

# Polyacrylate microspheres composite for all-solid-state reference electrodes

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A novel concept is proposed for the encapsulation of components within polyacrylate microspheres, prior to their incorporation into a membrane phase. Thus finer and better controlled dispersion of heterogeneous membrane components can be achieved. This concept was verified by using a poly(*n*-butyl acrylate) membrane-based reference electrode as an example. In this example the proper dispersion of solid constituents of the heterogeneous membrane and prevention of their leakage are both of primary importance. Potassium chloride-loaded poly(*n*-butyl acrylate) microspheres were prepared and then left in contact with silver nitrate to convert some of the KCl into AgCl. The material obtained was introduced into a poly(*n*-butyl acrylate) membrane. The reference electrode membranes obtained in this way were characterized with much more stable potential (both in different electrolytes and over time) compared with electrodes prepared by the direct introduction of KCl and AgCl to the membrane.

## Introduction

In recent years, the majority of research effort in analytical potentiometry has been orientated towards the improvement of indicator electrodes, with the emphasis on better analytical parameters and sensor construction optimization [*e.g.* ref. 1 and 2]. The new ideas as well as the instrumental techniques proposed/applied have resulted in significant improvements mainly in the field of ion-selective electrodes. Progress related to reference electrodes is however significantly less advanced. Although different systems based on *e.g.*, conducting polymers,<sup>3–8</sup> plastic membranes<sup>3,9–14</sup> or screen printed devices<sup>15,16</sup> have been proposed, the classical concept of reference electrodes, most often based on Ag/AgCl or saturated calomel electrodes, clearly dominates in laboratory practice. The excellent stability of these half-cells often compensates for all the drawbacks of (wet) internal solution containing reference systems. In our earlier works<sup>3,12,13</sup> we have shown that dispersion of solid Ag/AgCl and KCl within a polymeric matrix, either plasticized poly(vinyl chloride) or photopolymerized poly(*n*-butyl acrylate) based ones, leads to stable responses of such reference electrodes. From a practical point of view, one of the important advantages of preparing reference elements using poly(vinyl chloride)- or polyacrylate-based matrices, *i.e.* systems well known as membranes of ion-selective, indicator electrodes, is that the same material can be used for both electrodes.

Although this issue has not been studied in detail, it is quite clear that the most important step in the preparation of successful reference membranes, *i.e.* leading to electrodes characterized with stable and reproducible potentials and that are not sensitive to activity changes, is the dispersal of solid components of the heterogeneous mixture within the membrane polymer.

Some reports<sup>15</sup> have stressed the importance of the proper construction of electrode layers, *e.g.* for screen printed arrangements, in achieving stable responses. Therefore, the aim of this work was to study other methods for the preparation of well defined membrane mixtures.

The novel idea explored here is based on the application of polymeric microspheres as carriers for solid constituents introduced into a membrane. To the authors' best knowledge not many applications have been proposed so far of polymeric microspheres in the preparation of electrochemical membranes including the application of polymeric spheres for the encapsulation of heterogeneous membrane components.

In this work poly(*n*-butyl acrylate) microspheres were loaded with solid (powdered) KCl during their preparation. The microspheres were then treated with AgNO<sub>3</sub> to convert some of the KCl to AgCl (traces of Ag were also formed). The heterogeneous material thus obtained was dispersed in tetrahydrofuran containing dissolved poly(*n*-butyl acrylate), good dispersion of the active ingredients was achieved and resulted in the improved performance of reference electrode membranes containing microspheres compared to the performance of electrodes prepared by the direct application of KCl and AgCl to the membrane phase.

## Experimental

### Apparatus

Multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) were used for the potentiometric experiments. Pump systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibration solutions.

For the electrochemical impedance spectroscopy experiments a galvanostat-potentiostat CH-Instruments model 660A (Austin, TX, USA) and a conventional three electrode cell, with a platinum sheet as counter electrode, were used.

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For the potentiometric experiments a membrane-coated glassy carbon electrode (GC, surface area 0.07 cm<sup>2</sup>) and a double junction Ag/AgCl reference electrode with 1 M lithium acetate in the outer sleeve (Möller Glasbläserei, Zürich, Switzerland) were used. The recorded potential values were corrected for the liquid junction potential (occurring at the classical reference electrode outer sleeve/sample solution) calculated according to the Henderson equation.

