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Students' understanding of molar concentration

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This article presents and discusses the results of a study that investigates university students' comprehension of the concept of molar concentration, following teaching and evaluation of the subject. The specific problems underlying learning of this concept have not yet been focused on in sufficient detail or depth. A "Reasoning with molarity" questionnaire, which explores the logical–mathematical relationships between the variables *n*, *V* and *M*, was administered to 303 Argentine first-year university students. Results obtained from think-aloud interviews related to this questionnaire, which were performed with 18 students, are also analysed. These results reveal that approximately half the first-year university students have no clear conceptual understanding of molarity. The main difficulty arises in inverse proportionality tasks where the number of moles (extensive) and *M* (intensive) should be related qualitatively to determine which solution occupies the smallest volume. It was also established that much conceptual confusion, such as the lack of differentiation between *n* and *M*, lies behind the algorithmic, numerical solution strategy carried out exclusively by many students.

Introduction

Most biological processes and many chemical reactions occur between substances dissolved to form homogeneous mixtures or solutions. Their study requires consideration not only of the qualitative, but also the quantitative aspects of solutions associated with the concept of concentration. The subject of concentration of solutions is very important, since it is a basic, central concept in the chemistry curriculum both at secondary school and university levels. Specifically, the concept of concentration is a prerequisite applied to areas of chemistry such as stoichiometry, acids and bases, kinetic chemistry, equilibrium chemistry and electrochemistry (Calik *et al.*, 2010), to name but a few. However, this concept is not easily understood by the majority of secondary school (Adadan and Savasci, 2012) and university students (de Berg, 2012), which is problematic considering that it constitutes such a basic operational concept in experimental chemistry. The preparation of a solution with a specific concentration constitutes a primary goal in many general chemistry laboratories; notwithstanding, the procedure is poorly understood (Dunnivant *et al.*, 2002).

The review carried out by Gabel and Bunce (1994) showed this lack of comprehension on the part of secondary pupils. However, most research has focused on students' ideas about the nature of solutions and the process of dissolution rather than quantitative aspects. For example, in their bibliographical review article on learning about chemical solutions, Calik *et al.* (2005) did not include the concept of concentration.

Difficulties encountered when learning the concept of concentration have been discussed, together with secondary pupils, in many studies (Calik, 2005; Devetak *et al.*, 2009; Adadan and Savasci, 2012), but few articles have focused specifically on molar concentration (Duncan and Johnstone, 1973; Gabel and Samuel, 1986; Heyworth, 1999). Difficulties with the concepts of concentration (Pinarbasi and Canpolat, 2003; de Berg, 2012) and molarity (Niaz, 1995; Ryan, 2012) persist even in university students. Given the importance of these concepts, in comparison with other subjects dealt with in the area of research into chemistry teaching, very few studies centre on the learning process associated with the concept of concentration in general, and molar concentration in particular. This is particularly marked at university level; therefore, this study seeks to contribute to our knowledge of this process.

How the concept of concentration is learned was investigated in some studies in the context of the general characteristics of solutions (*e.g.* Adadan and Savasci, 2012). Learning of the concept of molar concentration has been explored as part of wider research, focusing for example on stoichiometry and the mole (Duncan and Johnstone, 1973; Johnstone, 1983; Dahsah and Coll, 2008; Khang and Sai, 2008), titration (Vincent, 1981; Anamuah-Mensah, 1986; Frazer and Servant, 1986), problem solving (Gabel *et al.*, 1984; Niaz, 1995; Heyworth, 1999; de Berg, 2012), analogous problems (Gabel and Samuel, 1986; Ryan, 2012) and proportional reasoning (Stavy, 1981; Gabel *et al.*, 1984; Ryan, 2012).

From the bibliographical review we can therefore appreciate the lack of articles that exclusively and thoroughly research

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understanding of the concept of molar concentration. This article aims to discover how first-year university students understand the concept of molarity, in an attempt to articulate contributions made in different areas, such as problem solving or conceptual learning. Results are also included from research in the field of mathematical education, related to proportionality.

Learning the concept of concentration of solutions

Many students find the concept of concentration difficult to understand (Calik, 2005) as it requires knowledge of previous concepts, such as substance and mixture, homogeneous mixture, dissolution, solute, solvent, and mass. It should be understood that concentration is an intensive property of a solution; that is, since the solution is a homogeneous mixture, its concentration is a constant property, irrespective of the size of the system under consideration. If, for example, a small amount of solution is removed, the remainder still has the same concentration. In contrast, the mass of solute and the volume of the solution are extensive variables, since their value depends on the quantities under consideration. Thus, if solute is added to a solution, its concentration increases, and if solvent is added, the concentration decreases. These relations hold true provided there is one constant variable in the system, as follows: (a) concentration is directly proportional to the amount of solute if the volume of the solution is constant, and (b) concentration is inversely proportional to the volume of the solution if the amount of solute remains constant (Stavy, 1981).

Stavy and Tirosh (1996) analysed the understanding of intensive properties in concepts like concentration and temperature. Their tasks consisted in presenting the subjects with two systems with identical intensive properties, but different sizes. Children between 6 and 10 years of age said that when two equally-concentrated sugar solutions are mixed, the resulting mixture will be more concentrated (sweeter). They justified their answers with two statements, "the container with more sugar is sweeter" and "the container with more water is sweeter".

Many erroneous conceptions about solutions were detected through particle representations (*e.g.*, molecules). At microscopic level, concentration is understood as the number of particles per unit volume. In some secondary (Devetak *et al.*, 2009) and university level (Smith and Metz, 1996; de Berg, 2012) studies, difficulty was found with correctly identifying and associating these variables; for example, some students focused more on the number of particles than on the number of particles per unit volume. Devetak *et al.* (2009) obtained better results in their study if the scenario presented had a constant volume, so that the students only had to consider the number of particles of solute to calculate the concentration; for example, where they had to draw twice the number of particles to double the concentration of a solution. The issues were more pronounced in scenarios where students were given two different volumes, since then they had to work with two different variables, the number of particles and the volume, to obtain two solutions of the same concentration, for example.

