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***Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth***

# INTERMOLECULAR INTERACTIONS OF 1- AND 2-BROMOPROPANE WITH SOLVENT MIXTURES STUDIED BY INFRARED SPECTROSCOPY

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**ABSTRACT.** The parameters of a vibrational band are sensitive to the environment created by solvents. The effects of the two solvent mixtures cyclohexane/tetrahydrofuran and carbon tetrachloride/acetonitrile on the frequency and half bandwidth of ν(C-Br) band of 1- and 2-bromopropane are investigated. The first mixture can be considered “ideal” and the frequency and half bandwidth of ν(C-Br) bands varies linearly on the mole fraction of the polar solvent. In the case of carbon tetrachloride/acetonitrile mixture, a process of “preferential solvation” with the maximum effect at 2 : 1 volume ratio was evidenced.

***Keywords:*** *infrared spectroscopy, 1-bromopropane, 2-bromopropane, intermolecular interactions, solvent mixtures, preferential solvation index Z*

## INTRODUCTION

Vibrational spectroscopy provides an effective mean of examining intermolecular interactions in non-aqueous solutions. The spectral band profile includes all information about the interactions of a normal vibrational mode with neighboring medium (first of all the static structural perturbations associated to the distribution of local configurations of the solvent).

The interaction of 2-bromopropane and *trans* and *gauche* conformational isomers of 1-bromopropane (named bromopropanes) with solvents is non-specific and is dominated by the dielectric properties of the solvents [1-3]. The Onsager reaction field [4] in which the solvent is represented by a continuum dielectric medium characterized by bulk dielectric constant $\varepsilon$ was a suitable model to describe the interaction of bromopropanes with neat solvents.

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Reported in this paper are the effects of two solvent mixtures prepared from solvents of different polarities cyclohexane/tetrahydrofuran (CH/THF) and carbon tetrachloride/acetonitrile ($CCl_4/CH_3CN$) on the frequency and half bandwidth of ν(C-Br) band of 1- and 2-bromopropane.

## RESULTS AND DISCUSSION

### *Dielectric properties of solvent mixtures*

A mixture of two individual solvents is a medium that generally does not act additively according to its composition.

Theoretically, a binary solvent mixture is “ideal” when a parameter $P_{mix}$ of the mixture is related with the parameters $P_1$ and $P_2$ of each solvent through the following relation:

$$P_{mix} = P_1x_1 + P_2x_2 \tag{1}$$

where $x_1$, $x_2$ are the mole fractions of the components.

Practically, because of the molecular interaction forces the total volume of the mixture is inferior to the sum of the individual volumes and is difficult to find an ideal mixture.

The solvent mixtures used in this study have been cyclohexane/ tetrahydrofuran (CH/THF) and carbon tetrachloride/acetonitrile ($CCl_4$/ $CH_3CN$). Every mixture contains a nonpolar solvent ($\mu = 0$) and a polar one. The dipolar moment of tetrafydrofurane is small ($\mu = 0.7$ D) while the molecule of acetonitrile is a very polar one ($\mu = 3.5$ D).

The mixture CH/THF is considered ideal. The values $\varepsilon^{e}_{mix}$ of the dielectric constant experimentally determined for different solvent mixtures come near the values $\varepsilon^{m}_{mix}$ calculated according to the relation (1) and vary linear with the mole fraction $x_P$ of tetrahydrofuran.

**Table 1**. Values of the dielectric constants $\varepsilon_{mix}$ for different solvent mixtures

| Nonpolar/ polar solvent volume ratio | CH/THF mixture | | | $CCl_4/CH_3$ CN mixture | | | |
|---|---|---|---|---|---|---|---|
| | $x_P$ | $\varepsilon^{m}_{mix}$ | $\varepsilon^{v}_{mix}$ | $x_P$ | $\varepsilon^{m}_{mix}$ | $\varepsilon^{v}_{mix}$ | $\varepsilon^{e}_{mix}$ |
| 1 : 0 | 0.000 | 2.024 | 2.024 | 0.000 | 2.234 | 2.234 | 2.234 |
| 30 : 1 | 0.042 | 2.255 | 2.200 | 0.058 | 4.233 | 3.337 | 3.004 |
| 20 : 1 | 0.062 | 2.365 | 2.282 | 0.084 | 5.129 | 3.854 | 3.381 |
| 10 : 1 | 0.116 | 2.662 | 2.524 | 0.155 | 7.576 | 5.370 | 4.502 |
| 5 : 1 | 0.208 | 3.167 | 2.936 | 0.269 | 11.505 | 7.955 | 6.617 |
| 2 : 1 | 0.397 | 4.206 | 3.854 | 0.479 | 18.743 | 13.711 | 11.797 |
| 1 : 1 | 0.568 | 5.145 | 4.822 | 0.648 | 24.568 | 19.467 | 17.576 |
| 1 : 2 | 0.725 | 6.008 | 5.684 | 0.786 | 29.324 | 25.188 | 23.727 |

