

The Study of Energy Transfer in Binary Organic Liquid Mixtures under Gamma-Irradiation

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The radiation induced light emission from various binary organic liquid mixtures, always with benzene as one component, has been measured using a new method. With this method it was possible to measure the emission intensity from each component in binary mixtures. Systems studied were composed from various alkanes, alcohols, acetates, and ketones, all with benzene. Parallel measurements of Gr value (radiolytic yields of free radicals) from the above liquid mixtures were performed using diphenyl picryl hydrazyl (DPPH). There was a close correlation between the variation of the emission intensities from alkanes, alcohols, and acetates in the mixtures with benzene, and that of Gr values from the mixtures with their compositions. In the case with a mixture of benzene and acetone there was no such correlation between both variations.. This fact was explained as due to the energy transfer between the lowest excited states of the both liquids. The experimental results suggest that energy transfer process exists between highly excited states of two components in the mixtures, and oxygen dissolved in the mixtures plays an important role in energy transfer process of radiation chemistry. Our results can also explain the fluorescent behaviors of liquid scintillator systems containing two solvents.

I. INTRODUCTION

Manion and Burton¹⁾ have reported that in radiolysis of a mixture of benzene and cyclohexane under electron bombardment excited cyclohexane molecule is protected by benzene. As the result of this protection, a yield of hydrogen is much less than that predicted by the assumption that the radiation energy absorbed by each component in the mixture is proportional to its mole fraction. This kind of protection and sensitization of a component to another in radiolysis of their mixtures have also been reported by several authors^{1,2,3)}.

Most of the methods used by these authors to investigate the indirect chemical effects in liquid mixtures were those by the measurements of Gr value from the mixtures by radical scavengers²⁾ and of fluorescence from small quantity of scintillator solute dissolved in the mixtures⁴⁾ and quantitative analysis of radiolitic products from the mixtures³⁾. In these methods it is always necessary to confirm that the chemical reactions following the primary process in radiation chemistry have no effect on the results of these measurements.

It will be required to know the behaviors of each component in a mixture under irradiation when detail discussions are needed about the sensitization and the protection. But none of these methods can make it clear how a component, say component A, is sensitized by another component, say component B, when com-

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ponent B is protected by component A or vice versa.

The method described here makes it possible to know the behaviors of each component in a mixture under irradiation. It is well known that the organic liquid under ionizing irradiation emits faint light. The light comes from excited and ionized species produced by the radiation in the liquid, and its intensity is proportional to the number of same. Because the excited and ionized species produced by the radiation are proper to the liquid, the emission spectrum from these is characteristic of the liquid. Therefore, if it is possible to distinguish the emission spectra of each component from the total emission of a mixture under the irradiation, it will be possible to know the relative numbers of excited and ionized species from both components over the complete range of composition, and the results obtained by this method will not be affected by the chemical reactions following the primary process, because the lights are emitted from these highly excited species within their very short life times, say 10^{-13} sec. This method is a new one in the study of energy transfer in binary liquid mixtures in radiation chemistry, and it is expected that the comparison of the results with those obtained by ordinary methods would give new knowledge about the systems.

However, under the irradiation where radiolysis of a mixture is negligible, the emission intensity from the mixture is so faint that it is difficult to investigate the emission spectrum. Although we did not measure the emission spectra from each component in a mixture, we distinguished the emission intensities from each component which contributed to the total emission intensity from the mixture using the method described in the following section. The measurement of the emission intensity was performed both in absence and presence of dissolved oxygen, and the results were compared with those from the measurement of Gr value.

II. EXPERIMENTAL

II.1. Principle

We let A and B be the components which compose a mixture. I_{A_0} and I_{B_0} are the respective emission intensities from each component under irradiation. When I_{A_0} and I_{B_0} are measured through a filter, these intensities will be reduced by factors α and β , respectively. As the emission intensity from the mixture, I_{A+B} , consists of the emission intensities from each component I_A and I_B , it follows that

$$I_{A+B} = I_A + I_B. \quad (1)$$

When this emission intensity is measured through the filter used to determine α and β , then emission intensity from the mixture, I'_{A+B} , will be expressed as follows:

$$I'_{A+B} = \alpha I_A + \beta I_B. \quad (2)$$

As I_{A+B} , I'_{A+B} , α , and β are the values obtained experimentally, it follows from Eqs. (1) and (2) that

$$I_A = \frac{I'_{A+B} - \beta I_{A+B}}{\alpha - \beta}, \quad (3)$$

$$I_B = \frac{\alpha I_{A+B} - I'_{A+B}}{\alpha - \beta}. \quad (4)$$

II.2. Apparatus

The experimental apparatus is shown in Fig.1. Gamma radiation from a 2 mC Co^{60} source was used to irradiate the mixtures contained in a stainless steel beaker.

