It's a displacement reaction because sodium ions are more reactive than zinc ions

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Abstract

Grade 10 (15 to 17 years old) students have difficulties in understanding ion-exchange reactions and complex salt formation involved in the tests for cations in basic inorganic chemistry qualitative analysis. Many students believed that when an insoluble hydroxide was produced from the reaction between an unknown cation and a hydroxide ion, a more reactive ion displaced a less reactive ion to form the precipitate. Students also explained that the reaction between several hydroxides and excess alkali as the precipitate dissolved when excess alkali was added because more solvent was added or that no new reagent was added and no further reaction was seen. Possible reasons proposed for such student conceptions included conceptual interference and perceptually-dominated thinking.

Introduction

Grade 10 students (15 to 17 years old) in Singapore sit for a national examination, the General Certificate of Education Ordinary Level (O-level) examinations, at the end of their school year. Students taking chemistry as a subject need to take one practical and two written papers. There is usually one question in the practical paper on basic inorganic chemistry qualitative analysis which requires students to carry out a series of procedures, observe and record what happens, and make inferences based on their observations.

Teachers in Singapore usually begin teaching qualitative analysis by reviewing the reactions involved and demonstrating some procedures that the students need to carry out. Using commercially available workbooks or teacher-prepared worksheets, students then do a series of tests for various cations, anions, gases, oxidising and reducing agents. After this initial stage, students will start on past years' examination questions to prepare for the practical paper. In the one-off practical examinations, students are assessed solely on their practical reports, and in qualitative analysis, this translates to the students' written observations of the reactions which occur when they execute a series of procedures, and to a lesser extent, the inferences they make based on their observations.

The content framework for qualitative analysis is given in Tan (2002). To understand the reactions in qualitative analysis, students mainly need to apply the knowledge they learned in the topic, 'Acids, Bases and Salts'. However, several studies (e.g. Carr, 1984; Hand & Treagust, 1988; Nakhleh & Krajcik, 1994; Schmidt, 1991, 1997) have found students have difficulties understanding the concepts and reactions of acids, bases and salts. For example, in qualitative analysis, many anions and cations are identified using ion-exchange reactions resulting in the formation of precipitates – Butts and Smith (1987) found that students could not relate the formation of a precipitate in an ion-exchange reaction to the low solubility of the salt, while Boo (1998), and Boo and Watson (2001) found that students believed the driving force for an ion-exchange reaction was the difference in reactivity between the metallic elements present in compounds involved.

Purpose of the study

The purpose of the study is to determine Grade 10 students' understanding of the ion-exchange reactions and complex salt formation involved in the tests for cations in basic inorganic qualitative analysis.

Method and procedure

In this study, interviews, a free response test in which students have to justify their answers, and a two-tier multiple choice diagnostic instrument (Treagust, 1995) were used to determine students' understanding of the procedures and reactions involved in qualitative analysis. Items in a two-tier multiple choice diagnostic instruments are specifically designed to identify alternative conceptions and misunderstandings in a limited and clearly defined content area. The first part of each item consists of a multiple choice content question having usually two or three choices. The second part of each item contains a set of four or five possible reasons for the answer to the first part. Incorrect reasons are derived from actual student alternative conceptions gathered from the literature, interviews and written tests. The Qualitative Analysis Diagnostic Instrument (QADI) (Tan et al, 2002) was used in this study, and the four items that are related to this topic of this paper are given in the Appendix. The QADI was administered to 915 Grade 10 students from 11 secondary schools. Sixty percent were females and forty percent were males.

In addition, twelve other students were interviewed using the QADI as the interview protocol to determine whether the students had difficulty understanding the wording of the items in the QADI, and to probe deeper into the thinking behind their answers.

