Dimerization of Carboxylic Acids in Solution up to High Pressures and Temperatures. 3. Acetic Acid

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Acetic acid in dilute solutions of n-heptane and of CCl_4 is studied via IR spectroscopy in the region of the $C=O$ and $O-H$ stretching fundamentals at pressures up to 2250 bar and temperatures up to 150 °C. Lambert-Beer's law is shown to be valid for the $C=0$ modes of the acid monomer and of the hydrogen-bonded cyclic dimer in both solvents, which enables the quantitative measurement of the dimerization equilibrium as a function of pressure and temperature. The pressure dependence of dimerization enthalpy and the temperature dependence of dimerization volume are reported and are compared with direct information on the monomer and cyclic dimer species as derived from their $O-H$ fundamental modes.

Introduction

The equilibrium between monomer and cyclic dimer molecules of carboxylic acids in dilute solution has been extensively studied in various solvents as a function of temperature and concentration [1]. First data on the pressure dependence of the dimerization equilibrium have been provided by Suzuki et al. from electrical conductance [2] and UV absorption work [3]. Within recent infrared experiments it turned out that the concentrations of acid monomers and cyclic dimers can be precisely obtained within an extended pressure and temperature region from the characteristic carbonyl stretching fundamentals of both species. For pivalic acid (PA) [4] and for benzoic acid (BA) [5], equilibrium constants and even a temperature dependence of dimerization volume were determined. For BA a remarkable observation is made in that, at and below ambient temperature, increasing pressure favours the monomer whereas, at higher temperature, increasing pressure shifts the equilibrium toward higher dimer concentrations. It seemed interesting to apply the quantitative IR-spectroscopic method to acetic acid (AA) which, at ambient pressure, is by far the most extensively studied system [1, 6–12]. The values reported for the dimerization enthalpy, however, differ largely, e.g. in CCl_4 solution between -33.9 $kJ \cdot mol^{-1}$ (derived from calorimetric studies [7]) and $-53.6\,kJ \cdot mol^{-1}$ (obtained from spectroscopic experiments [8]). The purpose of the present paper is to measure equilibrium constants, reaction enthalpies, and reaction volumes for the dimerization of AA in dilute n-heptane and in CCl_4 solutions at pressures and temperatures up to 2250 bar and 150 °C, respectively. From the characteristic $C=O$ and $O-H$ stretching fundamentals additional direct information about pressure and temperature effects on the monomer and cyclic dimer species may be derived.

Experimental

The optical cell for operation up to 3300 bar and 350 °C with windows from single-crystalline sapphire and, for studies at wavenumbers below 2000 cm^{-1}, from polycrystalline silicon is described in [13]. Details about the experimental set-up and about the experimental procedures used in the infrared investigation of pressurized carboxylic acid solutions are given in [4].

Pressures are recorded within ± 3 bar. Temperatures are measured with a sheathed thermocouple inside the sample fluid to better than ± 0.5 °C. Spectra are taken on a NICOLET 5 DX Fourier transform interferometer with a resolution of 4 cm^{-1}.

Acetic acid was of better than 99% purity (Gold Label, Aldrich) and CCl_4 and n-heptane were of UVASOL quality (Merck).

Results

Experimental absorbance spectra between 1660 cm^{-1} and 1810 cm^{-1} of a $1.12 \cdot 10^{-2}$ molar solu-

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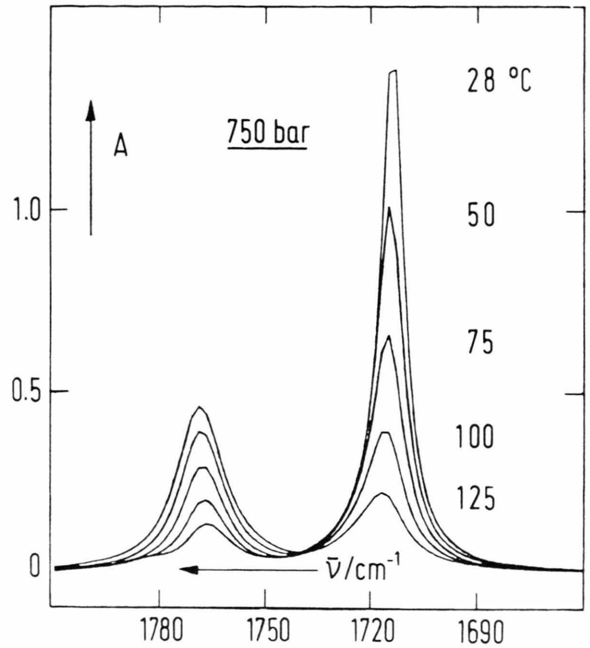

