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Solvent Extraction Studies by the AKUFVE Method

IV. Spectrophotometric Determination of the Distribution of Acetylacetone

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Using the AKUFVE method with spectrophotometric detection, the distribution of acetylacetone between different organic solvents and aqueous sodium perchlorate was investigated. It was found that the distribution constant (k_d) decreased with increasing ionic strength for the organic solvents benzene, toluene, xylene, mesitylene, ethyl benzene, and chloroform. At constant ionic strength, k_d decreased with increasing number of methyl groups in substituted benzene. Furthermore, k_d decreased with increasing temperature for the chloroform system, but remained nearly constant in the other systems. The results are discussed in relation to NMR measurements, and calculated ΔH and ΔS values.

Using the newly developed AKUFVE technique,[1,2] we have for some time in our laboratory determined thermodynamic constants for the formation and distribution of metal complexes between organic and aqueous solutions.[3,4] For these determinations it is necessary to know the distribution constant (k_d) of the complexing agent itself between the two liquid phases as a function of temperature, ionic strength and pH. In the present paper, the results for acetylacetone (HAA) are reported, using spectrophotometric determinations in both phases. This method of detection has been adopted to the AKUFVE technique to provide fast and continuous measurements. The apparatus is shown in Fig. 1.

SPECTROPHOTOMETRIC DETERMINATION OF k_d

The distribution constant k_d may be defined as

$$k_d = \frac{[HAA]_{org}}{[HAA]_{aq}} \quad (1)$$

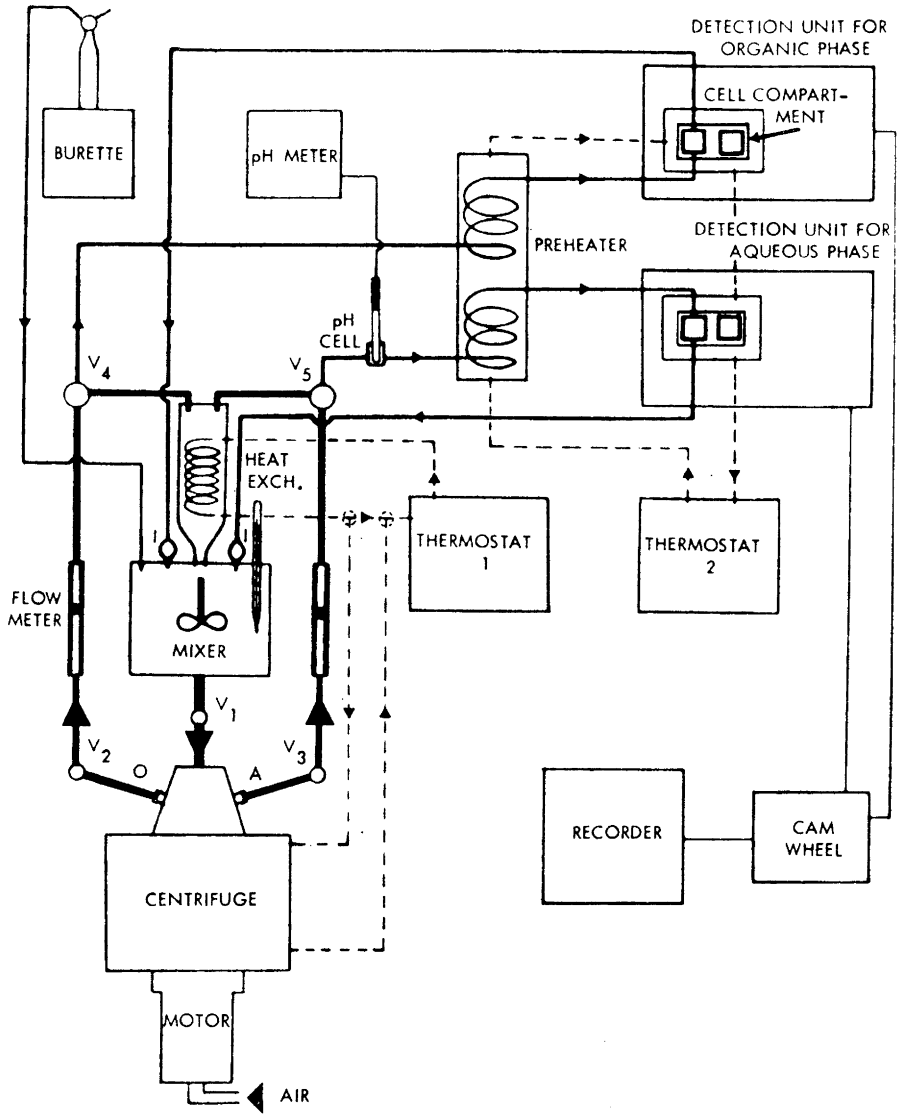

Fig. 1. The AKUFVE system for spectrophotometric detection. A and O are the aqueous and organic phase connections, respectively. I's are inspection glasses. V_1, V_2, and V_3 are valves for regulating the three main liquid flows. V_4 and V_5 are three-way stopcocks for regulating the side-streams to the detection units.

