

Automated electronic tongue based on potentiometric sensors for the determination of a ternary anionic surfactant mixture

Montserrat Cortina, Christina Ecker, Daniel Calvo, Manuel del Valle*

Sensors and Biosensors Group, Department of Chemistry, Autonomous University of Barcelona, Edifici Cn, 08193 Bellaterra, Spain

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Abstract

An automated electronic tongue consisting of an array of potentiometric sensors and an artificial neural network (ANN) has been developed to resolve mixtures of anionic surfactants. The sensor array was formed by five different flow-through sensors for anionic surfactants, based on poly(vinyl chloride) membranes having cross-sensitivity features. Feedforward multilayer neural networks were used to predict surfactant concentrations. As a great amount of information is required for the correct modelling of the sensors response, a sequential injection analysis (SIA) system was used to automatically provide it. Dodecylsulfate (DS^-), dodecylbenzenesulfonate (DBS^-) and α -alkene sulfonate (ALF^-) formed the three-analyte study case resolved in this work. Their concentrations varied from 0.2 to 4 mM for ALF^- and DBS^- and from 0.2 to 5 mM for DS^- . Good prediction ability was obtained with correlation coefficients better than 0.933 when the obtained values were compared with those expected for a set of 16 external test samples not used for training.

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1. Introduction

Surfactants are involved in numerous industrial and domestic purposes (emulsions for paints, pharmacology, detergents, etc.), where they are used in aqueous media but also in organic or hydroorganic media [1]. Mixtures of surfactants are often explored to enhance their performance properties; among these we can enumerate foaming, wetting, emulsification or solubilisation of soil, dirt and pharmacological active compounds [2]. Such a wide application of surfactants may result in the pollution of surface waters. Hence, the fact that their determination, as intermediates, in final formulation or in the environment, has been focused by many works with several analytical approaches, including titrimetry [3,4], spectrophotometry [5,6], spectrofluorimetry [7,8], chromatography [9,10] and electrochemical methods incorporating ion-selective electrodes (ISEs) sensitive to surfactants [11–13]. However, some of these methods, such as spectrofluorimetry and chromatography, need expensive equipment and special pretreatments.

Potentiometry using ISEs for anionic surfactants is a very convenient option, given its simple measuring scheme and the reduced efforts in pre-treatment of sample. Variants have been described for global detection of anionic, cationic or non-ionic surfactant types. However, simultaneous detection of several components by means of direct potentiometry is only possible in some cases, since highly selective sensors are needed and some limitations are imposed on the composition of the solution under analysis.

In ISEs sensitive to ionic surfactants, an ion association ($A^+ \cdot B^-$) is used as the electroactive element in a polymeric membrane, in which the anion B^- is an anionic surfactant and the cation A^+ is usually a cationic surfactant. Normally, sensors for surfactants employ a poly(vinyl chloride) (PVC) polymeric membrane specially formulated for an optimal response. Depending on the used ion-pair, different selectivity patterns are recorded for a set of surfactants. In the present work, an array employing surfactant ion-associations with larger selectivity, plus cyclic ligands and ion pairs of generic response are combined together in order to achieve the proper cross-sensitivity features.

For fast qualitative and quantitative examination of multi-component solutions, a multisensor approach, called “electronic

* Corresponding author.

E-mail address: manel.delvalle@uab.es (M. del Valle).

tongue”, has been proposed recently. It is based on the combination of an array of non-specific, poorly selective, chemical sensors with partial specificity (cross-sensitivity) to different compounds in a solution, and an appropriate chemometric tool for the data processing [14], for example by means of artificial neural networks (ANNs) [15,16].

ANNs have been presented as an optimal performance in the modelling of non-linear systems, such as the cross-term responses of potentiometric sensors [17,18]. The followed methodology requires training an ANN with a large number of standards, needed to establish a numerical response model [19,20]. The use of flow systems, in our case a sequential injection analysis (SIA) system, has been proposed to automatically provide the large amount of information required by this approach [21,22], minimizing the effort in building electronic tongue systems.