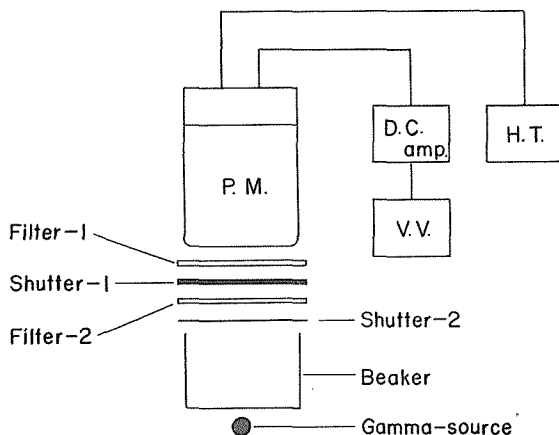


Fig. 1. Experimental apparatus for the study of γ -induced emission from organic liquids (schematic).

The light emission intensity was measured by a Toshiba MS-9SY photomultiplier. The voltage across the anode resistor was amplified by a vacuum tube voltmeter. The spectral sensitivity of the photomultiplier lies in the range of wave length between $2000\text{\AA}$ and $7000\text{\AA}$. Therefore, a photo-plate glass was always placed as Filter-1 in front of the photomultiplier to eliminate the effect of self-absorption in a mixture and the fluorescence from benzene. Filter-1 cuts the light of wave length shorter than $3200\text{\AA}$. It is necessary to eliminate the fluorescence from benzene, because this fluorescence is affected by energy transfer between the lowest excited states of benzene and another component. In order to get α , β , and I'_{A+B} a Toshiba UV-D25 glass filter (Filter-2) was placed under Shutter-1. This filter was operated manually and passed the light of wave length between about $2500\text{\AA}$ and $3900\text{\AA}$. Shutter-1 was used to shield the photomultiplier when a sample was exchanged. Shutter-2 was made of a sheet of black paper. After each measurement light emission from a mixture or components was shielded by the Shutter-2, and the dark current which was due to the direct effect of gamma radiation on the photomultiplier was measured.

When the measurement was performed with nitrogenated mixtures or components the apparatus except the associated electronic equipment was placed in a special box filled with dried nitrogen. Nitrogen was introduced by bubbling it through the mixtures or components, and they were transferred by a pipette into the beaker in the box.

II.3. Measurement of Gr Value.

Measurements of Gr value from liquid mixtures were performed using diphenyl picryl hydrazyl (DPPH). The gamma-ray irradiation of DPPH solutions was carried out in cylindrical glass cells of 12 mm inner diameter and 15 cm long. DPPH solutions of 10 cc concentration of which was 1×10^{-4} mol/l were used for each

irradiation. In the measurement with solutions containing no oxygen degassed solutions were used in stead of nitrogenated solutions. Preliminary experiments showed both solutions gave the same experimental results. The degassed solutions were prepared by the freeze-pump-thaw technique. Liquid nitrogen was used to freeze the solutions. Gamma-ray irradiations were performed with Co^{60} source⁵⁾ which was calibrated by the Fricke dosimety. Dose rate for the irradiation was 1000 r/hr. In the case of chloroform which is known to give very high Gr value⁶⁾, it was confirmed that under the irradiation of the above dose rate the DPPH concentration we used was sufficient to scavenge radicals produced from the solvent. All Gr values in this paper are the averages of three runs in different total doses.

II.4. Chemicals

All chemicals we used except DPPH and nitrogen gas were of guaranteed reagent grade from Nakarai Chemical Co. The purification processes of the above chemicals are as follows.

a) Benzene, cyclohexane, and chloroform were purified by shaking with sulphuric acid, washing with distilled water, drying with metallic sodium and then, distilling on fresh metallic sodium. But chloroform was dried on CaCl_2 , and distilled. All chemicals were distilled through a 30-theoretical-plate column, and the first and last 20 % of the distillate were discarded.

b) Acetone was purified by refluxing with KMnO_4 , drying on K_2CO_3 , and distilling.

c) Methyl acetate was purified by shaking with saturated sodium chloride solution, drying with MgSO_4 and distilling.

d) To obtain the anhydrous ethanol of high purity, 5 % benzene solution in ethanol was distilled, analyzing the purity of the distillate by gas chromatography at several stages of the distillation. The distillate whose purity was 99.99% or more was used for present experiment.

e) The analysis of gas chromatography showed the amount of impurities in the above chemicals except ethanol after purification were of trace or less.

f) DPPH was used as received from Tokyo Kasei Chemical Co.

g) Nitrogen gas was obtained from industrial gas cylinder and used as received because the analysis of gas chromatography showed the purity of gas was 99.99%.

III. EXPERIMENTAL RESULTS AND DISCUSSION

III.1. Comparison of the Variation of Emission Intensity and of Gr Value with the Composition of Mixtures

The molecule which had an interaction with ionizing radiation is excited to its highly excited states or becomes a highly excited molecular ion. The highly excited molecule or molecular ion decomposes within about 10^{-13} sec., producing many kinds of radicals, daughter ions, or becomes a lower-excited molecule, losing their excitation energy. We may expect that some of these radicals and ions are in their excited states and emit lights. Even if these products are in their excited states which have enough energy to dissociate an ordinary chemical bond, they will not be able to decompose another molecule by giving their excitation energy

to it. Because this energy will be distributed to many chemical bonds which compose the molecule, and the energy given to each chemical bond will not be sufficient to dissociate it. Therefore, the irradiation products do not take part in the energy transfer process in a binary organic liquid mixture.