Fig. 1. Absorbance spectra in the carbonyl stretching region of a dilute solution of acetic acid in CCl_4 at 750 bar and temperatures between 28 °C and 125 °C. The acid concentration prepared at ambient pressure and temperature is $c_0 = 1.12 \cdot 10^{-2}$ molar.

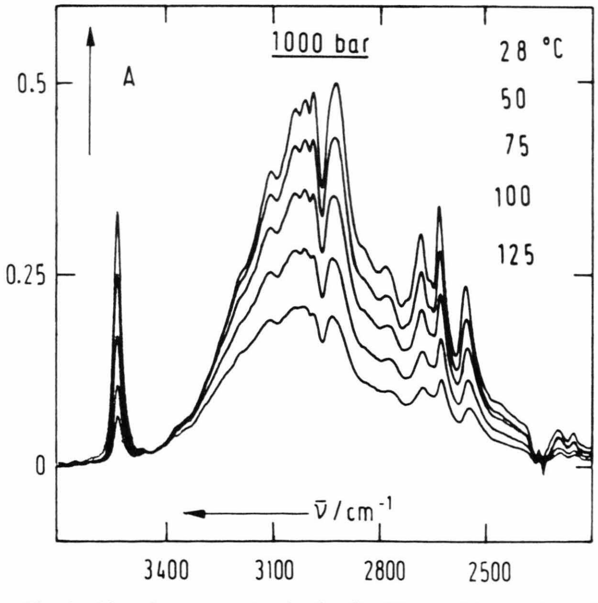

Fig. 2. Absorbance spectra in the O – H stretching region of a dilute solution of acetic acid in CCl_4 at 1000 bar and temperatures between 28 °C and 125 °C. The acid concentration prepared at ambient pressure and temperature is $c_0 = 4.97 \cdot 10^{-2}$ molar.

tion of acetic acid (AA) in CCl_4 measured at constant pressure (750 bar) and temperature variation between 28 °C and 125 °C are shown in Figure 1. The band at 1768 cm^{-1} is due to the C = O stretching fundamental of monomeric AA and the 1716 cm^{-1} component is assigned to the C = O stretch of the cyclic AA dimer. With increasing temperature the monomer band increases and the dimer absorption decreases. An isosbestic point occurs close to 1740 cm^{-1}. The appearance of the experimental spectra measured in the two solvents at various other pressures (up to 2250 bar) in n-heptane and (up to 1250 bar) in CCl_4 is very similar to the data in Figure 1.

Figure 2 shows experimental absorbance spectra in the O – H stretching region of a $4.97 \cdot 10^{-2}$ molar AA solution in CCl_4 at 1000 bar and temperature variation between 28 °C and 125 °C. The narrow band at 3535 cm^{-1} is due to the O – H fundamental in monomeric AA whereas the broad band between 3400 cm^{-1} and 2200 cm^{-1} is due to the O – H stretching fundamental in the dimer with absorption contributions around 3000 cm^{-1} from the C – H stretching modes in AA. The three satellite bands around 2650 cm^{-1} have been assigned to binary combination modes of fundamentals within the – COOH group [14]. Contrary to the situation in the C = O stretching region (Fig. 1), changing the relative amount of monomer and dimer species, at approximately constant overall AA concentration, yields large variations in the dimer spectrum as compared to minor changes on the monomer band. This observation demonstrates that the vibrational intensity of the O – H stretch within the dimer largely exceeds the corresponding quantity within the AA monomer molecule.

The O – H stretching region could not be studied in n-heptane solution as the C – H solvent absorption is too strong.

