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The Concept of a Vibrational Cell for Studying the Interface Chemical Kinetics. Vibrational Flow Structure

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Abstract: The problem for the optimization of mass-transfer on the interface of two immiscible liquids by means of vibrational hydromechanics is studied experimentally. A new vibrational cell of Lewis's type expressly conceived for such purposes is described. Flow is generated by activators in the form of disks inducing translational axial oscillations near the opposite end faces of the cavity. It is shown that such vibrating disks can lead to the onset of a large-scale toroidal whirlwind effectively mixing the liquid throughout the volume. According to the experiments, in particular, axisymmetrical radial flows are generated on both sides of the horizontal liquid interface (that remains steady). The structure and the intensity of these vibrational flows are investigated as a function of the amplitude and frequency of vibrations, and also the relative size of the activators. The method of vibrational excitation of large-scale streams is proven to be a relevant and effective strategy for efficient renewing of liquids near the interface and their simultaneous intermixing in the bulk.

Keyword: liquids interface, vibrations, averaged flows, mass transfer, solvent extraction.

1 Introduction

The control of mass-transfer on the interface of immiscible liquids is a problem of great interest in many chemical engineering processes Levich (1962); Danesi and Chiarizia (1980); Colombani (2000). Many researches have studied the kinetics of interfacial mass transfer in solvent extraction K'Zhero (1997); Buch (2001); Rabinovitch et al (1988); Bosland (2005) and different techniques have been considered such as the "single drop" technique Colombani (2000), the highly stirred cell Watarai (1982), and the rotating membrane cell Simonin and Weill (1998).

The most classical device, however, is the "constant interfacial area cell", commonly referred to as Lewis-type cell Danesi and Chiarizia (1980); Colombani (2000); K'Zhero (1997); Buch (2001); Bosland (2005); Nitsch and Hillekamp (1972); Zheng and Li (1996); Weigel et al (2001); Pareau et al (2005). In this case the problem is mainly related to the identification of the relationship between the concentration of the chemical components on the interface and measurable bulk concentrations.

Because of a significant lack of information about the properties of convection in the interfacial liquid boundary layer (except for the rotating cell Simonin and Weill (1998) or the recent laminar flow cell Zheng and Li (1996)), the problem appears to be quite complex; till date, in fact, no simple analytical solutions have been proposed Danesi and Chiarizia (1980).

For the aforementioned Lewis's cell classical device, in particular, the two immiscible liquids on the opposite sides of the interface are stirred with the help of mechanical mixers. At intensive stirring rate, the interfacial reagents concentration becomes thoroughly equal to the concentration in the bulk.

Restrictions of this method are generally related to the stability of the steady shape of the interface; in case of quick reactions this method is not effective (near to the interface diffusion boundary layers are formed).

There are various possible approaches which could be used to overcome these problems. To

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them concern: stabilization of the interface with the help of grids located at some distance from the border Colombani (2000); K'Zhero (1997); Bosland (2005); Pareau et al (2005); the account of diffusion layers thickness by calculation of concentration of chemical components on the border Simonin and Weill (1998); Zheng and Li (1996), etc.

It is also known, however, that vibrations can generate averaged flows in liquids Nyborg (1965), usually referred to as "acoustic streaming". Vibrational generators of streams, hence, can be an alternative to traditional mixers. The currents excited by bodies vibrating in a liquid possess high symmetry and can be of significant intensity.

The vibrational flows excited by the end face of a cylinder making longitudinal oscillations in a cylindrical glass filled with liquid were investigated experimentally and theoretically in Ivanova et al (1998). The case of relatively large cavity, $r \equiv R_1/R_0 = 4$ (here R_0 and R_1 – radii of the body and the cavity correspondingly) was considered. It was revealed that the vibrating body generates a jet of liquid directed along the axis of vibrations.

In general, the flow velocity is determined by the pulsation Reynolds number defined as $Re_p = b^2\Omega/\nu$ (here $\Omega = 2\pi f$ – radian frequency, b – amplitude of vibrations, ν – the kinematic viscosity of liquid) and essentially depends on the dimensionless frequency of vibrations $\omega = \Omega R_0^2/\nu$.

It is known that in the presence of an edge of large curvature the speed of the vibrational flows grows monotonously with the frequency until an asymptotic behavior is established for $\omega > 10^5$.

The purpose of the present research is to study the structure and intensity of such vibrational currents, using the PIV method, in a vertical cylindrical container filled in equal volumes by two immiscible liquids of different density.

