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Approximate Relations in pH Calculations for Aqueous Solutions of Extremely Weak Acids: A Topic for Problem-Based Learning

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ABSTRACT: This paper describes the implementation of problem-based learning in chemical education with regard to the impact that protolytic reactions have on equilibria. The problem-based task presented here is focused on extremely weak acids and calcuation of the pH value of their aqueous solutions. The task is based on comparisons of K_a ranges over which calculations using the universal cubic equation, quadratic equation with a nonlinear term, and the simplest equation for pH calculation (pH = $-\log[H^+]$) are each valid. Our students observed that an extremely weak acid can be defined as an acid with a pK_a greater than 8.13, with a relative error of 0.005 pH units, or 7.89, with a relative error of 0.01 pH units. Under these conditions, the quadratic equation without linear term serves as a universal formula. Students then solved a criterial equation using a quadratic equation without a linear term and the simplest formula to estimate the critical concentration, which is dependent on the pK_a value. Below this concentration, the simplest formula cannot be used. During practical applications, students observed that the critical concentration for hydrogen peroxide is very high (0.193 mol L^{-1}) and that the pH of its aqueous solution should be calculated according to a quadratic equation without a linear term in most of the practical examples. When traditional educational methods were used, students were unable to solve this problem properly, so we searched for a new way to solve this task. Taking into account the principles of problem-based learning, we designed a didactic cycle (as represented by a flowchart) for solving the above-mentioned problem. In this cycle, learning was aimed at the students, and the teacher only served as a facilitator. In this situation, the students' own work, research, and discovery were highlighted, together with the development of their chemical, mathematical, and IT skills.

KEYWORDS: *Second-Year Undergraduate, Analytical Chemistry, Equilibrium, Collaborative/Cooperative Learning, Problem Solving/Decision Making, Acids/Bases, Interdisciplinary/Multidisciplinary, pH, Student-Centered Learning*

■ INTRODUCTION

Protolytic equilibria is an integral component of chemical aqueous equilibria.[1−6] Understanding of this phenomenon is important in a chemist's training because it expands his or her chemical thinking.

Examples of protolytic equilibria should be simple to avoid complicated algebraic solutions that can only be solved using software, which in many cases, does not involve thinking about chemical systems using chemistry qualifications. In practice, teaching uses a common simple example that involves the calculation of the pH value in water as a solvent, which is achieved using the well-known formula:

$$\mathrm{pH} = -\log(a_{\mathrm{H_3O^+}}) = -\log([\mathrm{H^+}]\gamma) \qquad (1)$$

In analytical chemistry, $[H^+]$ is usually written instead of $[H_3O^+]$ as outlined in a study published in this *Journal*,[7,8] to avoid possible confusion in the proton solvation mechanism. In many cases, aqueous solutions are strongly diluted and the activity coefficient, γ, is equal to unity. The relation for the calculation of pH is

$$\mathrm{pH} = -\log[\mathrm{H^+}] \qquad (2)$$

Equation 2 is very simple, but calculation of the hydrogen ion equilibrium concentration $[H^+]$ is rather complicated. In practical calculations, the first step is to write equilibrium equations and find the species (cations, anions, and neutral molecules) that take part in the equilibrium process. The same number of equations as the number of species assures that the protolytic system can be solved. This procedure leads to relations in which the unknown parameter (in our case $[H^+]$) is present at a third or higher power; therefore, the solution of the problem is accessible only through iterative computation. For this reason, one should use some prerequisites to make the solution simpler by formulating approximate relations. The range of validity of these approximate formulas is poorly discussed in the literature to date and depends not only on the acid concentration but, in the case of weak acids, also on its strength. Derivations of the above-mentioned approximate formulas are readily accessible.[9] In the case of weak acids, derivation of the approximate formulas is based on the combination of the following equations: water autoprotolysis, charge balance, mass balance of the target acid, and a formula for the dissociation constant of a given acid. The derivation leads to the following formulas.