Results and discussion

The results of the Grade 10 students on the QADI are given in Figure 1. The students found the QADI difficult – the average mark was 5.8 out of a maximum of 19, with 87% scoring 9 marks or less. The reliability of the instrument (Cronbach alpha) is a moderate .68, consistent with the criterion-referenced nature of the test (Ross & Munby, 1991). The focus of this paper is on the Grade 10 students' understanding of the reactions involved in the testing of cations in basic inorganic qualitative analysis. These are ion-exchange reactions resulting in the formation of precipitates and the formation of complex salts when the precipitates react with excess alkali. The students' performance on the relevant items are given in Table 1. Alternative conceptions are considered significant if they existed in at least 10% of the student sample as a higher minimum value, say 25%, would possibly eliminate some valid alternative conceptions from the results (Tan et al., 2002). Data obtained during the development of the QADI, as well as data from interviews using the QADI as the protocol were used to support and illustrate the results obtained from the administration of the QADI.

Table 1 Performance of the Grade 10 students (N=915) on items 1, 2, 13 and 14.

Item	Content option	Reason option (1)	(2)	(3)	(4)	(5)
1	A	0.4	1.6	*24.9*	2.7	-
	B	4.8	7.8	7.1	**40.8***	-
	C	0	5.2	0.8	1.1	-
2	A	*28.6*	*15.7*	5.2	25.7	-
	B	.3	.4	2.7	**19.3***	-
13	A	2.4	4.7	3.2	*11.6*	-
	B	5.8	**44.9***	2.3	4.0	-
	C	*13.0*	1.9	1.2	1.0	-
14	A	4.3	*24.8*	*16.4*	15.5	-
	B	3.0	1.0	2.0	**29.1***	-

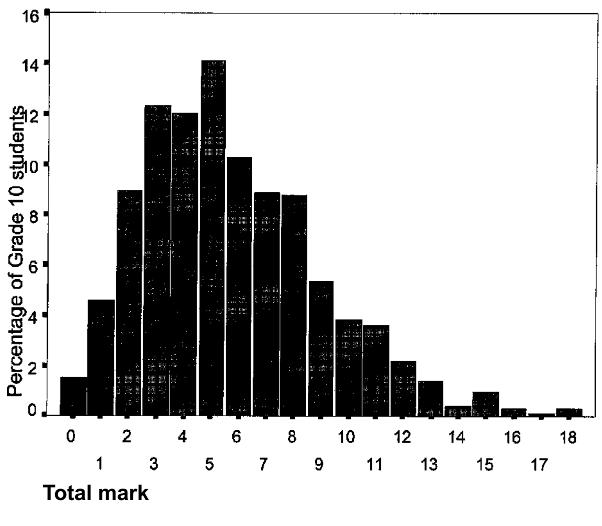

Figure 1 Distribution of Grade 10 students' scores (n=915

Unknown cations are identified in O-level qualitative analysis by reacting them with aqueous sodium hydroxide and/or aqueous ammonia. For example, zinc salt solutions react with aqueous sodium hydroxide to form a white precipitate, zinc hydroxide, which in turn will react with excess aqueous sodium hydroxide to form a colourless solution of sodium zincate, a complex salt. However, in item 1 (see Appendix and Table 1), only 41% of the students knew that the zinc and hydroxide ions combined to form the zinc hydroxide precipitate. Many students indicated that a displacement reaction resulted in the formation of the precipitate because the sodium ion was more reactive than the zinc ion (A3, 25%). This is similar to the finding of Boo (1998), and Boo and Watson (2001) mentioned in the introduction. This showed that students did not understand that the precipitate was the result of an ion exchange reaction, and that in a displacement reaction, a more reactive element displaced the ion of a less reactive element, rather than an ion of a more reactive metal displaced an ion of a less reactive metal. Another possible explanation is that students did not differentiate between the metal and its cation, thus the students believed that the two species had the same properties (Boo & Watson, 2001). In an earlier stage of the study, a free-response instrument, in which students had to write down their reasons for their first-tier options, was administered to a different batch of 203 students. For an item similar to item 1 of the two-tier diagnostic instrument, 21 students (10%) also supplied reasons to the effect that sodium was a more reactive metal than zinc, so it displaced zinc, or that the more reactive sodium ion displaced the zinc ion. These beliefs also appeared in interviews with students as illustrated below by two excerpts of interviews.

I: OK…so what actually happens that gives rise to this insoluble substance?