Adadan and Savasci (2012) also used microscopic representations and included an item on concentration where the solution was diluted to twice its volume. The following alternative conception was identified in the secondary pupils' answers: "If the volume of a solution increases due to dilution, the amount of solute dissolved per unit volume decreases, because the additional water increases the solubility of the sugar". This conception was attributed to the fact that these students conceived the molecular representations as undiluted sugar granules, and therefore, with the addition of water the number of granules diminished due to dissolution, and consequently they did not appear in the representation. This idea, that on diluting a solution the solute dissolves more, was also found among university students in the Niaz (1995) study when analysing the strategies they used to resolve chemistry exercises, though without using pictorial representations.

Some of the issues encountered may stem from the confusing characteristics of the submicroscopic representations used to assess understanding of the concept of concentration, given that these combine macroscopic aspects with submicroscopic elements (Andersson, 1990). In this respect, interpretation of chemical phenomena does not necessarily have to be reduced to the level of submicroscopic representation. Chemical explanations can focus on the macro and symbolic levels, using macro variables or properties of the system studied (Talanquer, 2011).

Difficulties in understanding molar concentration

Molar concentration, or molarity, is a measure of the concentration of a solute in a solution, in particular the number of moles of a solute per litre of solution. Its unit is mol L^{-1} or molar (M), and it is described by the formula $M = n/V$. Learning of this magnitude will depend on the level of comprehension of the concepts that make up its definition, especially the variable n (amount of substance) and its unit mole.

Concern for the difficulties encountered in learning about the mole is a recurrent theme in the literature (Novik and Menis, 1976; Dierks, 1981; Strömdahl *et al.*, 1994). As a product of the education they have received, students: (a) perceive the mole as a mass, or Avogadro's number (Staver and Lumpe, 1995); (b) associate the mole only with molecules, not with atoms or other entities (Krishnan and Howe, 1994); (c) do not differentiate between the concepts of molecule and mole (Dahsah and Coll, 2008); and (d) hold that if two substances have the same mass, they have the same number of submicroscopic entities (Dahsah and Coll, 2008).

Fang *et al.* (2014) proposed that comprehension of the concept of the mole goes beyond simply being able to state its SI definition, given that it includes the concepts of atomic or relative molecular mass, molar mass, and the connection between them, and in turn these involve concepts such as mass, atom, and molecule. These authors attribute the learning difficulties to the fact that for any given element, the molar mass in grams, the relative atomic mass and the mass of an atom in atomic mass units have the same numerical value, and to the high cognitive demand required to integrate the amount of substance at macroscopic level with the relative ideas of the atomic-molecular level.

A review of the literature revealed little previous research on the comprehension of molarity, especially in university students.

In addition, most articles dealing with the subject date before the year 2000, and as mentioned in the introduction, only addressed the topic as part of a wider study. One of the earliest studies to deal with difficulties in learning about molar concentration was an investigation carried out by Duncan and Johnstone (1973) on learning the concept of the mole. The results obtained from secondary pupils showed that 59% defined molar concentration as moles of solute per litre of water. Two thirds of the pupils were able to calculate which solution was more concentrated if the data were given in mL of solution and moles of solute. However, if the data were given in mL of solution and molarity, only 45% answered correctly. When asked which solution contained more solute, if the data were given in mL of solution and M, 38% answered correctly; approximately 50% failed to take volume into account and considered that whichever had more moles was more concentrated. These difficulties were attributed to a lack of knowledge regarding the definition of molarity, and confusion between molarity and number of moles.

Johnstone (1983) asked 16-year-old pupils which of the following solutions of sodium chloride was the most concentrated: (a) 1000 mL 2 M, (b) 800 mL 3 M, (c) 500 mL 4 M or (d) 200 mL 5 M. Half the pupils answered option b; that is, the one that had the highest number of moles. Using similar problems, Schmidt (1984) and Dahsah and Coll (2008) also identified confusion between molarity and number of moles.

The persistent failure of pupils to distinguish amount of substance (number of moles) from concentration (molarity) was observed, for example, in the teaching of titration (Vincent, 1981; Frazer and Servant, 1986) and pH (Khang and Sai, 2008). This confusion was also detected in two-thirds of pupils interviewed on chemical equilibrium (Bergquist and Heikkinen, 1990), and on applying Le Chatelier's principle (Quílez and Solaz, 1995).

This lack of differentiation may be reinforced by teaching if teachers are not mindful of the procedures used by students. For example, Raviolo *et al.* (2004) warned that when answering questions on the preparation of solutions, first-year university students write units of concentration where they should put units of amount of solute. If asked to prepare 500 mL of a 1.0 M solution, they write 1.0 M in 1000 mL, and therefore in 500 mL there would be 0.50 M, when both solutions should be 1.0 M. Reaching the correct numerical value of 0.50 reinforces this confusion between amount of substance and concentration.

Insufficient comprehension of the concepts involved could lie behind the algorithmic solving of molarity problems (Lutter *et al.*, 2019). Gabel *et al.* (1984) found that both successful and unsuccessful secondary pupils solved problems using algorithmic techniques and had difficulty answering questions about molarity due to a lack of conceptual understanding.

Some issues with problem solving may be related to establishing the proportionality relationships between molarity variables. For example, the study carried out by Anamuah-Mensah (1986) with secondary pupils identified two strategies used to solve traditional acid–base titration problems. One was based on formulas and the other on proportionality. The strategy based on formulas such as $M = n/V$ gave the greatest percentage of correct answers, even though it did not demonstrate qualitative comprehension of the problems or the relation between variables. Using the proportionality strategy, some pupils assumed there was a relationship of direct proportionality between the concentration and volume of a solution, which illustrates the confusion between n and M.

