Dimerization of Carboxylic Acids in Solution up to High Pressures and Temperatures. 1. Pivalic Acid

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Pivalic acid in dilute solution of n-heptane and of CCl_4 is studied via IR spectroscopy in the region of the C=O and O–H stretching fundamentals up to pressures of 2 kbar and temperatures of 175 °C. Lambert-Beer's law is shown to be valid for the C=O modes of the acid monomer and of the hydrogen-bonded cyclic dimer, which enables the quantitative measurement of the dimerization equilibrium as a function of pressure and temperature. Increasing pressure favours the dimerization in n-heptane to a larger extent than in CCl_4 solution. In both solvents this pressure effect increases with temperature. The hydrogen bond strength within the dimer species is slightly reduced toward high pressure. The data on the temperature dependence of the dimerization volume and on the pressure dependence of the dimerization enthalpy are compared with direct information on both species as derived from their O–H fundamental modes.

Introduction

The study of the self-association of carboxylic acids which dates back to Pfeiffer [1] who, in 1914, established a cyclic structure for the acetic acid dimer, is still an active field of experimental and theoretical research [2, 3]. The cyclic dimer species with two hydrogen bonds constitutes a relatively simple and well-defined model system for the investigation of more complicated hydrogen-bonded structures in chemistry and in biochemistry.

A large body of literature has accumulated on the carboxylic acid association [4–12] with an excellent survey being provided in [13]. The hydrogen-bonded system has been studied in various solvents as a function of temperature and concentration. With the exception of the work by Suzuki and his group [14, 15], information about the influence of pressure on the carboxylic acid dimerization is not available. Because of the intermediate strength of hydrogen bonds, application of moderately high pressures in the kbar range should affect the dimer structure. Thus it seemed interesting to study the vibrational IR spectrum of carboxylic acids in fluid solution up to high pressures and temperatures and to derive spectroscopic and thermodynamic data.

Within the present paper, pivalic acid (2,2-dimethyl-propionic acid), which at ambient pressure has already been studied by several groups [16–18] is measured in dilute solution (around 0.01 molar) of n-heptane and of CCl_4 up to a maximum pressure of 2 kbar and up to 175 °C. The monomer and dimer bands are studied in the region of the O–H and of the C=O stretching fundamentals which both probe the association.

Experimental

The optical high-pressure cell for operation up to 350 °C and 3300 bar is machined from stainless steel (RGT 601, Arbed Saarstahl). The cell is equipped with two (cylindrical) windows which, depending on the spectral range under investigation, are made from sapphire (for wavenumbers above 2000 cm^{-1}) and from polycrystalline silicon (for studies below 2000 cm^{-1}).

The distance between the internal surfaces of the windows is the optical path length l, which according to the acid concentration and to the specific mode under investigation has to be chosen such that the maximum value of the decadic absorbance A does not or not substantially exceed $A = 1$. l was mostly of the order of one millimeter. By means of a steel bellows fitted into a cross-bore at right angle to the light path, the acid solution is separated from the pressure generating system filled with water or with hydrocarbons. The bellows, which ensures zero pressure difference when maintained in about its normal length (which is controlled by an inductive transducer) enables the

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pressure to be measured on gauges in the pressurizing system at room temperature. The cell is heated from outside with sheathed resistance wire. Details about the optical high-pressure cell are given elsewhere [19].

Pressures are obtained within ± 3 bar. Temperatures are measured with a sheathed thermocouple inside the fluid sample solution to better than ± 0.2 °C. The optical cell is adjusted into the sample compartment of a NICOLET 5 DX Fourier transform interferometer which has a resolution of $\pm 4\,\text{cm}^{-1}$.

The C=O stretching modes of monomeric and dimeric pivalic acid are studied in several dilute solutions of n-heptane (between $1.0 \cdot 10^{-2}$ molar and $1.6 \cdot 10^{-2}$ molar) and of CCl_4 ($4.9 \cdot 10^{-3}$ molar and $1.1 \cdot 10^{-2}$ molar). Experiments in the O−H stretching region were only performed in CCl_4 solution ($5.0 \cdot 10^{-2}$ molar) since the overlap of the C−H modes of n-heptane with the O−H dimer band is too strong.

Pivalic acid was of 99.5% (GC) purity (Fluka). CCl_4 and n-heptane were of Uvasol quality (Merck). Because of decomposition within the stainless steel cell and because of reaction with pivalic acid, experiments with CCl_4 as a solvent were only performed up to 125 °C whereas n-heptane solutions were studied to 175 °C. A maximum pressure of 1250 bar has to be chosen in the CCl_4 experiments in order to prevent freezing of the solvent at ambient temperature. Solute reaction and solvent decomposition are detected from a comparison of spectra measured at identical pressure and temperature before and after an experimental run. If absorbances of these initial and final spectra differ by more than 2 per cent, the whole experiment is rejected.

