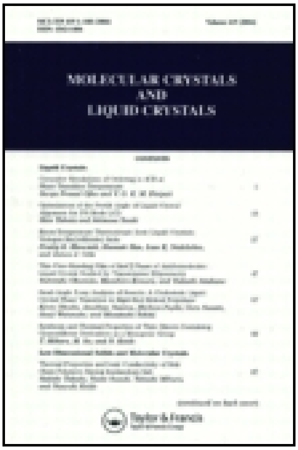

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Measurement of Transfer Efficiencies and Radiative Transfer of Aromatic Solvents at Very Low Solute Concentrations†

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1. Introduction

Many studies have been carried out on the measurements of luminescence yields as a function of the solute concentrations in aromatic solvents. Most of these have been done at moderate solute concentrations, between 0.1 and 20 g/l. The scope of this work was a study of the luminescence yield at low solute concentrations, down to 0.005 g/l. Only at these low concentrations is it possible to get information on other processes which might occur in the liquid scintillator solution system. Of particular interest is the measurement of the contribution to the luminescence yield of a possible radiative transfer process at low solute concentrations.

The earlier work of Berlman[1] has been extended to these low solute concentration solutions by use of new techniques which give very reliable data. A semi-empirical formula has been developed to explain the measured light yields. A computer program is used to evaluate the parameters of this equation. The luminescence yields were measured for liquid scintillator solutions excited by both alpha particles and electrons. Interesting differences in the parameters of the developed equation are obtained for the different mode of excitation. Also the luminescence yields were measured at two temperatures. The effects of temperature are discussed.

Other interesting information obtained from this work include measurement of the α/β ratio as a function of solute concentration, the rela-

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† Based on work performed under the auspices of the U.S. Atomic Energy Commission.

tive amount of dynamic quenching (or track quenching), the transfer efficiencies, and the fraction of observed light which arises from transfer by the radiative process. (This process does not reguire the emission and absorption of a real photon.)

2. Experimental

Equipment

A single multiplier phototube light measuring system was used. This has been described in detail in previous publications.[2] Two types of multiplier phototubes were employed, a DuMont 6292 operated at +750 v and cooled to −20°C and an RCA 8575 operated at + 1000 v and room temperature (24°C). Both of these tubes have good response to the wavelength of light emitted by the solutes studied. A difference in the spectral response curves is not important since only relative pulse heights are measured. The RCA 8575 has very low noise at room temperature but the DuMont 6292 has a much better energy resolution. The DuMont 6292 could not be used at room temperature due to the high noise levels encountered. A sample holder-light guide was made of special UVT-Lucite (ultraviolet transmissive) and was painted with a MgO reflecting paint to insure collection of all possible light emitted by the scintillating solution.[2]

Materials for Liquid Scintillators

The solvent used in this work was toluene, Research Grade from Phillips Petroleum. The two solutes used were 2,5-diphenyloxazole, PPO, and 1,4-Bis-2-(4-methyl-5-phenyloxazolyl) benzene, M_2-POPOP, scintillation grade from Packard Instrument Co. Stock solutions of various solute concentration were prepared by weighing amounts of solute which were dissolved in desired volumes of toluene. Intermediate concentrations were obtained by accurate dilutions. No dilutions greater than 1 : 4 were made on any one stock solution.

Radioactive Sources

Sn^{113} was used as the source for electron excitation and Pu^{238} as the source for alpha particle excitation. Sn^{113m} decays by electron capture to the 104 min half-life I_n^{113m} which decays by emission of a 50% internally

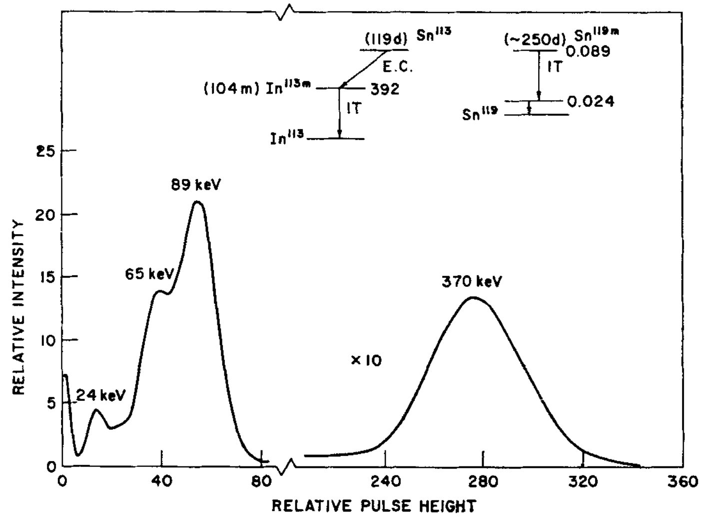


Figure 1. Differential pulse height spectrum of a Sn^{113} excited scintillator solution of 5.0 g/l PPO in toluene.

