437. *Vapour-phase Hetero-association of Trifluoroacetic Acid with Acetic Acid, Water, and Dioxan*

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The vapour-phase hetero-association of trifluoroacetic acid with acetic acid, water, and dioxan has been investigated by using a vapour-density technique. Formulæ for the most probable associated species and equilibrium constants for their formation from monomers are reported.

Although no technique for investigating self-association is more direct than the vapour-density method, little use has been made of vapour-density measurements in studying the hetero-association of hydrogen-bonding compounds. There are two probable reasons for this neglect: first, association reactions occur relatively infrequently in the vapour phase as compared to condensed phases; second, conventional vapour-density techniques are not easily adapted to studies of mixed vapours.

A vapour-density technique developed in this laboratory is well suited for studying mixed vapours.[1] We have used the method to investigate mixed vapours in the systems acetic acid–trifluoroacetic acid, water–trifluoroacetic acid, and dioxan–trifluoroacetic acid.

Experimental

The organic compounds were all of reagent grade, distilled through a 25-plate Oldershaw column and stored in vapour-contact with phosphorus pentoxide.

Except for a minor modification of the evacuation valve, the apparatus was the same as that described previously.[1] The flask and connecting tubing had a volume slightly greater than 3 l., and the entire system was immersed in a water-bath controlled to within $\pm 0{\cdot}1°$.

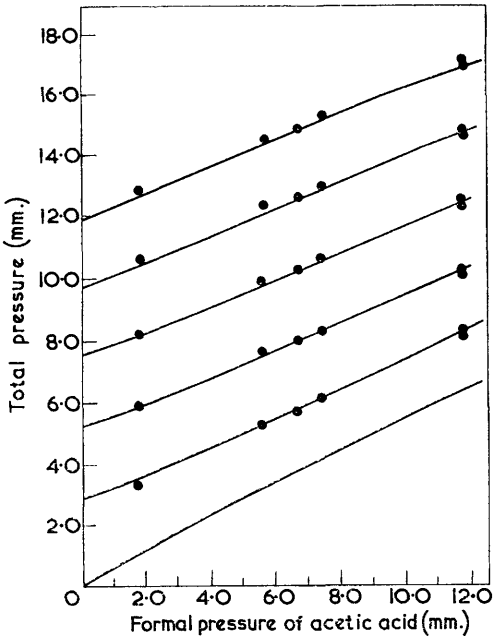


Figure 1. Plot of total pressure against formal pressure of acetic acid for formal pressures of trifluoroacetic acid of 19·67, 15·74, 11·80, 7·87, 3·94, and 0 mm., respectively, from top to bottom. Curves are calculated, points are experimental

Samples were introduced through the mercury-covered sintered-glass disc by means of a 2 ml. microburette made by Gelman Instrument Co., Chelsea, Mich. A sample of one of the components was added to the flask and the pressure measured; increments of the second component were then added and the pressure measured after each addition.

[1] Christian, Affsprung, and Lin, *J. Chem. Educ.*, 1963, **40**, 323; *J.*, 1964, 1848; Lin, Ph.D. Dissertation, University of Oklahoma (1964).

Care was taken not to extend measurements to pressures close to the saturation pressure, since experiments with pure polar compounds indicated that, at pressures near the dew point, apparent deviations from vapour-phase ideality occur. Previous results obtained with the vapour-density apparatus indicated that non-polar vapours such as cyclohexane, carbon tetrachloride, and benzene, at pressures up to at least 80 mm., obeyed the ideal gas equation.[1] Water vapour, also, has been shown to be ideal to within the limits of experimental error at pressures less than about 90% of saturation at room temperature. Thus, neither adsorption nor non-ideality of the individual species is likely to be a significant source of error at pressures in the range reported (0—18 mm.).

Figure 1 shows typical vapour-density results for one of the systems investigated. Total pressure is plotted against the formal pressure * of acetic acid, corresponding to various constant values of the formal pressure of trifluoroacetic acid. The formal pressure of the component added initially to the flask is plotted as the abscissa; hence, the points on each curve have been obtained from several independent runs and systematic errors in the individual runs tend to be randomised. Values for the other two systems were obtained for the following ranges of the measurables: system water–trifluoroacetic acid—total pressure, 0—12 mm., formal pressure of water, 0—7 mm., formal pressure of trifluoroacetic acid, 0—16 mm., 22 sets of values; system dioxan–trifluoroacetic acid—total pressure, 0—9 mm., formal pressure of dioxan, 0—6 mm., formal pressure of trifluoroacetic acid, 0—6 mm., 33 sets of values.†

