Solute-Solvent Interactions. III. Solvent Shifts of Carbon-Chlorine Infrared Stretching Frequencies of Some Chlorinated Hydrocarbons

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Abstract: The influence of various solvents on the C–Cl stretching frequencies of several incompletely chlorinated hydrocarbons has been studied. It is shown that the character of the hydrogen atoms on the carbon bonded to chlorine has an important influence on the C–Cl frequency observed in solution. When these atoms have little hydrogen-bonding ability, as in *n*-propyl chloride, the bulk dielectric constant of the solvent appears to be the dominant factor in producing frequency shifts, and the Kirkwood–Bauer–Magat treatment applies. On the other hand, when these atoms do have hydrogen-bonding ability, as in chloroform, the spectra are drastically affected as a result of complex formation with proton-acceptor solvents. Certain C–Cl stretching bands can be resolved in some solvents and solvent mixtures. These findings throw new light on the mechanism of solvent shifts of infrared spectra.

It is well known that solvents shift the characteristic infrared absorption bands of various groups. It has been shown that both the bulk dielectric constant of the solvent and specific association of solute with solvent may be important.[3-5] Bellamy, *et al.*,[6,7] found that the solvent shifts of X–H (for a large variety of X) and C=O stretching bands are primarily the result of local specific association with the solvent, rather than bulk dielectric effects. On the other hand, Hallam and Ray[8] concluded that for shifts in C–halogen stretching frequencies the dielectric constant of the solvent is the primary factor, although they emphasized that generally "the frequency displacement of a solute vibration is a complex function of the properties of both solute and solvent, and it is only in special cases such as X–H vibrations that one factor alone is sufficient to account for the greater part of the shift." Hydrogen bonding was not specifically considered.

We have carried out a further study of solvent shifts of the C–Cl stretching frequencies of selected chlorinated hydrocarbons in 13 solvents in an attempt to resolve the influence of whichever effects may be significant. The results clearly illustrate the relative importance of the bulk dielectric constant of the solvent and of an indirect effect caused by hydrogen bonding to proton-acceptor solvents of active hydrogen atoms attached to the C–Cl linkage.

Experimental Section

Measurements. All spectra were recorded using double-beam operation with a Beckman IR 8 spectrophotometer. Solutions were prepared as dilute as possible, commensurate with accurate measurement of intensity in mainly 0.1-mm liquid cells. In most cases the concentration was from 0.1 to 0.3 *M*, but in a few instances concentrations of up to 0.5 *M* had to be used because of weakness of absorption intensities. Liquid cells of 0.5 mm thickness could be used in a few cases where the transparency of the solvent was particularly favorable. The precision of the frequency values reported for sharp bands is ±1 cm^{-1}, and that for frequency shifts is ±0.5 cm^{-1}.

Materials. Practical grade acetonitrile[9] and acetone[10] were purified as described before. The sources of other chemicals are indicated as follows: Eastman White Label, EWL; Fisher Certified Grade, F; Fisher Certified Spectroanalyzed, FS. Chloroform (FS) and tetrachloroethylene (EWL) were shaken twice with concentrated sulfuric acid to remove ethanol preservative, then shaken with water, dried with anhydrous sodium sulfate, and finally distilled from phosphorus pentoxide immediately before use. *n*-Propyl chloride, isobutyl chloride, and *cis*-dichloroethylene (all EWL) were distilled from phosphorus pentoxide. Triethylamine (EWL) was dried over Linde 3A Molecular Sieves and then fractionally distilled at atmospheric pressure. Nitromethane (EWL) was dried over anhydrous calcium chloride and then twice fractionally distilled at atmospheric pressure. In all cases boiling points agreed with literature values. *n*-Hexane, cyclohexane, benzene, methylene chloride, carbon tetrachloride, carbon disulfide, and ethyl acetate (all FS), diethyl ether (EWL, Spectrograde), 1,4-dioxane (F, 99 mole % pure), and chloroform-*d* (Nuclear Magnetic Resonance Specialties and E. Merck A. G.) were used without further purification.