In the spurs produced by radiation in a liquid highly excited molecules or molecular ions exist densely, and their orbitals will overlap, having interactions with each other. Therefore, it will be appropriate to think that the energy transfer process exists in the highly excited states of molecules or molecular ions produced immediately after the interaction between radiation and molecules in a binary liquid mixture. If in a binary organic liquid mixture the energy transfer takes place between the highly excited states of each component, the kinds of radicals, ions, and lower-excited molecule produced from a component of the mixture are the same as those produced from the component when it exists alone. This fact was implicitly assumed in Eq. (1). As the gamma-induced light emission comes from the excited radicals and ions, and the lower-excited molecules produced from the highly excited molecules, there must be a parallel relationship between the emission intensity from a component and the number of radicals which give the Gr value of the component.

Figures 2(a), 3(a), 4(a), and 5(a) give the curves for the variation of the emission intensities from each component in the following liquid mixtures with their compositions, respectively: cyclohexane, ethanol, methyl acetate, and acetone, all with benzene in presence of oxygen. Figures 2(b), 3(b), 4(b), and 5(b) give the curves for the variation of Gr value from the above mixtures with their compositions, respectively.

As Gr value from benzene is very small, $Gr=0.8$ in presence of oxygen, con-

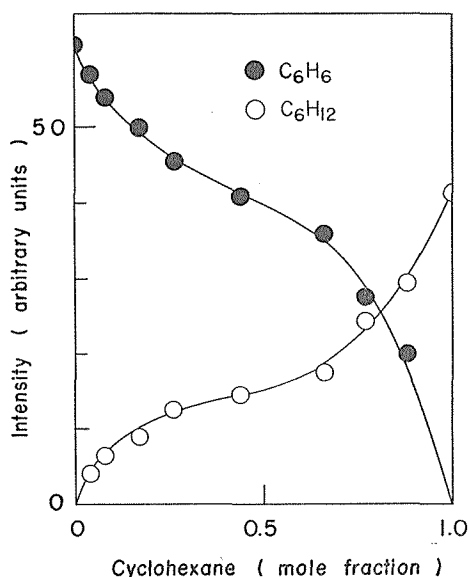


Fig. 2(a). Variation of emission intensities from benzene and cyclohexane in their mixture with its composition, in presence of oxygen.

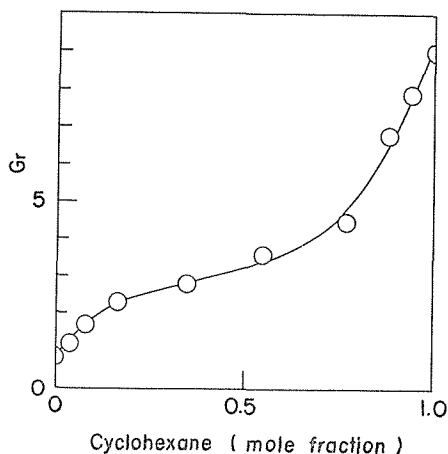


Fig. 2(b). Variation of Gr value from a mixture of benzene and cyclohexane with its composition, in presence of oxygen.

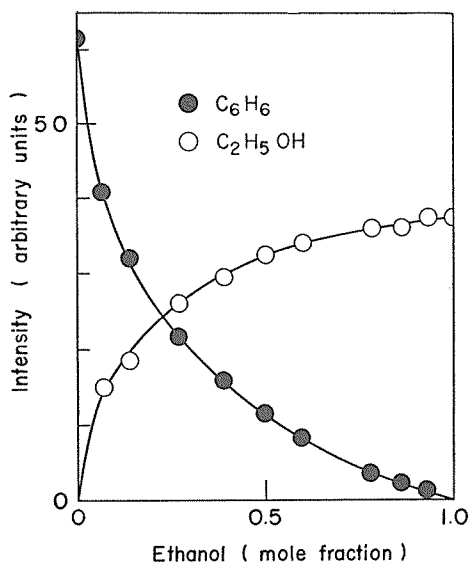


Fig. 3(a). Variation of emission intensities from benzene and ethanol in their mixture with its composition, in presence of oxygen.

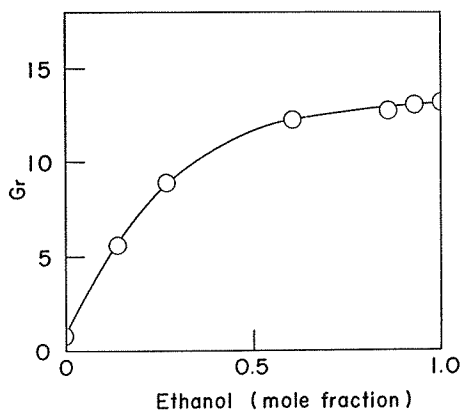


Fig. 3(b). Variation of Gr value from a mixture of benzene and ethanol with its composition, in presence of oxygen.

