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CONTENTS

Abstract ........................................................................................ 1
Problem Status .............................................................................. 1
Authorization ................................................................................ 1

HISTORICAL BACKGROUND ...................................................... 1

EVALUATION OF EXISTING THEORIES .................................... 3

The Kirkwood-Bauer-Magat Theory ............................................. 3
The Bellamy Theory of Specific Interactions .................................. 5
Composite Theories ....................................................................... 7

MIXED SOLVENT TECHNIQUES ................................................ 8

Calculation of Overlapped Band Contours ................................... 8
Applications ............................................................................ 11

SUMMARY ................................................................................ 13

REFERENCES ............................................................................ 14
Solvent-Induced Effects on Infrared Spectra

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The historical development of theories for solvent-induced infrared frequency shifts is given and several of these theories are then examined in the light of accurate experimental data. The bulk dielectric theory of Buckingham predicts that the ratio of the integrated intensity of an absorption band and the square of its frequency is an isotopic invariant. This prediction is checked using the C–H and C–D stretching bands of CHCl₃ and CDCl₃; CHCl₃Br and CDCl₃Br; and CHBr₃ and CDBr₃. Ratios of 1.73, 1.54, and 1.20, respectively, are observed. These values are in significant disagreement with the predicted value of unity. Bellamy-type plots are constructed for the C=O vibrations of a number of solutes and, in general, the resulting curves do not pass through the origin as predicted.

Theoretical band contours resulting from two overlapped bands are computed for various band maxima separations, and the effect of intensity changes of the individual bands on the shape of the resultant contour is discussed. These theoretical predictions are then applied to the interpretation of a number of mixed solvent studies which show the complexity of most solvent-solute interactions.

Finally, these techniques are applied to the interpretation of the 750 cm⁻¹ band of tetralin and the 680 cm⁻¹ band of benzene which are unusual bands in that they show a "blue-shift" with increasing solvent polarity. The observed behavior in the intensity and shape of the bands, as a function of solvent composition, cannot be explained in terms of either complex formation or bulk dielectric effects. These observations provide additional evidence that frequency shifts are probably due to a number of interactions which individually produce frequency shifts of different magnitude and direction.

HISTORICAL BACKGROUND

It is well-established that molecular interactions can give rise to a number of changes in molecular spectra. The frequencies of the normal modes of vibration may be either raised or lowered; the intensities of the bands may be changed by as much as an order of magnitude; and the half-width and shape of the bands may change drastically. In addition, these interactions can result in changes in the effective geometrical symmetry of the absorbing entity, which results in the appearance of previously forbidden transitions. Finally, combination bands involving simultaneous transitions in a molecule and one or more of its neighbors can result. The study and understanding of these spectral changes is an important approach to the determination of molecular dynamics and interactions in condensed media.

The magnitude of molecular interactions encompasses a considerable range of energies. At one extreme, one encounters the very strong interactions which result in the formation of relatively stable complexes. The strong hydrogen bonds which result in the formation of the carboxylic acid dimers represent a somewhat weaker interaction. The energy of such bonds is typically in the 10 to 15 kcal/mole range. At the other end of the scale one encounters the relatively weak interactions which involve bond energies of 2 to 3 kilocalories/mole. The complexing of chloroform and acetone is characteristic of such interactions. Finally, we have the very weak interactions which give rise to relatively small spectral changes and which have been the subject of a great many theoretical and experimental papers during the past 25 years. This report will be concerned primarily with these weaker effects. In particular, we shall be concerned with solvent-solute interactions as opposed to the modification of solute-solute interactions by means of dissolution in an essentially inert solvent.

The study of weak solvent-solute interactions began with the work of Kirkwood, as reported by West and Edwards (1), and Bauer and Magat (2). These investigators, working independently, derived a formula which relates the relative frequency shift experienced by an oscillator in going from an isolated environment to a condensed medium in terms of the dielectric constant of the medium. The theory is based on the concept of a reaction field which is the mean electric field acting...
on a molecule due to the polarization induced in neighboring molecules by its own charge distribution. The theory generally assumes a point dipole located in a spherical cavity surrounded by a uniform medium of dielectric constant, $\varepsilon$. The resulting equation is the well-known "Kirkwood-Bauer-Magat" formula (KBW)

$$\Delta\nu/\nu = C (\varepsilon - 1)/(2\varepsilon + 1)$$  \hspace{1cm} (1)

where $\nu$ is the frequency in the vapor or isolated state, $\Delta\nu$ is the frequency shift, $\varepsilon$ is the dielectric constant of the solvent medium, and $C$ is a constant which depends only on the properties of the vibrating molecule.

The KBM formula, which is the basis of the bulk dielectric theory of solvent effects, has been applied to a wide variety of solute-solvent systems (3-14). The general conclusion reached by most of these investigators is that the KBM relationship is valid for nonpolar solvents but fails in the case of polar solvents. In order to explain the frequency shifts in polar solvents, additional terms have been added involving the refractive index of the solvent and other parameters such as the molar volumes of both solute and solvent. However, most of these theories relate observed frequency shifts to bulk properties of the solvent and neglect specific interactions. Such modifications of the original KBM theory have been proposed by numerous investigators (5,6,15-19).

