

Demixing of Aqueous Polymer Two-Phase Systems  
in Low Gravity

S. BAMBERGER

Department of Neurology  
Oregon Health Sciences University  
Portland, Oregon 97201

J. M. VAN ALSTINE

Space Science Laboratory  
NASA/Marshall Space Flight  
Center, Alabama 35812

J. M. HARRIS

J. K. BAIRD

Department of Chemistry  
University of Alabama  
Huntsville, Alabama 35812

R. S. SNYDER

Space Science Laboratory  
NASA/Marshall Space Flight  
Center, Alabama 35812

J. BOYCE

Dept. of Pathology  
University of British Columbia  
Vancouver, Canada V6T 1W5

D. E. BROOKS

Departments of Pathology  
and Chemistry  
University of British Columbia  
Vancouver, Canada V6T 1W5  
and  
Department of Neurology  
Oregon Health Sciences University  
Portland, Oregon 97201

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## Abstract

When polymers such as dextran and poly(ethylene glycol) are mixed in aqueous solution biphasic systems often form. On Earth the emulsion formed by mixing the phases rapidly demixes because of phase density differences. Biological materials can be purified by selective partitioning between the phases. In the case of cells and other particulates the efficiency of these separations appears to be somewhat compromised by the demixing process. To modify this process and to evaluate the potential of two-phase partitioning in space, experiments on the effects of gravity on phase emulsion demixing were undertaken. The behavior of phase systems with essentially identical phase densities was studied at one-g and during low-g parabolic aircraft maneuvers. The results indicate that demixing can occur rather rapidly in space, although more slowly than on Earth. We have examined the demixing process from a theoretical standpoint by applying the theory of Ostwald ripening. This theory predicts demixing rates many orders of magnitude lower than observed. Other possible demixing mechanisms are considered.

## INTRODUCTION

When pairs of polymers are dissolved in aqueous solution two immiscible liquid phases often form. A common such pair is dextrane (a polymer of glucose units) and poly(ethylene glycol) (PEG), which form a PEG-rich phase floating on top of dextran-rich phase, both phases containing primarily water (i.e., 90% w/w). An important use of these phase systems is in purifying biological materials by partitioning between one or both phases and the phase interface (1-6).

On Earth, an emulsion formed by mixing the polymer phases rapidly demixes because of differences in phase density (1,2). The demixing process seems to occur in two steps: in the first step, droplets coalesce to form millimeter-sized phase regions, which in the second step, undergo rapid, gravity-induced convective streaming to produce two cleanly separated phases. Recent work on the mechanism of cell partition indicates that the rapid fluid flows that accompany phase demixing greatly reduce cell separation efficiency (2,7,8).

A major goal of our research is to carry out two-phase partition experiments in the low gravity ( $g$ ) environment of space. Low- $g$  is expected to present the advantages of reduced cell sedimentation and reduced rate of phase emulsion demixing, thus providing an opportunity to carry out unique cell purifications (7-11).

This manuscript examines phase demixing when gravitational effects are small. Five mechanisms which can potentially contribute to demixing of the aqueous polymer two-phase systems

in low-g are: Ostwald ripening (12-15), wall wetting (16-17), nucleation (18), spinodal decomposition (19), and coalescence (20-21). The Ostwald ripening mechanism, which has been used successfully to explain the growth of large crystals by transport of material from small crystals, is considered in detail in the present manuscript. A heuristic derivation of Ostwald ripening theory is given, and the resulting equations are used to predict the rate at which large phase droplets will grow at the expense of smaller droplets.

To test the predictions from Ostwald ripening theory we have measured the rate of phase demixing at one-g of isopycnic phase systems (i.e., systems with insignificant phase density differences), and we have also measured the rate of phase demixing of nonisopycnic phase systems during low-g parabolic maneuvers in a NASA KC-135 aircraft.

