INFRARED STUDY OF ACETIC ACID SOLUTIONS IN CCl_4

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Spectra of acetic acid solutions in carbon tetrachloride were taken at room temperature over the concentration range 0.025–0.00125 mol dm^{-3}. Solutions of acetic acid were modelled as an ideal mixture of monomers, and cyclic and linear dimers. Regression analysis effected separation of the experimental envelope into its component bands. Band shapes were approximated by a Lorenzian function with the resolved band peak frequencies 1 712 cm^{-1} for the cyclic dimer, 1 724 cm^{-1} for the linear dimer and 1 765 cm^{-1} for the acetic acid monomer. Mean values of equilibrium constants for the standard state of unit concentration are 2 700 for the cyclic and 393 for the linear dimer, respectively.

We, as human beings, are literally vitally dependent on H-bonded systems which play key roles in a wide variety of biological metabolism. Do we know enough about behavior of these H-bonded liquid mixtures? There exist three ways of describing these systems:

1. “Physical” way

All non-idealities are summed up in experimentally obtained activity coefficients. Their concentration dependence is sometimes difficult to correlate at the experimental error level by relations that are used for mixtures of nonelectrolytes.

2. “Chemical” way

The solution is regarded as a mixture of clusters of different types that all exhibit ideal behavior and therefore, having known all kind of species really present, the description of their mixture would be easy. Experimentally obtained data are used to fix chemical reaction constants of clusters present. The problem is that mixture exhibiting ideal behavior for one standard state does not behave ideally for another standard state when the concentration units differ. In other words as $\gamma_x \neq \gamma_c$ (where γ_x and γ_c stand for activity coefficients in mole fractions and in concentrations, respectively) they both can equal to one only in very dilute solutions.

3. “Pragmatic” way

Unsatisfactory description by the “chemical” way in higher concentrations is accounted for not knowing the activity coefficients of the real species. But the “chemical” way describes m-component mixture as n-component one, where $n > m$, and in most cases we do not know much about behaviour of these new pure components as it is impossible to separate them. We can only guess their pure component behavior from properties of their mixtures. The better model, the more reliable these pure component data.

As we deal with organic acids[1–4] knowledge of real species present would be a great help for us. As physical-chemists we are aware there have to hold not only chemical equilibrium relations in one phase, but also phase equilibrium conditions between different phases. What do we know about behavior of the lower carboxylic acids?

a) No trimers or higher polymers were observed in the vapor phase of acetic acid by the method of mass spectroscopy although sensitivity of the mass spectrometer enabled to detect trimers if their abundance were at least 1% (ref.[5]).

b) Equilibrium constants of dimerization in a vapor phase were obtained by measuring state behavior and, therefore, if there exist two types of dimers in the vapor phase there are indistiguishable and the final equilibrium constant is a sum of those for the cyclic and open dimer.

c) If there are two forms of dimers in the vapor phase, ΔH_{as} is a weight average of both ΔH_{as} that ought to differ substantially as there are two H-bonds in the cyclic form and only one in the open form. As temperature rises the amount of open dimers would grow and ΔH_{as} ought to be lower in absolute value. This situation is demontrated in Table I.

d) Both, acetic acid and propionic acid have nearly the same values of dimerization constants in vapor phase.

It can be concluded that while the existence of higher associates is highly improbable the existence of the open dimer cannot be excluded in vapor phase of the acid.

a) The bands ascribed to the cyclic dimer obtained by means of the infra-red carbonyl absorbtion are asymmetrical and have similar shoulders in both, solution and vapor phase.

b) Some evidence exist[10] that there are open chains in the solid phase of acetic and formic acid while in that of propionic acid cyclic dimers are postulated[10].

