

Chapter 4

Efficiency of Tritium Detection in Toluene—Cyclohexane—Polystyrene—PPO System

J. Gebicki, W. Reimschüssel and J. Rudzinski

Institute of Applied Radiation Chemistry, Technical University, Lodz, Poland.

INTRODUCTION

In the presence of polymer molecules in a liquid scintillation cocktail the efficiency of tritium detection was found to be dependent on the position of the radioactive site.¹ In a solution of the same composition the efficiency was different for tritium located in the macromolecule compared with tritium tagging the solvent molecules. The location effect has been explained in terms of non-uniform distribution of scintillator molecules between the solvent and the swollen macromolecules of polymer.

In this work we present the results of our studies on the detection efficiency of tritium in a similar system but with toluene-cyclohexane solvent. Toluene is a better solvent for polystyrene than cyclohexane and in addition is much more efficient in energy transfer to scintillators.^{3,4} These solvents were chosen not only for the differences mentioned above but also as two common and generally used solvents in macromolecular studies.

EXPERIMENTAL

The counting equipment, experimental conditions and preparation of non-labelled and tritiated polystyrene were as described previously.¹ Tritiated cyclohexane was synthesized by the reaction of bromocyclohexane and HTO.⁵ Labelled toluene was used as supplied by The Radiochemical Centre, Amersham, England. The viscosity-average molecular weights were the same for non-labelled and tritiated polystyrene and were equal to $\bar{M}_v = 2.41 \times 10^5$.

The measurements of efficiency of tritium detection were carried out in the following systems:

- A: Toluene-T-Cyclohexane-PPO
- B: Toluene-Cyclohexane-T-PPO
- C: Toluene-Cyclohexane-PS-T-PPO
- D: Toluene-T-Cyclohexane-PS-PPO
- E: Toluene-Cyclohexane-T-PS-PPO

In each case only one tritiated component was present in solution. The concentration of polystyrene varied in the range of $0.1-1 \text{ g l}^{-1}$. The volume fraction of cyclohexane V_c in the toluene-cyclohexane solvent varied in the range of 0-0.95. In all experiments PPO concentration was constant and equal to 4 g l^{-1} .

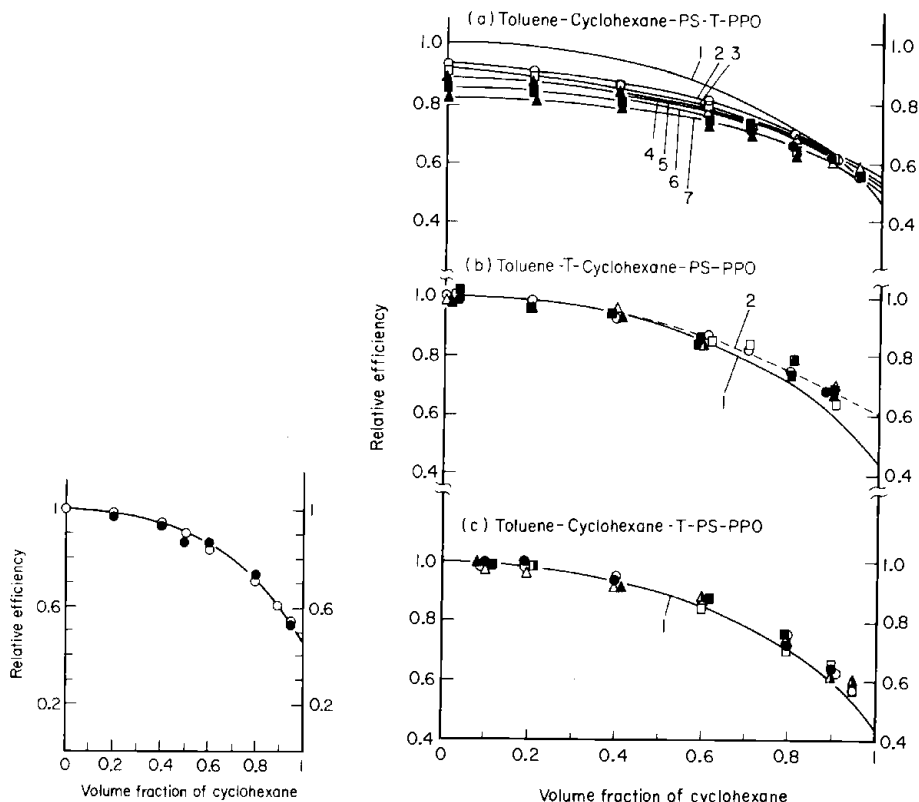


Fig. 1

Fig. 2

Fig. 1. Dependence of the relative efficiency of tritium detection on the volume fraction of cyclohexane for toluene-cyclohexane-PPO system. \circ - toluene-T; \bullet - cyclohexane-T.

Fig. 2. Dependence of the relative efficiency of tritium detection on the volume fraction of cyclohexane for toluene-cyclohexane-PS-PPO system. (a) Toluene-Cyclohexane-PS-T-PPO. Concentration of PS-T: 1 - 0.00, 2 - 0.10, 3 - 0.15, 4 - 0.20, 5 - 0.25, 6 - 0.50 and 7 - 1 g l^{-1} . (b) Toluene-T-Cyclohexane-PS-PPO. Concentration of PS: 1 - 0.00, \blacksquare - 0.10, \blacktriangle - 0.15, \bullet - 0.20, \square - 0.25, \square - 0.50 and \circ - 1 g l^{-1} . (c) Toluene-Cyclohexane-T-PS-PPO. Concentration of PS: 1 - 0.00, \circ - 0.10, \square - 0.15, \blacktriangle - 0.20, \triangle - 0.25, \bullet - 0.50 and \blacksquare - 1 g l^{-1} .