Discussion

The association of acetic acid in the gaseous state and in solution has been discussed in terms of a two component model with monomer and cyclic dimer species [7, 8, 11] and also by including a second type of monomer species and open-chain dimers [10] or higher associates such as trimers or tetramers [15–17]. There is, however, strong evidence that in AA solutions at pressures, temperatures, and concentrations as in the present paper, monomer and cyclic dimer molecules are by far the dominant species of the association equilibrium. This assumption is supported by the appearance of the spectra in the C=O stretching region. Moreover, the broad O–H absorption of associated AA is adequately described by models which only take cyclic dimer species into account [18].

Quantitative analysis of individual monomer and cyclic dimer concentrations via IR spectroscopy requires Lambert-Beer's law to be valid in the experimental pressure and temperature range. Thus the vibrational intensity B of the characteristic monomer and dimer modes should be independent of P and T.

$$B = \int \varepsilon(\bar{\nu}) \cdot \mathrm{d}\bar{\nu}\,, \qquad (1)$$

where $\varepsilon(\bar{\nu})$ is the molar absorptivity as a function of wavenumber $\bar{\nu}$. $\varepsilon(\bar{\nu})$ is related to the experimental (decadic) absorbance $A(\bar{\nu})$ by

$$\varepsilon(\bar{\nu}) = A(\bar{\nu})/(c\,l) \qquad (2)$$

with c and l being the concentration and the optical path length, respectively. Combination of (1) and (2) yields

$$\int A(\bar{\nu}) \cdot \mathrm{d}\bar{\nu} = c\,l\,B\,, \qquad (3)$$

which says that, if B is a constant, from the measured absorbance spectrum $\int A(\bar{\nu}) \cdot \mathrm{d}\bar{\nu}$, at known optical path length, the concentration c is directly obtained. Thus it is interesting to measure B-values for monomer and dimer species in both absorption regions: $B_M(C=O)$, $B_D(C=O)$, $B_M(O-H)$, and $B_D(O-H)$. For pivalic acid [4] and benzoic acid [5] it turned out that Lambert-Beer's law holds for the carbonyl stretching modes of the monomer and of the dimer and also for the monomer O–H stretch whereas it is not obeyed by the O–H stretching mode of the cyclic dimer. Using the same kind of analysis [4], the monomer and cyclic dimer C=O vibrational intensities of AA in dilute solution of n-heptane are obtained to be

$$B_M(C=O) = 96 \pm 8\ \mathrm{km \cdot mol_M^{-1}} \quad \text{and}$$
$$B_D(C=O) = 157 \pm 9\ \mathrm{km \cdot mol_M^{-1}}.$$

Within the experimental temperature range from 50 °C to 150 °C and up to 2250 bar, these values are demonstrated to be independent of P and T by plotting the sum of spectroscopically determined concentrations, $c_M + c_D$, versus the total acid concentration, $c(P, T)$, at identical P and T (Figure 3). c_M and c_D, at known optical path length l, are obtained via (3) from the integrated absorbance between 1861 cm^{-1} and 1740 cm^{-1} (for the AA monomer) and between 1740 cm^{-1} and 1632 cm^{-1} (for the AA cyclic dimer) using B_M and B_D, respectively. $c(P, T)$ is calculated from c_0, the precisely known AA concentration prepared at ambient temperature and pressure and from the pure solvent PVT data (CCl_4 [19], n-heptane [20]) according to

$$c(P, T) = c_0\,\varrho/\varrho_0\,, \qquad (4)$$

where ϱ is the solvent density at P and T and ϱ_0 is the corresponding value at ambient temperature and pressure. The good agreement of $c_M + c_D$ with $c(P, T)$ shows the validity of Lambert-Beer's law within the limits of experimental accuracy. Individual concentrations c_M and c_D are thus directly available from the carbonyl stretching region.

Analysis of the carbonyl spectra measured on dilute solutions of AA in CCl_4 along the same lines yields

$$B_M(C=O) = 105 \pm 3\ \mathrm{km \cdot mol_M^{-1}} \quad \text{and}$$
$$B_D(C=O) = 198 \pm 5\ \mathrm{km \cdot mol_M^{-1}}.$$

The $B_M(C=O)$ values are rather similar in CCl_4 and in n-heptane whereas the dimer intensity in CCl_4, as has already been found for pivalic acid and for benzoic acid, largely exceeds the corresponding value deter-

