

Formulation for the preparation of a beta scintillating plastic device

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Abstract

A new technique for the preparation of a beta scintillating plastic from a resin doped with fluorescent material is presented. The making of the plastic is easy, quick, and does not require any special laboratory equipment. This formulation for a polymerization kit enables to obtain a beta ternary plastic scintillator device with the shape and the size required by the user. The plastic can be either cast into a mould or machined to obtain a device, ready to be used as a nuclear detector in experiments involving beta emitters. It can be used for making radiochromatography cells, capillary electrophoresis devices, etc. The capability of the plastic has been tested in a diffusion experiment: the self-diffusion coefficient of labelled chloride $^{36}\text{Cl}^-$ in an aqueous electrolyte solution of 0.1 M sodium chloride has been measured by the closed capillary technique. The result is in good agreement with published values.

1. Introduction

For many years now, physico-chemical sciences (in particular Electrochemistry) have been using radiolabelled compounds as radiotracers, for the study of dynamical processes. Pure beta emitters such as phosphorus-32, chlorine-36 used at tracers concentrations, are particularly convenient for the study of dynamic processes such as diffusion. The linear range of the penetration of beta radiation within the condensed matter is very small (for instance $R = 550 \mu\text{m}$ in toluene for the 156 keV β^- emission of ^{14}C). This characteristic of beta radiation is a strong drawback for its nuclear detection.

The technique which was first found to circumvent this difficulty consisted to mix intimately the beta emitter and the scintillation liquid as a detector. It is the so-called beta liquid scintillation technique. Numerous

scientists such as nuclear, atomic and molecular physicists, organic chemists, photochemists have developed liquid scintillating detectors and their applications to analytical and physical chemistry. On this basis scintillating plastics have been devised for the particular use of Nuclear Physics research.

However, physical chemists who need beta scintillating plastic have two possibilities: either they purchase it from a specialized supplier, but they generally have to buy relatively large quantities at a rather high cost; or they can synthesize it, which requires a long procedure and a specialized technician. As a fact, the procedures described in the literature can last a few days and are composed of numerous steps [1,2]. Thus, an "easy-to-make" beta scintillating device would be interesting for laboratory uses involving small size detectors, such as radiochromatography cells, capillary electrophoresis devices, etc.

In this paper, we present a formulation for the synthesis of a beta scintillating plastic made from insatur-

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ated polyester resin. We chose this resin because it has the following advantages. It contains numerous π -bonds present in the insaturated esters and in the copolymer used (styrene, vinyltoluene,...). This abundance of π -bonding increases the fluorescence yield. Moreover, in the solid state, the resin has a high degree of reticulation, which confers good mechanical properties to the plastic.

In the first section we give the ingredients and methodology for the synthesis of the plastic from a doped resin. It is shown that the synthesis is easy (it does not require any special laboratory equipment), and it can be performed in a few hours. In the second section we present an application consisting in the fabrication of a cell for the measurement of self-diffusion coefficients of species in solution.

2. Experimental section

Apparatus. There is no special equipment needed for the synthesis of the plastic. The preparation of the resin needs a glass distillation apparatus. The making of the scintillating device requires a polishing metallographic bench (from Jaudoin-Prom-Somerec, Enghien les Bains, France) and a lathe for mechanical machining, the polishing accessories were purchased from Buehler Ltd. (Illinois, U.S.A.). In the diffusion experiment, an automated beta scintillator spectrometer (Tri-Carb 4660 from Packard) was used.

Reagents. Insaturated polyester resin GTS was obtained from Solo-plast Vosschemie (Saint Egrève, France). Styrene was purchased from Prolabo (France). This supplier was chosen because of the low content in stabilizing agent. The primary and secondary scintillators (from Merck, scintillation grade) were PPO (2, 5-diphenyl-oxazolyl-benzene) CARN [92-71-7] and POPOP (1, 4-bis(5-phenyl-2-oxazolyl)-benzene) CARN [1806-34-4]. The radiochemical used was radiochloride 36 in NaCl (Amersham, U.K.).

Preparation of the scintillating doped resin [3]. A sample of 100 cm³ of insaturated polyester resin is poured into a Pyrex[®] vessel. Then, 400 mg of primary scintillator (PPO) and 100 mg of the secondary scintillator (POPOP) is added. The latter doping agents must be mixed to the resin by gentle stirring to minimize the formation of air bubbles. At the same time the mixture must be heated moderately in an oil bath at

about 70°C in order to eliminate the curds. Moreover the heating reduces the viscosity of the mixture, which has two consequences: (i) the air microbubbles rise to the surface and disappear; (ii) the undissolved crystals of scintillator fall to the bottom and do not remain in suspension. This step is fundamental in the procedure to obtain a plastic of optimal optical properties.

