A Flow System for Video Demonstrations: Comparative Evaluation of the Stability of Some Cuprate(II) Complexes

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Abstract

An analytical flow system for class demonstrations is proposed. A digital camera monitors the flow-through cuvette, allowing images of the flowing sample to be real-time displayed on a large screen. The demonstration involves in-line formation and monitoring of different coloured cuprate(II) complexes. By taking into account the typical coloration of the gathered images, it is possible to classify the complexes according to their stability constants. Concepts of analytical selectivity and sensitivity are discussed. The flow system is rugged and portable, requiring minute amounts of solutions.

Keywords Video demonstration, stability constants, flow analysis

1. Introduction

For a truly formative education in Chemistry, use of different teaching methodologies involving e.g. video demonstrations and / or classroom experiments related to the chemistry of everyday life plays a key role [1]. Novel approaches to assist the knowledge transference become then essential. In this context, several strategies have been proposed to improve the teaching of chemistry, usually involving pedagogical kits, micro-scale laboratories, alternative materials and / or specific computer resources [2].

However, the teaching-learning process may still require innovations in order to become more dynamic. Aspects more related to stability of complexes in solution are within those needing particular attention. In general, the approach has been only theoretical, as a practical demonstration is usually limited by the need for large volumes of solutions involving relatively expensive reagents. Moreover, the experiments normally are not repeated at will [3]. This limitation can be overcome by using analytical flow systems which have been considered as excellent solution managers [4]. Among their main features the high sampling rate and the low sample and reagent required volumes can be highlighted.

Flow systems have been widely used for large scale analysis [5] but their use for practical activities in classrooms for improving the teaching of analytical chemistry is still incipient [6]. Most of these activities involve flow injection systems [7-11] into which classical experiments are implemented in a modern manner. This aspect plays a positive influence to increase the students' interest by practical demonstrations that, in their classical versions, would be tedious and repetitive. The analytical flow systems are recognized by their portability [12] and this feature is an additional positive factor in relation to their use in didactical experiments. In this context, images of the flowing sample can be obtained by resorting from computer facilities [13,14], photographs [15] or zone sampling [16]. For real-time image gathering, a slide projector [17] or a CCD digital camera [18] can be used.

This paper reports the use of an analytical flow system with a digital camera for video demonstrations. In this context, an experiment exploiting the formation of different complexes with the same element [19] was selected aiming at a qualitative and comparative evaluation of their stabilities. The Cu(II) complexes with water, ammonia, ethylenediaminetetraacetate (EDTA) and diethyldithiocarbamate (DDTC) as ligands were selected in view of their markedly different stability constants and their different colours in aqueous solution.

Among the above mentioned complexes, the tetraaquo-cuprato(II), $[Cu(H_2O)_4]^{2+}$, is the least stable [3], and can be formed by dissolving a cupric salt in water. The resulting solution is pale bluish.

When ammonia is added to a $[Cu(H_2O)_4]^{2+}$ solution, the water molecules of the complex are gradually replaced by ammonia molecules, leading to formation of aqua-ammonia complexes, and the colour is modified towards intense indigo [3,20]. The process ends up with the formation of the tetraaminocuprato(II) complex, $[Cu(NH_3)_4]^{2+}$, as this later complex is more stable relatively to $[Cu(H_2O)_4]^{2+}$ [3]. The overall process can be described by Eq. 1:

$$[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O \qquad \text{(Eq. 1)}$$
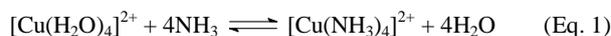
EDTA, a classical ligand, forms a stable complex with the cuprous ion [20] according to Eq. 2:

$$Cu^{2+} + [H_2EDTA]^{2-} \rightleftharpoons [Cu\text{-}EDTA]^{2-} + 2H^+ \qquad \text{(Eq. 2)}$$

where $[H_2EDTA]^{2-}$ = anion of the EDTA disodium salt.

Analysis of Eq. 2 reveals that the stability of the formed complex, $[Cu\text{-}EDTA]^2$, is dependent on the hydrogen ion activity (pH) in the reaction environment. The resulting aqueous solution is blue greenish.

DDTC has been widely used in spectrophotometric determinations of copper [21]. The complex is formed according to Eq. 3 and the resulting aqueous solution is brownish.

$$Cu^{2+} + 2[DDTC]^- \rightleftharpoons [Cu\text{-}(DDTC)_2] \qquad \text{(Eq. 3)}$$
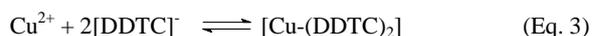
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In view of the different stability constants and colours of the involved solutions [19,21], an approach to classify the complexes according to their conditional stability constants can be proposed. To this end, similar volumes of two solutions involving the above-mentioned ligands are mixed together, and the colour of the resulting solution indicates the dominance of the more stable complex. By several times carrying out this procedure in order to include all the solutions, the stability constants can be comparatively evaluated. It becomes then possible to sort the complexes according their stabilities in water solutions.