The flows have been generated by two activators (round disks located along the axis of the cavity near to its face borders), which induce high-frequency longitudinal oscillations of small amplitude.

For the sake of comparison, the same experiments of Ivanova et al (1998) (where the flow was generated by an end face of the long cylinder plunged in the liquid and making longitudinal vibration) have been initially performed. In this case the flows structure has been studied using the method of photo-registration.

2 Vibrational currents in an open cylindrical glass

2.1 Experimental technique

As mentioned above, the flow generated by the end face of a vertical vibrating cylinder plunged in a liquid in a vertical cylindrical glass was studied in Ivanova et al (1998). In Ivanova et al (1998) the body size was relatively small, in the present study the body has the size comparable to the sizes of the cavity $r \equiv R_1/R_0 = 2$.

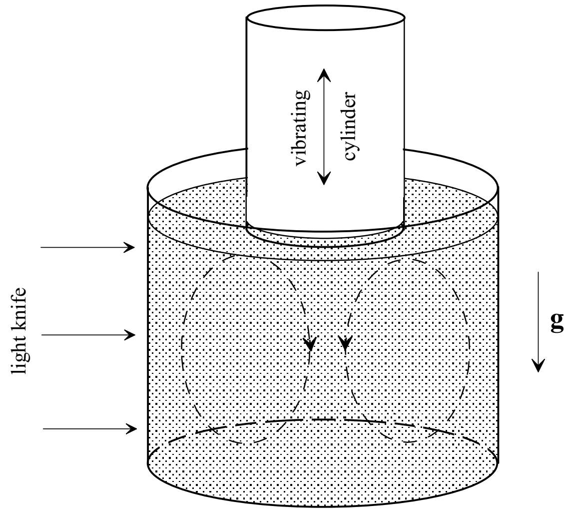


Figure 1: Schetch of the cavity.

In the present work the experimental setup includes an electrodynamic vibrator, a cylindrical cavity (Fig. 1) filled with a liquid and a coaxial vibrating body.

The method of photo-registration has been used for velocity field investigation.

A loudspeaker, used as vibrator, provides the longitudinal oscillations of the rigid cylinder with flat end. A generator with smooth adjustment of amplitude and frequency has been used; the vibration amplitude has been varied from 0 to 0.3 mm, the

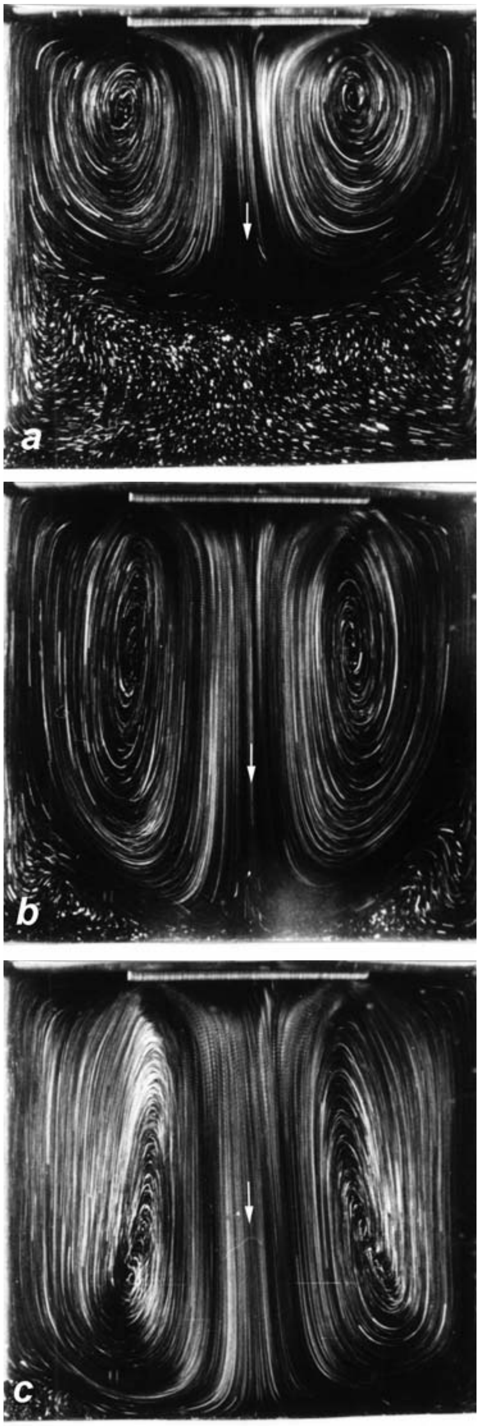


Figure 2: Vibrational flow patterns in the axial cross section of a cavity filled with alcohol. In the upper part of the photos one can see the flat end of a vibrating cylinder with the plunging depth of few millimeters; the free surface surrounds it. Photos *a*, *b* and *c* were obtained at $f = 60$Hz, $b = 0.20$, 0.25 and 0.29 mm ($Re_p = 10$, 16 and 20).

frequency from 50 to 500 Hz. The amplitude has been measured by a microscope with an accuracy of 0.02 mm.