Different potentiometric electronic tongues based on the combination of an array of ISEs and ANNs have been developed in last years, to simultaneously quantify mixtures of ions [22–25]. Very significant is the work from the group of Kulapina, in Saratov University (Russia), who has developed several approaches of electronic tongues for surfactants [26–29]. The present study demonstrates the use of an array of potentiometric sensors, with cross-response to anionic surfactants, in conjunction with a SIA system to facilitate the training of ANNs and enable dodecylsulfate, dodecylbenzenesulfonate and α -alkene sulfonate to be simultaneously quantified in aqueous samples.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared with doubly distilled water and reagents used were of analytical grade.

Ion-selective electrode membranes were prepared dissolving the sensing element, the plasticizer and the polymeric matrix in an organic solvent. Membranes were then solvent-casted on graphite-based, inner solid contact potentiometric sensors, of normal use in our laboratories [22,24]. Materials used for the preparation of the inner solid contact for the potentiometric sensors were the epoxy resin components Araldite M and HR hardener (Uneco, Barcelona, Spain) with graphite powder (50 μ m, BDH Laboratory Supplies, UK) as the conducting filler. Once formed, membranes were conditioned in a solution of their primary ion for 24 h. The analyte electroactive elements were the following ion pairs: tetraoctylammonium bromide (TOAB) (Fluka, Switzerland) for generic response to anions; Hy-DBS, synthesised from Hyamine 1622 (Hy) (Merck, Germany) and sodium dodecylbenzenesulfonate (NaDBS) (Carlo Erba, Italy) [30]; T12A-DBS, synthesised from tetradodecylammonium bromide (T12A) (Fluka, Switzerland) and NaDBS [30]; 7,13-bis(*n*-octyl)-1,4,10 trioxa-7,13 diazacyclopentadecane (L^1); and L^1 -(DS)₂, synthesised from L^1 and sodium dodecyl sulfate (NaDS) (Fluka, Switzerland) according to [31], comprised the cyclic ligand in order to induce changes in selectivity. Plasticizers

Table 1

Formulation of the ion-selective membranes employed in the construction of the potentiometric sensor array

Electrode	Ionophore	Plasticizer	PVC (%)	Reference
E1	Hy-DBS (1%)	<i>o</i> -NPOE (66%)	33	[32]
E2	T12A-DBS (1%)	<i>o</i> -NPOE (66%)	33	[32]
E3	L^1 (3.7%)	<i>o</i> -NPOE (55.32%)	40.98	[31]
E4	L^1 -(DS) ₂ (3.7%)	<i>o</i> -NPOE (55.32%)	40.98	[31]
E5	TOAB (4%) ^a	DBP (65%)	29	[33]

^a This membrane incorporates 2.00 wt.% PTCPB.

used were 2-nitrophenyloctylether (*o*-NPOE) and dibutylphthalate (DBP) (both from Fluka, Switzerland). The polymeric matrix was poly(vinyl chloride) (PVC) (Fluka, Switzerland) and the volatile solvent was tetrahydrofuran (THF) (Merck, Germany). An anionic additive was also used to formulate the generic membrane: potassium tetrakis-4-chlorophenylborate (PTCPB) (Fluka, Switzerland). Table 1 summarises the formulation of the different membranes, as taken from the literature. As all potentiometric measurements were performed with equivalent ionic media (carrier solution K₂SO₄, 5 mM), activity coefficients were considered to be constant. Calibration experiments were made with surfactants NaDS, NaDBS (source as above) and α -alkene sulfonate (ALF) (Molins Kao, Spain).

2.2. Instrumentation

The SIA system used in this determination is shown in Fig. 1. The flow system was made up of a Crison 2030 automatic micro-burette (Crison Instruments, Spain), fitted with a syringe of 5 ml (Hamilton, Switzerland) and controlled entirely by a PC; a six ports (Ref. HVXM R36760) Hamilton MVP valve (Hamilton, Switzerland), also controlled by computer; a 7 ml perspex mixing chamber with a conical base to aid emptying, used to homogenise the solutions; and a holding coil, formed by a PTFE tube (Bioblock, France) with an internal diameter of 1 mm and a total inner volume of 5 ml. The elements were connected together using low-pressure liquid chromatography connectors.

