Interaction between Methanol and the Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, BF₄⁻, SO₃CF₃⁻ and PF₆⁻ Anions Studied by FTIR Spectroscopy

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Kristiansson, O. and Schuisky, M., 1997. The Interaction between Methanol and the Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, BF₄⁻, SO₃CF₃⁻ and PF₆⁻ Anions Studied by FTIR Spectroscopy. – Acta Chem. Scand. 51: 270–273. © Acta Chemica Scandinavica 1997.

The interaction between methanol and the Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, BF₄⁻, SO₃CF₃⁻ and PF₆⁻ anions in dilute dichloromethane solutions has been investigated. The OH stretching vibration was used to monitor the hydrogen bonds formed between the anions and the methanol molecules, providing a direct measure of the hydrogen-bond strength. Concentrations of free and anion-bonded methanol molecules were measured and the equilibrium constants calculated. The wavenumber shift and the free energy of hydrogen-bond formation was found to be significantly correlated. For the anions studied it was found that the hydrogen-bond strength increases in the order: PF₆⁻ < BF₄⁻ < ClO₄⁻ < SO₃CF₃⁻ < NO₃⁻ < I⁻ < Br⁻ < Cl⁻.

When ions are introduced into a protic solvent, structural rearrangements of the hydrogen-bonded network of the liquid will occur. Vibrational spectroscopy is one of the most useful experimental methods to examine these structural changes. In this study we use the OH stretching vibration to investigate the hydrogen bonds formed between methanol molecules and a number of common anions.

The OH stretching vibration is used due to its particular sensitivity to the local environment. It is well known that an increased hydrogen-bond strength is accompanied by a shift to lower wavenumbers and an increase of the bandwidth and intensity.[1-3] Vibrational spectroscopy also allows detection of molecular aggregates with lifetimes of 10^{-13} s, which is shorter than most rearrangement processes occurring in solution. A number of studies of the solvation of anions in methanol with IR spectroscopy have been presented.[4-8] Of particular interest here is an investigation in which methanol in dilute carbon tetrachloride solutions of tetraalkylammonium halides (Cl⁻, Br⁻, I⁻) was studied.[9] OH stretching vibrations of the methanol–anion adducts were obtained and the concentration of free and hydrogen-bonded methanol molecules calculated. It was found that the frequency shifts were proportional to the formation constants obtained. In this paper, this method will be extended to a number of other common monovalent

anions. Owing to the solubility of the tetraalkylammonium salts, dichloromethane is preferred here as solvent.

Experimental

$(C_6H_{13})_4NCl$, $(C_8H_{17})_4NBr$, $(C_4H_9)_4NI$, $(C_4H_9)_4NPF_6$, $(C_8H_{17})_4NClO_4$, $(C_4H_9)_4NNO_3$, $(C_4H_9)_4NCF_3SO_3$ and $(C_6H_{13})_4NBF_4$ salts at purum or puriss grades were purchased from Fluka Chemie AG and used without further purification. The salts were dried under vacuum at room temperature during prolonged periods. For the Br⁻ and Cl⁻ salts a temperature of 55 °C was used. CCl₄ and CH₂Cl₂ of spectroscopic grade were dried with 4A molecular sieves. All solutions were prepared by weight in sealed, air-tight bottles. A dry-box was used when necessary.

Spectra were recorded on a Perkin-Elmer 1760 X FTIR spectrometer on line with a computer. A resolution of 4 cm⁻¹ was chosen. The solutions were contained in a cell with CaF₂ windows and a teflon spacer, giving a path length of 1.00(1) mm. The temperature was 26(1) °C as measured by a thermocouple inserted in the solution in the cell. Spectra were recorded of (a) x M CH₃OH and y M salt in CH₂Cl₂ and (b) y M salt in CH₂Cl₂. The spectra presented in the following are the resulting differences. Spectral evaluations were made with SpectraCalc®.[10]

Results and discussion

Spectra in the OH stretching region of solutions of 0.0275 M CH₃OH and 0.029–0.149 M (C₈H₁₇)₄NBr in