This demonstration involves several repetitions of a solution mixing procedure, and is then more efficiently accomplished in an analytical flow system. Moreover, the required volumes involved are quite small.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with analytical grade chemicals and distilled water.

The solution used to mimic the inserted sample (S - Fig. 1) was a 0.1 mol L^{-1} Cu solution prepared by dissolving 2.50 g $CuSO_4.5H_2O$ in 20 mL of a 0.07 mol L^{-1} HNO_3 solution and filling the volume up to 100 mL with water. The C carrier stream was a 0.1% (v/v) HNO_3 solution. Both S and C solutions were acidified in order to prevent Cu^{2+} hydrolysis and eventual precipitation of the formed products as a result of carry-over [22] with other alkaline solutions.

R_1 was a 0.03 mol L^{-1} NH_3 solution based on a 28% (v/v) NH_3 stock solution.

R_2 was a 0.13 mol L^{-1} EDTA solution, prepared by dissolving 5.0 g Na_2EDTA in about 70 mL of water, adding 10 mL of a 0.10 mol L^{-1} $Na_2B_4O_7$ solution, adjusting the pH to 10 with a 0.1 mol L^{-1} NaOH solution and filling the volume up to 100 mL with water.

R_3 was a 0.02 mol L^{-1} DDTC solution, prepared by dissolving 0.50 g Na_2DDTC in about 80 mL of water, adjusting the pH to 10 as above and filling the volume up to 100 mL with water [23].

The concentrations of EDTA and DDTC were set according to the corresponding methods for the spectrophotometric determination of copper [21]; a high ammonium concentration in R_1 was needed as a guarantee of quantitative formation of the $[Cu(NH_3)_4]^{2+}$ complex.

2.2. Apparatus

An IPC-08 Ismatec peristaltic pump with TygonTM pumping tubes was used for propelling the solutions. Three-way MTV-3-N1/4UKG Takasago solenoid valves controlled by computer through the PCL-711 Advantech interface card were used for inserting and directing the involved solutions.

Transmission lines and helical tubular reactors were made of polyethylene tubing with an internal diameter of 0.8 mm.

A digital camera (Webcam) with video output, was positioned near a 178-OS Hellma flow-cell (inner volume = 80 µL; optical path = 10 mm) in order to collect the images along the cell optical path. It was connected to a Legend LX-8 multimedia projector through a RCA cable. In this way, images of the solution inside the flow cell could be real-time gathered. Better contrast was attained against an illuminated white wall.

2.3 Flow diagram

The analytical flow system was designed to allow all possible combinations of the solutions involved. Flow rates of the involved streams and length of the RC main reactor were selected as 2.0 mL min^{-1} and 50 cm, respectively.
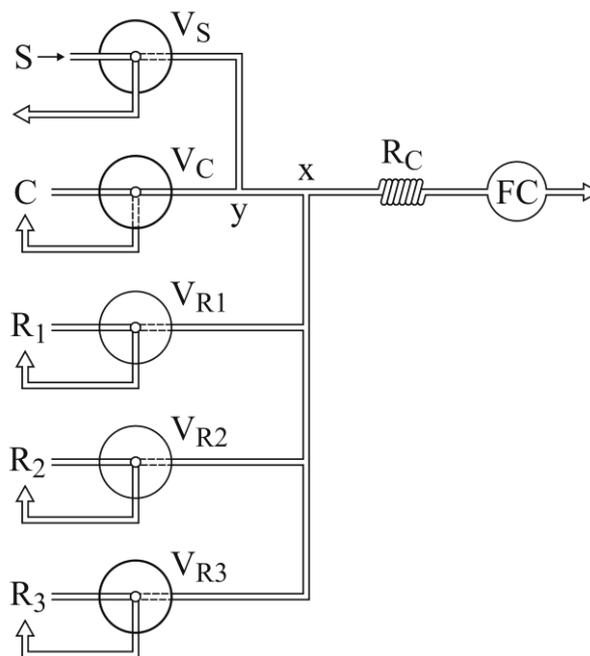

Fig. 1. Flow diagram of the system used to visualize the different formed complexes. S, C, R_i = solutions involved; V_i = solenoid valves; x, y = confluence points; R_C = coiled reactor; FC = flow-cell monitored with the digital camera. For details, V. text.