The vertical cylindrical glass container, $R_1 = 1.4$cm, has been filled with a liquid up to an height equal to the diameter.

The motion has been induced by vibration of the vertical coaxial cylinder of radius $R_0 = 0.7$cm with flat end, plunged into the liquid.

Experiments have been carried out with alcohol and water.

The liquid flow has been visualized with aluminum powder and illuminated in the axial section by a light sheet. To avoid the optical distortion the cylindrical container has been installed in a rectangular glass filled with the same liquid.

The velocity structure has been registered by a photo-camera. A stroboscopic illumination has been used for the quantitative measurement of liquid velocity – the light beam is being interrupted for half of a period with frequency 20 Hz. In the photographs with exposition time equal to 1 sec the markers draw the dotted traces. The photos are then processed on a computer. One can measure the velocity in the different points of the cavity according to the traces length. In the domains of low velocity its value could be found using the trace length during the whole exposition.

2.2 Experimental Results

As anticipated, high-frequency linear vibration of a cylinder in an incompressible liquid excites a time-averaged jet directed from the vibrating cylinder towards the cavity bottom. This jet produces an axisymmetrical toroidal circulation in the cavity (Fig. 2).

When vibrations have a sufficient intensity the jet reaches the bottom of the cavity and the circulation involves the whole cavity volume (Fig. 2 *c*).

It is worth mentioning that the radial flow is excited near the cavity boundary. Further increase of the vibration amplitude leads to the intensification of the flow; the axisymmetrical steady convection undergoes transition to an unsteady asymmetrical flow.

The intensity and structure of such vibrational flow does not depend significantly on the depth of body plunging. The distortion of the flow appears only when the end of the vibrating cylinder is in contact with the free surface and the excitation of surface waves takes place.

Experiments show that the vibrational flow structure is also very sensitive to the presence of a transversal component of cylinder vibration; it causes the infringement of the axial symmetry of the flow.

The velocity measurement demonstrates that the vibrational flow structure and intensity are determined by the dimensionless parameter $Re_p = b^2\Omega/\nu$. The dependence of the dimensionless maximum axial velocity $V = \upsilon R_0/\nu$ on Re_p is presented in Fig. 3; υ is the maximal axial velocity, measured on the cavity axis at the distance from the vibrating body equal approximately the body radius. The typical scattering of the data arising from the processing of several photos at definite vibrational parameters is represented by error bars.

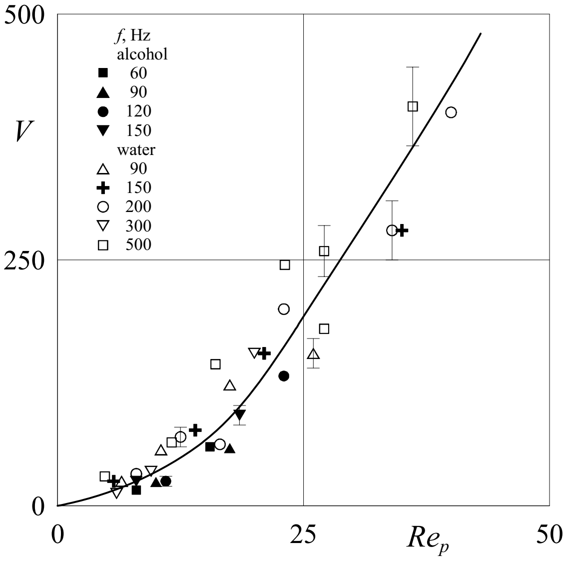


Figure 3: Dimensionless maximum axial velocity V versus Re_p.

At first glance all the points for different liquids in a wide range of frequencies concentrate near one curve, but one can notice that the velocity slightly increases with the increase of the dimensionless frequency. The results are in qualitative agreement with Ivanova et al (1998).