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CH_2Cl_2 are shown in Fig. 1. The spectra consist of two bands. The bands centred at 3627 cm^{-1} originate from monomeric methanol molecules, weakly interacting with surrounding solvent molecules.[11] These interactions are mainly non-specific and are small compared with the hydrogen-bonding interactions of interest here. When the salt concentration is increased, the intensity of this band is reduced and the intensity of a band centred at 3341(2) cm^{-1} increased. This band is interpreted as arising from methanol molecules hydrogen-bonded to the Br$^-$ anion. Band parameters for these spectra are given in Table 1. For comparison, corresponding spectra were also recorded and evaluated using CCl_4 as solvent. No change in the band parameters of the Br$^-$ band was

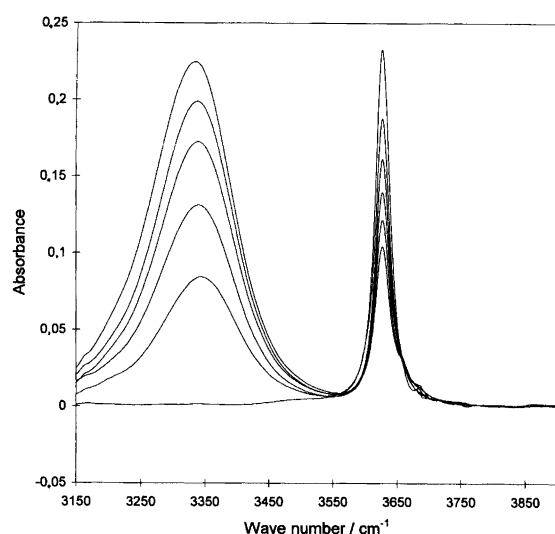Fig. 1. IR absorption spectra in the OH stretching region of 0.0275 M CH_3OH and various concentrations (0–0.1489 M) of $(C_8H_{17})_4NBr$ in CH_2Cl_2.

observed. The band originating from monomeric methanol molecules is found here at 3644 cm^{-1}. Spectra were also recorded using $(C_2H_5)_4N^+$ as cation. No changes in the band parameters could be observed.

The band maxima and widths are constant within experimental error in the concentration range studied. Ion-pair equilibria between the bromide and tetraoctyl-ammonium ions implies a concentration dependence. As the band parameters are invariant, we conclude that either no ion pairs or clusters are formed, which appears unlikely in view of the low dielectric constant of the solvent, or that tetraalkylammonium ions even in the proximity of the anions do not cause any significant perturbation of the anion–methanol interaction. The salt concentrations are in excess compared to methanol concentrations, making multiple-bonded anions statistically unlikely. These systems might consequently be regarded as idealised systems in which the methanol molecule interacts with one anion, forming 1:1 hydrogen-bonded complexes.

Band parameters of the anions studied are given in Table 1. The decrease in frequency of the OH stretching vibration upon adduct formation is accompanied by an increased bandwidth as illustrated in Fig. 2, where the full widths at half height, FWHH, are plotted versus the shift of the band maxima relative to the monomer frequency in the gas phase, Δv_{vapour}, found at 3687 cm^{-1}. Included are also the bands from methanol monomers in CCl_2H_2 and CCl_4. The increase in bandwidth with increasing hydrogen-bond interaction energies is well known for a large variety of hydrogen-bond donor and acceptor molecules, as is the relation between the OH stretching frequency and the acceptor–donor distances.[12,13] For oxygen acceptors, an exponential relation is established.[10] The methanol molecule will experience

Table 1. Absorption band maxima of the OH stretching vibration (v_{max}), frequency shifts relative monomeric methanol molecules (Δv), full bandwidths at half height (FWHH) and equilibrium constants (K) for various methanol–anion adducts.