In the situation specified in Fig. 1, the V_C valve directed the carrier stream towards detection, and the other valves were positioned to allow recycling of the corresponding solutions. Thereafter, V_C and V_S were simultaneously switched in order to insert the S solution into the analytical path and recycle the C solution. The S solution could merge with any other solutions (R_1, R_2, R_3) depending on the respective valves (VR_1, VR_2, VR3). Three or even all solutions involved could be combined to support the demonstration. When passing through the flow-cell, the image of the flowing sample was monitored and displayed on the large screen (Fig. 2). By analysing the colours resulting from the combination of all the solutions, it was possible to infer the relative stability of the different cuprate(II) complexes. Thereafter, the processed zone was directed to the flask for waste collection and treatment.

3. Results and discussion

The flow system proposed for video demonstrations proved to be very rugged and stable, as the images related to a given situation were always very similar to each other. Consequently, the different solutions could be real-time identified, according to the colour modifications (Fig. 2)
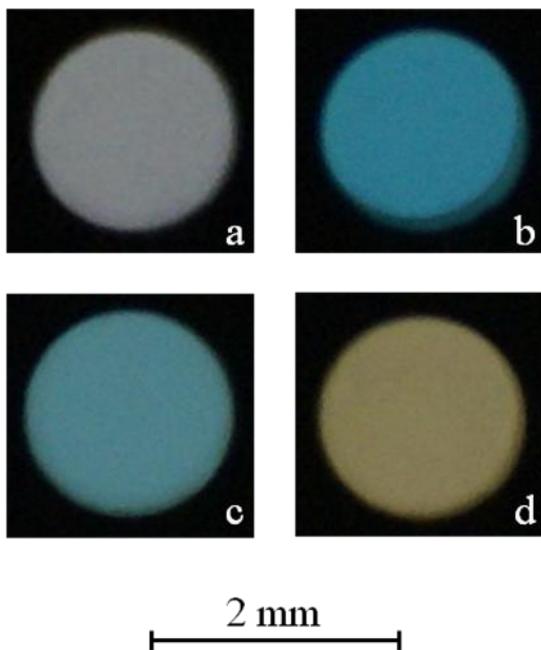
Fig. 2. Displayed images. Lettering a, b, c, d = tetraaquo, tetraamino, EDTA and DDTC cuprate(II) complexes.

The images were achieved ca 10 s after valve switching and the chemical equilibria were always reached. This later feature was confirmed by switching the peristaltic pump off when maximal colour intensity was noted: no further increase in coloration of the displayed image was observed. This aspect constitutes itself as a guarantee that the observed images truly reflected the chemical equilibria involved.

In aqueous solution, cupric ions are coordinated with water molecules, and the related pale blue tetraaquocuprate(II) complex is shown in (Fig. 2a). By adding the aqueous ammonia solution, the colour was changed to indigo blue (Fig. 2b) due to the ligands replacement (Eq. 1) and consequent formation of tetraaminocuprato(II).

Addition of EDTA led to the formation the complex outlined in Fig. 2c, as Cu^{2+} ions were quantitatively complexed during the residence time of the S solution inside the analytical path. The pH of the reaction medium plays a significant role in complex formation with this ligand, called chelation. The $[Cu\text{-}EDTA]^{2-}$ complex is stable in alkaline solutions and the decrease in pH reduces this stability, since hydrogen ions compete with cupric ions.

The importance of the pH value is less pronounced in relation to the copper complexation with DDTC, as it may occur in a wider [4-11] pH range [20]. In the presence of DDTC, the formation of a brown-yellowish suspension was noted (Fig. 2d). It should be stressed that the diethylditiocarbamate cuprate(II) complex can be extracted in organic solvents slightly miscible in water, such as e.g. carbon tetrachloride, and the strategy is often exploited in analytical procedures aiming at improvements in sensitivity and/or selectivity [24].

By taking into account the real-time displayed images of the flow-through cuvette, it was possible the elaborate Table 1, which is referred to the experiments involving all the possible combinations of S with the R_1-R_3 solutions and the consequent formation of the different complexes $[Cu(H_2O)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$, $[Cu\text{-}EDTA]^{2-}$ or $[Cu\text{-}(DDTC)^2]$. Analysis of

Table 1 allows one to conclude that these complexes can be ordered according to their stability constants: tetraaquo < tetraamine < EDTA < DDTC [3,19].

Tab. 1. Results from the video demonstration. Symbols as in Figs 1 and 2.

Solution	colour	dominant complex
C	colourless	nihil
S	a	$[Cu(H_2O)_4]^{2+}$
S + R_1	b	$[Cu(NH_3)_4]^{2+}$
S + R_2	c	$[Cu\text{-}EDTA]^{2-}$
S + R_3	d	$[Cu\text{-}(DDTC)_2]$
S + R_1+R_2	c	$[Cu\text{-}EDTA]^{2-}$
S + R_1+R_3	d	$[Cu\text{-}(DDTC)_2]$
S + R_2+R_3	d	$[Cu\text{-}(DDTC)_2]$
S + R_1+R_2+R_3	d	$[Cu\text{-}(DDTC)_2]$

4. Conclusions

The stability of a complex is related to the characteristics of both the metal ion involved and the ligand, and this aspect was confirmed by the formation of the different complexes according to combinations of involved solutions.