Discussion

The problem of determining equilibrium constants from measurements of vapour density and composition at low pressures may be reduced to that of solving the following equations.

$$p = \sum_{i,j} K_{ij} p_A{}^i p_B{}^j \quad (1)$$

$$\pi_A = \sum_{i,j} i K_{ij} p_A{}^i p_B{}^j \quad (2)$$

$$\pi_B = \sum_{i,j} j K_{ij} p_A{}^i p_B{}^j \quad (3)$$

where p is the total pressure, π_A and π_B are the formal pressures of species A and B, respectively, p_A and p_B are the partial pressures of the monomeric forms of the components and the K_{ij} values are equilibrium constants for the reaction of monomers to yield the complex A_iB_j. Note that by definition $K_{00} = 0$, $K_{10} = 1$, and $K_{01} = 1$. In formulating equations (1—3) it is assumed that each complex individually obeys the ideal gas equation.

We have developed a computer programme for determining the goodness of fit of the values for p, π_A, π_B data provided by a chosen set of values of the constants K_{ij}. The programme calculates p_A and p_B for each experimental point by simultaneous solution of equations (2) and (3) and uses these values in computing

$$E = \left\{ \frac{\sum_{k=1}^{N} [p^k \text{ calc.} - p^k \text{ exp.}]^2}{N - n} \right\}^{\frac{1}{2}}$$

where p^k calc. and p^k exp. are the calculated and experimental pressures for the experimental point k, N is the total number of points, and n is the number of adjustable constants used in the fit. Obviously, for a given choice of possible species, the best fit corresponds

* By analogy with formal concentration, the formal pressure of component X is defined as the pressure the compound would exert if present in the vapour phase solely as monomer obeying the ideal gas law, and is calculated from the expression

$$\pi_X = w_X RT/M_X V,$$

where w_X is the weight of the component in the flask, M_X is the molecular weight of the monomer of X, and V is the volume of the vapour phase.

† Tabulated results will be supplied by the authors on request.

to the lowest computed value of E. The minimum value of E is determined graphically by plotting computed values of E against K_{ij}. In Figure 2 a typical plot of E against K_{11} is shown for the trifluoroacetic acid–dioxan system. The probable error of each hetero-association constant is calculated from the probable error of the minimum value of E and knowledge of the variation of E with K in the vicinity of the minimum.

In treating results for the systems described here, the only hetero-associated complexes

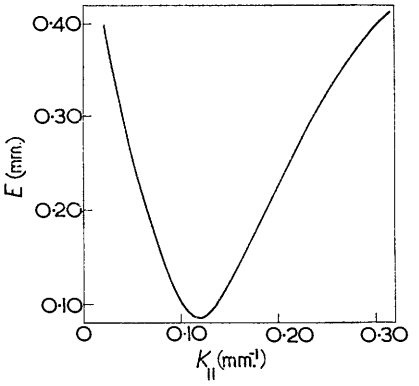


FIGURE 2. Dependence of E on K_{11} for the system trifluoroacetic acid–dioxan

considered were AB, AB_2, A_2B, and A_2B_2, and the only homo-associated species assumed to be present were the dimers of the acids. Self-dimerisation constants were obtained from measurements on the pure components. It was possible in each case to achieve a satisfactory fit of the values by postulating a single hetero-associated species.

Table 1 lists formulæ of the assumed complexes, values of equilibrium constants and the

TABLE 1

Equilibrium constants for postulated species

Temp. (°c)	System: Component A	System: Component B	Postulated complexes	Equilibrium constants	E (mm.)
20	Trifluoroacetic acid	Acetic acid	A_2, B_2, AB	$K_{02} = 3{\cdot}15 \pm 0{\cdot}15$ mm.$^{-1}$ $K_{20} = 0{\cdot}46 \pm 0{\cdot}03$ mm.$^{-1}$ $K_{11} = 14{\cdot}5 \pm 3{\cdot}5$ mm.$^{-1}$	0·099
20	Trifluoroacetic acid	Water	A_2, AB_2	$K_{20} = 0{\cdot}46 \pm 0{\cdot}03$ mm.$^{-1}$ $K_{12} = 0{\cdot}010 \pm 0{\cdot}003$ mm.$^{-2}$	0·161
40	Trifluoroacetic acid	Dioxan	A_2, AB	$K_{20} = 0{\cdot}11 \pm 0{\cdot}01$ mm.$^{-1}$ $K_{11} = 0{\cdot}12 \pm 0{\cdot}015$ mm.$^{-1}$	0·085

value of E corresponding to the best fit obtained for the results for each system. The solid curves in Figure 1 were calculated by using constants from the Table. Values of E for the three systems are comparable to expected uncertainties in p, computed from the probable errors in the volumes of liquid samples added.

