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Oscillation of evaporating liquids and ispalator paradoxes

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Contents

Abstract. The surface active properties of the vapor of volatile, inert fluorocarbon compounds such as C_6F_{14}, C_8F_{18}, and $C_{10}F_{18}$ have been discovered. In a newly observed phenomenon of capillary instability, permanent oscillatory and rotary motions occur in many fluids, due to a 10 – 30% reduction in the surface tension of a fluid when in contact with fluorocarbon vapors at room temperature. The features and possible uses of the effect and prospects for finding new types of volatile surfactants are discussed.

1. Introduction

Phenomena on liquid surfaces occur in a thin boundary layer of nanoscale size, where the composition and density of particles change by several orders. The properties of phase boundary surfaces attract the attention of a large number of specialists. Physicists are concerned with them when they investigate friction and lubricants, wetting and coating, production of high vacuum, memory units and sensors as well as two-dimensional monomolecular crystals based on Langmuir – Blodgett films. Specialists in hydrodynamics and aerodynamics are interested in interfacial phenomena as they analyze mechanical properties and processes in subsurface layers. The subject is also of concern to chemists who investigate corrosion, operation of catalyzers and efficiency of chromatographic separation of mixtures; to biologists who deal with membranes, processes in lungs as well as embryonic self-organization and cell specialization, and to geophysicists who model weather changes on the Earth with due regard for interactions between ocean surfaces and the atmosphere and the El Niño effect. Superficial layers are investigated experimentally with atomic-force scanning microscopes, by optical methods with the generation of summary frequencies and harmonics, or using X-rays and neutrons, as well as analytically and by mathematical modelling with the use of the most powerful supercomputers. The results of these investigations are reported in dozens of journals on surface phenomena, and a lot of reviews and books are published every year.

As pointed out in the scientific literature [1, 2], over the past three decades the thermodynamic properties of one-

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component liquids have been described theoretically in great depth unlike simple two-component mixtures, where a lot of problems are yet to be solved. Despite great practical interest and essential results of studies, interfacial phenomena remain something of an enigma and surprise. In this work we describe some easily accessible and readily reproducible experiments where one of the new such phenomena reveals itself and give an explanation for the results.

2. Experiments with ispalators

2.1 Description of an ispalator

An 'ispalator' [3 – 6] (the term is a contraction from the words 'evaporator' and 'oscillator' in Russian) is a device where unusual oscillations on liquid surfaces are observed. It is a simple glass or container containing several immiscible liquids. The shape of the container is of no concern; what matters is only the wettability of its walls and the choice of liquids. An open glass or container of diameter 3 – 6 cm and of height 4 – 6 cm is filled, for example, with three chemically inert liquids: water, dibutyl phthalate (DBP) specially colored with a dye, and the heavy fluorocarbon liquid (perfluoroctane) C_8F_{18}.

The rate of evaporation of liquids is proportional to the pressure of their saturated vapors. For water this value makes up about 20 Torr at room temperature. The boiling point of DBP is 340 °C; the pressure of its saturated vapor is rather low, and it virtually does not evaporate at room temperature [7]. Fluorocarbon liquid C_8F_{18} consists of linear molecules with completely saturated bonds [8]; its boiling point is 106 °C and density is 1.8 g cm^{-3}; finally, its vapor pressure at room temperature is about 20 Torr, as in the case of water. This substance is a liquid analogue of Teflon; it is absolutely inert and similar to other fluorocarbon liquids which are used in surgery as components of an artificial 'blue' blood [9, 10], since they transfer oxygen and carbon dioxide well (better than erythrocytes).

Due to peculiarities of interactions with the container walls and fluorocarbon liquid, a 4 – 5 mm thick water layer has two stable shapes. It can be either flat, being continuous, or have a shape of a torus or a ring adjacent to the container walls, the center of the ring being water-free and occupied by fluoride liquid. The upper level of the water ring is several millimeters higher than the level of the fluoride liquid; in the middle this water ring has a funnel shape with the wall covered by a colored DBP ring. Figure 1 depicts an ispalator photographed from the side through a transparent container wall [5, 6].