The measurement system comprised the detection system (sensor array incorporated into the system in series) and a Ag/AgCl double-junction reference electrode (Thermo Electron 900200). Reference and ISE signals were passed to conditioning amplifiers based on the INA116 (Burr-Brown, USA) instrumentation amplifier, to ensure that minimal current was drawn during voltage measurement. A low-pass filter (2 Hz) was used afterwards for each channel to reduce system noise [34].

Indicator electrodes, shown in the insert in Fig. 1, were all-solid-state, tubular, flow-through electrodes of normal use in our laboratories [35].

Communication between the computer (PC Pentium at 166 MHz) and the various apparatus of the SIA system was achieved by means of RS-232 protocol. To this end, a program written in LabVIEW6.1 (National Instruments, USA) was used [34].

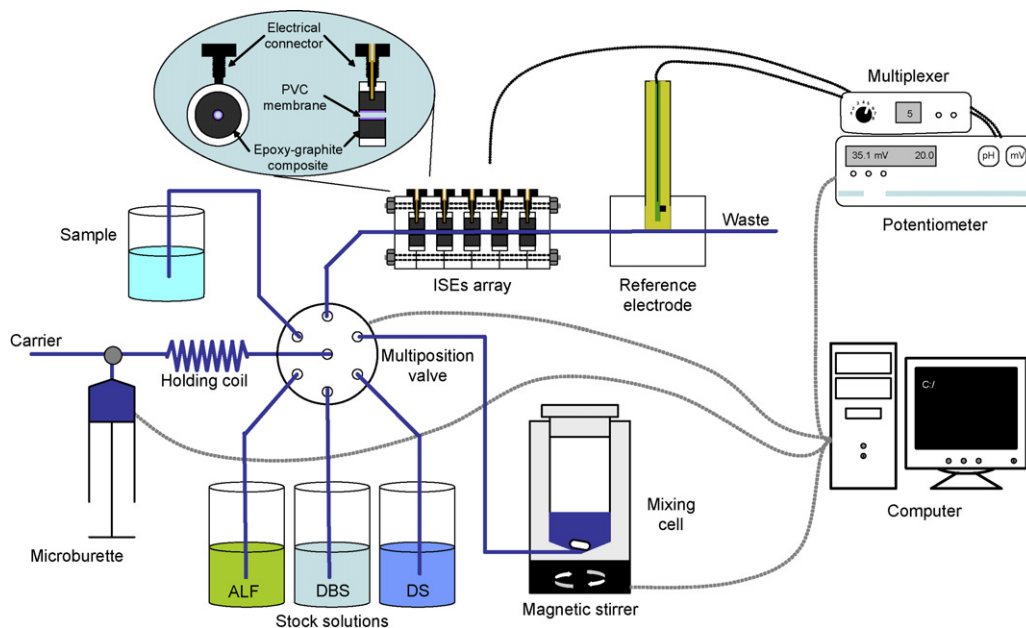


Fig. 1. Manifold of the SIA system employed in the study. The insert shows the design of the flow-through tubular all-solid-state electrode.

2.3. Procedures

ANNs were used to model the combined response of anionic surfactants ALF⁻, DBS⁻ and DS⁻. In order to build the calibration model, a set of standards with random concentration values was generated. This set consisted of 64 mixed solutions automatically prepared by the SIA system. Once calibration samples were measured, the complete set was randomly divided into two subsets: (1) a training set, which served to determine the model's parameters; and (2) a test set, which enabled the model's predictive ability to be evaluated [36].

Neural network processing was developed with MATLAB 6.1 (Mathworks, USA), using its Neural Network Toolbox (Neural Network Toolbox 4.0.2, Mathworks, USA). In all cases, ANNs used were feedforward and trained by employing back-propagation algorithm, viz. Bayesian regularisation (BR). One particularity of this algorithm is that it does not require an internal validation set of samples to avoid overfitting [37].

