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Infrared band intensities of 1,2-dibromoethane in solutions: Electrostatic effect and influence of hydrogen bonding on the conformational equilibrium

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Abstract

The conformational equilibrium of 1,2-dibromoethane (DBE) in various media (vapor phase, liquid, and solutions in *n*-hexane, carbon tetrachloride, toluene, carbon disulfide, bromoform, acetone, nitromethane, deuterated acetonitrile and deuterated dimethylsulfoxide) has been studied by IR absorption spectra. The enthalpy differences between *trans* (t) and *gauche* (g) conformers (ΔH_o) were determined from the dependencies of $\ln(I_t/I_g)$ upon T^{-1}, where I_t and I_g are the integrated intensities of the bands, belonging to different conformers. The values $RT\cdot\ln(I_t/I_g)$ and $(R\cdot\ln(I_t/I_g)+\Delta H_o/T)$ obtained at 296 K were used as measures of the free enthalpy (ΔG_o) and entropy differences of the conformers (ΔS_o) respectively, when considering their changes with solvent. To minimize the errors due to solvent and temperature effects on the IR-band absorption coefficients, four different band pairs of *trans* and *gauche* conformers were investigated. Good correlations between ΔG_o, ΔH_o and the function of dielectric permitivity of the medium $(0.5-(\ \ -1)/(2\ \ +1))^{1/2}$ were observed for all solvents except toluene. Significant changes of ΔS_o with the media have been found: they cover more than 1.5 cal mol^{-1} K^{-1} when going from the vapor phase to polar solvents. The ΔS_o values correlate with ΔH_o ones (compensation effect); the slope of the dependence $(\Delta\Delta S_o/\Delta\Delta H_o)=(1.0\pm0.3)\cdot10^{-3}$ K^{-1} is close to those determined earlier for 1,2-dichloro- and bromofluoro-ethanes, *trans*-1,2-dichlorocyclohexane and *o*-iodophenol. The overall integrated intensities in the CH$_2$-stretching ($\alpha_{A/B}$(str), 3200–2700, cm^{-1}) and deformational ($\alpha_{A/B}$(def), 1550–1300, cm^{-1}) regions were measured for neat DBE and its solutions in CCl_4, CD_3CN and $(CD_3)_2SO$. The $\alpha_{A/B}$(str) value noticeably increases when going from CCl_4 to proton acceptor solvents, while the $\alpha_{A/B}$(def) does not depend on the solvent. These results are interpreted within the framework of the formation of weak hydrogen bonds between CH$_2$-groups of DBE and proton acceptor groups of the solvents. The enthalpies of specific interaction of DBE with CD_3CN and $(CD_3)_2SO$ were estimated using the ‘intensity rule’. These values are about 1 kcal mol^{-1}. Nevertheless, poor correlation between ΔH_o, ΔG_o and basicity parameters of the solvents indicate the minor effect of the H-bond formation on the conformational equilibrium of DBE.

Keywords: 1,2-Dibromoethane; Hydrogen bonding; Electrostatic effect

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