where [ ] means concentration, "org" refers to the organic phase and "aq" to the aqueous phase. In the spectrophotometric analysis the relationship

$$A = c \cdot \varepsilon \cdot d \qquad (2)$$

is valid, where A is the absorbance, c the concentration of the substance (M), ε its molar extinction coefficient (M^{-1} cm^{-1}) and d the thickness of the cell (cm). Combining these equations one obtains

$$k_d = \frac{A_{org}}{A_{aq}} \cdot \frac{\varepsilon_{aq}}{\varepsilon_{org}} \cdot \frac{d_{aq}}{d_{org}} \quad (3)$$

ε depends on ionic strength (I), pH and temperature (T). In order to determine $k_d(I,\mathrm{pH},T)$ calibration curves for the absorbance of HAA in the organic solvents and in the sodium perchlorate solutions must be obtained, and the corresponding ε-values be computed, before eqn. 3 can be applied for the calculation of k_d. In order to extend the measurable concentration region it is practical to use different cell length in the two phases.

EXPERIMENTAL

Chemicals. The acetylacetone was of pract. quality (Fluka); it was purified according to Rydberg.[5] The sodium perchlorate solutions were made by titration of concentrated $HClO_4$ (Merck *p.a.*) with 10 M NaOH (pH-Tamm). Benzene, toluene, xylene, cyclohexane, hexane, carbon tetrachloride, chloroform, and methylene chloride, were all *p.a.* (Merck). Gas chromatographic analysis showed that the xylene consisted of about 3 % *p*-, 83 % *m*-, and 14 % *o*-xylene. Mesitylene and ethyl benzene were *puriss.* (Fluka).

Selection of wavelengths. Acetylacetone has an absorption maximum at 273.5 nm in sodium perchlorate solutions. In the organic solvents used the maximum occurs between 270 and 273.5 nm. Normally the absorbance was measured at the absorption maximum. This was done for all solvents but benzene and its homologues and kerosene. These solvents absorb to a certain extent at 273 nm. Because the solubility of these solvents