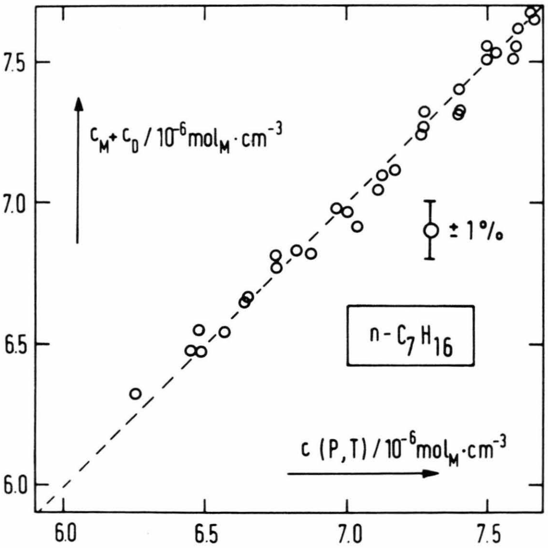

Fig. 3. Comparison of the spectroscopically measured sum of monomer and dimer concentrations, $c_M + c_D$, for acetic acid in n-heptane with the total acid concentration $c(P, T)$ obtained from the solvent PVT-data via (4).

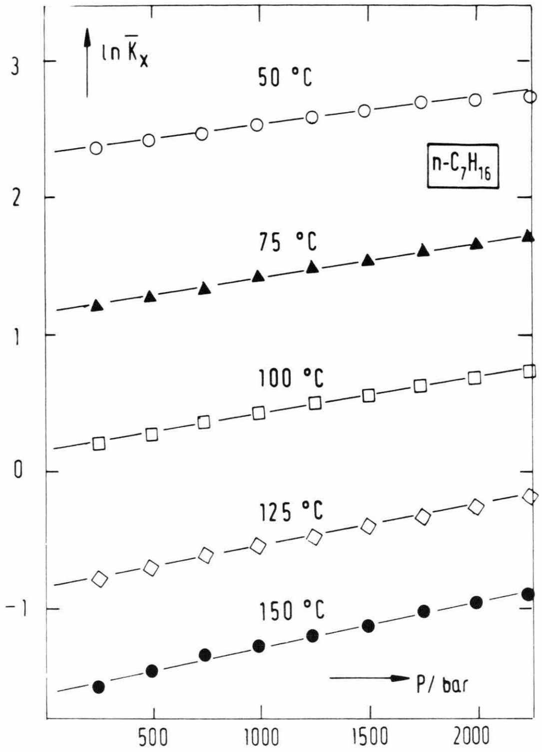

Fig. 4. Pressure dependence of the dimerization equilibrium constant $\bar{K}_x$ for acetic acid in n-heptane solution at several temperatures. $\bar{K}_x$ is obtained as an arithmetic mean value from three independent experiments with concentration c_0 between $6.93 \cdot 10^{-3}$ molar and $9.71 \cdot 10^{-3}$ molar.

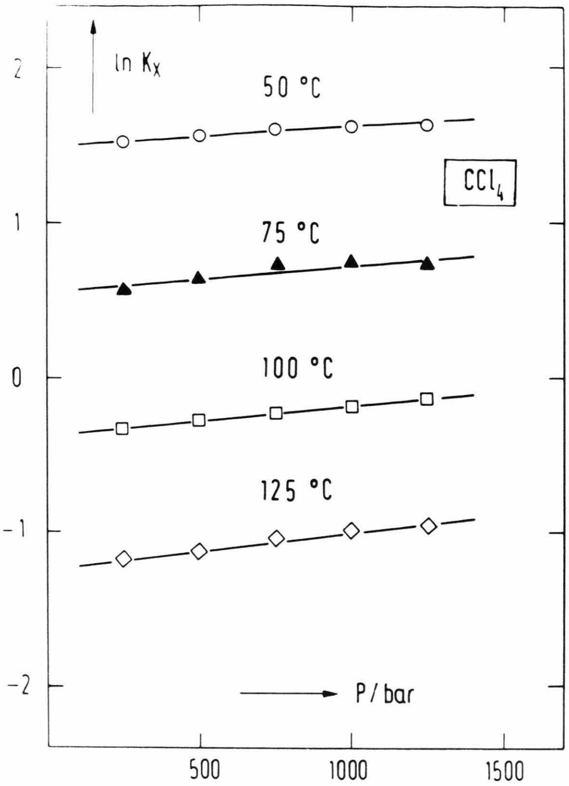

Fig. 5. Pressure dependence of the dimerization equilibrium constant K_x for acetic acid in CCl_4 solution.

mined for n-heptane solutions. The structural information contained in these B-values is not yet understood. Plotting $c_M + c_D$ versus $c(P, T)$ again yields good agreement as in Figure 3. This demonstrates that high-pressure high-temperature infrared spectroscopy on the characteristic C=O stretching fundamentals enables the quantitative study of the monomer-cyclic dimer equilibrium also in dilute CCl_4 solution.