Scanning electron microscopy (SEM) investigation was conducted using a microscope LEO 435 VP (Germany) coupled with a Roentec energy-dispersive X-ray (EDS) analyzer.

Prior to SEM observations the samples were sputter coated with a 1–2 nm layer of Pd–Au alloy using a Polaron SC 620 Mini Sputter Coater.

### Reagents

Tetrahydrofuran (THF), *n*-butyl acrylate, 1,6-hexanedioldiacrylate (hexane-1,6-diyl-bis-prop-2-enoate) (HDDA) and 2,2-dimethoxy-2-phenylacetophenone (2,2-dimethoxy-1,2-diphenylethanone) (DMPP), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500), regioregular polyoctylthiophene (POT), poly(vinylalcohol) (PVA), 2,2'-azobis(2-methylpropionitrile) (AIBN) were from Aldrich (Germany).

Doubly distilled and freshly deionised water (resistance 18.2 MΩ cm, Milli-Qplus, Millipore, Austria) was used throughout this work. All the salts used were of analytical grade and were obtained from POCh (Gliwice, Poland).

### Preparation of solid contact electrodes

Glassy carbon electrodes were polished with Al<sub>2</sub>O<sub>3</sub>, 0.3 μm and rinsed well with water.

Polyoctylthiophene (POT) layers (used as solid contact-ion-to-electron transducers) were prepared by applying 10 μl of polymer solution in chloroform (2.75 mg ml<sup>-1</sup>) on the surface of GC electrode, prepared as described above, placed in upside down position. The conducting polymer (CP) layer solvent was dried and the reference membrane was then applied.

### Synthesis and preparation of polyacrylic microspheres

The synthesis of poly(*n*-butyl acrylate) microspheres was carried out according to the method of Hall *et al.*,<sup>17</sup> with some modifications. A mixture of *n*-butyl acrylate (*n*BA) (1000 μl), HDDA (220 μl) and DMPP (10 mg) as initiator, containing 500 mg of solid (ground) KCl was prepared using an ultrasound probe (3 min). The mixture was then dispersed in 5 ml of aqueous 1% (w/v) polyvinyl alcohol solution, using an ultrasound probe (3 min) and was immediately photopolymerized.

The polymerisation step was conducted under a nitrogen atmosphere for 5 min using vigorous stirring of the emulsion.

Following polymerisation, 1 ml of mixture was combined with 1 ml of 1 M AgNO<sub>3</sub> solution, mixed thoroughly (5 min ultrasound) and left for 48 h. The solid fraction was then separated by centrifugation at 5800 rpm for 5 min. The solid material left was washed with a small amount of water and was used to prepare the reference electrode membranes. Due to obvious reasons excessive washing of the obtained spheres containing KCl with water was avoided.

For scanning electron microscopy (SEM) investigation, some microspheres were not treated with AgNO<sub>3</sub>, but were centrifuged directly after polymerisation, the solid material obtained was then tested.

Samples for SEM studies were prepared by deposition of 15 μl of post polymerisation suspension on brass sheets. After evaporation (12 h, room temperature) of liquid the solid material remaining was sputter covered with a layer of Pd–Au alloy film and studied.

### General procedure for the synthesis of acrylate polymers

A portion of *n*-butyl acrylate monomer (to yield pBA polymer) containing 1 wt % of AIBN was irradiated for 15 min under UV light and then heated under a nitrogen atmosphere for 8 h in a water bath (100 °C). A further portion of AIBN (1 wt %) was added and the mixture was heated for another 8 h under the above stated conditions. Finally, the reaction mixture was heated for 1 h (100 °C) under diminished pressure (water pump). The polymerisation yield was 96–98%.

### Reference electrodes membrane

200 mg of polyacrylate KCl/AgCl composite-microspheres and 8.2 mg of ETH 500 were dispersed in 0.6 ml of THF containing 200 mg of dissolved poly(*n*-butyl acrylate). For a control experiment solid 16.5 mg AgCl with traces of metallic Ag, 53.5 mg of solid KCl and 4.7 mg of ETH 500 were dispersed in 0.6 ml of THF containing 200 mg of poly(*n*-butyl acrylate).

The reference membranes were obtained by application of 40 μl (2 × 20 μl) of any of above described cocktails, on POT layer coated on supporting GC electrode while the latter was placed in upside-down position, in a similar manner to the method described earlier for indicator electrodes.<sup>1,3,12,13,20</sup>

The reference electrodes obtained in this way were conditioned in 3 M KCl prior to use and in-between measurements.