Results

Experimental absorbance spectra between $1660\,\text{cm}^{-1}$ and $1810\,\text{cm}^{-1}$ of a $1.58 \cdot 10^{-2}$ molar solution of pivalic acid (PA) in n-heptane measured at constant pressure (1000 bar) and temperature variation from 75 °C to 150 °C are shown in Figure 1. The band at $1760\,\text{cm}^{-1}$ is due to the C=O stretch of monomeric PA. The $1710\,\text{cm}^{-1}$ component is assigned to the C=O stretch of the cyclic PA dimer. Toward higher temperature the monomer absorption increases and the dimer band decreases. An isosbestic point is observed close to $1730\,\text{cm}^{-1}$. Experiments as in Fig. 1 are performed on several dilute solutions up to 2 kbar and 175 °C in n-heptane and up to 1.25 kbar and 125 °C in CCl_4. The appearance of the whole set of spectra is very similar: A pronounced temperature dependence occurs at constant pressure whereas the influence of pressure at constant temperature is weak. Experimental absorbance spectra in the O−H stretching region are shown in Fig. 2 for a $5 \cdot 10^{-2}$ molar PA solution in CCl_4 at 75 °C and pressures between 250 bar and 1250 bar. The narrow band at $3535\,\text{cm}^{-1}$ is due to the O−H stretching mode of monomeric PA whereas the broad absorption contour between $3400\,\text{cm}^{-1}$ and $2300\,\text{cm}^{-1}$ is assigned to the O−H stretch of the hydrogen-bonded PA dimer. The intense C−H stretching modes of the methyl groups in PA between $3000\,\text{cm}^{-1}$ and $2900\,\text{cm}^{-1}$ are observed on top of this dimer band. The spectra in Fig. 2 are shifted in the baseline in order to avoid strong intersection.

Discussion

In the preceeding section it has been tacitly assumed that only two species, monomers and cyclic dimers, occur in dilute fluid solution. Other species

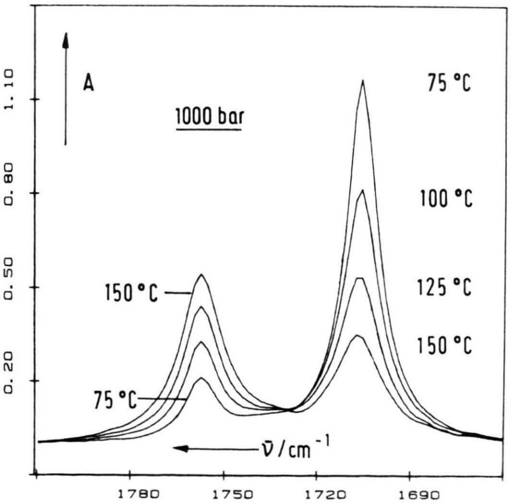

Fig. 1. Absorbance spectra in the carbonyl stretching region of a $1.58 \cdot 10^{-2}$ molar solution of PA in n-heptane at 1000 bar and temperatures between 75 °C and 150 °C.

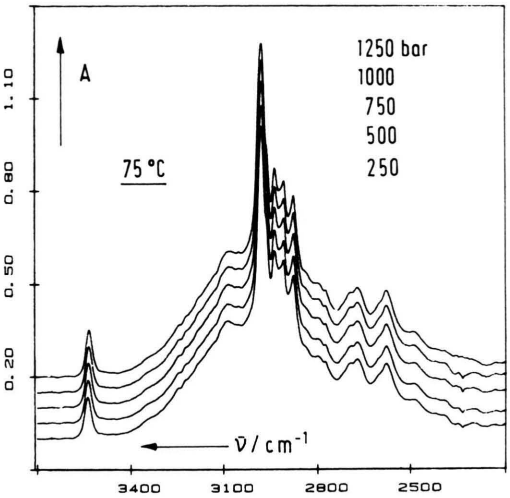

Fig. 2. Absorbance spectra in the O−H stretching region of a $5.0 \cdot 10^{-2}$ molar solution of PA in CCl_4 at 75 °C and pressures between 250 bar and 1250 bar (the curves are shifted in the base-line).

such as higher multimers, open dimers, and cis and trans monomers have also been considered in studies on carboxylic acids [5, 9, 12]. It turned out that the cyclic dimer is the dominant associated species in both, the gaseous and liquid phase. For pure liquid PA and for PA in CCl_4 solution the same result was obtained from Raman scattering data including the low wavenumber modes between $100\ \mathrm{cm}^{-1}$ and $400\ \mathrm{cm}^{-1}$ [16, 18]. The prevalence of a monomer-cyclic dimer equilibrium for PA mole fractions up to $7.5 \cdot 10^{-2}$ in cyclohexane ($8 \cdot 10^{-2}$ molar solution) was also demonstrated by NMR experiments [17]. A two-species model with monomer and cyclic dimer molecules has also been demonstrated to adequately describe the self-association of ε-caprolactam [20] and even of phenol [21] in CCl_4 at concentrations, pressures, and temperatures as in the present paper. Moreover, the very simple appearance of the C=O spectra (Fig. 1) within an extended temperature range supports the assumption of a two-species equilibrium. According to these arguments, within the subsequent text, pivalic acid in dilute solution (up to $5 \cdot 10^{-2}$ molar) is assumed to exclusively consist of monomer and cyclic dimer species.

