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Solvent Extraction Studies by the AKUFVE Method

II. A New Centrifuge for Absolute Phase Separation

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Three different commercial liquid-liquid flow centrifuges were tested with regard to absolute phase separation and general suitability for the requirements of the AKUFVE method. As a consequence a new type of centrifuge, the H-centrifuge was developed. A general description is given of its design and phase separation properties.

AKUFVE is an arrangement for the measurement of distribution ratios in liquid-liquid extraction. It consists of (a) a mixing vessel, in which a solute is distributed between two immiscible liquids, and connected to this is (b) a separating device in which the two liquid phases are separated from one another, and (c) detectors for on-line measurement of the concentration of the solute in the separated phases. Normally the separated phases then flow back into the mixer, forming a closed cycle system, in which the physical and chemical conditions can be changed by suitable means. The system makes possible accurate, fast, and continuous determination of the distribution factor of the solute. In a previous paper [1] the general problems of the system were discussed, particularly with regard to mixing and separation. The present paper deals with the practical aspects of phase separation.

The AKUFVE requires that the separator *rapidly provides absolute phase separation*, *i.e.*, each outgoing phase must be absolutely free of droplets of any other phase, liquid or gas. Though absolute phase separation can be achieved in many ways, centrifugation seems to be the only method which also meets the time requirement.

Many types of liquid-liquid flow centrifuges have been constructed.[2] They differ roughly with respect to the mechanical arrangement in the centrifuge bowl, where the phase separation takes place, and in the discharge arrangement by which the separated phases are removed from the rotating bowl. Three representative centrifuges were tested: a de Laval centrifuge,[3] a Luwesta centrifuge,[4] and a Sharples type centrifuge.[5] Because the AKUFVE only requires one stage, multiple stage extractors were not taken into consideration. Because none of these centrifuges was found to be satisfactory for

AKUFVE use, a new kind of centrifuge (the "H-centrifuge") was constructed.[6a]

CONTINUOUS LIQUID FLOW CENTRIFUGES

The conditions in a continuous liquid flow centrifuge can be described with the aid of Fig. 1. The two-phase mixture flows into the rotating centrifuge bowl through a separate entrance and then passes through a separation volume, where the phase separation takes place. The phase separation may be completed after the liquid has travelled only a fraction of the separation volume (*i.e.* the effective separation length). This length depends on the mechanical arrangement, running conditions (flow rate, speed of rotation, temperature, *etc.*) and the properties of the two-phase system (density differences, viscosity, surface tension properties, *etc*).[e.g. 1,2d] The separation volume may either be a hollow tube divided into sectors by radial vanes (as, *e.g.*, in the Sharples type centrifuges) or a bowl containing a large number of conical discs stacked on top of one another, with spacers in between (as, *e.g.*, in the de Laval and Luwesta centrifuges).

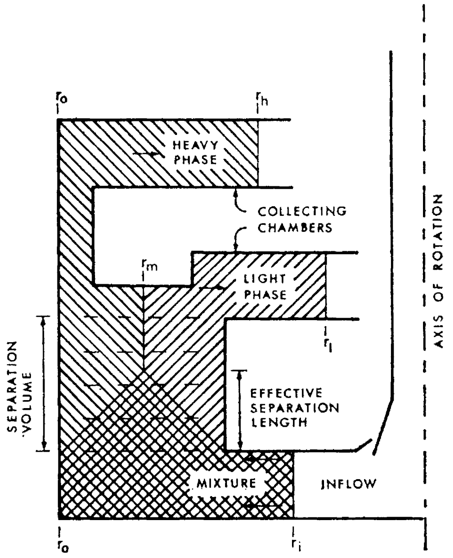

Fig. 1. Schematic diagram showing the liquid phase separation in a rotating bowl.

The separated phases are collected in different chambers and discharged from the bowl (or tube). Three methods can be used: (a) the liquids are allowed to flow over rotating weirs, which are part of the centrifuge bowl, into stationary catcher volumes, (b) stationary pump wheels dip down into the rotating liquids, and the internal pressure of the liquids forces them out, (c) tight bearings are used between the rotating collecting chambers and stationary tubes, and the liquids are forced out by applying pressure to the inflow. Only the first two arrangements are possible for AKUFVE usage, because in case (c) lubricating the bearings will contaminate the liquids.

ABSOLUTE PHASE SEPARATION

As pointed out above, absolute phase purity is a necessary requirement of the AKUFVE system. It can be checked by two independent methods. This will be exemplified with reference to the water-benzene system.