Conceptual difficulties can be aggravated if a solution undergoes transformations such as the addition or evaporation of solvent. For example, the research into chemistry problem solving carried out by Niaz (1995) with university students included two problems on the concentration of solutions. The first was a traditional problem, where students had to calculate molarity and molality from data on mass of solute and the volume and density of the solution. To answer the second problem, they had to choose the option correctly describing what happens to a solution with known molar concentration and density when a volume of water is added. The second problem, which is more conceptual and less algorithmic than the first, was correctly solved by few students because they did not take into account the constancy of the number of moles of solute. Similar results were found by Heyworth (1999) when interviewing secondary pupils.

Gabel and Samuel (1986) suggested that the issue lies in students not understanding what happens with molar concentration variables in processes like dilution or evaporation. When researching the difficulties shown by secondary pupils in solving molarity and similar problems based on everyday materials like lemonade, these authors found that the difficulties presented in the test using everyday materials were similar to those in the chemistry test, in scenarios where water was added to a solution (dilution) or it evaporated (increase in concentration). From these results they concluded that the issues go beyond lack of comprehension of terms like molarity, mole or molar mass, since these processes of dilution and increased concentration due to evaporation are not understood even in the daily environment.

Difficulties in establishing proportionality relationships

The study done by Stavy (1981) with pupils under 14 years of age concluded that the main difficulty in comprehending the concept of concentration was linked to the difficulty in understanding inverse proportionality; that is to say, understanding that an increase in the amount of solvent leads to a decrease in the concentration of the solution.

The topic of concentration of solutions was chosen to exemplify situations in studies on proportionality in mathematical education. In some of these studies, depending on the age of the participants, concentration was presented with qualitative scales such as: a stronger flavour of lemonade (Cramer and Post, 1993), greater sweetness in solutions of sugar in water (Hilton *et al.*, 2013) or a stronger orange flavour in solutions of powdered orange juice in water (Park *et al.*, 2010). Other interdisciplinary educational studies linked mathematics and chemistry, such as the work of Ramful and Narod (2014), who investigated proportional reasoning in stoichiometry, or Bakker *et al.* (2014) who analysed quantitative comprehension of the dilution process. These studies highlight the situated nature of mathematical abstraction in specific situations such as chemistry, where proportional reasoning is applied. They concluded that the complexity of this type of understanding of chemical processes lies in the units of concentration, since from a mathematical perspective only simple multiplication and division operations are involved.

Studies on proportional reasoning in mathematical education usually identify three types of task involving proportions (Cramer and Post, 1993): (a) problems of numerical comparison, (b) problems with a missing value and (c) problems of qualitative comparison or prediction. In numerical comparison problems four variables are given (a, b, c, and d), and the objective is to determine the order relation (more, less, the same) of a/b and c/d. In the missing value problems, three of the four values are given of the proportion a/b = c/d, and the missing value must be found. The qualitative comparison problems involve comparisons that do not depend on specific numerical values, and the problems may not even include them. Examples of this classification, which we have formulated to apply to the concept of molarity, are shown in Table 1 below.

Park *et al.* (2010) indicate that what is necessary are approaches that link ratios with proportions in specific situations, thus going further into the mathematical connections. This can be extended to the concept of concentration, given that teaching on solution concentration generally focuses more on situations involving proportions than on reasoning. Common problems include finding the missing value, cross multiplication, or the rule of three. What should be strengthened is the use of ratios, clarifying that quantity of solute per unit volume of solution is involved; *i.e.*, taking into consideration that it is an intensive quantity when reasoning proportionally.

A central aspect of proportional reasoning is its immersion in a context that supposes, simultaneously, the covariance of quantities and the invariance of ratios or products (Lamon, 2007). Covariance refers to simultaneous change in two variables between which there is a relation that links them, while invariance refers to constancy of the relation between the two variables, in one or various transformations. In the case of molarity, the number of moles and the volume of the solution can vary proportionally such that the ratio between the variables or molarity can remain constant. This is key to the complete understanding of concentration of solutions, and to correctly answering conceptual questions such as those investigated in this work.

The bibliographical review presented here reveals a lack of research focusing exclusively on the difficulties university students encounter when dealing with the concept of molarity. This article seeks to tackle this problem from a perspective that integrates different approaches (conceptual learning, problem resolution and the development of reasoning) in the discussion of the results obtained in this work.

Objective and research question

This study investigates comprehension of the concept of molar concentration in students in their first semester of university, following teaching and evaluation of this topic.

We aim to answer the following research question: What difficulties do first-year university students have with the variables involved in the concept of molarity (n, V and M) even after they have received teaching on the subject of solutions in general, and molar concentration in particular?

Methodology

Within the context of qualitative research on education, a theoretical framework guides the research questions and the methods of data collection and analysis (Bodner and Orgill, 2007; Merriam, 2009). This work takes a constructivist approach, which is a useful theoretical framework for a study that seeks to understand the construction of knowledge, alternative conceptions, and conceptual change over time. In research based on the constructivist perspective, the data collection methodology must be designed to help the researcher comprehend the concepts held by participants, where the aim is to investigate how knowledge is actively built by the mind of a learner who is trying to give meaning to an experience (Ferguson, 2007).

The design of this study follows the tradition of an interpretative and descriptive qualitative study (Merriam, 2002), where data is obtained from a questionnaire and interviews. The questionnaire (described in the next section) was designed to provide information on different types of conceptual and proportional reasoning, in accordance with the material found in the bibliographical review, and taking the research question into account. To aid interpretation of the completed questionnaire think-aloud interviews were conducted, a technique which allows participants to explain what they were thinking as they resolved the tasks (Herrington and Daubenmire, 2014).

Think-aloud interviews have been used with secondary level students in connection with chemistry subjects linked to the concept of concentration, to investigate how they solve problems dealing with moles, stoichiometry, gas laws and molarity (Gabel *et al.*, 1984), and volumetric analysis (Anamuah-Mensah, 1986; Heyworth, 1999). They have also been used with university students working on the concept of the mole (Staver and Lumpe, 1995).