The thermodynamic analysis, as in the previous papers on pivalic acid and benzoic acid [4, 5], is based on the equilibrium constant K_a in terms of activities, $K_a = a_D/a_M^2$, with the standard state of the solute being chosen as the hypothetical pure substance with interactions such as in an infinitely dilute solution. Assuming activity coefficients at low concentration as in the present study to be close to unity, yields the equilibrium constant K_x in terms of mole fractions:

$$K_x = x_D/x_M^2, \qquad (5)$$

which after substitution of mole fractions by concentrations becomes

$$K_x = c_D \cdot c/c_M^2 = K_c \cdot c. \qquad (6)$$

K_c is directly obtained from the spectroscopically measured concentrations, and the total acid concentration c at the experimental pressure and temperature is calculated according to (4).

Toward higher pressures and toward lower temperatures the dimerization equilibrium constant of AA in n-heptane (Fig. 4) and in CCl_4 (Fig. 5) increases. $\bar{K}_x$ in Fig. 4 indicates that these equilibrium constants are derived as arithmetic mean values from three independent experiments. At identical temperature, K_x is larger in n-heptane than in CCl_4, which appears to be due to stronger attractive acid monomer-solvent interactions in CCl_4. This assumption is supported by closer inspection of the band maximum position of the acid monomer C=O stretching modes. The arithmetic mean of the shift toward lower wavenumbers on going from n-heptane to CCl_4 solution for AA, BA, and PA is $5.5 \pm 2.0\ cm^{-1}$. The C=O modes within the dimer species are less influenced by changing the solvent. The corresponding mean value of the low wavenumber shift of the C=O fundamental in the AA, BA, and PA dimers is only $2.5 \pm 2.0\ cm^{-1}$. This small solvent dependence provides additional support for the occurrence of cyclic dimers with their C=O and O−H bonds being essentially engaged in mutual hydrogen bonds.

The accuracy of the equilibrium constant data is estimated to be better than ± 10%. Their relative accuracy is considered to be sufficient for a study of the standard dimerization enthalpy ΔH^0 as a function of pressure and of the standard dimerization volume ΔV^0 as a function of temperature:

$$-\Delta H^0 = (\partial(R \ln K_x)/\partial(1/T))_p \qquad (7)$$

and

$$-\Delta V^0 = (\partial(R\,T \ln K_x)/\partial P)_T. \qquad (8)$$

Replacement of K_x in (7) and in (8) by K_c yields the dimerization enthalpy $-\Delta H$ and the dimerization volume $-\Delta V$. ΔH^0 and ΔH differ by a term containing the isobaric expansion coefficient of the solvent. For AA in CCl_4 and in n-heptane, both quantities are plotted versus pressure in Figure 6. The (negative) dimerization enthalpy is larger in n-heptane than in CCl_4. This result fully agrees with the monomer C=O band position showing a larger redshift in CCl_4 than in n-heptane thus absorbing closer to the dimer C=O fundamental band as has been mentioned above.

