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Infrared Band Broadening and Interactions in Polar Systems

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The width and shape of bands in the infrared spectrum of a material are determined by a number of factors. Absorption bands have a "natural" width associated with the uncertainty principle, Doppler broadening, collisions in the liquid state, and so on, but in addition, there are instrumentation and data processing contributions, problems with sample preparation (e.g., polymer films of uneven thickness), and, the topic of concern here, interactions between neighboring molecules or polymer segments.

Recent work in our laboratory has focused on connectivity and spacing effects in hydrogen-bonded polymer blends. We have found that "spacing" the hydrogen-bonding functional groups along a polymer chain with "inert" (i.e., non-hydrogen-bonding) segments such as ethylene results in a much greater propensity to form hydrogen bonds, as measured by equilibrium constants describing intermolecular interactions (e.g., between the phenolic OH group of poly(vinyl phenol) and the acetate carbonyl group of ethylene/vinyl acetate random copolymers).[1] During the course of this work we observed significant changes in the width of carbonyl bands (measured at half peak height), as a function of dilution or "spacing" of these groups. For example, the spectra of poly(vinyl acetate) and various ethylene/vinyl acetate random copolymers obtained at 100 °C (above the melting point of any ethylene sequence crystallinity) in the carbonyl stretching region are compared in Figure 1. (Our experimental protocols are described in detail in refs 1 and 2.) Clearly, as the amount of ethylene is increased, the width at half-height diminishes considerably. Great care in experimental methodology is necessary here, as uneven films, or those that are too thick (hence outside the linear Beer/Lambert law range), can lead to "artificial" broadening (see ref 2 for a detailed discussion). However, exactly the same trend can be seen in the spectra of solutions of ethyl isobutyrate in cyclohexane, obtained using thin, sealed liquid cells or "smears" sandwiched between sealed KBr windows, as shown in Figure 2. The width at half-height of both the polymer and this low molecular weight analogue as a function of dilution with nonpolar segments or molecules is shown in Figure 3. The width at half-height approaches the same limiting value of ~11 cm^{-1} at high dilution. Furthermore, in both systems there is a frequency shift of the carbonyl stretching mode from about 1738 cm^{-1} in the concentrated regime to near 1742 cm^{-1} at high dilution.

This is a result that at first sight might appear to be only of interest to spectroscopy afficionados. However, we believe there are broader implications that are related to the use of vibrational spectroscopy as a probe of intermolecular interactions and molecular force measurements (for example, see ref 3). The results reported here are, we believe, almost certainly due to transition dipole coupling and would depend on the angular correlation of dipoles in these polar materials.

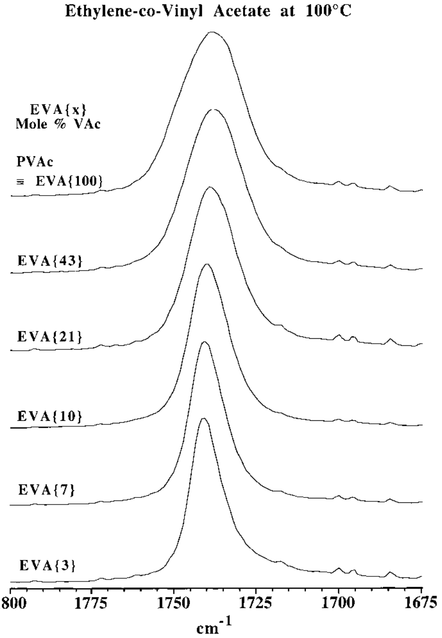

Figure 1. Carbonyl stretching region of the infrared spectra of ethylene-*co*-vinyl acetate copolymers, EVA{x}, where x = mole percent of vinyl acetate.