converted 392 keV gamma ray. The conversion is predominately in the *K* shell which gives rise to 370 keV conversion electrons. A typical differential pulse height spectra obtained from a 5.0 g/l solution of PPO in toluene using the DuMont 6292 multiplier phototube at —20°C is shown in Figure 1. The peaks observed at the lower energy arise from conversion electrons from the decay of some Sn^{119m} present in the sample. The Pu^{238} decays by emission of 5.5 MeV alpha particles.

These radioactive sources are dissolved directly in the scintillator solution by use of the di-(n-octyl) phosphoric acid complexes of Sn and Pu. This technique is described in previous publications.[2] About 3 μl of a 25% solution of the complex in toluene is used in each sample. At these concentrations there is essentially no quenching of the light.

Sample Preparation

As described in previous publications[2] small samples of 250 μl were used. Argon was used to purge oxygen. Thin walled quartz tubing (6 mm O.D. and 5 mm I.D.) was used for sample containers. The sample was frozen with liquid nitrogen, evacuated and permanently sealed by use of a torch. This technique gave samples that were stable for long periods of time. It is very important that all oxygen be removed so that the dynamic (or track) quenching can be studied. The small volumes minimize the probability of self absorption of the light emitted by the solute.

3. Results

The differential pulse height spectrum was measured for each concentration of solute. Some typical spectra are shown for Sn^{113} excitation of PPO solutions, Fig. 2, and Pu^{238} excitation of PPO solutions, Fig. 3. Using the maximum of each distribution as a measure of the lumines-

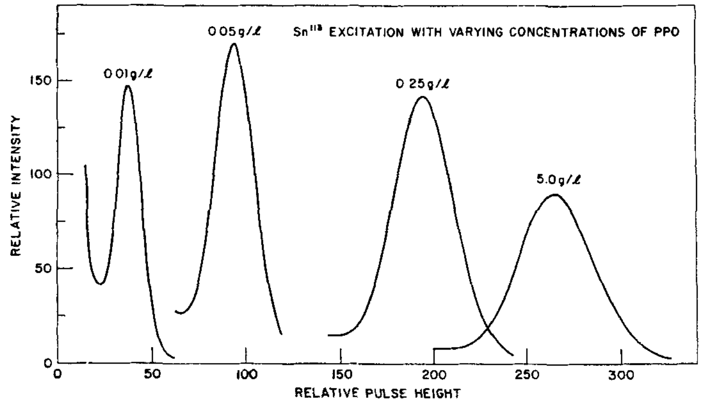


Figure 2. Several differential pulse height spectra of the 370 keV conversion electrons from Sn^{113} at different concentrations of PPO in toluene.

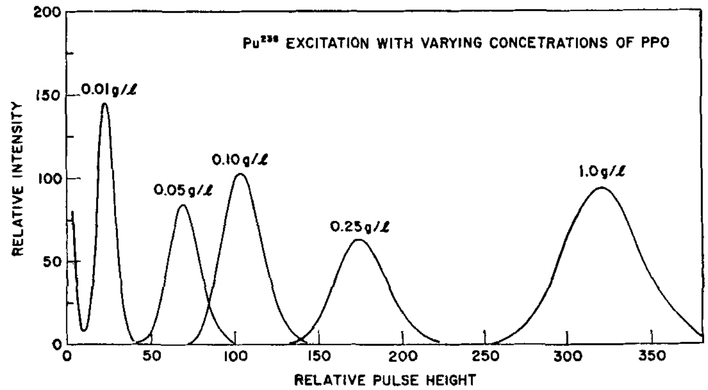


Figure 3. Several differential pulse height spectra of the 5.5 MeV alpha particles from Pu^{238} at different concentrations of PPO in toluene.

cence yield, plots of the relative pulse height versus concentration were obtained, Fig. 4, 5 and 6.