Table 1 Examples of molar concentration questions classified according to the three types of proportionality task proposed by Cramer and Post (1993)

Types of proportional task	Example
Numerical comparison problems	Which of the following solutions is more concentrated? (a) 0.20 moles of solute in a 200.0 mL solution or (b) 0.40 moles of solute in a 500.0 mL solution.
Missing value problems	How many moles of solute are there in 200.0 mL of a 0.500 M solution?
Qualitative comparison or prediction problems	If you have two solutions with the same molar concentration, which contains more moles of solute? (a) the one that has less volume or (b) the one with more volume.

No study was found in the bibliographical review that used think-aloud protocols to investigate how university students reason when considering the concept of concentration.

Reasoning with molarity questionnaire (RWM)

The instrument used in this work is based on the relationships between the macroscopic variables involved in the molarity concept, to avoid difficulties related to the use of submicroscopic representations.

Molarity is a concept that links three variables pertaining to solutions: two independent extensive variables, n and V, and one dependent intensive variable, M. Understanding the concept of molarity implies establishing the correct relations between these three variables, which demands reasoning that involves management control of the variables and proportionality, in a chemical context that is not familiar to the students.

The logical-mathematical analysis of the $M = n/V$ equation is shown in Fig. 1.

The ''Reasoning with Molarity'' (RWM) questionnaire (Fig. 2) was drawn up to investigate the 6 mathematical relationships between the concentration variables, using qualitative comparative proportionality tasks (Cramer and Post, 1993). The result is a quickly-administered tool that enables in-depth study of comprehension of the molar concentration concept, without the potential interference of other factors such as the difficulties encountered by some students in the interpretation of particle diagrams. This questionnaire was tried out and discussed by a pilot group of 20 teachers who took part in a course on teaching the concentration of solutions, carried out during a national conference on chemistry teaching. This group of teachers agreed with the content and structure of the questionnaire, but following the discussion some improvements were made in the formulation of the questions.

The questionnaire evaluates whether the students can distinguish between the variables involved in the definition of molarity (n, V and M), and whether they are able to establish relationships of direct and inverse proportionality between them. It also assesses understanding of the molar concentration concept in scenarios where one of the variables remains constant and the other two must be compared. Determining the relation between two of the three variables requires proportionality reasoning that includes covariance and invariance simultaneously, in a single scenario (Lamon, 2007). Although mol dm^{-3} is the proposed SI unit, both the text books and teaching received by these students used mol L^{-1}.

$M.V = n$ k = proportionality constant

If M is constant:	V.k = n	higher V, higher n	lower n, lower V
If V is constant:	M.k = n	higher M, higher n	lower n, lower M
If n is constant:	$M.V$ = k	higher M, lower V	lower V, higher M

Fig. 1 Logical mathematical relationships between the variables included in the definition of molarity.

1) Which of the following 2 M solutions has the highest number of moles of solute?
   a. 300 mL
   b. 500 mL
   c. 100 mL

2) Which of the following 1.5 M solutions occupies the smallest volume?
   a. has 0.10 moles of solute
   b. has 0.50 moles of solute
   c. has 0.25 moles of solute

3) If you have 800 mL of each of the following solutions, which one has the highest number of moles of solute?
   a. 0.10 M
   b. 0.20 M
   c. 0.40 M

4) If you have 500 mL of each of the following solutions, which one has the lowest molarity, M?
   a. has 1.0 moles of solute
   b. has 0.25 moles of solute
   c. has 0.50 moles of solute

5) If all the following solutions have 0.10 moles of solute, which one has the highest molarity, M?
   a. 100 mL
   b. 300 mL
   c. 500 mL

6) If all the following solutions have 0.20 moles of solute, which one occupies the smallest volume?
   a. 0.80 M
   b. 1.0 M
   c. 1.4 M

Fig. 2 ''Reasoning with Molarity'' (RWM) questionnaire.

Participants

The questionnaire was answered by 303 first-year university students who were taking their first chemistry subject (Introduction to Chemistry or General Chemistry), with an average age of 20.3 years, standard deviation 3.2. Although the age range extended from 17 to 40, 71% of the students were between 18 and 20 years old. The sample consisted of 176 female students and 127 males who were taking a variety of courses (BSc in Biology or Chemistry, Engineering, and teaching degrees in Physics or Chemistry) in 5 national Argentine universities: Comahue, Río Negro, Río Cuarto, Litoral and Tecnológica. This study forms part of the 40-B-749 research project, approved by Rio Negro national university. The students were informed of the objectives of this work, and answered the questionnaire voluntarily.

The participants, who had recently begun university, had been taught chemistry for one or two years in secondary school, which implies that at this stage they should be familiar with the topic of solutions and have basic knowledge of its quantitative aspects (Ministerio de Educación, 2011). Over the preceding months these students had attended theoretical, problem solving, and practical laboratory classes, and had sat an exam that included the subject of molar concentration. Due to access-related issues, the interviews were conducted with a subset of the population that had completed the questionnaire, consisting of those living in the same locality as the researchers. Eighteen student volunteers from the Río Negro and Comahue Universities of the city of Bariloche were interviewed.

Procedure

The RWM questionnaire was administered (in Spanish) halfway through the university term, after the students had undergone evaluation in the subjects of chemical quantities, stoichiometry and solutions. It was given to participants in paper form at the end of a class, and they completed it in pencil.

Participants were informed that calculations should be done mentally – no calculator or paper and pencil should be used – to discourage the use of numerical resolution. In this way mechanical calculations were made more difficult, thus favouring the use of proportional reasoning, despite the presence of numerical values for the variables. This allows more in-depth analysis of the reasons for conceptual confusion (Lutter *et al.*, 2019). The average time taken to answer was approximately 15 minutes.

