

Solvent Extraction Studies by the AKUFVE Method

III. Experimental Technique for Equilibrium Studies Using Radioactive Tracers

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An experimental technique for the investigation of complex formation in liquid-liquid extraction systems by distribution measurements using the AKUFVE apparatus has been developed. Its main advantages are great speed and precision. An experimental system with radiometric detectors and a datalogging unit is described. The experimental procedure is discussed in detail with reference to experiments with the chemical system copper(II)-acetylaceton-benzene-1 M sodium perchlorate and experimental results are given. Future development of the measuring system and the technique is outlined.

The study of complex formation in solution, based on measurement of distribution factors in liquid-liquid extraction systems, has attracted great interest during the last two decades. The experiments are usually carried out by mixing an organic and an aqueous phase of known compositions until equilibrium is established, and analysing the two phases after separation. These batchwise experiments are laborious and need advanced sampling and analysing techniques to avoid large errors. The number of experiments needed is great, measurements at temperatures considerably different from room temperature are often quite difficult, and studies of reaction kinetics are usually limited to slow processes.

The recently developed AKUFVE apparatus,^{1,2} see Fig. 1, removes many of these limitations. In this apparatus, the mixing and separation goes on continuously while the phases are circulating. The system may be regarded as two pure phases in mixing equilibrium. This makes it possible to measure the concentration of different solutes by suitable liquid flow detectors in the pure phases. After a change in the conditions, *e.g.* by addition of a reagent to the mixing chamber, new values of the concentrations can be measured as soon as mixing equilibrium is established. Each change in the conditions corresponds to a conventional "test-tube experiment". If reaction kinetics

are not too fast, the concentrations can be measured as a function of time. The experiments are easily performed at different temperatures.

This paper describes an AKUFVE system with radiometric detectors, instrumentation, and datalogging unit, and its use for measurements of distribution ratios for metals in liquid-liquid extraction systems with the aid of radioactive tracers. Experimental details given refer to experiments with the system copper(II)-acetylaceton-benzene-1 M sodium perchlorate.

1. DETERMINATION OF EQUILIBRIUM CONSTANTS BY DISTRIBUTION MEASUREMENTS

General surveys of the theory for the investigation of complex equilibria in solutions by distribution measurements have been given by several authors; *cf.*, *e.g.*, Refs. 3–6. If we only consider the complex formation between a metal M^{N+} and a chelating agent, the weak acid HA, complexes of the general composition.



may be formed in the two-phase H_2O -Org system. Using low concentrations and constant ionic strength, [Org] and $[H_2O]$ may be regarded as constant. If only uncharged complexes are extracted the distribution ratio D_M of the metal between the organic (index org) and the aqueous (index aq) phases then becomes (omitting the charges on the ions and using [] for concentrations)⁴

$$D_M = \frac{\sum_m \sum_x m \beta_{m,x,mN} \lambda_{m,x,mN} [M]_{aq}^m [HA]_{aq}^x [H]_{aq}^{-mN}}{\sum_m \sum_x m \beta_{m,x,y} [M]_{aq}^m [HA]_{aq}^x [H]_{aq}^{-y}} \quad (1)$$

where $x = n + r$ and $y = n + p$, and the distribution constants λ and the stability constants β are defined in the usual way.

From the determination of D_M as a function of the concentrations of the different reactants in eqn. 1, the predominating complexes may be identified (*cf.*, *e.g.*, Refs. 3,4) and the corresponding λ and β values calculated by one of the different methods given in the literature (*cf.*, *e.g.*, Refs. 5,7,8).

In the technique described in this paper, D_M is determined with the aid of radioactive tracers. The ratio between the radioactivities in the organic and aqueous phases is directly proportional to D_M . If D_M is found to be independent of the metal concentration, only mononuclear complexes ($m=1$) have to be considered.

[HA] is changed by addition from a stock solution. If the total amount of HA, b_{HA} , is much greater than the total amount of metal, the fraction of HA complexed by M can be neglected. This simplifies the calculations and $[HA]_{aq}$ can be determined from the relation

$$[HA]_{aq} = b_{HA} / (k_d V_{org} + V_{aq} + V_{aq} k_a [H]_{aq}^{-1}) \quad (2)$$

where k_a is the acid dissociation constant of HA, k_d is the distribution constant of HA between the two liquid phases, and V_{org} and V_{aq} are the organic and aqueous phase volumes. [H] is measured in the aqueous phase using, *e.g.*, a glass electrode.

2. USE OF THE AKUFVE APPARATUS TO DETERMINE D_M ([M], [HA], [H], T)

We shall here consider the practical aspects of using the AKUFVE for determination of D_M as a function of the temperature and the concentrations of the different reactants in the solution, *e.g.* [M], [HA], and [H].