An interesting fact obtained from this data is that 100% of the 370 KeV conversion electrons and 5.5 MeV alpha particles are counted even at the lowest solute concentrations. Thus every particle must produce a measurable and statistically equivalent number of excited solute molecules. The homogeneity of the scintillator solutions is shown by plots of the resolution (full width at half maximum divided by the pulse height of the maximum of the distribution) versus the reciprocal of the square root of the pulse height of the maximum of the distribution. If there are no local concentration effects this plot should be a straight line. Figure 7 shows the straight line plots obtained with typical data. This same type of plot was obtained at a constant solute concentration and different energy particles, Fig. 8. The increase in the resolution is due to a decrease in the number of photons produced and not to any local

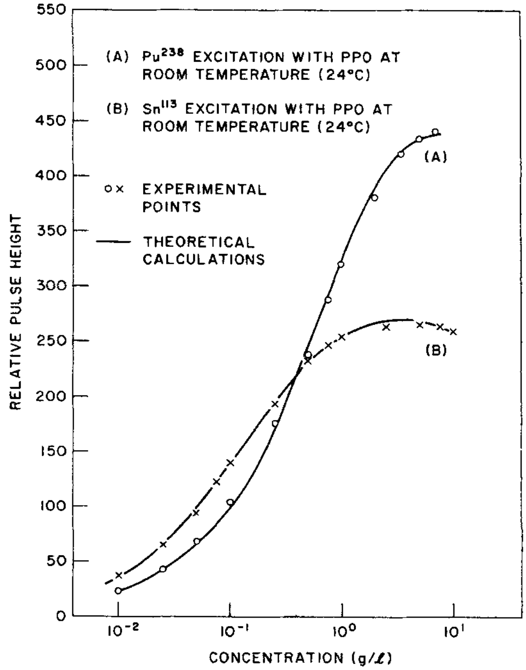


Figure 4. Luminescence yield (relative pulse height) of PPO-toluene solutions at 24°C for Sn^{113} and Pu^{238} excitations as a function of PPO concentration. Experimental and theoretical data.

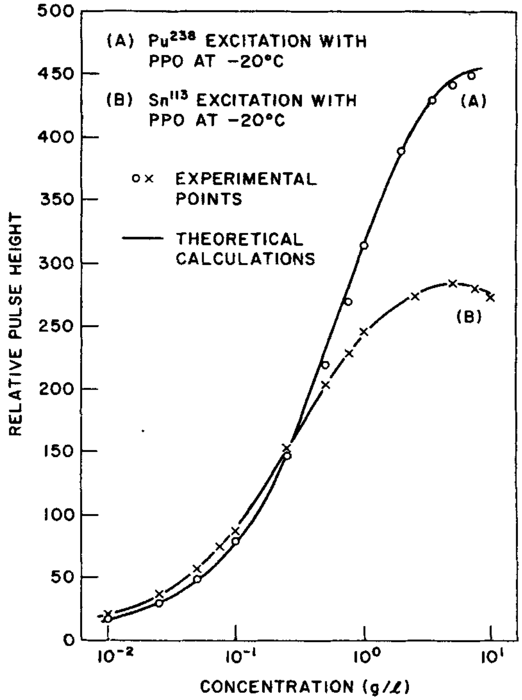


Figure 5. Luminescence yield (relative pulse height) of PPO-toluene solutions at −20°C for Sn^{113} and Pu^{238} excitations as a function of PPO concentrations. Experimental and theoretical.

concentration effects. Thus the solutions are homogeneous over the range of solute concentrations employed.

From the data the α/β ratio can be obtained as a function of the solute concentration, Fig. 9. This ratio is defined by the equation:

$$\alpha/\beta = \frac{\mathrm{RPH}_\alpha/5.5}{\mathrm{RPH}_\beta/0.370} \tag{1}$$

where RPH_α is the pulse height of the maximum of the alpha distribution and RPH_β is the pulse height of the maximum of the electron distribution. It should be noted that because the alpha energy-pulse height response function [2, 3] is nonproportional, different α/β ratios will be obtained with different energy alpha particle emitters.