Monomer and dimer concentrations may be derived from experimental spectra on the premises that Lambert-Beer's law is valid, which requires that the integrated molar absorptivity (vibrational intensity) B is independent of pressure and temperature in the concentration range under investigation. B is defined as

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

where the integral may be taken over the total band of a characteristic mode or, if overlapping bands occur, over band sections, e. g. from the maximum toward the low-frequency or toward the high-frequency absorption limit. The molar absorptivity $\varepsilon(\bar{\nu})$ is the experimental decadic absorbance $A(\bar{\nu})$ reduced to unit concentration c and unit optical path length l:

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

Equation (1) applies to monomer and to dimer absorption in both, the C=O and O−H stretching regions. The molar integrated absorptivities for both species, $B_{\mathrm{M}}(\mathrm{C{=}O})$, $B_{\mathrm{D}}(\mathrm{C{=}O})$, $B_{\mathrm{M}}(\mathrm{O{-}H})$, and $B_{\mathrm{D}}(\mathrm{O{-}H})$, are not directly calculated, as the individual monomer and dimer concentrations, c_{M} and c_{D}, are not immediately available. (It should be noted that the B-values will probably depend on the solvent.) To derive these B-values, the following procedure is applied: Individual monomer and dimer absorbance bands which are determined by integration from the minimum between the two bands (e. g. Fig. 1) to the high and to the low wavenumber absorption limits are divided by the optical path length l and by the total acid concentration c, which yields

$$B_{\mathrm{M}}^{+} = (c \cdot l)^{-1} \int A_{\mathrm{M}}(\bar{\nu})\, \mathrm{d}\bar{\nu} \quad \text{and} \qquad (3)$$
$$B_{\mathrm{D}}^{+} = (c \cdot l)^{-1} \int A_{\mathrm{D}}(\bar{\nu})\, \mathrm{d}\bar{\nu}\,,$$

respectively. The total acid concentration c at the experimental pressure P and at temperature T, for very dilute solutions, is obtained from c_0, the precisely known concentration prepared at ambient temperature and pressure and from pure solvent PVT data taken from the literature (CCl_4 [22], n-heptane [23]):

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

where ϱ is the pure solvent density at P and T, and ϱ_0 is the corresponding value at ambient temperature and pressure. The concentrations of both, monomers and dimers, are given in moles monomer per cm³. The notation B^+ in (3) indicates that these quantities are not integrated molar absorptivities in the sense of (1), as the infrared absorbance of a monomer or dimer component band, A_M or A_D, is reduced by the total PA concentration c. To remove this unclear physical meaning of the experimental B_M^+ and B_D^+ values, for a series of spectra measured within an extended pressure and temperature region, the sum of B_M^+ and B_D^+ is plotted versus B_D^+. The result for the C=O stretching region of PA in n-heptane is shown in Figure 3. The experimental points closely fit onto a straight line. Extrapolation toward $B_D^+ = 0$, where the total concentration c equals the monomer concentration c_M, yields $B_M(C{=}O) = 104 \pm 3$ km · mol$_M^{-1}$. The intersection of the straight line through the data points with the diagonal, which corresponds to the situation $c_M = 0$, yields $B_D(C{=}O) = 154 \pm 4$ km · mol$_M^{-1}$.

The arithmetic means of the vibrational intensity obtained from extrapolations as in Fig. 3 on four independent experimental data sets at PA concentrations in n-heptane between $1.0 \cdot 10^{-2}$ molar and $1.6 \cdot 10^{-2}$ molar are

$$B_M(C{=}O) = 106 \pm 4 \text{ km} \cdot \text{mol}_M^{-1} \quad \text{and}$$

$$B_D(C{=}O) = 156 \pm 3 \text{ km} \cdot \text{mol}_M^{-1}.$$

The vibrational intensity of the carbonyl mode thus is markedly enhanced upon hydrogen bond formation. It should be noted that $B_M(C{=}O)$ and $B_D(C{=}O)$ refer to PA in dilute solution of n-heptane. From these values, via (1) and (2), monomer and dimer concentrations, c_M and c_D, may be calculated:

$$c_M = \int A_M(\bar{\nu})\, d\bar{\nu}/(l \cdot B_M) \quad \text{and}$$

$$c_D = \int A_D(\bar{\nu})\, d\bar{\nu}/(l \cdot B_D) \qquad (5)$$

if both vibrational intensities, B_M and B_D, remain constant throughout the whole temperature and pressure range under investigation. To examine whether this assumption holds, the sum of spectroscopically determined (5) monomer and dimer concentrations, $c_M + c_D$, is plotted versus the known total acid concentration, $c(P, T)$, as obtained from (4). The agreement of both sets of data within ± 1.0 per cent, as is shown in Fig. 4, demonstrates the validity of Lambert-Beer's law for the carbonyl stretching mode of pivalic acid monomer and dimer dissolved in n-heptane.

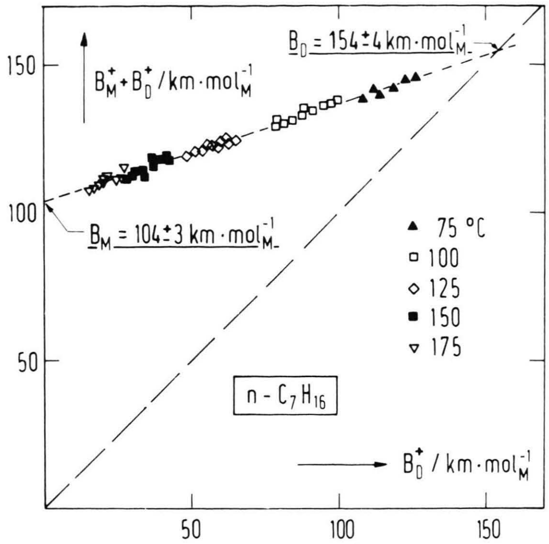

Fig. 3. Sum of monomer and dimer integrated intensities $B_M^+ + B_D^+$, plotted versus B_D^+ for a $1.07 \cdot 10^{-2}$ molar solution of PA in n-heptane studied in the C=O stretching region up to 2 kbar and 175 °C (B_M^+ and B_D^+ are obtained according to (3), see text).