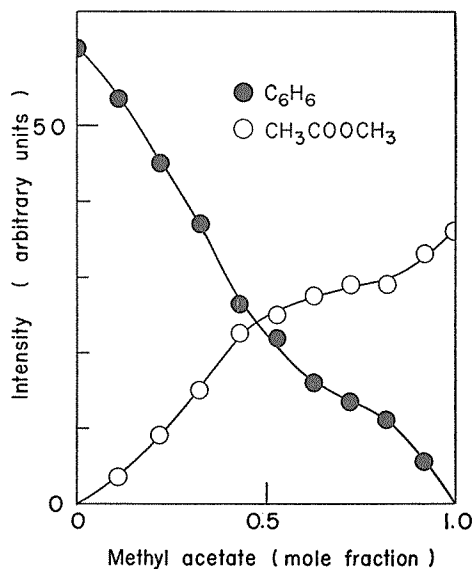


Fig. 4(a). Variation of emission intensities from benzene and methyl acetate in their mixture with its composition, in presence of oxygen.

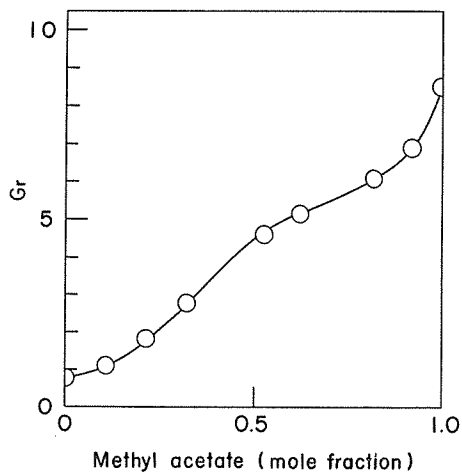


Fig. 4(b). Variation of Gr value from a mixture of benzene and methyl acetate with its composition, in presence of oxygen.

tributions to Gr value from the mixtures mostly come from cyclohexane, ethanol, methyl acetate or acetone. When the comparison is made between the curves of Gr value from the mixtures and of emission intensity from cyclohexane, ethanol, and methyl acetate in the mixtures, it is found that there is a close correlation between both curves. The correlation which was expected from the above discussion

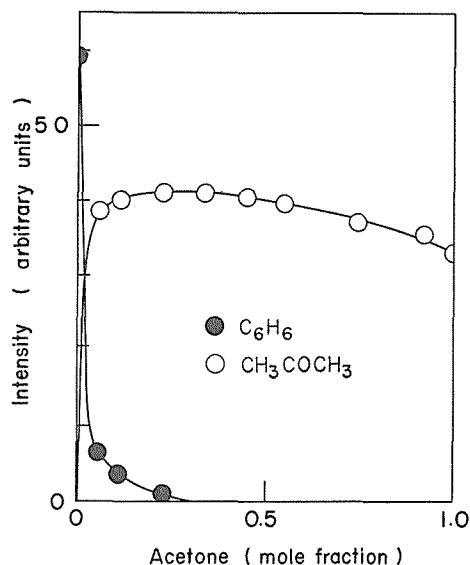


Fig. 5(a). Variation of emission intensities from benzene and acetone in their mixture with its composition, in presence of oxygen.

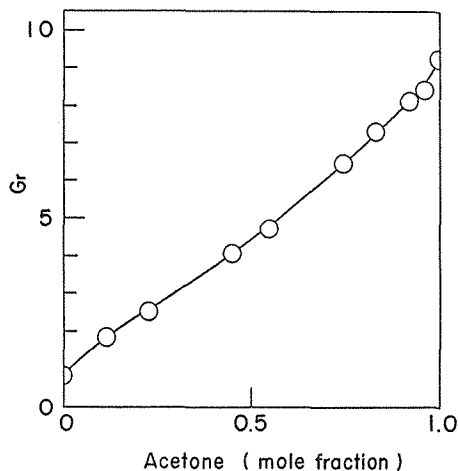


Fig. 5(b). Variation of Gr value from a mixture of benzene and acetone with its composition, in presence of oxygen.

was also found in the following mixtures studied: n-hexane, n-heptane, propanol, butyl acetate, and benzyl acetate, all with benzene in both cases of presence and absence of oxygen.

In the mixture of acetone and benzene there is no correlation between both curves as shown in Figs. 5(a) and 5(b). The reason for this fact is considered as follows; acetone has an absorption band in near-ultra-violet region and when acetone vapour is irradiated with ultra-violet radiation, it emits the fluorescence which has its maximum intensity around $4000\text{\AA}$ ⁷. This fluorescence is not cut by Filter-1, and there exists excitation transfer from excited benzene to acetone.