3. Results and discussion

3.1. Characterisation of the sensor array

Calibrations towards each surfactant were made to check their response and the cross-sensitivity features. Typical potentiometric calibrations were therefore performed, with the automated SIA system preparing a number of standards; this consisted in the sequential dilution of the stock solution and the measurements of the ISE array in parallel [21]. In this way a concentration range of four decades was covered. Measured sensitivities are summarized in Table 2, where the slopes of the middle logarithmic response region (between the potentiometric limit of detection and the critical micelle concentration) are indicated. The reproducibility of the calibrations was better than 5% for

two different-day consecutive verifications. The potentiometric limit of detection corresponding to the above calibrations are also presented on the table, confirming a resolution capability ca. the μM level.

Regarding the slopes, it can be seen that the E3 ISE, using in its membrane the cyclic ionophore L¹, showed the highest response (supernernstian) towards the three analytes. Apart, a different selectivity pattern is shown for the different considered surfactants. Sensors E1 and E4 showed a higher sensitivity for DS than for the other surfactants, while E2, E3 and E5 showed a highest response for DBS. Besides, the five used sensors presented secondary response for the third surfactant, ALF. This cross-sensitivity behaviour is what permitted to build an electronic tongue for the resolution of surfactant mixtures.

Further, the used sensors were characterised by means of high-dimensionality calibrations with respect to two analytes, taking profit of the versatility shown by the automated SIA system. This characterisation represents an interference study

Table 2

Summary of calibration results of the five flow-through ISEs used in the sensor array vs. the three surfactants considered

ISE	E1	E2	E3	E4	E5
Sensitivity (mV/dec)					
Analyte					
ALF	-66.315	-77.73	-118.52	-69.43	-81.915
DBS	-77.88	-93.005	-131.795	-69.995	-97.085
DS	-78.67	-86.635	-108.55	-74.83	-87.835
Potentiometric limit of detection (mM)					
Analyte					
ALF	0.0058	0.0018	0.0058	0.0094	0.0003
DBS	0.0025	0.0052	0.0025	0.0067	0.0049
DS	0.0146	0.0020	0.0146	0.0055	0.0028

Calibrations carried out from a surfactant stock concentration of 10 mM. Fitted equation: $E \text{ (mV)} = K + s \log C$.

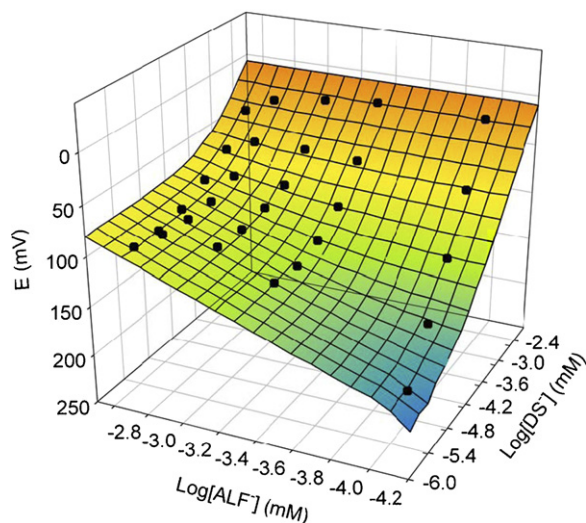


Fig. 2. Response surface for the sensor based on Hy-DBS, where DS^- is considered to be the principal analyte and ALF^- the interferent.

of great practical utility, since the value of the potentiometric selectivity coefficients in the Nikolskii–Eisenman equation (K^{pot}) [38] could be obtained with two degrees of freedom, varying the concentration of both the analyte and the interferent. As example, Fig. 2 shows the response surface for the sensor based on Hy-DBS (E1), considering DS^- as the primary analyte and ALF^- as the interferent. The figure illustrates the experimental points prepared automatically with the SIA system, as well as the three-dimensional response surface which corresponds to the Nikolskii–Eisenman expression, fitted with non-linear regression methods. It can be clearly seen how, with low concentrations of the primary ion, the curvature gets steeper as the concentration of the interferent ion increases. The $\log K_{\text{DS}^-, \text{ALF}^-}^{\text{pot}}$ obtained from the surface fitting was -0.254 .