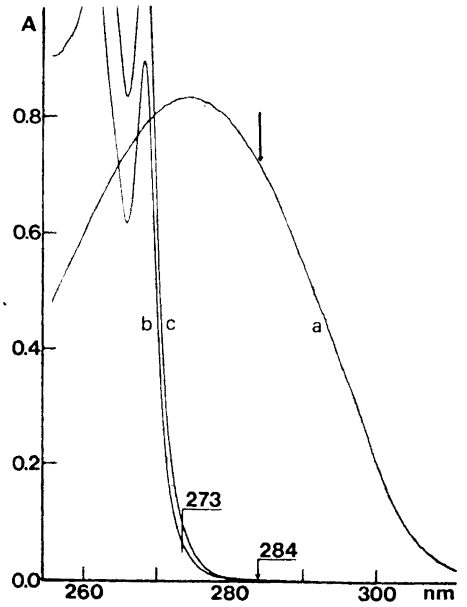

Fig. 2. Spectrum of (a) acetylacetone in 1 M $NaClO_4$ +0.001 M $HClO_4$, (b) 1 M $NaClO_4$+0.001 $HClO_4$ saturated with toluene at 5°C, and (c) same as (b) but at 40°C. The arrows indicate the wavelength chosen for quantitative determination of acetylacetone in the presence of toluene.

in sodium perchlorate varied with temperature and ionic strength it was necessary to measure the absorbance on the slope of the acetylacetone absorption peak, where the influence from the solvents was almost negligible (Fig. 2). Wavelengths chosen for the different systems are listed in Table 1.

After calibration curves for a system had been obtained, the spectrophotometer settings were not changed at any time until all experiments on the system had been finished. This is particularly important for measurements made on the slope of an absorption peak.

Apparatus. In the AKUFVE system (Fig. 1) equal volumes of organic and aqueous phases are brought into contact in a mixing chamber, from which the mixture flows down into the centrifuge, in which absolute phase separation [1,6] takes place. The pure light and heavy phases pass through identical arrangements. The main fraction of each phase flows through a flow meter and a heat exchanger back into the mixer. The heat exchanger and the cooling jacket around the centrifuge are connected to a thermostat, which removes the heat developed in the centrifuge. The thermostat can either be used to keep the temperature constant, or to allow the temperature to rise slowly during a run. A very accurate thermometer is placed in the mixer.

During an AKUFVE run different parameters can be changed, *e.g.* concentration of complexing agent, ionic strength, pH, and temperature. When starting a run, equal volumes of organic and aqueous phases (about 300 ml each) are introduced to the mixer, air pressure is applied to the centrifuge motor, the stirrer is started, and the valve V_1 between mixer and centrifuge opened. Both phases leaving the centrifuge must be clear and free from air bubbles, which can be accomplished by adjusting the throttling valves V_2 and V_3 if necessary. The temperature of the system is set on the desired value with the thermostat 1, and the temperature in the detection unit is set a few degrees higher with the thermostat 2. The three-way stopcocks V_4 and V_5 can now be opened enough to give the proper flow rate over the pre-heater to the cell compartments of the spectrophotometers, which are connected to the same thermostat. The cell compartments contain a reference cell and a flow-through cell from which the solution flows back to the mixer *via* inspection glasses where the flow rates can be checked.

The two phases leaving the centrifuge are saturated with respect to each other. If the temperature in the measuring part becomes lower than the temperature in mixer and centrifuge, oversaturation occurs, and droplets of the dissolved phase will precipitate in the previously clear phase. This would make spectrophotometric detection impossible. It is therefore necessary to keep the detection arrangement at a slightly higher temperature than mixer and centrifuge.

Two Metrohm burettes containing $NaClO_4$ and $HClO_4$ are connected to the mixer. The emf in the aqueous phase is measured with a glass electrode in the side-stream, where the flow rate is slow enough to avoid disturbances in the measurement.[4] When the aqueous phase is the lighter one it is necessary to interchange the phase output connections on the centrifuge.

The centrifuge is made of titanium. Tube connections, valves and some parts in the mixer are made of stainless steel. The three-way stopcocks, pH-cell, mixer top and bottom, and all tubes are made of teflon. Heat exchangers, mixer walls, flowmeters and flow-through cells are made of glass. The centrifuge is driven by an air compression motor, which gives the centrifuge bowl a rotation speed of up to 18 000 rpm.

The absorption measurements are made with Beckman double beam spectrophotometers. For simultaneous registration of both phases, two such spectrometers are used, connected to a Beckman 10-inch recorder *via* a cam wheel switch, which provides recording in 30 sec intervals alternating between the two spectrometers.