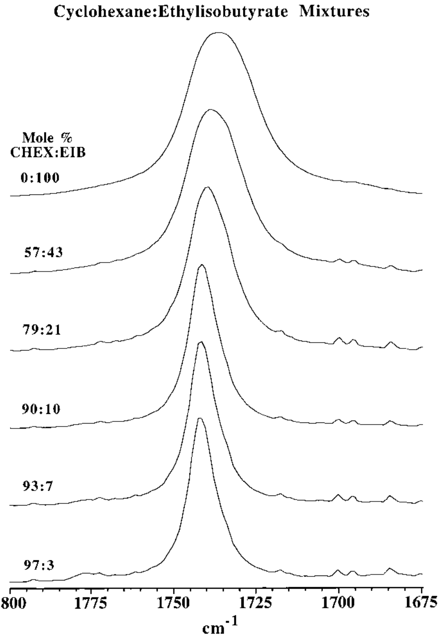

Figure 2. Carbonyl stretching region of the infrared spectra of solutions of ethyl isobutyrate in cyclohexane.

There is a wealth of literature concerning solvent effects in infrared spectroscopy, and it is well-known that changes in the dielectric constant of the medium, which would occur as a result of dilution with a nonpolar segment or solvent, can also result in frequency shifts. However, the evidence indicates that in the type of system studied here (i.e., carbonyl-containing molecules or segments diluted by nonpolar material) a simple

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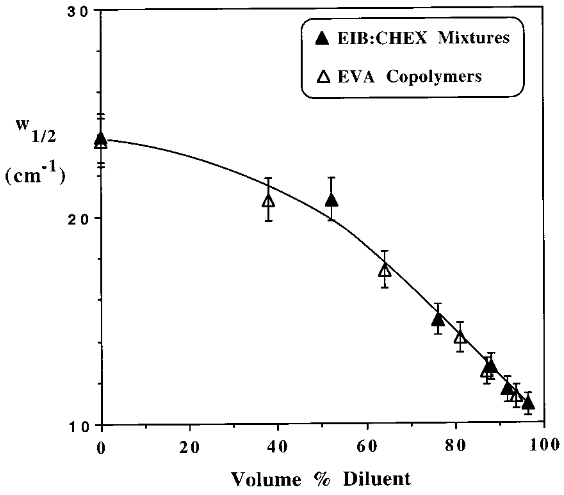

Figure 3. Plot of the width at half-height of the carbonyl bands shown in Figures 1 and 2 as a function of volume percent of the diluent.

dielectric “reaction field” effect provides an inadequate description, and dipole interactions dominate.[4-6] Furthermore, in a definitive and comprehensive body of work Krimm and co-workers (see refs 7–9 and citations therein) have demonstrated how transition dipole coupling results in a significant “splitting” in the amide I mode (carbonyl stretch) of ordered polypeptides and makes a large contribution to the splitting of carboxyl stretching modes in formic acid dimers. Similarly, Kobayashi and Sakashita have shown how this type of interaction explains morphology-dependent bandshifts in the infrared spectra of poly(oxymethylene) and poly(ethylene oxide).[10] These are ordered systems, of course, but it is a relatively straightforward task to show how this mechanism would lead to band broadening in amorphous polymers or liquid small molecule systems of the type studied here.

The interaction potential between two dipoles, A and B, can be written in the following form:

$$V_{dd} = -\mu_A \mu_B X_{AB} \tag{1}$$

where X_{AB} is a geometrical factor

$$X_{AB} = [\hat{\mathbf{e}}_A \cdot \hat{\mathbf{e}}_B - 3(\hat{\mathbf{e}}_A \cdot \mathbf{r}_{AB})(\hat{\mathbf{e}}_A - \mathbf{r}_{AB})]/r_{AB}^3 \tag{2}$$

while $\hat{\mathbf{e}}$ is a unit vector describing the direction of the dipole moment and r_{AB} is the distance between the centers of the dipoles. It is the *transition* dipole moment, however, that determines frequency shifts (and intensities) in the infrared spectrum, and the usual procedure is to express the dipole moment as a power series with respect to the normal coordinate (or other displacement coordinates). To first order (i.e., neglecting interactions between different normal modes) the frequency shift of the ith normal mode due to V_{dd} is then[7]

$$\Delta\nu_i = \frac{V_{dd}}{hc} = \frac{84862}{\nu_i}\left[\frac{\partial\mu}{\partial Q_i}\right]^2 X_{AB}^i \tag{3}$$

where X_{AB}^i is in Å^{-3}, the unperturbed frequency ν_i is in cm^{-1}, and $\partial\mu/\partial Q_i$ is in D Å^{-1} u$^{-1/2}$ (u = atomic mass units).