3.2. Building of the response model

As previously specified, 64 mixed solutions of ALF^- , DBS^- and DS^- were automatically prepared with the SIA system in order to build the 3-analyte response model. Concentration of the three anionic surfactants ranged from 0.2 to 4 mM for ALF^- and DBS^- and from 0.2 to 5 mM for DS^- . This set of solutions was randomly subdivided in two different subsets (viz. training and test) needed for the correct training of the network and checking its performance. The compositions of the prepared set are shown in Fig. 3 and no non-random trend is revealed. In our case, the training set comprised 48 points and the test set 16 (ca. 75 and 25% of the total amount, respectively). In this step, the precaution of reserving the extreme values for the training subset was taken, avoiding the need for extrapolating these points out of the obtained model.

For each point generated by the SIA system, the corresponding potential values for the array of five potentiometric sensors were recorded. These values were the input information to the ANN for each sample. Thus the number of neurons at the input layer equalled the number of sensors used, five. The output layer

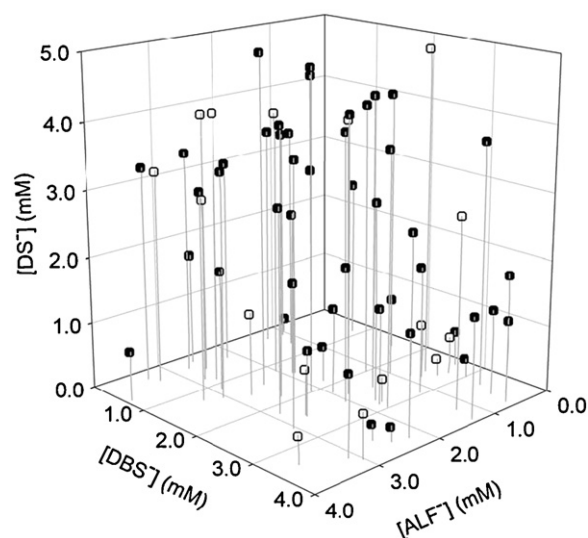


Fig. 3. Distribution of concentrations of the three anionic surfactants for the training (●) and test (○) samples prepared automatically employing the SIA system.

was also defined a priori: it required three neurons, one for each species to be quantified (ALF^- , DBS^- and DS^-). Only structures with a single hidden layer were assayed, as research suggests that the results obtained are as good as those produced with two layers [39].

On the basis of previous experience [40], some configuration details were fixed a priori. These details comprised the specific parameters for the learning algorithm, the learning rate (α) and momentum (β), which took the values of 0.1 and 0.4, respectively; also, the transference functions used within each neuron layer were preset as sigmoidal for the hidden layer and linear for the input and output layers. Prior to training, data were range-scaled between -1 and 1 .

A study of the ANN architecture was performed in order to optimise the quantification of the three surfactants considered. All possible combinations of transfer functions in the hidden (*tansig* and *logsig*) and output (*purelin* and *tansig*) layers were tested, as well as the number of neurons in the hidden layer (between 3 and 12). For each of the 28 configurations tested, root mean square error (RMSE) [41] values were recorded for the test subset, the total value and according to each surfactant considered. To select the best ANN, a direct comparison of modelling performance for each analyte was performed. For this purpose, predicted concentration values were plotted against expected, and the regression line of the comparison was calculated. A good ANN configuration should display small RMSEs and, for each ion, comparative lines with a good correlation and slope equal to 1 with zero intercept.

To ensure that the results obtained did not correspond to local minimums, the weight values were reinitialised at random and the ANN retrained to see if the model showed convergence in similar situations or whether it reached local minima. This was done by repeating the network's learning through resetting the weight values three times and then evaluating the results obtained.