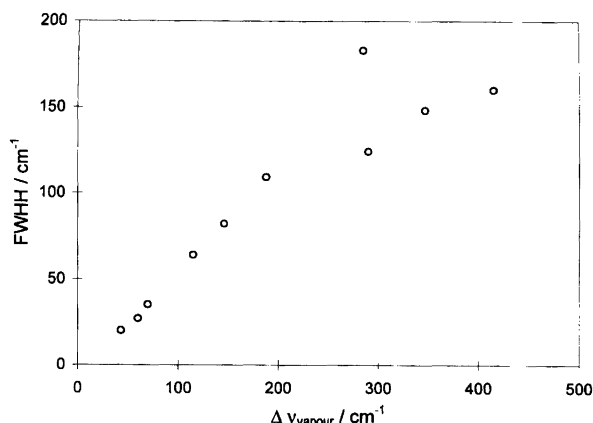| Anion	[CD$_3$OH]/ mol l^{-1}	[(C$_n$H$_{n+1}$)$_4$NX]/ mol l^{-1}	v_{max}/ cm^{-1}	Δv/ cm^{-1}	FWHH/ cm^{-1}	K/M^{-1}
Br$^-$	0.0275(1)	0.0289(1)	3340(4)	283	145	10.6(5)
		0.0589	3339	287	150	9.1
		0.0872	3338	287	148	9.2
		0.1167	3341	288	147	9.8
		0.1489	3340	291	155	10.2
Cl$^-$	0.0230(1)	0.0740	3271	356	160	14.0
		0.1483	3272	355	158	13.2
I$^-$	0.0275(1)	0.0729	3397	230	122	3.8
		0.1448	3394	233	124	3.7
NO$_3^-$	0.0275(1)	0.0747	3402	225	185	5.1
		0.1419	3401	226	181	5.1
SO$_3$CF$_3^-$	0.0275(1)	0.0736	3500	127	111	2.6
		0.1341	3497	130	110	2.6
ClO$_4^-$	0.0275(1)	0.0745	3545	87	82	3.1
		0.1492	3545	86	82	3.0
BF$_4^-$	0.0275(1)	0.0698	3571	56	64	2.3
		0.1458	3572	55	64	2.1
PF$_6^-$	0.0275(1)	0.0734	3618	9	32	1.3
		0.1477	3617	10	39	1.5

Fig. 2. The bandwidths at half heights (FWHH) as a function of the frequency shift of the band maxima relative to vapour-phase methanol molecules (Δv_{vapour}) for a number of anion-methanol adducts. Included are also monomeric methanol in CCl_4 and CH_2Cl_2.

a distribution of interaction distances, r, originating both from low frequency methanol–anion vibrational modes and from orientational disorder in the liquid. When the frequency, v, decreases, dv/dr increases, which results in an increased bandwidth. The band associated with the NO_3^- anion is comparatively broad. With its D_{3h} symmetry, the nitrate anion offers the possibility of both radial and axial coordination, which probably causes a broad distribution of interaction energies. A similar relatively broad band originating from the NO_3^- anion is also observed in aqueous nitrate solutions.[14]

The equilibrium constants, K, for adduct formation are calculated according to the reaction

$$X^-(CH_2Cl_2) + CH_3OH(CH_2Cl_2)$$

$$= CH_3OH \cdots X^-(CH_2Cl_2)$$
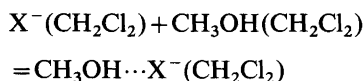
where $X^- = Cl^-$, Br^-, I^-, NO_3^-, ClO_4^-, BF_4^-, $SO_3CF_3^-$ or PF_6^-. The concentration of monomeric methanol is determined from the intensity of the $3627\ cm^{-1}$ band. The concentration of anion-bonded methanol is obtained by difference. Since in many cases severe band overlap occured, a band-shape analysis was performed. The bands observed are well described by a mixed Gaussian–Lorenzian band profile. All band parameters were allowed to vary freely. In all cases, the band parameters of the $3627\ cm^{-1}$ band remained constant. An example of the observed and fitted spectra including the component bands involving the BF_4^- anion is given in Fig. 3. For the dilute solutions studied, activity coefficients are assumed to be equal to unity. The free energy changes are calculated from $\Delta G^\circ = -RT \ln K$. In Fig. 4 ΔG° is plotted versus the shift of the band maxima, Δv (= $v[CH_3OH \cdots X^-(CH_2Cl_2)]-v[CH_3OH(CH_2Cl_2)]$). We observe a significant correlation. Linear dependencies relating the hydrogen-bond enthalpy ΔH with the wavenumber shift Δv have been reported for a number of different H-bond donor systems.[2] Iogansen[15] suggested
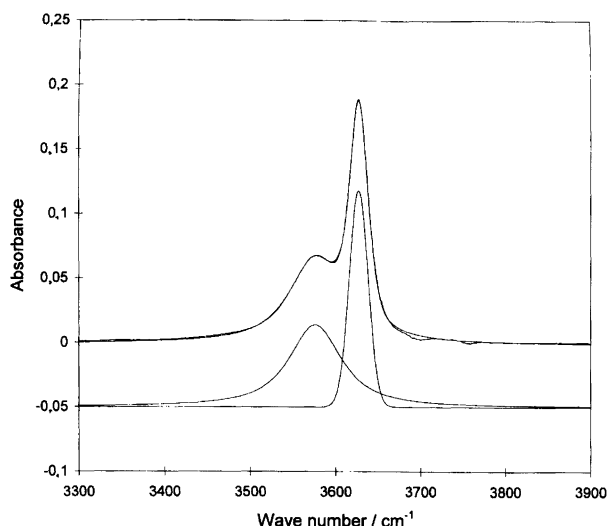

