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Determination of the Equilibrium Constants of Association from IR-Studies in the Acetone—Chloroform System

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From IR-studies a method was developed for the determination of the equilibrium constant of association in the acetone—chloroform system. The method is based on the separation of the $C=O$ stretching vibration band of the ketone mixed with chloroform and cyclohexane (mixed solvent method).

(Keywords: IR-Spectroscopy; $C=O$ *Stretching vibration; Association constant; Mixed solvent method)*

Bestimmung der Gleichgewichtskonstanten der Assoziation aus IR-spektroskopischen Messungen in Aceton—Chloroform-Mischungen

Aufgrund infrarotspektroskopischer Untersuchungen wurde eine Methode zur Bestimmung der Assoziations-Gleichgewichtkonstanten in Aceton—Chloroform Mischung entwickelt. Die Methode beruht auf einer Auftrennung der Absorptionsbande der $C=O$ Valenzschwingung des Ketons in Mischungen mit Chloroform und Cyclohexan (sog. "mixed solvent" Methode).

Introduction

It is well known from vapour-liquid equilibrium and heat of mixing data, that the acetone—chloroform system shows a great negative deviation from *Raoult*'s law[1,2]. The strong interactions between molecules of the components can be explained by the hydrogen bonds. In earlier works the association of acetone (and other ketones) with chloroform was considered to involve only 1 : 1 complexes.

Among others *Kearns*[2] and *Lascombe*[3] have proposed that 1 : 2 acetone—chloroform complexes also can exist in this type of mixtures.

Several methods are available for the determination of equilibrium constants of association form IR studies. The *Nash* method[4] is, however, suitable only for the determination of the equilibrium constant of the 1 : 1 complexes. *Huyskens* et al.[5] and also *Whetsel* and *Kararise*[6,7] determined the two association constants for systems containing an OH group in the proton donor component. For the ketone-chloroform system the equilibrium constant of the 1 : 2 complex is only an estimated value[7]. In this work a method is presented for the calculation of the two equilibrium constants of the association.

The method is applied to the system aceton—chloroform.

Theory

The A—AB—AB_2—B type model of ideal associated mixtures was used[8]; so it was supposed that the self-association effect of chloroform or acetone could be neglected. The presence of two complexes having aceton-chloroform ratios 1 : 1 and 1 : 2 can be indicated among others from IR-spectra.

The carbonyl band of acetone will be shifted in the direction of lower wave numbers and two new bands occur with increasing chloroform concentration. These absorption peaks were investigated by means of the mixed solvent technique, namely the concentration of acetone was constant while the quantity of chloroform and of course that of the solvent were varied. The first three curves (Fig. 1) could be obtained this way. The first curve is the absorbance of acetone in solution versus the wave number. The effect of chloroform on the C=O band can be seen in the second and third curve (C′, C″ chloroform, C_0 acetone concentration). These two bands consist of three overlapped absorption peaks. Those are due to the —C=O, —C=O...H—, and the $\text{—C=O}\begin{smallmatrix}\cdot\cdot\text{H—}\\ \cdot\cdot\text{H—}\end{smallmatrix}$ stretching vibration respectively. The first step of the method is the separation of the band. It can be made point by point if the two equilibrium constants are known. K_1 and K_2 must be estimated as the starting values of the calculation.

With the K values the real composition of the mixture can be calculated as follows:

$$K_1 = \frac{X_{AB}}{X_A X_B} = \frac{C_{AB}(C_A + C_{AB} + C_{AB_2} + C_B)}{C_A \cdot C_B} = \frac{C_{AB}(C_0 + C - C_{AB} - 2C_{AB_2})}{(C_0 - C_{AB} - C_{AB_2})(C - C_{AB} - 2C_{AB_2})} \tag{1}$$

$$K_2 = \frac{X_{AB_2}}{X_{AB} X_B} = \frac{C_{AB_2}(C_A + C_{AB} + C_{AB_2} + C_B)}{C_{AB} \cdot C_B} = \frac{C_{AB_2}(C_0 + C - C_{AB} - 2C_{AB_2})}{C_{AB}(C - C_{AB} - 2C_{AB_2})} \tag{2}$$