## MATERIALS AND METHODS

### Two-Phase Systems

The preparation and physicochemical characterization of aqueous polymer two-phase systems has been described previously (3-11). Isopycnic dextran-ficoll two-phase systems were prepared following the description of their existence by Albertsson (1). Small amounts of PEG were added to the systems to achieve equal phase density at lower total polymer concentration. All two-phase systems were prepared by mixing appropriate weights of the following aqueous stock solutions: 30% (w/w) dextran (D) T500 ( $\bar{M}_w = 461,700$ ,  $\bar{M}_n = 181,700$ , Pharmacia Fine Chemicals, lot 3447), 30% (w/w) DT40 ( $\bar{M}_w = 40,000$ ,  $\bar{M}_n = 33,000$ , lot F1-18974), 30% ficoll (F) 400 ( $\bar{M}_w = 400,000$ , lot 7867), 30% PEG 8000 ( $\bar{M}_w = 6650$ , Union Carbide, lot B529-9104), 0.60 M sodium chloride, 0.24 M sodium phosphate buffer pH 7.5. All reagents were ACS grade or better from various sources.

Dextran concentrations were determined polarimetrically and PEG concentrations were determined by gravimetric and refractive index measurements (3,11). Once compounded the systems were filtered (0.45  $\mu\text{m}$  filter, Sybron Nalge, Inc.) and allowed to equilibrate for 24 hours at the operating temperature.

Phase systems were physically characterized (Table I) by measuring: (a) bulk phase electrostatic potentials (dextran-rich phase negative) generated by the asymmetric partition of ions between the phases (3,11,24); (b) interfacial tensions, using the rotating drop method (22); (c) phase diagram tie-line lengths (11); (d) phase densities and (e) phase viscosities.

(11,22,24). In order to obtain these measurements isopycnic systems were altered by increasing or decreasing the PEG concentration 0.3% w/w from the isopycnic values, in order to float one phase on top of the other, and interpolating values for the isopycnic compositions. The data given in Table I represent the averages of at least ten independent determinations.

Phase systems are designated, according to convention (3,11), as (a,b,c)d where a, b, and c refer to the % (w/w) concentration of dextran T500, PEG and ficoll, respectively, in the system. Systems containing dextran T40 are designated with an asterisk: e.g., (a\*,b,c)d. Parameter d refers to buffer composition: I = 109 mM Na<sub>2</sub>HPO<sub>4</sub>, 35 mM NaH<sub>2</sub>PO<sub>4</sub>, pH 7.2; V = 150 mM NaCl, 7.3 mM Na<sub>2</sub>HPO<sub>4</sub>, 2.3 mM NaH<sub>2</sub>PO<sub>4</sub>, pH 7.2; and VI = 85 mM Na<sub>2</sub>HPO<sub>4</sub>, 25 mM NaH<sub>2</sub>PO<sub>4</sub>, pH 7.5.

In order to better visualize phase demixing, the PEG-ficoll-rich phases were dyed by including (0.05 mg/ml) Trypan Blue (Aldrich) in the systems.

#### Unit-g and Low-g Emulsion Demixing Experiments

One-g and low-g emulsion demixing experiments were undertaken using an apparatus (Figure 1) consisting of a Nikon F3 camera with Kodacolor ASA 400 film and a 55 mm, 1.28 Nikon Macrolens anchored to a platform holding a removable phase-module which was backlit by a fluorescent light box. The clear plexiglass module contained four chambers 30 mm high, 8 mm wide and 6 mm thick (light path axis) and a digital clock. Each chamber contained a 5 mm diameter stainless steel ball to

facilitate complete emulsification of the phases when the module was shaken manually. Usually the air-liquid interface aids in emulsification upon shaking, but in low-g and control demixing chambers air spaces were eliminated.

An experiment involved mixing the phases by quickly inverting the module 20 times, starting the timer, localizing the module on the experimental platform and taking 10 pictures at 1- to 2-second intervals (Figures 2-4).

Low gravity experiments were performed aboard NASA KC-135 aircraft. The aircraft flew a series of parabolas in which the experiments and personnel on board experienced up to 30 seconds of low-g (Figure 1)(8,25). The acceleration experienced by the partition module was monitored by three accelerometers (Sundstrand Data Controls, Model 300A1) mounted to the experimental platform on orthogonal axes, one of which was parallel to the sample vertical axis and two of which were parallel to the aircraft's major axes. For a typical maneuver the low-g acceleration on all axes averaged less than  $10^{-2}$  g.

Demixing experiments with isopycnic systems at one-g (Figures 3,4) were conducted under conditions similar to those described above using plexiglass chambers 50 mm high, 10 mm wide, and 10, 7.5, 5, or 2.5 mm thick. Mixing was accomplished by manually stirring the phase system with a plastic rod.