Results and Discussion

Tables I–III contain the observed C–Cl stretching frequencies in wave-number units, as well as the relative frequency shifts, $10^3\Delta\nu/\nu$, calculated on the basis of the vapor-state frequencies. Some data from the literature[8,11] are also included.

In Figure 1 the relative frequency shifts of the C–Cl stretching vibration bands of isobutyl chloride, methylene chloride, and chloroform are plotted against the corresponding shifts of ν_{C-Cl}(asym) of *cis*-dichloroethylene, the "standard" C–halogen absorption recommended by Hallam and Ray,[8] who reported that each of these compounds gave a good straight line for the series of solvents studied. However, our results show that several points fall well off the straight lines. This deviation from linearity is even more striking when the relative shifts in ν_{C-Cl} of these three compounds are plotted against the corresponding shifts for *n*-propyl chloride, as in Figure 2a and b. Only isobutyl chloride gives a linear plot, while extensive

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Table I. Solvent Effects on the C–Cl Stretching Frequencies of *n*-Propyl Chloride and Isobutyl Chloride

			n-Propyl chloride				Isobutyl chloride			
	Solvent	ε^a	ν, cm^{-1} (*trans*)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (*gauche*)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (*trans*)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (*gauche*)	$10^3\Delta\nu/\nu$
	Vapor		743^b		660^b		745.5^c		698^c	
1	*n*-Hexane	1.9	735	10.8	655.5	6.8	735	14.1	692	8.6
2	Cyclohexane	2.0	734.5	11.4	655	7.6	734.5^c	14.7	691.5^c	9.3
3	1,4-Dioxane	2.2	722.5	27.6	647	19.7	725.5	26.8	683.5	20.8
4	Carbon tetrachloride	2.2			653	10.6			689^c	12.9
5	Benzene	2.3	725	24.2			726.5	25.3		
6	Tetrachloroethylene	2.3	731	16.2	653	10.6	732.5^c	17.4	689^c	12.9
7	Triethylamine	2.4			653	10.6			689	12.9
8	Carbon disulfide	2.6	730	17.5	652	12.1	731^c	19.4	688^c	14.3
9	Diethyl ether	4.3	728.5	19.4	651	13.6	730	20.8	687	15.8
10	Ethyl acetate	6.0	723.5	26.2	647.5	18.9	726.5	25.3	684	20.1
11	Acetone	20.7	721	29.6	645.5	22.0	724.5	28.2	682	22.9
12	Acetonitrile	36.0	720	31.0	644.5	23.5	723	30.2	681	24.4
13	Nitromethane	36.7	719	32.3			722	31.5		

[a] Dielectric constant values for 20–25°, taken mainly from A. A. Maryott and E. R. Smith, "Table of Dielectric Constants for Pure Liquids," NBS Circular 514, 1951. [b] C. Komaki, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 330 (1955). [c] Reference 11.

Table II. Solvent Effects on the C–Cl Stretching Frequencies of Methylene Chloride and *cis*-Dichloroethylene

		Methylene chloride				*cis*-Dichloroethylene	
	Solvent	ν, cm^{-1} (asym)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (sym)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (asym)	$10^3\Delta\nu/\nu$
	Vapor	759^a		724.5^a		857^b	
1	*n*-Hexane	745^a	18.4			850.5^a	7.6
2	Cyclohexane	744^a	19.8	710^a	20.0		
3	1,4-Dioxane	734^a	32.9	701.5^a	31.7	842^a	17.5
4	Carbon tetrachloride			708	22.8	849^a	9.3
5	Benzene	737.5^a	28.3			844^a	15.2
6	Tetrachloroethylene			708	22.8	849^a	9.3
7	Triethylamine			703	29.7	846	12.8
8	Carbon disulfide	740.5^a	24.4	707.5^a	23.5	847^a	11.7
9	Diethyl ether	737.5	28.3	703	29.7		
10	Ethyl acetate	736	30.3	702	31.1		
11	Acetone	734.5	32.3	701	32.4	842	17.5
12	Acetonitrile	735	31.6	702	31.1	843.5	15.8
13	Nitromethane	736	30.3	702	31.1	843.5	15.8

[a] Reference 8. [b] H. J. Bernstein and D. A. Ramsay, *J. Chem. Phys.*, **17**, 556 (1949).

