolic reagent, which indicated a very rapid dissolution rate of the salt. When analyzing the propyl acetate standards, however, the recovery was found to be no better than 97%, indicating a problem with the stoichiometry of the KF reaction.

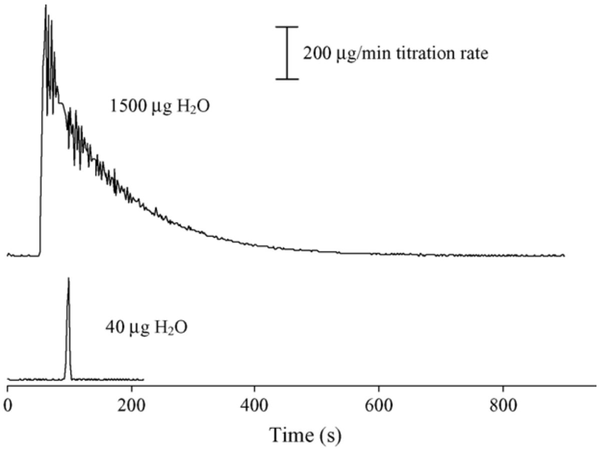

Fig. 2. Titration of 50 µL 30 wt.% LiBOB in THF. Upper curve is with a methanolic reagent (Hydranal Coulomat AG-H) and the lower with an NMF-based reagent.

2.2. Optimization of reagent composition

A series of reagents was prepared to find an optimum composition. As expected from previous studies [20], a high imidazole concentration was advantageous because of the faster kinetics of the main reaction. This is clearly seen from the shape of the titration curves in Fig. 3. However, when the imidazole concentration was 2.5 M and higher, an increase in the background (drift value) was observed. High sulfur dioxide concentrations resulted in poor recoveries, especially for larger samples and prolonged titration times. Sulfur dioxide should therefore be held at as low a concentration as possible, with the capacity of the reagent as the limiting factor. Presumably this is due to the increased formation of sulfite/bisulfite, which is susceptible to oxidation by species other than iodine, i.e. oxygen and hypoiodite (Fig. 1). This may also explain the positive effect of a high iodide concentration on the recovery, since the SO_2I^- complex may form and thereby lower the amount of free sulfur dioxide (Fig. 1). A problem with high iodide concentration is the increased auto-oxidation of iodide to iodine, which results in a negative contribution to the background. In some cases this contribution was even higher than that from the intruding moisture and the cell had to be shielded from light to avoid overshooting the end point. Reagents resulting in recovery rates of 99% or better were achieved by dissolving 1–2 M of imidazole, about 1 M of imidazolium iodide, 0.10–0.15 M of sulfur dioxide, and 50 mM of iodine in NMF.

As long as iodine is in excess to water the KF reaction will be very rapid and the time non-reacted water is available for competitive reactions will be minimized. Because of this the recovery rates eventually dropped as the sample size was increased and the titration process thereby prolonged. A selection of the optimization results, shown in Table 1, illustrates how this effect was pronounced in some mixtures and almost unnoticeable in others. In the best reagents it was possible to maintain close to 100% recovery up to at least 240 µg of water, which is good enough for making reliable trace water determinations.

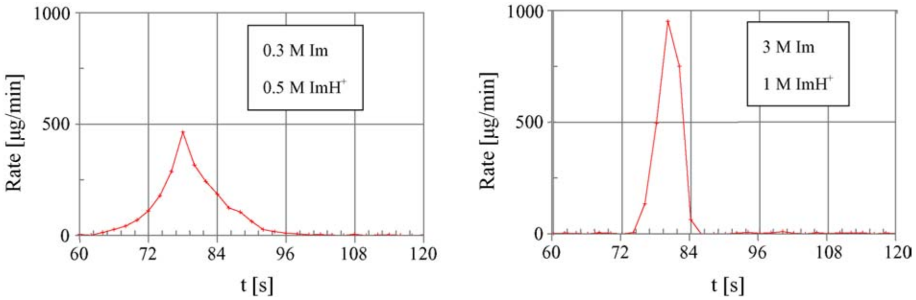

Fig. 3. Comparison of the kinetics in two NMF reagents. Amount of water in the sample ~80 µg.