The proponents of the bulk dielectric theory have long recognized the existence of specific interactions between solvent and solute molecules, and have explained the exceptions to KBM-type theories in terms of such interactions. Thus it is generally agreed that solvent-induced frequency shifts are due to both dielectric effects and to specific interactions. However, little has been done to evaluate the relative magnitude of the individual contributions to the total shift. It is interesting to note that most of the vibrational frequencies which have been utilized to check the validity of the KBM-type formulas are due to functional groups which are known to form hydrogen bonds. These include such groups as $\text{N} \cdot \cdot \cdot \text{H}$, $\text{O} \cdot \cdot \cdot \text{H}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$, and the $\text{C} \cdot \cdot \cdot \text{H}$ group in chloroform. Thus one is naturally skeptical about the relative significance of bulk dielectric effects.

In rather sharp contrast to the bulk dielectric theory of solvent effects, a second school of thought has more recently developed which tends to explain solvent effects solely on the basis of specific interactions. This school of thought has been given its greatest impetus by the work of Bellamy and co-workers (20-24). The approach taken by these investigators is to compare the frequency shifts of two different solutes in a variety of solvents. By this means, Bellamy, et al. (20) reasoned that one could eliminate those properties of the solvents which operated to similar extents in the two cases. They further reasoned that if the frequency shifts depended upon some property of the solvent such as the dielectric constant, a simple linear relationship with a slope of 45 degrees would result, but if the properties of the solute molecules are also involved, a line of different slope would result. Bellamy and co-workers have studied a number of solute molecules and have been able to show that the slopes of the resulting straight lines differ considerably and can be correlated with the proton-donating or accepting power of the vibrating entity. On the basis of these data they have suggested that specific interactions are responsible for solvent-induced frequency shifts, and have given considerable supporting evidence for this hypothesis by studying frequency shifts in mixed solvents (22). By this means they were able to show that the solvent shifts exhibited by a number of X-H stretching vibrations were due to local or specific interactions rather than nonlocalized dielectric effects.

The first systematic attempt to isolate the individual contributions made by specific and dielectric effects to the total frequency shift was made by Caldow and Thompson (25). They attempted to fit a number of sets of experimental data to an equation of the type

$$\Delta\nu/\nu = C_1 + C_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + C_3 \frac{n^2 - 1}{2n^2 + 1} + C_4 \sigma^a,$$  \hspace{1cm} (2)

where $\varepsilon$ is the dielectric constant, $n$ the refractive index, $\sigma^a$ the Taft inductive factor (26,27), and the $C_i$'s are constants characteristic of a given solute vibrational mode. While this approach was partially successful in fitting the observed data, it was not adequate to isolate or indicate the relative importance of the various factors contributing to the frequency shifts.

In a recent series of papers, Whetsel and Kagarise (28-30), utilizing the technique of mixed solvents, have been able to partially isolate the contribution which complex formation makes to
solvent-induced frequency shifts. In general, the specific effects exceed what could possibly be attributed to bulk dielectric effects. More recently Heald and Thompson (31) have suggested that dispersion forces are quite significant in the case of CO₂ and several C=O group containing compounds. It therefore seems quite certain that any theory for solvent-induced frequency shifts must consider the contribution from specific intermolecular interactions be they dipole-dipole, dipole-induced dipole, or dispersion forces.

In this report we shall present data which serves two purposes. First, it will demonstrate that existing theories are inadequate to explain the observed facts. Secondly, it will discuss some techniques which should prove useful in isolating the various factors which give rise to solvent effects.

EVALUATION OF EXISTING THEORIES

The Kirkwood-Bauer-Magat Theory

The bulk dielectric school of thought, as exemplified by the KBM-type equations, has reached its most sophisticated state of development in the work of Buckingham (17,19). One of the consequences of this theory is that the integrated intensity of an absorption band divided by the square of the frequency \( \frac{A}{\nu^2} \) is independent of isotopic substitution. The intensity data, which Buckingham used to check this prediction (the C-H and C-D stretching band of CHCl₃ and CDCl₃), were obtained in different laboratories using prism instruments, and therefore subject to considerable experimental error. The quantity \( \Delta \nu/\nu \) is likewise an isotopic invariant, according to the Buckingham theory.

The integrated intensity of the C-H and C-D stretching vibrations of several haloforms, both as pure liquids and in dilute CCl₄ solutions, have been measured, and the results are given in Tables 1 and 2.

These data were obtained with a Perkin-Elmer Model 112 double-pass spectrophotometer equipped with a 75 line/mm diffraction grating. The spectral slit width used was about 0.5 cm⁻¹. With this resolution, it is felt that the intensity measurements are reliable to ±10% in an absolute sense and considerably more reliable in a relative sense.

An examination of the data given in Tables 1 and 2 shows that the prediction that \( \Delta \nu/\nu \) is an isotopic invariant is substantiated. However, it should be pointed out that the ratio \( \frac{\langle \Delta \nu/\nu \rangle}{\langle \Delta \nu/\nu \rangle_0} \) is slightly greater than unity in every case and there seems little doubt that this is a real effect.