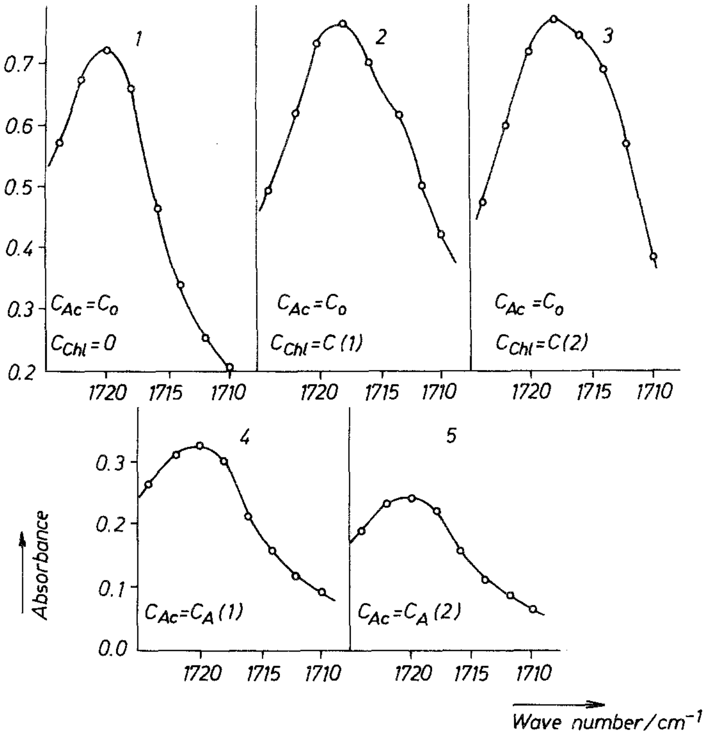

Fig. 1. Spectra of acetone in mixtures of chloroform and cyclohexane (curve *1, 2, 3*) and spectra of free acetone in the mixture (curve *4, 5*)

C_0 and C mean the nomical concentration of acetone (A) and chloroform (B), X means the molar fraction.

Since the concentration of the non-associated acetone can be calculated from the equations (1) and (2) we can have its absorption curve: it can be measured or calculated according to *Beer's* law (curves 4 and 5 in Fig. 1). The points of this peak will be subtracted from the points of the peak of the corresponding mixture. The obtained "remainder" absorption band is due to the C=O stretching vibration of the two 1 : 1, 1 : 2 acetone-chloroform complexes (curve 1 in Fig. 2).

If this process will be repeated at another chloroform concentration (C'', curve 2 in Fig. 2) the band separation can be made point by point from the two obtained remainder curves.

In this way two separate C=O bands of the AB and AB_2 complexes will be available (curves 3, 4 in Fig. 2). The separation must be made once again at another chloroform concentration pair.

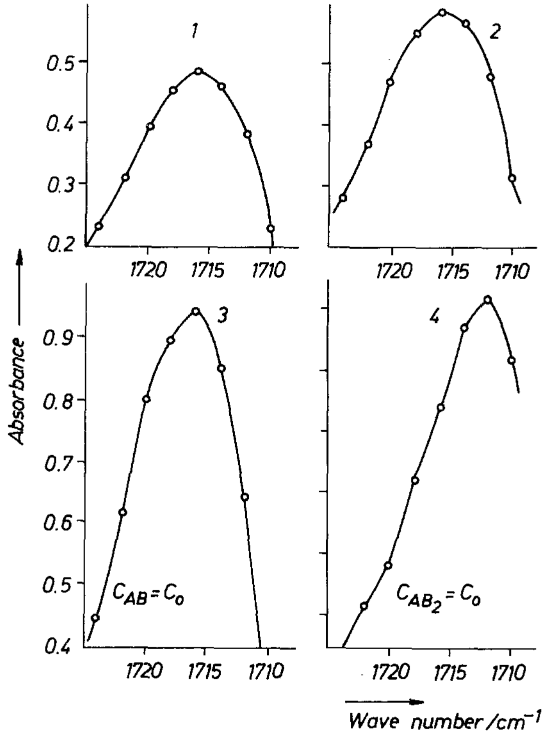

Fig. 2. Calculated "remainder" spectra of the two complexes (curve *1*, *2*) and separate C=O band of the AB (curve *3*) and AB_2 complex (curve *4*)

If the same separated C=O bands for the two complexes can be obtained from several (minimum two) concentration pairs of chloroform, then the estimated *K* values are correct. If the points of the curves show a greater deviation than a given error, the procedure must be repeated with modified *K* values.

Experimental

Apparatus and Materials

A SPECORD-IR 75 type spectrophotometer equipped with KBr optics was used for the measurements. All measurements were made with 0.0434 mol/dm^3 acetone and difference concentrations of chloroform in a cyclohexane solvent. The cell thickness was 0.413 mm determined from interference fringes.

