Aqueous biphasic systems and biofuels: Implementation of a formative experiment for students in chemical engineering

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Abstract

The present experiment intends to get the students familiarized with aqueous biphasic systems, a new type of liquid-liquid equilibrium that is currently being used in different biotechnological processes due to its benign character. Therefore, an aqueous solution of bioethanol will be concentrated after a preliminary definition of the binodal curve.

Keywords

Formative experiment, Aqueous biphasic systems, Bioethanol, Purification, Salt, Sustainability

Introduction

The production of bioethanol for its use as fuel in mixtures with gasoline is under the subject of a great academic interest. Although the so-called first generation of bioethanol was obtained from primary agricultural raw materials like wheat or cane sugar, which led to increased food prices (Drabik et al, 2016), the second and third generations bet in lignocellulosic materials or algal cells (Shuba and Kifle, 2018). However, the high costs associated to the latter are still hindering the extension and generalization of these technologies.

In this scenario, chemical engineers are called to play a relevant role to design novel green and competitive strategies for processing these raw materials. One of the steps bearing high processing costs is the bioethanol purification, which usually demands the installation of distillation units. To illustrate the necessity of applying new separation methods, the students will be trained in liquid-liquid extraction technique as an appealing alternative to energy-intensive vapor-liquid-based processes.

Considering the current education trends, where the students play a more active role, this laboratory practice intends to strengthen the theoretical knowledge on Operation Units acquired during the previous course of Chemical Engineering. Apart from that, the concepts of environmental sustainability and competitiveness will be prioritized to make the students aware of the skills that future chemical engineers should pursue during their professional life.

Among the possible options, aqueous biphasic systems (ABS) have been highlighted due to several advantageous features: low cost, availability of segregation agents at bulk quantities, low energy consumption and spontaneous phase disengagement (Freire et al, 2012). These systems are composed of two hydrophilic compounds that become immiscible over a certain mass composition, thus leading to two aqueous phases (Albertsson, 1986). Therefore, the aqueous mixtures of bioethanol can be salted out by several high density charge inorganic salts containing phosphate, carbonate or dihydrogenphosphate anions. These salts have been chosen in order to compel the students to analyze which one would entail the greater salting out effect. To do that, the well-known Hofmeister series must be consulted, and important thermodynamic concepts tackled in the course "Thermodynamics and heat transfer" (belonging to the second year of Chemical Engineering degree, as established in the official curriculum) like Gibbs free energy or entropy of hydration will be required.

Therefore, the construction of the binodal curve in an ABS will be the basis for this formative experiment in undergraduate Chemical Engineering laboratories, as a preliminary step to apply the obtained data to a real aqueous sample containing bioethanol. Additionally, the lecturers have envisaged the visit to a real bioethanol manufacturing plant in order to ease the grasp of the biotechnological process.

Student learning

The experiment was addressed to 26 students from the 3rd year in the degree of Chemical Engineering, working in pairs. Prior to developing the experimental procedure, the students had to read the information regarding bioethanol, aqueous biphasic systems, Hofmeister series, Gibbs free energy and entropy of hydration. Then, during the first part of the laboratory class, a discussion was favored by the teacher in order to elucidate which salt would be the best for being employed in the ABS determination. Analogously, the correct way to determine the binodal curve was approached by explaining them the main underlying concepts. Afterwards, each group started the experiment by the cloud point method. Briefly, the students used a glass tube to prepare a binary mixture of water and ethanol (about 50 % wt) and the selected inorganic salt was added until a turbid solution was observed. Once the mass of inorganic salt was quantified, water was drop-wise introduced in the glass tube until a transparent solution was obtained. Again, the mass of water was ascertained, and the operation was repeated for 12 times at room temperature and under magnetic stirring. The visual aspect of the turbid and transparent solutions can be seen in figure 1.

Figure 1**.** Glass tube containing a transparent (left) and turbid (right) solution.

Once the binodal curve was determined, the students were instructed to represent their experimental data in an orthogonal representation instead the conventional triangular diagram, and the results obtained are presented in figure 2. As an example, the data of 5 groups have been included in this figure and they allow concluding that most of the experimental data fall in the same place, which confirms the success of almost all the groups to map the boundaries of the biphasic region. It should be noted that the first points are crucial for a proper determination of the binodal curve, so the teacher should pay a special attention during this part of the experiment.