3 Two-liquid system with interface located within a closed cavity

3.1 Experimental Technique

Vibrational flows in a two-liquid system have been studied in a closed cylindrical container of radius $R_1 = 2.5$cm and height $L = 7.3$cm (Fig. 4). The cell has been fastened vertically and filled with water (density $\rho_1 = 1$gr/sm^3 and viscosity $\nu_1 = 1$cSt) and dodecan ($\rho_2 = 0.87$gr/sm^3, $\nu_2 = 1.12$cSt) in equal amounts.

An axisymmetrical motionless reflector (1) has been fastened in correspondence of the interface between the liquids. The radius of the reflector is 1.26 cm; the height is 0.9 cm (fastening of the reflector is provided with three thin radial rods, not shown in the figure). Thus the liquids interface has the form of a ring and is at the level of the sharp edge of the reflector.

The flows have been generated by two identical activators (2) located symmetrically in the different liquids at equal distances from the end walls. The activators have the form of short cylinders of radius $R_0 = 1.00$, 1.25 or 1.50 cm and height 0.60 cm. They are fastened on the light mobile metal rod 3 (radius 1.5 mm) located at the axis of cavity and freely moving through an aperture in the reflector.

Translational oscillations of the rod with the activators have been produced by the vibrator (built on the basis of loud-speaker MONACOR – SP 150, acoustic generator HAMEG Instruments – HM 8030-6 and an amplifier PRISMAUDIO MTK50 PS 50 W).

The mean liquid velocity has been analyzed by means of a PIV-method. The measuring complex Dantec includes a pair of pulse lasers New Wave Research – Minilase-15, and CCD-camera Dantec Dynamics. For visualization, light-scattering particles Rilsan Fine Powder (diameter 50 microns) with neutral buoyancy in water are used. A laser beam in the form of a vertical knife of 2 mm thickness "cuts" the cavity along the axis. The mean velocity field has been studied by averaging the results over 100 measurements. For elimination of the optical distortions caused by cylindrical lateral cavity surface the cell has been located in a rectangular basin filled with distilled water.

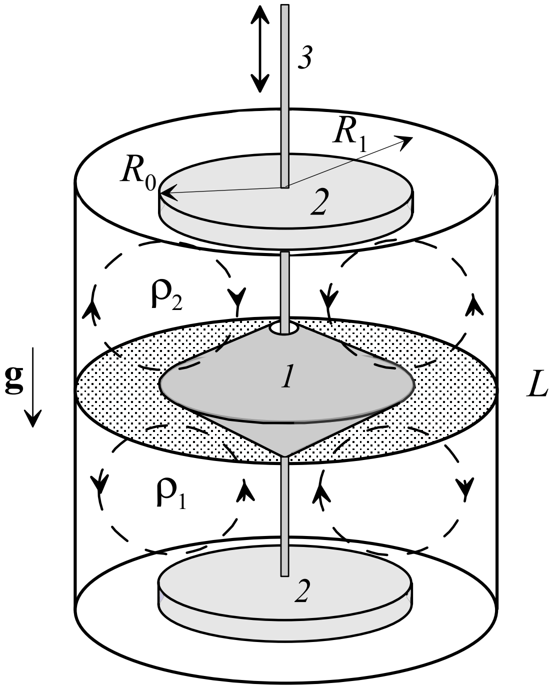
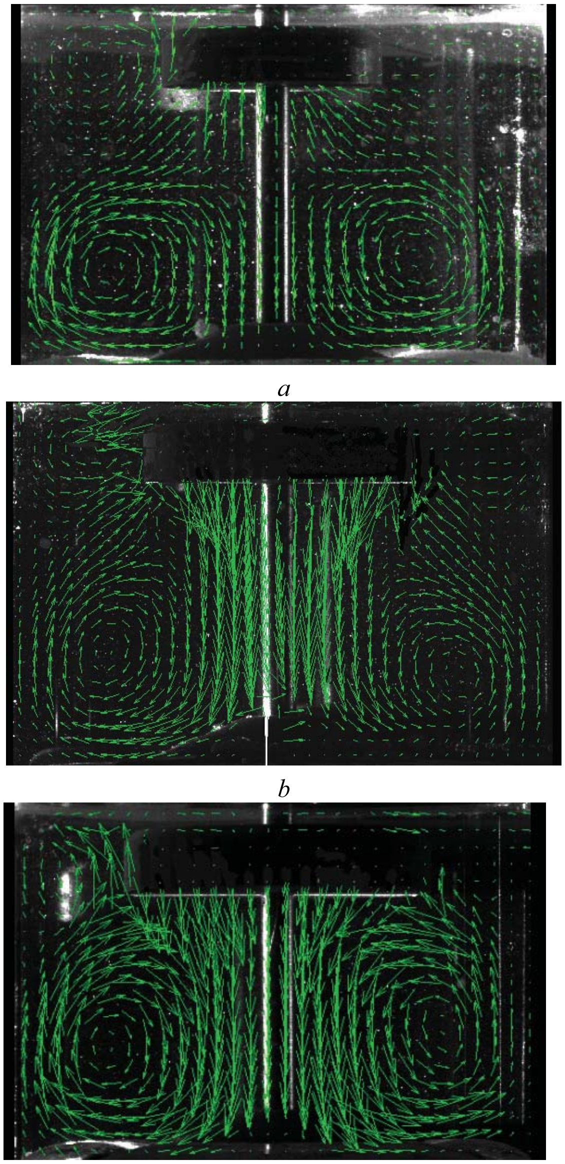