AKUFVE RUNS

At high pH-values, acetylacetone dissociates ($k_a = 10^{-8.9}$). The AA^- ion absorbs stronger than undissociated HAA; the maximum value of ε for AA^- occurs at 290 nm, and is about 14 times higher than for undissociated HAA. Even at 273.5 nm, where HAA has its ε-maximum in aqueous solution, the

ε-value of AA^- is about 7 times that of undissociated HAA. It is therefore necessary to make all distribution measurements of HAA in slightly acidic solutions (pH<6) in order to avoid interference from AA^- in the spectrophotometric measurements.

When the AKUFVE apparatus works properly, *i.e.* the temperature is the desired one and two absolutely pure phases pass through the detection cells, the recorder is started and gives zero values of the absorbances of both phases, indicated by A_{org}^0 and A_{aq}^0 in Fig. 3. This registration is continued for some time, until constant A^0 values are reached. After changing the conditions in the system, as HAA concentration, ionic strength or temperature, new absorbance values A_{org}' and A_{aq}' are obtained, see Fig. 3. Because the

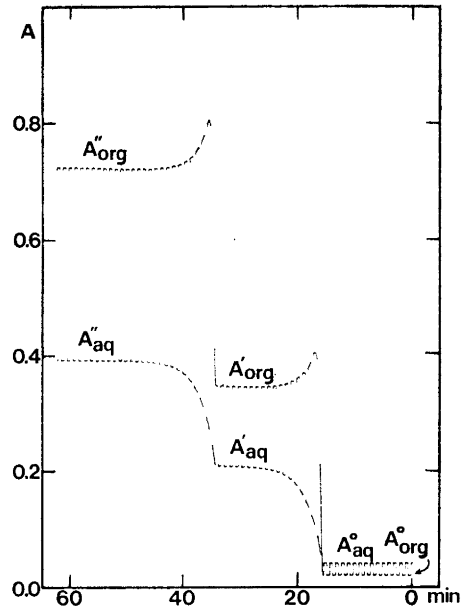

Fig. 3. Automatically recorded rate of approach to distribution equilibrium for acetylacetone in the system toluene-1 M $NaClO_4$+0.001 M $HClO_4$ at 25°C. For each phase A^0 is absorbance without HAA, A' after one addition, and A'' after two additions of HAA.

corresponding ε-values are known from calibration runs, k_d can be calculated from these measured values, using eqn. 3, where $A_{org}=A_{org}'-A_{org}^0$, and $A_{aq}=A_{aq}'-A_{aq}^0$. Further changes give A_{org}'' and A_{aq}'', *etc.*

HAA-concentration dependence. When the k_d dependence on the concentration of HAA was to be studied at a certain ionic strength, pH, and temperature, the A_{org}^0 and A_{aq}^0 were recorded and a small volume (0.2–2.0 ml) of 0.1 M HAA in the organic solvent was then added to the mixer. The absorbance was continuously recorded, reaching the equilibrium values indicated A_{org}' and A_{aq}' in Fig. 3.

By successive additions of HAA, a series of A_{org} and A_{aq} values was obtained, from which k_d was computed as described above. The HAA concentration was increased in this way until one of the phases had reached an absorbance close to 2.0.

If k_d is independent of [HAA] (see below), k_d can be calculated in 6 different ways after 3 HAA additions, and in $\frac{1}{2}n(n+1)$ ways after n additions. This improves the reliability of the calculated k_d-values.

Ionic strength dependence. When the dependence of k_d on the ionic strength (I) was to be studied at constant pH and temperature, this was done by adding a very concentrated $NaClO_4$ solution to the mixer which contained 0.001 M $HClO_4$ as aqueous phase from the beginning. Due to the limited volume of the mixer, an I-value of 1.0 could not be achieved in this way. Therefore AKUFVE runs were normally done at different but constant ionic strengths, while other parameters like concentration of HAA or temperature were varied.