Table III. Solvent Effects on the C–Cl Stretching Frequencies of Chloroform and Chloroform-*d*

		Chloroform				Chloroform-*d*			
	Solvent	ν, cm^{-1} (asym)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (sym)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (asym)	$10^3\Delta\nu/\nu$	ν, cm^{-1} (sym)	$10^3\Delta\nu/\nu$
	Vapor	772.5^a		678^a		746^b		655^b	
1	*n*-Hexane	762.5^a	12.9	671^a	10.3	736.5	12.7	650.5	6.9
2	Cyclohexane	762^a	13.6	670.5^a	11.1	736	13.4	650.5	6.9
3	1,4-Dioxane	756	21.4	665	19.2	733	17.4	646	13.7
4	Carbon tetrachloride			669.5	12.5			650	7.6
5	Benzene	757.5	19.4			733	17.4		
6	Tetrachloroethylene			669.5	12.5			650	7.6
7	Triethylamine			659	28.0			640	22.9
8	Carbon disulfide	759	17.5	669	13.3	733.5	16.8	649.5	8.4
9	Diethyl ether	756	21.4	665	19.2	734	16.1	645.5	14.5
10	Ethyl acetate	756.5	20.7	665.5	18.4	734	16.1	646.5	13.0
11	Acetone	756	21.4	665.5	18.4	734	16.1	646.5	13.0
12	Acetonitrile	758	18.8	666	17.7	734.5	15.4	647.5	11.4
13	Nitromethane	759	17.5			735	14.7		

[a] Reference 8. [b] R. B. Bernstein, A. A. Gordus, and F. F. Cleveland, *J. Chem. Phys.*, **20**, 1979 (1952).

scatter of points occurs with methylene chloride and especially with chloroform.

In many cases the dipoles in a given family such as X–H (X = B, C, N, O, S, halogens; ref 6), C═X (X = O, S; ref 7), C–halogen,[8] etc., exhibit a common pattern of solvent effects, with the result that the Δν/ν values of any one compound measured in different solvents can be plotted against the corresponding values of any other compound in the family to give a straight line (Bellamy–Hallam–Williams (B–H–W) relationship[6]). Conse-

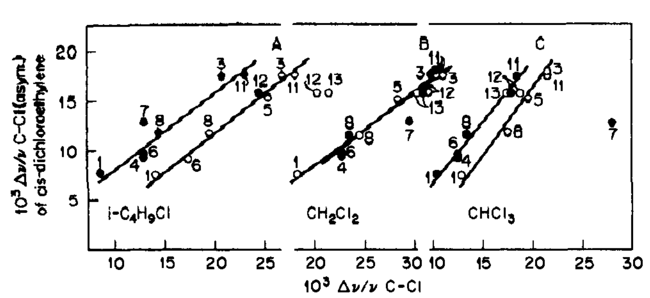

Figure 1. Relative frequency shifts of ν_{C-Cl} bands of (A) isobutyl chloride, (B) methylene chloride, (C) chloroform, plotted against the corresponding shifts of *cis*-dichloroethylene; numbers of solvents refer to Table I: (A) ○, *trans*; ●, *gauche*; (B and C) ○, asym; ●, sym.