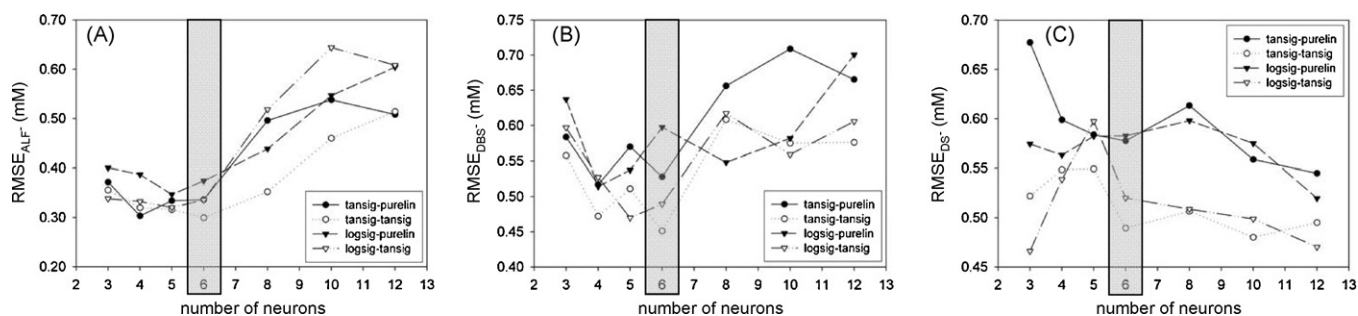


Fig. 4. Selection of the configuration of the final ANN model. Obtained RMSEs values for ALF^- (A), DBS^- (B) and DS^- (C) for different transfer functions in both hidden and output layers and varying number of neurons in the hidden layer.

Table 3

Summary of the goodness of fits obtained for the three surfactants with training ($n = 48$) and external test sets ($n = 16$)

	Slope	Intercept (mM)
Training		
ALF^- ($r = 0.895$)	1.022 ± 0.151	-0.05 ± 0.30
DBS^- ($r = 0.892$)	1.065 ± 0.160	-0.13 ± 0.36
DS^- ($r = 0.941$)	1.042 ± 0.111	-0.13 ± 0.3
Test		
ALF^- ($r = 0.933$)	0.891 ± 0.197	0.22 ± 0.45
DBS^- ($r = 0.936$)	0.915 ± 0.197	0.36 ± 0.47
DS^- ($r = 0.954$)	0.835 ± 0.150	0.44 ± 0.41

r is the correlation coefficient. Confidence intervals calculated at the 95% confidence.

As can be seen in Fig. 4, the configuration yielding the best model had six neurons in the hidden layer and used the *tansig* transfer function in both hidden and output layers.

Table 3 contains the regression values of comparison between obtained versus expected data for both the training and the external test subsets by using the optimal ANN configuration. In both cases, very good correlation was obtained with comparison lines indistinguishable from the theoretical values. It must be remarked that the data used in the external test subset is not employed at all for the modelling, so goodness of fit is a measure of the accomplished modelling performance.

In order to show a typical laboratory application, five synthetic samples were prepared by appropriate dilution in K_2SO_4 background, processed with the SIA system and interpolated in the formerly trained ANN model. Results are sketched in Table 4, where the concordance between obtained versus expected results can be visualized; the advantages of the proposed method are

Table 4

Results obtained in the resolution of the manually prepared synthetic samples employing the finally trained electronic tongue

Sample	Expected surfactant concentration (mM)			Obtained surfactant concentration (mM)		
	ALF	DBS	DS	ALF	DBS	DS
A	2.67	2.44	0.69	2.82	2.54	0.68
B	1.34	1.82	3.90	1.40	2.24	4.08
C	2.84	0.76	2.79	2.83	0.88	2.54
D	3.63	3.35	0.41	3.34	3.00	0.42
E	3.31	0.42	3.24	2.89	0.51	3.23

evident in the accurate resolution of the surfactant mixture with an extremely simple experimental procedure, once all the system is fine-tuned.

4. Conclusions

An automated potentiometric electronic tongue has been developed by coupling a SIA system to an array of potentiometric sensors, to simultaneously quantify the surfactants dodecylsulfate, dodecylbenzenesulfonate and α -alkene sulfonate in aqueous samples in the mM concentration range. The SIA system was able to generate automatically, and with a high-degree of randomness, the information necessary for training ANNs, which were used to model the response of the sensor array, having a cross response to anionic surfactants. The structure providing the best modelling was a single hidden layer containing six neurons.

The performance of the electronic tongue was checked with samples not participating in the training process, where only slight differences between the obtained and expected concentrations were found. The obtained results permitted the resolution of a mixture of three anionic surfactants, an achievement normally attainable only with chromatographic techniques, this time reached by a very simple and direct use of appropriate sensors plus advanced chemometric treatment.

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