The remarkable observation from the data in Fig. 6 is that the monomer-dimer enthalpy difference within both solvents decreases toward higher pressures. The wavenumber resolution of C=O band positions within the present experiments is not sufficiently high to detect differences in peak positions between acid monomers and dimers as a function of pressure. From studies on hydrogen-bonded systems [1, 21] it is, however, known that the vibrational intensity of O−H stretching modes strongly increases with hydrogen bond strength. The monomer and dimer O−H vibrational intensities are not available by the procedure used for the determination of $B_M(C=O)$ and $B_D(C=O)$ as Lambert-Beer's law is violated for the dimer. Taking the monomer and dimer concentrations, however, from the quantitative analysis in the C=O stretching region, enables $B_M(O-H)$ and $B_D(O-H)$ to be directly calculated from the measured integrated absorbances between $3628\ cm^{-1}$ and $3481\ cm^{-1}$ and from $3481\ cm^{-1}$ to $2109\ cm^{-1}$, respectively. The data are plotted in Figure 7. The vibrational intensity of the monomer, as has also been observed for pivalic acid [4] and benzoic acid [5], within the limits of experimental accuracy, is independent of P and T: $B_M(O-H) = 36 \pm 2\ km \cdot mol^{-1}$, whereas $B_D(O-H)$ varies with temperature and with pressure. The vibrational intensities of the C−H stretching fundamentals and of the binary combination modes which, as has been mentioned above, also contribute to $B_D(O-H)$, are considered to be independent of P and T. Thus the observed changes of $B_D(O-H)$ with pressure and temperature should be essentially due to the O−H dimer mode. The lowering of $B_D(O-H)$ intensity, as it occurs toward the $B_M(O-H)$ monomer intensity, is interpreted as a weakening of hydrogen bonds within the cyclic dimer. Higher pressures and higher temperatures thus decrease the hydrogen bond strength of the dimer species. This result agrees with the measured pressure

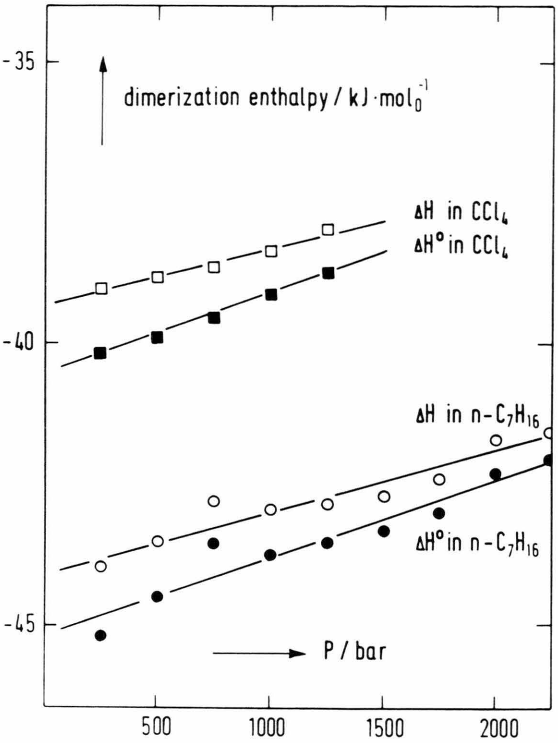

Fig. 6. Pressure dependence of the dimerization enthalpies ΔH^0 and ΔH for acetic acid in n-heptane and in CCl_4.

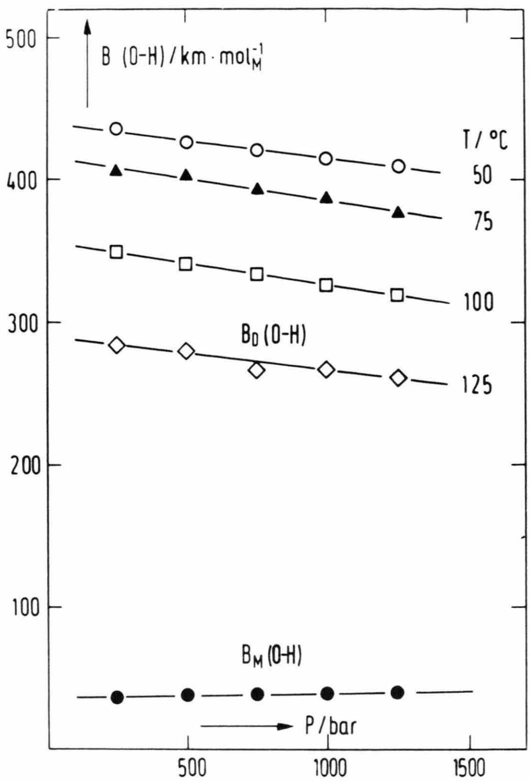

Fig. 7. Vibrational intensities $B_M(O-H)$ and $B_D(O-H)$ of acetic acid monomers and cyclic dimers in CCl_4 solution ($c_0 = 4.97 \cdot 10^{-2}$ molar) up to 1.25 kbar and 125°C. The dimer intensity contains some absorption due to $C-H$ stretching fundamentals and due to combination and overtone modes in the acetic acid molecule.