### Results and discussion

Looking at literature reports it is quite clear that an heterogeneous Ag/AgCl system in the presence of KCl in the lipophilic membrane can be successfully used as a reference membrane.<sup>3,12–15</sup> A conducting polymer, POT, was applied in the studied system as a solid contact in order to enhance the redox capacitance of electrodes containing membranes in which Ag/AgCl/KCl had been dispersed.<sup>3</sup> An additional benefit of the POT layer is to provide hydrophobic contact between the membrane and electrode support thereby reducing the risk of thin water layer formation. However application of the heterogeneous mixture (membrane cocktail), and preparation of the membrane usually requires skill or the application of alternative membrane preparation methods, such as screen printing of the solid components. The main idea behind the preparation of the reference electrode membrane cocktail using poly(*n*-butyl acrylate) microspheres was to assure better control of dispersion (ideally uniform) of heterogeneous constituents within the polymeric membrane (compared to application of solid, ground Ag/AgCl and KCl). In other words, encapsulation of Ag/AgCl and KCl within a polyacrylate matrix that can be further suspended in a membrane cocktail is in principle advantageous over application of

powdered material;<sup>3,12,13</sup> this approach seems to be especially attractive for tetrahydrofuran (THF) based cocktails as cross-linked polyacrylate material is known to swell in this solvent.<sup>18</sup> The swelling of the polyacrylate spheres is expected to result in an improvement in the dispersion of encapsulated Ag/AgCl and KCl through the membrane thickness, especially when compared to non-encapsulated solid material. Taking into account that after application of the membrane cocktail evaporation of solvent requires some time, during which gravitation enhanced sedimentation of solid membrane constituents (Ag/AgCl and KCl) can occur, pre-organization (due to swelling/sticking to each other) of membrane material introduced in the polyacrylate encapsulated form can be highly beneficial.

Moreover, the application of microspheres is expected to result in a reduction in the release of encapsulated constituents from the membrane, *i.e.* adding an extra level of control/minimizing component leakage from the heterogeneous membrane. The risk of leakage/release upon contact with sample solution of solid dispersed material is especially pronounced for linear polyacrylate polymers membrane matrices, *e.g.* tetrahydrofuran soluble ones, materials which are known to accumulate pronounced amounts of water.<sup>20</sup> Thus, it can be expected that this approach will result in better and longer lasting stability of potential readings compared to similar systems in which the components are directly dispersed in the membrane.

Previous experiences<sup>19</sup> with encapsulation of compounds insoluble in acrylate monomer but soluble in water have proved that entrapped chemicals can be relatively well retained within the spheres; however, some losses occurring in the course of emulsion polymerisation are inevitable. Thus, to assure high loading of the membrane with KCl, a relatively high ratio of KCl solid to liquid *n*-butyl acrylate was applied. It was anticipated that upon introduction of aqueous PVA solution some of the KCl applied would be dissolved and would be present in the aqueous phase of the emulsion. The SEM pictures of the obtained spheres are presented in Fig. 1A. As can be seen in

Fig. 1A1 polymerisation has resulted in the formation of spheres: some of them are partially or totally collapsed, especially those dispersed in solid material, which were found to be rich in potassium and chlorine when analysed by EDS. Other spheres, found more in the centre of the sample, Fig. 1A2, are relatively well shaped; however, on their surface particulates other than polymer material—presumably KCl—are also found.

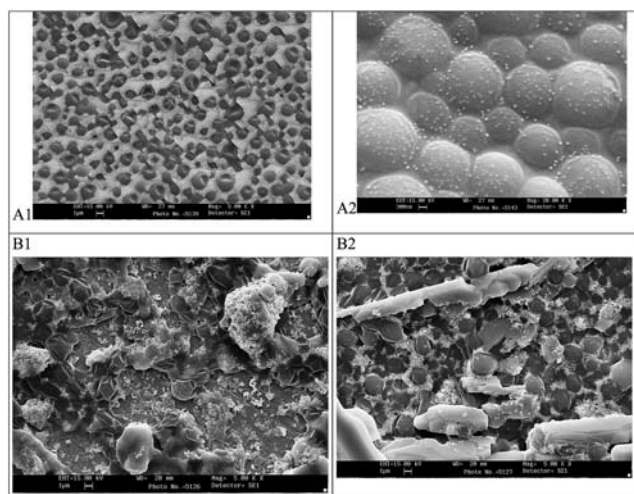
On the basis of the SEM pictures discussed above it can be concluded that the spheres formed behave differently depending on the thickness of the polymer crust. For spheres containing more polymer, release of KCl to the solution is less pronounced, resulting in only small particulates of KCl present in the well shaped spheres, Fig. 1A2. On the other hand, spheres containing less polymer and higher amounts of KCl, possibly due to a thin shell of poly(*n*-butyl acrylate), tend to release KCl.