(1) If the organic phase leaving the separator contains large droplets of water or air, these are easily visible to the naked eye because the refractive indices are rather different (1.33 for water and 1.50 for benzene relative to air). Both water droplets and air bubbles will therefore scatter light. The phase purity can then be measured by means of absorption spectrometry. The benzene phase is allowed to pass a cell placed in a spectrophotometer, with a reference cell containing benzene saturated with water. Because of the temperature dependence of the solubility of water in benzene (approx. a 4 % increase per °C), the optical cells must be kept at a slightly higher temperature than that of the AKUFVE-separator during on-line measurements on the outgoing organic phase, *cf.* Ref. 7. If the absorption in the flow cell and in the reference cell is the same over the measured range of wavelengths region, the droplet entrainment is $\gtrsim$ 0.01 % (using a Beckman DB Spectrophotometer). This can be taken as a practical criterion on absolute phase separation. Haze at ~ 0.1 vol.% is easily visible to the naked eye.

(2) Solubility data of binary liquid systems are readily available from the literature.[8] The values do not always agree, because different methods of investigation may cause over- or undersaturation, and the analytical procedures can be of different sensitivity. For the AKUFVE system one may assume that phase equilibrium is reached after a long circulation time in the closed cycle system. Thus, for the example above, if analysis of the benzene phase shows more water than given by the solubility data, this may be taken as an indication that the investigated phase contains droplets of the other phase. In such experiments, the temperature must be kept constant within fine limits and any evaporation of the phases must be prohibited.

Both methods are open to criticism, but used together they give a useful measure of the degree of phase purity which the separator achieves.

INVESTIGATION OF COMMERCIAL CENTRIFUGES

Tests on the ability of the centrifuges to achieve absolute phase separation were carried out in a closed cycle arrangement similar to that shown in Fig. 2. The figure specifically refers to the tests on the H-centrifuge, but does not differ much from the test arrangement used on the Luwesta centrifuge (type LG 205, bowl volume 0.66 l). For the de Laval centrifuge (type 1225, bowl volume 0.45 l) and Sharples type centrifuge (according to Ref. 5c, bowl volume 16 ml), it was nesessary to insert pumps in order to recycle the liquids.

Two methods of starting the system were used. The centrifuge was allowed to attain maximum speed, and then either the mixture from A was allowed to enter it through the needle valve V_M, or the centrifuge was first filled with heavy phase before intermixed light phase was introduced into the centrifuge. The interface radius r_m can be varied on the Luwesta centrifuge by applying different counter pressures using the needle valves V_H and V_L, and on the

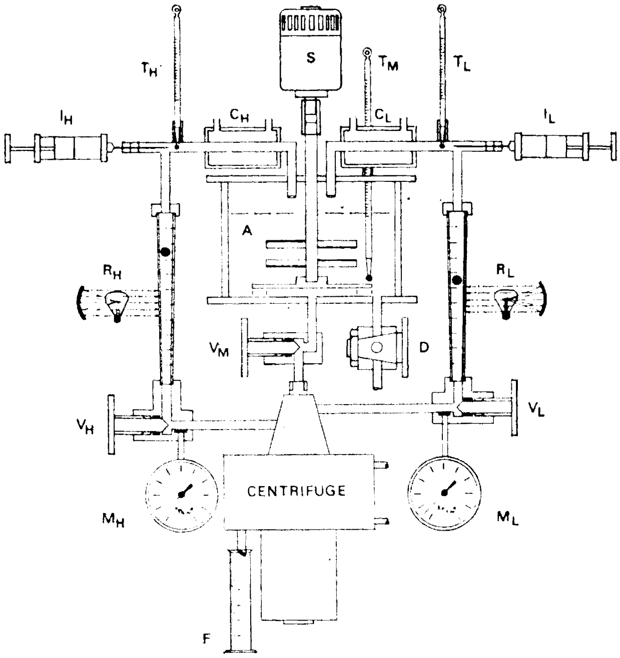

Fig. 2. Test arrangement for the H-centrifuge showing manometers (M), valves (V), flow meters with inspection lamps (R), injection and sample collection arrangement (I), thermometers (T), and heat exchangers (C) for the light (L) and heavy (H) phases respectively. A is the mixing vessel, V_M the inflow valve for the mixture, D a drain valve, and S a stirrer motor. The other centrifuges were tested in arrangements of principally the same design.

two other centrifuge types by changing the diameters of the weirs which control the radii r_h and r_l.