For the cubic equation

$$[\mathrm{H^+}]^3 + K_a[\mathrm{H^+}]^2 - (K_a c_a + K_W)[\mathrm{H^+}] - K_a K_W = 0 \qquad (3)$$

This equation is an exact relation for any weak acid concentration (c_a) and dissociation constant (K_a), where K_W is

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the dissociation constant of water. If $[OH^-]$ is comparable to $[H^+]$, eq 3 can be simplified to a quadratic equation:

$$[H^+]^2 + K_a[H^+] - K_a c_a = 0 \quad (4)$$

With a physically relevant solution

$$[H^+] = \frac{(-K_a + \sqrt{K_a^2 + 4K_a c_a})}{2} \quad (5)$$

Furthermore, if $[OH^-]$ is comparable to $[H^+]$ and $[H^+]$ is negligible in comparison with the concentration of an acid c_a, the well-known and simplest approximate formula for the calculation of the pH of a weak acid solution is obtained:

$$[H^+] = \sqrt{K_a c_a} \quad (6)$$

However, in the case of an extremely weak acid, where $[H^+]$ is negligible in comparison to the concentration of an acid c_a, but $[OH^-]$ is not negligible in comparison to $[H^+]$, then the quadratic equation without a linear term approximately describes the $[H^+]$ calculation:

$$[H^+] = \sqrt{K_a c_a + K_W} \quad (7)$$

The calculation of the validity range of certain approximate formulas is based on a criterial equation defined, for example, as

$$\frac{[H^+]_{(4)} - [H^+]_{(3)}}{[H^+]_{(3)}} \times 100\% = 2.28\% \quad (8)$$

The equilibrium concentrations of hydrogen ions were calculated according to eqs 3 and 4 at constant K_a, over a wide concentration range for c_a. The concentration of a weak acid that fulfills eq 8 is called the critical concentration (c_c). Below the critical concentration, the relative error between the equilibrium concentration of hydrogen ions, calculated according to eqs 4 and 3, is higher than 2.28%, which corresponds to 0.01 unit on the pH scale, and the quadratic equation cannot be used to calculate pH correctly. In this case, the critical concentration is very low; therefore, the cubic equation should only be used for stronger weak acids when the solutions are very dilute. A more interesting case is when quadratic eq 4 is compared to the simplest formula (eq 6). The critical concentration[9] has an exact expression

$$c_c = K_a\left[\frac{1 + x}{(1 + x)^2 - 1}\right]^2 \quad (9)$$

where x is defined as the error in percent divided by 100. As seen from this equation, the critical concentration depends not only on the pK_a value (acid strength) but also on the error, which has multiple definitions, but we used the above-mentioned value of 2.28% (0.01 pH). For stronger weak acids, e.g., oxalic acid (the second dissociation step was omitted), the critical concentration is unrealistically high. This result indicates that, according to this criterion, the simplest formula is not valid in all practical cases and a quadratic equation should be used instead. In our previous study,[3] we did not pay significant attention to extremely weak acids.

In the case of the equilibrium concentration of hydrogen ions in the aqueous solutions of extremely weak acids, $[H^+]$ comes from two significant sources, namely, from acid dissociation and autodissociation of water. The second source might be crucial for the pH value of extremely weak acid solutions; therefore, a pH value slightly below 7 is expected.

In this paper, we present a definition for extremely weak acids based on their protolytic behavior and the validity ranges of the calculations used for approximate relations for pH calculations in aqueous solutions. Both aspects were performed by students implementing problem-based learning (PBL) methods. We hope that this study not only will be useful as a PBL topic, but also will inspire teachers when generating calculation examples for protolytic equilibria in their courses.

■ BRIEF DESCRIPTION OF THE PBL METHOD

Implementation of PBL as an active learning teaching methodology has been published in a number of articles that describe its meaning, principles, benefits, and inclusion in various areas of education.[10−15] Our purpose is not to precisely define and describe the PBL method but to specifically demonstrate one approach in the topic of chemistry. We would like to mention only basic PBL principles that were applied in the task described here.

PBL is considered an inquiry-based instructional model, in which students are engaged with an authentic, ill-structured problem that requires further research.[16] Students identify gaps in their knowledge, conduct research, and apply their learning to develop solutions and present their findings.[17] In PBL learning, students learn how to analyze a problem; to identify relevant facts, generate hypotheses, and identify the necessary information/knowledge for solving the problem; and to make reasonable judgments about the solution of the problem.

Yew and Schmidt[18] elaborate on the cognitive constructivist process of PBL:

- Students activate their prior knowledge on the presented problem, and through discussion within their group.
- In their group, students create possible theories or hypotheses to explain the problem. Together, they identify learning issues to be researched and construct a primary model to explain the problem. Facilitators provide scaffolding, a framework for students to construct knowledge relating to the problem.
- After the initial teamwork, students work independently in self-directed study to research the identified issues.
- Finally, students return to the group to discuss their findings and refine their initial explanations based on what they discovered.