The frequency shift obviously depends on the orientation of the transition dipoles with respect to one another and the proximity of the molecules. In ordered systems this geometry is well-defined, but in the liquid-state one would expect a distribution that will depend on the dipole strength and the shape of the molecules, which can impose barriers to the rotation of a molecule or segment relative to its immediate neighbors. In other words, although it is the transition dipole moment that determines intensities and the extent of frequency shifts from “unperturbed” values, dipolar interactions also play a role through their effect on the geometry-dependent term, X_{AB}^i, in eq 3.

In systems where dipolar interactions are relatively weak (with respect to kT) dipolar interactions can be averaged over all orientations to give the Keesom interaction energy

$$\bar{V}_{dd} = -\frac{2\mu_A^{\,2}\mu_B^{\,2}}{3r^6kT} \tag{4}$$

Because the time period of a molecular vibration ($\sim10^{-13}$–10^{-14} s) is much faster than that of molecular reorientation ($\sim10^{-11}$ s in low molecular weight liquids at ordinary temperatures), the infrared spectrum essentially “sees” all of the interactions between a reference molecule and its neighbors, giving rise to a symmetrically broadened band which can be considered a superposition of frequency shifts (from the unperturbed stretching mode) from all possible relative orientations of the molecules. As the system is diluted with nonpolar molecules, the number of neighboring polar groups decreases, and the band narrows and shifts closer to the unperturbed value observed in the dilute state (i.e., $\Delta\nu_i \rightarrow 0$ in eq 3).

This is apparently what we observe in the ester- and acetate-containing molecules and copolymers described above. However, if the spectra are examined carefully, it appears that in the concentrated regime the bands are broadened asymmetrically on the low-frequency side. Care must be taken here, because factors such as noise, the resolution used to obtain the spectrum (which affects the measured frequency of maximum absorption), and so on can lead to errors in judgment. Nevertheless, it is useful in concluding this note to show that the appearance of asymmetry or even a second peak would be expected in systems where there are strong dipolar interactions, because there is a tendency for the dipoles to align. Kirkwood[11] described short-range orientational correlations between a dipole and its z immediate neighbors using a correlation factor g defined as

$$g = 1 + z\,\overline{\cos\gamma} \tag{5}$$

where $\overline{\cos\gamma}$ is the average of the cosine of the angle γ between the dipole of the reference molecule and one of its neighbors. For pairwise interactions ($z = 1$), values of g close to two indicate a strong parallel (in-line) association, while values near zero indicate a strong antiparallel alignment. The geometry term in eq 3 could be replaced by some average that depends on g (actually $g - 1$) with the following result. For systems with strong dipolar interactions there would be a tendency for antiparallel alignment (which is energetically more favorable than a parallel arrangement of dipoles), resulting in a distribution of imperfectly aligned molecules or segments. In ordered systems consisting of a finite number of such coupled oscillators, one observes various bands that map the dispersion curve of the theoretically infinite oscillator chain. For disordered systems one would therefore expect to see a superposition of the effect of finite chain lengths and imperfect alignment. This could result in bands asymmetrically broadened on the low-frequency side when there is a tendency to antiparallel alignment [and on the high-frequency side if there is a tendency to parallel (in-line) alignment, see ref 12]. We will investigate systems with strong dipolar interactions in future work in order to check this prediction.

To summarize, these results show that there is an interesting sensitivity of the half-widths and possibly the shapes of infrared bands to dipolar interactions, and this could prove useful in studying dipolar interactions and correlations in polar materials.

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