LETTERS TO THE EDITOR

EINSTEIN COEFFICIENT OSCILLATOR STRENGTH AND THE LIFETIME MEASUREMENT IN THE B 1 - X 1Σ SYSTEM OF PbO

Relatively few of the important band systems observed in the spectra of cosmic bodies and also commonly found on earth have been fully or partly studied from an intensity point of view.

Knowledge of intensity gives a clear understanding of the transitions, and therefore the states and conditions of reactions responsible for excitation and its surroundings. The expression for the intensity of a v', v" transition in emission is given as

\[ I_{v', v''} = \frac{64}{3} \pi c N_v \langle \psi_{v'} \psi_{v''} \rangle \left[ \int \psi_{v'}^* \psi_{v''} \, dv \right]^2 \]

where c is the velocity of light, \( \nu \) the frequency of the transition, \( N_v \) the population in the excited state, \( R_e \) is the electronic transition moment assumed to be independent of the internuclear distance, and the quantity \( [ \psi_{v'} \psi_{v''} ] \) is the Franck-Condon factor.

The preceding equation can also be written as

\[ I_{v', v''} = N_v \langle E_{v'} \rangle R_e^2 \left( \langle v' \rangle \langle v'' \rangle \right) q_{v'} q_{v''} \]

where \( E \) is the energy of the transition, \( R_e^2 \) is the electronic transition moment expressed as a function of r-centroids and q_{v'} q_{v''} is the Franck-Condon factor for the transition.

\[ R_e^2 \left( \langle v' \rangle \langle v'' \rangle \right) q_{v'} q_{v''} = \left[ \int \psi_{v'}^* R_e(r) \psi_{v''} \, dr \right]^2 = S_{v' v''} \]

where \( S_{v' v''} \) is called the band strength expressed in atomic units.

The expression relating the Einstein coefficient and the band strength is given by Penner as:

\[ A_{v' v''} = \frac{2 \cdot 026 \times 10^6 S_{v' v''}}{g_{v''}^3} \text{ sec}^{-1} \]

where \( A_{v' v''} \) is the Einstein coefficient, \( g_{v''} \) is the statistical weight of the upper level and \( \lambda \) is the wavelength in microns.

Further expression relating the Einstein coefficient and the oscillator strength is given as

\[ f_{v' v''} = 1.5 \times 10^{-8} \lambda^2 A_{v' v''} \]

where \( f_{v' v''} \) is the oscillator strength, \( \lambda \) is the wavelength in microns and \( A_{v' v''} \) is the Einstein coefficient in sec\(^{-1}\).

The band strength for the B1-X 1Σ system of PbO has been determined by Dube et al. exciting the PbO B1-X 1Σ system in an arc. On the basis of the measurements of the band strengths, calculation of the Einstein coefficient, oscillator strength and lifetime is done. The results are tabulated in Table I. The lifetime of the zeroth vibrational level of the upper state is calculated to be \( 2.526 \times 10^{-6} \) sec.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\( V' \), \( V'' \) & \( \lambda \) (A) & \( S_{v' v''} \) & \( g_{v''}^3 \) & \( A_{v' v''} \) \text{ sec}^{-1} & \( f_{v' v''} \) \\
\hline
0, 1 & 4655 & 13.5 \times 10^{-4} & 13 \cdot 54 + 3 & 4 \cdot 075 - 5 \\
0, 2 & 4917 & 28.7 \times 10^{-4} & 28 \cdot 65 + 3 & 6 \cdot 045 - 5 \\
0, 3 & 4984 & 40.7 \times 10^{-4} & 33 \cdot 3 + 3 & 12 \cdot 85 - 5 \\
0, 4 & 5162 & 56.8 \times 10^{-4} & 28 \cdot 74 + 3 & 10 \cdot 881 - 5 \\
0, 5 & 5333 & 26 \cdot 8 \times 10^{-4} & 17 \cdot 60 + 3 & 7 \cdot 605 - 5 \\
\hline
\end{tabular}
\caption{Table I}
\end{table}

\( \text{N.B.: The numbers against the quantities with plus and minus signs are the powers of ten to be multiplied.} \)

In some cases it has been possible to use lifetime measurements to place relative band strength on an absolute scale. The same method has been applied to aeronomic and non-aeronomic band systems. Attempts have also been made to interpret band intensity measurements in terms of effective electronic oscillator strengths for the complete band system, although it is doubtful if the concept is meaningful to more than an order of magnitude.