Many hundreds of runs were made on these centrifuges, such as varying centrifuge condition (counter pressures, weir sizes, and speed of rotation), physical conditions of the liquids (flow rate, aqueous/organic volume ratio, density differences, temperature) and chemical conditions (water with and without acid or salt, different organic solvents with and without dissolved reagents). All centrifuges could rather easily give one very pure phase, which is satisfactory for most industrial purposes. Discharge over rotating weirs, which was used on the de Laval and the Sharples type centrifuges, gave often air or gas bubbles in one or both of the outgoing phases, and produced foam with some chemical systems. This did not occur to the same extent, when pump wheels were used for discharge, as used on the Luwesta centrifuge. On the other hand it was found almost impossible to obtain two absolutely pure phases with the Luwesta centrifuge.

Several mechanical improvements to the centrifuges were introduced in order to obtain absolut phase separation and steady conditions, but non entirely successful.

THE H-CENTRIFUGE

Design. Consideration of the flow of a drop in a centrifugal field under the action of various forces (centrifugal, gravitational, Coriolis acceleration, inertial and frictional)[9] showed that the phase separation could be improved by using mechanical devices somewhat different from those in the commercial centrifuges. Supported by a great number of experiments on droplet movements and interface positions in the streaming liquid of a centrifuge, a new mechanical arrangement was designed.[6]

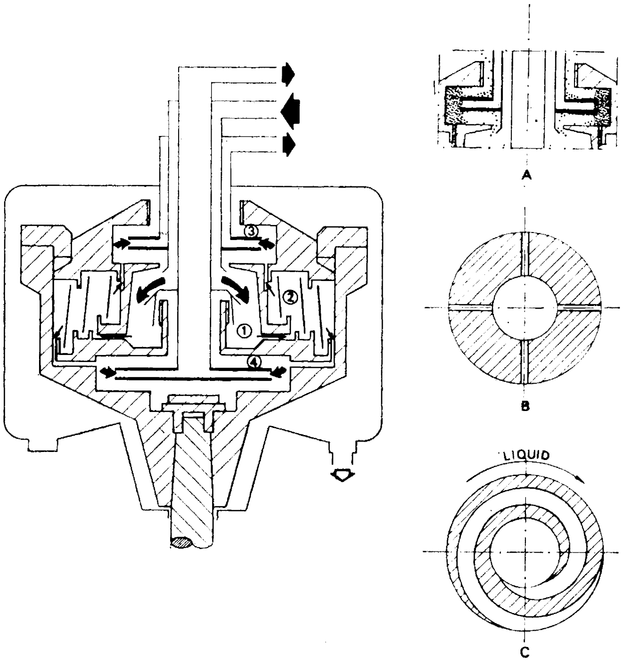

Fig. 3. The principle design of the H-centrifuge, showing flow pattern and (A) flow around the upper pump wheel, (B) a (potential pressure) pump wheel, and (C) a (dynamic pressure) turbine pump wheel.

Fig. 3 shows the present H-centrifuge.[6b] The mixture enters centrally into the centrifuge bowl and is accelerated in the inlet chamber (1) from which it passes into the separation volume (2). This contains an arrangement of eight sector shaped chambers totally separated from each other. The liquid flow in these chambers is a zigzag motion, caused by peripheral partition walls with interspersed baffle ridges. One collecting chamber is above, and the other below the separation volume. The light phase goes to the upper collecting chamber (3), and the heavy phase to the lower one (4). These chambers are not connected with each other, except through the separation volume. From these chambers the separated phases are taken out axially upwards with pump wheels of different types (B and C).

Heat is generated in all centrifuges through friction in the liquid during its acceleration and retardation, in the gear box and in the motor, and in the air space between the rotating bowl and the stationary casing. In a closed cycle AKUFVE the temperature of the liquid is therefore continually increasing. The rise amounts to 2—20°C/h in 1 liter of liquid, depending on centrifuge design. It is therefore necessary to introduce cooling coils into the system. This heating is a serious problem in AKUFVE usage. The mutual solubility of the two liquid phases leads to saturation at a temperature which may differ from that in the AKUFVE detection cells, where droplets then may precipitate. This may seriously affect many detection devices.[7]

The H-centrifuge is driven by a pneumatic motor of 0.6 H.P. or an 800 W variable speed induction motor, which provides a maximum of 18 000 rpm. The bowl volume is 100 ml and has a maximum flow capacity of 200 l/h. Materials in contact with the solutions are pure titanium and teflon (viton).

Phase purity test. The H-centrifuge was tested in the closed cycle arrangement shown in Fig. 2. The outgoing phases returned by their own pressure to the mixing vessel, from which the mixture flowed down into the centrifuge. At the start, the centrifuge was allowed to attain maximum speed before the mixture from A was allowed to enter it. Quite often, though not always, two visually pure phases were obtained right from the start. In other cases this same result could be achieved either by applying counter pressure with the valves V_L and V_H, or adjusting the rotational speed, or inflow rate (V_M). Clear phases were obtained for systems consisting of pure water and one of the following organic phases: benzene, toluene, hexane, kerosene, hexon, chloroform or carbontetrachloride. Addition of salt to the aqueous phase, and/or complexing agents such as acetylacetone or oxine to benzene, or tributylphosphate or trilaurylamine in moderate amounts to kerosene (avoiding third phase formation by pH-adjustments) showed no influence on the phase purity.