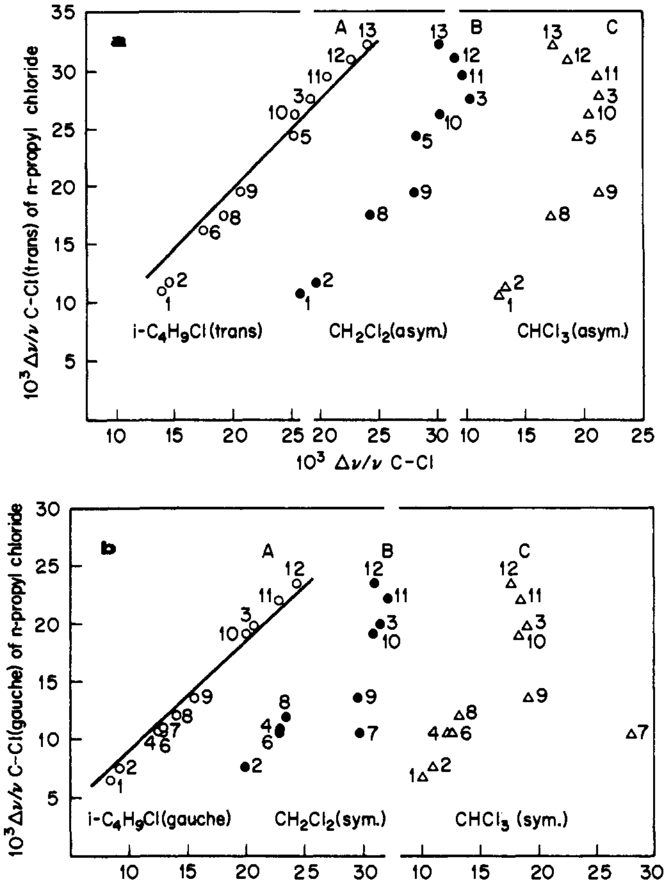

Figure 2. Relative frequency shifts of ν_{C-Cl} bands of (A) isobutyl chloride, (B) methylene chloride, (C) chloroform, plotted against the corresponding shifts of *n*-propyl chloride; numbers of solvents refer to Table I.

quently, the method of solvent variation is often useful for the identification of group frequencies of polar links.[12,13] However the above results clearly show that all C–Cl dipoles do not exhibit the same solvent dependence, and that deviations from the B–H–W relationship occur in proton-acceptor solvents.

The fact that the CH groups of certain halogenated hydrocarbons can act as hydrogen-bond donors is well established.[14] Allerhand and Schleyer[15] concluded from infrared evidence that the ability of a CH group to act as a hydrogen-bond donor depends on the carbon hybridization, increasing in the order C(sp^3)-H < C(sp^2)-H < C(sp)-H, and increasing as expected with an increasing number of electron-withdrawing groups, such as halogens. Likewise, McClellan and Nicksic[16] found an increasing trend in nmr hydrogen-bond shifts with decreasing number of protons in many halomethanes and haloethanes.

For *n*-propyl chloride and isobutyl chloride, which have little hydrogen-bonding ability, our results support previous conclusions[8] that the bulk dielectric constant of the solvent is the dominant factor in determining the magnitude of the C–Cl stretching frequency shift that occurs in solution. With these two compounds the relative shifts of ν_{C-Cl} bands increase in the order *n*-hexane < triethylamine < diethyl ether < acetone < acetonitrile < nitromethane, essentially as the dielectric constants of the solvents increase. Furthermore, except for 1,4-dioxane (point 3) and benzene (point 5) as solvents, the quantitative representation of this dependence by the Kirkwood–Bauer–Magat treatment[17,18] is reasonably successful, as shown in Figure 3, again in agreement with previous conclusions.[8] The anomalously large shifts observed in 1,4-dioxane and benzene are puzzling and may indicate that these solvents are much more polar locally than their low dielectric constants would indicate. Hydrogen bonding of *n*-propyl chloride or isobutyl chloride to dioxane or benzene is not likely to occur and cannot be invoked in order to rationalize these large shifts.

We also have carried out measurements in mixtures of polar with nonpolar solvents. For *n*-propyl chloride and also for isobutyl chloride the (single) C–Cl band gradually shifts to lower frequencies as the proportion of polar solvent increases. Figure 4 shows the results for *n*-propyl chloride in mixtures of acetone with cyclohexane, covering a range of dielectric constants from 2.0 to 20.7.