Fig. 1 shows a schematic picture of the AKUFVE liquid flow system.* It has a total liquid volume of about 1200 ml, and the volume of the mixer is about 1000 ml. After the centrifuge has run up in speed and about 450 ml of each phase has been added to the mixing chamber, the stirrer is started and valve 1 is adjusted to obtain suitable flow rates, normally 500–1500 ml/

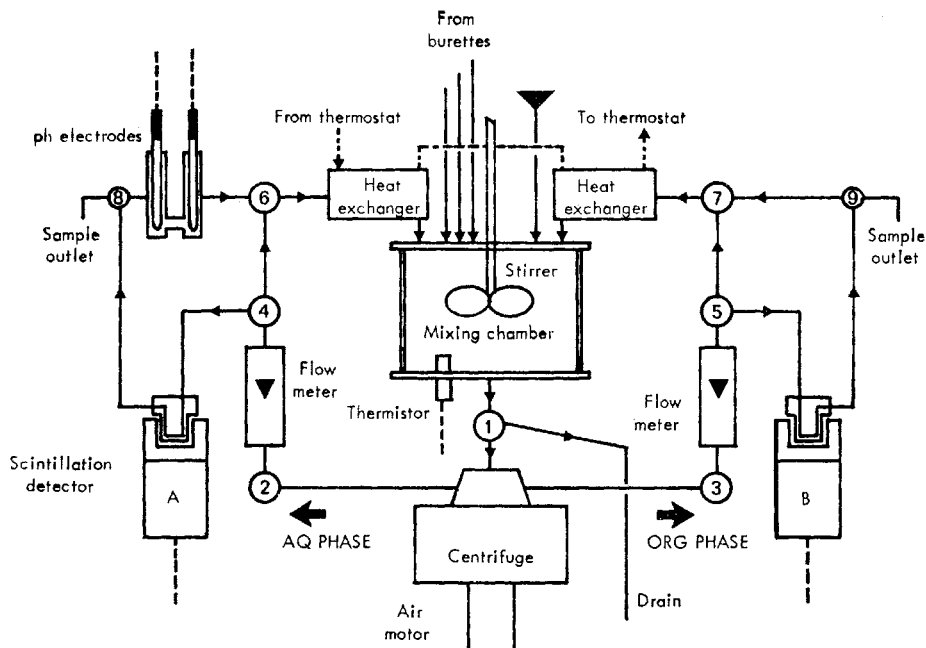


Fig. 1. Diagram of the AKUFVE liquid flow system. ○ indicate valves.

min for each phase. By adjusting valves 2 and 3, and the speed of the centrifuge, pure phases are normally obtained. The phase purity is checked by visual observation at the flow meters.² Not until the phases appear absolutely clear are they allowed to pass through the detector system. This is accomplished by switching the three-way valves 4–7.

The temperature of the system is kept constant with a thermostat. The thermostat liquid is ethanol to electrically insulate the thermostat from the

* The commercial unit made by Incentive Research and Development AB, Stockholm, differs in some respects from the unit described here.

liquid flow system; ground currents may otherwise disturb the pH-measurements. The temperature is measured with a calibrated thermistor in the mixing chamber. The practical temperature range is 10–60°C.

At elevated temperatures, the evaporation of volatile solvents must be considered. In experiments lasting many hours, losses of ~100 ml may occur. Because the phase volumes must be known throughout the experiment it may be necessary to take out samples and analyse them for the complexing agent concentration. V_{org} can then be calculated from eqn. 2 assuming V_{aq} is known from the added volumes.

Liquid reagents, *e.g.* solutions of M, HA, HClO₄, NaOH, *etc.* can be added to the mixing chamber with pipettes or from motor-driven burettes (*e.g.* Metrohm Dosimat E415P). These burettes are equipped with electrical transducers for external registration of the added volumes. With the flow rates and phase volumes mentioned it takes 30–120 sec to reach mixing equilibrium.¹

When the operation of the liquid flow system is satisfactory, *i.e.* constant temperature and absolutely pure phases^{1,2} flowing through the detectors, a solution corresponding to about 50 μCi of a gamma-emitting radioisotope of the metal to be investigated is added. This activity is sufficient for measuring distribution ratios in the range 10^{-3} to 10^{+3} with good precision, using well type scintillation crystals and flow cells with a volume of about 10 ml.

Extreme radiochemical purity is required for the radioactive tracer. Even small amounts of radioactive impurities will influence the D_{M} values. The purity is most efficiently checked by gamma-ray spectrometry and half-life determinations on samples from the phases taken at both high and low D_{M} values during the experiment. The radioactivity measurements from which D_{M} is calculated involve several factors which influence the precision. These are discussed in detail in section 3.

The most common "distribution curves" involve measurement of D_{M} as a function of the free ligand concentration, [A], keeping temperature, ionic strength, *etc.* constant. Such curves can be obtained as follows. After addition of the complexing agent HA from a stock solution, the hydrogen ion concentration is changed in steps by additions of base or acid from the burettes. It is measured with a glass-calomel combination electrode, which is calibrated during the distribution experiment. This involves special problems which are discussed in detail in section 4.

All values are registered with a datalogging unit, described in section 5. The time for a complete measuring cycle depends on the radioactivity counting time chosen and is between 15 and 150 sec. At each hydrogen ion concentration, several measuring cycles, with at least two after reaching equilibrium, are carried out. If chemical equilibrium is rapidly established, a distribution curve with 50 to 100 equilibrium points can be obtained in a few hours. When the pH range of interest has been investigated, the total amount of complexing agent or metal is changed by addition from the stock solution and the procedure is repeated to obtain the next curve.

If one AKUFVE apparatus is to be used for experiments with different radioactive tracers, complete decontamination between the experiments is essential because remaining activity may otherwise distribute between the

phases during the subsequent experiments and confuse the results. Radioactive tracers with comparatively short half-lives, *i.e.* of the order of some hours to a week, is therefore to be preferred. Because the materials in contact with the solutions are glass, teflon, and titanium, cleaning can be done with concentrated acids. Detergents should be avoided, because they may contain complexing agents which are difficult to wash out, and surface active agents which may interfere with the functioning of the centrifuge.

