Solvent Extraction Studies by the AKUFVE Method

Part 1. Principle and General Problems

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AKUFVE is an apparatus for the continuous measurement of the distribution factor of a solute in liquid-liquid extraction. It consists mainly of a mixer, a centrifuge for absolute phase separation and on-line detectors, which are either connected in a once-through or in a closed-cycle arrangement. In this paper, the general properties and possible uses of the AKUFVE are discussed. Experimental results will be given in subsequent papers.

Solvent (or liquid-liquid) extraction is a fundamental separation process, which is widely used in all fields of chemistry. Though its basic principle, the Nernst distribution law, is very simple, a detailed understanding of the process requires thorough knowledge concerning the thermodynamics of solutions, complex formation, multicomponent phase diagrams, phase transport theories, etc. Since it is not yet possible to predict the extraction behaviour of a solute accurately, data must be collected experimentally. The information thus gained is often both of great interest to the theoretical chemist, and helps the applied chemist to evolve better and more efficient separation procedures.[1–4]

The experimental procedure now in common use is very simple:[5] The liquid two-phase system, which contains various solutes, is shaken in a vessel for some time, after which the phases are separated in a gravitational or centrifugal field and analyzed for species of interest. Because a large number of such experiments are required to obtain a thorough picture of the solute behaviour, the procedure is tedious and the risk for the incurrence of accidental errors is great. This primitive technique not only hampers the efficient development of solvent extraction processes, but also limits advancement in solution chemistry in general.

Though progress has recently been made in the treatment of solvent extraction data, e.g.[6] no comparable improvements have been made in the experimental procedure. A new technique, with which it is possible to obtain solvent extraction "points" 10—100 times faster and with less scatter than with the test-tube procedure, has been developed and is based on an apparatus

known as the AKUFVE, which is a Swedish abbreviation for "apparatus for continuous measurement of distribution factors in solvent extraction".[7,8] The new technique also simplifies the study of such solvent extraction phenomena as temperature dependence, kinetics, etc. The general features of the new technique are discussed in this paper. Experimental details will be given in subsequent papers.

1. DISTRIBUTION RATIO AND DISTRIBUTION CONSTANT

In 1891 Walter Nernst formulated the distribution law, which can be written

$$\lambda_A = \langle A \rangle_1 / \langle A \rangle_2 \tag{1}$$

where λ_A is the distribution (or partition) constant of the pure compound A between the solvents indexed 1 and 2, and $\langle \ \rangle$ indicate chemical activities. The distribution constant, λ_A, must not be confused with the distribution (or partition) factor (or ratio) D, which is defined

$$D_X = [X]_1 / [X]_2 \tag{2}$$

where [ ] indicate concentrations and [X] is the sum of all species with a common atom or group of atoms X in either phase, e.g. $[X]_1 = [XA]_1 + [XA_2]_1 + +[XB]_1 + [X_2C]_1$, etc. The dependence of the distribution factor D_X on a variable Z (which may be temperature, pH, concentration of the solute X or of another solute, etc.), i.e. $D_X(Z)$, is referred to as the distribution (or extraction) curve of X. Since distribution curves provide a basis for all studies and applications of solvent extraction processes we shall in this paper consider the determination of D-values only.

2. THE PRINCIPLE OF THE AKUFVE

The principle of the AKUFVE is illustrated in Fig. 1. In the mixing chamber the chemical compositions of the two liquid phases are adjusted through addition of suitable reagents. The two-phase mixture then flows down into a continuous flow centrifuge, in which *absolute phase separation* takes place, i.e. the out-going light and heavy phases are absolutely free from droplets of any size of the other phase. The pure phases then pass through suitable measuring devices for flow, temperature, etc., and through detectors, which continuously register the concentrations of the species of interest. The liquids then either flow back into the mixing vessel, thus making a closed cycle, or out into separate collecting vessels, in a once-through arrangement.