In PBL, student attention centers on a complex problem that does not have a single correct answer. Students work in collaborative groups to identify what they need to learn to solve the problem. They are engaged in self-directed learning (SDL) to apply their new knowledge to problem solving and reflect on what they learned. The teacher helps facilitate the learning process instead of providing facts. The goals of PBL include helping students to develop flexible knowledge, effective problem-solving skills, SDL skills, and effective collaboration skills.[19]

Problem solving is a highly effective approach for acquiring knowledge based on student-centered learning (SCL). Learning is focused on the learners, allowing them to conduct their research and integrate theory and practice.[20] PBL is an inductive learning method, namely, the learning of specific concepts leading to more general knowledge.[21,22] Jansson[23] applied this approach to environmental chemistry teaching and found several educational advantages, including enhanced

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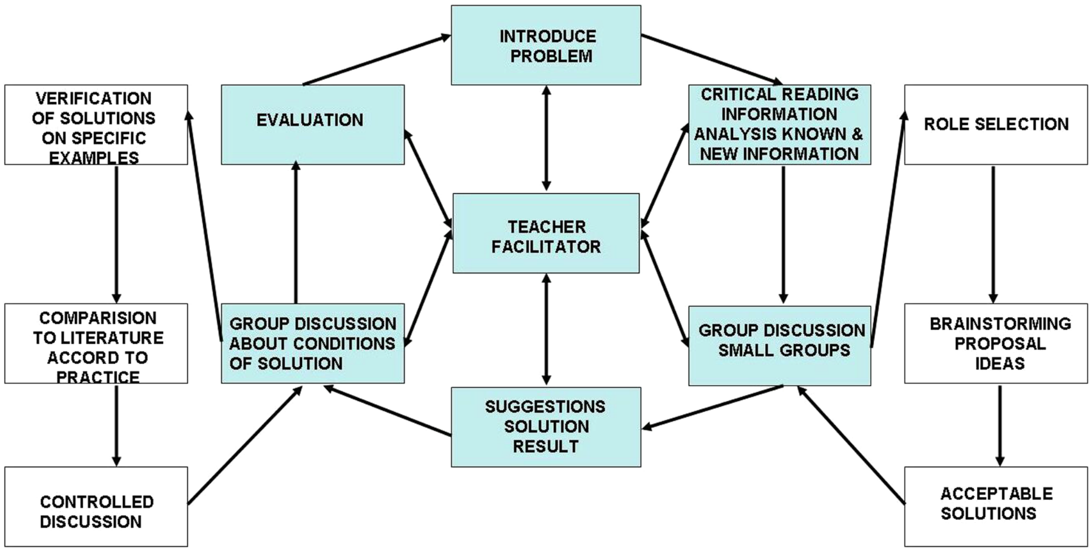

Figure 1. Didactic interpretation cycle (white boxes indicate work in groups).

creative thinking ability, self-regulated learning skills, and self-evaluation in Master's level courses.

■ DIDACTIC INTERPRETATION OF THE PROBLEM TASK

When compiling a problem or task, we tried to link the task to a subject lesson with the presence of an unknown element (problem), forcing researchers to acquire new information, relationships, and knowledge based on logical interconnections, and to develop an inductive approach that would lead to the solution.

As mentioned in the Introduction, the presented task focused on extremely weak acids; therefore, the exact assignment given to the students was stated as follows.

Derive exact and approximate relationships for calculating the pH for simple cases of protolytic equilibria in extremely weak monobasic acids in dilute aqueous solutions. Determine the range of validity of the individual relationships and when they can be used to calculate the pH with sufficient precision.

This task was given to undergraduate students studying subject combinations: chemistry−computer science and chemistry−mathematics. On the basis of the above-mentioned principles of the PBL method and using our specific problem, we developed a didactic interpretation cycle (presented as a flowchart) to solve the problem, which is shown in Figure 1.

This task was an extension of previously acquired knowledge on weak acids and stimulated student interest because they had already worked with acids in chemistry classes and in real life.