Temperature dependence. When the temperature dependence of k_d was studied, the run was started up as described earlier, but the two thermostats were adjusted to different temperatures before the A^0 absorbances were recorded. Thermostat 1, which was connected to mixer and centrifuge, was set on a value slightly lower than the temperature wanted in the mixer. The difference in temperature between mixer and thermostat was about 2 degrees at room temperature and about 5 degrees at 10°C in the mixer. Thermostat 2, which was connected to the detection units, was set at the highest temperature that was to be reached in the mixer during the run, thus eliminating variations in the ε-value during the experiment.

When the temperatures in the mixer and the cells became constant, the zero absorbances were recorded for about half an hour to see that A_{org}^0 and A_{aq}^0 were constant. Then a proper amount of HAA was added to the mixer. When it was seen on the recorder that equilibrium had been reached, the temperature of mixer and centrifuge was slowly raised. This was best done by switching off thermostat 1, so that only the pump worked. The heat developed in the centrifuge then was enough to raise the temperature slowly in the mixer. This temperature rise could be varied by changing the volume of the water in the thermostat, or by changing the speed of the centrifuge. Usually a rise of 1 degree per 10—15 min occurred.

There were some limitations to this technique. At temperatures over 45°C, small air bubbles were formed in the detection cells after some time. In the flow-through cells they were removed with the liquid flow, which went upwards through the cell, but in the reference cell the bubbles stuck to the cell walls and changed the absorbance.

The flow rate in the side-stream always had to be so slow, that the liquid reached the detection cell with the right temperature. With a temperature difference of 25°C between mixer and detection cell, the delay was about 2 min, but with a temperature difference of 10°C, it was possible to increase the flow rate to give a delay of only 30 sec.

Experiments made by ordinary shaking technique. When the ionic strength was chosen to be 1 M, it was not possible to reach pH-values below 1 by adding 1 M $HClO_4$ because of the limited liquid volume of the AKUFVE system. When studying the dependence of k_d at high acidities (Table 2), it was therefore necessary to complement the AKUFVE runs by experiments using manual shaking technique: A lot of glass ampoules with equal amount of organic and aqueous phase, with HAA, and with pH between 0 and 3, and I = 1 M ($NaClO_4$), were shaken in a thermostated room for 2 h. Then the phases were separated, centrifuged, and analysed spectrophotometrically for HAA. Because the absorbance depended on pH at pH < 3, calibration curves for each pH had to be made in advance.

Similar experiments were also made with 0.001 M $HClO_4$ and several other organic solvents (Table 1).

RESULTS

For ionic strength between 0.001 and 1 M, k_d was found to be independent of the HAA concentration in the measured concentration range, 0.03—3 mM, for all solvent systems studied. Higher concentrations could not be directly measured spectrophotometrically because of the high absorbancy. The k_d values in 0.001 M $HClO_4$ are listed in Table 1.

The dependence of k_d on ionic strength is shown in Fig. 4. For the organic solvents benzene and chloroform k_d was measured both as a function of acidity and ionic strength in the concentration region 0.001—1 M (Table 2). It is obvious that the cation had a considerable influence on the distribution

Table 1. Wavelengths chosen for the different systems and the measured k_d values at 25°C using 0.001 M $HClO_4$. Manual experiments are marked *a*; otherwise the AKUFVE technique was used. When the absorbance was measured on the maximum this is marked *b*.