The validity of the content is based on the fact that the questionnaire exhaustively covers the six logical-mathematical relations between the three variables included in the definition of molarity. A Cronbach's Alpha reliability coefficient of 0.61 was obtained, a low value (George and Mallery, 2003). This value is acceptable for this study, whose aim is to investigate students' comprehension with an instrument that takes into account the logical-mathematical relations between variables involved in the concept of molarity. We are not dealing with an attitude scale, but rather a test that constitutes a construct that measures comprehension of a scientific concept (Taber, 2018), oriented towards investigating the reasoning that comes into play.

Think-aloud interviews

Think-aloud interviews are useful for gathering information concerning the cognitive processes followed when someone solves a problem (Ericsson and Simon, 1993). They also provide insight into how and why a participant used a certain piece of knowledge, process, or algorithm to solve a problem or complete a task (Herrington and Daubenmire, 2014).

These interviews were carried out (in Spanish) in order to investigate the knowledge, strategies and reasoning used by students to answer the RWM questionnaire. The literature confirms the value of think-aloud protocols as a way of exploring the thinking processes of individuals when the task offers an effective cognitive challenge, as the questionnaire used in this study does, and the interview can provide an authentic outlet for the internal process (Charters, 2003).

Students participated from each of two courses we had access to, and from each of these the first 9 who volunteered to take part were selected. The interviews were carried out the week after the questionnaire had been completed. There had been no discussion of the questionnaire following its administration. The procedure consisted in giving each student their completed questionnaire, without subsequent modification, and then asking how they had solved each of the 6 items, taking the questions in order. Audio recordings of the interviews, which lasted an average of 8 min, and complete transcriptions were made. The interviewees read the problem aloud, then stated how they had solved it and which answer they had given. In many cases this process of review and explanation of what they had done led to the correction of their answer they had originally arrived at. The interviewer did not interrupt them until they had finished explaining an item and tried to move on to another. Feedback was only given to let the participants know that their contributions were valuable, and to offer encouragement to expand on or confirm an answer, should it be necessary (Herrington and Daubenmire, 2014).

On completion of the interview, if participants had not mentioned it while doing the questionnaire, they were asked whether they had resorted to any type of representation, whether they had imagined something concrete other than calculations while solving the problems. Analysis of the interview transcriptions was performed separately by the three researchers, each identifying categories that were then compared and discussed before arriving at the categories finally agreed on. They then returned to the data to quantify the appearances of these categories and extract example paragraphs to illustrate each category.

Results

In order to evaluate the questionnaire, one point was allocated to each correct answer and zero points to incorrect answers. On a scale from 0 to 6, the average general result was 4.1, with a standard deviation of 1.4. The results are shown in Table 2:

The percentages of the options chosen, according to whether it was the correct, intermediate, or opposite answer, are shown in Table 3. The opposite answer is when they selected the opposite tendency, *i.e.*, the smallest value when the correct answer is the largest, or *vice versa*.

Of all the options chosen by the students, 67.8% corresponded to a correct answer, 26.2% to an opposite answer and only 5.4% to an intermediate one. This affirms that the questionnaire options were not chosen randomly, but followed

Table 2 Frequency of answers given for each option (N = 303). The correct answer is shown in bold

Item	1	2	3	4	5	6
Option a	12	**207**	30	58	**212**	153
Option b	**206**	75	9	**217**	9	22
Option c	82	18	**264**	28	78	**126**
Did not answer	3	3	0	0	4	2
Total	303	303	303	303	303	303

Table 3 Percentages of answers for each option (N = 303)

Item	1	2	3	4	5	6
Correct option	68.0	68.3	87.1	71.6	70.0	41.6
Opposite option	27.1	24.8	9.9	19.1	25.7	50.5
Intermediate option	4.0	5.9	3.0	9.2	3.0	7.3

some kind of reasoning. The tendency to polarization increases if we analyse only the items with the lower scores.

The correct answer was chosen in items 1 to 5 by over two-thirds of the sample, but they encountered particular difficulties when answering item 6, which involved inverse proportionality reasoning. Only 17.8% of the students answered all 6 questions correctly and only 1 student (0.3%) answered with the opposite option in every case.

The 18 students interviewed obtained an average of 4.4 (standard deviation 1.0) in the questionnaire, similar to the average for the entire sample. The results of the interviews are presented below, grouped by category, and representative quotes are given as examples.

Analysis of the interview results

Given that the students were thinking about specific exercises, the range of answers was not large and could be classified into hypothetical categories, many of which were reported in the literature review. Even though each researcher was alert to new findings in their independent reading, the inductive process of categorising the results was influenced by knowledge of the issues encountered by other researchers, such as: (a) the conceptual lack of differentiation between *n* and *M*, (b) algorithmic solving based on numbers, or (c) difficulties encountered in inverse proportionality reasoning.

Many students presented more than one type of reasoning during the interviews. The final categories are presented below, together with some transcription excerpts selected as being representative of said categories. These results are discussed in the following sections.

(a) Correct answers based on direct proportionality between two variables, while a third remains constant, in accordance with the proportionality attributes of covariance and invariance. These students can detach themselves from the numbers, and state the relation between two variables (11 students, in items 1–4 about direct proportionality):

"In the same quantity of 800 mL, the highest molarity, that is of moles, you get the highest quantity of moles." (S9, item 3)

"Obviously, if we have the same volume, the one with the highest quantity of moles of solute will be the most concentrated, because that is exactly what molarity tells us." (S11, item 3)

While no interviewee explicitly used the terms intensive or extensive, some students referred indirectly to these properties, mentioning that it had to do with the amount of solute per unit volume of solution, for each litre of solution:

"Molar concentration is the quantity of moles per litre. I think that per litre there are..." (S10, item 4)

"Because they all have the same molarity, it would be the same quantity of moles per volume, so the one with the lowest quantity of moles would have the least volume, so as to be equivalent." (S14, item 2)

Others explained the concept of proportion, saying, "the proportion is maintained":

"...as the volume increases, I'll have a greater quantity of solute, because the proportion is still the same..." (S11, item 1)