For the preparation of reference electrode membranes the occurrence of two types of poly(*n*-butyl acrylate) KCl loaded spheres is very fortunate. It can be expected that KCl released from the spheres/or not-dissolved and present either as solid material or in solution after polymerisation can be transformed to AgCl. Taking into account that the molar ratio of KCl to AgNO<sub>3</sub> used was about 1.2, it is expected that KCl will remain in the mixture. Possibly, a lot of KCl, encapsulated within polymer rich spheres will not take part in AgCl formation, and then act as a reservoir of KCl in the reference electrode membrane. The emptied capsules (crust of microspheres) of polymer will contribute to the polymer matrix of the membrane.

The SEM picture, taken close to the edge, Fig. 1B1, of a sample treated with AgNO<sub>3</sub>, shows a frosty looking deposit on the remaining polymeric spheres. A picture taken closer to the sample centre, Fig. 1B2, shows the same frosty looking deposit; however, the presence of crystalline material is also visible. EDS analysis of the frosty looking deposit has shown the presence of silver and chlorine (presumably AgCl); the bigger structures found were rich in potassium and nitrogen (probably KNO<sub>3</sub>). The majority of the spheres shown in Fig. 1B2 are partially collapsed but covered with a fine deposit of AgCl. It seems probable that upon treatment with AgNO<sub>3</sub>, potassium chloride diffuses slowly out of the spheres forming a AgCl precipitate on the surface, or that nanocrystals of AgCl formed preferably build up on the polymer. Potassium and nitrate ions remain in the sample, under the SEM experimental conditions (*i.e.* following evaporation of solvent) forming a crystalline deposit. Thus the treatment of the spheres with AgNO<sub>3</sub> has resulted in the formation of fine structures of silver chloride, well dispersed within the matrix of polymeric spheres.

The presence of fine AgCl material, taking into account the grey-violet colour of the mixture indicates traces of spontaneously formed Ag.

It should be stressed that even the presence of debris of polyacrylate microspheres that have released KCl is beneficial for the preparation of reference electrode membranes. It is expected that when the solid material described above is dispersed in THF, the polymer (microsphere building material) swelling will induce thickening of the cocktail and thus help to retain fine spatial distribution of the components within the membrane. To further enhance the process of polymer matrix formation, the poly(*n*-butyl acrylate) was dissolved in the THF used. Ultimately the membrane composition obtained resembles other Ag/AgCl



**Fig. 1** SEM images of microspheres prepared in the course of this work. A, spheres loaded with KCl, B, above spheres after overnight contact with AgNO<sub>3</sub> solution: A1/B1, edge of the sample, A2/B2, centre of the sample.



reference systems<sup>3,12,13</sup> with the additional advantage of better distribution of its components. A longer lifetime of this system can also be expected.