Dept. of Spectroscopy, Prem Shankar Dube, Banaras Hindu University, Varanasi-5, October 5, 1970.


SOLUTION PROPERTIES OF POLY (BUTYL ACRYLATE) AND POLY (BUTYL ACRYLATE-CO-STYRENE)

Studies on configurational and frictional properties of Poly (butyl acrylate) have not so far been carried out. We have investigated monodisperse Poly (butyl acrylate), PBA, in good solvent, methyl ethyl ketone, (MEK), at 35°C. and the effect of introducing styrene units

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in poly (butyl acrylate) on the solution properties by a study of poly (butyl acrylate-co-styrene) PBAS, in methyl ethyl ketone and toluene at 35°C.

**Experimental**

PBAS was prepared by solution and bulk polymerization of butyl acrylate with azobisisobutyronitrile or benzoyl peroxide as initiators in various solvents at 35°C and 60°C. in nitrogen atmosphere with restricted conversion, ca < 15%. The purified polymer was fractionated into eight fractions with MEK as solvent and methanol-water (6:1 vol.) as a precipitant. Bulk co-polymerization of styrene and butyl acrylate was carried out with benzoyl peroxide as catalyst in nitrogen atmosphere at 60°C ± 1°C. with restricted conversion, ca < 5% to yield PBAS in 1:1 composition and the purified co-polymer was fractionated (8 fractions) with MEK and methanol as solvent and non-solvent respectively. The composition and microstructure of co-polymer was determined by nuclear magnetic resonance.¹² The appearance of shoulder in the phenyl proton peak at 3-03 τ and the ratio of the area of phenyl proton peak to the O-CH₃ proton peak at 6-03 τ being unity, indicated the absence of alternation but the proportion of the two units to be 1:1 as expected from kinetics.⁴ The molecular weights of PBAS fractions in different solvents of varying refractive index increments were almost same, indicating the composition heterogeneity to be narrow. Intrinsic viscosities [η] of the purified and fractionated samples of PBA and PBAS were measured in MEK and toluene respectively at 35°C. in the suspended level dilution viscometer (PCL, Colchester Instruments Ltd., U.K.), for [η] < 300 and in a variable shear rate viscometer for [η] > 300. The scattered light intensities were measured for the carefully centrifuged and filtered solutions at 45-135° angles in the light scattering photometer (Brice-Phoenix Universal 1,000 series; Phoenix Precision Instrument Company, Philadelphia) for incident unpolarized light λ = 4356 Å. The refractive index increments of polymer samples were also measured at the same wavelength in differential refractometer (Brice-Phoenix Instruments Company, Philadelphia). The light scattering data were processed using computer IBM 1,130 and results were treated according to Zimm⁵ for the determination of weight average molecular weight and other parameters. The number average molecular weight Mₙ was determined with Osmometer (Pinner-Stabin; Colchester Instruments Ltd., U.K.).

**Results and Discussion**

(i) From the intercepts of the plots of nsp/c vs. c and (lnη/η₁)/c vs. c, [η] = 101-800 ml./gm.⁻¹ for PBA in MEK at 35°C. for Mertia = 0.48-11.37 × 10⁶ and [η] = 64 to 179 ml./gm.⁻¹ for PBAS in MEK at 35°C. and [η] = 78 to 198 ml./gm⁻¹ for PBAS in toluene at 35°C. for Mertia = 2.7 × 10³ were obtained. The Huggins' constant k' ranged from 0.33 to 0.35 for PBA in MEK and 0.30 to 0.37 and 0.28 to 0.38 in MEK and toluene respectively for PBAS.

(ii) From log [η] vs. log (Mertia) plots the following equations were obtained:

[η] = 2.41 × 10⁻² Mertia⁻⁰·⁶⁴ for PBA in MEK at 35°C.

[η] = 0.85 × 10⁻³ Mertia⁻⁰·₇₅ for PBAS in acetone at 35°C.

[η] = 3.09 × 10⁻³ Mertia⁻⁰·₈₁ for PBAS in MEK at 35°C.

[η] = 1.45 × 10⁻¹ Mertia⁻⁰·₇₁ for PBAS in toluene at 35°C.

The low value of 'α' (0.64) for PBA/MEK compared to PBA/acetone indicated that methyl ethyl ketone is a more ideal solvent than acetone. The lower value of 'α' for PBAS/toluene than for PBAS/MEK indicated that toluene is more ideal than MEK. The high value of 'α' for PBAS/MEK compared to PBA/MEK (α = 0.64) and poly styrene (α = 0.62) at 35°C. indicated the increased thermodynamic interaction between PBAS and MEK.