If the signals from the detectors are I_L from the light phase, and I_H from the heavy phase, they can be related to the concentration of the solute X in the two phases and to the distribution factor:

$$D_X = [X]_L / [X]_H = a \times I_L / b \times I_H \tag{3}$$

The value of the variable, Z, is registered by the signal I_Z:

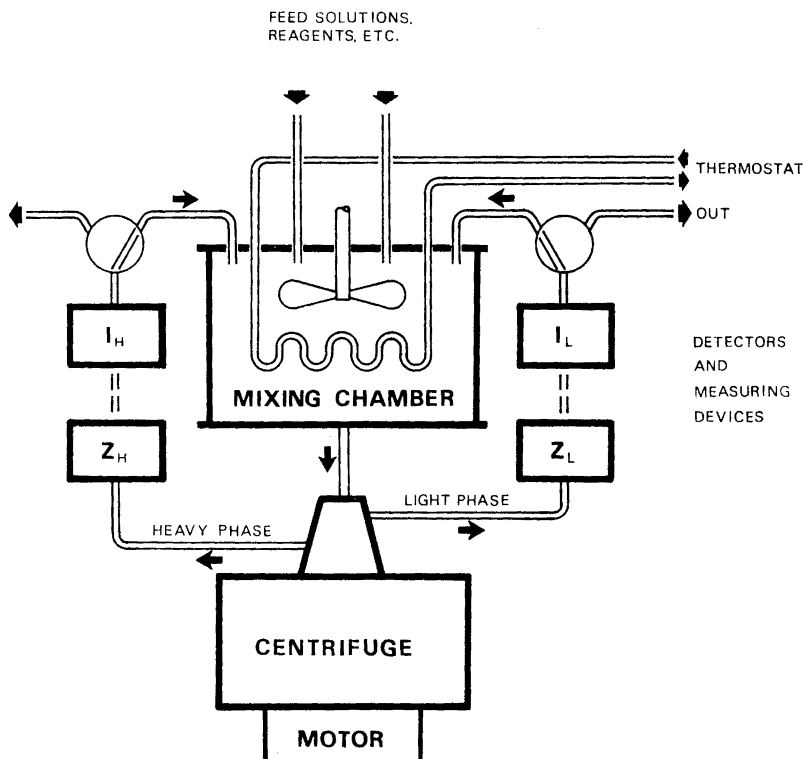$$Z = c \cdot I_Z \tag{4}$$

FEED SOLUTIONS,
REAGENTS, ETC.

Fig. 1. Schematic arrangement of the AKUFVE.

and a, b, and c are calibration values. With suitable equipment it is possible to directly obtain a plot of D_X as a function of Z.

In the "perfect" AKUFVE

(a) mixing and phase separation are instantaneous,
(b) the length of mixing and the time from mixing to separation are variable from zero upwards,
(c) absolute phase separation takes place,
(d) there is no time lag between separation and detection,
(e) a large variety of detection systems may be used: radiometric, spectrophotometric, refractive index, pH, etc.
(f) all liquid volumes are small in order to permit work with dangerous or expensive substances,
(g) the temperature is kept constant at a selected value in the range 0—100°C.

Contemporary technology and nature impose, however, limitations on that which may be achieved. These limitations will now be discussed.

3. KINETICS OF TWO-PHASE EQUILIBRIA

The rate by which equilibrium for a solute in a two-phase liquid system is established depends on mixing efficiency, contact time in the mixer, and on the rates of the various chemical reactions.[1,9-11]
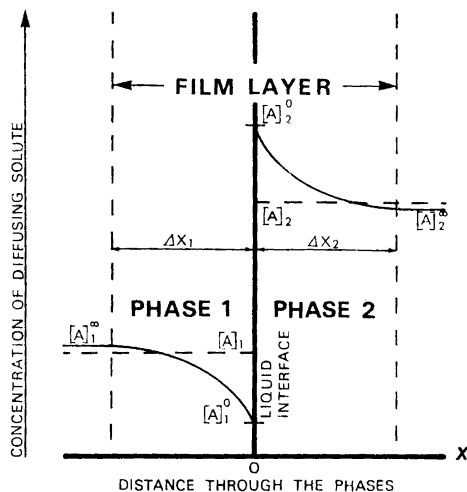

Fig. 2. Concentration gradients at interface during transfer of solute A from phase 1 to phase 2.