The fluorescence yield is increased by adding styrene (10% in volume). Before use, the commercial styrene must be purified because the stabilizing agent (tert-butyl-4-pyrocatechol) and the impurities are potential quenching agents. The small amount of stabilizing agent (phenolic compound) and impurities is eliminated by a purification procedure now described:

First step: Solvent extraction by an aqueous solution of sodium hydroxide is performed. The aqueous alkaline solution is selected because of the good solubility of the sodium salt of phenolic compound in water. Emulsion phenomenon is often formed in solvent extraction with alkaline aqueous solution thus rendering a clean separation impossible, so the emulsion may be broken by increasing the concentration of ionic species [4]. Thus, the mass fraction of sodium hydroxide is 10% wt. After several strong shaking in a separatory funnel, the mixture of the two liquids has a rest time of ten minutes. The lower layer (styrene) is run off and separated as possible. The styrene is washed with fresh distilled water. The washing operation is continued to completely free alkaline reaction by pH measurement of washing water.

Second step: The styrene is drying on anhydrous sodium carbonate and filtered through a phase separating paper (Whatman).

Third step: The styrene is purified by distillation under diminished pressure of argon (“vacuum” distillation). The complete apparatus for vacuum distillation is depicted in Fig. 1. (A) is a three-necked round-bottomed flask, which contains a metallic sodium wire, fitted with a Vigreux column (G). The bulb of the thermometer (L) should be just below the level of the side arm. The left-hand neck (H) is fitted with a feeding reservoir of pure styrene. This reservoir is a bottle flask (I) which contains a drying agent (Na₂CO₃) at the bottom, and a sintered glass (J) filter through which the styrene pass before entering in the flask (A) by depression. The styrene is introduced by a cylindrical funnel (K) which contains a molecular sieve, the right-hand neck (C) of which carries a screw

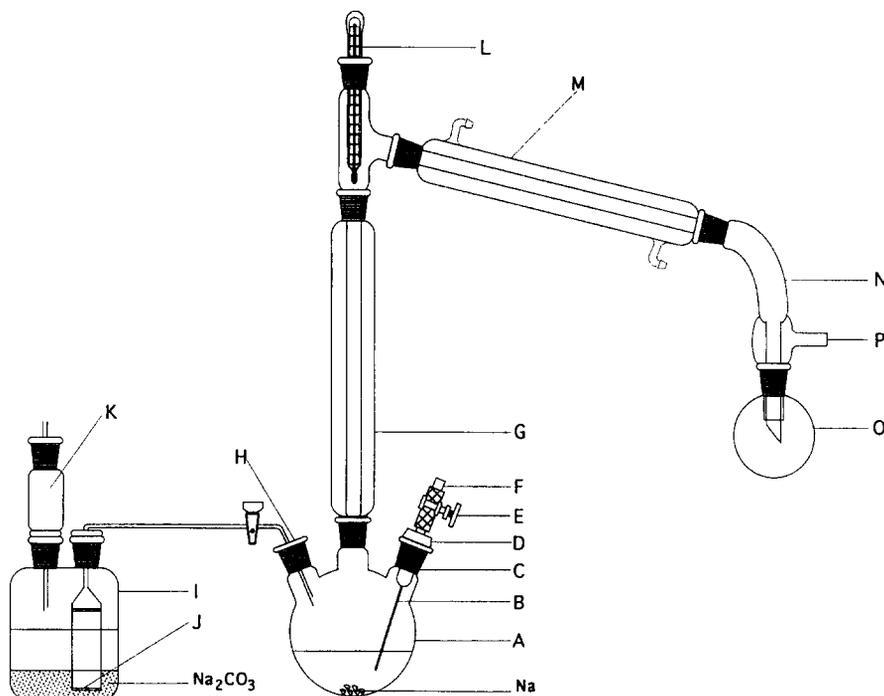


Fig. 1. Apparatus for distillation under diminished pressure.

cap adapter (D) through which is inserted a glass tube of appropriate diameter drawn out to a capillary (B) at its lower end. The tube carries at its upper end a short piece of pressure tubing (F) connected to an argon circuit and a screw-clip (E). The West condenser (M) carries a receiver and an adapter (N) connected via a suitable liquid nitrogen trap and manometer to an oil vacuum pump (P). The flask is heated by means of a silicon oil bath.

The pure styrene is very sensitive to any source of activation energy (thermal, ultraviolet, ..) which can release hazardous polymerization. The pure styrene is conserved under argon in a cool place, in an inactinic recipient to prevent its decomposition. The amount of water in the styrene is periodically measured by the Karl Fischer method.

To clarify the doped resin, it is left at rest at room temperature during about three hours away from light and pollution. The final doped resin is obtained by decantation of the floating part. It is glass-like transparent, with a typical blue reflected light aspect.