Special care was taken to be sure that light emitted by the solvent was not being measured. A sample of toluene and Sn^{113} complex (with no

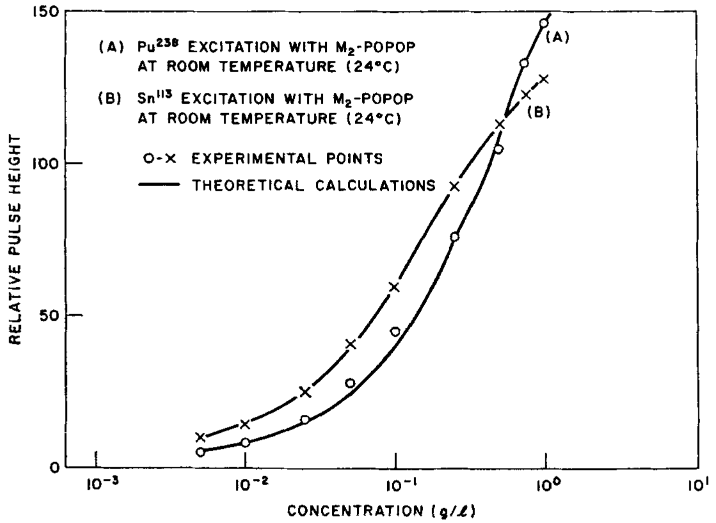


Figure 6. Luminescence yield (relative pulse height) of M$_2$-POPOP-toluene solutions at 24°C for Sn^{113} and Pu^{238} excitations as a function of M$_2$-POPOP concentrations. Experimental and theoretical.

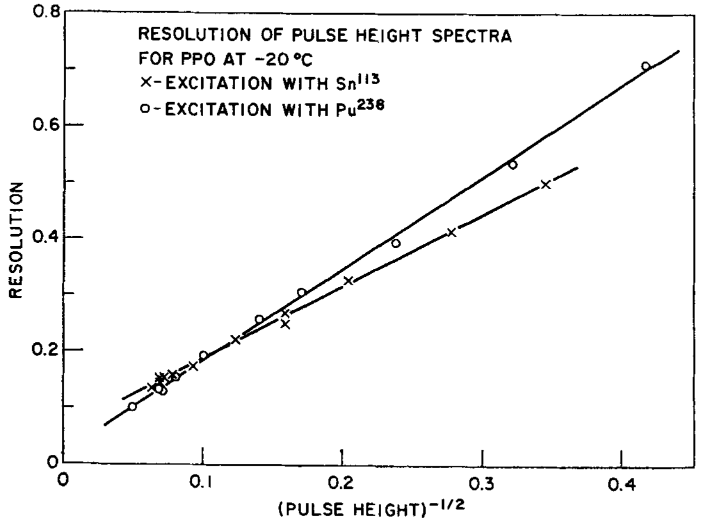
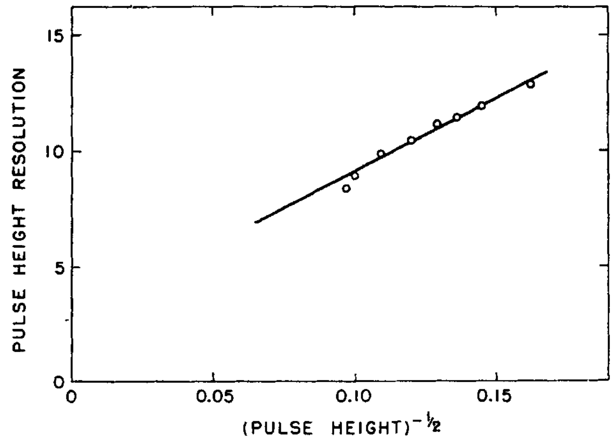


Figure 7. Resolution of pulse height spectra as a function of relative pulse height for Sn^{113} and Pu^{238} excitations of PPO-toluene solutions at —20°C for varying PPO concentrations.



Pulse height resolution-pulse height relationship as a function of alpha particle energy.

Figure 8. Resolution of pulse height spectra as a function of the relative pulse height for alpha particle excitation of a solution of 5.0 g/l PPO in toluene for varying alpha particle energy.

solute) was measured and no detectable light was observed with either multiplier phototube.