3. DETERMINATION OF DISTRIBUTION RATIOS BY RADIOACTIVITY MEASUREMENTS

In the AKUFVE experiments it is convenient to use gamma or hard beta emitting isotopes for the measurement of D_M . In order to evaluate the precision in these measurements it is necessary to consider the influence of the background activities R_0 , of the measuring efficiencies ϕ , of the amount of radioactive tracer added (disintegration rate Q), and of the detector arrangement. The distribution ratio D_M is given by

$$D_M = \frac{(R_{m, \text{org}} - R_{0, \text{org}})v_{\text{aq}}\phi_{\text{aq}}}{(R_{m, \text{aq}} - R_{0, \text{aq}})v_{\text{org}}\phi_{\text{org}}} \quad (3)$$

v_{org} and v_{aq} are the detector cell volumes (not to be confused with V_{org} and V_{aq} , which are the total phase volumes in the system) and $R_{m, \text{org}}$ and $R_{m, \text{aq}}$ are the measured radioactivities. By suitable choice of measuring time and of the amount of tracer added, the relative error in R_m can be made much smaller than the relative errors in R_0 , v and ϕ . v_{org} and v_{aq} are constants provided that the detector flow cells are without traps or pockets. The same applies to ϕ_{org} and ϕ_{aq} for a given radioactive tracer and chemical system. Thus, the factors $v_{\text{org}}\phi_{\text{org}}$ and $v_{\text{aq}}\phi_{\text{aq}}$ can be regarded as constants for a given chemical system and may be accurately determined. The main source of error in D_M will then be $R_{0, \text{org}}$ and $R_{0, \text{aq}}$. Their relative importance depends on the value of D_M .

It is of interest to evaluate the error in D_M which is introduced by neglecting $R_{0, \text{org}}$ and $R_{0, \text{aq}}$. We define

$$D_M' = \frac{R_{m, \text{org}}v_{\text{aq}}\phi_{\text{aq}}}{R_{m, \text{aq}}v_{\text{org}}\phi_{\text{org}}} \quad (4)$$

Rearrangement of eqn. 3 gives

$$D_M = \frac{(1 - R_{0, \text{org}}/R_{m, \text{org}}) R_{m, \text{org}}v_{\text{aq}}\phi_{\text{aq}}}{(1 - R_{0, \text{aq}}/R_{m, \text{aq}}) R_{m, \text{aq}}v_{\text{org}}\phi_{\text{org}}} \quad (5)$$

The relative error a introduced by using D_M' instead of D_M is

$$a = 1 - D_M'/D_M \quad \text{for } D_M > 1 \quad (6)$$

$$a = D_M'/D_M - 1 \quad \text{for } D_M < 1 \quad (7)$$

The maximum and minimum D_M values that can be measured to within the maximum allowed relative error, a , when the background activities are neglected, can now be estimated

$$D_M(a)_{\text{max}} \approx \frac{aQ v_{\text{aq}} \phi_{\text{aq}} - R_{0, \text{aq}} V_{\text{aq}}}{(1-a) V_{\text{org}} R_{0, \text{org}}} \quad (8)$$

$$D_M(a)_{\min} \approx \frac{a R_{0, \text{org}} V_{\text{aq}}}{(1+a) (Q V_{\text{org}} \varphi_{\text{org}} - a R_{0, \text{org}} V_{\text{org}})} \quad (9)$$

As R_0 is usually a function of Q (see below) the increase in the measurable range of D_M values with increasing Q is limited. To further increase either this range, or the precision, it is desirable to determine the background values.

The experimental background in one phase R_0 is the sum of the contributions from several sources

$$R_0 = R_n + R_s + R_a + R_t \quad (10)$$

R_n is the natural background which is always encountered in radioactivity measurements. It depends on the volume of the detector crystal (not the flow cell) and on the shielding around the detector. For a given detector and shield it is a constant, which can be accurately determined from measurements before the start of an AKUFVE experiment.

R_s is the increase in background which is caused by the radiation from the radioactive tracer in the AKUFVE apparatus outside the detector shield. If the volumes of the pure phases outside the mixer and the centrifuge are small, close together in space or well shielded, R_s is independent of D_M . R_s for a given gamma ray energy, E_γ , can then be considered as a function of the shielding efficiency, $k_{\text{sh}}(E_\gamma)$, the geometrical arrangement of AKUFVE and detectors, a factor k_g , and the total disintegration rate, Q .

$$R_s = k_{\text{sh}}(E_\gamma) k_g Q \quad (11)$$

R_s can be calculated from measurements on a sample of the actual tracer isotope, with known disintegration rate, placed in different significant positions, *e.g.* at the centrifuge, the mixer, *etc.* These measurements are weighted with the volume fractions present in these places during the actual experiment and multiplied by the disintegration ratio between the sample and Q to obtain R_s . R_s can also be estimated from the background measured at the beginning of the actual experiment with the tracer put into the AKUFVE apparatus, but before the solutions are passed through the detector cells.

