A SOLID POLYELECTROLYTE TO DETECT ETHANOL IN HYDROCARBONS

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Abstract.

An interpenetrating polymer network based on poly(glycidyl methacrylate), diethylenetriamine, poly(4-vinyl pyridine) and 1,4-dibromobutane has been investigated as sensitive material to build a sensor for the detection of ethanol in hydrocarbons. Preliminary tests has been carried out by impedance spectroscopy in ethanol/cyclohexane mixtures. The sensor showed a measurement range between 5% and 100%, good reversibility and fast response time.

*Key words*: Ethanol sensors; Impedimetric sensors; Chemoresistors; Functional polymers; Impedance spectroscopy.
1. Introduction.

The progressive heating of the Earth, the reduction of crude oil stocks and the instability of oil price induce to develop urgently renewable fuels [1]. In the short term, ethanol coming from agriculture is one of the most promising renewable fuel [2] because Otto-cycle engines can burn it, or its mixtures with gasoline, simply setting correctly the spark-ignition [3]. Fuel ethanol is a market already developed in Brazil but, in other countries, it is going to became an additive for gasoline and the world consumption is estimated to increase from five to ten times up to 2030 [4]. However, in the practical use of ethanol/gasoline blends the change in composition due to the different vapour pressure of the components [5], the phase separation due to water sorption [6] or, simply, the attempt at swindle, are phenomena that must be continuously checked to avoid detrimental effects on the fuel quality. Consequently, the market of ethanol/hydrocarbons mixtures will need new user-friendly sensors.

Capacitive sensors [7] or CMOS technology [8] were already investigated to discriminate between ethanol/gasoline blends on the base of their permittivity. Other electronic sensors, based on the conductivity changes of conjugated polymers, were patented in 1994 [9] and further developed later [10].

The present paper reports a preliminary investigation on the electric properties of a polyelectrolyte-based impedimetric sensor for the measurement of ethanol in hydrocarbons as an alternative of the previous systems. The selected polyelectrolyte is an interpenetrating polymer network (IPN) containing poly(4-vinylpyridine) (P4VP) cross-linked with 1,4-dibromobutane (DBB) and poly(glycidyl methacrylate) (PGMA) cross-linked with diethylenetriamine (DETA). This IPN was successfully used as sensitive material for the detection of humidity in air [11-14] and for the detection of moisture in several organic liquids [15-17]. It was also exposed to ethanol vapour showing that its humidity-sensitive properties have not been damaged [18].

The water sensing mechanism of polyelectrolytes can be explained as follows: the polymer sorbs water that interacts with the ions constricted in the vicinity of their polymeric counterparts by
electrostatic forces and frees them to provide current transport. At the same time, because of the high relative dielectric constant \((\varepsilon_r)\) of the water \((\varepsilon_r=71.1)\), the capacitance of the material increases.

However, the intimate mechanism of the water-polyelectrolyte interaction is very complicated because it involves the structure of the polymer, the ion concentration and Onsager-type interactions. An interpretation of the variation of the electric conductivity of polymer electrolytes and polyelectrolytes as a function of the relative humidity (RH) in air, where water is the dominant dipolar component, was reported in previous papers [19-21].

When a sensor based on an insoluble polyelectrolyte is dipped into an organic liquid containing water, the organic liquid interacts with the polymer stronger than air because of its higher density, polarisability and eventual polarity, thus, the adsorption of organic liquid becomes competitive with that of water. Moreover, organic liquids penetrate into the polymer pores inducing their modification. In this environment, water probably diffuses to the most polar groups of the polymer and solvates the ions producing a layer with an increased concentration of water in which solvated ions can move [17]. In principle, the mechanism of water sensing purposed for polyelectrolytes in moist organic liquids can be extended to every mixture of liquids with a reasonably difference in \(\varepsilon_r\), in the present paper cyclohexane \((\varepsilon_r=2.0)\) and ethanol \((\varepsilon_r=25.8)\) have been considered.

2. Experimental.

The sensors were prepared by dipping glass supported interdigitated gold electrodes in a dimethyl sulphoxide solution containing P4VP and DBB with a mole ratio 1:3, PBMA and DETA with a mole ratio 1:1, and having P4VP/PGMA weight ratio 1:1. After the dipping process, the sensor was heated to 90°C for 10 hours giving IPN solid films [22]. P4VP and PGMA preparations, and interdigitated electrode specifications, were described elsewhere [21].

The water content in cyclohexane (Merck, pro analysis) stored for almost 12 hours over 0.3 nm molecular sieves (Merck, activated at 380°C for 4 hours) was 10 ppm whereas water-saturated
cyclohexane contained 50 ppm of water. Ethanol absolute (Normapur analytical reagent) was mixed with cyclohexane and the mixtures were stored almost 12 hours over molecular sieves before use. The water content of these mixtures increases with the ethanol content reaching 30 ppm in pure ethanol. The tests on the sensor have been carried out in the presence of the molecular sieves to avoid that water contamination affects the results. Water content was measured by Karl-Fischer titration (Metrohm, KF756 Coulometer) before and after the sensor testing.