The quantity \( A/\nu^2 \) on the other hand, is quite sensitive to isotopic substitution. For chloroform CHCl₃, the ratio is about 1.75, both in the pure liquid and in CCl₄ solution. This value decreases as the degree of bromine substitution increases. Thus the data clearly demonstrate that \( A/\nu^2 \) is rather sensitive to isotopic substitution. This sensitivity is probably related to the reduced amplitude of the deuterium atom as compared to the hydrogen atom during the stretching motion. In a previous study (32) it was shown that the energy

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparison of Frequency and Intensity of C-H and C-D Stretching Vibrations of Some Haloforms in the Pure Liquid</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>HCCl₃</th>
<th>DCCl₃</th>
<th>HCClBr</th>
<th>DCClBr</th>
<th>HCBr₂</th>
<th>DCBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu ) (vapor)*</td>
<td>3033.4</td>
<td>2263.6</td>
<td>3040.3</td>
<td>2267.1</td>
<td>3048.7</td>
<td>2272.2</td>
</tr>
<tr>
<td>( \nu ) (liquid)</td>
<td>3020.2</td>
<td>2254.6</td>
<td>3020.6</td>
<td>2252.8</td>
<td>3020.6</td>
<td>2251.9</td>
</tr>
<tr>
<td>( \Delta \nu )</td>
<td>13.2</td>
<td>9.0</td>
<td>19.7</td>
<td>14.3</td>
<td>28.1</td>
<td>20.3</td>
</tr>
<tr>
<td>( \Delta \nu/\nu \times 10^4 )</td>
<td>4.35</td>
<td>3.97</td>
<td>6.47</td>
<td>6.51</td>
<td>9.22</td>
<td>8.93</td>
</tr>
<tr>
<td>( A/\nu^2 )</td>
<td>706.6</td>
<td>227.7</td>
<td>1177.5</td>
<td>425.7</td>
<td>2174.8</td>
<td>1010.6</td>
</tr>
<tr>
<td>( A/\nu^2 \times 10^4 )</td>
<td>77.5</td>
<td>44.8</td>
<td>129.0</td>
<td>83.8</td>
<td>238.4</td>
<td>199.3</td>
</tr>
<tr>
<td>( \langle \Delta \nu/\nu \rangle )</td>
<td>1.09</td>
<td>1.02</td>
<td>1.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \langle A/\nu^2 \rangle )</td>
<td>1.78</td>
<td>1.54</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All frequencies are expressed in cm⁻¹

\( \Delta \nu = \nu \) (vapor) - \( \nu \) (liquid)

Integrated intensity in units of liters mole⁻¹ cm⁻²
Table 2
Comparison of Frequency and Intensity of C-H and C-D Stretching Vibrations of Some Haloforms in CCl₄ Solution

<table>
<thead>
<tr>
<th></th>
<th>HCCl₄</th>
<th>DCCl₄</th>
<th>HCCl₄Br</th>
<th>DCCl₄Br</th>
<th>HBr₂</th>
<th>DCBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(vapor)*</td>
<td>3033.4</td>
<td>2263.6</td>
<td>3040.3</td>
<td>2267.1</td>
<td>3048.7</td>
<td>2272.2</td>
</tr>
<tr>
<td>ν(in CCl₄)</td>
<td>3019.8</td>
<td>2254.1</td>
<td>3023.9</td>
<td>2254.0</td>
<td>3050.1</td>
<td>2258.7</td>
</tr>
<tr>
<td>Δν</td>
<td>15.6</td>
<td>9.5</td>
<td>16.4</td>
<td>12.1</td>
<td>18.6</td>
<td>15.5</td>
</tr>
<tr>
<td>Δν/ν × 10⁴</td>
<td>4.48</td>
<td>4.20</td>
<td>5.52</td>
<td>5.34</td>
<td>6.10</td>
<td>5.94</td>
</tr>
<tr>
<td>A‡</td>
<td>1558.9</td>
<td>170.8</td>
<td>753.8</td>
<td>279.8</td>
<td>1463.1</td>
<td>679.0</td>
</tr>
<tr>
<td>A/ν² × 10⁶</td>
<td>61.3</td>
<td>35.6</td>
<td>82.4</td>
<td>55.0</td>
<td>159.3</td>
<td>135.1</td>
</tr>
<tr>
<td>(Δν/ν)₁/₁[(Δν/ν)₀]</td>
<td>1.07</td>
<td>1.03</td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>(A/ν²)₁/₁[(A/ν²)₀]</td>
<td>1.82</td>
<td>1.50</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
</tr>
</tbody>
</table>

*All frequencies are expressed in cm⁻¹.
†Δν = ν(vapor) - ν(liquid).
‡Integrated intensity in units of liters mole⁻¹cm⁻¹.

of the haloform-acetone complex decreases as one goes from chloroform to bromoform. Since the intensity changes in the band due to the C-H or C-D stretching mode are closely associated with complex formation, it is perhaps not too surprising to observe the above-mentioned changes in A/ν² with isotopic substitution.

In many of the earlier attempts to check the validity of the KBM relationship, solvents were chosen primarily on the basis of their transparency in the region of interest and on the basis of their dielectric constant and refractive index values. While this resulted in the widest possible range of values for the function (n² - 1)/(2n² + 1), it did not provide an opportunity to study systematic changes in solvent properties. To remedy this situation the carbonyl frequency of acetone has been studied in a number of halogen-substituted methanes and benzenes. The observed frequencies and frequency shifts and computed (n² - 1)/(2n² + 1) values are listed in Table 3. These data are also shown in Fig. 1, where the frequency of the carbonyl group stretching mode is plotted as a function of the quantity (n² - 1)/(2n² + 1). It is obvious from these data that the KBM relationship is inadequate. However, it is possible to note some linear relationships if one considers solvents of similar structure.

