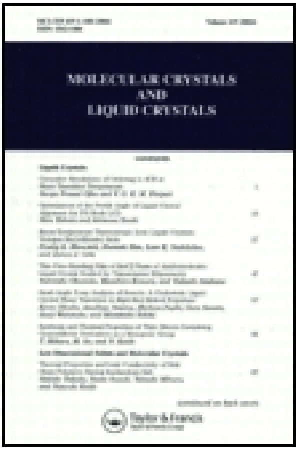

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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J. W. Van Loben Sels [a] & J. T. Dubois [a]
[a] Aerospace Research Laboratories, Wright-Patterson Air Force, Base, Ohio

Version of record first published: 21 Mar 2007.

To cite this article: J. W. Van Loben Sels & J. T. Dubois (1968): Solvent-Solvent Energy Migration in Liquid Scintillators. Part II, Molecular Crystals, 4:1-4, 33-44

To link to this article: http://dx.doi.org/10.1080/15421406808082899

Molecular Crystals, 1968. Vol. 4, pp. 33–44

Printed in Germany

Solvent-Solvent Energy Migration in Liquid Scintillators. Part II

J. W. van LOBEN SELS* and J. T. DUBOIS

Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio

Recieved Aug. 9, 1966
Revised Oct. 28, 1966

Abstract—The quenching of benzene monomer fluorescence by biacetyl at 28°C is studied as a function of dilution with hexane and cyclohexane. The component of the overall transfer rate constant, attributable to solvent-solvent energy migration is shown to vary linearly with benzene concentration and is independent of the diluent. The results are discussed in the light of the work of other authors.

The transfer of electronic excitation energy in an organic liquid scintillator results ultimately from a resonance interaction between solvent molecules (donor) and solute molecules (acceptor).[1] It has been suggested[2,3] that the transferring species are promoted to their critical transfer distances either by solvent to solvent migration of the excitation energy (a resonance interaction between the solvent molecules) and/or by material migration, i.e., diffusion. Thus, in general, the overall rate of energy transfer in such systems is expected to depend on the strengths of the resonance interactions mentioned and on the simultaneous effect of the mutual diffusion of the transferring species during the lifetime of the excited state of the donor. Since the theoretical treatment of the combined effect of diffusion and long range resonance transfer has thus far not been of general application,[4,9] the task of extricating and evaluating the contribution of solvent-solvent energy migration in liquid scintillators has proved difficult. It has been shown recently[10] that if a suitable acceptor is used, long range resonance transfer can by eliminated and the overall transfer process with a rate constant k_t can be reduced to a competition between material migration with rate constant k_d, and solvent-solvent energy migration with rate constant k_A, permitting

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* In partial fulfillment for the M. S. degree, Air Force Institute of Technology Wright-Patterson Air Force Base, Ohio.

a less ambiguous assessment of the contribution of the latter. In this manner it was demonstrated that the rate constants k_t for the quenching of the monomer fluorescence of neat (undiluted) benzene, toluene and p-Xylene by biacetyl in aerated and in degassed systems at room temperature, were at the very least twice the values k_d expected on the basis of the diffusion process alone, and increased in the order benzene, toluene and p-Xylene. These results established with certainty a contribution other than diffusion, to the overall rate constant for the transfer process. This contribution $k_A = k_t - k_d$ is the rate constant due to "solvent-solvent migration".

The aim of the present study was to obtain, for benzene, the functional dependence of k_A on donor concentration in order to shed more light on the mechanism responsible for its manifestation and to probe the reasons for the apparently conflicting reports[2, 11-16] about the existence of this process in scintillator systems. The diluents hexane and cyclohexane were chosen because their viscosities lie respectively below and above that of benzene, causing decreasing and increasing diffusional rates in the mixtures, with increasing benzene concentration.

1. Experimental

Materials

Biacetyl, spectroquality benzene, hexane and cyclohexane were obtained from Matheson, Coleman and Bell. The biacetyl was distilled in the dark, the middle fraction being retained for the experiments. The other materials were used without further treatment.