Table 1
Optimization of reagent composition

	Reagent composition					Recovery %			
	$[Im]_0$ (M)	$[ImH^+]_0$ (M)	$[I^-]_0$ (M)	$[I_2]_0$ (mM)	$[SO_2]_{work}$[a] (mM)	80 µg H_2O		240 µg H_2O	
						30 Mv[b]	90 mV[b]	30 mV[b]	90 mV[b]
A	0.26	0.50	0.50	50	60	98.9	95.9	99.1	96.0
B	0.26	0.50	0.50	50	470	98.8	93.4	96.9	90.5
C	1.0	1.0	1.0	50	90	99.1	–	99.2	–
D	1.0[c]	1.0[c]	0	100	50	96.6	–	94.9	93.5
E	2.0	1.0	1.0	50	40	100.0	–	99.9	97.9
F	2.0	1.0	1.0	50	510	99.1	–	98.8	97.8

[a] 0.15 M added initially. The content in solutions B and F was increased by further addition.

[b] Bipotentiometric end-point potential; 50–60 µM iodine excess at 30 mV, and 10 µM at 90 mV.

[c] 2 M Im + 1 M benzoic acid is assumed to produce 1 M ImH^+.

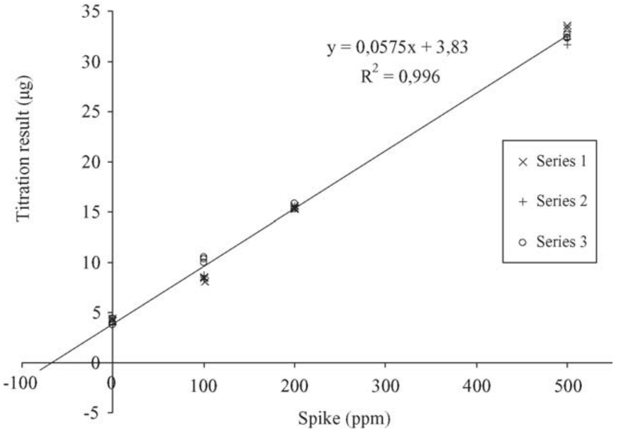

Fig. 4. Standard addition of water to LiBOB samples dissolved in an ethylene carbonate/ethyl methyl carbonate mixture.

2.3. Analytical results

An NMF reagent composed of 2 M imidazole, 1 M imidazolium iodide, and 0.08 M sulfur dioxide was used for water determination in samples of LiBOB dissolved in a carbonate mixture. The three series were analyzed one at a time within two days, using the same reagent. All results are plotted in Fig. 4 and from the linear regression line a water content of 67 ppm can be calculated for the non-spiked sample. This is well in accordance with the value of 68 ppm calculated directly from the mean of all results of the non-spiked samples, indicating that no significant interference occurred. The spread in the results can be assumed to originate from three major sources; sample preparation, transportation, and the determination. It is difficult to decide which of them contributes most, but the clear deviation of one series of 100 ppm samples was most likely due to the preparation process. The water content in the dissolved LiBOB (12 wt.%) was calculated to be 570 ppm, assuming that all water was from the solid substance. It was, however, not investigated to what extent moisture was able to leak into the vials between the preparation and the analysis.

In order to estimate the detection limit of the method, eight 50-µl portions of dried NMF were titrated using 30 mV and 100 mV end-point potentials. The minimum titration rate of the Metrohm titrator was unnecessarily high and was therefore adjusted to a minimum (from 15 µg/min to 0.3 µg/min). The average result was 1.8 µg in both cases, but the standard deviation increased from 0.17 µg to 0.35 µg as the end-point potential was lowered. By taking three times the standard deviations the detection limits were estimated to be 0.5 µg water at 100 mV end-point potential, and 1 µg at 30 mV. This difference simply reflects the greater sensitivity of the bipotentiometric indicating system at the higher potential.

3. Conclusions

In comparison to coulometric KF reagents based on alcohol-type compounds, the reagents based on NMF allow for the titration of solid LiBOB and LiBOB solutions, without the severe side reaction observed with standard KF reagents. Thus, the NMF reagent described in this paper will constitute a valuable complement to the commercially available methanolic reagents for the determination of water in polar samples and in situations where the alcohol component causes interference effects, such as with active carbonyl compounds. The very rapid kinetics exhibited in this type of reagent will improve the kinetic discrimination of side reactions such as those caused by iodine-consuming sample constituents, or the irreversible formation of bisulfite addition complex in the presence of active carbonyl compounds. Unfortunately, the bipotentiometric and biamperometric indication systems commonly used in commercial instruments do not allow for end points at very low iodine levels. The use of alternative techniques with response also at lower concentrations, such as zero-current potentiometry, would make it possible to further minimize the background-correction error caused by iodine-consuming side reactions, as well as to increase the positive effect of the kinetic discrimination. Future studies of NMF-based reagents will be focused on a better understanding of the equilibriums and complex reactions involved, with the aim of maintaining a 1:1 stoichiometric ratio also for samples containing larger amounts of water.

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