"...I considered it as proportion as well. The one with the lowest quantity of moles would have to have less volume, because it's the same molar value, it doesn't matter what the value is." (S18, item 2)

(b) Correct answers based on the inverse proportionality of two variables, stating that a third remains constant, in accordance with the proportionality attributes of covariance and invariance. These students can detach themselves from the numbers, and state the relation between two variables (11 students, in items 5 and 6 on inverse proportionality):

"Of course, if you have the same quantity of solute in them all, where there is less volume, it will be more concentrated." (S11, item 5)

"In all of them I have the same number of moles; c is more concentrated, so it must have the smallest volume. (S2, item 6)

(c) Numerical resolution: students specified that they were looking for the missing value or using the rule of three. They compared numbers, and did not generalize; they were unable to detach themselves from the numbers (9 students):

"I did the calculations in my head. 2 M means 2 moles in 1000 mL, that means 1 mole... in 300 mL. I tried to compare the highest with the lowest." (A3, item 1)

"I did the rule of three, in my head... 1.5 moles in 1000 mL of solution, so which is smaller...and so then you do the relation and that gives you the lower volume...I didn't do the exact calculation but you can tell..." (S1, item 2)

"2 M means that there are two moles in 1000 mL, in 500 mL, so many moles...it says which is the highest... I did the calculations... I answered them all in the same way." (S9, item 1)

(d) No conceptual differentiation between the number of moles and molar concentration (9 students):

"...this one that has a higher number of moles will have less volume, because this quantity of moles will be in less volume because the concentration is the same...; I mixed up the number of moles with concentration, yes, because what I thought was the opposite, with a higher quantity of moles, it has to be less volume..." (S2, item 2)

"So you have 0.20 in 1000... You have 0.20 concentration, 0.20 molar." (S4, item 6)

"In all of them you have 2 moles." (S17, item 1)

Some associated the solution with the highest volume as having the highest concentration (given a constant number of moles):

"I have the three solutions with 0.10 moles of solute; in the 500 mL one I have higher molarity." (S7, item 5)

"But it is more concentrated, the most concentrated occupies most volume." (S15, item 6)

Others assigned the lowest concentration to the solution with the smallest volume (given a constant number of moles):

"Since they all have the same quantity of moles, the one with the lowest molarity will also occupy the lowest volume." (S12, item 6)

Of the 9 students who solved the problems numerically, 6 showed a lack of conceptual differentiation between *n* and *M*.

(e) Reasoning that depends on some kind of concrete representation (7 students).

The representations used were macroscopic. None of the interviewees spontaneously used particle representations, with molecules for example:

''I did it with reasoning (with no calculations)...I imagined little balls, so I have the same (volume), in this one I have 10 balls, in this one 20 balls, and in this one 40 balls...I decided that 0.40 M was more, it's the one that has the highest number of moles of solute.'' (S1, item 3)

''I imagined an Erlenmeyer flask with water and a coloured liquid; the lighter the colour, the more dilute it is.'' (S10, item 4)

Asking the participants at the end of the interview whether they had resorted to any type of internal imagery or representation, if they hadn't already mentioned this, was an exploratory question. It was designed to reveal the type of representation they imagined while completing the questionnaire, basically whether they resorted to imagery with particles, and specifically, whether in their reasoning they considered the number of particles per unit of volume quantitatively, in line with the difficulties encountered in previous studies (Devetak *et al.*, 2009; de Berg, 2012).

The answers given to item 6 of the questionnaire are especially interesting, where a significant number of incorrect answers was obtained (58.4%). Five of the 18 interviewees chose the correct answer to this item, based on the inverse proportionality between the variables. Within the incorrect answers: six solved it numerically, four showed lack of differentiation between n and M, three stated that with a larger volume of solution the concentration is higher, and one said that with a smaller volume of solution the concentration is lower. Of the six students who solved it numerically, four showed confusion between n and M.

Discussion

Conceptual undifferentiation

The results obtained from the questionnaire can be explained to some degree by undifferentiation between the n and M concepts. As evidenced by the examples included in the previous section, in items 1, 2, 5 and 6, inversion of the n and M concepts in the questions led to selection of the opposite answer, which was the answer chosen by approximately 26% in items 1, 2 and 5, and 50.5% in item 6. This did not happen in items 3 and 4 since they dealt with constant volume, and confusion between n and M would lead to the same results. For example, if item 6 was ''read'' changing n for M, ''Which of the following solutions occupies a smaller volume if all have 0.20 M?'' the option with 0.80 moles would be chosen (the incorrect option selected by 50.5% of the students). This lack of differentiation was observed in the interviews in 9 out of 18 interviewees, some of whom recognised it explicitly, like S2: ''I mixed up the number of moles with concentration''.

Novik and Menis (1976) suggest that introducing molarity contributes to students' confusion, since concepts with similar phonetics are added, like mole, molecule, molecular and molar, which are all introduced to the students within a short lapse of time. The written form of the units also increases this confusion; for example, some students tend to abbreviate molarity as ''mol'' (Heyworth, 1999). In addition to the phonetical similarity between moles and molarity, there is equivalence in the numerical value: ''1.20 M implies 1.20 moles in...'', which contributes significantly to the lack of conceptual differentiation.

Confusion between the number of moles and molarity were explicitly mentioned in the research conducted by Dahsah and Coll (2008), Duncan and Johnstone (1973), and Johnstone (1983) and Schmidt (1984). In other studies this confusion was not evident because the scenarios presented had a constant volume (when n increased, M also increased, or *vice versa*), as for the example in the item assessed by Calik (2005) or the first problem of the study conducted by Devetak *et al.* (2009). As mentioned above, several studies show how the lack of differentiation between the amount of substance and molar concentration appears in later subjects on the curriculum, such as titrations, pH, and chemical equilibrium.