Apparatus and Technique

The quenching measurements were made in aerated solutions at 28°C with an excitation wavelength $\lambda = 2400$ Å. The apparatus used was the AMINCO spectrophotofluorometer, equipped with a 150 W Hanovia 901C-1 source, a 1P28 photomultiplier and front face attachment. Background corrections an general procedure were as described previously.[10] In the front face mode, the benzene concentrations were kept in the range 1.6–11.25 M to preserve the viewing geometry of the detecting system. The quenching coefficients for the infinitely dilute benzene solutions in hexane and in cyclohexane were obtained from observations at 90° to the incident radiation.

2. Approach and Results

The kinetic scheme applicable to neat-donor/acceptor systems has been discussed previously.[10] It is repeated here, without discussion, for the convenience of the reader.

$D + h\nu \rightarrow D^*$	[1]	$A + h\nu \rightarrow A^*$	[1′]
$D^* \rightarrow D + h\nu_D$	[2]	$A^* \rightarrow A + h\nu_A$	[2′]
$D^* \rightarrow D$ or ^3D	[3]	$A^* \rightarrow A$ or ^3A	[3′]
$D^* + D \rightarrow D_2^*$	[4]	$A^* + A \rightarrow$ quenching	[4′]
$D_2^* \rightarrow D^* + D$	[5]		
$D_2^* \rightarrow 2D + h\nu_{D_2}$	[6]		
$D_2^* \rightarrow 2D$ or $^3D_2^*$	[7]		
$D^* + O_2 \rightarrow$ quenching	[8]	$A^* + O_2 \rightarrow$ quenching	[8′]

$$D^* + A \xrightarrow{kt} D + A^* \qquad [9]$$

The Stern-Volmer expressions applicable are

$$F_D^0/F_D = 1 + k_t\tau_D[A] = 1 + K_Q[A] \qquad (1)$$

$$(F_D^0/F_D)_2 = 1 + k_t(\tau_D)_{O_2}[A] = 1 + (K_Q)_{O_2}[A] \qquad (2)$$

where F_D^0 and F_D refer to the emission of the neat donor in the absence and in the presence of A, K_Q and $(K_Q)_{O_2}$ are the quenching coefficients in the degassed and aerated liquids and τ_D and $(\tau_D)_{O_2}$ are the corresponding lifetimes. In the case of air saturated solutions,

$$(\tau)_{O_2} = \{k_2 + k_3 + k_4\,[D]\,(1 - k_5\tau_{D_2}) + k_8\,[O_2]\}^{-1} \qquad (3)$$

where τ_{D_2}, the actual lifetime of the excimer is defined as $\tau_{D_2} = (k_5 + k_6 + k_7)^{-1}$.

Approach

The approach taken for this work was similar to that described previously[10]. Biacetyl was used as the acceptor in order to insure short-range, diffusion-controlled transfer. Under these conditions, the contribution of solvent-solvent migration k_A to the overall rate constant k_t for the transfer process is defined as $k_A = k_t - k_d$, where k_d is the contribution from material migration (diffusion). The object here is to obtain k_A for the system benzene/biacetyl as a function of the diluents hexane and cyclohexane. For this purpose, k_t was obtained experimentally by the method described below, whereas k_d was calculated from an appropriate form of the Smoluchowski equation also discussed below.

Determination of k_t

k_t was obtained from measured quenching coefficients $(K_Q)_{O_2} = k_t(\tau_D)_{O_2}$ and from measured values of $(\tau_D)_{O_2}$, the actual lifetime of the aerated donor benzene. Thus $k_t = (K_Q)_{O_2}/(\tau_D)_{O_2}$. The quenching coefficients needed were obtained from the slopes of Stern-Volmer diagrams Eq. (2) for the quenching of benzene monomer emission by biacetyl at 28°C. These were measured at various dilutions of benzene with hexane and cyclohexane and the results are shown in the first two rows of Table 1.

The lifetimes of benzene monomer emission at the corresponding concentrations of benzene in aerated hexane were determined by Ivanova et al.[17] and are listed in row 3 of Table 1. The corresponding values of the lifetimes in cyclohexane were not available and were estimated from the relative intensities of benzene monomer emission in hexane F_D^H and F_D^C in cyclohexane, according to the approximate relation

$$\tau_D^C \approx \tau_D^H(F_D^C/F_D^H)\,(n_H/n_C)^2$$

where τ_D^C and τ_D^H = benzene monomer lifetime in aerated cyclohexane and hexane respectively; n_C and n_H = refractive index of cyclohexane and hexane. The lifetimes in cyclohexane obtained in this manner are reported in row 4 of Table 1. From these lifetimes and the measured quenching coefficients, the overall rate constants $k_t = (K_Q)_{O_2}/(\tau_D)_{O_2}$ were calculated and are reported in Rows 5 and 6 of Table 1.