Solvent	λ_{org} nm	λ_{aq} nm	k_d
Benzene	278	278	5.93 ± 0.02
Toluene	284	284	4.57 ± 0.02
Xylene	288	288	3.69 ± 0.01
Mesitylene	290	290	2.73 ± 0.02
Ethyl benzene	286	286	3.31 ± 0.02
Cyclohexane [a,b]	270.5	273.5	1.03 ± 0.01
Hexane [a,b]	270	273.5	0.95 ± 0.01
Kerosene [a]	290	290	1.00 ± 0.01
Carbon tetrachloride [a,b]	272.5	273.5	3.31 ± 0.01
Chloroform [b]	273.5	273.5	23.80 ± 0.30
Methylene chloride [a,b]	273	273.5	22.50 ± 0.50

Table 2. k_d for HAA in the chloroform-water and benzene-water systems at various I ($NaClO_4$+$HClO_4$) and pH($HClO_4$) at 25°C. Manual experiments are marked *a*; otherwise the AKUFVE-technique was used.

$[H^+]$	Organic solvent: $CHCl_3$			Organic solvent: C_6H_6		
M	I = 0.001	I = 0.1	I = 1	I = 0.001	I = 0.1	I = 1
0.001	23.8 ± 0.3	23.3 ± 0.4 (23.5)[7]	19.5 ± 0.3	5.93 ± 0.02	5.75 ± 0.01 (5.75)[8]	4.80 ± 0.02
0.1	—	20.7 ± 0.4[a]	18.1 ± 0.3[a]	—	5.43 ± 0.03[a]	4.55 ± 0.03[a]
1	—	—	14.3 ± 0.3[a] (16.2)[10]	—	—	3.63 ± 0.02[a] (3.49)[10]

constant. Fig. 4 also shows the dependence of k_d on acidity for benzene and chloroform. The results agree closely with those found by Rydberg [5,7] Rudenko and Stary,[8] Salvinien and Garrigues,[9] Peshkova and Peng-Ang,[10] and fairly well with values obtained by Wakahayashi *et al.*[11]

The temperature dependence was studied for systems with benzene, toluene, xylene, mesitylene, ethyl benzene, and chloroform as organic phase and sodium perchlorate solutions of different ionic strength as aqueous phase, buffered to pH 3 with $HClO_4$. For the benzene, toluene, xylene, mesitylene and ethyl benzene systems no marked dependence of temperature was found between +20 and +40°C.

k_d for the $CHCl_3$ system, however, decreased with increasing temperature as is seen from Fig. 5, where log k_d is plotted as a function of T^{-1}. The filled symbols indicate three consecutive runs on the AKUFVE, starting at 15°C

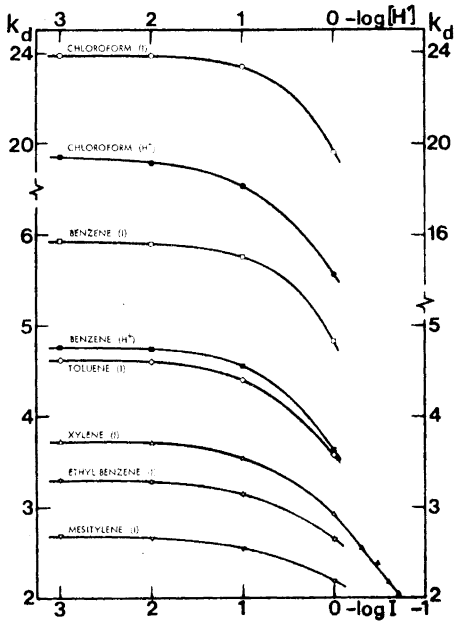

Fig. 4. Dependence of k_d on (a) ionic strength in $NaClO_4+0.001$ M $HClO_4$ (open symbols, marked *I*), and (b) on acidity in 1 M $NaClO_4+HClO_4$ (filled symbols, marked H^+).