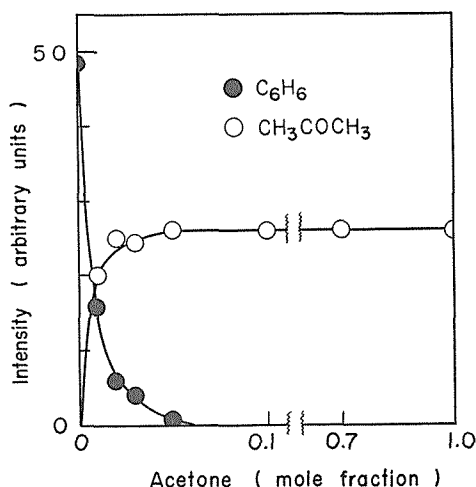


Fig. 6. Variation of fluorescent intensities from benzene and acetone in their mixture with its composition under $2537\text{\AA}$ U. V. irradiation, in presence of oxygen.

This fact is clearly shown in Fig. 6 where the curves for the variation of fluorescent intensity from benzene and acetone in their mixture with its composition under 2537Å ultra-violet irradiation are given.

As the extinction coefficient of benzene is much greater than that of acetone at 2537Å, most of the radiation energy is absorbed by benzene, but the fluorescent intensity from acetone is efficiently sensitized by benzene. No correlation found in the mixture of benzene and acetone can be explained by the fact that the fluorescence from the lowest excited state of acetone was not be eliminated from the emission of the mixture. Accordingly, if we measure the light emission in the range of wave length where the fluorescence from the lowest excited state of acetone dose not exist, a good agreement will be obtained between the curves of Gr value and of the emission intensity in this system of liquid mixture. However, at present time there is a technical difficulty because in the region of wave length longer than about 4000Å the emission spectra from benzene is almost the same as that from acetone; this fact makes it impossible to calculate the correct I_A 's and I_B 's from Eqs. (3) and (4).

III.2. Effect of Oxygen on Light Emission and Gr Value from Mixtures

Table I gives the emission intensities and the factor α 's from benzene and cyclohexane in presence and absence of oxygen.

Table 1. Emission intensities and factor α 's from benzene and cyclohexane.

	Intensity*		Factor α	
	in presence of oxygen	in absence of oxygen	α_{O_2}	α_{N_2}
Benzene	0.64	1.00	0.561	0.673
Cyclohexane	0.44	0.44	0.468	0.468

*) All intensity values are referred to the value of benzene in absence of oxygen as 1.

It is clear from the Table 1 that the emission intensity and the factor from cyclohexane are not affected by the presence of oxygen while those of benzene are markedly affected by oxygen. Figure 7 gives the curves of emission intensity from benzene and cyclohexane in the nitrogenated and non-nitrogenated mixture of them.

In the nitrogenated mixture the emission intensity from benzene is always sensitized by cyclohexane, but on the contrary, in the non-nitrogenated mixture the emission intensity from cyclohexane is sensitized by benzene in the range of cyclohexane concentration less than about 0.5 mole fraction. As shown in Table 1 the emission intensity of nitrogenated benzene, $I(N_2)_b$, is reduced to the intensity of its 64 % in presence of oxygen while that of nitrogenated cyclohexane, $I(N_2)_c$, does not change in presence of oxygen. If oxygen did not play any role in energy transfer process in the mixture, the emission intensity from benzene in non-nitrogenated mixture would always be 64 % of $I(N_2)_b$ (shown with a dotted line in Fig.7), and the emission intensity from cyclohexane would always be the same as that in nitrogenated mixture. Therefore, the differences between the dotted line

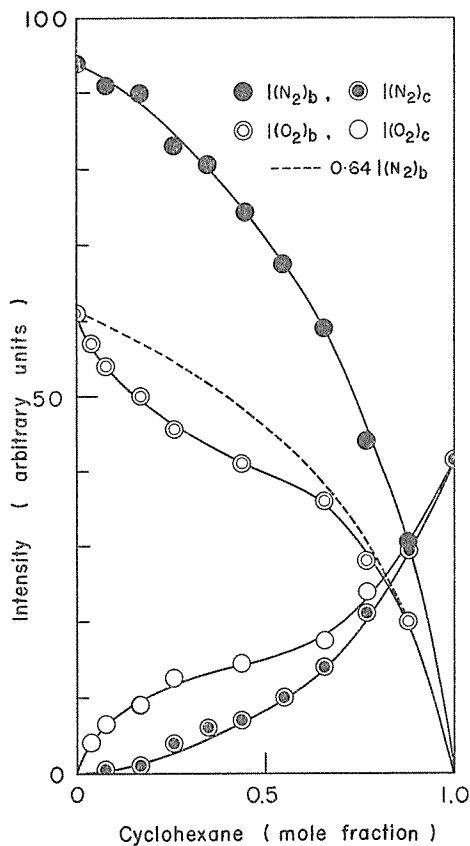


Fig. 7. Variation of emission intensity from benzene and cyclohexane in their mixture with its composition, in presence and absence of oxygen.