## Quantitation and Demixing Process

Slides taken of demixing phase systems at defined time intervals were projected, the outlines of connected domains traced on paper, and the area of each domain estimated using an IBM-PC computer equipped with a Microsoft Mouse mechanically fixed to a single orientation. A program was developed which used the screen cursor movement, created by tracing the domain outlines with the Mouse, to digitize and store the pictures of the areas as polygons. The domain area was calculated by adding the areas of the trapezoids formed from the individual sides of the polygon and the projection of each side onto the horizontal axis.

An example of the result of each stage is shown in Figure 5 where a distribution of the drop areas measured is also provided. The mean and standard deviation of each such histogram was calculated, the radius of a circle of area equal to the mean area determined, and the results expressed as a function of time on a log-log plot. These plots were then subjected to linear regression analysis (Table II); the line of best fit is illustrated (Fig. 6).



## RESULTS AND DISCUSSION

### Ostwald Ripening

When two immiscible liquids of different density are emulsified, a mixture of droplets forms. In the presence of a gravitational field, these droplets will agglomerate by sedimentation and the emulsion will demix. If, however, the two liquids are of identical density, or if there is no sensible gravitational field acting, sedimentation plays no role. Rather, the two emulsified liquid phases might be expected to demix in order to minimize the surface area of contact between them and to preferentially localize one phase next to the container wall (16). In the following discussion we treat the dynamics of this separation process as an example of Ostwald ripening. This concept has been successfully used to explain how large crystals grow at the expense of small crystals (15). We have derived the equations required to apply this same concept to the transport of materials from microscopic regions to large droplets of one polymer-enriched phase suspended in the other.

Consider a chemical substance A, which is partitioned between a submicroscopic droplet of radius R and an exterior phase. The concentration of A just outside the droplet is  $C_A(R)$ . In the limit that the two phases are separated by a flat surface (infinite radius of curvature), the equilibrium concentration is  $C_A(\infty)$ . The two concentrations are related by the Gibbs-Kelvin equation:

$$C_A(R) = C_A(\infty) \exp(2\sigma v_A / Rkt) \quad (1)$$

$\sigma$  is the interfacial tension between the phases,  $v_A$  is the molar volume of A,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature.  $C_A(\infty)$  is the thermodynamic concentration in the exterior phase given by the appropriate phase equilibrium. Equation 1 shows that the concentration of A in the exterior phase outside a droplet of radius  $R$  is always greater than  $C_A(\infty)$ . When two phases, initially having a flat surface of contact between them, are shaken, droplets with a distribution of sizes are formed. Immediately after mixing  $C_A(R) = C_A(\infty)$  for all  $R < \infty$ , but as shown in Eq. 1, at equilibrium  $C_A(R) > C_A(\infty)$  for all  $R < \infty$ , so A will diffuse from the droplets to the exterior phase. That is, initially, these regions begin to shrink. This causes the concentration of A in the exterior phase to rise. At some point, the concentration of A reaches the value  $C_A(R_n)$  which is the concentration of A in equilibrium with a droplet of radius  $R_n$ .  $R_m$  is the radius of the largest droplet in the distribution.  $R_n$  represents a distribution of smaller droplets. When the concentration of A in the exterior phase around the small droplet of radius  $R_n$  exceeds  $C_A(R_m)$  the largest droplet begins to grow by accretion of A. Droplets of radii smaller than  $R_m$  continue to shrink. As the time  $t$  approaches  $\infty$ , droplets with radii smaller than  $R_m$  disappear, leaving behind the largest region or droplet, whose radius has grown to the point that it approaches equilibrium with the flat surface concentration  $C_A(\infty)$ .

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of A. This may be because the concentration of B is so much higher or because the diffusion coefficient of B is much greater than that of A. In either case, the physical result is that when a molecule of A reaches the surface of the droplet by diffusion through the exterior phase, there is already present at the surface enough B so as to maintain the correct equilibrium composition of the droplet upon incorporation of an additional molecule of A. If the mole fractions of A and B in the droplet are  $x_A$  and  $x_B$ , respectively, then upon incorporation of  $x_A$  moles of A,  $x_B$  moles of B are also incorporated. If the molecular volumes are  $v_A$  and  $v_B$ , respectively, the average molecular volume in the droplet is  $\bar{V}$  where  $\bar{V} = x_A v_A + x_B v_B$ . The volume of the droplet is proportional to  $R_m^3$ , so that the number of molecules in the droplet is  $R_m^3/\bar{V}$ . If the rate of incorporation of molecules into the droplet by diffusion is  $D_A R_m (C_A(R_m) - C_A(\infty))$ , then the rate growth of the number of molecules in the droplet is given by