4. Discussion

The luminescence yield, *L*, of a liquid scintillator solution which is free of external quenchers, i.e. oxygen, can be described at higher solute

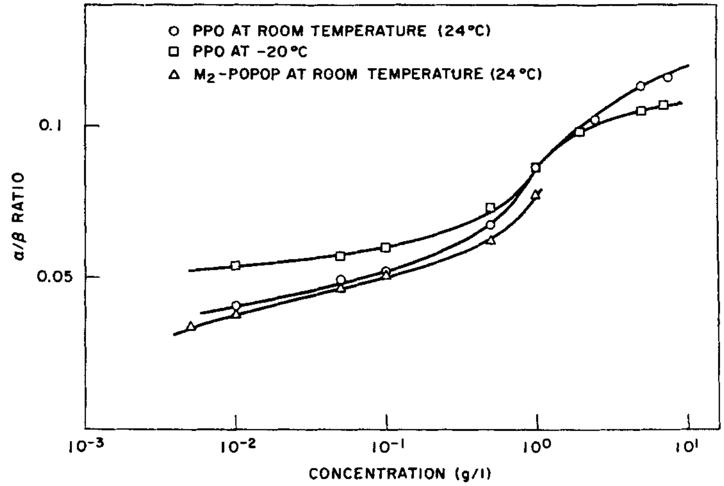


Figure 9. Value of α/β ratios as a function of solute concentration.

concentrations by the equation:

$$L = L'\left(\frac{p_t}{p_e + p_q + p_t + p'_q}\right)\left(\frac{P_e}{P_e + P_i + P_q}\right) \tag{2}$$

where p_t, p_e, p_q and p'_q are the probabilities/sec, respectively, for energy transfer from solvent to solute, for solvent emission of the excitation energy, for inter- and intramolecular quenching of the solvent and for dynamic (or track) quenching of the solvent, and P_e, P_i and P_q are the probabilities/sec, respectively, for emission from the solute, for internal quenching of the solute and for self quenching of the solute. Both p_t and P_q are concentration dependent. L' is determined by the number of solvent molecules which are excited to the electronic level which is responsible for the transfer and emission processes (this is, in most cases, the first excited singlet state of the solvent molecule). Upon rearranging Eq. (2) one gets:

$$\text{RPH} = A\left(\frac{Bc}{1 + Bc + D}\right)\left(\frac{1}{1 + Ec}\right) \tag{3}$$

where c is the concentration of the solute,

RPH is the measured pulse height of the maximum of the pulse height distribution,

A is $\dfrac{L'(P_e + P_i)}{P_e}$, and includes a normalizing factor for the light collection efficiency of the apparatus,

Bc is $\dfrac{p_t}{p_e + p_q}$,

D is $\dfrac{p'_q}{p_e + p_q}$, and is proportional to the amount of dynamic quenching, and

Ec is $\dfrac{P_q}{P_e + P_i}$, and is proportional to the amount of self quenching.

This equation describes the data very well at solute concentrations above 1 g/l. However, at lower concentrations the measured RPH was always higher than that calculated from Eq. (3). Thus a new process of energy transfer must become important at the low solute concentrations. This could very likely be some sort of radiative transfer of energy from the excited solvent molecule to the solute molecule. A semi-empirical formula was developed to give the best fit to the measured RPH values. Several functions of the solute concentration were tried with the follow-

TABLE 1 Computer Determined Values of the Constants of Equation (4)

Solute	Temp. °C	Excitation Mode	A	B	D	E	F	G	H
PPO	24	Sn^{113}	292	7.0	0.0	0.011	0.043	0.0230	0.000147
PPO	24	Pu^{238}	510	7.0	3.0	0.011	0.088	0.0225	0.000137
PPO	—20	Sn^{113}	316	7.0	1.0	0.011	0.025	0.0167	0.000094
PPO	—20	Pu^{238}	540	7.0	4.0	0.011	0.041	0.0191	0.000112
M_2-POPOP	24	Sn^{113}	148	6.5	0.0	—	0.0087	0.0085	0.000025
M_2-POPOP	24	Pu^{238}	213	6.5	2.0	—	0.026	0.0120	0.000037

ing equation giving the best agreement over the range of solute concentrations investigated:

$$\mathrm{RPH} = A\left[\frac{Bc + Fc^{-1/2}(1 - Gc^{-1} + Hc^{-2})}{1 + Bc + D}\right]\left[\frac{1}{1 + Ec}\right] \tag{4}$$

where $Fc^{-1/2}$ is proportional to the number of solvent molecules which are in an excited state which could transfer its energy to the solute molecule by this radiative process,

and $(1 - Gc^{-1} + Hc^{-2})$ is the fraction of these excited solvent molecules which produce excited solute molecules.