S7: What actually happens?

S8: Is displacement possible?

I: Why do you say that?

S8: Because…because sodium is a metal higher in the reactivity series. So er…any cation that is below it may be displaced.

I: …if a precipitate is formed, can you tell me why…or what leads to its formation?

S33: Displacement.

I: Why displacement?

S33: Why displacement…the more reactive one displace the less reactive.

S34: Sodium…displaces the…

S33: Sodium is very reactive…so it displaces things under it in the reactivity series.

I denotes the interviewer, and S7, S8, S33 and S34 denote students.

The authors believed that the 'more reactive ion displaces a less reactive ion' conception could have resulted from conceptual interference (McDermott, 1988) as well as failure to differentiate the metal from its cation (Boo & Watson, 2001). Students were taught that a more reactive metal displaced a less reactive metal from its compounds in the topic 'Reactivity of Metals', and they also were required to memorize the reactivity series, a list of several metals arranged in order of decreasing reactivity. Thus, what they learned in 'Reactivity of Metals' could have become more prominent compared to what they learned about ion-exchange reactions. This could have caused students to inappropriately apply knowledge from previous learning, that is, reactivity and displacement, to explain ion-exchange reaction. This hypothesis was supported by the following excerpt of an interview with Students 52 and 53.

S52: Because…sodium hydroxide will displace the…zinc chloride…cos…the zinc chloride is less stable than sodium chloride…so…a displacement reaction will happen.

I: Why did you think of a displacement reaction?

S53: We've got the reactivity series…then we learn the displacement…so we apply.

I: Why did you think of the reactivity series…is there any reason?

S53: We were made to memorise the reactivity series…so it comes naturally.

S52: The teacher always stresses the importance of the reactivity series, so the moment you see sodium…you see metals like sodium…any metal from the reactivity series, even though it is an ion, you think of reactivity series right away.

Item 13 is very similar to item 1 in that an alkali (aqueous ammonia) is added to an aqueous solution of copper(II) sulfate(VI) resulting in the formation of insoluble copper(II) hydroxide. The results showed that 15% of the 915 students indicated in item 13 that a displacement reaction had occurred because copper(II) ion was less reactive than ammonium ion (A4, 12%) or because copper(II) ion was more reactive than the ammonium ion (A3, 3%). However, the ammonium ion does not appear in the reactivity series at all! A possible reason for the alternative conception was that the students concentrated on the copper(II) ion and associated it with copper metal which they knew was low in the reactivity series, and applied their knowledge erroneously. This is illustrated again by the comments of Students 52 and 53.

S52: I said…displacement…because the copper ion is less reactive than ammonium ion.

I: Is the ammonium ion in the reactivity series?

S52: Not really, no.

S53: No.

I: Then why do you choose that reason.

S52: Because a blue solid, so it's like the presence of copper(II) precipitate, there will be copper(II) ions…and furthermore copper is very low down in the reactivity series… easily displaced.

I: Why do you think of the reactivity series?

S53: The low position [of copper(II)] supports our answer…with the presence of copper…copper(II) ions right, there will be light blue precipitate …so then since copper is so low down the reactivity series, it supports our answer.

Some clarification has to be made at this point. Displacement is an example of a redox reaction, so option C can be considered to be an umbrella term (Towns & Robinson, 1993) for option A in items 1 and 13. However, in the interviews and in the earlier versions of the diagnostic instrument which required students to write the reasons for their first-tier choices, a vast majority of students only associated the 'reactivity' of the ions with displacement, and the gain/loss of oxygen with redox. The percentages of students choosing option C3 in item 1 (1%), and C3 and C4 in item 13 (2%) also showed that students tended not to consider redox as an umbrella term for displacement. Thus, displacement and redox were retained as first-tier options in items 1 and 13.