Fig. 2 depicts a hypothetical interface between two solvents, the vertical thick line $x=0$ being the geometrical interface. On both sides of this interface there is a layer (thickness Δx_1 and Δx_2, respectively) forming a "film", which can be assumed to be stationary. The film thickness depends on the solutes and the solvent pair, and varies from 10^{-2} to 10^{-6} cm, a common figure being $\lesssim 10^{-4}$ cm for not especially surface active solutes.[11] Solute transport occurs through this film in a laminar and diffusion controlled manner. At the interface the solute may react "physically", i.e. orientate itself, displace surface active agents, etc., but the transport over the interface is supposed to be momentary. The force, which drives a solute A, originally present only in phase 1, to phase 2, is related to a negative concentration gradient through the layers Δx_1 and Δx_2, as indicated in the figure. The solute flux N through the film can be described by the expression.[1]

$$N = K_1 \ ([A]_1^\infty - [A]_1^0) = K_2([A]_2^0 - [A]_2^\infty) \ (\text{mole} \cdot \text{s}^{-1} \cdot \text{m}^{-2}) \qquad (5)$$

where $[A]_1^\infty$ and $[A]_2^\infty$ are the concentrations of A just outside the film, and are assumed to be the same as in the bulk of the drops. $[A]_1^0$ and $[A]_2^0$ are the concentrations at the geometrical interface, measured in a small volume element. K_1 and K_2 are mass transfer coefficients (cm/s). Eqn. 5 is closely related to the Fick diffusion law, where the diffusion coefficient $D=Kx$. Thus K depends both on film thickness and diffusion coefficient.

The ratio $[A]_1^0/[A]_2^0$ is known as the "interface equilibrium distribution". For ordinary solutes, i.e. those which are not highly surface active, interface

equilibrium is established very rapidly. The rate depends on the properties of solute and solvents, but is independant of mixing efficiency.

The solute is transported from inside the drop to the surface (and *vice versa*) through diffusion and convection. As true equilibrium is approached, $[A]_1^\infty$ and $[A]_1^0$ approach $[A]_1$ (and correspondingly for phase 2), and the interface distribution approaches $D=[A]_1/[A]_2$. The chemical potential of the solute is then equal in both phases. Since vigorous stirring creates smaller droplets and thus a greater surface area, the diffusion controlled transport from phase 1 to phase 2 increases. If, however, the solute transport within the droplets were diffusion controlled only, it would take seconds to minutes to reach equilibrium in an ordinary mixture. Fortunately, convection in the drops is very intense, partly depending on the absolute value of the difference $[A]^0-[A]^\infty$, and increases the transport rate $10-100$ times. Coalescence and new droplet formation further increase the rate by which the two-phase equilibrium is approached. By means of vigorous stirring, producing droplets of magnitude $\lesssim 0.01$ cm, the "physical two-phase equilibrium" is reached in less than 1 s.

The solute may undergo chemical reaction in order to be extracted. For example oxidation-reduction reactions and/or complex formation may be necessary preliminary steps before extraction can take place. Such reactions may be considered to take place in the bulk of the solvents. Desolvation-resolvation (*e.g.* $A \cdot H_2O \rightarrow A \cdot ether$) may, however, take place either in the bulk or in the film. Further, if the interface contains layers of surface active agents, it may be necessary for the solute to react chemically with these in order to move over into the other phase, or it may simply have to push away the hindering barrier. In all these cases the transfer will be slowed down, as compared to the physical transport reaction described above.

The AKUFVE can be used to study the rate of these latter chemical reactions, provided the two-phase system has reached its physical phase equilibrium. For chemical reactions with halftimes down to ~ 1 s, vigorous mixing of the two phases, producing very small droplets, is necessary.