| Nonpolar/ polar solvent volume ratio | CH/THF mixture | | | CCl$_4$/CH$_3$ CN mixture | | | |
|---|---|---|---|---|---|---|---|
| | $x_P$ | $\varepsilon^m_{mix}$ | $\varepsilon^v_{mix}$ | $x_P$ | $\varepsilon^m_{mix}$ | $\varepsilon^v_{mix}$ | $\varepsilon^e_{mix}$ |
| 1 : 3 | 0.798 | 6.409 | 6.146 | 0.846 | 31.392 | 28.080 | 26.896 |
| 0 : 1 | 1.000 | 7.520 | 7.520 | 1.000 | 36.700 | 36.700 | 36.710 |

$\varepsilon^e_{mix}$: dielectric constants experimentally determined for different solvent mixtures
$\varepsilon^m_{mix}$: dielectric constants of solvent mixtures calculated according to relation (1)
$\varepsilon^v_{mix}$: dielectric constants calculated according to relation (2)

For a CCl$_4$ / CH$_3$CN mixture, an important deviation from linearity in the dependence of $\varepsilon^e_{mix}$ on the mole fraction $x_P$ of acetonitrile was noticed. The experimental dielectric constants of this system are better approximated by the $\varepsilon^v_{mix}$ values calculated according to the empirical relation (2):

$$\varepsilon^V_{mix} = \varepsilon_N V_N + \varepsilon_P V_P \qquad (2)$$

where V is the volume fraction of solvents and the indexes N and P indicate the nonpolar and respectively the polar solvent from the mixture.

From the thermodynamic point of view the dielectric Onsager functions calculated [5] using different dielectric constants $\varepsilon_{mix}$ are not suitable to describe the effects of a mixture of solvents even if this is considered ideal. The mixture composition or the non-homogeneity of the mixture in the vicinity of solute can modify even the dielectric constant of the individual solvents.

### *Frequency shift of ν(C–Br) infrared bands of bromopropanes*

If the solute sample does not disturb the solvent structure, the maximum of the infrared absorption band should be shifted linearly with the mole fraction of the polar solvent from the mixture. This kind of variation was observed for the bromopropanes solved in the mixture CH/THF considered ideal (see Figure 1).

The dependence of the maximum of ν(C–Br) bands on the mole fraction of acetonitrile is non-linear under the effect of CCl$_4$/CH$_3$CN mixture (Figure 1). The effect is more pronounced at smaller concentrations, proving the importance of local effects of the medium in the proximity of the solute.

Generally, a non-linear dependence of the frequency of the absorption band on the mole fraction $x_P$ is considered as a proof for a specific association solute-solvent, for example hydrogen bonding, but also as a result of a “dielectric enrichment” of the solvent shell around the dipolar solute molecule. If the mixture contains solvents having very different polarities, a process of “preferential solvation” occurs that disturbs their distribution into the electric field of a dipolar solute molecule. The composition of the solvent shell in the vicinity of solute could be different by the composition of the bulk mixture.

The process of “preferential solvation” in $CCl_4/CH_3CN$ mixtures can be characterized by the index *Z* that expresses [6] the relation between the mole ratios $X = x_N/x_P$ and $Y = y_N/y_P$:

$$Y = X e^{-Z}$$

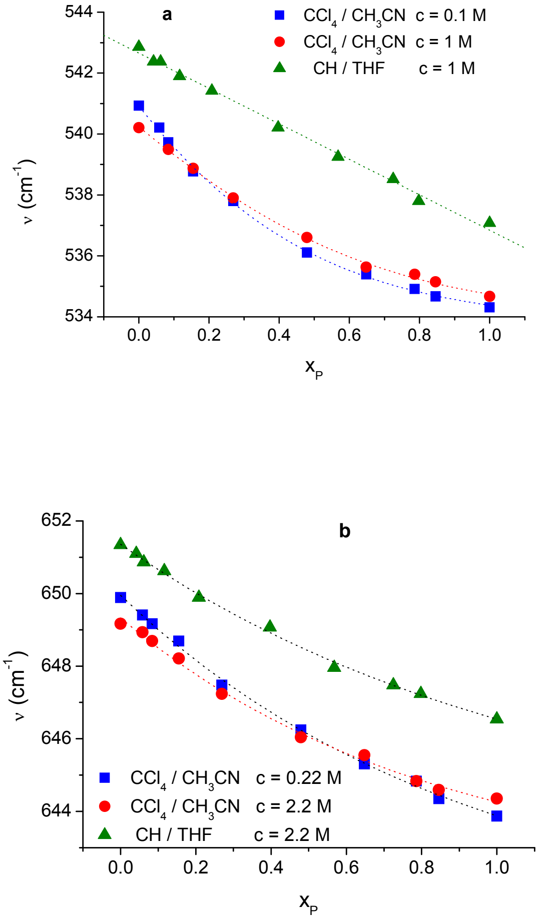

**Figure 1.** Dependence of ν(C-Br) frequency of (**a**) 2-bromopropane and (**b**) *trans* 1-bromopropane on the mole fraction of the polar solvent in CH/THF and $CCl_4/CH_3CN$ mixtures (*c* is the molar concentration of the solute)

The mole fractions $y_P$ of acetonitrile in the solvation shell of bromopropanes were calculated assuming a linear dependence of ν(C–Br) frequency on it. Because of small differences between the ν(C–Br) frequency values, the calculated index *Z* has an uncertainty of ±0.1.

**Table 2.** Mole fraction of polar solvent in the solvation shell $y_P$ and index *Z* of "preferential solvation" of bromopropanes in $CCl_4/CH_3CN$ mixtures (c= molar concentration of solutes)

| $x_P$ | $y_P$ | | | | | |
|---|---|---|---|---|---|---|
| | 2-bromopropane | | *gauche* 1-bromopropane | | *trans* 1-bromopropane | |
| | c=0.11M | c=1.00 M | c=0.22 M | c=2.20 M | c=0.22 M | c=2.20 M |
| 0.058 | 0.149 | 0.120 | 0.125 | 0.097 | 0.106 | 0.090 |
| 0.084 | 0.208 | 0.169 | 0.176 | 0.138 | 0.150 | 0.129 |
| 0.155 | 0.344 | 0.289 | 0.300 | 0.243 | 0.260 | 0.228 |
| 0.269 | 0.512 | 0.450 | 0.461 | 0.392 | 0.414 | 0.372 |
| 0.479 | 0.724 | 0.671 | 0.691 | 0.617 | 0.639 | 0.597 |
| 0.648 | 0.840 | 0.804 | 0.811 | 0.763 | 0.780 | 0.748 |
| 0.786 | 0.913 | 0.891 | 0.895 | 0.866 | 0.876 | 0.856 |
| 0.846 | 0.940 | 0.924 | 0.927 | 0.906 | 0.913 | 0.898 |
| 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Z | 1.05 | 0.80 | 0.84 | 0.55 | 0.65 | 0.48 |

It can be noticed that *Z* value increases in the following order: *trans* 1-bromopropane < *gauche* 1-bromopropane < 2-bromopropane.

The decrease of solute concentration in $CCl_4$/ACN mixture determines also an increase of index *Z.* For all solutes, the difference $y_P–x_P$ has a maximum value for $CCl_4$ : $CH_3CN$ volume ratio of 2 : 1 ($x_P$ ~ 0.4). At this concentration the maximum half bandwidth was also evidenced.

### *Half bandwidth of ν(C-Br) infrared bands of bromopropanes*

The changes observed in the parameter half bandwidth ($\Delta\nu_{1/2}$) of ν(C-Br) bands are related with the complexity of solvent medium in the vicinity of solute molecule, more exactly the part of molecule implied in the studied vibrational mode.

According to Yoshino [6] the greatest modification of the half bandwidth of an absorption band is expected for a value 0.5 of the mole fraction of the polar solvent from a solvent mixture if the difference between the solvation energy of the solute in the individual components of the mixture is zero.

The parameter $\Delta\nu_{1/2}$ of C-Br stretching band increases monotonously with the mole fraction of polar solvent from the bulk CH/THF mixture which is considered ideal (Figure 2).