The doped resin associated to the catalyst (methyl-ethyl-ketone peroxide) constitutes a polymerisation kit for the preparation of scintillating plastic. The resin can

be polymerized by adding 2% (v/v) of catalyst. The polymerization takes about three hours.

A plastic of still better quality can be obtained by gamma irradiation of doped resin, without catalyst added. With this method the fluorescence yield is increased. However, this technique demands an access to gamma irradiator facilities.

Making of the diffusion cell. The cell consists of two cylindrical sections of different materials which are glued together. A bore of 1 mm diameter is drilled through the center of this cylinder. The bottom section, of length L , is made from scintillating plastic and the top of the same length is made of non-scintillating plastic [5]. In the present work we chose $L = 1.5$ cm. This device is called a closed capillary. A sketch of the closed capillary is given in Fig. 2.

The making of the cell is conducted as follows. A cylinder of non-scintillating plastic (made from the same resin, but without scintillators) is wrapped up in a sheet of terphane[®]. Both sides of the cylinder have been previously polished (ultimate step: 0.25 μm diamond past) to obtain optical standard. Doped resin (with the catalyst added) is then poured slowly on the top of the cylinder.

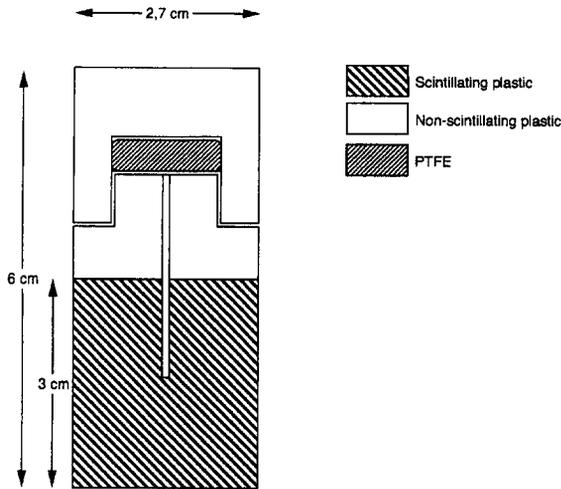


Fig. 2. Closed capillary cell.

After having removed the sheet of terphane[®] the top side of the rod is polished, and the lateral side is machined with screw-cutting lathe (both operations performed at optical standard). Eventually, the end of the non-scintillating section is thread. This pitch circle permits to close the capillary with a cap. A bore of 1 mm diameter is drilled through the center of the cylinder in such a way that the length of the capillary in the scintillating section is equal to that of the non-scintillating section.

The closed capillary technique. The closed capillary method for the determination of self-diffusion coefficients of ions in electrolyte solutions has been developed by Liukkonen, Passiniemi, and co-workers [6–8]. The method employs continuous monitoring of radioactivity in the capillary. Its reliability and precision have been demonstrated in previous works [9–11].

A diffusion experiment is performed in the following way. Initially the bottom section of the capillary is filled with a solution of 0.1 M NaCl spiked with a tracer amount of radiochloride 36. The counting rate of the tube, n_0 , is measured in the chamber of the scintillation counter. Then unlabelled 0.1 M NaCl solution is carefully added in the non-scintillating, top half of the capillary and the counting rate, $n(t)$, is recorded as a function of time.

3. Theory

It has been shown [6,7] that the counting rate $n(t)$ detected by the photomultiplier can be expressed as

$$n(t) = n(t = \infty) + \sum_{m=1}^{\infty} n_m \exp(-m^2 \pi^2 D t / 4L^2), \quad (1a)$$

where L stands for the half-length of the capillary, D for the diffusion coefficient, and t is the time. This expression should be valid after some short time of diffusion (of the order of half an hour) when the effect of the cylindrical perturbation arising from the filling disappears. Setting

$$P(t) = n(t) / n_0 \quad (1b)$$

and noticing that $n_0 = 2n(t = \infty)$, it can be shown that

$$P(t) = 1/2 + (4/\pi^2) \sum_{k=0}^{\infty} \exp[(-q_k^2 D t) / (2k+1)^2], \quad (2a)$$

where we set $q_k = (2k+1)\pi/2L$, and where only odd arguments appear because of the initial condition that only the bottom of the tube is filled with radioactive solution.

As mentioned [9], a practical experiment consists in measuring the integrated pulse counts over time intervals Δt (in our case $\Delta t = 30$ min), and thus one introduces the quantity

$$P(t) = (1/\Delta t) \int_{t-\Delta t}^t P(u) du, \quad (2b)$$

which is the mean value of $P(t)$ over the interval of time Δt and the observable quantity.