R_a is the activity from tracer adsorbed in the flow cell. It depends on the metal concentration, the charge of the metal, the hydrogen ion concentration, the complexing agent and its concentration, the temperature, the surface material, and other experimental conditions. It is usually different in the two phases. In many cases it is possible to choose experimental conditions and material so that R_a is negligible compared with $R_n + R_s$. If this is not the case it is possible to use a detector arrangement by which R_a may be evaluated during the experiment.

R_t is the contribution from small volumes of solution which may be trapped in pockets inside the cell and do not take part in the circulation. Their activity is changed very slowly by diffusion of the tracer into or out of the pockets. If mistakes are made when adjusting the AKUFVE to obtain pure phases, small drops of the other phase may temporarily occur and adhere to the cell walls. These will then give an effect similar to that caused by the pockets. R_t is a function of the cell construction, and of Q , and may vary in an

unpredictable way during an experiment. It must therefore be minimized or eliminated by suitable cell construction.

The background values $R_{0, \text{org}}$ and $R_{0, \text{aq}}$ should be determined at regular intervals during an experiment. This can be done in several ways.

(1) When the D_M value is low or high, samples are taken from the pure phases and equal volumes of these are counted in an external counting device. For the external measurements, ϕ is constant and the background r_0 can be determined without difficulty. The relation between the externally measured activities from the two samples, r , and the AKUFVE measurements R at the time when the samples were taken is then

$$\frac{(R_{m, \text{org}} - R_{0, \text{org}}) \phi_{\text{aq}} v_{\text{aq}}}{(R_{m, \text{aq}} - R_{0, \text{aq}}) \phi_{\text{org}} v_{\text{org}}} = \frac{r_{\text{org}} - r_0}{r_{\text{aq}} - r_0} \quad (12)$$

For low D_M values $R_{0, \text{aq}}$ can be neglected in comparison with $R_{m, \text{aq}}$ and $R_{0, \text{org}}$ can be calculated. For high D_M values $R_{0, \text{aq}}$ can be neglected and $R_{0, \text{aq}}$ calculated in the same way.

(2) The R_0 values may be directly measured by flushing the cell with an inactive solution of otherwise identical composition as the active one, provided that the amount of radioactive tracer adsorbed and trapped in the flow cell is unchanged by this procedure. Stopcocks may be inserted immediately before and after the cell for this purpose. The method is tedious and may introduce new errors, but it is easy to carry out.

The R_0 values determined in this manner can then be used to evaluate $R_a + R_t$ from the previously determined values of R_n and R_s , using eqn. 10. From the determinations of R_a the value of R_t can be estimated. If R_t is negligible R_a can be calculated from R_0 . Values between determinations are estimated by linear interpolation.

Measuring system used in the experiments. As pointed out above, it is convenient to use gamma or hard beta emitting isotopes. These are measured with flow cells, which are placed in well type NaI(Tl) scintillation crystals mounted on Landis & Gyr EPQ3. 1 detectors. The detectors are supplied with high voltage from Landis & Gyr EES1e units. Each flow cell and detector is enclosed in a 7 cm thick lead shield. The cells have an efficient volume of 10 ml. When a larger cell volume can be tolerated, a very simple flow cell can be made by winding a few turns of, e.g., teflon tubing around the scintillation crystal and fixing it in position. To obtain the same ϕv factor, the volume must be about three times larger than that of the well type cell. This teflon tubing cell type eliminates probably most of the pocket problem.

As shown in Fig. 5, the detector signals pass two prescalers, Landis & Gyr ELB5, where they are scaled by a factor of 1, 10, or 100, and are then fed to a Picker Nuclear "Dual Rate computer", comprising a timer with preset time facility, two independent 5-decade scalers, and a cycle index. The maximum counting rate for less than one percent dead time loss is about 10^6 cpm. With the arrangement described this corresponds to a total activity of about 100 μCi in the system.

4. DETERMINATION OF HYDROGEN ION CONCENTRATIONS

Knowledge of the hydrogen ion concentration in the aqueous phase is essential for the calculation of the free ligand concentration in the types of experiments discussed. The determination is made by measuring the electromotive force between an electrode, reversible to hydrogen ion, in the sample solution, and a reference electrode connected to the sample solution through a salt bridge. For continuous measurements in flowing liquids, a glass electrode with a built-in calomel reference electrode is preferable because of its rugged

construction, rapid response, and easy handling. It also has the salt bridge outlet close to the active glass surface, which minimizes the influence of the liquid flow on the emf.

At constant ionic strength, the hydrogen ion activity factor is approximately constant, and the emf, E , of the electrode combination is given by

$$E = E_{\text{H}}^{\circ} + \eta \frac{RT}{F} \ln[\text{H}^+] - E_j \quad (13)$$

E_{H}° is the potential difference between the reference electrode and the glass electrode in the standard state. E_j is the liquid-junction and asymmetry potential. η is an ideality factor for the electrode.* In a given solution E_j is approximately constant in the pH ** range 2–10 and may be included in E_{H}° .

When 1 M sodium perchlorate is used as ionic medium in the experiments, a salt bridge with potassium chloride solution is impractical due to precipitation of potassium perchlorate which gives an unstable junction potential. The use of 1 M sodium perchlorate in the reference electrode gives satisfactory results. In the electrodes used (Radiometer GK2025C), the salt bridge is in direct contact with the solid calomel. The substitution of potassium chloride for sodium perchlorate gives an unsymmetrical electrode combination. The asymmetry can usually not be compensated for on an ordinary pH-meter, which makes it impossible to read the pH directly. The emf must therefore be measured, and the hydrogen ion concentration calculated from eqn. 1. E_{H}° , including E_j , and η are determined by calibration of the electrode.