4. ABSOLUTE PHASE SEPARATION

Suppose we have two solvents with limited mutual solubilities (*e.g.* benzene and water) and pour the lighter on top of the heavier one. If no droplets have been formed, we may say that we have absolute phase separation. The two solvents will slowly dissolve in each other until the phases are saturated with respect to each other, but the phases will remain clear: we still have absolute phase separation. Absolute phase separation can then be defined in the following ways: (1) the phases shall be absolutely clear (*i.e.* show no Tyndall effect) and contain no droplets of the other phase and (2) each phase shall not contain more of the other phase than the maximum solubility permits. Using these definitions, deviations from absolute phase separation can be measured.

Absolute phase separation is a necessary requirement of the AKUFVE for exact on-line determination of distribution factors. One reason is that some detection devices require absolutely clear phases. For example, droplets

of a foreign phase will seriously interfere in optical densitometry and refrac-
tometry. Though some detection methods are less sensitive to the presence
of droplets, *e.g.* emf-measurement, conductometry, and radiometry, a droplet
which gets caught in the detection cell may seriously distort the results. Further
the errors caused in the measured distribution factors owing to the presence
of droplets may be quite large, even if the detectors are insensitive to droplets
per se. For example, if the distribution factor of a radioactive substance is
measured with radiation detectors, and the lighter phase contains droplets
of the heavier phase corresponding to x_H volume percent, then the measured
distribution is

$$D' = (I_L \ (1-x_H)+I_H \times x_H)/I_H \tag{6}$$

while the true distribution is given by eqn. 3 (assuming $a=b$). We can then
define the relative error R.E. as

$$\text{R.E. (light phase impure)} = \left|\frac{D-D'}{D}\right| = \left|x_H \ \frac{(D-1)}{D}\right| \tag{7}$$

At very small D-values the error is large. With increasing D the error first
diminishes and becomes zero at $D=1$, and then increases towards x_H.

It is obvious that in certain D-regions a small impurity in one of the phases
may be accepted and corrected for, but this requires separate analyses and
diminishes the practical value of the AKUFVE-technique. In many practical
cases, however, a small impurity may be tolerated since it "drowns" in the
noise and background of the detectors. Conversely, noise and background
limit the measurable D-region.

5. CENTRIFUGAL SEPARATION

Many methods, such as gravitational settling, the use of hydroclones,
centrifuges, electrostatic separators, membranes, *etc.*, can be used to achieve
absolute phase separation. Only the liquid flow centrifuge,[12,13] however, fits
all the requirements of AKUFVE.

The rate of phase separation in a cylindrical centrifuge rotating at an
angular speed ω follows approximately [13] the expression

$$v_c = \frac{\Delta\varrho \cdot d^2 \cdot \omega^2 \cdot r}{18\mu} \tag{8}$$

where v_c is the speed of sedimentation of a droplet of diameter d at the cen-
trifuge radius r for a density difference $\Delta\varrho$ between the droplet phase and the
stationary phase. A practical example may be $\Delta\varrho=0.1$ g/cm³, $d=0.001$ cm
(*i.e.* 10 μm), $\omega=2\pi \times 10\ 000/60$ rad/s (*i.e.* 10 000 rpm), $r=5$ cm and $\mu=0.01$
poise (*e.g.* water). One then obtains $v_c=30$ cm/s. For $d=1$ μm one obtains
$v_c=0.3$ cm/s. The time to achieve phase separation in the centrifuge thus
depends heavily on the droplet size: the smaller the droplets, the longer it
takes to separate the phases.

This affects the capacity of the centrifuge, which can be defined as the
maximum flow rate necessary in order to achieve absolute phase separation.