For example, the C=O frequencies for the four haloforms lie on straight line (curve A) as do the points for the three methylene halides (curve B). Similarly, although with somewhat greater scatter, the data for the halogenated benzenes (curve C) and the three completely halogenated methanes (curve D) fall on straight lines. However, these various curves are separated both in intercept and slope by significant amounts. One would certainly conclude from these data that the KBM relationship is not adequate. One can further test this theory by varying the quantity (n² - 1)/(2n² + 1) for a particular solvent by simply varying the temperature. As one lowers the temperature, the density increases and the refractive index n increases. The effect of such a temperature-induced change in n on the carbonyl stretching frequency is shown by curve E. Although the relationship is quite linear, the slope of this line differs considerably from that of curve A. One must therefore conclude that the change in frequency in at least one or perhaps both of these cases is not due solely to changes in the refractive index of the solvent.

It should be pointed out that several other solvent properties vary in an essentially linear manner with the function (n² - 1)/(2n² + 1). Two of these seem to be particularly significant as will be pointed out later. The first of these is the electronegativity of the substituents. In the case of the haloforms it is reasonable to assume that the hydrogen bonding ability of the hydrogen atom is related to the electronegativity of the substituent atoms. In Fig. 2, the sum of the electronegativities of the substituent atoms is plotted as a function of (n² - 1)/(2n² + 1) and the presence of linear relationships is apparent. Secondly, if the solvent shifts are due to dispersion type interactions one
Table 3
Frequency of the C=O Band of Acetone in Some Halogenated Methanes and Benzenes

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \nu_{c=0} ) (cm(^{-1}))</th>
<th>( \Delta \nu )</th>
<th>( \Delta \nu/\nu \times 10^5 )</th>
<th>( n^2 - 1/2n^2 + 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl(_4)</td>
<td>1717.2</td>
<td>19.8</td>
<td>11.4</td>
<td>0.215</td>
</tr>
<tr>
<td>CCl(_2)Br(_2)</td>
<td>1714.1</td>
<td>22.9</td>
<td>13.2</td>
<td>0.234</td>
</tr>
<tr>
<td>CBr(_4)</td>
<td>1708.0</td>
<td>29.0</td>
<td>16.7</td>
<td>0.253</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>1711.1</td>
<td>25.9</td>
<td>14.9</td>
<td>0.210</td>
</tr>
<tr>
<td>CHCl(_2)Br</td>
<td>1710.0</td>
<td>27.0</td>
<td>15.5</td>
<td>0.228</td>
</tr>
<tr>
<td>CHCl(_2)Br(_2)</td>
<td>1708.9</td>
<td>28.1</td>
<td>16.2</td>
<td>0.242</td>
</tr>
<tr>
<td>CHBr(_3)</td>
<td>1710.0</td>
<td>29.0</td>
<td>16.7</td>
<td>0.255</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>1712.1</td>
<td>24.9</td>
<td>14.5</td>
<td>0.204</td>
</tr>
<tr>
<td>CH(_2)Br(_2)</td>
<td>1709.9</td>
<td>27.1</td>
<td>15.6</td>
<td>0.239</td>
</tr>
<tr>
<td>CH(_2)I</td>
<td>1707.0</td>
<td>30.0</td>
<td>17.3</td>
<td>0.287</td>
</tr>
<tr>
<td>C(_6)H(_6)F</td>
<td>1715.6</td>
<td>21.4</td>
<td>12.3</td>
<td>0.219</td>
</tr>
<tr>
<td>C(_6)H(_6)Cl</td>
<td>1715.3</td>
<td>21.7</td>
<td>12.5</td>
<td>0.235</td>
</tr>
<tr>
<td>C(_6)H(_6)Br</td>
<td>1714.2</td>
<td>22.8</td>
<td>15.1</td>
<td>0.244</td>
</tr>
<tr>
<td>C(_6)H(_6)I</td>
<td>1713.1</td>
<td>25.9</td>
<td>15.7</td>
<td>0.260</td>
</tr>
<tr>
<td>Vapor</td>
<td>1737.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 1 - Plot of the carbonyl frequency of acetone vs the refractive index function \( (n^2 - 1)/(2n^2 + 1) \), for various halogenated solvents: Curve (A), the haloforms; curve (B), the dihalomethanes; curve (C), monohalobenzenes; curve (D), perhalomethanes; curve (E), at various temperatures in chloroform.

The Bellamy Theory of Specific Interactions

The position that solvent-induced frequency shifts are due primarily to specific interactions has been defended most strongly by Bellamy and his co-workers (20-24). They have based this on the so-called Bellamy plots in which the \( \Delta \nu/\nu \) terms for a series of solutes is plotted as a function of \( \Delta \nu/\nu \) for a reference solute. According to the arguments proposed by Bellamy, those solutes which interact more strongly with the solvents should yield straight-line plots of the slope less than 45 degrees, while solutes having weaker interaction energies should have steeper slopes.
there is no reason why they should be equal for any two given solute molecules. Thus we see that bulk dielectric theory would also predict plots similar to those predicted by Bellamy on the basis of specific interactions only.