TABLE 1 The Effect of Benzene Concentration on Transfer Parameters

Benzene Concentration	11.25*	8.4	5.6	2.8	1.6	4.1 × 10^{-4}	moles/liter^{-1}
$(K_Q)_{O_2}$ in hexane	262	226	212	194	191	214	l. mole^{-1}
$(K_Q)_{O_2}$ in cyclohexane	262	243	224	188	168	170	l. mole^{-1}
$(\tau_d)_{O_2}$ in hexane	7.8	7.3	6.6	6.0	6.0	6.5	n. sec
$(\tau_d)_{O_2}$ in cyclohexane	7.8	8.4	8.4	9.0	9.6	13	n. sec
k_t in hexane	3.4	3.1	3.2	3.3	3.2	3.5	l. mole^{-1} sec^{-1} × 10^{-10}
k_t in cyclohexane	3.4	2.9	2.7	2.1	1.8	1.2	l. mole^{-1} sec^{-1} × 10^{-10}
k_d in hexane	1.7	2.0	2.3	2.7	3.0	3.5	l. mole^{-1} sec^{-1} × 10^{-10}
k_d in cyclohexane	1.7	1.8	1.7	1.5	1.4	1.2	l. mole^{-1} sec^{-1} × 10^{-10}
k_A in hexane	1.6	1.2	0.9	0.5	0.2	0	l. mole^{-1} sec^{-1} × 10^{-10}
k_A in cyclohexane	1.7	1.2	1.0	0.6	0.4	0	l. mole^{-1} sec^{-1} × 10^{-10}

* The neat donor, benzene.

Estimation of k_d

The diffusion controlled rate constants k_d were estimated as before[10] from the relation*

$$k = 8\,RT/2000\,\eta_{DX} \tag{4}$$

where R is the gas constant, T the absolute temperature and η_{DX} the viscosity of the mixture benzene/diluent. For ideal mixtures of D and X the viscosity is given by the Kendall equation

$$\log\frac{1}{\eta_{DX}} = x_D \log\frac{1}{\eta_D} + x_X \log\frac{1}{\eta_X} \tag{5}$$

where η_{DX}, η_D and η_X are the viscosities of the mixtures and of the pure components and x_D and x_X are the mole fractions of D and X in the mixture. $\eta_{DX}^{28°}$ is obtained by using values of η_X and η_D interpolated to 28°, from existing experimental data. It is noteworthy that the scant data available on viscosities of mixtures hexane/benzene and cyclohexane/benzene at other temperatures follows Eq. (5) reasonably well. The contribution k_d to the overall rate constant k_t for the transfer process calculated from Eqs. (4) and (5) is shown in rows 7 and 8 of Table 1 and graphically in Fig. 1.

Rate Constant k_A

The rate constants k_A for solvent-solvent migration calculated from $k_A = k_t - k_d$ and the data in Table 1 are shown graphically in Fig. 1. As can be seen from Fig. 1, k_A varies linearly with donor concentration and, as might be expected, is independent of the diluents, even when the latter have been chosen to produce entirely different viscosity profiles in mixtures with the donor.

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* This form of the Smoluchowski equation "with slip"[18] is chosen over that "with no slip" ($8RT/3000\eta$) because it appears to represent more closely the diffusion process in pure liquids and because the pure liquid benzene in this work is only diluted by a maximum factor of seven. In any case it can be shown that either choice does not alter the final conclusions.