If the centrifuge has a volume V, through which the liquid mixture flows at a rate F, the hold-up time in the centrifuge is V/F. This should be identical with the time it takes for a droplet moving with speed v_c to pass through a stationary phase h cm thick. Thus

$$V/F = h/v_c \qquad (9)$$

If the thickness h of the stationary phase is small compared to the centrifugal radius r, eqn. (9) may be combined with (8) to compute maximum flowrates. Thus, assuming $V=0.2$ l and $h=1$ cm, one obtains $F=6$ l/s for $d=10$ μm, and 0.06 l/s for 1 μm. The hold-up times will be 0.033 and 3.3 s, respectively. Commercial liquid flow centrifuges usually require larger hold-up times, even when absolute phase purity of only one phase is achieved.

6. AKUFVE FOR FAST CHEMICAL REACTIONS

The aim of our work has been to design an AKUFVE for rapid studies of chemical equilibria. It might, however, be appropriate at this point to ask ourselves the question: how fast is the fastest chemical reaction which we could successfully expect to study with the AKUFVE method and present technology?

For fast reactions one has to use a "once-through" AKUFVE, consisting of a mixer, a centrifuge and detectors placed very close together. Suppose we could make a mixer of a few ml producing a narrow droplet size spectrum around 10 μm; physical phase equilibrium would then be achieved in much less than 1 second. With a centrifuge of 30 ml liquid volume, rotating at 30 000 rpm, and a flow rate of about 50 ml/s, it should be possible to separate a 3 μm droplet mixture in about 0.3 s. With a geometrical distance between the mixer and the detectors of 10 cm, it would take about 0.2 s from the mixer to the detectors. Obviously, chemical reactions with halftimes down to some tenths of a second could probably then be measured.

Such an AKUFVE does not exist, but can eventually be built. It certainly would require some innovations and much technological effort. One difficulty, perhaps the most serious one, is that when the liquids emerging from the mixer strike the rotating parts of the centrifuge, shearing will produce droplets much smaller than those leaving the mixer. This will considerably increase the time necessary to achieve absolute phase separation.

In the following, only the "closed-cycle AKUFVE", which has been successfully constructed,[8,14] will be discussed. It should, however, be noted, that this AKUFVE can also be used for studies of chemical reaction rates, though at present only for reactions with halftimes down to $\sim$10 s.

7. AKUFVE FOR EQUILIBRIUM STUDIES; THE MIXING PROBLEM

The closed-cycle AKUFVE can be regarded as consisting of two connected liquid parts, one with turbulent flow only and one with laminar flow only. Turbulent flow occurs from the inflow to the mixing chamber to that place in the centrifuge where phase separation is complete, laminar flow occurs

from this point through the pipes and the detectors back to the inflow to the
mixing vessel. If the concentration of a solute in the mixing chamber is changed,
it will take some time (the "mixing time"), independent of the rate of chemical
reactions or interface transport, before the solute is homogeneously distributed
in both the turbulent and laminar parts of the solvent ("mixing equilibrium").

Let us for simplicity consider only one solvent phase, with a turbulent
volume V_{turb} and a laminar volume V_{lam}. If at time $t=0$ we add m moles
of substance A to the turbulent volume, the concentration in the mixing
chamber becomes

$$C_{turb}(t = 0) = m/V_{turb} = C_0 \tag{10}$$

which is also the concentration at the outflow from the chamber (point I
in Fig. 3).

It takes a time $\tau = V_{lam}/F$ for a molecule of A to pass through the laminar
volume from point I to point II. We will call the composition at point II
the laminar concentration. Thus