The problem was given to the students at the beginning of the course both verbally and in written form to familiarize students with the main objective, to precisely define and elaborate the specific goals (Table 1). Motivation in the course was ensured by requiring critical reading (searching for data) from various sources on compounds that are classified as weak or extremely weak acids. The findings regarding their real-life interactions with weak acids were very interesting. Students began to have a stronger interest in the problem. During the task, students and teachers critically assessed what they already knew about the task and what needed to be learned from different sources. By using appropriate remarks, the teacher directed the students to think about how weak and strong acids behave in aqueous solutions and how the dissociation process proceeds. From group discussions, students concluded that weak acids behave according to the Brönsted theory because they do not completely dissociate, and using acetic acid as an example of a weak acid cited in their textbook, they described a weak acid equilibrium system. In the solution process, they used the relationship for the dissociation constant K_a[10] and had no problem observing the conditions that influenced the concentrations of undissociated molecules and ions in the aqueous solution. They also used the relationship for the water ionic product K_W.[11] At the same time, they derived the neutrality condition of the solution[12] and the acid mass balance.[13] By using the subsequent mathematical operations, students derived the relationship for the dissociation constant of acid.[14]

$$K_a = \frac{[A^-][H^+]}{[HA]} \tag{10}$$

$$K_w = [H^+][OH^-] \tag{11}$$

$$[H^+] = [A^-] + [OH^-] \tag{12}$$

$$[HA] + [A^-] = c_a \tag{13}$$

$$K_a = \frac{\{[H^+] - (K_W/[H^+])\}[H^+]}{c_a - [H^+] + (K_W/[H^+])} \tag{14}$$

Students also solved eq 14 for $[H^+]$, leading to relation 3which is a universal cubic equation.

The next step was to create study groups, at which point the students received their roles. Each group included students in the second year of their bachelor studies that were studying chemistry, mathematics, and informatics. The participants of the "Selected Chapters on Analytical Chemistry" course had access to analytical chemistry textbooks, chemical tables, computers running Word and Excel software, and the Internet. The two research groups worked independently and exchanged the knowledge they gained at the end of the course. They compared the obtained results and discussed what caused the most severe problems in each group. This information was beneficial not only to the investigators but also to the teacher.

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Table 1. Concretization of the Objectives of the Given Problem Task

Specific Objective	Students' Initial Finding	Expected Solution	Equation
Describe the equilibrium system of very weak acids and derive relation for K_a in water solutions	Basic knowledge from protolytic equilibria, K_a, K_W	The condition of solution electrical neutrality	12
	Mathematical skills required for equation solving	Acid balance	13
		Relation for dissociation constant of the acid	10
		Relation for ionic product of water	11
		Final relationship for K_a	4
Express the exact solution for $[H^+]$ and find the simplifying relations for calculating $[H^+]$ under specific conditions	Mathematical and IT skills required for solving equations (cubic, quadratic) and the ability to make approximate	Cubic equation	3
		Quadratic equation	4
		Quadratic equation without a linear term	7
		The simplest relationship	6
On the basis of the protolytic behavior of weak acids, decide when (at which pK_a) it is possible to talk about extremely weak acids	Ability to process numeric and graphical data and mathematical solutions of equations, knowledge of iterations	At an error tolerance of 1.14% (0.005 pH) at a pK_a value over 8.131, it is possible to use a quadratic equation without a linear term	7
		There is an error tolerance of 0.01 pH units (2.28%) for a pK_a over 7.891	
Determine when is it possible to utilize the simplest relationship for calculation of pH	Ability to make mathematical operations in equations	Use the criterial equation for the simplest relationship instead of a quadratic equation without a linear term	18
Verify the results on real examples of extremely weak acids	Ability to navigate the literature, searching known facts about acids	HCN, HBrO, H_2O_2, C_6H_5OH	

Students followed specific objectives (Table 1, column 1), which gradually led them to the solution of the problem.

RESULTS AND SOLUTIONS

Two partial tasks were solved in the groups: on the basis of the protolytic behavior of weak acids, decide when (at which pK_a) it is possible to talk about extremely weak acids and which equation should be used for calculating the pH value. The solution of this problem was reached by the active participation of all course members because they analyzed the problems in groups that included students from computer science and mathematics. The students knew the principles and procedures of the calculation process, as well as understood the problem from a chemical standpoint. Chemistry students without these approbations learned how to complete chemical computations using software. Chemical, mathematical, and IT literacy was increased to a higher level using this method.

Cubic equation 3 is unusable for manual calculations; it is rather difficult to find a real root. The teacher managed students' ideas, which were rather chaotic. He guided them in such a way that there were different possibilities regarding how to solve the given equation, either using numerical methods of calculation or considering a modification of eq 3 under certain simplifying assumptions. Numerically, students solved the cubic equation using Newton's or Cardan's method.