Calibration. The AKUFVE distribution experiments are usually carried out with stepwise additions of acid and base to obtain different hydrogen ion concentrations. Electrode calibrations during the actual experiment are thus easily performed. Influences of the organic solvent, of the complexing agent, and of the liquid flow are then included. From the known additions of acid and base, the equivalence point is calculated by Gran's method,⁹ as described by Rossotti.¹⁰ The hydrogen ion concentrations can then be calculated from the added volumes and reagent concentrations in the pH-range where the buffer capacity of the complexing agent can be neglected. Values near the equivalence point are useless due to the large influence of even a small error in the equivalence point. These calculated pH-values and the measured emf values are used to estimate E_{H}° and η according to eqn. 13.

Determination of the equivalence point according to Gran. When a strong acid, volume V , is titrated with a strong base, a function ψ_{H} may be defined in the acidic range as

$$\psi_{\text{H}} = (V+v)10^{EF/2.303RT} \quad (14)$$

where v is the volume of base added. A similar function ψ_{OH} may be defined in the alkaline range

$$\psi_{\text{OH}} = (V+v)10^{-EF/2.303RT} \quad (15)$$

It can be shown¹⁰ that if the hydrogen ion activity factor, E_j and the water ion product remain constant throughout the titration, the functions $\psi_{\text{H}}(v)$ and $\psi_{\text{OH}}(v)$ are linear

* The potential difference across the glass membrane can be regarded as a voltage source in series with a high resistance. Due to the limited insulation provided by the glass in the main body of the electrode, a leakage current is always drawn from the voltage source. If the internal resistance of the membrane is R_i and the insulation resistance is R_g , the apparent emf will be less than the correct one by the factor $\eta = R_g/(R_i + R_g)$. In a new electrode $R_g \gg R_i$ and η equals unity.

** pH denotes $-\log [\text{H}^+]$

and intersect the v -axis at the point $(v_e, 0)$ where v_e is the volume of base added at the equivalence point. Thus, the value of v_e can be determined by plotting ψ_H or ψ_{OH} against v and extrapolating the straight line to cut the v -axis at the point $v=v_e$ as shown in Fig. 2. The fitting of the straight line can be made by a linear least squares method which yields both v_e and the statistical error in v_e .

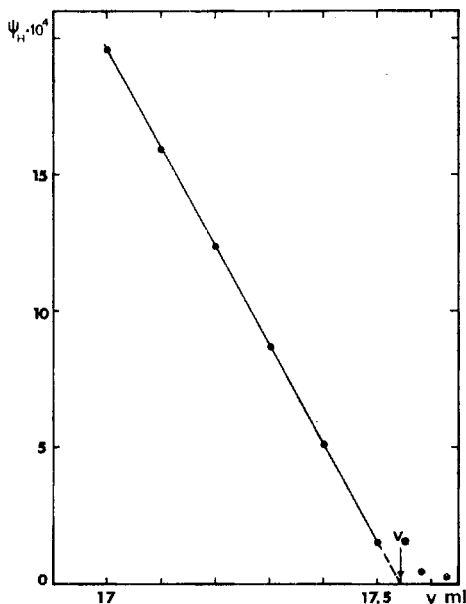


Fig. 2. An example of a plot of the Gran function, ψ_H , versus the volume of base added, v . The straight line is extrapolated to $\psi_H=0$ to obtain the equivalence volume, v_e .

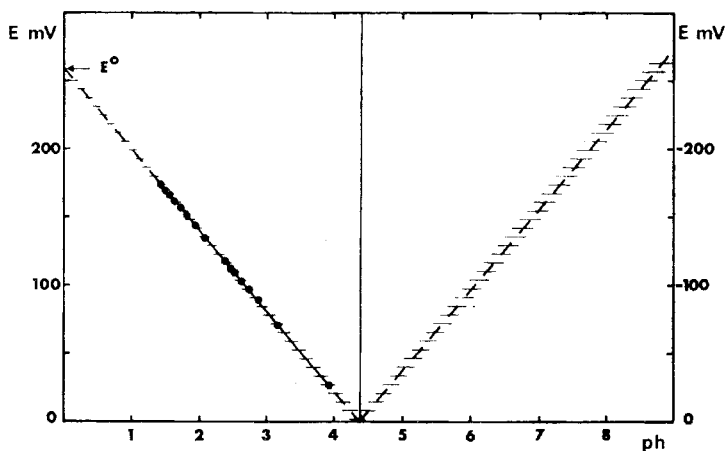


Fig. 3. Graphical electrode calibration. The measured E -values are plotted against the calculated ph values. The dashed lines are extrapolations from the measured values to cover the ph range used. For negative E -values, *i.e.* $ph > 4.3$, the scale to the right must be used. The hatched area indicates 95 % confidence limits for the calibration line calculated from the points shown.