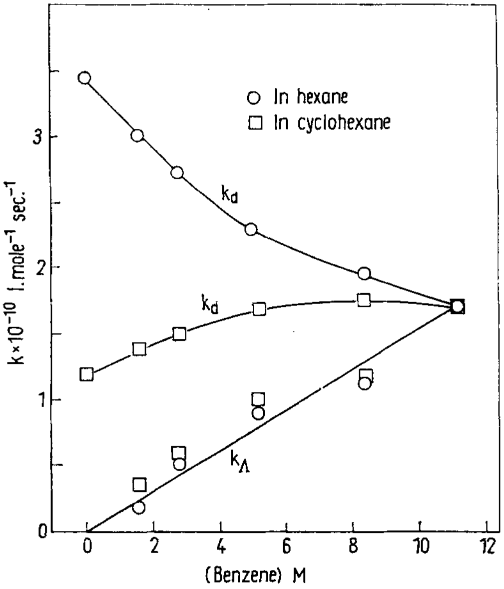

Figure 1. Change of diffusional rate constants and solvent-solvent migration rate constants with benzene concentration.

Internal Consistency of the Measurements

One way to judge the internal consistency of the measurements on the benzene system is by considering the following equalities:

$$\frac{(K_Q)_{O_2}}{K_Q} = \frac{k_t(\tau_D)_{O_2}}{k_t\tau_D} = \frac{(\tau_D)_{O_2}}{\tau_D} \qquad (6)$$

In Table 2 we have listed $(K_Q)_{O_2}$ obtained in this work for aerated neat benzene as well as the corresponding K_Q measured previously in degassed solutions.[10] Listed in the same table are the corresponding lifetimes obtained by Ivanova[17] as well as the ratios defined by Eq. (6). The agreement between the ratios of quenching coefficients and lifetimes for the neat benzene is seen to be excellent.

The internal consistency of the measurements on the benzene system can be further revealed through the oxygen quenching coefficients defined as $K_{O_2} = k_8\tau_D$. Oxygen quenching coefficients are usually larger than hydrocarbon quenching coefficients because of the larger diffusivity of oxygen in a given solvent.[19, 20] The oxygen quenching coefficients can

TABLE 2 Quenching Coefficients and Lifetimes for Neat Benzene

Experimental Parameter	Benzene	Units
K_Q	746	l. mole^{-1}
$(K_Q)_{O_2}$	262	l. mole^{-1}
τ_D	21.8	n. sec.
$(\tau_D)_{O_2}$	7.8	n. sec.
$(K_Q)_{O_2}/K_Q$	0.35	—
$(\tau_D)_{O_2}/\tau$	0.36	—
$K_{O_2}^a$	1260	l. mole^{-1}
α^b	2.4	—

^{a}Calculated from Eq. (7).
^{b}Calculated from Eq. (8).

be obtained from the relation[19]

$$K_{0_2} = \frac{1}{[O_2]}\left\{\frac{K_Q}{(K_Q)_{0_2}} - 1\right\} \tag{7}$$

where $[O_2]$ is the molar concentration of oxygen in the solvent. With the oxygen concentration in neat benzene estimated from the work of McKeown and Hibbard,[21] and the quenching coefficients given in Table 2, Eq. (7) gives $K_{0_2} = 1260$ liters per mole. It can be shown readily that if solvent-solvent migration is included, the excess diffusion of oxygen over that of biacetyl in the neat benzene is given by

$$\alpha \cong \frac{K_{0_2}}{K_Q}\left(1 + \frac{k_A}{k_d}\right) - \frac{k_A}{k_d} \tag{8}$$

where all the symbols have already been defined. Using the values of K_{0_2}, K_Q, k_A and k_d for neat benzene from Tables 1 and 2, it is found that $\alpha \simeq 2.4$ which is in good agreement with the excess diffusion of oxygen over biacetyl ($\alpha = 2.3$) in cyclohexane.[19]

3. Discussion

Figure 1 confirms the contribution of k_A to the overall transfer process in benzene, shows that the magnitude of this contribution increases linearly with benzene concentration and is independent of the diluents hexane and cyclohexane. The independence of k_A on diluent is the more remarkable if one observes that the k_d's for the diluents chosen are entirely opposite functions of the benzene concentration.

Since there has been no general agreement about the contribution of solvent solvent migration in neat liquids it is of interest to dwell briefly on previous reports.