$$C_{lam}(t) = C_{turb} \ (t-\tau) \tag{11}$$

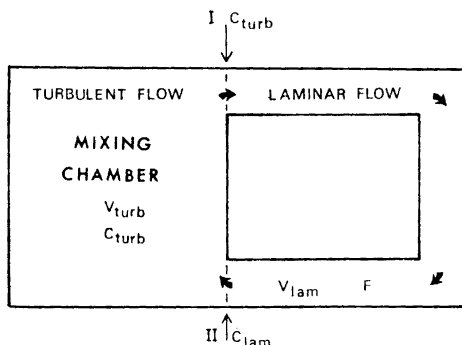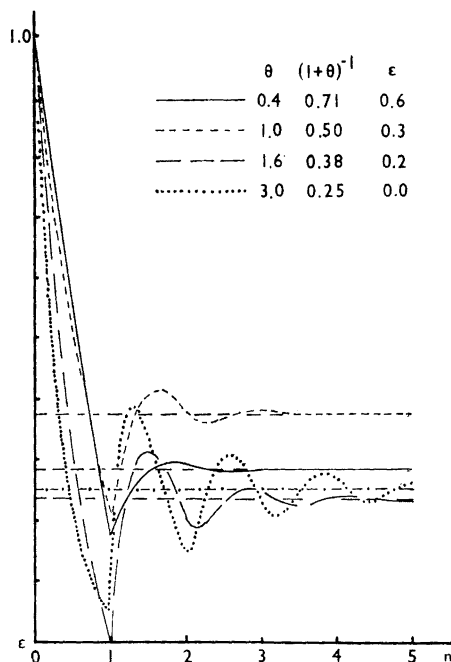| θ	$(1+\theta)^{-1}$	ε
0.4	0.71	0.6
1.0	0.50	0.3
1.6	0.38	0.2
3.0	0.25	0.0

Fig. 3.

Fig. 4. Approach to mixing equilibrium
as a function of the number of laminar
volumes n passing through the arrangement
in   figure   3   for   various   values   of
$\theta = V_{lam}/V_{turb}$. The vertical scale varies
with the factor ε.

Table 1. Approach to mixing equilibrium, $100(C_t - C_\infty)/C_\infty$, for various ratios $\theta = V_{lam}/V_{turb}$ as a function of the number n of laminar volumes (V_{lam}/F). At zero time $n=0$ and $C_0 = 1$.

θ \ n	0.1	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	2.0	4.0
1	-0.4679	-1.7523	-6.155	-12.19	-19.12	-26.42	-33.74	-40.82	-47.51	-59.40	-90.84
2	0.0135	0.0879	0.444	0.877	1.044	0.64	-0.53	-2.55	-5.41	-13.30	-63.20
3	-0.0004	-0.0024	-0.003	-0.083	0.357	0.87	1.62	2.46	3.24	3.92	-25.39
4	-0.0002	-0.0001	0.0001	-0.020	-0.054	-0.068	0.013	0.28	0.86	2.65	3.09
6	-0.0002	0.0000	-0.0001	0.0001	0.002	0.005	0.0007	-0.029	-1.07	-0.43	7.67
10	-0.0001	-0.0001	-0.0002	0.0000	-0.0002	-0.0003	-0.0002	-0.0005	10.002	-0.006	-0.41

The mass balance requires that the amount of A in the turbulent and laminar volumes is constant

$$C_{\text{turb}}(t) \times V_{\text{turb}} + \int\limits_{t-\tau}^{t} C_{\text{turb}}(t) \times F \ \mathrm{d}t \ = \ C_0 \times V_{\text{turb}} \tag{12}$$

The equation exhibits discontinuities at $t = n \, \tau$, where n is a whole integer; n indicates the number of laminar volumes which have passed point I or II. It can be shown that

$$C_{\text{turb}}(t = n \, \tau; \ n = 1, 2, 3 \ . \ .) \ = \ C_0 \sum_{k=0}^{n-1} \frac{\theta^k \, e^{\theta \ (k-n)}}{k!} \ (n-k)^k \tag{13}$$

where $\theta = V_{\text{lam}}/V_{\text{turb}}$. The equilibrium value

$$C_{\text{turb}(\infty)} \ = \ (1 + \theta)^{-1} \tag{14}$$

is slowly approached as n increases; see Table 1.