A computer program was used to evaluate these constants to give the best fit to the measured RPH values. A was evaluated by normalizing the Eq. (4) at the experimental value of the RPH at 1 g/l. The values of B, D and E are obtained from the data at the higher concentrations and agree quite well with those found by Berlman[1] for PPO. The computer gave the values shown in Table 1.

The curves calculated with these parameters are shown as the solid lines in Fig. 4, 5 and 6. The agreement is very good in all cases.

From these values the transfer efficiency of a solvent-solute system can be calculated;

$$\mathrm{T.E.} = \frac{Bc + Fc^{-1/2}(1 - Gc^{-1} + Hc^{-2})}{1 + Bc + D} \tag{5}$$

which is the first part of Eq. (4). The T.E. values as a function of solute concentration are plotted in Figures 10 and 11. In every case the transfer efficiency is higher for electron excitation than alpha particle excitation. Also with PPO the transfer efficiency is lower at —20°C than 24°C.

Figure 12 shows the fraction of the observed light which comes from this radiative transfer process. At high solute concentrations the competition for transfer of energy by other methods essentially eliminates this radiative transfer process. A greater fraction of the light comes from this radiative transfer at 24°C than —20°C and for alpha particle excitation than for electron excitation. These observations are partly indicated by the larger values of F at the higher temperature, for a given mode of excitation, and for alpha particle excitation, compared to electron excitation at the same temperature. The higher *F* values indicate that the number of solvent molecules excited to the state which can transfer

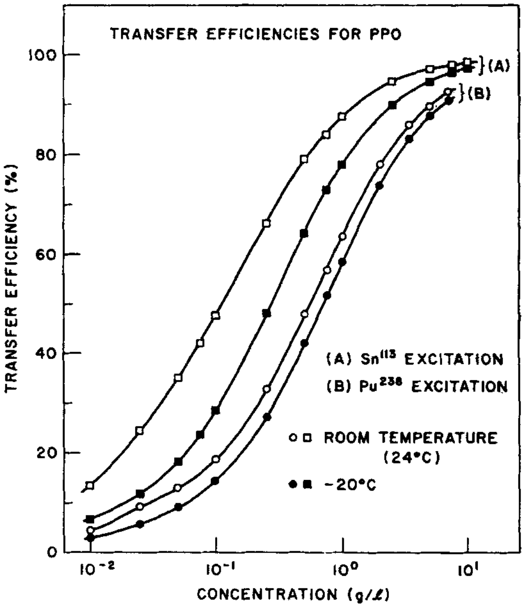


Figure 10. Transfer efficiencies of PPO-toluene solutions as a function of PPO concentrations.

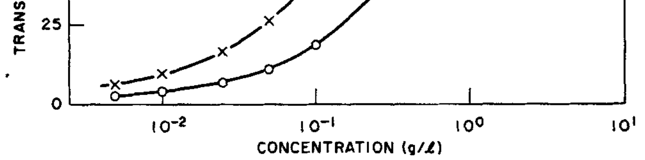


Figure 11. Transfer efficiencies of M_2-POPOP-toluene solutions as a function of M_2-POPOP concentration.

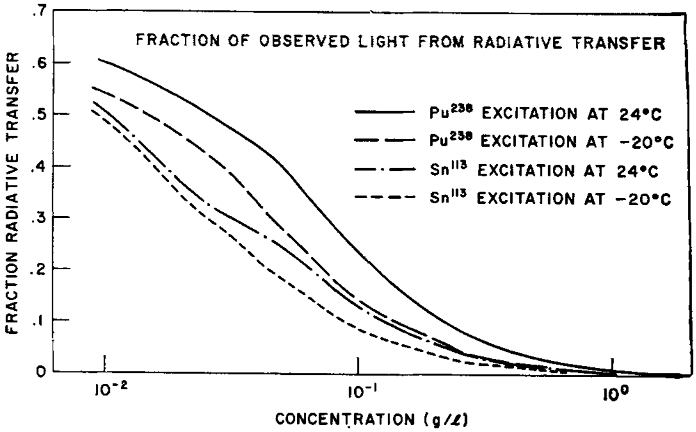


Figure 12. Fraction of observed light which is produced by radiative transfer in PPO-toluene solutions as a function of the PPO concentrations.