When the phases appeared clear, thus meeting the first of the requirements of absolut phase purity, the second "test of mutual phase solubility" could be applied. For this purpose the systems pure water-benzene and water-chloroform were chosen. Some typical results are given in Table 1 together with some experimental details. Two types of centrifuge were used, an "older" and a "newer" model, with minor mechanical differences; this did not affect the phase separation properties.

Table 1 reveals some general features. The AKUFVE runs are not systematically higher or lower than the test-tube runs, and the two sets of experiments seem to agree well within the 95 % confidence interval. This is to be expected for absolute phase purity when the same analytical methods are used. Run c is an example of phase impurity: in a series of experiments, the benzene phase was allowed to contain some water. The volume percentage value increased from 0.044 (absolute phase purity) to 0.152 (slightly visible impurity). This indicated that it may be difficult to visually observe phase impurities below 0.1 vol. %. Though the sensitivity of the analytical procedure *per se* may be as good as 0.002 vol. %, the accuracy is rarely better than 0.01 vol. % (one standard deviation) as an average of several runs.

Table 1. Investigation of phase separation behaviour of the H-centrifuge. Errors given in vol.% correspond roughly to the 95 % (2σ) confidence interval.

AKUFVE runs	Phase investigation	Temp. °C	Volume % found			
			AKUFVE	Test-tube	Lit.	Ref.
a	Benzene in water	20	0.15 ±0.04	0.20 ±0.03	0.199	10,11
b	»	28–31	0.13 ±0.02	0.13 ±0.02	0.214	
c	Water in benzene	20	0.044–0.152	0.046±0.008	0.048	10,12
d	»	28–31	0.042±0.014	0.050±0.008	0.065	
e	Chloroform in water	20	0.36 ±0.04	0.39 ±0.03	0.55	13
f	»	22–23	0.37 ±0.08	0.37 ±0.03	0.53	
g	Water in chloroform	20	0.12 ±0.02	0.134±0.020	0.100	13d
h	»	22–23	0.14 ±0.04	0.114±0.015	0.110	

Experimental conditions: AKUFVE runs a and e: One run, gaschromatographic analysis. Run b: Five runs under different conditions (phase ratios 0.54–1.02, flow ratios 0.96–1.53 l/min), spectrophotometric analysis. Runs c and g: As a, but water analyzed according to Karl Fisher. Run d: As b, but water analyzed according to Karl Fisher. Run f: Six runs under different conditions (phase ratios 0.22–2.17, flow rates 0.77–1.58 l/min), analysis according to Nicloux. Run h: As f, but water analyzed according to Karl Fisher.

The corresponding test-tube runs (mixing for 3–24 h, separation by centrifugation or standing for 1 day) were analyzed as for the AKUFVE runs, each value corresponding to the average of five experiments.

The literature values are selected as the most probable values considering all references.[8,10-12] The uncertainty is commonly about ±0.01 vol.%. This leads to some definite deviations between our experiments and those of other authors. The explanation may lie in the different analytical procedures. Usually the literature values are obtained from measurement of the temperature at which one single clear phase occurs in a mixture of known composition. This may lead to a higher solubility value than in our experiments, as is found for runs a-f; for exception (runs g-h), only one literature value is known. Another explanation may be that some fraction of the dissolved phase has evaporated during the analysis. Though precautions against this was taken, our analytical procedure which involved one pipetting, is open to this criticism. However, the reproducibility of the analysis does not favour this explanation.

DISCUSSION

One might deduce from Table 1 that the AKUFVE-runs do not lead to complete *phase equilibrium*. We do not believe this to be true for the following reasons: The temperature recorded is that of the mixer, but in the system the temperature varies slightly; the liquids leave the centrifuge at 0.1—0.3°C higher than in the mixer. The temperature is restored by the cooling coils. This, we believe, leads to very good phase equilibrium at the mixer temperature. In experiments with radioactive trace metals (*e.g.*^{64}Cu, Ref. 13) distribution ratios of the order of 10^{+3} and 10^{-3} have been recorded with good precision, which values agree completely with our own test-tube values and with the literature. This would not be the case if phase equilibrium were not reached.

The main conclusion to be drawn from Table 1 is, therefore, that the H-centrifuge provides absolute phase separation in the sense defined in this paper, and it thus meets the AKUFVE requirement.

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