Acetone was dried with anhydrous $CaSO_4$, then distilled. Chloroform was washed with water to remove the ethanol, than dried and refluxed with P_2O_5 and distilled. Cyclohexane was a high purity chemical, and since good agreement was found between its physical properties and the corresponding data in the literature, no further purification was effected.

Results and Discussion

The method outlined above was applied to the system acetone—chloroform. The calculations are based on the experimental absorbance data of Table 1. The blockscheme of the program is showed in Fig. 3. According to this scheme the calculation can be made for N chloroform concentrations [$N(N—1)/2$ concentration pairs] and M measured points of the C=O band.

From the measured absorbance data the following association equilibrium constants have been calculated:

$$K_1 = 1.42 \pm 0.05$$
$$K_2 = 0.52 \pm 0.02$$

The average deviation—the average value of mean deviation of each of the three [$N = 3$, $N(N—1)/2 = 3$] calculated absorbances—was smaller than 0.04.

Several literature values are given for comparison: *Kearns*[2] obtained values of $K_1 = 0.967$ and $K_2 = 1.117$ from enthalpy of mixing data for the system acetone-chloroform. For a system containing acetone—chloroform and cyclohexane *Whetsel* and *Kagarise*[7] obtained $K_1 = 1.2 \pm 0.3\,\mathrm{dm^3\,mol^{-1}}$ (by the method of *Nash*) and $K_2 = 0.2\,\mathrm{dm^3\,mol^{-1}}$ (estimated value).

The equivalent values in mole fraction units are about 1.45 and 0.24, respectively.

Table 1. *Absorbance values of the carbonyl stetching vibration band in the acetone—chloroform—cyclohexane system*

$C_{\mathrm{acetone}}/\mathrm{mol\,dm^{-3}}$	0.0434	0.0434	0.0434	0.0434
$C_{\mathrm{chloroform}}/\mathrm{mol\,dm^{-3}}$	0.0000	0.0512	0.1210	1.0180
Wave number/cm^{-1}	Absorbance			
1 725	0.4841	0.3651	0.3188	0.2845
1 723.75	0.5311	0.4039	0.3541	0.3174
1 722.5	0.5624	0.4506	0.4122	0.3843
1 721.25	0.5785	0.4812	0.4619	0.4414
1 720	0.5467	0.5152	0.5113	0.5095
1 718.75	0.4583	0.5420	0.5601	0.5510
1 717.5	0.3820	0.5645	0.6000	0.6275
1 716.25	0.3175	0.5492	0.6141	0.6502
1 715	0.2660	0.4932	0.5722	0.6262
1 713.75	0.2320	0.4037	0.4813	0.5437
1 712.5	0.2104	0.3140	0.3721	0.4234
1 711.25	0.1812	0.2441	0.2822	0.3167
1 710	0.1586	0.1995	0.2223	0.2425
1 708.75	0.1466	0.1694	0.1828	0.1950
1 707.5	0.1361	0.1488	0.1565	0.1634

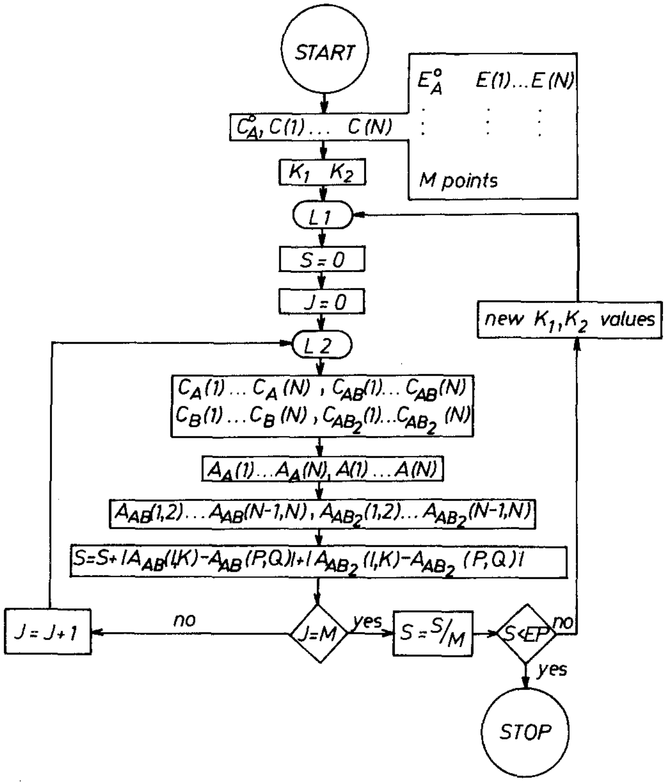

Fig. 3. The blockscheme of the computer program of the method

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