When solving the cubic equation according to approximate relationships, the students found three simplifications: a quadratic eq 4, the simplest relation 6, and a quadratic equation without a linear term 7, as described in the Introduction. Then, they were able to solve the problem according to these simplified equations.

All of the groups of students monitored the change in pH value in all four equations for a given range of pK_a and for highly diluted solutions and compared the obtained values (the deviation between individual results). Students also drafted a graphical representation of pH dependence with concentration for a given pK_a value in the concentration range between 1 and 1×10^{-16} mol L^{-1}. It was necessary to monitor all 4 equations. The students were advised to monitor how pH changes as a function of pK_a value and identify significant changes. The students found it is useful to look at the relation between pH_{eq3} (according to the cubic equation) and pH_{eq7} (according to the quadratic equation without a linear term).

Figure 2 shows the dependence of ΔpH calculated as the difference between the pH value calculated according to the cubic equation and the pH value calculated using the quadratic equation without a linear term for pK_a values of 6, 7, 8, and 9, vs the concentration. As seen from this dependence for pK_a = 9, the ΔpH value does not exceed 0.005 of pH units over the entire concentration range. It means that the cubic equation can be fully substituted by a quadratic equation without a linear term as a universal formula and that a weak acid with a pK_a value of 9 can be considered to be an extremely weak acid.

It was clear that the pK_a value defining an extremely weak acid lies between pK_a values of 8 and 9. Further calculations showed that the limiting value is 8.131 (Figure 3). This limiting value of pK_a, which determines whether a given weak acid is extremely weak or not, also depends on the error of the pH calculation. In our further calculations, one group of students observed that if the acceptable error of the pH calculation is 0.01 pH units, then the limiting pK_a value for the determination of an extremely weak acid is equal to 7.891.

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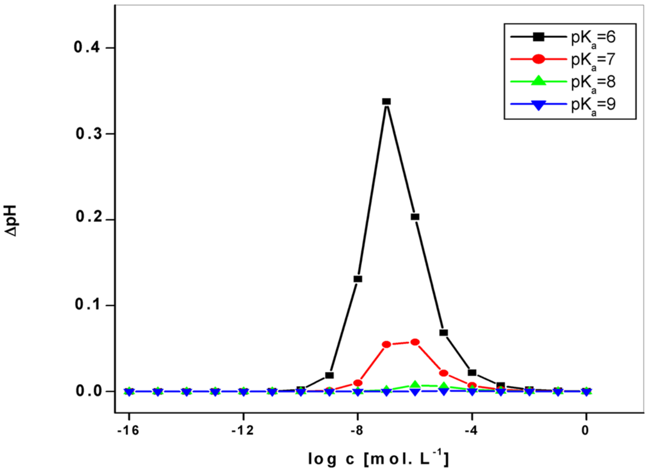

Figure 2. Dependence of ΔpH ($pH_{eq3} - pH_{eq7}$) on the concentration for pK_a = 6, 7, 8, 9.

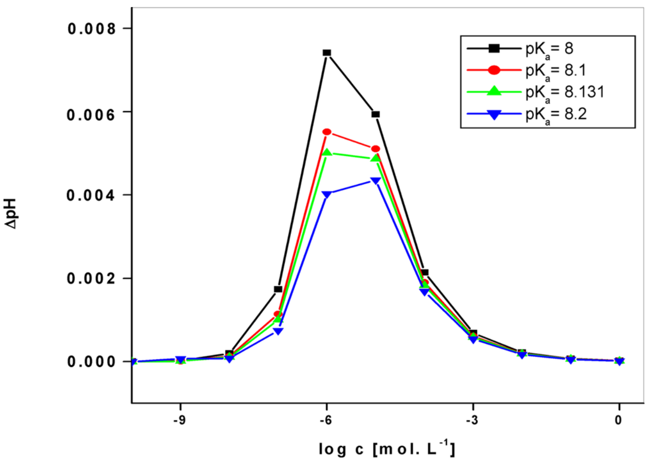

Figure 3. Dependence of ΔpH ($pH_{eq3} - pH_{eq7}$) on the concentration for pK_a = 8.0, 8.1, 8.2, 8.131.