When a least squares method is used for the estimation of E_H° and η , statistical standard errors can be obtained. In Fig. 3, a plot of E versus ph is shown with 95 % confidence limits indicated by the hatched area around the line. In the ph -range shown, Δph varies from about 0.04 to 0.18 ph -units. In most cases the calibration errors are smaller.

ph measurements in the AKUFVE experiments. As pointed out above, the hydrogen ion concentration is conveniently determined by measuring the emf of a modified glass-calomel combination electrode immersed in the aqueous phase. The electrode is calibrated *in situ* several times during a given experiment and the hydrogen ion concentration is then calculated according to eqn. 13. Usually two electrodes, placed in a flow cell according to Fig. 4, are used.

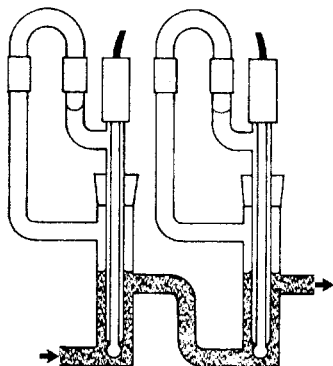


Fig. 4. Flow cell, made of glass, for the ph electrodes.

If one of them fails, the values from the other may save the experiment. One electrode is connected to a millivoltmeter (Radiometer 26). The other is connected to a digital voltmeter (Dynamco DVM 2025, range 0—1.9999 V) through an operational amplifier, used as a voltage follower with very high input impedance.

As the internal resistance of the glass electrode may be several hundred megohms, the need for the very high input impedance is obvious. This makes the measurements very sensitive to electrical disturbances. Efficient screening and earthing of all cables is necessary. The electrical stirrer motor is equipped with an interference suppressor. The liquid flow system apart from the radioactivity detectors is enclosed in a plexiglas cabinet and is well insulated from earth to avoid disturbances from ground currents. An air motor is used to drive the centrifuge.

5. DATA COLLECTION AND PROCESSING

The AKUFVE experiments yield a large number of measured values in a short time. The calculations necessary for obtaining D_M and concentration values are tedious and this makes the use of digital computers highly desirable. Recording of data should be made in a way which facilitates direct transfer to a computer. Fig. 5 shows the measuring system with datalogging unit, which is used to record all values on punched tape.

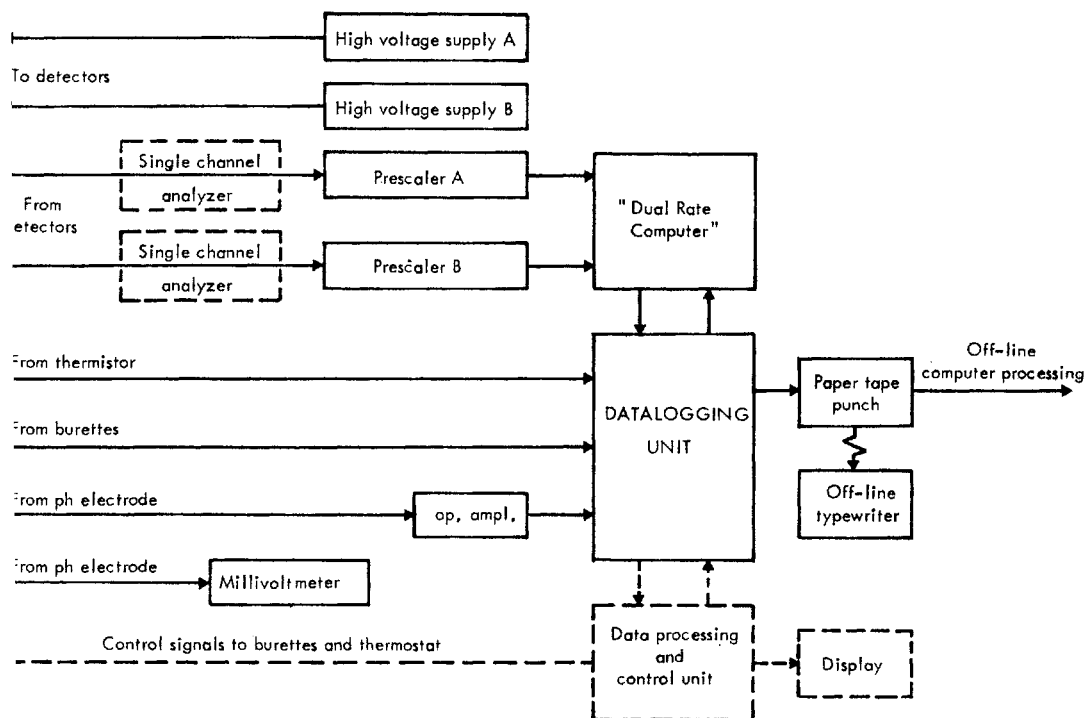


Fig. 5. Block diagram of the AKUFVE measuring system (some future developments are indicated by dashed lines).

Datalogging. Most of the instruments indicated in Fig. 5 have digital displays and readings can be recorded manually. The inherent speed of the AKUFVE technique, however, makes measurements with short time intervals desirable, and this is not feasible with manual recording. To take full advantage of the experimental capacity of the AKUFVE apparatus a datalogging unit, designed and built by SAAB Electronics AB, Göteborg, has been connected to the AKUFVE measuring system. The unit comprises the digital voltmeter mentioned above, a Wheatstone bridge for the thermistor, a digital clock, five registers for burette volumes, inputs for digital information from the radioactivity counters, a paper tape punch driving unit, a keyboard for manual punching, switching networks, and logic circuits.