Values of $C_{\text{turb}} \, (t)$ for fractional values of n are most easily obtained by considering each n-interval at a time. The material balance in the turbulent volume requires that

$$\mathrm{d}C_{\text{turb}} \ V_{\text{turb}} \ = \ \mathrm{d}V[C_{\text{lam}}(t) - C_{\text{turb}}(t)] \tag{15}$$

Because $F = \mathrm{d}V/\mathrm{d}t$ and $C_{\text{lam}}(t) = 0$ in the interval $0 \le n \le 1$ one obtains

$$C_{\text{turb}} = C_0 \times \exp(-Ft/V_{\text{turb}}) \ = \ C_0 \times \exp(-\theta n) \qquad (0 \le n \le 1) \tag{16}$$

In the time interval $1 \le n \le 2$, we can again use eqn. (15), but $C_{\text{lam}}(t)$ is now equal to C_{turb} of eqn. (16). By solving the resulting equation, one obtains

$$C_{\text{turb}} \ = \ C_0 \cdot e^{-\theta n}(1 + \theta \cdot e^{\theta} \, (n-1)) \quad (1 \le n \le 2) \tag{17}$$

etc. By means of a computer program C_{turb} has been calculated for the first five intervals using different θ-values, see Fig. 4. It should be noted that the extreme values of an interval do not necessarily coincide with maximum deviation from the equilibrium value $C_{\text{turb}} \, (\infty)$.
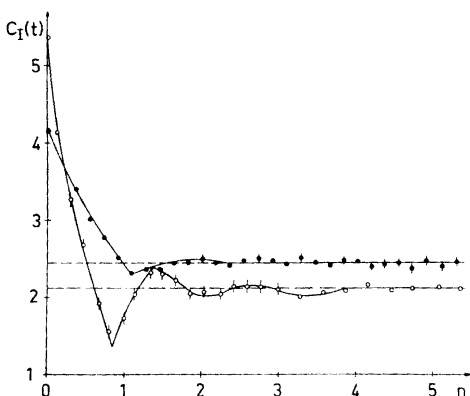

Fig. 5. Experimental verification of the approach to mixing equilibrium in a beaker with a stirrer (turbulent volume) and a long rubber tube (laminar volume), with ^{60}Co as tracer. V_{lam}/F 1.4 min, filled circles θ 0.63, open circles θ 1.45.

The equations for mixing equilibrium have been tested experimentally using a ^{60}Co tracer. Fig. 5 shows that the results generally agree with the calculated values. The reason that the approach to mixing equilibrium in Fig. 5 shows less marked fluctuations than in Fig. 4 is due to the fact that some turbulence also occurs in the laminar part. Mixing equilibrium will therefore be reached somewhat more rapidly in practice. Semilaminar pockets may, however, exist in the connecting pipes, valves etc. of the AKUFVE, and these may take a considerable time to wash out. Such pockets should therefore be avoided.

In Table 2 the conditions for reaching mixing equilibrium in an AKUFVE with an assumed total laminar volume of 300 ml and a centrifuge of 150 ml

Table 2. Conditions for reaching mixing equilibrium in a closed-cycle AKUFVE.

Centrifuge liquid volume, ml			150		
Other laminar volumes, ml			150		
Hold-up time in centrifuge, s			5		
Flow rate, ml/s			30		
$\theta = V_{lam}/V_{turb}$	0.3	0.6	1.0	1.5	3.0
n for 100 $(C_t - C_\infty)/C_\infty \leq 0.1$	3	3	4	6	32
Mixer liquid volume (V_{turb}), ml	1000	500	300	200	100
Mixing equilibrium time, s	30	30	40	60	120
Total liquid volume, ml	1300	800	600	500	400

liquid volume and a hold-up time of 5 s, are summarized. At reasonable mixer volumes, mixing equilibrium cannot be achieved in less than 30 s, though the hold-up time in the centrifuge is only 1/6 of this time. These figures are close to those which have been achieved practically.[15] Only 1—3 "equilibrium points" per minute can therefore be obtained at present. By diminishing the laminar volume and the hold-up time in the centrifuge, it is, however, possible to push this value up to one equilibrium point in every 5—10 sec.