A second indication that the Bellamy approach is inadequate is that many plots do not pass through the origin. Examples of this are shown in Fig. 3 where $\Delta\nu/\nu$ for five solutes have been plotted as a function of $\Delta\nu/\nu$ for ethyl acetate. The solvents used included cyclohexane, methyl iodide, acetonitrile, 1,2-dichloroethane, nitromethane, methylene chloride, sym-tetrachloroethane, chloroform, and bromoform. An examination of this figure reveals that most of the lines do not pass through the origin. Moreover, with those which do the intercept may be either positive or negative. If one makes the reasonable assumption that the frequency shifts are due to several factors, including both dielectric and specific effects, the complexity of a Bellamy plot becomes apparent.

For this purpose let us use the formula proposed by Caldow and Thompson (25) which is

$$\Delta\nu/\nu = C_1 + C_2 \left( \epsilon - 1 \right)/(2\epsilon + 1)$$

A similar equation applies to a second solute and is given using primed quantities for the solute dependent terms

$$\Delta\nu'/\nu' = C_1' + C_2' \left( \epsilon - 1 \right)/(2\epsilon + 1) + C_4\sigma^*.$$

Equation (5) is solved for $\sigma^*$ and substituted in Eq. (4) to give

$$\Delta\nu/\nu = C_1 - \frac{C_1C_1'}{C_1'} + \left( C_2 - \frac{C_1C_2}{C_1'} \right) \left( \frac{\epsilon - 1}{2\epsilon + 1} \right)$$

$$+ \left( \frac{C_1C_1'}{C_1'} \right) \left( \frac{n^2 - 1}{2n^2 + 1} \right) + \frac{\Delta\nu'/\nu C_4}{\nu C_4'}. \tag{6}$$

Using the data of Caldow and Thompson (25), we have evaluated the constants $C_1$, $C_2$, $C_3$, and $C_4$ for the carbonyl stretching mode of acetone, dimethyl acetamide, and acetyl pyrrolidine. In general, Eq. (6) will result in a complex relationship. However, in practice the range of values in
Fig. 3 - Plots of $\Delta \nu / \nu$ for the carbonyl stretching frequency of ethyl acetate vs the corresponding quantity for various carbonyl groups containing compounds dissolved in various common solvents.

Fig. 4 - Plot of $\Delta \nu / \nu$ for the $C=O$ band of acetone vs $\Delta \nu / \nu$ for the $C=O$ bands of $n$-acetyl pyrrolidine and dimethyl acetamide in various common solvents. The solid lines are theoretical curves based on the Caldow-Thompson equation for solvent-induced frequency shifts.

$$(\varepsilon - 1)/(2\varepsilon + 1)$$ and $$(n^2 - 1)/(2n^2 + 1)$$ is rather limited and one can consider them to have a constant value which is close to their median value. Substituting constant values of 0.45 for $$(\varepsilon - 1)/(2\varepsilon + 1)$$ and 0.2 for $$(n^2 - 1)/(2n^2 + 1)$$ in Eq. (6) yields the straight lines shown in Fig. 4. The solid line having the greater slope depicts the relationship between $\Delta \nu / \nu$ for acetone and dimethyl acetamide, while the other line is that for acetone and acetyl pyrrolidine. The experimental points are shown by the circles and these agree reasonably well with the predicted lines.

Composite Theories

On the basis of the foregoing discussion it is quite apparent that solvent induced frequency shifts cannot be satisfactorily explained in any simple manner. The assumption of either bulk dielectric effects or specific interactions as being the predominant factor is a gross oversimplification. Thus it seems certain that if one is to understand the nature and origin of solvent-induced shifts, an experimental approach must be developed which will enable the isolation or separation
of the various factors which are responsible for these shifts. The need for such an approach has been recognized and pointed out by Heald and Thompson (31). They have attempted to eliminate some of the many possible interactions such as dipole-dipole and dipole-induced dipole by studying the effect of solvents on the infrared absorption of CO$_2$, a molecule which does not possess a permanent dipole moment. These results indicate that specific intermolecular interactions predominate and that dielectric effects are secondary. However, because such an approach is limited to a relatively small number of molecules, it cannot be applied to the majority of solute molecules. Therefore, the need exists for a more general approach. In the next section we shall discuss some of the progress that has been made at this Laboratory towards meeting this need.

**MIXED SOLVENT TECHNIQUES**

The use of mixed solvents has already been shown to be a powerful approach to an understanding of solvent-induced frequency shifts (13,22,28-30,32). If the solute absorption frequencies in the two solvents are well separated, i.e., $\Delta \nu$ is at least several times the half-widths of the bands, the interpretations of the solute absorption in mixtures of these two solvents is relatively straightforward. If bulk dielectric effects predominate, one observes a progressive shift in frequency as the solvent composition is varied from one extreme to the other. However, if specific interactions predominate, two separate and distinct bands are observed in the mixtures and their relative intensities change with composition, the frequencies remaining essentially constant.