Fig. 3. IR absorption spectra in the OH stretching region of 0.0275 M CH_3OH and 0.1477 M $(C_6H_{13})_4NBF_4$ in CH_2Cl_2. The upper spectra are the observed and the the fitted bandshapes and the lower spectra are the component bands.
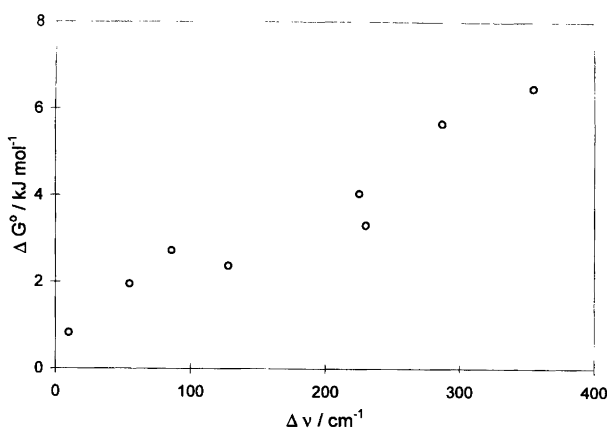

Fig. 4. The free energy of formation, ΔG° (kJ mol^{-1}), as a function of the frequency shift of the band maxima relative monomeric methanol, Δv, for a number of methanol–anion adducts.

for methanol the equation $-\Delta H = 18\Delta v/(\Delta v + 720)$, where ΔH is given in kcal mol^{-1}. Applying this equation to the present data yields $-\Delta H$ values 2–3 times higher than corresponding $-\Delta G$ values, suggesting that entropy effects are indeed important. It is, for example, seen that for the NO_3^- and I^- anions, the equilibrium constants and the shift of band maxima are reversed as compared with the order of the other anions. This might be attributed to entropy contributions. In a future this study might be extended in a broader temperature range to extract such components unambiguously.

In a study on H_2O/salt/dichorometane ternary systems, the v_1 symmetric stretching vibration of the water molecules interacting with the ClO_4^-, NO_3^-, Br^-, CO_3^{2-} and F^- was found at 3531, 3414, 3364, 3345 and 3302 cm^{-1}, respectively.[16] The water monomer band is found at 3602 cm^{-1}. The v_1 absorption band of the H_2O

molecule is unfortunately complicated by overlapping v_3 and $2v_2$ bands, making quantitative properties difficult to extract. The relative proton acceptor strength in 1:1 water–anion complexes is nonetheless as observed in this study. Spectra of the OD stretching vibration of isotopically dilute HDO molecules hydrogen-bonded to various anions in aqueous solution have been obtained with a double difference technique.[14,17] It can be concluded that the relative order of interaction strength of anions in aqueous solution closely agrees with that of 1:1 anion–methanol adducts. In a later paper, a similar double difference technique will be applied to methanolic electrolyte solutions.

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