The efficiency of tritium detection was calculated in relation to the efficiency measured for the standard solution i.e. toluene-PPO (4 g l^{-1}). The absolute efficiency of tritium detection for the standard solution equals 49% and for simplicity was further assumed to be equal to unity.

RESULTS AND DISCUSSION

The dependence of the relative efficiency of tritium detection on the volume fraction of cyclohexane, V_c , for systems A and B is shown in Fig. 1. No influence of tritium location on its detection efficiency has been observed. Decrease of detection efficiency with increased cyclohexane volume fraction is due to less efficient energy transfer to the scintillator observed in cyclohexane compared with toluene as solvent.

The results obtained for the solution with polymer as solute were compared and related to the curve shown in Fig. 1. In the presence of tritiated polystyrene, system C (Fig. 2(a)), the detection efficiency is a function of the volume fraction

of cyclohexane in a manner similar to the reference curve in Fig. 1 and it depends also on the concentration of polymer. Similar results in connection with solvent composition were obtained for system D when tritiated toluene was used. The addition of polymer, however, in this case causes an increase of detection efficiency but there is no measurable effect of polymer concentration. In system E (Fig. 2(C)) with labelled cyclohexane the increase of efficiency of tritium detection can also be noticed but is much less distinct compared with that presented in Fig. 2(b).

The results presented in this work can be discussed, at this stage, only qualitatively. For toluene solutions of polymers the differences in detection efficiency were attributed to non-homogeneous distribution of PPO molecules in the inner and outer spheres of the polymer. In the case of mixed solvent we have to deal also with the variable composition of the solvent within the macromolecular volume and its bulky, macroscopic environment. Because of selective adsorption of toluene molecules by swollen macromolecules of polystyrene one can imagine greater contribution of toluene than of cyclohexane inside macromolecules. The selective adsorption process is due to the different molecular interactions which also determine different thermodynamic properties of toluene and cyclohexane as polystyrene solvents.

The results presented above can be conveniently compared in the form of the diagram shown in Fig. 3. In Fig. 3 the difference, ΔE , in tritium detection is related to the solution without polymer (level 1). The comparison has been made for solution containing 95 volume percent of cyclohexane. In the system of the chosen composition a significant fraction of toluene molecules is probably enclosed within the volume of the macromolecules. As seen from Fig. 3, values of ΔE are similar for mixtures with labelled toluene (level 3) and tritiated polystyrene (level 4). In both cases due to selective adsorption labelled molecules are accumulated in microregions of a swollen macromolecule 'filled' with toluene molecules. A small ΔE value for solutions with labelled cyclohexane (level 2) can also be explained in terms of our model. In this case neither polymer nor toluene can contribute to energy transfer processes and efficiency observed is practically the same as for the toluene-cyclohexane-PPO system.

In another paper (p.32)¹ we have shown that energy acceptor, PPO molecules are displaced from the volume of macromolecules causing a relative deficit of PPO molecules. The selective adsorption of toluene by swollen polystyrene macromolecules discussed in this paper ensures a high local concentration of donor molecules. These two phenomena act simultaneously and the situation is therefore somewhat confused. Quantitative discussion of results obtained will be possible only when more data on the microstructure of the polymer solution in mixed solvent become available.

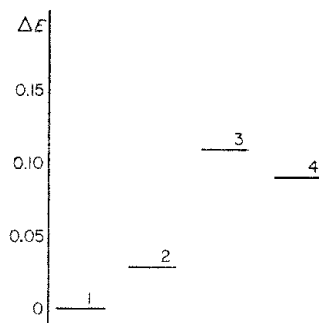


Fig. 3. The diagram of the difference in the efficiency of tritium detection, ΔE , for toluene-cyclohexane-PS-PPO system. Volume fraction of cyclohexane $V_c = 0.95$ and concentration of PS = 0.25 g l^{-1} . 1 - without PS, 2 - Cyclohexane-T, 3 - Toluene-T and 4 - PS-T.

REFERENCES

1. W. Reimschuessel, J. Gebicki and Z. Tołwinska-Stanczyk, in Liquid Scintillation Counting, Vol. 5 (M.A. Crook and P. Johnson, Eds) Heyden, London, 1978, p.32.
2. W.N. Cwietkow, W.J. Eskin and S.J. Frenkel, in Macromolecular Structure in Solutions, in Polish, WNT, Warsaw, 1968, p.256.
3. F.N. Hayes, Nucleonics, 13, 1 (1955).
4. H. Kallmann and M. Furst, Phys. Rev. 79, 857 (1950).
5. A. Murray and D.L. Williams, in Organic Syntheses with Isotopes, Interscience, New York, 1958, p.573.
6. R. Ewart, C. Roe, P. Debye and N. McCartney, J. Chem. Phys. 14, 687 (1946).

DISCUSSION

B.E. GORDON: How did you make sure that the polystyrene-T was not adsorbed on the vial walls? Once you have less than 10^{-7} or 10^{-8} molar in the counting vial, adsorption is a serious problem and gets worse with increase in molecular weight.

J. GEBICKI: Polystyrene is an example of non-polar polymer and its molecules should not be adsorbed on the vial walls in the solutions investigated. However, we have taken into consideration this fact and experimentally confirmed the lack of polystyrene adsorption to vial walls.

E.D. BRANSOME: To follow up Dr Gordon's question with a reference to other polymers: I suspect that the lack of adsorption of polystyrene to vial walls cannot be generalized to all polymers. Polyethyleneglycol, for instance, is notorious for its adsorption to vial walls.* Other oxygenated polymers (e.g. nucleic acids) in concentrations less than 2×10^{-6} M can also be expected to adsorb.

* W.G. Crouthamel and K. Van Dyke, Anal. Biochem. 66, 234 (1975).