On the other hand, the behavior of methylene chloride, *cis*-dichloroethylene, chloroform, and chloroform-*d*, which have the capacity to hydrogen bond to proton-acceptor solvents, depends much less on the bulk dielectric constant of the solvent. The Kirkwood–Bauer–Magat treatment fails for these compounds, as shown in Figure 5 for chloroform. The solvent dependence of chloroform and chloroform-*d* especially contrasts with that of *n*-propyl chloride or isobutyl chloride, and it does so in two main respects. First, the relative shifts of the ν_{C-Cl} bands of the two former compounds actually increase in the reverse order from that of the two latter, namely, nitromethane < acetonitrile < acetone < diethyl ether < triethylamine. This order, which is the same as that for the relative shifts of X–H stretching bands, such as N–H of pyrrole, O–H of water, etc.,[6] also is the order of hydrogen-bond acceptor power.[19,20] Second, the ν_{C-Cl}(sym) absorption bands of chloroform and chloroform-*d* show characteristic shoul-

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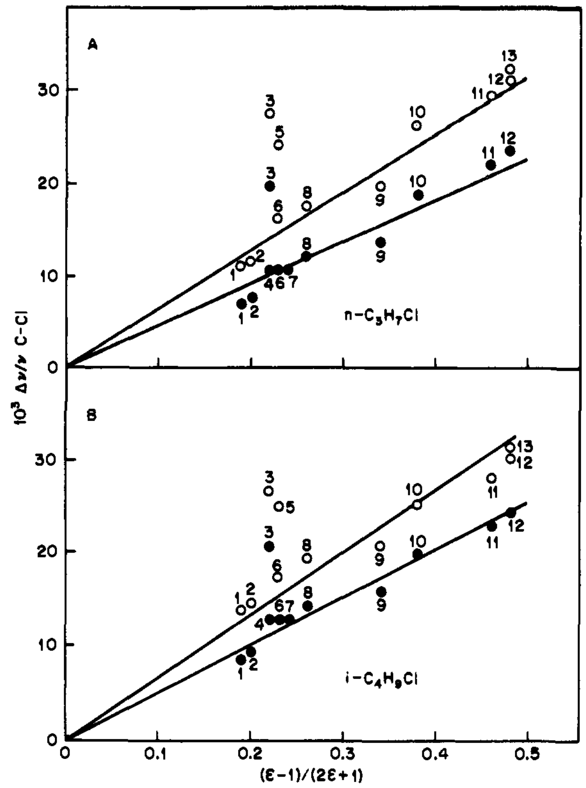

Figure 3. Relative frequency shifts of ν_{C-Cl} bands of (A) *n*-propyl chloride, and (B) isobutyl chloride, as a function of the dielectric constant of the solvent; numbers of solvents refer to Table I: ○, *trans*; ●, *gauche*.

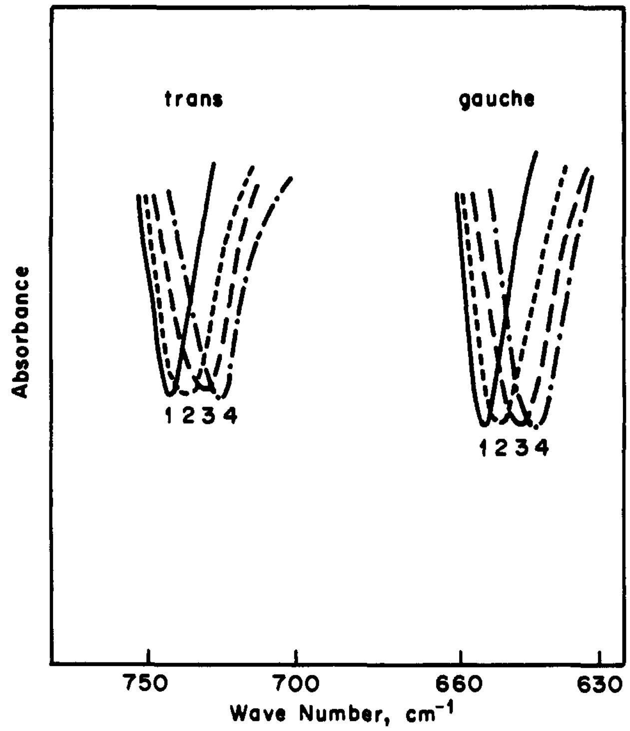

Figure 4. The C–Cl stretching bands of *n*-propyl chloride in mixtures of cyclohexane and acetone: volume fraction of acetone, (1) 0, (2) 0.17, (3) 0.50, (4) 1 (*n*-propyl chloride concentration 0.19 *M*; 0.5-mm cells).