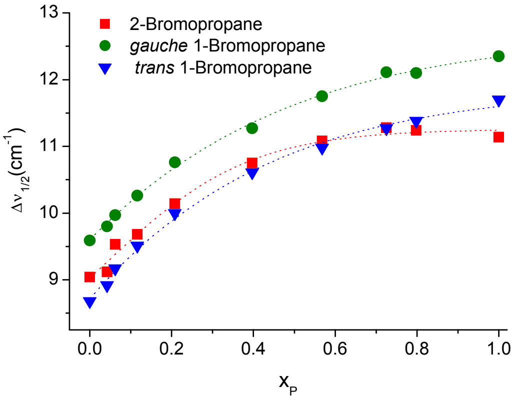

**Figure 2.** Dependence of the half bandwidth $\Delta\nu_{1/2}$ of $\nu$(C-Br) band of 2-bromopropane (*c*=1.06 M) and 1-bromopropane (*c*=2.2 M) on the mole fraction $x_P$ of tetrahydrofuran from the CH/THF mixtures

A different behaviour is noticed under the effect of $CCl_4/CH_3CN$ mixture (Figure 3). A maximum half bandwidth for the mole fraction of acetonitrile ~0.4 is observed. This corresponds to a $CCl_4$ : $CH_3CN$ volume ratio of 2 : 1 where, in the conditions of preferential solvation, the difference $y_P$-$x_P$ is the greatest.

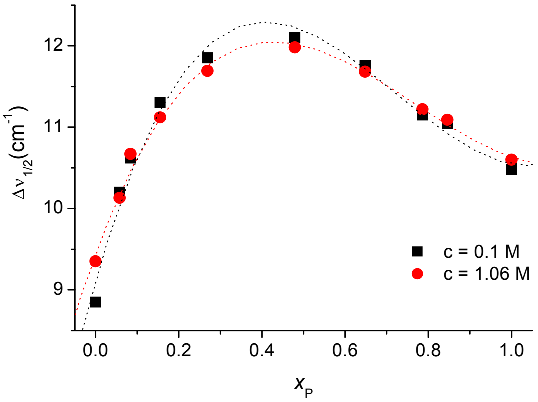

**Figure 3.** Dependence of the half bandwidth $\Delta\nu_{1/2}$ of 2-bromopropane $\nu$(C-Br) band on the mole fraction $x_P$ of acetonitrile from the $CCl_4/CH_3CN$ mixtures (c is the molar concentration of solute)

In Figure 3 is presented the case of 2-bromopropane, but the graphs for the conformational isomers of 1-bromopropane are similar.

The maximum half bandwidth of ν(C-Br) band observed for values of mole fraction of acetonitrile smaller than 0.5 indicate a difference between the solvation energies of bromopropanes in the individual components of the $CCl_4$ / $CH_3CN$ mixture

## CONCLUSIONS

The solutes 2-bromopropane and 1-bromopropane do not disturb the “ideal” CH / THF solvent mixture.

The deviation from linear dependence of ν(C-Br) band frequency on mole fraction of acetonitrile observed under the effect of $CCl_4$/$CH_3CN$ mixture is determined by the local “dielectric enrichment” of the solvation shell. The process of “preferential solvation” in this mixture can be characterized by the index *Z* which increases in the following order: *trans* 1-bromopropane < *gauche* 1-bromopropane < 2-bromopropane.

The maximum half bandwidth of ν(C-Br) band was observed for values of molar fraction of acetonitrile smaller than 0.5, indicating an increase of the difference between the solvation energy of bromopropanes in the individual components of the $CCl_4$/$CH_3CN$ mixture. More exactly, the maximum broadening of ν(C-Br) band corresponds to the composition 2:1 of solvent mixture, for which the difference between mole fraction of acetonitrile in the bulk and in the vicinity of solute is the greatest.

## EXPERIMENTAL SECTION

The analyzed spectra were collected using a JASCO 610 FTIR spectrometer, with a resolution of 0.5 $cm^{-1}$ and sealed KBr cells of 0.012 and 0.062 cm path length. The spectra were obtained by subtracting the spectrum of pure solvent (multiplied with a proper factor which depends on the solute concentration) from that of the solution using the Spectra Analysis software of the spectrometer.

The frequency of ν(C-Br) vibrational mode of bromopropane compounds studied as neat liquids is 538.3 $cm^{-1}$ for 2-bromopropane, 563.1 $cm^{-1}$ for *gauche* isomer and 647.5 $cm^{-1}$ for *trans* isomer of 1-bromopropane respectively.

The solvent mixtures used in this study, cyclohexane/ tetrahydrofuran (CH/THF) and carbon tetrachloride/acetonitrile ($CCl_4$/$CH_3CN$), were prepared from spectral grade solvents.

The solute concentrations were of 1.06 M for 2-bromopropane and 2.2 M for 1-bromopropane in both solvent mixtures and of 0.1 M and 0.22 M respectively, in $CCl_4/CH_3CN$ solvent mixture.

The concentrations of 2-bromopropane were 0.1 M and 1.06 M and of 1-bromopropane were 0.22 M and 2.2 M in both solvent mixtures (CH/TH and $CCl_4/CH_3CN$).

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