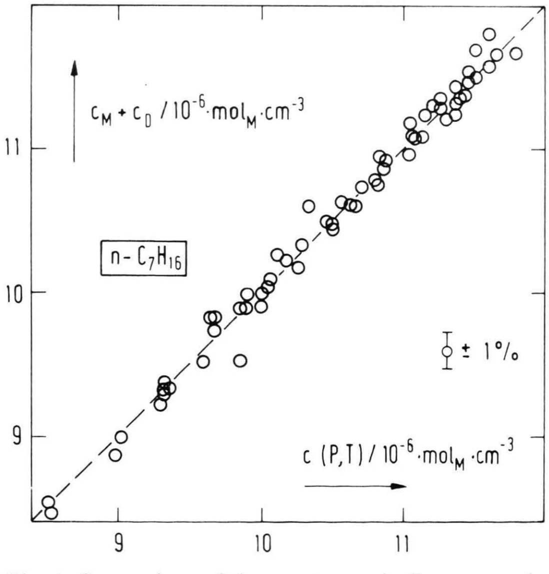

Fig. 4. Comparison of the spectroscopically measured sum of monomer and dimer concentrations, $c_M + c_D$, for PA in n-heptane solution (same experiment as in Fig. 3) with the total concentration $c(P, T)$ as obtained via the solvent PVT data (4).

The corresponding analysis of the PA spectra measured in CCl_4 solution is shown in Figure 5. The arithmetic mean values of the vibrational intensity from two independent experiments are

$$B_M(C{=}O) = 111 \pm 4\ \text{km} \cdot \text{mol}_M^{-1} \quad \text{and}$$
$$B_D(C{=}O) = 191 \pm 3\ \text{km} \cdot \text{mol}_M^{-1}\,.$$

The vibrational intensities of the monomer and dimer carbonyl modes in CCl_4 are larger than in n-heptane solution. This may be interpreted as an indication of stronger monomer-solvent interactions and of more stable hydrogen bonds in the dimer if CCl_4 is chosen as the solvent. The information contained in these condensed state vibrational intensities, however, is still far from being fully understood.

Plotting the sum of monomer and dimer concentrations (from (5)) for the CCl_4 data against the total PA concentration obtained from PVT data via (4), again yields good agreement (Figure 6). The conclusion from Figs. 4 and 6 is that infrared vibrational spectroscopy on the carbonyl stretching fundamentals enables monomer and cyclic dimer concentrations for PA in dilute solutions of n-heptane and of CCl_4 to be determined.

Analysis of the O−H stretching region of PA in CCl_4 along the same lines yields an approximately linear $B_M^+ + B_D^+$ vs. B_D^+ plot comparable to the data for the C=O stretching modes (Figs. 3 and 5). The sum of monomer and dimer concentrations as obtained from extrapolated B_M(O−H) and B_D(O−H) vibrational intensities, however, fails to agree with the total PA concentration, which demonstrates that, for the O−H stretch, Lambert-Beer's law is not valid and at least one of the vibrational intensities, B_M(O−H) and B_D(O−H), appreciably varies with temperature and pressure. As has been shown above, individual monomer and dimer concentrations are, however, available from an investigation of the C=O stretching region. Thus vibrational intensities of the narrow monomer and of the broad cyclic dimer O−H bands can easily be obtained ((1) and (2)). B_M(O−H) is determined by integration between 3630 cm^{-1} and the absorbance minimum at 3464 cm^{-1} (Figure 2). The contribution of C−H stretching absorption from the methyl groups in PA which overlap the O−H dimer band (Fig. 2) is calculated from the known C−H vibrational intensity of hydrocarbons [24] and subtracted from the primary intensity data which result from direct

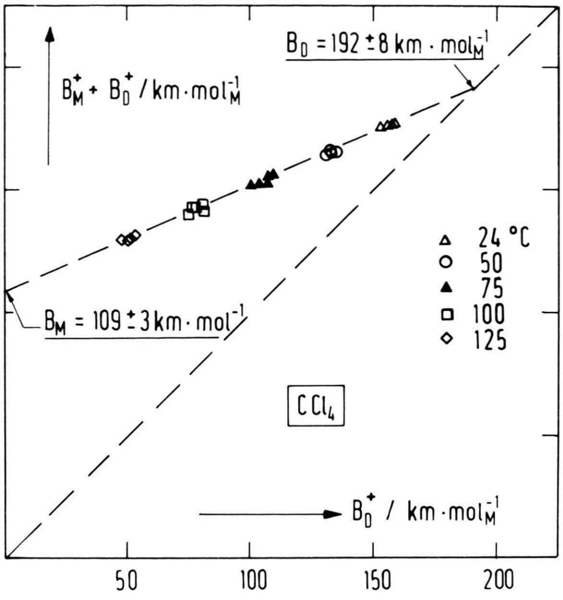

Fig. 5. Sum of monomer and dimer integrated intensities, $B_M^+ + B_D^+$, plotted versus B_D^+ for a $5.0 \cdot 10^{-2}$ molar solution of PA in CCl_4 studied in the C=O stretching region up to 1.25 kbar and 125 °C (B_M^+ and B_D^+ are obtained according to (3), see text).