The confusion between molarity (M) and number of moles (n) can be considered a problem of conceptual undifferentiation, characterized by Talanquer (2006) as heuristic reasoning that enables students to simplify problem analysis or interpretation of concepts, reducing the factors under consideration. These naive ways of thinking underlie many alternative conceptions. In general, when people make decisions they tend to reduce the factors they analyse, focusing on one variable and ignoring others (Talanquer, 2014). This is a form of reduction where two different concepts are used indistinctly, without taking into account important aspects or conditions of their definitions.

It was discovered in the interviews that some students allude to representations when answering the questions, and that these representations are macroscopic, related to the density and colour intensity of the solution and the number of little balls within a volume. They do not spontaneously resort to using submicroscopic representations like molecules, which highlights how important it is that chemical phenomena are not reduced only to the level of submicroscopic representation (Talanquer, 2011) and that relationships between the macroscopic variables are discussed.

Proportionality reasoning

Difficulties in understanding the concept of concentration were attributed to inefficient reasoning related to basic proportionality (Devetak *et al.*, 2009; Adadan and Savasci, 2012) or to an inability to discern whether a situation involves direct or inverse proportionality (Anamuah-Mensah, 1986). Ryan (2012) considers that the difficulties encountered by students entering university do not lie in proportional reasoning fallacies, but in a lack of knowledge as to how to apply it in chemistry and in solutions in particular.

Half of the students interviewed solved at least one of the items numerically. They deliberately compared numbers, looking for the missing value, without working out a general idea of the relations between the variables involved. On the other hand, two-thirds of the students applied, in at least one item, reasoning of direct or inverse proportionality between two variables, recognising a third as constant. In these cases they were able to detach themselves from the numbers and state the order relation between two variables, relations like: when there is a greater volume of solution there is also a greater number of moles if concentration is constant, showing understanding of the covariance and invariance attributes of proportionality (Lamon, 1993).

In accordance with the results obtained by Stavy (1981), the principal confusion arose in item 6, which required reasoning on inverse proportion: if the number of moles is constant, the most concentrated solution will occupy least volume. Stavy and Tirosh (1996) consider that students' answers in situations of comparison, in different contexts of subject content and demands in terms of reasoning, are governed by a small number of intuitive rules, such as "more A means more B". In items 1, 2, 3 and 4, applying this rule leads to the correct result, while in items 5 and 6 it leads to the opposite, incorrect result "the most concentrated solution occupies most volume" (with an equal number of moles of solute). This tendency to generalise is reinforced by experiences that are apparently similar in educational and everyday contexts, and is considered intuitive reasoning, since to the person it seems obvious and gives them security. Although this rule is found frequently in children, it is not abandoned with age and can reappear in contexts that are unfamiliar to the person, such as in chemistry.

As in mathematics education, teaching on the concentration of solutions frequently highlights approaches with proportions (find the missing value, cross multiplication, or rule of three) more than on the ratios (Park *et al.*, 2010). For the concept of concentration, what should be emphasised is the use of ratios, stating explicitly that it involves a quantity of solute per unit volume of solution, *i.e.*, it must be taken into account that you are operating with an intensive quantity when reasoning proportionally.

A perspective that integrates different approaches

Thorough conceptual comprehension of molarity would imply knowledge and integration of the following aspects: (a) identification and differentiation of the variables involved in the definition of molarity (n, V and M), (b) recognition of the nature of these variables (extensive: n and V, intensive: M), and (c) establishment of the relations between them (of direct or inverse proportionality).

The low number of correct answers in item 6, in comparison with the others, may be explained by the complexity of a task associated with the type of variable they have to work with, and whether they are dealing with extensive or intensive properties. The notable difference (statistically significant, $t = 7.33$, $p < 0.01$), seen between the two items that required inverse proportionality reasoning, items 5 (70%) and 6 (41.6%), is due to the fact that in item 5 the student considers, or visualises, the number of moles in different volumes and arrives at the correct answer; that is, less volume, greater concentration. In contrast, in item 6 they have to consider the number of moles in different concentrations; that is, the relation between n and n/V, and conclude that higher concentration means less volume. In item 5, they are required to compare 0.10 moles in 100 mL, 0.10 moles in 300 mL and 0.10 moles in 500 mL, and a relation of inverse proportion is arrived at from the two extensive variables. In item 6, on the other hand, the student has to arrive at this relation of inverse proportion from one extensive variable and one intensive variable (a ratio). This generates greater cognitive load, as many variables have to be processed in the working memory at the same time, and the students were visibly perturbed when they faced this item on the questionnaire. The complexity of the content to be learned may result in cognitive overload, since information processing and knowledge construction are subject to the limitations of the learner's working memory (Sweller, 1994).

The intensive nature of concentration was considered and discussed in the study conducted by Ryan (2012), when issues arose in tasks where the students were presented with solutions of different volumes but with the same molarity. To many students these containers held the same amount of solute. By not reasoning in intensive terms, they thought the same molarity implied the same amount of solute. Some students who reasoned in extensive terms explicitly stated that "*M* is moles", confusing concentration with amount of solute. It was concluded that, for this type of simple task, students starting university do have proportional reasoning skills, but do not employ them correctly in tasks involving solutions. For these students, the ability to reason proportionally is based on a set of relatively simple explanations like the extensive reasoning framework, with a certain lack of mathematical rigor, due to not considering the intensive properties as proportionality constants (Wink and Ryan, 2019).

Stavy and Tirosh (1996) suggest that children (aged 6 to 10), who have no knowledge of the concept of intensive properties, are guided by the perceptible aspects of the total quantity of solution and apply reasoning of the "more A means more B" type. This was also observed in the work of Fassoulopoulos *et al.* (2003), who researched the ideas of Greek pupils (ages 12 and 15) regarding density. Twenty-five percent held the extensive perspective on density, that "density is greater in the glass with more water". They observed that most of the students that saw density as an intensive property, *i.e.*, independent of quantity, did so because they perceived density as dependent on the type of material more than due to proportionality reasoning that relates mass and volume variables. Students who have an extensive perspective tend to reduce the two variables (intensive and extensive) into one, according to the perceptual characteristics of the task. As pointed out by Johnstone (1983), for secondary level pupils the fact that the substances are in a solution makes it more difficult for them to understand aspects related to stoichiometry, due to the additional problem of differentiating intensive and extensive properties.