TABLE I

Dependence of ΔH_{ass} on temperature in the vapor phase of acetic acid

Temperature range, °C	ΔH^0_{as}, kJ	Reference
25–40	–68.55	6
95–155	–65.63	7
110–184	–57.64	8
165–200	–56.85	9
260–300	–48.49	9

What do we know about structure of these substances in the liquid phase? Although the association of acetic acid has been one of the most widely studied of association equilibria, there still does not exist a unique picture of true species in the liquid phase. The most explicit knowledge of the true species can be obtained from spectral studies – and these studies on fatty acids are quite numerous in literature. As we went through them, we found out there exist two extreme cases:

a) qualitative studies

leading after a band resolution to the postulation of many different clusters[11,12]

b) quantitative studies

restricted in nearly all cases on a monomer-dimer equilibrium only, although several authors suggested existence of two types of dimers[13–15].

We found on examination that the work already done on these molecules[11–28] did not provide us with sufficient information. Moreover, the existence of two types of dimers could explain discrepances in values of dimerization constants obtained by different techniques[14,17]. On the other hand we could not a priori exclude existence of resonance bands in the region. As the equilibrium associate bands have to fulfil some constraints we believed we will be able to exclude a possible influence of resonances a posteriori. As it was impossible to process newly data already obtained we repeated much of the past work.

EXPERIMENTAL

Spectra were taken with a SPECORD model M-80 infrared spectrophotometer. The carbonyl stretching region from 1 800 to 1 600 cm^{-1} was scanned. The cell used for the solution measurements, of path length 0.632 mm as determined by interference measurement, had sodium chloride windows separated by platinum spacers.

In order to rule out a possible influence of invalidity of the Lambert–Beer law, solutions of benzophenone in carbon tetrachloride in the concentration range 0.001–0.05 mol dm^{-3} were examined as we believed this carbonyl group was a non-hydrogen-bonding one. The experimental points did not deviate from the expected straight line relationship more than by ±0.05 in integrated intensities.

Tetrachloromethane (p.a., Lachema Brno) was dried over P_2O_5 and distilled on a packed column prior to use. Acetic acid (p.a., Lachema Brno) was refluxed with a small of acetic anhydride and $KMnO_4$ and then fractionally distilled. Analysis on a GLC column on Separon with a catharometer showed the product to be 99.9 wt.% with a content of water less then 0.03 wt.%.

Solutions in the concentration range 0.025–0.00125 mol dm^{-3} were prepared by diluting from concentrated solution, and were used immediately after preparation. All spectra were taken three times at 21 ± 1 °C (room temperature).

RESULTS AND DISCUSSION

The asymmetrical dimer spectrum was interpreted as a superposition of the cyclic and open form. As suggested before[15], we were looking for four bands occurring in the vicinity of 1 782, 1 767, 1 722 and 1 715 cm^{-1}. These were assigned to the nonbonded carbonyl stretching modes of an open dimer, monomer, bonded carbonyl stretching modes of open dimer and cyclic dimer, respectively. The first band was, unfortunately, very weak and, therefore, to no use for further calculations. Our consistency test was thus limited on the three other bands. The monomer band, also weak, was probable source of errors leading to a scatter in resulting equilibrium constants. The dimer band was subjected to a numerical curve fitting. The treatment of data assumed that

a) the equilibria involve existence of two types of dimers,

b) the Lambert–Beer law is valid for all three bands i.e. monomer and linear and cyclic dimer bands,

c) there are no resonance bands in this region,

d) the shape of the true absorbtion bands may be represented by a Lorentzian curve

$$\log\left(\frac{I_0}{I}\right)_{\tilde{\nu}} = \frac{a'}{1 + b'\,(\tilde{\nu} - \tilde{\nu}_0)^2}\ ,$$

where on the left hand side of the equation is absorbance at a given wavenumber, a' and b' are constants and $\tilde{\nu}_0$ the wavenumber of the band center.

The band resolution of digitized dimer spectra into two bands was unambiguous. To be certain that the assignment of bands is justed we did not check only their concentration dependence but also some constraints between them resulting from equilibrium conditions at constant temperature, namely $A_{2C} : A_{2L}$ = const (resulting from $K_C/K_L = c_{2C}/c_{2L}$, $A_{2C} : A_1^2$ = const′(resulting from $K_C = \mathrm{c}_{2C}/c_1^2$, $A_{2L} : A_1^2$ = const″(resulting from $K_L = c_{2L}/c_1^2$, which would be redundant if the first two relations are sharply valid. Here A denotes integrated intensities, subscript 2C denotes cyclic dimer, 2L linear dimer and 1 monomer.