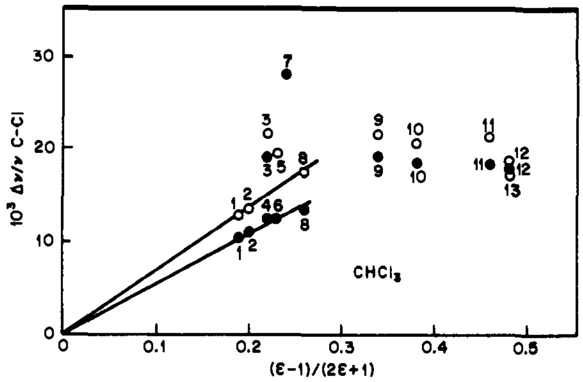

Figure 5. Relative frequency shifts of ν_{C-Cl} bands of chloroform as a function of the dielectric constant of the solvent; numbers of solvents refer to Table I: ○, asym; ●, sym.

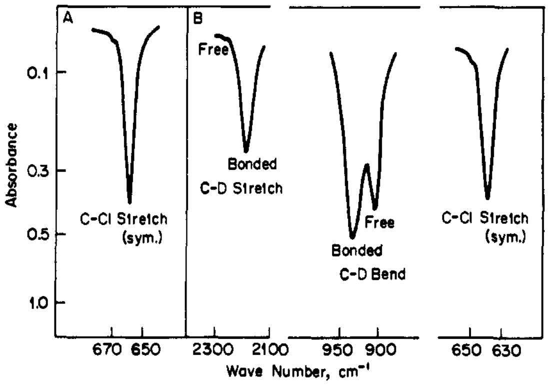

Figure 6. The infrared spectra of chloroform (A) and chloroform-*d* (B) in triethylamine (concentration 0.47 *M*; 0.1-mm cells).

ders in certain solvents, indicating the presence of a reasonably stable solute–solvent adduct. Typical examples are illustrated in Figure 6. Judging from the correspondence to ν_{C-D} and δ_{C-D} absorption bands of chloroform-*d*,[21,22] it seems reasonable to assume that the strong main bands correspond to the hydrogen-bonded species and the shoulders to the residual nonbonded species.

The importance of hydrogen bonding as an indirect cause of C–Cl frequency shifts is further illustrated by results obtained in mixed solvents. Figure 7 represents the ν_{C-Cl}(sym) stretching bands of chloroform in mixtures of acetone with cyclohexane, and triethylamine with cyclohexane. In each case two bands were obtained. While the relative intensities of these bands depend upon the composition of the solvent mixture, the positions of both peaks are essentially invariant. The association constant of the chloroform–acetone adduct (assumed to be a 1:1 complex) was estimated using the method described by Nash[23] from the intensity at 665.5 cm^{-1} for 0.4 *M* chloroform and up to 2.2 *M* acetone in cyclohexane. Our

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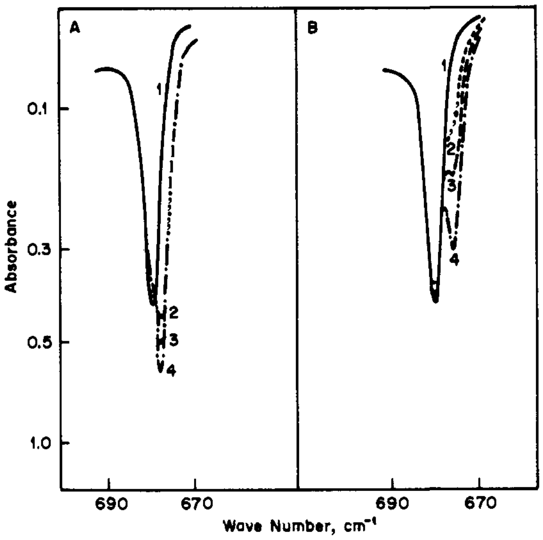