8. SOME GENERAL COMMENTS

The main purpose of the AKUFVE is to facilitate the rapid and accurate collection of solvent extraction data. From the foregoing it is clear that only a few points can be collected every minute with the closed cycle system. In one day, however, a couple of hundred points might be obtained, which corresponds to one or a few solvent extraction curves. This is at least 10 times faster than conventional techniques. The rapid collection of data, each point comprising 5—10 pieces of information (*e.g.* temperature, pH, radioactivity of aqueous and organic phases, kinds and amounts of reagents added, *etc.*), may put some strain on the "information collector", the most suitable one being a system of electronic or mechanical registers. In a later paper [15] we shall describe such an arrangement for the collection of data.

Suppose the liquid volume in an AKUFVE-experiment is 600 ml, and 300 points have been collected. In a corresponding test-tube extraction, in which each experiment requires 10+10 ml solvents, the total liquid consump-

tion would be $300 \times 20 = 6000$ ml. The AKUFVE thus uses smaller amounts of chemicals than test-tube experiments. It is, of course, easy to diminish the volumes in both methods, but the AKUFVE can usually "beat" the test-tubes. This is of practical importance, expecially when the chemicals are expensive or dangerous.

An important feature of the AKUFVE is that the distribution factor of the solute investigated is registered continuously, using suitable detectors.[15] If the addition of a reagent (e.g. alkali) should cause D to change drastically when passing through a sensitive and important region, it may be easy to push D back into the proper region with another reagent (e.g. acid). This possibility which is often exploited in practice, merits the consideration of the use of the AKUFVE for process control on a larger scale. Such a project is under way.

Many chemical reactions proceed with half-reaction times slow enough to be measured easily with the "closed-cycle" AKUFVE, i.e. with half-reaction times >10 s. Reaction kinetics in solvent extraction, previously rarely studied for such short times, can thus be investigated. With the "once-through" AKUFVE the possibilities are still better. Perhaps, through such investigations, better separation processes may also be developed. Since D is measured continuously, control of industrial processes operating under non-equilibrium conditions, might even be possible. The fast "once-through" AKUFVE might also be used to investigate shortlived extractable species formed under special conditions as, e.g., in radiation fields.

D can easily be measured at various constant temperatures both with the AKUFVE and in test-tube experiments. Only the AKUFVE permits, however, the continuous measurement of D as a function of temperature.[16] Independent of the technique chosen, there is a great need for more thermodynamic data for solvent extraction processes, and particularly for distribution constants (λ). It is hoped that the AKUFVE will inspire much work in this field.

Finally, some limitations of the AKUFVE should be noted.

In certain solvent-solute systems emulsions are easily produced. This may be due to phase transport phenomena rather than to stirring.[11] The AKUFVE cannot be used to break up emulsions, which cannot be destroyed either by long time standing or intense centrifugation.

The study of solvent extraction processes involving slow reactions as, e.g., the polynuclear hydrolysis of metal ions, which may take several days to reach equilibrium, will be little improved by using the AKUFVE.

One of the basic principles of the AKUFVE is the on-line measurement of a certain solute. Practically, all detection techniques can be adapted to on-line measurement, though not necessarily continuous ones. One example is the measurement of α-radioactivity: at present no simple detector for continuous α-measurement of both organic and aqueous (acid as well as basic) solutions is available. In cases like this, either new detectors must be developed, or fast discontinuous (e.g. sampling) techniques must be adopted, if the AKUFVE is to be used.

Requirements for all on-line detectors are that they are insensitive to flow-rate, have a short response time and show no memory effects. This is not always the case: e.g., EMF-measurements are slightly sensitive to flow

rates, and the response time varies from a few seconds up to minutes or more for precise determinations. Radiometric detection cells may show memory effects at trace concentrations of highly charged metal ions, *etc.* These problems can, however, usually be mastered and they will be discussed further in subsequent papers.

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