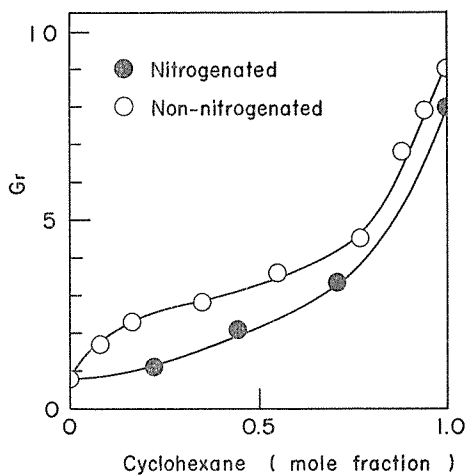


Fig. 8. Variation of Gr value from nitrogenated and non-nitrogenated mixtures of benzene and cyclohexane with their compositions.

and $I(O_2)_b$ and between $I(O_2)_c$ and $I(N_2)_c$ must be considered as due to the result that energy is transferred from benzene to cyclohexane by the intervention of

dissolved oxygen into the transfer process. $I(\text{O}_2)_b$ and $I(\text{O}_2)_c$ are the emission intensities from benzene and cyclohexane in the non-nitrogenated mixture of them, respectively.

The same effect of oxygen on radiolysis was observed in the mixture. Figure 8 shows the curves of Gr value from a nitrogenated and non-nitrogenated mixture of benzene and cyclohexane.

Gr values from nitrogenated and non-nitrogenated cyclohexane are 8.0 and 9.0, respectively. Therefore, with reference to Fig. 7 most of the differences between the two curves of Gr value are considered as due to the fact that the decomposition of cyclohexane is sensitized by the action of oxygen which transfers energy from benzene to cyclohexane.

It was seen in all the systems studied the oxygen played a significant role in energy transfer process. Table 2 gives a summary about the directions of energy transfer in nitrogenated mixtures and those by the action of oxygen in non-nitrogenated mixtures.

Table 2. Directions of energy transfer.

Systems	Direction in nitrogenated mixtures	Directions due to the effect of oxygen
Benzene-Alkanes	←	→
Benzene-Alcohols	→	→
Benzene-Acetates	→	←

III.3. Fluorescent Behavior of Binary Liquid Mixtures Containing Scintillator Solute

When the solution containing scintillator solute is irradiated by ionizing radiation, a part of the radiation energy absorbed in the solvent is transferred to the solute and emitted as fluorescence of the solute. In the case that solvent molecule contains the conjugated double bonds like benzene, the energy is transferred to the solute molecule from the lowest excited singlet state of the solvent molecule. However, the solvent molecule containing no conjugated double bonds has no such stable excited states. In the case of cyclohexane, Burton⁹⁾ suggested the energy was transferred to the solute from the ionized states of cyclohexane. This idea may be applied to other solvent molecules which do not contain the conjugated double bonds. As the lowest excited singlet state comes from the highly excited states, the fluorescent intensity from the solute is proportional to the number of the highly excited molecules or molecular ions. Therefore, if there exists energy transfer process between the highly excited states of molecules or molecular ions produced from each component in a binary liquid mixture, there must be a parallel relationship between the fluorescent intensity and the gamma-induced emission intensity because the excited products which give the gamma-induced emission are also produced from the highly excited molecules or molecular ions. Therefore, the fluorescent behavior of scintillator solute dissolved in a binary liquid mixture will be understood by the measurement of the gamma-induced emission intensity from the mixture without scintillator solute. Figure 9 shows the fluorescent be-

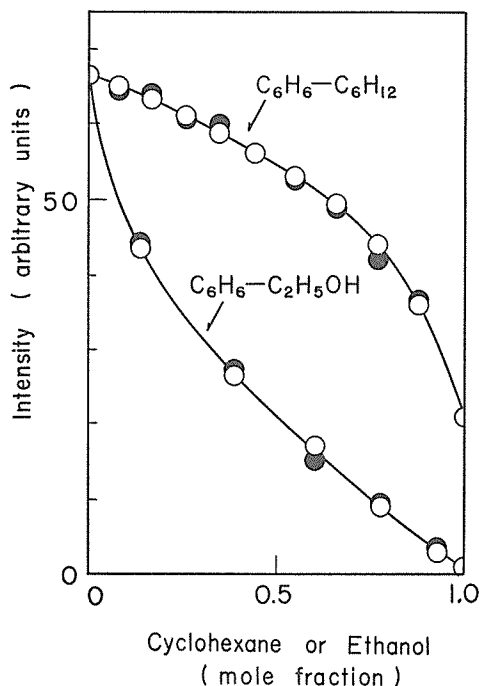


Fig. 9. Variation of fluorescent intensities from p-terphenyl (0.5g/l) in benzene-cyclohexane and benzene-ethanol system, in absence of oxygen.

○.....experimental values, ●.....calculated values from Eq.(5) and(6).

haviors of p-terphenyl (0.5g/l) dissolved in benzene-cyclohexane and benzene-ethanol systems, both in absence of oxygen.

Table 3 shows the gamma-induced emission intensities of benzene, cyclohexane, and ethanol, fluorescent intensities of p-terphenyl dissolved in each of above solvents, and the ratio of both kind of intensities with respective solvents.

Table 3. Gamma-induced emission intensities and fluorescent intensities.