The treatment of the result can be handled in two ways:

(i) One gets an approximate value of D by performing a linear regression (LR) on the experimental set of points $[t, P'_{\text{exp}}(t)]$. Approximating $P'(t)$ by $P(t)$ (the two quantities should differ only slightly as Δt is not large), one can rewrite Eq. (2a) for t sufficient large (depending in practice on the actual value of D) as

$$P(t) \cong 1/2 + (4/\pi^2) \exp(-\pi^2 D t / 4L^2). \quad (3)$$

We set

$$s(t) = \ln[P'(t) - 1/2] \cong -(\pi^2 D / 4L^2)t + \ln(4/\pi^2), \quad (4)$$

and the LR is performed on the set $[t, s_{\text{exp}}(t)]$, where $s_{\text{exp}}(t) = \ln[P'_{\text{exp}}(t) - 1/2]$. We get from the slope the

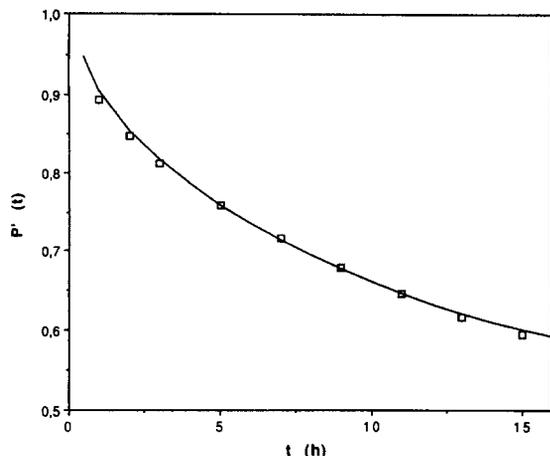


Fig. 3. Experimental points and result of LR plot for $^{36}\text{Cl}^-$ in 0.1M NaCl. Squares (\square): experimental data; continuous line (-): LR result.

value of D and, from the value of $s(t)$ extrapolated to $t=0$, a test for the consistency of the method. By keeping the first mode as in Eq. (3), we obtain a good estimate for D .

(ii) To obtain a more accurate result for D from experimental data, we used a non-linear regression procedure (NLR) based on a Simplex method. It consists of least squares using the expression for $P'(t)$ derived from (2b) and (2a) taking 10 terms for the expansion of $P'(t)$. Only the parameter D is adjusted; it is determined by the requirement for minimizing the quantity

$$Q = \sum_i [P'(t_i) - P'_{\text{exp}}(t_i)]^2,$$

where $\{t_i\}$ is the set of times at which the measurements were made ($t_{i+1} - t_i = \Delta t$). From $Q(D)$, one can compute the standard deviation of D in an experiment. It should be emphasized that in this method only one parameter needs to be adjusted whereas, in the linear regression, both the slope and the value at $t=0$ are determined from experimental data.

4. Results and discussion

The treatment of the experimental data with the LR leads to the value of the diffusion coefficient of $^{36}\text{Cl}^-$ in 0.1 M NaCl: $D(\text{Cl}^-) = (2.29 \pm 0.02) \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ($n=3$). The treatment with the NLR yields $D(\text{Cl}^-) = (2.20 \pm 0.02) \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ($n=3$). A typical LR plot and the corresponding NLR plot are shown respectively in Fig. 3 and in Fig. 4.

These results show that the LR and NLR methods give appreciably different values of the diffusion coefficient D . Anyhow, the more accurate value of D is the NLR result. The latter value is in good agreement with a previously published value [10] $D(\text{Cl}^-) = (2.10 \pm 0.02) \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ obtained with commercial NE 102 A (NE Technology Ltd., U.K.) scintillating plastic.

5. Conclusion

The diffusion experiment performed with a cell made from our home-made scintillating plastic yields results identical to those obtained with a cell made from commercial plastic.

Upcoming research. The preparation of a ternary beta scintillating plastic device is presented. The technique is applied to the measurement of diffusion coefficients of species in solution by the closed capillary method.

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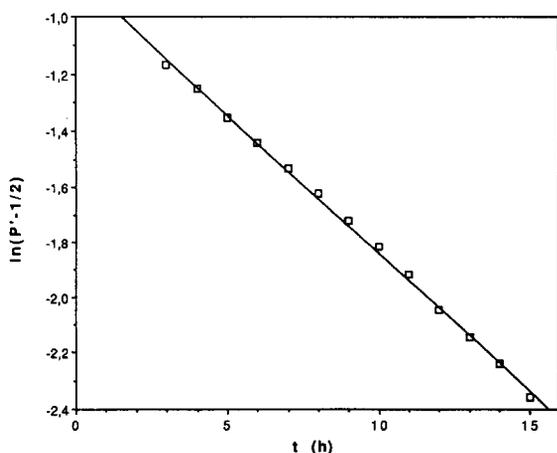


Fig. 4. Experimental points and result of NLR plot for $^{36}\text{Cl}^-$ in 0.1M NaCl. Squares (\square): experimental data; continuous line (-): NLR result.

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