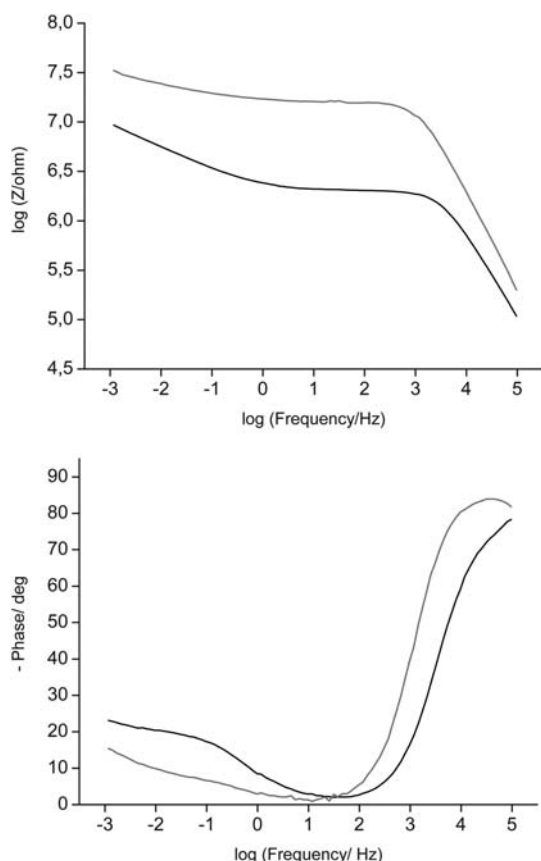
Fig. 2 presents electrochemical impedance spectra (in the form of Bode plots, *i.e.* showing dependence of phase angle or logarithm of impedance on frequency applied) recorded for a reference electrode membrane containing microspheres (prepared as described above) and a reference electrode membrane prepared by the direct application of solid KCl and Ag/AgCl to the membrane. The results recorded within the frequency range from  $10^0$  to  $10^2$  Hz show that the impedance determined by membrane resistance (concluded from a phase angle close to zero) is about one order of magnitude lower for microspheres containing membrane compared to other types of membrane tested and is close to  $10^{6.3}$   $\Omega$ . However, the resistance value obtained for microspheres containing membrane is higher than previously reported for poly(*n*-butyl acrylate) membrane reference electrodes,<sup>12</sup> but is significantly lower than typical resistance values obtained for ion-sensing poly(*n*-butyl acrylate) membranes.<sup>20</sup> The lower resistance obtained for microspheres containing membrane can be related to the more uniform dispersion of compounds within the membrane and/or higher overall content of potassium salts (KCl/KNO<sub>3</sub>) within the membrane. For higher frequencies (higher than  $10^2$  Hz), for

both membrane types tested, the impedance starts to be affected by the capacitance of the system (because the phase angle approaches  $-90^\circ$ ). For simplification it can be assumed that the membrane can be represented by a parallel connection of resistance (membrane resistance) and capacitance elements (geometrical capacitance of the membrane). Therefore, for a higher frequency,  $f$ , range, where the phase angle approaches  $-90^\circ$ , the impedance,  $Z$ , is determined by capacitance,  $C$ ,  $C = 1/(2\pi \cdot f \cdot Z)$ ; the calculated capacitance is above  $10^{-11}$  F. This value is typical for geometric capacitance of photopolymerized polyacrylate membranes.<sup>12</sup>

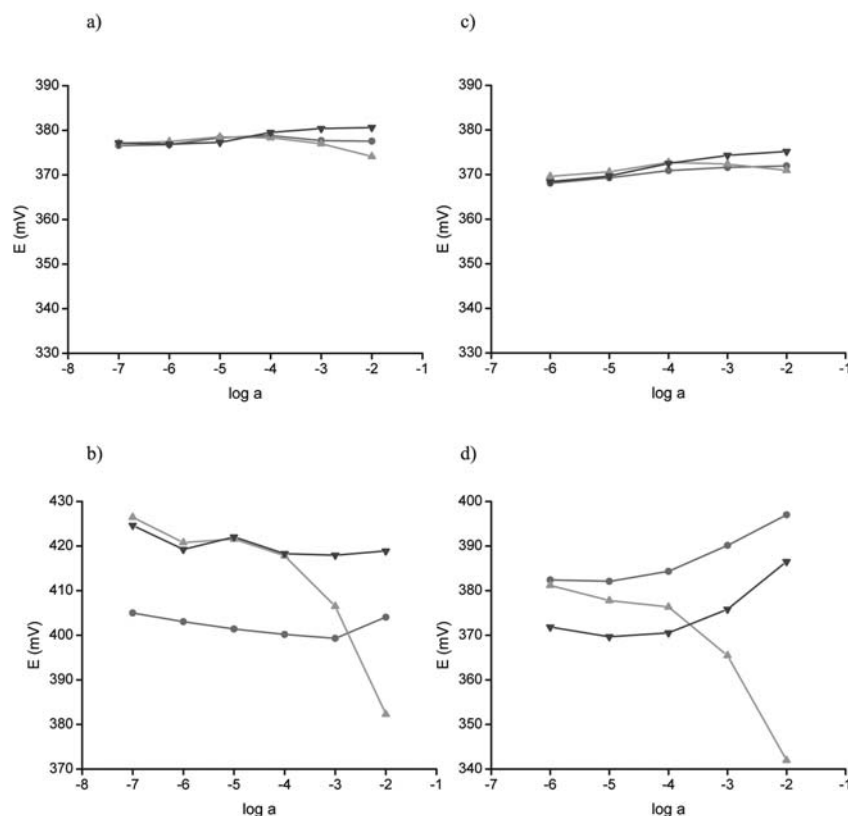
The potentiometric responses obtained for a microspheres-containing reference electrode and a reference electrode membrane, where compounds were introduced directly (microspheres-free membrane), are shown in Fig. 3. As can be seen from Fig. 3(a), potentials recorded for microspheres-containing membrane are practically independent of type of anion ( $\text{Cl}^-$  or  $\text{NO}_3^-$ ) or cation ( $\text{Na}^+$  or  $\text{K}^+$ ) and of salt concentration after three days conditioning in 3 M KCl. Only in  $\text{NaNO}_3$  solutions of highest activity tested ( $10^{-2}$  M changed to  $10^{-3}$  M) was a 4 mV potential change observed. As can be seen from Fig. 3(b), a significantly different picture was observed for the electrode with a microspheres-free membrane. Not only has the change of electrolyte from KCl to NaCl resulted in a shift of about 20 mV, but also for  $\text{NaNO}_3$  solutions a change of activity from  $10^{-4}$  to  $10^{-2}$  M resulted in a change of potential of about 35 mV. The results presented in Fig. 3 clearly show the beneficial effect of the introduction of microspheres containing KCl and AgCl into the membrane. A similar experiment performed more than three weeks after the electrodes were prepared (and after testing them during this time), Fig. 3(c) and 3(d), confirmed the superior performance of microspheres-containing membranes. Fig. 3(c) and 3(d) show that quite stable potential values were recorded for different types of electrolyte and activity change, over 3 weeks of testing/storage of this type of reference electrode resulted in a change of about 5 mV of the potential values recorded. In contrast, for the microspheres-free reference electrode membrane, Fig. 3(d), a pronounced potential change for both electrolytes tested and for activity change was observed. In the time frame between these two experiments being carried out, see Fig. 3(b) and 3(d), the change in potential values recorded for this electrode change was close to 45 mV.