$$1/\bar{V} (dR_m^3/dt) = D_A R_m (C_A(R_m) - C_A(\infty)) \quad (2)$$

which is an equation of motion for  $R_m$  taken as a function of time. To integrate Eq. 2 we first evaluate Eq. 1 at  $R = R_m$  and expand the exponential for the case  $(2\sigma v_A/R_m kT) \ll 1$ . The result is

$$C_A(R_m) = C_A(\infty) (1 + 2\sigma v_A/R_m kT) \quad (3)$$

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Ignoring the factor of 2 in Eq. 3, we substitute this result into the right hand side of Eq. 2 to obtain

$$1/\bar{V}(dR_m^3/dt) \approx D_A R_m [C_A(\infty)(1 + \sigma v_A/R_m kT) - C_A(\infty)] \quad (4)$$

By cancelling common factors, this equation can be rewritten

$$dR_m^3/dt = D_A C_A(\infty) \sigma \bar{V} v_A / kT \quad (5)$$

Since  $R_m(t)$  at large  $t$  is much larger than  $R_m(0)$ , we may take  $R_m(0) = 0$  and integrate Eq. 5 directly to obtain

$$R_m^3(t) = D_A C_A(\infty) \sigma \bar{V} v_A / kT \cdot t \quad (6)$$

which shows that  $R_m^3(t)$  increases linearly with the time  $t$ .

In the rigorous derivation which this derivation replaces,  $R_m(t)$  is replaced by  $R(t)$ , the radius of the average droplet in the distribution. The maximum radius,  $R_m(t)$ , is just 50% larger, a difference which is unimportant in a heuristic derivation. Also, in the rigorous derivation, the right hand side of Eq. 6 appears multiplied by a factor of 8/9, which is again of the order of unity (15).

Our results may be summarized by saying that as the small phase regions dissolve, we are left with a single droplet. According to Eq. 6, the radius,  $R_m(t)$ , of this droplet grows asymptotically with time as  $t^{1/3}$ , while the volume of the droplet grows linearly with  $t$ .

can apply Equation 6 to the specific case of demixing in  
 us-polymer phase system, identifying dextran as compound  
 G as compound B. Dextran of  $\bar{M}_n$  185,000 has a molar  
 of  $0.611 \text{ cm}^3/\text{gm}$  (2) hence its molecular volume can be  
 ed to be  $1.83 \times 10^{-19} \text{ cm}^3/\text{molecule}$ . Similarly, PEG  
 550 has a molar volume of  $0.833 \text{ cm}^3/\text{gm}$  (2) and a molecular  
 of  $9.20 \times 10^{-21} \text{ cm}^3/\text{molecule}$ . We have chosen a typical  
 ystem (1) in which the composition of the exterior phase  
 % dextran (mole fraction  $x_{\text{dex}} = 1.13 \times 10^{-6}$ ), 5.7% PEG ( $x_{\text{PEG}}$   
 $10^{-4}$ ), and 93.25% water ( $x = 1$ ,  $\bar{V} = 2.99 \times 10^{-23} \text{ cm}^3/\text{gm}$ ).  
 r average molecular volume in the droplet,  $\bar{V}$ , is calculated to  
 $10^{-23} \text{ cm}^3$ . For this system we have measured  $\sigma$  as  $0.02$   
 $D(\text{dex}) = D_A = 2 \times 10^{-7} \text{ cm}^2/\text{sec}$ . The concentration of  
 in the exterior phase,  $C_a(\infty)$ , is given by  $x_A/\bar{V}$   
 $10^{16} \text{ molecules}/\text{cm}^3$ .

Inserting these parameters into Equation 6 gives

$$R_m^3(t) = (2 \times 10^{-20} \text{ cm}^3/\text{sec}) t \quad (7)$$

Using this equation we then calculate that 10 weeks will be  
 needed to grow a droplet one micron in diameter (starting at  
 $10^{-4}$  cm). For a droplet to grow to ten microns is calculated to  
 take 9 years.

In conclusion, if Ostwald ripening is to provide the  
 dominant mechanism by which the two aqueous-polymer phases demix  
 in the absence of density differences, this demixing can be  
 expected to take years.