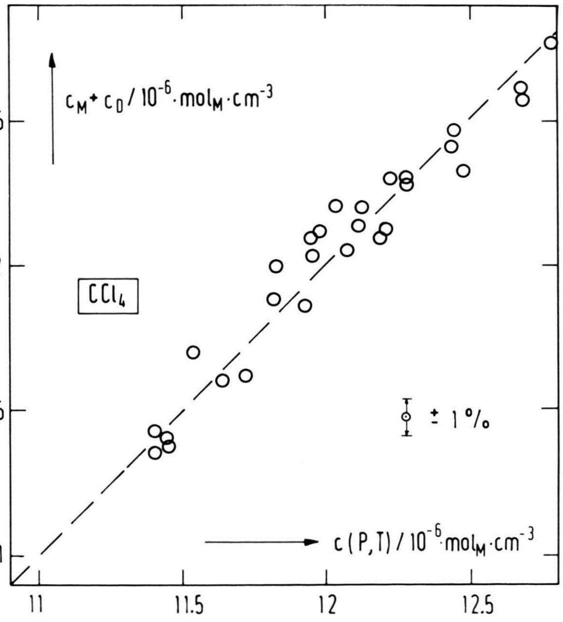

Fig. 6. Comparison of the spectroscopically measured sum of monomer and dimer concentrations, $c_M + c_D$, for PA in CCl_4 solution with the total concentration $c(P, T)$ as obtained via the solvent PVT data (4).

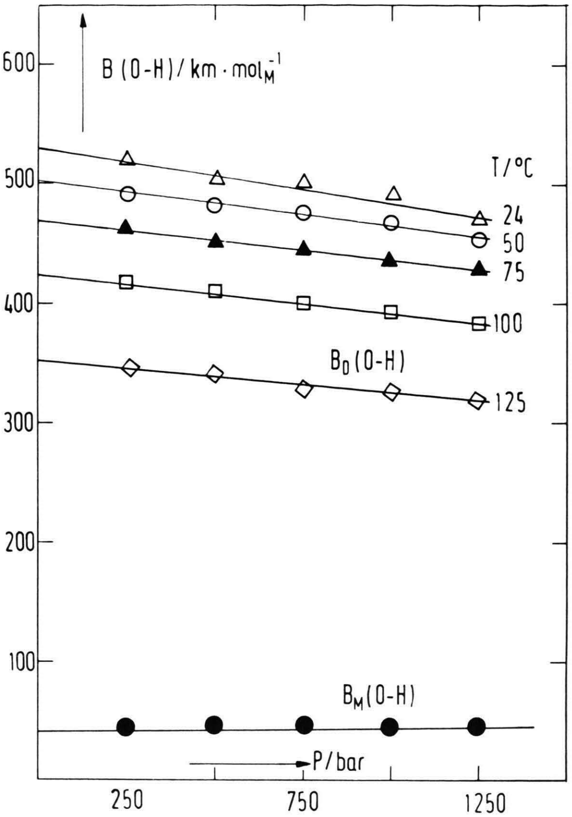

Fig. 7. Vibrational intensities B_M(O−H) and B_D(O−H) of PA monomers and cyclic dimers, respectively, in CCl_4 solution ($5.0 \cdot 10^{-2}$ molar) up to 1.25 kbar and 125 °C (the full circles for B_M(O−H) refer to temperatures between 24 °C and 125 °C).

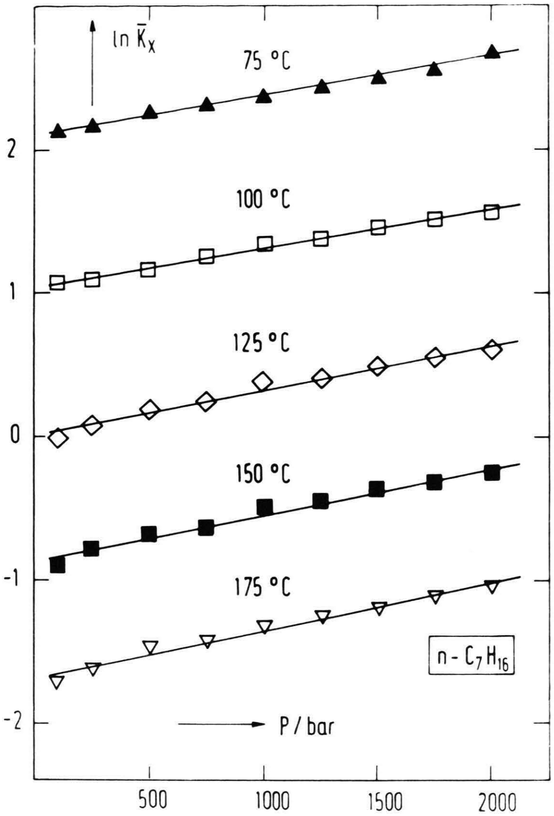

Fig. 8. Pressure dependence of the dimerization equilibrium constant $\bar{K}_x$ for PA in n-heptane solution at several temperatures. $\bar{K}_x$ is obtained as the arithmetic mean from four independent experiments at acid concentrations c_0 between $1.0 \cdot 10^{-2}$ molar and $1.6 \cdot 10^{-2}$ molar.