Figure 4: Sketch of the cell: 1 – motionless reflector at the level of liquids interface, 2 – vibrating bodies (activators), 3 – a rode making vertical vibration on which the activators are fastened.

Longitudinal oscillations of the activators excite an axisymmetrical toroidal whirlwinds in the volume of both liquids; along the axis the liquid streams are directed towards the interface; near to the horizontal liquids interface a radial movement is formed.

As a whole the convective structure is similar to the one observed near the end face of the long cylinder in Fig. 2. The difference consists of the excitation of an additional vortical flow near the face border of the cavity (Fig. 5).

The intensity of whirlwind near the wall essentially depends on the relative size of the activators and the distance between the activator and the wall (especially in the case of activator of small size).



a

b

c

Figure 5: Structure of the vibrational streams generated in the upper half of the cell (in dodecan) by the activator of radius $R_0 = 1.00$, 1.25 and 1.50 cm (*a*-*c*); $b = 0.784$, 0.457 and 0.588 mm ($f = 50$Hz).

Taking into account the mirror symmetry of the problem the velocity field has been investigated only in the upper part of the cell, in the liquid of lower density – dodecan.

Activators of different size located at various distance from the ceiling (bottom) of the cavity have been considered.

The frequency has been varied in an interval f = 25 – 100Hz and has been kept constant during the experiment with an accuracy of 0.2 Hz; the amplitude of vibration varies in the range b = 0 – 1.0mm; the optical micrometer with an accuracy $\sim 10^{-2}$mm has been used for measurement of the amplitude (the error not exceeding 5%).

3.2 Results

The structure and the intensity of the vortical flow excited by the activator depend on the distance between the activator and the cavity ceiling.

The following characteristic quantities have been considered as significant parameters to monitor: the axial velocity υ below the center of the activator at a distance equal to its radius and the velocity of radial flow u near the interface and below the center of the toroidal whirlwind.

Measurements performed several times at given parameters of vibration and vibrating body position have been used for the definition of mean values and the error bars. The scattering of the results may be ascribed to changes of the flow structure caused by a varying location of the vibrating body.

In experiments with activators with radius less than half of the cavity radius it has been found that the flow intensity (at definite values of amplitude and frequency of vibrations) grows with decreasing the distance between the activator and end face of the cavity (Fig. 6).

At large vibration amplitude one can see a nonmonotonous dependence of main whirlwind intensity on the distance h between the top border of the vibrating body and the end face of the cavity (marks 1 in Fig. 6 *a*, and *b*). This occurs especially for the activator of small diameter. According to the flow structure (Fig. 5) one can conjecture that the nonmonotonous behavior of the velocity is connected with the variation of the relative size of the toroidal whirlwind located near the face border.

For small vibration amplitudes (b = 0.1 – 0.2 mm) the vibrational current has low intensity; the jet does not reach the interface, and the velocity of liquid near the interface has a nonmeasurable small value. This is in agreement with the results obtained with the long cylinder (Fig. 2 *a*).