The characteristics inherent to the proposed flow system, especially the portability and low consumption of solutions (about 0.5 mL) are appropriate for video demonstrations. This feature, and the excellent image visibility, makes the strategy more attractive when too many students are in the classroom. The better interaction student / teacher during the demonstrations, as well as the possibility of multiple repetitions of the experiments, should also be emphasised.

The cuprate(II) complexation depends on the activity of the chemical species considered (concentration, ionic strength), reaction stoichiometry, pH value, temperature, metal-ligand affinity, possibility of hydrolysis and acid-base dissociation of the ligand in the medium. These theoretical aspects should be discussed apart from the video demonstration. This limitation

was not critical in the present situation, as the chemical systems were characterized by stability constants very different from each other. Moreover, the determination of the stability constants was not aimed at.

By modifying the concentration of the S solution (Fig. 1), concepts related to sensitivity and detection limit could be also discussed, as well as the sequences of reactions involved in the analytical procedures. To this end, a simpler flow system with only one confluent reagent, eventually manually operated, could be used.

References

[1] T. R. Alvim, J. C. Andrade, *Quim. Nova*, **29**, 168, (2006).

[2] D. G. Abreu, C. R. Costa, M. D. Assis, Y. A. Iamamoto, *Quim. Nova*, **29**, 1381, (2006).

[3] E. J. Slowinski, W. L. Masterton, W. C. Wolsey, Chemical Principles in the Laboratory, W.B. Saunders Company, Philadelphia, 1977, p. 219.

[4] F. J. Krug, H. Bergamin-Filho, E. A. G. Zagatto, *Anal. Chim. Acta*, **179**, 103, (1986).

[5] Y. Iida, FIA bibliography (53). *J. Flow Injection. Anal.*, **27**, 74, (2010).

[6] B. R. Kowalski, J. Ruzicka, G. D. Christian, *Trends Anal. Chem.*, **9**, 8, (1990).

[7] E. H. Hansen, J. Ruzicka, *J. Chem. Educ.*, **56**, 677, (1979).

[8] J. A. Nobrega, A. A. Mozeto, R. M. Alberici, *J. Chem. Educ.*, **68**, 966, (1991).

[9] J. A. Nobrega, F. R. P. Rocha, *J. Chem. Educ.*, **74**, 560, (1997).

[10] R. P. Sartini, E. A. G. Zagato, C. C. Oliveira, *J. Chem. Educ.*, **77**, 735, (2000).

[11] F. R. P. Rocha, P. B. Martelli, B. F. Reis, *Quim. Nova*, **23**, 119, (2000).

[12] S. D. Kolev, I. D. Mckelvie, Advances in Flow Injection Analysis and Related Techniques. In: Comprehensive Analytical Chemistry, D. Barceló (Ed), Wilson & Wilson's, Amsterdam, 2008, p. 777.

[13] J. T. Vanderslice, A. G. Rosenfeld, G. H. Beecher, *Anal. Chim. Acta*, **179**, 119, (1986).

[14] H. Wada, S. Hiraoka, A. Yuchi, G. Nakagawa, *Anal. Chim. Acta*, **179**, 181, (1986).

[15] T. Korenaga, F. –H. Shen, H. Yoshida, T. Takahashi, K. K. Stewart, *Anal. Chim. Acta*, **214**, 97, (1988).

[16] E.A.G. Zagatto, O. Bahia-Filho, H. Bergamin-Filho, *Anal. Chim. Acta*, **193**, 309, (1987).

[17] I. D. McKelvie, T. J. Cardwell, R. W. Cattrall, *J. Chem. Educ.*, **67**, 262, (1990).

[18] N. Maleki, A. Safavi, F. Sedaghatpour, *Talanta*, **64**, 830, (2004).

[19] Wellington College UK. A2 Experiment 14.5(2) – Ligand exchange in copper(II) complexes. http://intranet.wellingtoncollege.org.uk/resource.aspx?id=15576, accessed on December 2010.

[20] Vogel, A.I. Análise Química Quantitativa; LTC. Press: Rio de Janeiro, Brazil, 1992.

[21] A. P. Smirnova, V. V. Chernysh, M. A. Proskurnin, *J. Anal. Chem.*, **59**, 424, (2000).

[22] R. E. Thiers, R. R. Cole, W. J. Kirsch, *Clin. Chem.*, **13**, 451, (1967).

[23] D. D. Perrin, B. Dempsey, Buffers for pH and Metal Ion Control; Chapman & Hall Press, New York, 1974.

[24] Z. Marczenko, Separation and Spectrophotometric Determination of Elements; John Wiley & Sons Press: New York, 1986.