(iii) The molecular weight heterogeneity

\[ \frac{M_w}{M_n} = 1.25 \text{ for PBA and PBAS was found.} \]

(iv) The following relationships were established at 35°C.

\[ (φ')_{w}^{1/2} = 0.98 M_w^{-0.52} \text{ for PBA in MEK.} \]

\[ (φ')_{w}^{1/2} = 0.43 M_w^{-0.56} \text{ for PBAS in MEK.} \]

The higher value of the exponent for PBAS shows more thermodynamic interaction between PBAS + MEK than PBA + MEK.

(v) Relationship between second virial coefficient A₂ and Mertia was established from log (A₂) vs. log Mertia.

\[ A₂ = 4.35 × 10⁻³ M_w^{-0.22} \text{ for PBA in MEK at 35°C.} \]
(vi) Flory's constant $K$, for PBA and PBAS from $[\eta]$ and $M_w$ data were obtained by various well-known methods.\textsuperscript{6-9} All methods gave the same value of $K = 12.54 \times 10^{-2}$ for PBA/MEK and PBAS/toluene ($11.02 \times 10^{-2}$). Flory-Fox method was not applicable to PBAS/MEK since a negative intercept was obtained and all the other methods for this system also gave lower value of $K = 6.0 \times 10^{-2}$. For poly (methyl acrylate) in methyl ethyl ketone, a similar observation was made.\textsuperscript{10} It may be emphasized that method due to Flory-Fox and other methods give lower value for unperturbed dimension when the extension of the chain is large (indicated by the exponent in Mark-Howink equation $a = 0.8$).

![Figure 1](image)

**FIGURE 1**

$\bar{P}_o^2 / (\bar{P}_o^2)^{1/2}$ unperturbed end to end distance for PBA (782 A to 3545 A) and PBAS (429 A to 595 A) by Stockmayer-Fixman-Bau- man\textsuperscript{11} method and the linear expansion factor $a$ (1.07 to 1.17) for PBA/MEK and (1.16 to 1.28) for PBAS/MEK were obtained. The expansion parameter and unperturbed root mean square radius of gyration increase with molecular weight as expected.

(viii) The Flory's universal parameter $\phi = <[\eta]/\bar{P}_o^2 (\bar{P}_o^2)^{1/2}>$ for PBA was found to be $1.0 \times 10^{-23}$ which is slightly lower than the ideal value ($2.87 \times 10^{-23}$) for flexible chain polymers but compares well with that calculated from reported values for acrylate polymers. $\phi = (2.78 \times 10^{-23})$ for PBAS/MEK is in excellent agreement with expected value.

(ix) The orders of magnitude for extensions of polymeric chain due to long range and steric effects $[\bar{P}_o^2 (\bar{P}_o^2)^{1/2}]$ being 4-48 to 4-92 for PBA/MEK and 4-08 to 4-32 for PBAS/MEK and values for the extension due to steric effects alone $(\bar{P}_o^2)^{1/2}$ being 4-18 for PBA and 3-45 for PBAS were evaluated. The value for PBA is greater than that (3-61) for poly (methyl acrylate).\textsuperscript{12}

(xi) From the slopes of the plots of $(\bar{P}_o^2)^{1/2}$ vs. (DP)$^{1/2}$ (DP = degree of polymerization) the value of the length of the statistical chain element, $b = 9.09$ A for PBA and 5.48 A for PBAS were obtained.


**STRUCTURE OF IXIOILITE**

The structure of ixiolite, a naturally-occurring mineral essentially a tantalite of manganese, has not been sufficiently studied. Tavora\textsuperscript{1} took the X-ray photograph of the sample, but it was not indexed and the system was not known. Reference\textsuperscript{2} shows it to be tetragonal. We have synthesised the sample (MnTa$_2$O$_6$) and made a structural study.

The sample was prepared by mixing appropriate proportions of MnO and Ta$_2$O$_5$ and firing the mixture at 1,100° C. for 20 hours, and at 1,350° C. for five hours in air. Finally, the sample was quenched to room temperature. The powder thus obtained was passed through a 300 mesh and the diffractometer pattern was taken using Mo Kα radiation filtered through Zr foil. The diffractometer was operated at 30 K. watts and 15 amps. and was driven at the rate of 1° per minute. The chart thus obtained was used to calculate the lattice dimensions.