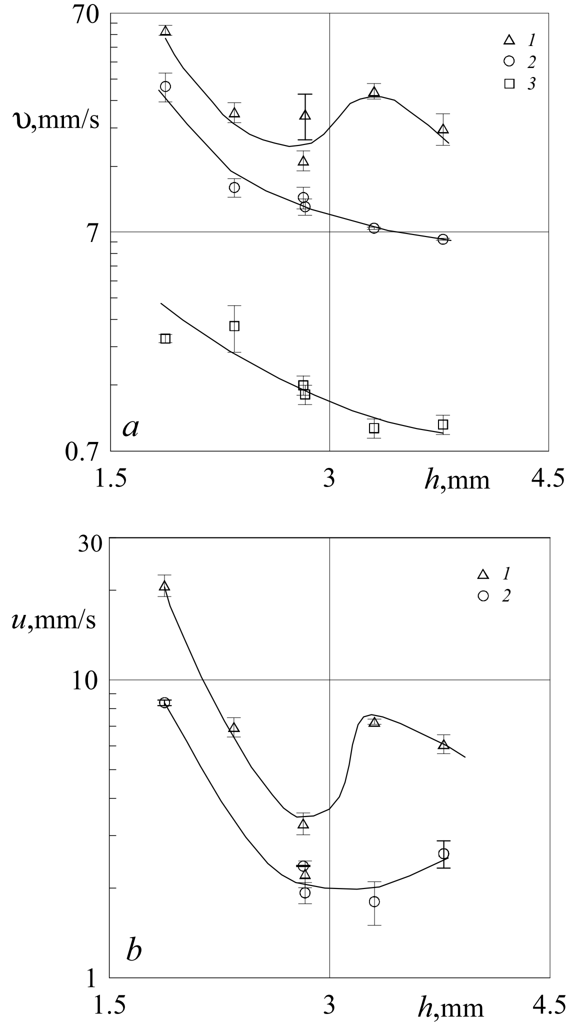


Figure 6: Mean flow velocity versus the distance h between the vibrating body and the cavity cover; a – axial flow, b – radial one; amplitude of vibration $b = 0.457, 0.326, 0.196$ mm (marks 1–3), $f = 50$Hz; radius of activators $R_0 = 1.25$cm.

The increase of vibration amplitude results in flow intensification and growth of the whirlwinds size. The axial velocity υ surpasses the radial one u.

One can see on the interface a spatial periodic system of vortices rotating in the opposite direction. The diameter of the rolls on the interface is close to the distance between the reflector and the lateral cylindrical cavity wall.

The structure and intensity of vibrational flows are essentially determined by the activator size. A decrease of the activator radius results in the intensification of the toroidal whirlwind near the end face of the cavity (its size becomes comparable with the size of the basic whirlwind, see Fig. 5 *a*).

The increase of the activator radius results in suppression of the near-wall vortex (the basic toroidal whirlwind occupies practically all the volume, see Fig. 5 *c*, and its intensity practically does not depend on the distance h between the wall and the activator, see Fig. 7).

Detailed investigation of the intensity of averaged flow as a function of the parameters of vibrations (at definite h) has been carried out with the activator of $R_0 = 1.50$cm, which provides the most effective intermixing of liquid in the bulk.

The axial velocity in the center of a cavity υ and radial one u near to the interface monotonously grow with the increase of vibration amplitude b at definite f (Fig. 8 *a*, and *b*).

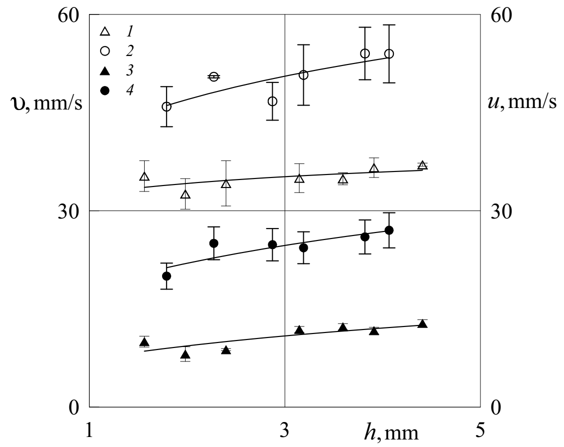


Figure 7: Flow velocity versus the distance between the activator and an end face of the cavity for $R_0 = 1.50$cm; marks 1 and 2 represent the axial velocity υ at $b = 0.457$ and 0.588 mm, 3 and 4 – the velocity of radial motion u at $b = 0.457$ and 0.784 mm.

With increasing f (at definite b) the intensity of currents also increases. In a wide interval of amplitudes the flow intensity (axial component υ) increases with the amplitude as $\upsilon \sim b^2$. At relatively large amplitude, $b \sim 1$mm, the velocity growth rate decreases with frequency.