Unfortunately, many situations are encountered where the two frequencies are not well-resolved. In these cases the separation and the half-width are comparable and one never observes two clearly defined bands. Instead one observes band asymmetries, changes in intensities and changes in the half-width. Thus it is considerably more difficult to discern between dielectric effects and specific interactions. With overlapped bands either effect will result in a progressive change in the frequency of the absorption maximum. We have therefore synthesized a number of hypothetical overlapped band systems in order to elucidate the spectral changes which occur as the relative intensities are varied. It is felt that an appreciation and understanding of these spectral changes can be invaluable in leading to a proper interpretation of mixed solvent data.

**Calculation of Overlapped Band Contours**

The starting point in any calculation of the contour of overlapped band systems is, of course, the shape of the individual bands. A recent study of frequency shifts by differential spectroscopy has indicated that absorption bands may be described fairly satisfactorily by means of the well-known Lorentzian band shape. Deviations from the Lorentzian shape were in many cases due to overlapped bands and not to an intrinsic change in band shape. Thus, all the calculations reported in this investigation are based on the assumption of Lorentzian band shapes. Certain other assumptions were made in order to simplify the calculations. These are summarized below, together with the band shape expression.

1. The bands have a Lorentzian shape, i.e., $A = a/(\nu - \nu_0)^2 + b^2$ where $A$ is the absorbance, $\nu$ the frequency, and $\nu_0$ the frequency at the absorption maximum. The constants $a$ and $b$ are related to absorbance maximum and the width at half intensity by the equations $A_{max} = a/b^2$ and $\Delta \nu_{1/2} = 2b$.

2. The two component bands have equal widths at half intensity.

3. The resolution of the spectrometer is adequate to give true band shapes.

The various parameters used to describe the shape of the resultant band are shown in Fig. 5. The system illustrated consists of two bands (dashed curves), Lorentzian in shape and separated by 1.2 $b$ or 0.6 $\Delta \nu_{1/2}$. The individual bands have maximum absorbance values of 0.5 and 0.3, respectively.

The resultant band, which is obtained simply by adding the absorbances of the two component bands, is shown by the solid curve. Most of the quantities used to describe this band are self-explanatory and need not be discussed. However, the parameters $\delta \nu_1$ and $\delta \nu_2$ require further explanation, since they are used to describe a very important property of the composite band, namely, the asymmetry. Their sum, $\delta \nu_1 + \delta \nu_2 = \Delta \nu_{1/2}$, is the width of the band at half intensity. Their difference, $\delta \nu_1 - \delta \nu_2$, represents the asymmetry. This quantity is zero for symmetrical bands and
increases in absolute value as the band becomes more asymmetrical.

The procedure used in computing curves similar to that shown in Fig. 5 was as follows. For a given value of $\Delta \nu$, the quantities $A_1$ and $A_2$ were varied in a stepwise fashion such that their sum, $A_1 + A_2 = 0.8$. A typical family of curves obtained from such a procedure is illustrated by Fig. 6. The value of $\Delta \nu$ used in this instance was $1.2 \, b$. This corresponds to bands separated by 0.6 of their half-width. Thus for a half-width ($2\, b$) of 10 cm$^{-1}$, $\Delta \nu$ would equal 6 cm$^{-1}$.

The four curves shown in Fig. 6, correspond to the intensities of $A_1$ and $A_2$ listed in the upper right-hand corner. There is, of course, an additional set of four curves which one obtains by interchanging the values of $A_1$ and $A_2$. However, these are mirror images of the first set (with respect to the $f = 0.6$ line) and have not been shown in order to avoid confusion.
Similar families of curves have been constructed for values of $\Delta \nu$ equal to 0.4 $b$, 0.8 $b$, 1.6 $b$ and 2 $b$. For the two higher $\Delta \nu$ values, one obtains two distinct maxima when the component bands are of equal intensity. At other intensity values, the weaker band appears as a shoulder on the stronger band.

Having obtained the above described set of curves, it was possible to relate such quantities as $A_{\max}$, $\delta \nu_1 + \delta \nu_2$, and $\delta \nu_1 - \delta \nu_2$ to the relative intensities and separation of the component bands.

In Fig. 7 are plotted various quantities as a function of the relative intensity $A_2/(A_1 + A_2)$. In the present calculations $A_1 + A_2$ was maintained at a constant value of 0.8. Figure 7a shows the effect of varying the relative intensity on the half-width. In the absence of overlap, the half-width would be 2 $b$. Thus if bulk dielectric effects were responsible for the observed frequency shift between two solvents, the half-width would remain constant in mixtures of the two solvents. It is assumed, of course, that the band half-widths are the same in both pure solvents.

For specific interactions which result in two distinct bands whose relative intensities change with the composition of the mixture, a fundamentally different change in half-width occurs as shown in Fig. 7a. The half-width first increases, reaching a maximum at a relative intensity of 0.5 and then decreases to its original value of 2 $b$. For two bands separated by 0.4 $b$, the maximum half-width is 2.12 $b$. Thus for $\Delta \nu/\nu_0 = 10$ cm$^{-1}$, the change in half-width would be 0.6 cm$^{-1}$, which is comparable to the experimental error.