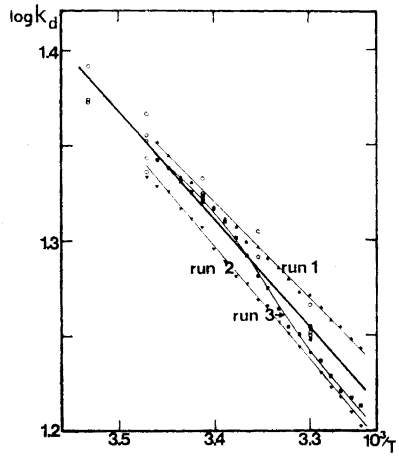

Fig. 5. Dependence of k_d on temperature (*T*) for the system chloroform-1 M $NaClO_4+0.001$ M $HClO_4$ at temperatures between 10°C and 35°C.

and ending at 35°C. The circles are values from AKUFVE runs at constant temperature, where other parameters were varied. The large scatter is due to the very low absorbance in the aqueous phase (1 cm cell length), while the absorbance was very high in the organic phase (0.1 cm cell length). The difference between runs 1 and 2 might have been due to a systematic error. It is still small compared with errors commonly obtained by conventional technique, and can probably be further decreased. The reason for the S-formed shape of run 3 is unknown.

By use of a least squares computer program considering all points, the heavy line was obtained. With the well known relationship

$$\log k_d = -\frac{\Delta H}{RT \ln 10} + \frac{\Delta S}{R \ln 10} \qquad (4)$$

the slope of the heavy line in Fig. 5 gives $\Delta H = -2.62 \pm 0.16$ kcal·mole^{-1} and $\Delta S = -2.93 \pm 0.19$ cal·mole^{-1} (e.u.).

For CH_2Cl_2 k_d was also found to be temperature dependent, though to a less extent than for $CHCl_3$ ($k_d \simeq 20$ at 3°C, and 16 at 25°C). No temperature dependence was found with CCl_4 ($k_d \simeq 2.9$ at 3—25°C).

DISCUSSION

From Table 1 it can be seen that the distribution constant k_d decreases with decreasing aromatic and increasing aliphatic character of the organic solvent. This is clearly demonstrated in Fig. 6, where k_d is plotted against the number of methyl groups in substituted benzene, $C_6H_{6-n}(CH_3)_n$.

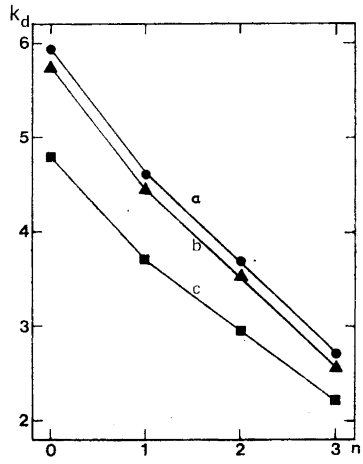

Fig. 6. Change in k_d with increasing number of methyl groups (n) in substituted benzene, $C_6H_{6-n}(CH_3)_n$, at 25°C and at I = 0.001 in (a), 0.1 in (b), and 1.0 M in (c).

In all two-phase systems investigated by us, k_d decreased with increasing ionic strength and acidity of the aqueous phase (Fig. 4). This is in line with the increasing solubility of HAA in salted and acid aqueous solutions, see Table 3.

Table 3. Solubility in g/100 ml of acetylacetone in aqueous solutions of various ionic strength and acidity at 25°C.

Concentration	0 M	1 M	2.5 M	5 M
$NaClO_4$	19.2	35.6	55	∞
$HClO_4$	19.2	48.8	∞	∞

The k_d values in Table 1 can be roughly divided into three groups, with values around 1 (hexane, kerosene, and cyclohexane), 3—6 (in increasing order mesitylene, carbon tetrachloride, ethyl benzene, xylene, toluene, and benzene), and around 23 (methylene chloride and chloroform). For the first group the dielectric constants are ≤ 2, for the second group 2.2—2.4, and for the third group 5—9. Because acetylacetone is polar (dielectric constant 25) one expects it to interact with other polar solvents, and accordingly be more easily dissolved in them, as Table 1 indicates.

Table 4. NMR measurements on pure acetylacetone, and pure organic solvents, and solutions containing 20 % acetylacetone in these solvents.