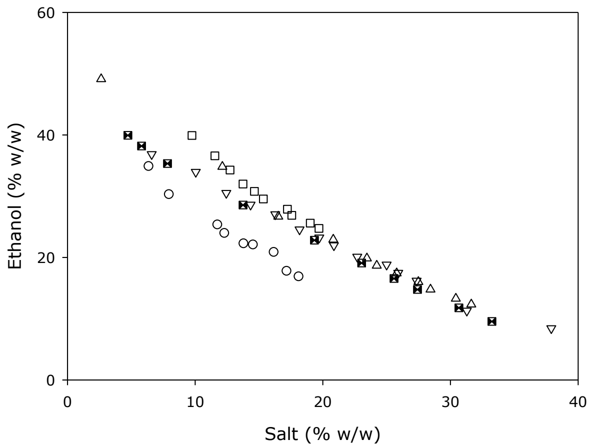

Figure 2. Binodal curves for the ternary systems ethanol, salt and water.

Then, the students were asked to apply an empirical mathematical model developed by Merchuk et al (1998).

$$Y = A\exp\left[\left(BX^{0.5}\right) - \left(CX^{3}\right)\right]$$

where *Y* and *X* are the ethanol and inorganic salt mass composition, respectively. *A*, *B* and *C* are the fitting parameters, which values were calculated by the students after minimizing the root mean square deviation with the Solver function in Microsoft Excel.

Finally, the students applied the system to a real sample obtained from the bioreactor of a bioethanol manufacturing plant, and they were able to concentrate the bioethanol in the upper phase by leaving the sample in a decanter for 15 min. Therefore, by simple mass balance, the students were able to calculate the tie-line and concentrate the bioethanol from 18% to 50%.

After having finished the practice six different items were evaluated to learn about the student performance. The results are presented in figure 3.

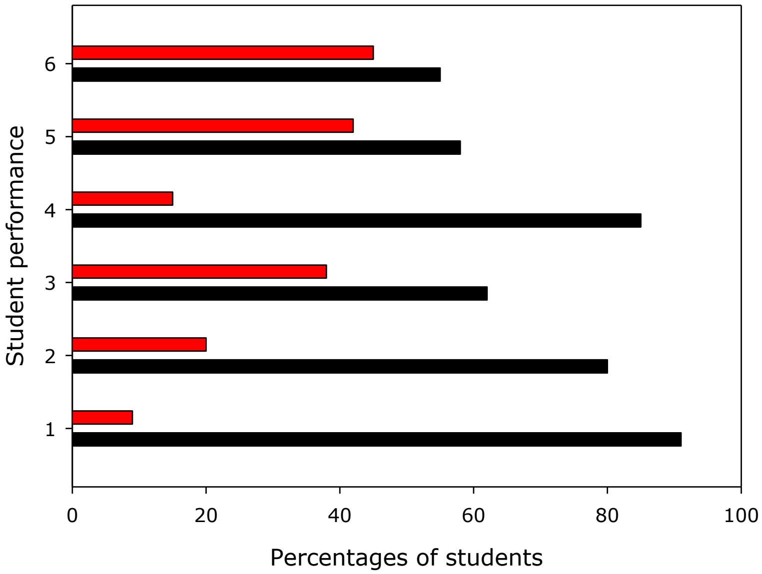

Figure 3. Students performance of the different parts of the experiment: 1.-The students understood the cloud point method; 2.- The students got the orthogonal representation; 3.- The mass balances to represent binodal curves were correctly carried out; 4.- The biphasic and monophasic regions were suitably identified in the phase diagram; 5.- The students were able to detect the alcohol and salt rich phases; 6.- The data modelling was appropriately performed

All the students were able to finish the experiment in the scheduled time (two hours), and different degrees of academic performance can be detected depending on the task under evaluation. Thus, three items were easily understood by most of the students, like the development of the cloud point method, the transformation of ternary systems into orthogonal representations and the identification of the biphasic and monophasic regions.

On the contrary, most of the learning difficulties are focused on the calculation of the mass balances to represent each point of the binodal curve, the identification of the main components in top and bottom phases, and the modelling of the experimental data. The reason behind this is that, at this stage, the students knowledge in liquid-liquid equilibrium is mainly based on theoretical concepts acquired during master classes, so the translation to the lab experiments is always challenging. Therefore, it is recommended that the students should be given a special support during the calculations, phases identification and data modelling.

Conclusions

The main premise for introducing this experimental practice for students is the 3rd year of the degree in Chemical Engineering is to get them familiar with experimental issues related with the liquid-liquid extraction technique. However, even if students had done some conventional liquid–liquid extraction experiments, the present laboratory practice makes up an innovative approach getting together concepts of green chemistry and biocompatible separation strategies. Terms like salting out agents, Hofmeister series, molar Gibbs free energy of hydration, molar entropy of hydration, cloud point method or orthogonal and triangular representations will be awoken and incorporated by the students in their academic skills, at the framework of a booming field like biofuels production.

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