For a band separation of 0.8 $b$, and a half-width of 10 cm$^{-1}$, the maximum change in half-width is 2.4 cm$^{-1}$. While such a change can be measured with reasonable accuracy, it would appear that the measurement of half-widths is not a particularly satisfactory means of differentiating between bulk dielectric effects and specific interactions. This is particularly true if the half-widths of the individual bands are not exactly equal, a situation which is commonly observed in practice.

A second possible means of differentiating between bulk dielectric and specific effects is illustrated in Fig. 7b. For bulk dielectric effects one would expect $\delta \nu_1 - \delta \nu_2 = 0$ for all values of $A_2/(A_1 + A_2)$. Specific interactions, on the other hand, would result in the curves shown. The magnitude of $\delta \nu_1 - \delta \nu_2$ is strongly dependent upon $\Delta \nu$ as one might suspect. For $\Delta \nu = 0.4$ $b$, the effect is too small to be observed. However, at larger $\Delta \nu$ values one can probably observe the S-shaped character of the curve with a fair degree of reliability.

Finally, one can use the changes in band intensities to distinguish between the two effects, i.e., bulk dielectric and specific interactions. If bulk effects are operative, $A_{\max}$ should remain constantreg

![Fig. 7](image)

Fig. 7 - Predicted changes in band parameters as a function of the relative intensities of the two overlapped bands and for various separations; (a) right, shows change in half-width, (b) upper left, band asymmetry, and (c) lower left, absorbance maximum.
at all compositions. In the case of overlapped bands, one would predict the behavior shown in Fig. 7c. The absorbance maximum first decreases in intensity, reaching a minimum value at \( A_1/(A_1 + A_2) = 0.5 \) and then increases to its initial value. Moreover, the sensitivity of this intensity change is good. For half-widths of 10 cm\(^{-1}\) and a separation of 0.8 \( b \) (4 cm\(^{-1}\)), the change in absorbance is 0.11, which corresponds to a transmittance change of 0.046. It would appear, therefore, that the behavior of the absorbance maximum as a function of composition is a good criterion for differentiating between bulk dielectric effects and specific interactions.

Applications

The results presented in the preceding section have been used previously to interpret a variety of mixed solvent-solute systems (28-30,32). In most instances the frequencies in the two solvents have been sufficiently different to permit an unambiguous interpretation in terms of two distinct bands. In the present investigation several systems have been studied which represent borderline cases between two overlapped bands and the continuous shift predicted by bulk dielectric theory.

The first example is that of the band due to the C-H stretching vibration of chloroform dissolved in various mixtures of carbon tetrachloride and carbon disulfide. The spectral data were obtained with the Perkin-Elmer Model 112 grating instrument described previously. The observed spectra, obtained at the indicated solvent compositions, are shown in Fig. 8. While the band shapes shown in Fig. 8 possess some asymmetry, there is certainly no direct evidence of two overlapped bands. However, there is a marked change in peak intensity and band half-width. These are plotted in Fig. 9. One notes that the change in frequency of the absorption maximum occurs in a very regular and in an essentially linear manner. Such a change is most consistent with the bulk dielectric theory although one obtains similar results with two closely spaced bands which are changing in relative intensity. The observed changes in the half-width and peak absorbance values on the other hand, are most readily explained on the basis of two distinct absorption frequencies which are badly overlapped. The curves shown in Figs. 9a and 9b are quite similar to those shown in Figs. 7a and 7c. Bulk dielectric effects could not result in the observed changes. Thus one is led to the conclusion that the chloroform molecule interacts in a specific manner with carbon disulfide and carbon tetrachloride, both of which are nonpolar solvents. Since the shift in C-H stretching frequency going from solution in \( \text{CCl}_4 \) to solution \( \text{CS}_2 \) is only 10 cm\(^{-1}\), one is obviously dealing with a relatively weak interaction. However, the total frequency shift in going from the vapor phase to \( \text{CCl}_4 \) solution is about 14 cm\(^{-1}\), so that even if this total shift is due to dielectric effects, the two shifts are comparable in magnitude. It still remains to be shown that the 14 cm\(^{-1}\) shift is due solely to bulk dielectric effects.

Since the ability to resolve two overlapped bands depends primarily upon the ratio of the separation of the bands and their widths at half intensity, it is advantageous to study narrow absorption bands. Two bands which ideally satisfy this criterion are the 750 cm\(^{-1}\) band of tetralin (1,2,3,4-tetrahydronaphthalene) and the 680 cm\(^{-1}\) band of benzene. Moreover, both bands are extremely intense which means that one can use both thin cells (and thereby reduce solvent interference) and reasonably dilute solutions. The observed frequency and half-widths of these two bands in a variety of solvents are listed in Tables 4 and 5.
The most interesting aspect of these data is the fact that the frequency increases, rather than decreases, as the dielectric constant of the solvent increases. Since it is well-known that hydrogen-bonding usually increases the frequency of bending modes, one naturally assumes the existence of specific interactions. Both vibrations in question are essentially bending modes involving the out-of-plane motion of the aromatic ring hydrogen atoms. Therefore, it seemed logical to apply the technique of mixed solvents in an attempt to demonstrate the existence of specific interactions or, more precisely, solvent-solute complexes. The 680 cm\(^{-1}\) band of benzene was studied in mixtures of cyclohexane and acetone. The frequency difference in these two solvents is about 10 cm\(^{-1}\), while the half-widths are 6 cm\(^{-1}\) and 11.8 cm\(^{-1}\), respectively.