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90% into the ficoll-rich phase in this system. Within 3 seconds following mixing at unit gravity the emulsion demixes into dispersed visible domains of each phase. By 12 seconds, sedimentation begins and convective streams are present by 25 seconds. This streaming occurs for approximately 30 seconds during which time clear regions of each phase appear at the top and bottom of the chamber. As demixing progresses, the middle emulsion region slowly contracts to form a planar interface. In keeping with sedimentation being the dominant demixing mechanism, shortening chamber height decreased the time required for demixing, while decreasing chamber thickness exhibited no effect. Undyed and Trypan-blue dyed systems exhibited identical behavior. Demixing of this non-isopycnic system at low-g in KC-135 aircraft mimicked the behavior of isopycnic systems at unit gravity, even to the extent of early preferential localization of PEG-ficoll-rich phase at the container walls. Also, demixing of the isopycnic systems was unchanged at unit-g and low-g.

Figures 5 and 6 and Table II give the quantitative results obtained by the imaging analysis process described in Materials and Methods. Note that phase streaming prevents use of this procedure in analyzing the demixing of non-isopycnic systems in unit-g. The data fit a log-log plot, thus implying a power law relationship between domain area and time. The log-log plot was less obviously linear in the case of the (7\*,5,0) V system. Presumably, this reflects the limited time scope of the KC-135 experiments.

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The preceding experiments show that aqueous polymer two-phase systems, which are characterized by moderately high viscosities and low interfacial tensions, will demix, following mixing by agitation, in the absence of appreciable gravitational influences. The mechanisms by which this demixing occurs are not known. Calculations based on our approximate treatment of Ostwald ripening strongly suggest that this mechanism is not of importance in the present case. Not only does the estimate of the years required to produce a 10 micron domain wildly differ from that observed, but measured power law coefficients (Table II) differ significantly from the  $t^{1/3}$  dependence predicted. It does not seem likely that either nucleation or spinodal decomposition are also involved, since the mixing/demixing process takes place at constant temperature and, presumably, constant phase composition. We have no evidence that the mixing process perturbs the composition of the phases from their equilibrium values. Hence, there seems to be no reason why these phase separation mechanisms should be relevant.

Coalescence of phase drops in the concentrated emulsions certainly occurs, and the disposition of the separated phases appears to be governed by preferential wetting of the chamber walls by the ficoll-PEG-rich phases. If coalescence does prove to be the dominant mechanism, the present data provides a basis for testing theories describing the processes involved. Consequently, we suggest that the coalescence process is driven by fluid motion associated with PEG-rich regions or droplets displacing dextran-rich phase from the wall.

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... the structures of immiscible metal alloys and  
... al systems solidified under microgravity conditions  
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... mary, our results suggest that emulsions of the type  
... re will demix by a different mechanism and at a slower  
... w-g than on Earth. The final disposition of demixed  
... d to some extent the rate of demixing, can be  
... by manipulation of chamber geometry and surface  
... havior. Application of polymer phase systems to space  
... ing is in progress.

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### CONCLUSIONS

... mmary, our results show that emulsions of aqueous  
... o-phase systems will demix in the absence of  
... nally-driven convection. The mechanism for this  
... s unclear, but we propose that preferential wetting of  
... ner walls provides fluid movement which leads to  
... e of droplets. Clearly, Ostwald ripening for these  
... too slow to be an important demixing mechanism.

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Table I. Composition and Physical Properties of Phase Systems<sup>a</sup>

| Composition <sup>a</sup><br>(% w/w)<br>(D, PEG, F) | Phase Viscosity <sup>b</sup><br>(CP)<br>PEG-F-rich | D-rich | Bulk Phase <sup>b</sup><br>Potential<br>(mV) | Phase Diagram <sup>b</sup><br>Tie Line Length<br>(% w/w) | Interfacial <sup>b</sup><br>Tension<br>( $\mu$ N/m) | Phase Density <sup>b</sup><br>(g/ml)<br>PEG-F<br>Dextran |       |        |
|--|--|--------|--|--|---|--|-------|--------|
| (7*, 5, 0)   | V  | 4.96   | 12.2   | 0.0  | 11.69   | 6.0  | 1.027 | 1.0578 |
| (5.5, 0.7, 9.5)                                    | VI   | 39.6   | 19.4   | ND   | ND  | 3.9  | 1.072 | 1.072  |