The percentages of students choosing the correct answer for item 1 (B4, 41%) and item 13 (B2, 45%) are very similar, but closer inspection of the results showed that only 278 students (30%) had both items correct. Twenty-three students (3%) who had item 1 correct stated that a displacement reaction had occurred in item 13 because of the difference in reactivity of copper(II) and ammonium ion (A3 and A4), while 46 students (5%) who had item 13 correct indicated that in item 1, a displacement reaction had occurred because the sodium ion is more reactive than the zinc ion (A3). These students seemed uncertain that the same type of reaction had occurred in both cases. On the other hand, though 25% in item 1 and 15% in item 13 thought that displacement occurred because of 'difference in reactivity of the ions', only 73 students (8%) consistently indicated so in both questions. The lack of consistency could indicate that the students had several alternative ideas from which students could choose depending on the context (Palmer, 1999; Taber 1999), or that they had little idea of the ion-exchange reactions involved in the testing of cations and resorted to either guessing or on-the-spot thinking.

Another alternative conception was determined in item 13 – a redox reaction had occurred because aqueous ammonia 'gained' oxygen in forming ammonium sulfate(VI) and copper(II) sulfate(VI) 'lost' oxygen in forming copper(II) hydroxide (C1, 13%). As suggested in Tan et al. (2002), the cause of this alternative conception appears to be the use of an inappropriate model, the oxygen model (Garnett & Treagust, 1992). However, a similar option (C2) in item 1 only attracted 5% of the students, with only 14 students (2%) consistently choosing the redox combination in both items 1 and 13. It is also interesting to note that 51 students (6%) who selected the C1 in item, 13, chose A3 (more reactive ion displacing less reactive ion) in item 1. This lack of consistency again showed that students could have either more than one conception of the reaction depending on the context, or had resorted to guessing or on-the-spot thinking.

A further step in the test for cations is to add excess alkali to the precipitate to determine if the precipitate reacts with it to form a complex salt. Hydroxides of zinc, aluminium, lead(II) are amphoteric, and will react with excess aqueous sodium hydroxide to form the zincate, aluminate or plumbite salt, while zinc and copper(II) hydroxide will react with aqueous ammonia to form the respective ammines. The percentages of students getting items 2 and 14 correct are 19% and 29%, respectively, while 125 students (14%) had both items correct. Many students indicated in items 2 and 14 that the precipitate dissolved in, instead of reacted with, the excess alkali because more alkali added meant more space/volume for the precipitate to dissolve (Item 2 - A1, 29%; Item 14 - A2, 25%), or that no new reagent was added and no further reaction except for the disappearance of the precipitate was seen (Item 2 - A2, 16%, Item 14 - A3, 16%). The number of students consistently choosing A1 in item 2 and A2 in item 14 was 154 (17%), while 87 students (10%) consistently chose A2 in item 2 and A3 in item 14. Many students could not relate the disappearance of the precipitate to the formation of the complex salt. This difficulty also surfaced during the interviews.

I: OK…is a precipitate insoluble?

S12: Yes.

S13: Yes.

I: Then why should it dissolve in excess?

S13: Because before adding excess, that solution perhaps could be concentrated, so…it gives out a precipitate. By adding excess sodium hydroxide, you're giving more volume for the…you're creating more space for precipitate to actually dissolve in it.

Data from the administration of the free-response test mentioned in an earlier section showed that 108 (51%) of them wrote reasons to the effect that 'no further reaction was seen except the disappearance of the solid', 'a colourless solution was obtained', 'no new products were formed', or 'excess solvent allows more solid to dissolve' to support their answer that the white solid dissolved in excess sodium hydroxide. Thus, the above results seemed to indicate that the students mainly used perceptually-dominated thinking (Ebenezer & Erickson, 1996) – if a solid disappeared in a liquid, then it dissolved in the liquid. In addition, Ribeiro, Pereira and Maskill (1990) reported that if students do not see a new substance being formed, they tended not to refer to the change as a reaction. This problem was further compounded by students being taught to write that the precipitate dissolved in excess reagent, a 'standard' answer required in the examinations to describe the disappearance of the precipitate. When several student were asked why they used the term 'dissolve', they either said that they were taught to do so or that it was given in the datasheet that they used for qualitative analysis practical work. Thus, formal instruction could have caused students to have the idea, in the first instance, that dissolution took place, and perceptually-dominated thinking provided the explanation.