In Fig. 10 are shown the observed changes in the maximum absorbance, half-width, and frequency of the 680 cm\(^{-1}\) band as a function of the volume fraction of acetone. The band remains symmetrical within the limits of experimental error. On the basis of the separation and half-widths of the 680 cm\(^{-1}\) band in the two pure solvents, one would predict a resolvable doublet in the mixed solvent cases if specific interactions predominate.

In the case of 750 cm\(^{-1}\) band of tetralin, essentially identical results were obtained. The solute was studied in mixtures of cyclohexane and p-dioxane. The band remained symmetrical
interaction between the dipole of the C-H bond and the dipole of the solvent molecule. However, such an interpretation is comparable to the assumption of complex formation and is in disagreement with the mixed solvent data. Moreover, Buckingham (17) has shown that the frequency shift is proportional to \( (U'' - 3U'\omega_0^2) \), where \( U' \) and \( U'' \) are the first and second derivatives of the interaction potential function. This leads to a modification of the KBM relationship of the form \( \Delta \nu/\nu = C_1 + C_2 (\epsilon - 1)/(2\epsilon + 1) \) where \( C_1 \) is either positive or negative depending upon the signs and magnitudes of \( U' \) and \( U'' \). Thus one cannot discount a bulk dielectric effect on the basis that it should always produce a "red-shift."

SUMMARY

Although many competent investigators have studied the problem of solvent-induced frequency shifts, both from a theoretical and experimental point of view, it must be concluded that very little is known about the origin of these shifts. This lack of understanding must be attributed, in large measure, to the complex nature of the liquid state itself. The assumption that the solute molecule is located in a spherical cavity surrounded by a uniform dielectric medium, while facilitating a mathematical solution to the problem, cannot be considered as more than an extremely crude approximation to the actual situation. Unfortunately, progress towards an understanding of solvent effects has been retarded by an overzealous application of this theory, the so-called Kirkwood-Bauer-Magat relation.

As a natural reaction to this oversimplified dielectric theory, the Bellamy school of thought developed which tended to explain all frequency shifts in terms of specific interactions. Such an extreme approach is likewise unrealistic and cannot hope to form the basis of a general theory. In recent years it has become increasingly more apparent that solvent-induced frequency shifts arise from a variety of sources. Certainly specific interactions play an important role, particularly with those functional groups such as H, H, O-H, C=O, C=N, and C-H groups adjacent to halogen atoms, and they are characterized by larger frequency shifts in comparison to such groups as C=C, C=C, and

Fig. 10 - The 680 cm\(^{-1}\) band of benzene in acetone-cyclohexane mixtures: the effect of solvent composition on peak absorbance (top curve), band width at half intensity (middle curve), and frequency of absorption maximum (bottom curve)
most C–H groups. Based on our current knowledge, it seems reasonable to conclude that if a frequency shift exceeds 20 cm⁻¹, one should suspect the presence of specific interactions. Numerous examples of even smaller shifts due to complexing have been pointed out in recent investigations.

Significant progress toward an ultimate understanding of solvent effects appears to depend upon several factors. First, experimental methods must be developed which permit one to differentiate between the various possible sources of frequency shifts. For example, one can use nonpolar solvents and solutes and thereby eliminate dipole-dipole and dipole-induced dipole interactions. In addition, mixed solvent methods and temperature studies appear to be quite useful in elucidating the presence of complexed species. Secondly, the experimentalist must become cognizant of the importance of band shapes and band intensities. He must come to realize that many asymmetrical bands are not inherently so, but rather consist of two or more badly overlapped symmetrical bands. Finally, the theoretician must accept the experimentally proven fact that specific interactions do indeed exist and must be an integral part of any theory of solvent-induced frequency shifts.

REFERENCES

The historical development of theories for solvent-induced infrared frequency shifts is given and several of these theories are then examined in the light of accurate experimental data. The bulk dielectric theory of Buckingham predicts that the ratio of the integrated intensity of an absorption band and the square of its frequency is an isotropic invariant. This prediction is checked using the C-H and C-D stretching bands of CHCl₃ and CDCl₃, CH₃Br and CD₃Br, and CHBr₃ and CDBr₃. Ratios of 1.79, 1.14, and 1.20, respectively, are observed. These values are in significant disagreement with the predicted value of unity. Bellamy-type plots are constructed for the C=O vibrations of a number of solutes and, in general, the resulting curves do not pass through the origin as predicted.

Theoretical band contours resulting from two overlapped bands are computed for various band maxima separations, and the effect of intensity changes of the individual bands on the shape of the resultant contour is discussed. These theoretical predictions are
then applied to the interpretation of a number of mixed solvent studies which show the complexity of most solvent-solute interactions. Finally, these techniques are applied to the 750 cm\(^{-1}\) band of tetralin and the 680 cm\(^{-1}\) band of benzene which are unusual bands in that they show a "blue-shift" with increasing solvent polarity. The observed behavior in the intensity and shape of the bands, as a function of solvent composition, cannot be explained in terms of either complex formation or bulk dielectric effects. These observations provide additional evidence that frequency shifts are probably due to a number of interactions which individually produce frequency shifts of different magnitude and direction.