integration of the overlapping bands. B_D(O−H) thus is essentially due to the dimer O−H stretch although combination modes will contribute to this vibrational intensity. The values of B_M(O−H) and B_D(O−H) of PA are shown in Figure 7. Several interesting conclusions may be drawn: The monomer vibrational intensity $B_M(O-H) = 39 \pm 1$ km · mol^{-1}, within the limits of experimental accuracy, is independent of P and T (the full circles correspond to experiments at temperatures from 24 °C up to 125 °C). Thus Lambert-Beer's law is valid for the monomer O−H stretching mode whereas strong variations occur in the vibrational intensity of the O−H fundamental of the acid dimer, which is by about one order of magnitude above B_M(O−H). Association via hydrogen bonds thus leads to an enormous increase in vibrational intensity as is well known for other hydrogen-bonded materials [13]. Toward higher temperatures and higher pressures B_D(O−H) is clearly reduced. As a decrease of B_D(O−H) corresponds to a change toward the monomer (characterized by B_M(O−H)), the observed variation in dimer vibrational O−H stretching intensity may be assigned to a decreasing strength of the hydrogen-bonded PA dimers toward higher pressures and higher temperatures. Another argument from Fig. 7 is that the assumption of only two species is very approximate since, within an extended P and T region, only the monomer seems to be a well-defined species characterized by a single B_M(O−H) value whereas the term dimer encompasses a plethora of species with properties (such as B_D(O−H)) varying substantially as a function of pressure and temperature. A special advantage of the carboxylic acid system relates to the possibility of calculating numbers for the vibrational intensity of bonded species, as their concentration is known. It should be noted that the large difference in vibrational intensity of monomeric and hydrogen-bonded O−H stretching modes poses severe problems to an analysis of IR bands in terms of "free" and "H-bonded" O−H groups, as the observed bands are mostly dominated by the intense absorption of hydrogen-bonded species. Intensity data such as in Fig. 7 are especially interesting with respect to studies on aqueous solutions [25].

The C=O dimer mode, as is illustrated in Figs. 4 and 6, appears to be insensitive to structural changes induced by P and T and thus enables the study of the PA association equilibrium. The equilibrium constant K_a is defined as

$$K_a = a_D / a_M^2 \tag{6}$$

with a_D and a_M being the dimer and monomer activities, respectively. For sufficiently dilute solutions, activity coefficients are close to unity (with the standard state of the solute being chosen as a hypothetical pure substance with interactions such as in an infinitely dilute solution) and activities may be replaced by mole fractions x:

$$K_x = x_D / x_M^2 \,. \tag{7}$$

Substitution of mole fractions by concentrations yields

$$K_x = c_D \, c / c_M^2 \,. \tag{8}$$

The equilibrium constant in terms of mole fractions, K_x, is thus directly obtained from the spectroscopically measured monomer and dimer concentrations and from the total acid concentration c at the experimental pressure and temperature (4). Throughout the subsequent text, the simplifying assumption of experimental concentrations being sufficiently dilute to replace activities by mole fractions is made.

Equilibrium constants $\overline{K_x}$ are calculated as arithmetic means from several independent series of experiments at different concentrations of PA in n-heptane and in CCl_4 (see above). A systematic concentration dependence of K_x (at identical temperature and pressure) could not be observed within the narrow concentration range under investigation.

The increase of ln $\overline{K_x}$ toward higher pressure and lower temperature is illustrated for PA in n-heptane in Fig. 8 and for PA in CCl_4 in Figure 9. At identical temperature, the equilibrium constant in n-heptane exceeds the corresponding value in CCl_4. The solvent dependence of the monomer-cyclic dimer equilibrium has been reported to be essentially due to changes in the solvent-monomer interactions [11]. CCl_4 thus is a less "inert" solvent for the PA monomer than is n-heptane. The stronger attractive interactions are responsible for the lower $\overline{K_x}$ values (Fig. 8 and 9). This result is in good agreement with literature data on the PA association in CCl_4 and in cyclohexane [17]. It should, however, be noted that the clear difference in B_D(C=O) between n-heptane and CCl_4 suggests that also the stability and structure of the dimer vary with the solvent.