Figure 7. The C–Cl symmetric stretching band of chloroform in two-component solvent mixtures: (A) cyclohexane and acetone: molarity of acetone, (1) 0, (2) 0.65, (3) 1.31, (4) 2.18; (B) cyclohexane and triethylamine: molarity of triethylamine, (1) 0, (2) 0.12, (3) 0.23, (4) 0.46 (chloroform concentration 0.40 *M;* 0.5-mm cells).

value of *ca.* 0.9 l./mole is in reasonable agreement with the literature value of 1.2 ± 0.3,[24] which was determined from the intensity of the hydrogen-bonded C═O stretching absorption of acetone in cyclohexane.

As shown in Figure 8, in a mixture of triethylamine, diethyl ether, and *n*-hexane, chloroform shows three distinct ν_{C-Cl}(sym) absorption bands. These bands occur at essentially the same frequencies as in the three pure solvents individually. In this case the three solvents have similar dielectric constants, yet changes in the proportions of the mixture cause corresponding changes in the relative intensities of the three bands.

Hitherto all efforts to resolve C–halogen stretching frequencies have been unsuccessful, and it has been believed that the influence of the dielectric factor masks any possible doublet arising from the existence of solute–solvent complexes.[5,8]

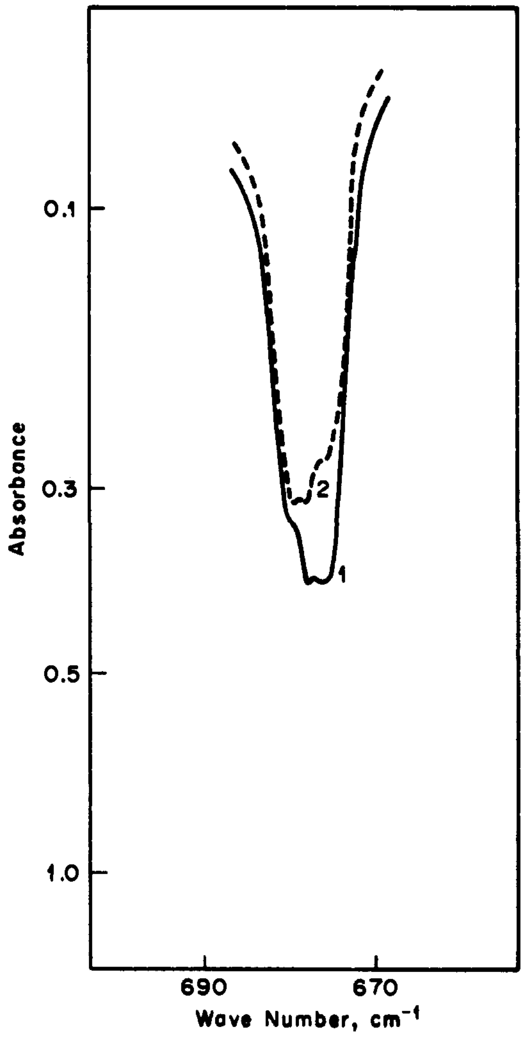

Figure 8. The C–Cl symmetric stretching band of chloroform in three-component solvent mixtures: (1) 83.4 vol % *n*-hexane + 8.3% diethyl ether + 8.3% triethylamine; (2) 90% *n*-hexane + 5% diethyl ether + 5% triethylamine (chloroform concentration 0.40 *M;* 0.5-mm cells).

In conclusion, it is clear that at least two factors can contribute to solvent shifts of C–Cl stretching absorption bands: the dielectric constant of the solvent and a specific indirect effect arising from hydrogen bonding to proton-acceptor solvents. Large fluctuations in solvent effects can occur, depending on the relative importance of these two factors.

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