The measuring cycle is started manually, or automatically with a preset time interval of up to 99 sec. Simultaneously, the "Dual Rate Computer" starts counting the phase activities for a preset time shorter than the cycle interval. When it stops, the datalogging unit scans the input signals and the registers, punching all readings on paper tape. This is completed in about 3 sec and the datalogging unit awaits the next starting signal. An electric typewriter is used to get a listing of the punched tape during the experiment.

The slow speed of the typewriter makes direct connection to the datalogging unit impossible.

The output from the datalogging unit together with some experimental notes regarding concentrations of stock solutions, background values *etc.* contains all information needed for the calculation of the equilibrium constants. A brief description of the various steps involved in the computer processing of the measurements is given below.

Data processing. To facilitate the removal of nonequilibrium measurements, selection of values for electrode calibrations, correction of errors *etc.*, the punched tape is converted by a computer program (CKRUT) to punched cards. A printed list of the measurements with indications of detected punch errors in the tape is produced. Each punched card contains all values from one measuring cycle. The card deck obtained is corrected according to the printed list and the notes taken during the experiment.

Selected values are used for the calculation of the equivalence point (program CKRGR1). These same values and the equivalence points determined are then used for the calculation of the electrode characteristics (program CKRSQLI). Both these calculations use the least squares method, and confidence limits are obtained for the values determined.

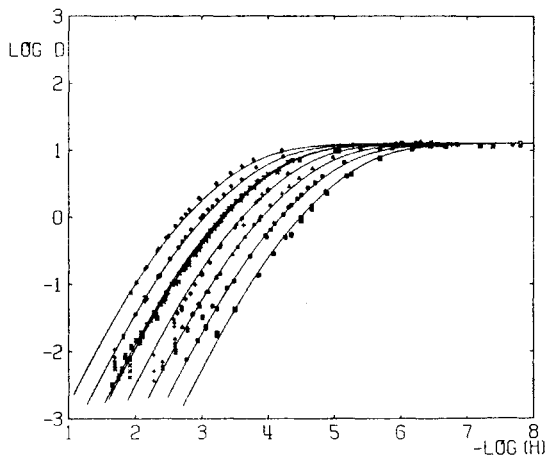


Fig. 6. Computer plot (machine drawn) of $\log D_{\text{Cu}}$ versus $-\log[\text{H}]$ for the system copper(II)-acetylaceton-benzene-1 M sodium perchlorate at 25°C. $[\text{HAA}]_{\text{aq}}$ is from left to right 46.2, 24.3, 13.6, 12.5, 6.4, 3.3, 1.7, and 0.9 mM.

All non equilibrium measurements are removed. Background values, ligand concentrations, and electrode constants are then added to the remaining data. This new data set is used for the calculation of distribution ratios and stability constants. The computer program (CKRJVT) used is a modified version of the one described by Sullivan *et al.*¹¹

Diagrams of $\log D_{\text{M}}$ versus pH and $\log D_{\text{M}}$ versus pA, are obtained by suitable plotting programs. In these plots, distribution curves calculated

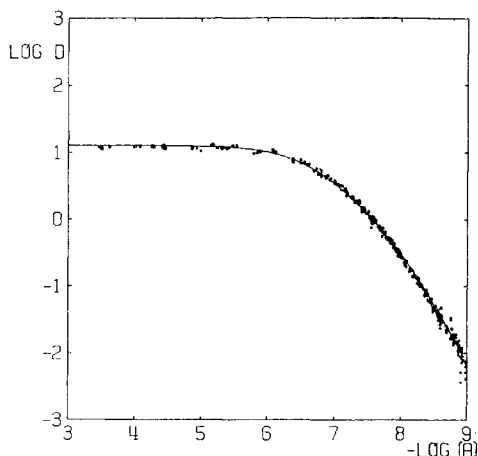


Fig. 7. Computer plot of $\log D_{\text{Cu}}$ versus $-\log[A]_{\text{aq}}$ for the system copper(II)-acetylacetonone-benzene-1 M sodium perchlorate at 25°C. [A] denotes the concentration of the free acetylacetonate ion. The experimental points are the same as in Fig. 6.

from the constants determined are drawn, together with the experimental points, as shown in Figs. 6 and 7.

All computer programs have been developed for use with the IBM 360 system.

6. INVESTIGATION OF THE COPPER(II)-ACETYLACETONE SYSTEM

The system copper(II)-acetylacetonone (HAA)-benzene-1 M sodium perchlorate was investigated at 25°C with the AKUFVE technique described, using ^{64}Cu as radioactive tracer.

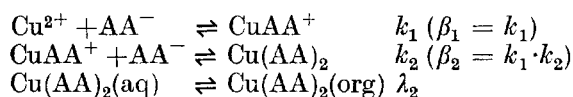
Chemicals. The ^{64}Cu (half-life 12.8 h) was obtained by neutron irradiation of pure copper metal. The radiochemical purity was checked by gamma ray spectrometry and half-life determinations. The copper was dissolved in concentrated nitric acid and evaporated several times with concentrated perchloric acid to remove the nitric acid. The remaining copper(II) perchlorate was dissolved in 1 M perchloric acid. The total copper concentration in the experiment was 2×10^{-6} M.

ph was varied by the addition of 1 M perchloric acid, 1 M sodium hydroxide in 1 M sodium perchlorate, or 0.1 M sodium hydroxide in 1 M sodium perchlorate.