It has to be acknowledged that it is difficult to judge whether the disappearance of a white solid in a colourless liquid involves a reaction or mere dissolution. For example, the addition of sugar to water, and calcium oxide to dilute hydrochloric acid look similar at the macroscopic level, but sugar dissolves in water whereas calcium oxide reacts with the acid. Thus, students needed to know what the substances involved were and if they would react – the Grade 10 students were taught the formation of complex salts though they were not required to write the relevant equations. It could also be argued that at the microscopic level, the formation of the zincate ion is similar to the hydration of zinc ions when zinc salts are dissolved in water, the only differences being the ligands. However, when the solution is evaporated, sodium zincate is recovered and not zinc hydroxide, thus zinc hydroxide should be considered to react with sodium hydroxide rather than dissolve in it.

The authors decided not to consider students stating that a precipitate dissolved in a reagent because it formed a soluble compound with the reagent as an alternative conception (Item 2 – A4, 26%; Item 14 – A4, 16%; A4 in both items, 10%). Though the term 'dissolve' was inappropriate in the situations, the authors believed that the students could have understood what had occurred leading to the disappearance of the precipitate, and agreed with Brosnan (1999) that understanding of the phenomenon in this case was more important than the terms used to categorise the phenomenon. Clerk and Rutherford (2000) also argued that students' alternative understanding of labels should not be considered as alternative conceptions if they understood the concepts involved. In addition, as mentioned early, students were taught to describe the phenomenon as dissolving, so they could have continued to describe it as such even though they understood what had occurred. To consider that the precipitate dissolved in, instead of reacted with, the excess alkali because more alkali added meant more space/volume for the precipitate to dissolve (Item 2 - A1, 29%; Item 14 - A2, 25%), or that no new reagent was added and no further reaction except for the disappearance of the precipitate was seen is a different matter altogether. They did not indicate any understanding of the underlying reaction and hence, had to be considered as alternative conceptions.

Conclusion and caution

The results showed that Grade 10 students had difficulties in understanding the reactions involved in the testing for cations. Many students believed that a more reactive ion displaced a less reactive ion to form a precipitate when aqueous sodium hydroxide or ammonia was added to a salt solution resulting in the formation of a precipitate. This could be because of their 'stronger' learning of the reactivity series and displacement reactions of metals. Many students also believed that the precipitate formed (insoluble hydroxide) dissolved when excess alkali was added because more solvent was added or that no new reagent was added and no further reaction was seen. Perceptually-dominated thinking and the students being taught to describe such a phenomenon as 'precipitate dissolving in excess alkali' could be the cause of such alternative conceptions. However, cross-tabulation of the students' answers showed the lack of consistency of their alternative conceptions. This could be due to students holding several different conceptions and selecting a particular one depending on contextual cues, or having little understanding or thoughts about the reactions and either resorting to guessing or on-the-spot thinking.

The two-tier multiple choice diagnostic instrument on qualitative analysis used in the study was "both an outcome of a research process and an instrument for data collection in that same research venture" (Taber, 2000, p. 471). The instrument was developed from data derived from the first author's teaching experience and observations of qualitative analysis practical work, literature on student difficulties of chemical concepts related to qualitative analysis, student interviews, and students' justification of their first-tier choices in the early versions of the diagnostic instrument. Thus, the data from the administration of the diagnostic instrument acted "both to triangulate the interpretation of the existing data base and to broaden the 'sample size'" (Taber, 2000, p. 471). However, being a pen-and-paper test, it has inherent weaknesses of such tests. For example, students' language abilities, reading accuracy and interpretation of the items, test-taking ability, sincerity, carelessness, impulsiveness and anxiety could all affect their performance on the diagnostic instrument (Griffard & Wandersee, 2001; Clerk & Rutherford, 2000; Taber, 1999). The content framework which guided the development of the instrument also has to be considered (Hashweh, 1986) by the teacher before administering the instrument. This would prevent the testing of any concept if it was not taught to the students, or if it was not the aim of the course to foster understanding of the concept at the level tested. Using the diagnostic instrument developed for higher grades then it was intended for could be also problematic as students possessing additional knowledge of the concepts tested might be penalised when the additional knowledge causes the distracters to be more plausible to them (Griffard & Wandersee, 2001).