<sup>a</sup> Equal volumes of each phase, containing the polymers dextran (D) T500 or \*dextran T40, PEG 8000 and ficoll (F) 400, and the buffer salts noted in Materials and Methods. Buffers I and VI contain sodium phosphate while V is phosphate buffered saline. ND=not determined. Only systems containing buffer VI were isopycnic

<sup>b</sup> Measured as described in Materials and Methods, mean of ten or more determination S.D.  $\pm$  < 10% x. Bulk phase potential PEG-F-rich phase positive

NOTE: Square brackets refer to values given to JVA by SB in letter 5/19/84. They suggest viscosity values for (5.5, 0.7, 9.5) may need checking (e.g. reversed?) Potentials can be measured in Vancouver by JVA, TLL's by S.B.

Table II. Regression Parameters of Phase System Demixing Kinetics

| System <sup>a</sup>       | Power Law Parameters <sup>b</sup> |      |       |
|---------------------------|-----------------------------------|------|-------|
|                           | A                                 | B    | r     |
| <u>Isopycnic; lg</u>      |                                   |      |       |
| (5.5,0.7,9.5) VI          | -3.49                             | 1.51 | 0.992 |
| (7,0.3,12) VI             | -2.13                             | 1.21 | 0.978 |
| <u>KC-135: &lt;0.01 g</u> |                                   |      |       |
| (7*,5,0) II               | -1.37                             | 1.18 | 0.891 |

<sup>a</sup> Equal volumes of each phase. Phase system composition as noted in Table I and in Materials and Methods.

<sup>b</sup>  $\log(\text{radius; mm}) = A + B \log(t; \text{sec}); r = \text{correlation coefficient}$

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KC-135 low-g phase demixing experiment.

Droplet growth with time in a (5.5,0.7,9.5) VI isopycnic system containing 0.05 mg/ml Trypan Blue dye. Chamber dimension; 50 mm x 10 mm x 2.5 mm (thick).

Demixing in a (7,0.3,12) VI isopycnic phase system at different times after mixing. Chamber dimension; 50 mm x 10 mm x 10, 7.5, 5 or 2.5 mm.

Unit-g and low-g demixing of (7\*,5,0) V two-phase system containing 0.05 mg/ml Trypan Blue dye.

Quantitation of demixing in isopycnic system in Figure 3.

- (a) Detail 90 minutes after mixing
- (b) Tracing of dyed and undyed areas
- (c) Distribution of traced areas

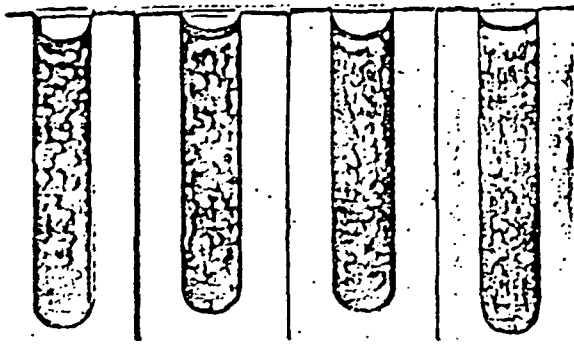
Plot of log time after shaking versus log (equivalent domain via meter) for (7,5,0) V system at low-g ( ) and isopycnic (5.5,0.7,9.5) VI system at unit-g (0). Bars represent the standard deviation for the individual size distribution. (Stephan redo please)

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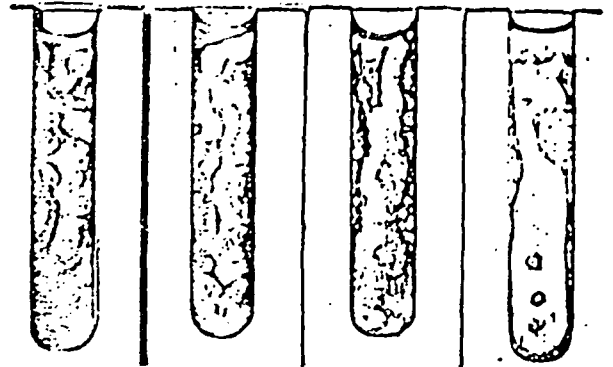