The potentiometric responses recorded after 3 months dry storage of the microsphere-containing membrane followed by 48 h conditioning were also independent of the change of KCl activity within the range  $10^{-1}$  to  $10^{-6}$  M.

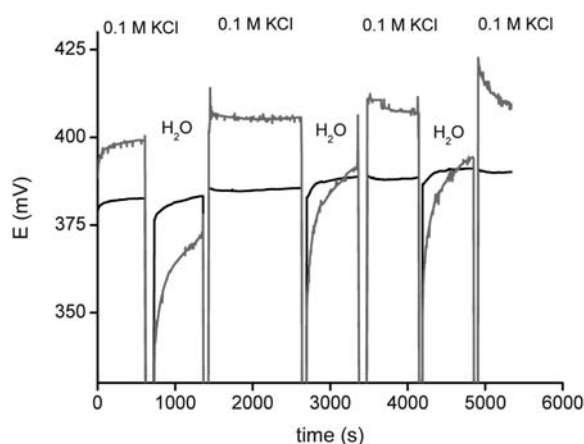
A challenging potentiometric experiment conducted for both types of membranes tested in parallel was repeated contact with 0.1 M KCl solution (50 ml each portion) and stirred deionized water (each time a new portion of 350 ml water was used, water was stirred at a speed close to 500 rpm during the test), Fig. 4. As can be seen from Fig. 4, the microsphere-containing membrane was characterized by a relatively stable potential, only small changes (about 2 mV) were recorded upon transfer of the electrode from water to KCl solution. Although a slow potential drift was observed for the microspheres-containing membrane (8 mV for the whole experiment), upon transfer to water, except for the first contact with  $\text{H}_2\text{O}$  where potential change was observed for the whole time, a drift was observed only for about



**Fig. 2** Bode plots recorded for a reference electrode with a microspheres-containing membrane (black line) and a reference electrode with a microspheres-free membrane, *i.e.* where KCl and AgCl were introduced directly to the polyacrylate (grey line), recorded in 3 M KCl at 350 mV, using 50 mV amplitude within the frequency range  $10^5$  to  $10^{-3}$  Hz.



**Fig. 3** Potentiometric responses, dependence of potential on logarithm of activity, of a microspheres-containing reference electrode membrane (a) and (c) and a reference electrode with a microspheres-free membrane, where KCl and AgCl were introduced directly to the polyacrylate (b) and (d) recorded in (▼) KCl, (▲)  $\text{NaNO}_3$  and (●) NaCl, on the 3rd, (a) and (b), and 23rd, (c) and (d), day after electrode preparation.