The present work on the variation of k_A with benzene concentration is in complete agreement with Weinreb's observations[11,12] of the intensitivity of transfer efficiencies to donor concentration. The transfer efficiency in air saturated solutions, defined as the fraction of energy transferred, is given by

$$\varepsilon = \frac{k_t[A]}{1/(\tau_D)_{O_2} + k_t[A]} = \frac{(K_Q)_{O_2}[A]}{1 + [(K_Q)_{O_2}[A]]} \qquad (9)$$

Substitution of the transfer coefficients given in Table 1, for fixed acceptor concentrations, yields the curves in Fig. 2. These curves are similar to those reported by Weinreb and co-workers[11,12] for aerated systems except that these authors assumed them to be concave between their two data points at about 1 M and 10 M; their other data points are below 1 M. Dilution with solvents other than cyclohexane may be expected to yield even more insensitive functions of donor concentration.

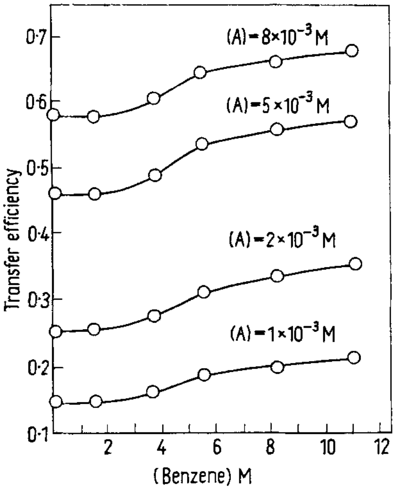

Figure 2. Variation of energy transfer efficiency with donor concentration; diluent is cyclohexane.

It is evident from Eq. (9) and Fig. 2 that the transfer efficiency is not a suitable parameter for indications of solvent-solvent energy migration, a fact which has been recognized previously.[14]

Melhuish[16] argues that solvent-solvent energy migration cannot be important since k_t for the system 9-methyl anthracene/perylene (in which this process is not possible) is larger than the k_t's found by him for systems neat toluene/hydrocarbons. However, on the basis of a Förster calculation, it can be shown that the critical transfer distance for 9-methyl anthracene/perylene is 39 Å, and therefore the large transfer rate constant found for that system, ($k_t = 9 \times 10^{10}$ l. mole^{-1} sec^{-1}) is fully expected. Further, this rate constant should not be compared with that for the short-range systems toluene/anthracene ($R_0 = 9$ Å) and toluene/perylene ($R_0 = 6$ Å). The energy transfer rate constants found by Melhuish for these two systems, (5.2×10^{10} and 4.1×10^{10} l. mole^{-1} sec^{-1} respectively) are very close to that found previously for toluene/biacetyl, where solvent-solvent migration is indicated.[10]

Kallmann and Furst[2] suggested that solvent-solvent migration may be an order of magnitude larger than diffusion. The present work indicates that the migration process in benzene is as important as diffusion and previous observations in toluene and in p-Xylene[10] indicate that it is twice as important as diffusion in the latter systems.

Finally the question arises about the nature of the mechanism responsible for this phenomenon. On the basis of an octopole-octopole interaction between solvent molecules, Voltz and co-workers[3, 22] were able to show that for benzene and toluene, solvent-solvent migration could be, as found here, of the order of material migration, leading to transfer rates $k_\Lambda\,[D] \sim 10^{11}$ sec^{-1}. We note, however, that according to a calculation made by Förster,[23] such large transfer rates would require an interaction energy of ~ 20 cm^{-1}, an order of magnitude larger than that assumed by Voltz for octopole-octopole interaction. An alternative suggestion by Birks[24] equates the lifetime of excimers τ_{D_2} in the neat liquid with the time of solvent-solvent migration, $\tau_{\mathrm{mig}} = (k_\Lambda[D])^{-1}$. Since the excimer lifetimes in benzene and its methyl derivatives are governed by the very fast rate of monomer reformation,[25] $\tau_{D_2} \simeq (k_5)^{-1}$. A comparison of $\tau_{\mathrm{mig}}{}^{-1}$ and $\tau_{D_2}{}^{-1}$ in Table 3 reveals that energy migration may be an order of magnitude faster than monomer reformation. Thus the nature of the mechanism of solvent-solvent migration remains unresolved.