As in problem-solving in other areas, many of the difficulties encountered when learning the concept of concentration can be attributed to the use of algorithms when there is little understanding of the underlying concepts and the relationships between them (Nurrenbern and Pickering, 1987; Dahsah and Coll, 2008). An algorithmic problem is one that can be solved using a memorized set of procedures, whereas a conceptual problem requires the student to work from the understanding of a concept to a solution to the problem (Cracolice *et al.*, 2008). For these authors, the fact that most students in high school and college chemistry courses rely almost exclusively on an algorithmic approach is counterproductive for their longer-term needs in terms of chemistry coursework, since memorization of an algorithm does not lead to the development of cognitive skills such as those employed in scientific reasoning.

The fact that the RWM questionnaire had to be resolved mentally, with no help from a calculator or paper notations, discouraged the use of algorithms; nevertheless, half the interviewees were unable to detach themselves from the numbers and make general statements about the relationships between the variables involved in the concept of molarity. The algorithmic method used by these pupils consisted in introducing numbers into a formula or finding the missing value in the a/b = c/d equation.

Formula-based algorithmic resolution, an approach promoted by most textbooks, and mechanical numerical resolution can hide underlying issues in comprehension of the three conceptual aspects related to molarity. For example, in research carried out by Anamuah-Mensah (1986) it was observed that many students that tried to qualitatively solve traditional titration problems, without mechanically using formulas, assumed a directly proportional relation between concentration and volume of the solution, showing a lack of knowledge of the relation between variables. In the interviews carried out in this study, it was found that of the nine students that used a numerical resolution, six also showed no conceptual differentiation between n and M.

Knowing how to calculate concentrations is procedural knowledge that can be learnt by rote memorisation (Lutter *et al.*, 2019). This is reinforced by the most frequently used university text books, which present concentrations with formulas (with an unknown variable to be found), and in particular, they present molarity as a conversion factor between moles of solute and volume of solution. Cramer and Post (1993) admit that students can use memorized routines to solve numerical comparison and missing value problems, and that qualitative comparison problems (as in the reasoning required by the RWM questionnaire) are more conceptual, since they require understanding of the meaning of a proportion. They assert that this qualitative thinking enables the appropriate parameters for the problem scenario to be established, and the viability of the answers to be checked, which is necessary before carrying out calculations.

Conclusions

The results obtained from the questionnaire and interviews show that approximately half of the first-year university students do not have a thorough conceptual understanding of molarity, given that they show difficulties in one or more of the following, previously mentioned aspects: (a) identification and differentiation of the variables involved in the definition of molarity (n, V and M), (b) recognition of the nature of these variables (extensive: n and V, intensive: M), and (c) establishment of the relations between them (of direct or inverse proportionality).

Mastery of the concept of concentration involves solid understanding that enables the student to resolve any scenario involving the concept, regardless of its complexity. This means understanding the nature of solutions and the variables involved, recognising concentration as an intensive variable that links two extensive variables, and carrying out direct and inverse proportionality reasoning where one of the three variables is a constant.

While the main source of confusion arose in an inverse proportionality item, where intuitive answers of the "more X means more Y" type are not valid, understanding and applying the concept of concentration in this case go beyond the domain of this reasoning, as shown by the results obtained from item 6. We verified that the difficulty lies in the complexity of the task due to the types of variable that they have to associate. It is notably harder for them to apply inverse proportionality when they have to qualitatively relate the number of moles (extensive) to M (intensive) to determine which solution occupies less volume, than when they have to relate the two extensive variables to each other (item 5).

To understand and apply the concept of molar concentration, a student must have knowledge of the nature of the variables involved, and their behaviour in different situations. When a scenario appears complex, due to the kind of reasoning required or the number of variables to be manipulated simultaneously, many students resort to conceptual undifferentiation; that is, they simplify the number of variables by assuming different variables to be equal. In particular, they assume the amount of solute and the concentration to be equal, considering concentration as an extensive variable.

Solving concentration problems by relying on the mechanical use of algorithmic procedures hinders the students from seeing beyond the numbers and grasping the qualitative-conceptual relations between the variables involved, which would allow them to handle them correctly. In traditional education students are not usually faced with conceptual questions concerning solutions, as they were in the RWM questionnaire. In the interviews it was observed that merely by reasoning aloud the students recognised their mistakes and corrected the answers they had originally written in their questionnaires.

With respect to investigating students' difficulties in learning the concept of concentration, this study is limited to the specific case of molar concentration, which requires knowledge of the amount of substance and its unit, the mole, which students find very difficult to learn. To continue with this research, in the future we intend to produce another questionnaire for Argentine students, similar to the RWM one but with familiar magnitudes, like grams of solute per litre of solution, thus going into the concept of concentration in greater depth without mentioning units like molarity and molality that include the elusive (Nelson, 1991) concept of the mole. In addition, the study of internal images or representations used by the students in their reasoning, which was exploratory in character in this study, will also be further developed during another stage of this investigation.

As to the implications for teaching, we suggest presenting students with tasks where they apply proportionality reasoning aimed at qualitative prediction and comparison, like those presented in this study. During this type of task, it is advisable to encourage students to specify that they are analysing the relation between two variables while leaving a third variable constant. Class or small group discussion of the answers given individually in the questionnaire could be a helpful strategy.

Chemical conceptual comprehension and mathematical proportional reasoning must complement and reinforce each other simultaneously. In general, students have no difficulty with proportional reasoning, but rather with how to apply it to chemistry. The concept of molarity is learned in depth when all the mathematical relationships established between the variables involved are brought into play, which facilitates transfer of the concept of proportionality and its attributes of covariance and invariability to other areas such as chemistry.

Conflicts of interest

There are no conflicts to declare.

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