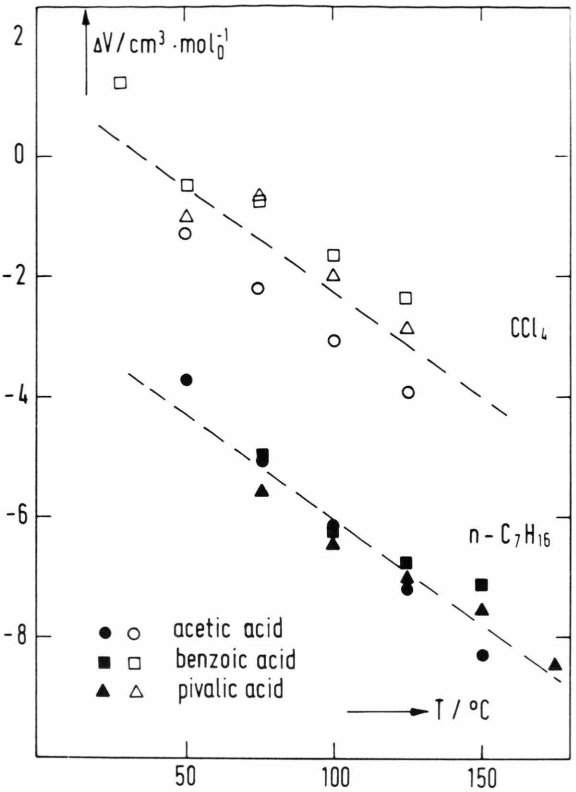

Fig. 8. Temperature dependence of the dimerization volume ΔV for the monomer-cyclic dimer equilibrium of acetic acid, benzoic acid, and pivalic acid in CCl_4 (open symbols) and in n-heptane (full symbols).

dependence of ΔH^0 (Figure 6). The spectroscopic analysis of the association equilibrium via $B_M(O-H)$ and $B_D(O-H)$ indicates that the variation of enthalpy difference with pressure mainly results from effects on the dimer species.

Extrapolation of the ΔH values in Fig. 6 toward ambient pressure yields $\Delta H = -39.4 \pm 0.8$ kJ · mol$_D^{-1}$ in CCl_4, which is almost exactly the arithmetic mean of the corresponding literature values by Zaugg et al. (-33.9 ± 0.8 kJ · mol$_D^{-1}$, [11]) and by Affsprung et al. (-44.8 ± 5.0 kJ · mol$_D^{-1}$, [7]). Reference data for the ambient pressure value in n-heptane, $\Delta H = -44.1 \pm 1.5$ kJ · mol$_D^{-1}$, are not found in the literature.

The change of dimerization enthalpy with pressure (Fig. 6) is associated with a pressure dependence of dimerization entropy which, from thermodynamic arguments, is equivalent to a temperature dependence of dimerization volume. In Fig. 8, ΔV values obtained from ln K_c versus P are plotted together with the corresponding data for pivalic acid [4] and benzoic acid [5] as a function of temperature. The data for each solvent may be represented by a straight line. The dimerization volume clearly changes with temperature. Toward higher temperature the molar volume of the dimer decreases with respect to that of two monomer species. The volume difference in n-heptane exceeds the value observed in CCl_4 solution. This is to be expected from the stronger attractive interactions between the acid monomers and CCl_4 which should be accompanied by a smaller molar volume of the monomer species. The change in the sign of ΔV which has been found for benzoic acid [5] around room temperature (see also Fig. 8), in AA seems to occur at a somewhat lower temperature. Positive ΔV says that increasing pressure favours the dissociation of acid dimers into monomer molecules.