After defining an extremely weak acid, students solved the next partial task that focused on the applicability of the simplest equation instead of the quadratic equation without a linear term for the pH calculation of an aqueous solution of an extremely weak acid. This task is based on the determination of a value for the critical concentration. Below this value the simplest formula cannot be used. The critical concentration value also depends on the error of the pH calculation, which is defined as

$$x = \frac{[H^+]_{(7)} - [H^+]_{(6)}}{[H^+]_{(7)}} \times 100\% \tag{15}$$

We used two values for x (x = 1.14% is equal to 0.005 on the pH scale and 2.28% corresponding to 0.05 on the pH scale). The critical concentration was determined from the following equation:

$$\frac{[H^+]_{(6)}}{[H^+]_{(7)}} = 1 - x \tag{16}$$

Hence:

$$\frac{\sqrt{K_a c_a}}{\sqrt{K_a c_a + K_W}} = 1 - x \tag{17}$$

The solution for critical concentration is

$$c_c = \frac{(x-1)^2}{2x - x^2} \times \frac{K_W}{K_a} \tag{18}$$

After this step, a group discussion was performed with the teacher participating as a facilitator providing constructive feedback to the groups to make the results more systematic. Finally, the results were applied to concrete examples of extremely weak acids.[24−27] Students suggested examples (Table 2) and found those with pK_a values above 8.131. They also discussed ambiguities for these values present in the literature. Students further verified the validity of the quadratic equation without a linear term compared to the simplest formula and calculated the critical concentration, as summarized in Table 2. As seen from this table, the critical concentration increases with the acid weakness (i.e., higher pK_a), and for H_2O_2, the value is so high that all real examples (diluted solutions) should be calculated only according to a quadratic equation without a linear term.

■ CONCLUSIONS AND FUTURE OUTLOOK

Students had an active connection with the entire process of problem solving (a student-centered learning, SCL approach). On the basis of their previous and novel knowledge, students determined suitable problem-solving strategies, literature references, procedures, and goals. They also monitored advances in their own education process (a self-directed learning, SDL approach).

The teacher had two purposes in the educational process. The first was to organize teaching activities for the students, and the second was to serve as an information source. Due to its many advantages, the PBL method cannot be overvalued. Procedures for using the method should be re-evaluated for a given topic to reach the highest effectiveness for the teaching

Table 2. Comparison of Critical Concentration Values for Selected Extremely Weak Acids

extremely weak acid (example)	pK_a	Exact equation		Critical concentration [mol.L^{-1}] error = 0.005pH		Simplest equation
HBrO	8.6	$[H^+] = \sqrt{K_a c_a + K_W}$	<	1.71629.10^{-5}	<	$[H^+] = \sqrt{K_a c_a}$
HCN	9.32	$[H^+] = \sqrt{K_a c_a + K_W}$	<	9.00072.10^{-4}	<	$[H^+] = \sqrt{K_a c_a}$
C_6H_5OH	9.89	$[H^+] = \sqrt{K_a c_a + K_W}$	<	3.346491.10^{-3}	<	$[H^+] = \sqrt{K_a c_a}$
H_2O_2	11.68	$[H^+] = \sqrt{K_a c_a + K_W}$	<	0.192570478	<	$[H^+] = \sqrt{K_a c_a}$

0 ⟶ extremely weak acid concentration

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process. Teacher training before might be time-consuming as well as dependent on students' abilities to solve problems. When creating problems and tasks, knowledge of the level and abilities of students for independent study should be considered.

Pedagogical Outcomes

It was not our purpose to investigate the PBL method but to develop a concrete problem task in a university course using the principles of PBL. This method has the potential to merge chemistry knowledge with other scientific fields (in this case mathematics and informatics). One of the main advantages of this teaching method is cooperation among students in groups. Our research showed that students' results were improved if they worked in a creative environment while simultaneously forming verbal and communication skills in the framework of group cooperation.

The topic presented here was implemented in a novel compulsory–facultative course called "Selected Chapters on Analytical Chemistry". This course includes extended teaching topics on analytical chemistry with problem-divergent tasks, with a focus on solving skills for analysis, synthesis, and evaluation.

Our aim was fulfilled because, in this course, when teaching was performed according to the proposed didactic model, the students solved the given problem task correctly, but in the case of traditional teaching, the students were unsuccessful.

Finally, students liked this task, and the PBL was an effective learning method for them, not only because of the enforcement of active learning but also due to development of understanding of the presented equations from a mathematical and chemical perspective. The metacognitive abilities of the students were enhanced. Additionally, students positively evaluated their ability to acquire and keep knowledge for a longer time due to the logical derivation of formulas and their validity over a concentration range dependent on the pK_a value when working in groups with teacher management. These observations are very promising and demonstrate the positive efforts for students to be active in their studies in university courses.

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Notes

The authors declare no competing financial interest.

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