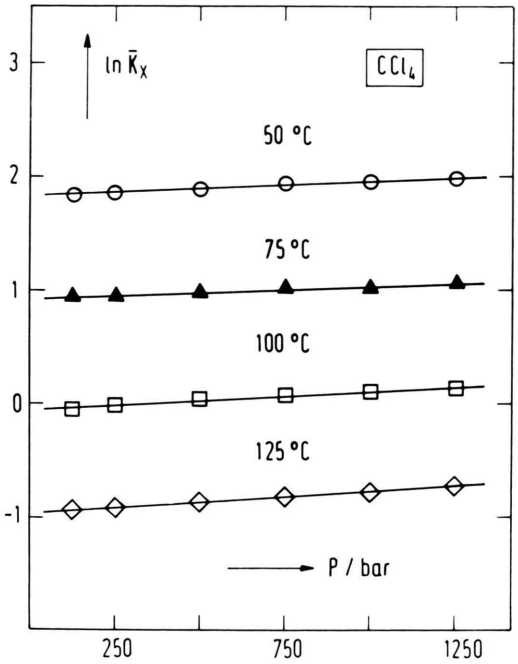

Fig. 9. Pressure dependence of the dimerization equilibrium constant $\overline{K_x}$ for PA in CCl_4 solution at several temperatures. $\overline{K_x}$ is obtained as the arithmetic mean from two independent experiments ($4.9 \cdot 10^{-3}$ molar and $1.1 \cdot 10^{-2}$ molar).

The accuracy of the $\overline{K_x}$ values is limited by the uncertainty of several quantities, such as integrated absorbances ($\int A_M \cdot d\bar{\nu}$ and $\int A_D \cdot d\bar{\nu}$), vibrational intensities (B_M and B_D), pressure, temperature, concentration c_0, and solvent PVT-data. It should, however, be better than ± 5%. The relative uncertainty of K_x data determined from subsequent series of experiments is estimated to be better than ± 3%

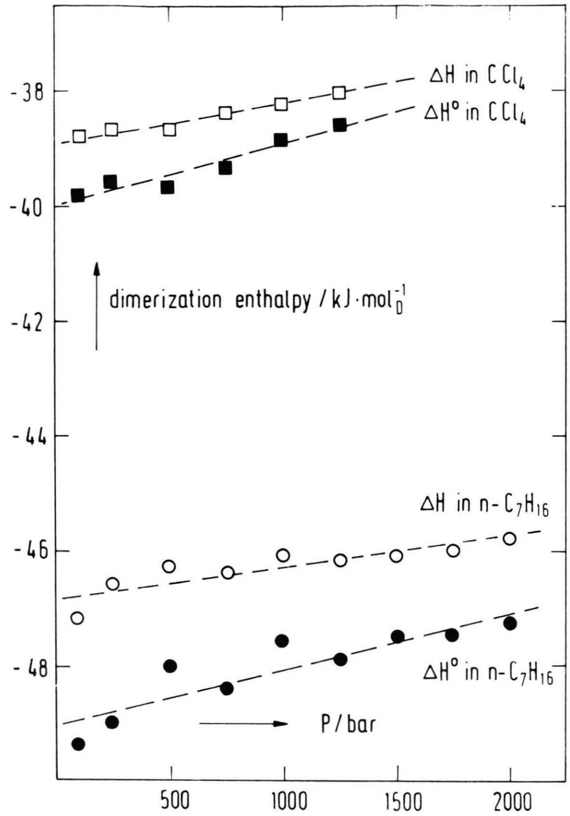

Fig. 10. Pressure dependence of the dimerization enthalpies ΔH^0 and ΔH for the PA monomer-cyclic dimer equilibrium in n-heptane and in CCl_4. The data are derived from equilibrium constants $\bar{K}_x$ and $\bar{K}_c$, respectively, which are obtained as mean values from independent experiments at several low acid concentrations (see text).

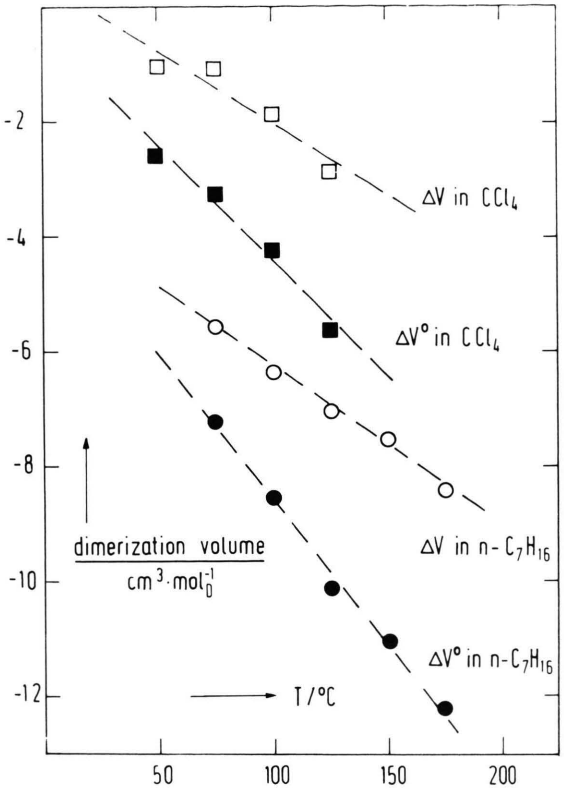

Fig. 11. Temperature dependence of the dimerization volumes ΔV^0 and ΔV for the PA monomer-cyclic dimer equilibrium in n-heptane and in CCl_4. The data are derived from equilibrium constants $\bar{K}_x$ and $\bar{K}_c$, respectively, which are obtained as mean values from independent experiments at several low acid concentrations (see text).