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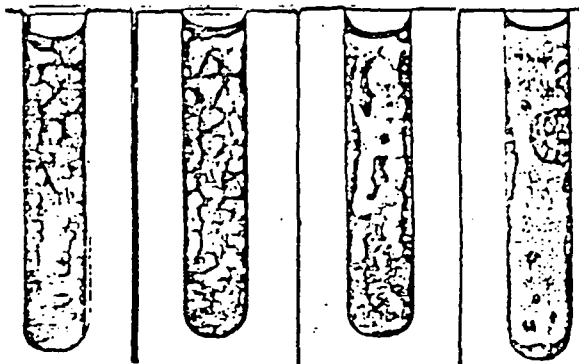
3 - <sup>44-</sup>Stephan



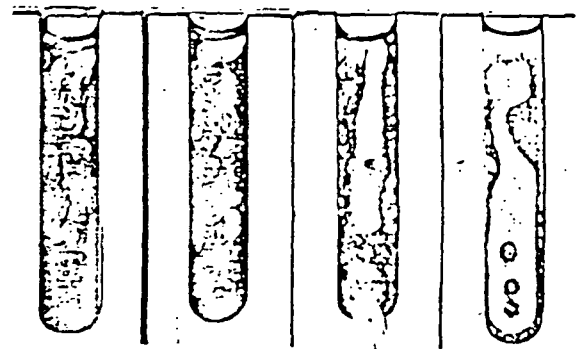
2 min



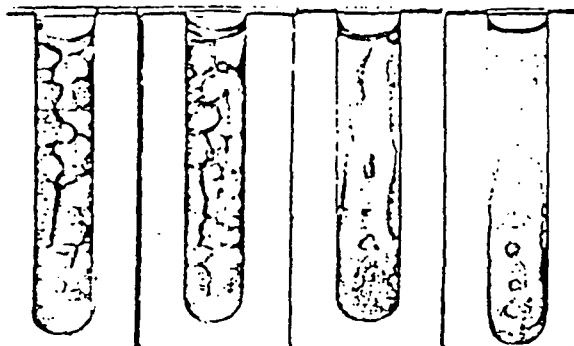
5 min



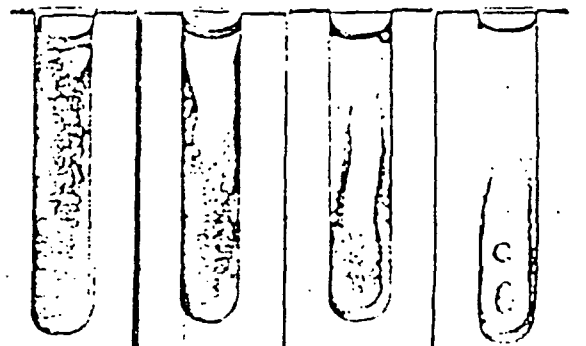
3 min



7 min

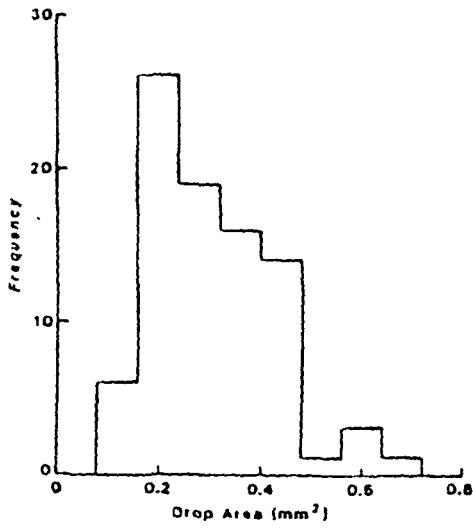
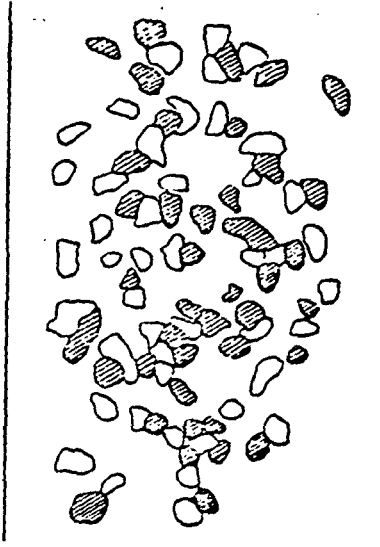


4 min



10 min

5



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