The resolved maximum band wavenumbers and integrated intensities obtained by the least square method are presented in Table II, the validity of relations given above is

TABLE II
Resolved band parameters

c, mol dm^{-3}	$\tilde{\nu}_{0C}$, cm^{-1}	A_{2C}	$\tilde{\nu}_{0L}$, cm^{-1}	A_{2L}	$\tilde{\nu}_{01}$, cm^{-1}	A_1
0.025	1 712.4	20.75	1 723.13	2.08	1 765.9	2.15
0.01	1 712.6	8.01	1 724.2	0.77	1 765.7	1.30
0.005	1 712.7	3.77	1 724.5	0.28	1 765.4	0.74
0.0025	1 712.8	1.79	1 724.6	0.13	1 765.5	0.59
0.00125	1 712.8	0.83	1 724.7	0.2	1 764.5	0.39

shown in Table III. The value 0.2 of integrated intensities of linear dimer in the last row of Table II is much to high and was not considered in the following calculation. As for the bulk concentration c_A of the acid holds

$$c_A = 2c_{2C} + 2c_{2L} + c_1 \tag{1}$$

and the Lambert–Beer law

$$A = alc \quad , \tag{2}$$

TABLE III
Ratia of integrated intensities

Ratio	c, mol dm^{-3}				
	0.025	0.01	0.005	0.0025	0.00125
$A_{2C} : A_{2L}$	9.4	10.3	13.5	13.5	5.2
$A_{2C} : A_1^2$	4.5	5.0	6.8	5.5	5.4
$A_{2L} : A_1^2$	0.44	0.46	0.48	0.42	1.3

TABLE IV
True species concentrations and equilibrium constants

c_A mol dm^{-3}	$c_{2C} . 10^3$ mol dm^{-3}	$c_{2L} . 10^4$ mol dm^{-3}	$c_1 . 10^4$ mol dm^{-3}	K_C[a]	K_L[b]
0.025	9.81	16.8	20.8	2 265	388
0.01	3.78	6.27	12.6	2 374	394
0.005	1.78	2.28	7.19	3 443	441
0.0025	0.844	1.07	5.53	2 759	349
0.00125	0.390	–	3.80	2 700	–

[a] Standard state of unit concentration.

where a is absorptivity and l is the sample path length, is valid for all three kinds of true species, the following equation results

$$c_A = k_{2C} A_{2C} + k_{2L} A_{2L} + k_1 A_1 \ . \qquad (3)$$

The constants were obtained by the least square method, values of al product are: $(al)_{2C} = 1\,058 \pm 36$ dm^3 mol^{-1}, $(al)_{2L} = 1\,244 \pm 108$ dm^3 mol^{-1}, $(al)_1 = 1\,029 \pm 102$ dm^3 mol^{-1}.

Their knowledge enables to calculate the true species concentrations and equilibrium constants of association given in Table IV. Mean values of equilibrium constants are

$$K_C = 2\ 700 \pm 461,\ K_L = 393 \pm 38.$$

Therefore, provided that our presumptions were correct, there is about seven times more cyclic dimers then linear ones in liquid acetic acid at room temperature. The sum of our equilibrium constants is somewhat lower than value obtained by Affsprung and coworkers[21] from IR measurements at the monomer O–H frequency. Their values $K_{25°} = 3\ 200 \pm 400$ and $\Delta H_{as} = -44.7$ kJ yield $K_{21°} = 4\ 100 \pm 500$.

Combining our constants, the equilibrium constant for cyclic dimer to linear dimer reaction can be obtained. Our value 0.15 ± 0.05 corresponds well with Tabuchi[27] value $K_{20°} = 0.212$, obtained from ultrasonic relaxation measurements.

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