All chemicals were of *p.a.* quality and were used without further purification, except sodium perchlorate and acetylacetonone.¹²

Results. The variation of D_{Cu} with hydrogen ion concentration at eight different acetylacetonone concentrations was determined. $\log D_{\text{Cu}}$ as a function of ph is shown in Fig. 6, and $\log D_{\text{Cu}}$ as a function of pAA in Fig. 7.

Equilibrium constants for the reactions



were calculated from eqn. 1 according to the procedure outlined in sections 1 and 5. The results are given in Table 1. In the calculations, a value of 8.996

Table 1. Equilibrium constants for the system copper(II)-acetylaceton-benzene-1 M sodium perchlorate. Values for $\mu=0$ are from Ref. 14. Errors given for our values are statistical 95 % confidence limits.

Temp. °C	μ	$\beta_1 \times 10^{-8}$	$\beta_2 \times 10^{-14}$	$\lambda_2 \times 10^{-1}$
20	0	2.04 ± 0.10	14.5 ± 2.3	
25	1.0	1.65 ± 0.06	6.51 ± 0.26	1.27 ± 0.04
30	0	1.66	8.93	

was used for the pk_a of HAA, and a value $k_d=4.91^*$ for the distribution of undissociated HAA between the phases at 25°C.

7. DISCUSSION

*Precision** and accuracy** in AKUFVE measurements.* Figs. 6 and 7, and Table 1, illustrate the good precision obtainable with the AKUFVE technique. This is largely due to the absence of sampling errors and to the good phase separation. The figures contain 741 measured points, all obtained in one single run lasting about 20 h. This shows the high experimental rate obtainable when chemical equilibrium is rapid.

The accuracy in AKUFVE experiments depends on several factors, and the relative importance of these can only be roughly estimated. Errors in the calibration of the pH electrodes, as described in section 4, affect the accuracy of the calculated equilibrium constants. Such errors originate from errors in the concentrations of the acid and base used, from impurities affecting the buffer capacity, from systematic errors in the burettes *etc.* Errors in the determination of the ratio between the counting efficiencies, or between the cell volumes of the radioactivity detectors, introduce systematic errors in the measured D_M values. This affects only the accuracy of the distribution constant λ . It is important to keep the above-mentioned errors as small as possible if the good precision obtainable with the AKUFVE is not to be wasted. All other errors seem to have comparatively little influence on the accuracy.

At high and low D values, the influence of errors in the determined background values lowers the precision considerably. The background can be decreased by the use of heavier lead shielding and single channel pulse height analysers. The use of such analysers also makes the measurements less sensitive to radioactive impurities.

* In a more recent investigation k_d was found to slightly depend on acidity even at constant ionic strength.¹³ This will influence our β -values in a complicated manner, but not by more than 2 %.

** *Precision* denotes here the spread in measured values around their mean. It is commonly estimated by the statistical standard deviation or mean square error. *Accuracy* refers here to the magnitude of the difference between the determined value and the true value, and includes both systematic and random errors.

Improvements to the technique. By using a multichannel analyser, giving energy spectra for the activity of both phases, it is possible to investigate the distribution of two or more metals simultaneously. This will be of special value, e.g. in studies of metal-metal synergism, or of isotopes having short-lived daughters.

Another interesting feature of this technique is the possibility of eliminating conventional pH measurements. pH is estimated from D_M values measured for a second metal in the system, having a precisely known distribution curve in the chemical system in question. Other distribution curves and equilibrium constants can then be determined with reference to this "standard metal", eliminating systematic errors in the comparison of metal ion properties.

One of the inherent features of the AKUFVE system is the ease and rapidity with which measurements are made. It is undesirable to slow down the rate of measurements, as this determines the time between electrode calibrations and background determinations, the influence of evaporation and of the decay of short-lived tracers. To achieve this aim, it is at present necessary to plan the AKUFVE experiment in detail beforehand. During the experiment, the time for planning is very limited. The operator is constantly occupied in checking the operation of the liquid flow system, determining when equilibrium is reached, adding reagents and making rough calculations of pH and D_M values. Although observations made during an experiment may suggest changes in the original plan, the evaluation possible is usually incomplete and may lead to unwise decisions.

These problems can be solved by connecting a small computer on-line to the datalogging unit (cf. Fig. 5). A complete evaluation of the measurements can then be made continuously as the measurements proceed. This will not only yield the extraction curves as they are measured, but will also permit the evaluation of these curves to test different theories of complex formation and extraction in the early stages of an experiment. This information can then be used to perform the measurements in such a way that the most promising theories are tested. Thus, the number of experiments with little significance, the labour of evaluation, and the consumption of expensive chemicals and radioisotopes may be decreased. Furthermore, all reagent additions can be accurately calculated to obtain desired values of the concentrations and the mechanical manipulation itself can be automatically performed under control of the computer. The electrode calibrations can be performed to obtain a predetermined precision. The same applies to radioactivity measurements, pH measurements, and to the establishment of equilibrium. It is also possible to follow continuously the occurrence of adsorption in the flow cells, and of evaporation, by balance calculations on the radioactivity. Consequently the time for an experiment and the number of experiments can be decreased by avoiding all unnecessary measurements and errors.

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