which appears to be sufficient for an investigation of the temperature and pressure dependence of equilibrium constant. The dimerization enthalpy ΔH^0 referring to the standard state defined above is actually measured as a mean value from several low concentration experiments:

$$-\Delta H^0 = (\delta (R \cdot \ln \bar{K}_x)/\partial (1/T))_P . \qquad (9)$$

The corresponding temperature dependence of $\bar{K}_c$, the equilibrium constant in terms of the individual (spectroscopic) concentrations: $K_c = c_D/c_M^2$, yields ΔH. Both dimerization constants are closely related: $K_x = K_c \cdot c$ (see (8)) which corresponds to ΔH^0 and ΔH differing only by one term containing the isobaric expansion coefficient of the solvent [20]. The dimerization enthalpies as is shown in Fig. 10, with full symbols referring to ΔH^0 and open symbols to ΔH, are pressure-dependent in both solvents (circles for n-heptane and squares for CCl_4). ΔH in n-heptane (-46.8 ± 0.8 kJ · mol_D^{-1}) is close to Kimtys' value of -47.3 kJ · mol_D^{-1} for pivalic acid in cyclohexane at ambient pressure [17a]. The difference in dimerization enthalpies (at ambient pressure) of PA in n-heptane and CCl_4, exceeds the literature value [17b] by about 4 kJ · mol_D^{-1}. As is required by thermodynamic consistency, the dimerization volume ΔV^0 "at infinite dilution", which is obtained from

$$-\Delta V^0 = (\partial (RT \cdot \ln \bar{K}_x)/\partial P)_T \qquad (10)$$

varies with temperature is shown in Figure 11.

The ΔV values which are also plotted in Fig. 11, are obtained from the pressure dependence of $\ln \bar{K}_c$. ΔV^0 and ΔV only differ by one term containing the isothermal compressibility of the solvent [20]. The variations of dimerization enthalpy with P and of dimerization volume with T, although being very small, appear to occur beyond the limits of experimental accuracy. They are observed within each of the experimental runs at constant concentration.

The data in Fig. 10 are in reasonable agreement with the suggestion derived from vibrational intensities $B_D(\mathrm{O-H})$ in Fig. 7, that increasing pressure reduces the strength of hydrogen bonds in the cyclic PA dimer. The concentration of dimers, however, increases with pressure at constant temperature (Figs. 8 and 9). The classical thermodynamic study which provides the correlation of states by Δ-quantities, such as ΔH, ΔV, and ΔS is thus appreciably extended by the spectroscopic analysis which enables characterization of the individual species. The higher strength of hydrogen bonds (at lower pressure) is probably associated with a more planar dimer structure which corresponds to larger molar volume.

The analogous explanation for the decrease of ΔV^0 toward higher temperature (Fig. 11) is: Cyclic dimers of higher stability (bond enthalpy) and thus of higher molar volume occur at lower temperature. The volume difference between a dimer and two monomer acid molecules is smaller than at higher temperature where, due to weaker hydrogen bonds, a cyclic dimer of less planar structure (which allows denser packing) is formed. This interpretation, in principle, is close to arguments which have been put forward to explain the reaction volumes observed for the cyclic dimerization via hydrogen bonds of ε-caprolactam in CCl_4 [20] ($\Delta V^0/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} = -1.3 \pm 0.3$) and of benzoic acid in n-heptane [15] ($\Delta V^0/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} = 0.4 \pm 0.9$). These numbers are appreciably larger than reaction volumes between $-3\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ and $-6\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ which are reported for the formation of a single (non-cyclic) hydrogen bond. The authors [15, 20] suggest that two competing effects occur: (i) a decrease of volume due to hydrogen bond formation and (ii) an increase of reaction volume due to cyclization as the center of the ring constitutes an excluded volume region.

Formal extrapolation of the n-heptane data in Fig. 11 suggests that at temperatures below 0 °C, applying pressure might shift the equilibrium toward the monomer. In CCl_4, this situation may occur close to 0 °C. The smaller values of (negative) dimerization volume in CCl_4 are consistent with the results on the carbonyl vibrational intensity (Figs. 3 and 5). They suggest that, compared with n-heptane, the monomer-solvent interactions in CCl_4 are stronger which corresponds to smaller molar volume whereas more stable hydrogen bonds in the cyclic dimer are associated with larger molar volume. Thus $-\Delta V$ is smaller in CCl_4 than in n-heptane. The pressure influence extrapolated for lower temperature which is also reported for benzoic acid in n-heptane at 25 °C [15], is not as unexpected as it might appear. The melting of ice and also the denaturation of proteins are well-known examples for pressure-induced transitions from almost perfect hydrogen-bonded structures to situations with less stable hydrogen bonds but with higher overall packing density. The carboxylic acid experiments are remarkable in that effects similar to the collapse of perfect hydrogen-bonded structure in three dimensions are also indicated for the two dimensional acid association.

In conclusion, quantitative high-pressure high-temperature infrared spectroscopy turns out to be a valuable technique for the study of the association of carboxylic acids in fluid solution. In addition to purely thermodynamic data which correlate states, e.g. by differences in enthalpy and volume, the spectroscopic analysis enables a direct study of the individual monomer and dimer species within a wide range of temperatures and pressures. Unfortunately, the information about the dimer structure, which is contained in the strong variation of O−H vibrational intensity is not yet adequately understood. In a subsequent paper the self-association of other carboxylic acids via hydrogen bonds will be studied up to high pressures and temperatures [26].

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