At low intensity of vibrations ($b < 0.4$mm at $f = 25$Hz) the velocity is insufficient for the generation of flows near the liquids interface. The scattering of data can be explained according to axial shifts of the vibrating body (variation of the distance to the end wall).

4 Discussion

The nature of the vibrational flows excited by oscillating activators in incompressible liquids is known to be connected to the generation of a mean vorticity in the Stokes boundary layers near the solid surfaces, known as Schlichting mechanism Schlichting (1951).

According to Ivanova et al (1998) the structure of such vibrational flows is essentially defined by the shape of the vibrating body, in particular, by the presence of sharp edges whose curvature radius is comparable with the thickness of Stokes layers.

The results of velocity measurement in a dimensionless form are presented in Fig. 9; ν/R_0 is used as a velocity unit: $V \equiv \upsilon R_0/\nu$, $U \equiv uR_0/\nu$. The velocity grows with Re_p monotonously (Fig. 9). It is in agreement with Ivanova et al (1998) (vibrational streams under the end face of the vibrating cylinder plunged in the liquid).

The dependence V (Re_p) confirms that the parameter Re_p determines the intensity of axial current. This parameter becomes the only governing one in the limit case of high frequency when the thickness of Stokes boundary layers $\delta \equiv \sqrt{2\nu/\Omega}$ is much less than the radius of curvature $\tilde{r}$ of the sharp edge of the vibrating body.

Stratification of the curves on the plane of the chosen parameters proves that the condition $\tilde{r} \gg \delta$ is not satisfied and besides the Reynolds number the flows depends on the dimensionless frequency.

Following Ivanova et al (1998) we have introduced the parameter V/Re_p whose value should be constant within the high frequency limit. The dependence of V/Re_p on the dimensionless frequency $\omega = \Omega R_0^2/\nu$ at a definite value of $Re_p = 100$ is shown in Fig. 10 (marks 1).

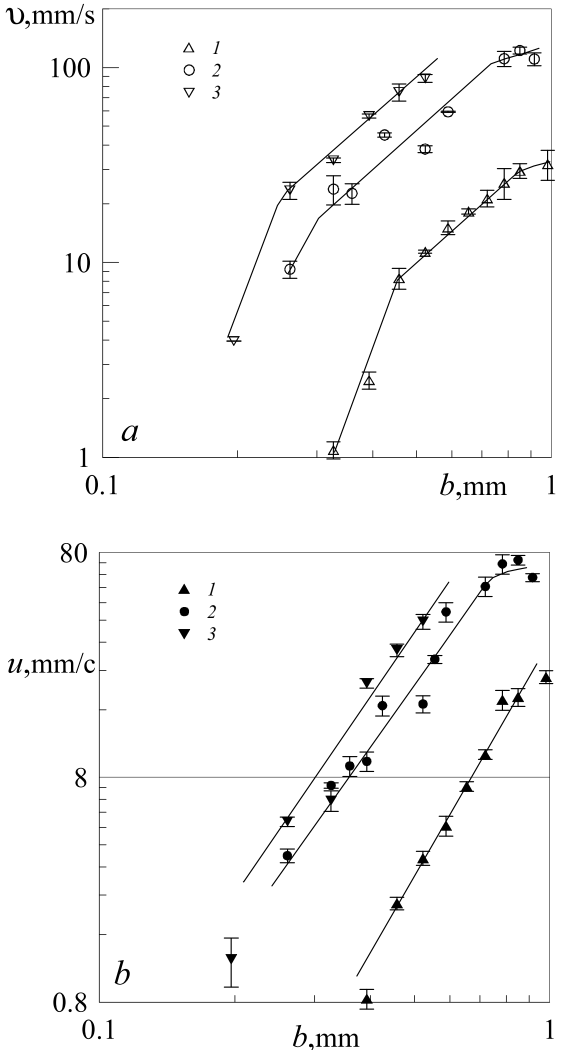


Figure 8: The velocity of axial (a) and radial (b) flows versus the amplitude of vibrations for the frequency $f = 25$, 50 and 75 Hz (marks 1–3); $R_0 = 1.50$cm, $h = 2.2 \pm 0.2$mm.