TABLE 3 Comparison of Solvent-Solvent Energy Migration Rates, in Neat Donors, with Rates of Monomer Reformation Obtained by Birks

Experimental Parameter	Benzene	Toluene	p-Xylene	Units
${\tau_{\mathrm{mig}}}^{-1} = k_\Lambda[D]$	1.9	3.4	6.6	$\sec^{-1} \times 10^{-11}$
$\tau_{D_2}^{-1} \sim k_5$	2.2	3.2	7.0	$\sec^{-1} \times 10^{-10}$

It is concluded that in addition to material diffusion, some other process (solvent-solvent migration) contributes at least equally to the diffusion of electronic excitation energy in neat benzene liquid. The magnitude of this additional component decreases as the benzene is diluted with a transparent solvent and appears independent of the solvent chosen. In neat benzene, toluene and p-Xylene, the rates of solvent solvent migration are an order of magnitude larger than those for monomer reformation. The mechanism responsible for solvent-solvent migration is not as yet well defined but, if an octopole-octopole interaction plays a role, the interaction energy involved may be substantially larger than had been supposed.

REFERENCES

1. Birks, J. B., *The Theory and Practice of Scintillation Counting*, Macmillan Co., New York, 1964.
2. Kallmann, H. and Furst, M., *Liquid Scintillation Counting*, Ed. Bell, C. G. and Hayes, F. N., Pergamon Press, London, 1958.
3. Voltz, R., Laustriat, G., and Coche, A., *Compt. Rend.* **257**, 1473 (1963).
4. Belikova, T. P. and Galanin, M. D., *Opt. i Specktroscopiya* **1**, 168 (1956).
5. Weinreb, A., *Proc. of the University of New Mexico Conf. on Organic Scintillation Detectors*, 1960, U.S. Atomic Energy Commission TID 7612, p. 59.
6. Vasil'ev, I. N., Kirsanov, B. P. and Kronganz, V. A., *Kinetics and Catalysis* **5**, 697 (1964).
7. Bagdasaryan, Kh. S. and Muler, A. L., *Optics and Spectroscopy* **18**, 990 (1965).
8. Feitelson, J., *J. Chem. Phys.* **44**, 1497 (1966).
9. Feitelson, ibid., **44**, 1500 (1966).
10. Dubois, J. T. and Loben Sels, J. W. van, *The Physics and Chemistry of Scintillators*, Ed. Riehl, N. and Kallmann, H., Karl Thiemig Kg., Munich, 1966, p. 74.
11. Cohen, S. G. and Weinreb, A., *Proc. Phys. Soc.* (*London*) **B69**, 593 (1956).
12. Bar, V. and Weinreb, A., *J. Chem. Phys.* **29**, 1412 (1958).
13. Brown, F. H., Furst, M. and Kallmann, H. P., ref. 5, p. 37.
14. Weinreb, A., *Luminescence of Organic and Inorganic Materials*, Ed. Kallmann, H. P. and Spruch, G. M., John Wiley and Sons, New York, 1962, p. 44.
15. Voltz, R., Laustriat, G. and Coche, A., *Compt. Rend.* **257**, 1473 (1963).

16. Melhuish, W. H., *J. Chem. Phys.* **40**, 1369 (1964).
17. Ivanova, T. V., Mokeeva, G. A. and Sveshnikov, B. Ya., *Optics and Spectroscopy* (Engl. transl.) **12**, 325 (1962).
18. Tyrrell, H. J. V., *Diffusion and Heat Flow in Liquids*, Butterworth, London, 1961, p. 127.
19. Stevens, B. and Dubois, J. T., *Trans. Faraday Soc.* **59**, 2813 (1963).
20. Ware, W. R., *J. Am. Chem. Soc.* **83**, 4374 (1961).
21. McKeown, A. B. and Hibbard, R. R., *Anal. Chem.* **38**, 1490 (1956).
22. Voltz, R., *et al.*, *Symposium on Nuclear Electronics*, Paris, 1963.
23. Forster, Th., *Comparative Effects of Radiation*, Ed. Burton, M., Kirby-Smith, J. S. and Magree, J. L., John Wiley and Sons, New York, 1960, p. 300.
24. Ref. 1, page 312.
25. Birks, J. B., Brga, C. L. and Lumb, M. D., *Proc. Roy. Soc.* **283**, 83 (1965).