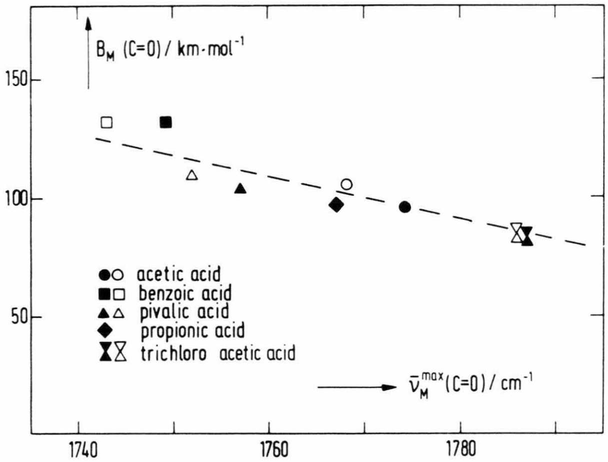

Fig. 9. Plot of the acid monomer vibrational intensity, $B_M(C=O)$, versus the wavenumber of the monomer band maximum, $\bar{\nu}_M^{max}(C=O)$, for several carboxylic acids in CCl_4 (open symbols) and in n-heptane (full symbols) solutions. The band positions are mean values refering to the pressure and temperature range of this work.

The variation of ΔV with temperature is interpreted by assuming more stable and also more planar hydrogen-bonded acid dimers of larger volume to exist at lower temperature whereas less perfect and less planar dimers occur at higher temperatures. Due to the smaller volume of these species, pressure favours the dimerization at elevated temperature. A pressure-induced shift toward monomer species is of some relevance with respect to systems such as ice or proteins where the stability of the three-dimensional hydrogen-bonded structure can also be reduced by applying pressure. The dimerization equilibrium of carboxylic acids in solution thus appears to be an interesting model system for the study of hydrogen-bonded structures.

The correlation between spectroscopic information, such as on band positions and vibrational intensities of monomer and dimer species, with thermodynamic evidence (which is also, but independently derived from spectroscopy) should be noted: (a) the decreasing monomer-dimer enthalpy difference on changing the solvent from n-heptane to CCl_4 corresponds to a lowering of the separation between the monomer-dimer $C=O$ band maximum positions, and (b) the decrease in enthalpy difference toward higher pressure (Fig. 6) corresponds to a reduction of the difference between $B_D(O-H)$ and $B_M(O-H)$ as is shown in Figure 7.

The highest sensitivity toward structural changes is contained in $B_D(O-H)$ as, for a given acid within a given solvent, pressure and temperature influences are detected. The dimer carbonyl intensity, $B_D(O-H)$, appears to be independent of P and T but largely changes with the solvent. The wavenumber accuracy, as has been pointed out, was not sufficient to detect small effects. The analysis of the $C=O$ positions, however, demonstrates that the cyclic dimer is less solvent-dependent than the monomer. The information contained in the dimer band positions and especially in the vibrational intensities is not yet understood. For the monomer species, a rather uniform picture is obtained by plotting the vibrational intensity $B_M(C=O)$ of several carboxylic acids in n-heptane and in CCl_4 solution versus the corresponding position of the monomer $C=O$ band, $\bar{\nu}_M^{max}(C=O)$, (Figure 9). Correlations of that type have already been reported for the oxygen-hydrogen stretching fundamental in the spectrum of pure water within an extended pressure and temperature range [21] and also for the $H-Cl$ fundamental in hydrogen chloride at strong variation of molecular surroundings [22]. The relation in Fig. 9 can be helpful to estimate vibrational intensities $B_M(C=O)$ from $\bar{\nu}_M^{max}(C=O)$ which is much easier to be obtained. From $B_M(C=O)$, at known total concentration $c(P, T)$, the dimerization equilibrium may be calculated from the integrated absorbance of the monomer band.

The variations in $\bar{\nu}_M^{max}(C=O)$ brought upon by changing the acid are of the same size as the difference between monomer and dimer maximum positions of the same acid. Trichloroacetic acid has a fairly high $\bar{\nu}_M^{max}(C=O)$ and the dimer band maximum occurs around 1750 cm^{-1} which is thus close to the monomer positions in pivalic acid [4] and in benzoic acid [5]. Because of the stronger corrosion of CCl_3COOH at elevated temperatures and pressures, the dimerization equilibrium could not be studied with comparable accuracy. There are, however, indications [23] that trichloroacetic acid differs from the behaviour of PA, BA, and AA where an increase of dimerization volume toward higher temperature and a decrease of dimerization enthalpy toward higher pressure have been established.

Acknowledgements

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