Solution at 32°C	Enol %	Keto %	H in enol OH, cps	H in solvent, cps	Ratio $-OH/-CH=$
HAA	75	25	924	—	1.0
HAA in CCl_4	93	7	915	—	1.0
$CHCl_3$				436	
HAA in $CHCl_3$	83	17	825	445	0.5
HAA in $CHCl_3$ at 60°C	66	34	812	441	0.8
CH_2Cl_2				320	
HAA in CH_2Cl_2	81	19	900	323	0.9
C_6H_6				429	
HAA in C_6H_6	74	26	945	431	0.9

In Table 4 some NMR measurements on acetylacetone solutions are recorded. HAA in the enol form is characterized by one HO-group for each =CH- group. As expected, the ratio HO-/=CH- is about 1 in the non-polar solvents CCl_4 and C_6H_6. However, in $CHCl_3$ the ratio is only 0.5 (32°C), indicating a change in the surrounding of the enol group. The chemical shift from about 920 to about 820 cps indicates a weakening of the enol hydrogen bond. A chemical shift is also observed for the hydrogen in $CHCl_3$ when HAA is dissolved. The conclusion must be drawn that $CHCl_3$ and HAA interact with each other over the hydrogen in $CHCl_3$ and in the neighbourhood of the enol-group in HAA. Probably the intramolecular hydrogen bond of the enolic form is changed by the formation of a new hydrogen bond between the carbonyl group and the chloroform hydrogen.

Increasing the temperature leads to an increase in the HO-/=CH- ratio, indicating a dissociation of the HAA—$CHCl_3$ bond. Since k_d also decreases with temperature, it may be assumed that "unsolvated" HAA is less soluble in $CHCl_3$ than is "solvated" HAA.

The assumption that a dipole-dipole bond is formed between HAA and $CHCl_3$, as well as between HAA and CH_2Cl_2, is further supported by the fact that k_d is temperature dependent in these systems only. Our investigation indicates that there is no effect of temperature on k_d for benzene, and a ΔS value of about 3 e.u. can be estimated. This is about 6 e.u. higher than that for the $CHCl_3$ system ($\Delta S = -3$ e.u.), which indicates that a more ordered structure is formed in the $CHCl_3$ phase, and a less ordered structure in the C_6H_6 phase, when HAA is extracted into these solvents from aqueous solutions.

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REFERENCES

1. Rydberg, J. *Acta Chem. Scand.* **23** (1969) 647. (Part I of this series).
2. Reinhardt, H. and Rydberg, J. In Dyrssen, D., Liljenzin, J. O. and Rydberg, J., Eds., *Solvent Extraction Chemistry*, North-Holland Publ. Co. 1967, p. 612.
3. Liljenzin, J. O., Stary, J. and Rydberg, J. *Proc. Intern. Conf. Solvent Extraction Chemistry*, Jerusalem 1968.
4. Andersson, C., Andersson, S., Liljenzin, J. O., Reinhardt, H. and Rydberg, J. *Acta Chem. Scand.* **23** (1969) 2781. (Part III).
5. Rydberg, J. *Svensk Kem. Tidskr.* **62** (1950) 179.
6. Reinhardt, H. and Rydberg, J. *Acta Chem. Scand.* **23** (1969) 2773. (Part II).
7. Rydberg, J. *Svensk Kem. Tidskr.* **65** (1953) 37.
8. Rudenko, N. P. and Stary, J. *Trudy Kom. Analit. Khim.* **9** (1958) 28.
9. Salvinien, J. and Garrigues, C. *Compt. Rend.* **242** (1956) 504.
10. Peshkova, V. M. and Peng-Ang. *Zh. Neorg. Khim.* **6** (1961) 2082.
11. Wakahayashi, S., Oki, T., Omori, T. and Suzuki, N. *J. Inorg. Nucl. Chem.* **26** (1964) 2255.

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