by this radiative process depends on the specific ionization of the particle; a greater fraction of this type of excited solvent molecules are produced by the higher specific ionization. This might be a possible indication that this radiative transfer process is associated with ion formation. The temperature effect on the value of F might be due to a diffusion factor. At the lower temperature the quench centers and the excited solvent molecules are held together for a longer period leading to a greater probability for quenching of the excitation energy.

Since the values of G and H are nearly the same regardless of the mode of excitation, for a given solute and temperature, the transfer process must be a simple emission absorption process which depends only upon the solute concentration.

The values of D give an indication of the degree of dynamic quenching which is a quenching of the excited solvent molecules which can contribute to the energy transfer processes. This is different from static quenching which affects all excited solvent molecules; often leading to conversion of energy into heat, and occurs much faster than the dynamic quenching. The value of D is very dependent on the specific ionization of the exciting particle. The greater specific ionization produces a higher concentration of some kind of quencher. The value of D is also temperature dependent. This may also be due to the diffusion process. At —20°C the D values are greater possibly due to an increased probability of the quenchers and excited solvent molecules coming in contact due to smaller diffusion parameters. It is very interesting that at —20°C there is a dynamic quenching for electron excitation of PPO solutions.

The value of B is constant for PPO excitation regardless of the mode of excitation or temperature (at least over the temperature range of this experiment). The value of B might be an indication of the degree of overlap of the toluene emission spectrum and the solute absorption spectrum. The value of B and the overlap are less for M_2-POPOP than for PPO. Another indication of the degree of overlap is obtained from the calculation of the fraction of light produced by this radiative transfer process. There is much less radiative transfer with M_2-POPOP than with PPO.

The value of E for excitation of PPO solutions in this work is higher than that reported by Berlman[1] but still comparable, 0.011 as compared to Berlman's 0.006. The value of E for M_2-POPOP could not be obtained from this data due to its low solubility in toluene.

The change of the α/β ratio with solute concentration is somewhat complicated as shown in Fig. 9. For PPO solutions the α/β ratio at —20°C is less than that at 24°C at the higher PPO concentrations but is greater at the lower temperature for lower PPO concentrations. For the small volumes of scintillator solution at room temperature an α/β ratio as big as 0.116 was obtained with 7.5 g/l of PPO.

5. Conclusions

From the data presented in this work it appears that a radiative energy transfer process becomes quite important at very low solute concentrations. At solute concentrations of 0.01 g/l as much as 60% of the observed light is a result of the radiative energy transfer process. Some of the parameters obtained from the semi-empirical equation, which relates the measured luminescence yield and solute concentration, give information on other processes which occur in the liquid scintillators:

Dynamic Quenching—increases with increasing specific ionization of the exciting particle and with decreasing temperature.

Excited Solvent Molecules which Produce Radiative Transfer—the fraction of these molecules increases with increasing specific ionization of the exciting particle and with increasing temperature.

Fraction of Radiative Transfer which Actually Transfers to Solute—mostly independent of mode of excitation (for α or e^-) and only slightly dependent on temperature.

Transfer Efficiencies—greater for excitation particles of lower specific ionization and for higher temperatures.

Overlap of Spectra of Solvent Emission and of Solute Absorption—an indication of the relative amounts of overlap for different solutes.

The α/β ratio—a complex function of temperature and solute concentration.

This work gives a method which can be used to obtain information about the energy transfer processes with any solvent-solute system. Thus, for different solutes, information can be obtained to correlate between solute constitution and the above listed properties of the scintillator solution.

REFERENCES

1. Berlman, I. B., *J. Chem. Phys.* **34**, 598 (1961).
2. Horrocks, D. L., *Rev. Sci. Instr.* **35**, 334 (1964); *Nucl. Instr. and Meth.* **27**, 253 (1964) and *Nucl. Instr. and Meth.* **30**, 157 (1964).
3. Flynn, K. F., Glendenin, L. E., Steinberg, E. P. and Wright, P. M., *Nucl. Instr. and Meth.* **27**, 13 (1964).