Sanger and Greenbowe (2000) contended that there was no guarantee that students actually had the alternative conceptions indicated by their answers, or that they did not have other alternative conceptions which were not addressed. Taber (1999) cautioned that only the most common alternatives were likely to be diagnosed as the test writer, based on previous research, would have to leave out the less common ones to avoid too many distractors. Voska and Heikkinen (2000) also noted that two-tier tests had the disadvantage of detecting far fewer conceptions than students may actually possess within a content domain and that a multiple choice test in which students had to supply their reasons for their choices could detect more alternative conceptions. They, however, did also acknowledge that the use of such approach within large classes was not feasible, and that the teacher's analysis and interpretation of results might be fraught with errors without formal training and without the benefit of information from student interviews. Thus, the selection of a multiple choice test with free response justification or a two-tier multiple choice test depends on the goals of the teacher in using the test. An alternative would be to give the option to students to write their reasons if they found that their reasons were not among those given in the second-tier. Students were given the option to do so during the administration of the QADI but less than 3% did so, and many of their reasons corresponded to the less popular ones which were eliminated in the early stages of the development of the diagnostic instrument. Thus, the teacher has to consider his/her goals, the strengths and weakness of such instruments, as well as the content framework of the instruments available before using them in their classes.

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Appendix: Examples of items in the QADI

Experiment A

Step	Test	Observations
a	To a sample of aqueous zinc chloride, add aqueous sodium hydroxide until a change is seen.	*A white solid is obtained.*
b	Add excess of aqueous sodium hydroxide to the mixture from (a).	*White solid disappears in excess reagent to give a colourless solution.*

1. What happens when aqueous sodium hydroxide is added to aqueous zinc chloride resulting in the white solid?

A Displacement
B Precipitation
C Redox

Reason/Justification

(1) The solution is too concentrated with sodium chloride so the sodium chloride comes out of the solution as a solid.
(2) Sodium hydroxide loses oxygen in forming sodium chloride and zinc chloride gains oxygen in forming zinc hydroxide.
(3) Sodium ion is more reactive than zinc ion.
(4) Zinc ions combine with the hydroxide ions.

2. In step (b), a colourless solution is obtained because the white solid _____ the excess sodium hydroxide.

A dissolves in
B reacts with

Reason/Justification

(1) More solvent is added so there is more space for the white solid to dissolve.
(2) No further reaction is seen except for the disappearance of the white solid, and no new reagent is added.
(3) Sodium ion displaces the cation from the white solid.
(4) The white solid forms a new soluble compound with the excess sodium hydroxide.

Experiment C

Step	Test	Observations
a	To a sample of aqueous copper (II) sulfate(VI), add aqueous ammonia until a change is seen.	*A light blue solid is obtained.*
b	Add excess of aqueous ammonia to the mixture from (a).	*Light blue solid disappears in excess aqueous ammonia solution.*

13. What happens when aqueous ammonia is added to aqueous copper (II) sulfate(VI) in step (a)?

A Displacement
B Precipitation
C Redox

Reason/Justification

(1) Aqueous ammonia gains oxygen in forming ammonium sulfate(VI) but copper (II) sulfate(VI) loses oxygen in forming copper (II) hydroxide.
(2) Copper (II) ions combine with the hydroxide ions.
(3) Copper (II) ion is more reactive than ammonium ion.
(4) Copper (II) ion is less reactive than the ammonium ion.

14. In step (b), why does the light blue solid disappear?

A It dissolves in aqueous ammonia.
B It reacts with aqueous ammonia.

Reason/Justification

(1) Ammonium ion displaces the cation from the light blue solid.
(2) More solvent is added so there is more volume for the light blue solid to dissolve in.
(3) No further reaction is seen except for the disappearance of the light blue solid, and no new reagent is added.
(4) There is a chemical reaction between the light blue solid and excess ammonia forming product(s) which is/are soluble