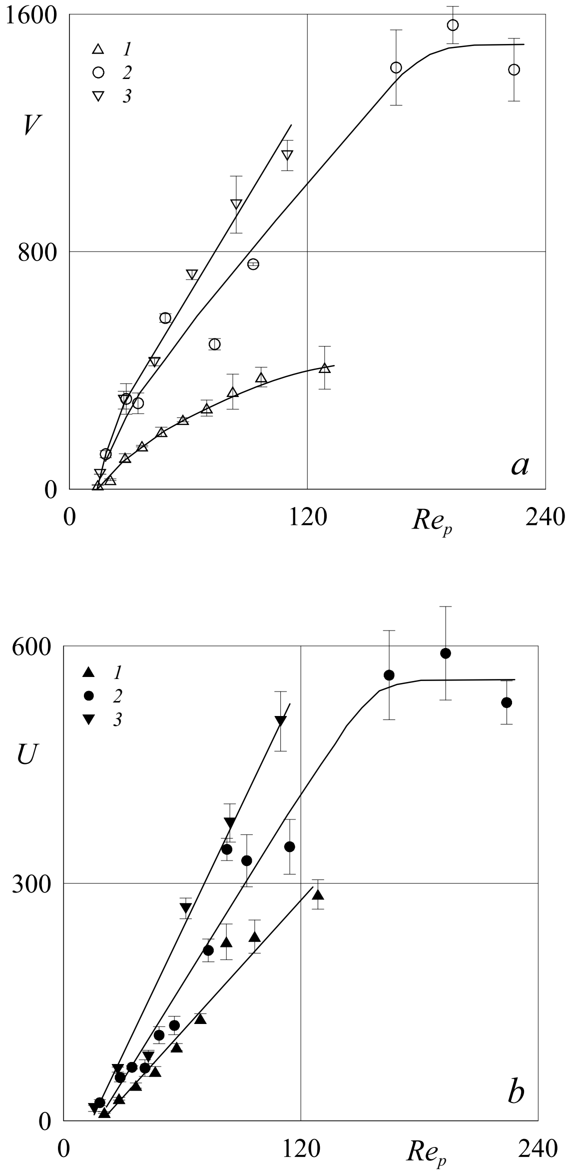


Figure 9: Dimensionless axial velocity (a) and radial (b) versus the Reynolds number; for the marks see caption of Fig. 8.

In the investigated range of frequencies a monotonous increase of V/Re_p with ω has been observed. It confirms the expected increase of efficiency of the vibrational mechanism of flows generation with the increase of ω.

In the area of low frequencies the obtained results are in qualitative agreement with the marks 2 Ivanova et al (1998), corresponding to $Re_p = 20$.

One can see the asymptotical behavior at high-frequency $\omega > 2 \cdot 10^5$. Despite of differences in the consired problems (a closed container with a small disk as an activator, $r = 1.66$ in the considered case; a free surface, the end face of a long cylinder, $r = 4$ in Ivanova et al (1998)), some qualitative similarities hold.

5 Conclusions

A new vibrational cell of the Lewis-type has been conceived and used for systematic experimental investigation.

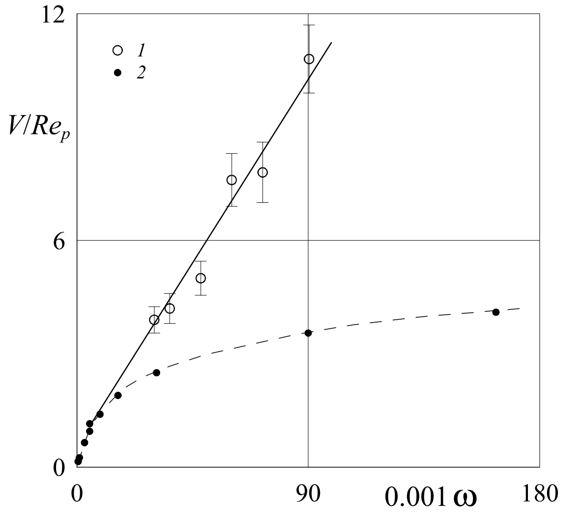


Figure 10: Parameter V/Re_p versus the dimensionless frequency ω; marks 1 refer to $Re_p = 100$, 2 – results Ivanova et al (1998) (different geometry) correspond to $Re_p = 20$.

By using a vibrational mechanics an intense axisymmetrical radial flow of liquid from both sides of the interface has been excited. When such flows carry away the superficial layer (in the absence of solid particles and surface active surfactants on the interface) they provide the most effective renewal of liquid close to the surface.

In particular, it has been shown that activators of large relative diameter generate whirlwinds involving practically the whole liquid volume and providing its complete homogenization.

The possibility of using vibrational excitation of large scale axisymmetrical vortical flows for providing effective interfacial mass transfer, therefore, has been proven.

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