Solvents	γ -induced emission intensities; I_1	Fluorescent intensities of p-terphenyl; I_2	I_2/I_1
Benzene	94.0	66.5	0.71
Cyclohexane	41.5	21.0	0.51
Ethanol	32.4	1.0	0.03

From above-mentioned discussions the fluorescent intensities from p-terphenyl in benzene-cyclohexane and benzene-ethanol systems will be expressed as follows:

$$I = r_1 I_b + r_2 I_e, \quad (5)$$

$$I = r_1 I_b + r_3 I_e, \quad (6)$$

where I , I_b , I_e , I_e , r_1 , r_2 , and r_3 are the fluorescent intensity of p-terphenyl in the respective liquid mixture, the emission intensities from benzene, cyclohexane, and ethanol, respectively, and the ratio, I_2/I_1 in the table 3 with benzene, cyclohexane,

and ethanol, respectively. Figure 9 also shows the plots of I 's calculated from the above Eqs. (5) and (6). The fact the Eqs. (5) and (6) fit very well with the respective fluorescent intensity shows the correctness of our assumption that energy transfer in a binary liquid mixture takes place between highly excited molecules and molecular ions.

III.4. Energy Transfer in Radiation Chemistry

The assumption that energy transfer process exists between the two organic liquids in their mixture under irradiation gives the functional relationship which expresses the emission intensities in terms of mole fraction of a component except benzene in the mixture. We let A be the component which is transferred energy from the component B in a mixture of them and let the description A^* , B^* and $[X]$ be the highly excited molecules and molecular ions of A and B, and molar concentration of X, respectively.

In a stationary state

$$\frac{d[A^*]}{dt} = \alpha_0[A] - \alpha_1[A^*] + k[A][B^*] = 0, \quad (7)$$

$$\frac{d[B^*]}{dt} = \beta_0[B] - \beta_1[B^*] - k[A][B^*] = 0, \quad (8)$$

where α_0 (β_0), α_1 (β_1) and k are the respective rate constants of production of A^* (B^*), of disappearance of A^* (B^*) by its decomposition or transition to its ground state, and of energy transfer from B^* to A. It follows from Eqs. (7) and (8) that

$$[A^*] = \frac{[A]}{\alpha_1} \{ \alpha_0 + k[B^*] \}, \quad (9)$$

$$[B^*] = \frac{\beta_0[A]}{\beta_1 + k[A]}. \quad (10)$$

As emission intensities I_A and I_B are proportional to $[A^*]$ and $[B^*]$, respectively, it follows from Eq. (10) that

$$\frac{I_{B_0}}{I_B} \frac{[B]}{[B_0]} = 1 + \frac{k}{\beta_1} [A], \quad (11)$$

where I_{B_0} and $[B_0]$ represent I_B and $[B]$ when $[A]$ is equal to 0. A plot of $\frac{I_{B_0}}{I_B} \frac{[B]}{[B_0]}$ vs. $[A]$ should be linear, and its slope will determine $\frac{k}{\beta_1}$. Figure 10 gives the curve of emission intensity from the mixture of benzene and ethanol in absence of oxygen. Figures 11 and 12 show the plots of Eq. (11) with the mixtures of ben-

Table 4. k/β_1 values from several organic liquid mixtures.

Mixtures	k/β_1
Benzene - Cyclohexane	2.8
Benzene - n-Hexane	1.7
Benzene - n-Heptane	0.3
Benzene - Propanol	3.85
Benzene - Ethanol	1.45

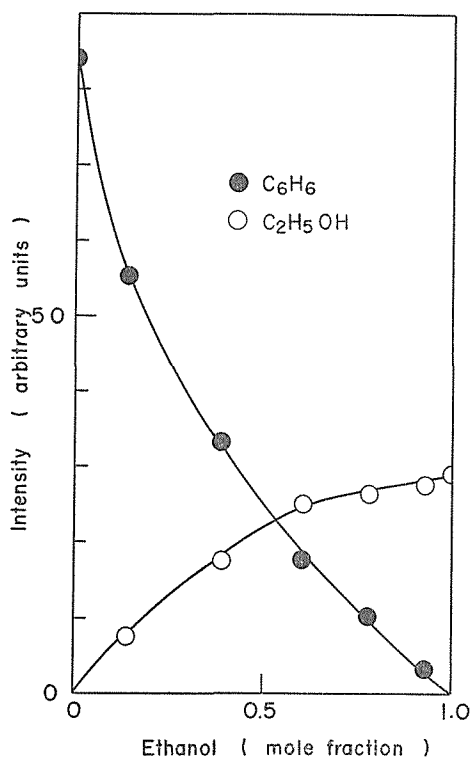


Fig. 10. Variation of emission intensity from benzene and ethanol in their mixture with its composition, in absence of oxygen.