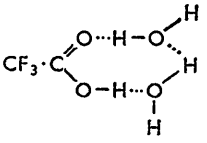
The trifluoroacetic acid–acetic acid system has been studied previously by Hansen and Christian,[2] who obtained values for the hetero-dimerisation constant of about 6 mm.$^{-1}$ (extrapolated to 20°) by using a somewhat less precise vapour-density method. The present value of $14{\cdot}5 \pm 3{\cdot}5$ mm.$^{-1}$ agrees reasonably well with the earlier results and indicates that the hetero-dimer is strongly favoured over either of the homo-dimers. Affsprung *et al.*[3] observed and discussed a similar effect in the formation of hetero-dimers of acetic acid and trichloroacetic acid in carbon tetrachloride solution.

With the trifluoroacetic acid (A)–water (B) system, it was possible to obtain a satisfactory fit of vapour-density results by assuming a single hetero-associated species, AB_2,

[2] Hansen and Christian, unpublished work; Christian, Ph.D. Dissertation, Iowa State College (1956).

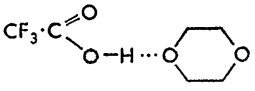
[3] Affsprung, Christian, and Melnick, *Spectrochim. Acta*, 1964, **20**, 285.

but, it was not possible to obtain a reasonable fit by assuming any other single hetero-complex. Further, it was not possible to find any combination of two hetero-species that would lead to a lower value of E than that obtained by using $K_{12} = 0{\cdot}10$ mm.$^{-2}$. A plausible structure for the 1 : 2 complex is



in which each water molecule is doubly hydrogen-bonded. This species might be expected to be more stable than the 1 : 1 complex, which would probably not be a cyclic structure. Infrared spectra provide evidence that both the carbonyl and the hydroxyl stretching modes are affected by hydration. When water vapour is introduced into an infrared gas cell containing anhydrous trifluoroacetic acid vapour, new absorption peaks appear on the long wavelength side of the frequencies characteristic of both the hydroxyl and carbonyl fundamental stretching modes of the trifluoroacetic acid monomer.

In the trifluoroacetic acid (A)–dioxan (B) system, the 1 : 1 complex is sufficient to explain the vapour-density results at 40°. It was not possible to determine vapour densities accurately at 20°, because of the low vapour pressure of the binary azeotrope (about 2 mm.). For this system, a slightly reduced minimum value of E was obtained by assuming both the complexes AB and A_2B to be present. If $K_{11} = 0{\cdot}090$ mm.$^{-1}$ and $K_{21} = 0{\cdot}006$ mm.$^{-2}$, $E = 0{\cdot}083$ mm. Since the estimated uncertainty in E is 0·008 mm., this is not significantly lower than the value $E = 0{\cdot}085$ mm. obtained by using $K_{11} = 0{\cdot}12$ mm.$^{-1}$. The 1 : 1 complex may have the structure



and it is reasonable to expect that the 2 : 1 complex will be formed by the attachment of another trifluoroacetic acid molecule at the second dioxan oxygen. Assuming that hydrogen-bond formation at one of the dioxan oxygens does not alter the *a priori* probability of bond formation at the other oxygen, it may be shown that K_{21} should equal $K_{11}^2/4$. In fact, if the values of the constants are taken to be $K_{11} = 0{\cdot}105$ mm.$^{-1}$ and $K_{21} = K_{11}^2/4 = 0{\cdot}0028$ mm.$^{-2}$, E is found to be only slightly greater than 0·083 mm. Hence, although it is likely that doubly-bonded dioxan molecules exist at the higher pressures of trifluoroacetic acid, the present results do not allow the calculation of K_{21} with any degree of confidence.

It is expected that the apparatus and technique developed during the present investigation will be valuable in studies of the comparative basicity of oxygen atoms in various classes of organic compounds. Trifluoroacetic acid contains an extremely acidic hydrogen, and should hetero-associate with numerous volatile bases, including ketones, ethers, and esters. The primary advantage of investigating this type of interaction is that solvation effects, which are always present in solution, are absent in the vapour phase.

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