**Fig. 4** Potentiometric responses of microspheres-containing reference electrode membrane (black line) and reference electrode with microspheres-free membrane, where KCl and AgCl were introduced directly to the polyacrylate (grey line), recorded in 50 ml of 0.1 M KCl and 350 ml of stirred deionized water, a new portion of water/KCl was used for each change of solutions.

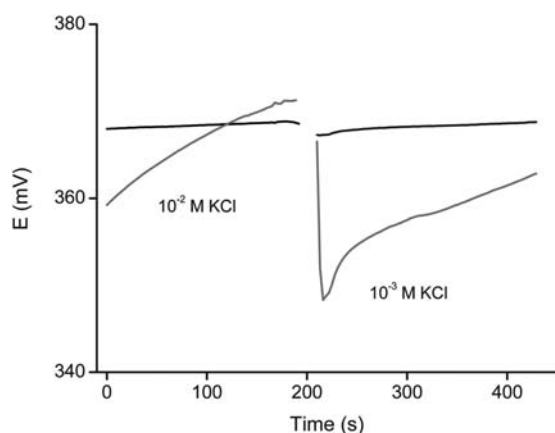
200 s after immersion of the electrode in water, with an overall potential change close to 5 mV each time.

A significantly different picture was obtained for the electrode with a microspheres-free membrane. The potential difference between water and KCl solution was close to 35 mV. Moreover,

potentials recorded in KCl solution following transfer from water changed over time, especially when the transfer was repeated for the 3rd or 4th time, suggesting that some of the “loosely”, entrapped KCl is lost when the membrane is in contact with water. Also for the electrode with this type of membrane, the potential started to increase at a significant rate of about 30 mV for 10 min, directly after immersion in water.

The results presented in Fig. 4 clearly demonstrate that encapsulation in microspheres is fulfilling the role of active, soluble, components leakage retarder, leading to more stable responses of reference electrodes.

Fig. 5 presents the potential change of the two types of reference electrodes, discussed above, in  $10^{-2}$  M KCl and then in  $10^{-3}$  M KCl, recorded after more than 3 weeks of continuous testing. As can be seen from Fig. 5 for the reference electrode containing microspheres in the membrane, stable potentials were recorded both in  $10^{-2}$  and  $10^{-3}$  M KCl. The KCl activity change results in a potential change of about 1 mV; however, after some time the potential recorded reached the value obtained in a more concentrated solution. For the electrode with a microspheres-free membrane, where KCl and AgCl were introduced directly to the polyacrylate matrix of the membrane, the potential drift observed was close to 10 and 15 mV, for  $10^{-2}$  M and  $10^{-3}$  M KCl, respectively. For this type of electrode, a change in KCl solution activity resulted in potential “overshoot”, *i.e.*, a rapid decrease followed by gradual increase in recorded values. This effect suggests that in contact with sample solution microspheres-free



**Fig. 5** Potentiometric responses of microspheres-containing reference electrode membrane (**black line**) and reference electrode with microspheres-free membrane, where KCl and AgCl were introduced directly to the polyacrylate (**grey line**) recorded in  $10^{-2}$  M KCl and after changing the KCl concentration to  $10^{-3}$  M.

membrane exchanges ions with solution and possibly releases KCl, ultimately leading to potential dependence on the log of activity of KCl in a similar manner as shown in Fig. 3(d). This type of behavior is not unexpected for a relatively loose network of THF soluble polyacrylate-based membrane. Thus, under these experimental conditions the introduction of microspheres together with KCl and AgCl to the membrane seems to be the best option for obtaining stable potentials of reference electrode membranes.

## Conclusions

The studies herein reported relate to a novel concept of encapsulation of components of a heterogeneous membrane in microspheres. This approach was studied using as an example, reference electrode membranes, where proper retention of components within the membrane is crucial. Comparison of electrodes with and without microspheres has proved the superiority of the microsphere-containing system. It was shown that encapsulation of KCl within poly(*n*-butyl acrylate) and partial conversion to AgCl results in the uniform distribution of finely dispersed heterogeneous material and that significant stabilization of potential readings was obtained after introduction of this

material to a poly(*n*-butyl acrylate)-based reference electrode membrane. The reference electrode membrane thus obtained was also more robust under conditions of repeated contact with stirred deionized water and solutions of various composition and concentration.

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