Impedance spectra were recorded 5 minutes after the dipping in the mixtures by a Solartron 1255 Frequency Response Analyser coupled with a Solartron 1294 Impedance Interface. Ten impedance values per decade of frequency has been recorded in the range 1 Hz - 1 MHz, with a bias potential of 0 V and a sinusoidal voltage of 1 V. The impedance spectra were fitted on the base of the most simple equivalent circuit [23]. The impedance was also measured versus time at 2 kHz when the sensor, coming from air, was dipped into the mixtures. All measurements were carried out at (291±3) K.

3. Results and discussion.

Fig. 1 shows the impedance spectra of the sensor dipped into ethanol/cyclohexane blends. The spectrum shape at ethanol content lower than 1% has only a line slightly divergent from the ordinate. At 5% of ethanol, this line becomes a semicircle then, increasing the ethanol content, an oblique line appears at frequency lower than that of the semicircle. The equivalent circuit that fits these results is shown in Fig. 1 but, at low ethanol content, the Warburg element ($Z_w$) and the resistor are not detectable.

Fig. 2 reports the variation of both resistance and capacitance as a function of the ethanol content in cyclohexane. The resistance is not valuable up to 5% but it decreases about six order of magnitude in the range between 5% to 100%. The capacitance is measurable in the whole concentration range and, even if at low ethanol concentration the data are scattered, it increases
linearly with correlation coefficient 0.9904, standard deviation 0.3, and slope $(0.059 \pm 0.003)$ pF per percent unit of ethanol.

Because of its high $\varepsilon_r$, water is the main interferent in the measurement of ethanol in cyclohexane, however, the water content in these experiments is lower than 30 ppm and the IPN resistance and capacitance exposed to such a concentration of water has been evaluated in 13 G$\Omega$ and 4 pF, respectively [15,17]. The resistance of IPN becomes detectable only when ethanol concentration is higher than 5% and the resistance measured in this conditions is lower than that due to water. On the other hand, the capacitance remains about 4 pF up to the concentration of ethanol is 10% hence the contribution of water to the capacitance is not negligible.

Also the parameters of $Z_w$ were evaluated by fitting the impedance spectra of the sensor in ethanol/cyclohexane mixtures with the equivalent circuit of Fig. 1. The resulting values of admittance ($Y^\circ$) are reported in Fig. 3. The coefficient at the exponent of the admittance ($n$), needed to represent $Z_w$, indicate that, at low frequency, diffusion processes are active, in fact $n$ has the average value $0.49 \pm 0.05$ but it ranges from 0.7 to 0.3 affecting the distribution of the related $Y^\circ$ data [23]. However, a rough linear fitting gives correlation coefficient 0.9916, standard deviation 0.05 and slope $(0.0107 \pm 0.0006) \Omega^{-n}s^n$ per percent unit of ethanol.

The sigmoidal curve of Fig. 3 shows the variation of the impedance module at 2 kHz with the ethanol percentage. 2 kHz has been selected because it gives a strong variation of the impedance with the ethanol concentration but is high enough to avoid the formation of the diffusion layer that could damage the material. The imposition of a constant frequency represents the easiest way to drive the sensor, but it needs some operations to convert the output signal in the linear scale of the concentrations.

After the dipping in the seven mixtures and in the pure ethanol, the impedance of the sensor was yet measured in pure cyclohexane. The variation of the capacitance was about 10% but that of the impedance module was smaller than 1% thus the hysteresis can be considered negligible.
Furthermore, after several hours of test, the sensor did not show meaningful performance variations indicating a promising life-time.

Fig. 4 shows the module of impedance at 2 kHz when the sensor passed from air with 23% RH to the ethanol/cyclohexane mixtures. The maximum variation in the impedance module after the dipping in pure ethanol occurs in 3 s, then the impedance module slightly increases reaching the steady state in 12 s. These data are a preliminary estimation of the sensor response time that can be considered satisfactory.

4. Conclusions

The IPN obtained from the cross-linking of PGMA and P4VP with DETA and DBB, already known as sensitive material for water in air and in organic liquids, has been used to produce a polyelectrolyte-based sensor for the detection of ethanol in cyclohexane. The operative range resulted 5-100% with satisfactory sensitivity and without significant hysteresis. The response time ranged from few to about ten seconds with a promising life-time. The use of a solid polyelectrolyte to detect ethanol in hydrocarbons represents a new approach for the quality control of the next future fuel.

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References.

Fig. 1. Equivalent circuit and Nyquist plots of the impedance spectra in ethanol/cyclohexane mixtures.
Fig. 2. Resistance and capacitance in ethanol cyclohexane mixtures.
Fig. 3. Module of impedance at 2 kHz and admittance of the Warburg element in ethanol/cyclohexane mixtures.
Fig. 4. Module of the impedance at 2 kHz passing from air to ethanol/cyclohexane mixtures.