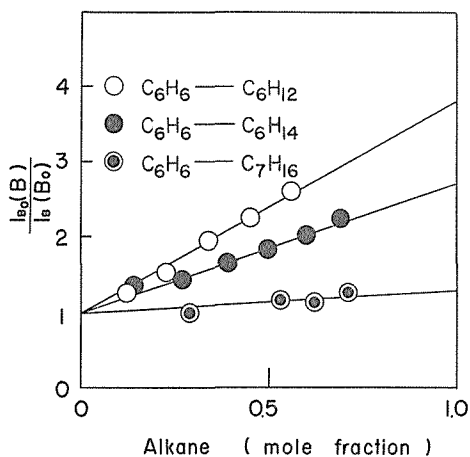


Fig. 11. Plots of Eq. (11) with the mixture of benzene and alkanes.

zene-alkanes and benzene-alcohols. The values of $\frac{k}{\beta_1}$ obtained from the above systems are given in Table 4.

The mechanism of the indirect chemical effects in binary liquid mixtures under irradiation has been discussed by many authors as ionization transfer¹³, excitation transfer¹³, dissociative electron attachment³⁰. However, ionization transfer

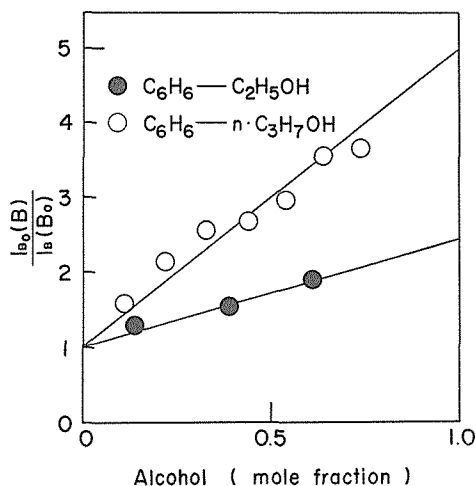


Fig. 12. Plots of Eq. (11) with the mixture of benzen and alcohols.

process will be excluded here by the fact that according to the present experimental results, the emission intensities from alcohols and acetates are sensitized by benzene whose ionization potential is lower than those of alcohols and acetates. Therefore, there may be ionization transfer between components in binary liquid mixture of them, but we do not think the component which has higher ionization potential always transfers its energy to the component of lower ionization potential.

It was concluded by Kallmann and Furst⁹⁾ that in a liquid scintillator system energy transfer between the lowest excited states of solvent and solute molecules plays a dominant role. It is known that benzene and acetone emit fluorescence

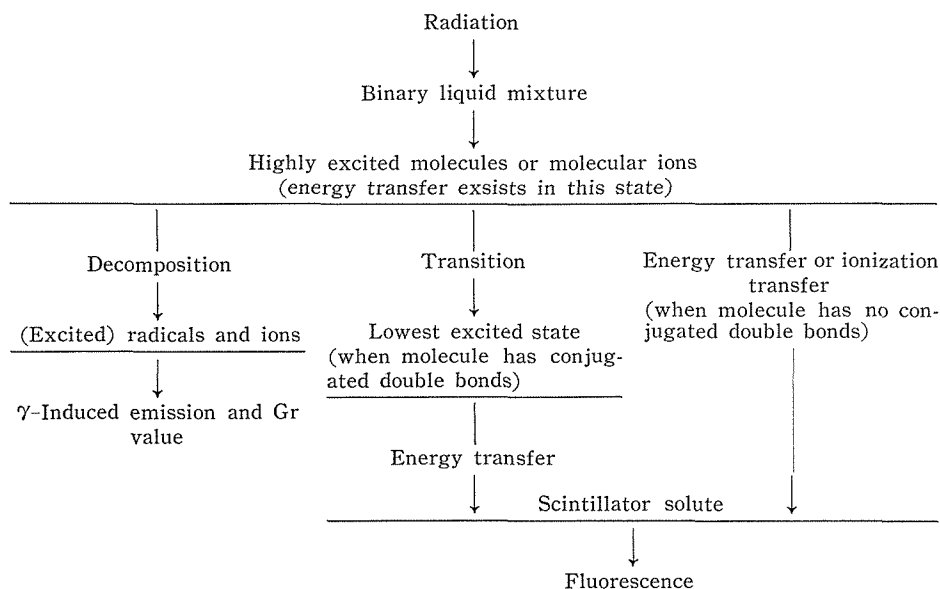


Fig. 13. The relationship between γ -induced emission intensity, Gr value, and fluorescence from scintillator solute, all from binary organic liquid mixture.

from their lowest excited states, but other organic liquids we used do not emit any fluorescence. As the fluorescence from benzene is shielded by Filter-1 in our measurement, the energy transfer between the lowest excited states has no effect on the present experimental results, except the example of the mixture of benzene and acetone. The mechanism of dissociative electron attachment will not be able to explain the close correlation between both variations of the gamma-induced emission intensity and of Gr value with the composition of binary liquid mixtures.

Following the discussions mentioned already, we consider that the indirect chemical effect in binary mixtures is due to the energy transfer between highly excited states of both components. Figure 13 shows the relationship between the gamma-induced emission intensity, Gr value, and fluorescence from scintillator solute. The Figure also shows the assumption that the energy transfer in radiation chemistry takes place between highly excited states gives an satisfactory understanding for the close correlation between both variations of the gamma-induced emission intensity and of Gr value with the composition of binary liquid mixtures, and for the variations of fluorescence intensity from scintillator solute.

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