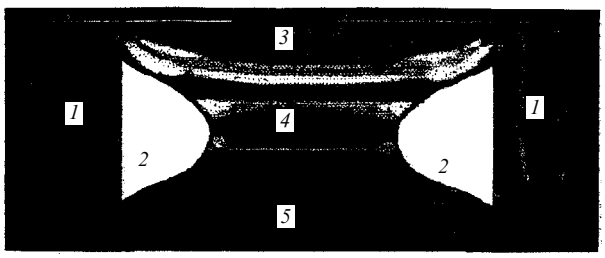

Figure 1. Side view of an ispalator containing three liquids: *1* — container walls (distance between the walls is 20 mm); *2* — a toroidal water 'roll' of height 5 – 8 mm, adjacent to the container walls; *3* — air; *4* — colored DBP ring of height 2 – 5 mm, diameter 8 – 15 mm, and thickness 0.2 – 1 mm, which is in contact with water; *5* — bottom layer of C_8F_{18} liquid.

Water, DBP, and fluorocarbon liquid C_8F_{18} do not mix; after shaking and mixing they separate again in a matter of minutes and do not enter into any chemical reactions between themselves. In a closed container they can remain in one of the stable forms for an arbitrarily long time, for example, in the one depicted in Fig. 1: a water ring adjacent to the container walls, the free surface of a fluoride liquid in the middle and a colored ring of a small amount of DBP at the interface between water and fluorocarbon liquid. All the three liquids have a common upper surface.

The DBP ring formed in a closed container and bearing a laser dye is a ready laser unit. We investigated the peculiarities of such units, which are naturally produced and are the cheapest laser resonators and waveguides of unusual shape (having ideal, unimpaired, optically smooth surfaces sensitive to external actions), where lasing with optical pumping takes place due to total internal reflection of light from interfaces [5, 11, 12]. But here we will not dwell upon the laser properties of such rings.

2.2 Waves propagating from the surface ring

In an open container where liquids are free to evaporate, an unusual intense motion arises on their surfaces in a matter of minutes, which outwardly has no analogues among physical systems and requires detailed consideration. The colored DBP ring becomes as if alive and starts spontaneously ejecting waves of colored DBP. The waves have the form of thin films which propagate along the inclined water surface with an amplitude of about 1 cm and period 1 – 3 ejections per several seconds, the number of ejections varying in different sectors of the ring (Fig. 2). Then the waves on the water surface transform into drops, which come back to the central DBP ring across the inclined water surface due to their proper weight. The whole cycle lasts several seconds and then resumes again. Once started this closed process of mechanical oscillations of the nonvolatile DBP ring lasts for hours and days, till one of the liquids evaporates almost totally. The pattern of motion of the two-dimensional waves is virtually independent of the shape of the container or environmental temperature (the latter was checked at temperatures in the range from 0 to 100 °C). At room temperature 20 °C, the total mass evaporating from the container does not exceed 0.1 g h^{-1}. In a closed container the oscillations come to a stop in 5 – 10 minutes, when the pressure of the vapors reaches equilibrium. Inside the container these vapors can be condensed on a cool trap and returned to the fluids as drops. So, in a hermetically closed ispalator the oscillations are perpetual (already several years).

The choice of liquids for ispalators is rather wide. DBP can be changed for another fluid, which does not mix with water and fluorocarbon [turpentine, dimethyl phthalate (DMP), oil, ether, cyclohexane, etc.]. Perfluoroctane C_8F_{18} can be replaced with other fluorocarbon liquids such as perfluorohexane C_6F_{14}, perfluorodecaline $C_{10}F_{18}$ [8], and so forth. No special precautions are required in this case, since these saturated fluorocarbons are absolutely harmless fluids without smell, flavor, color, and completely chemically inert.

2.3 Drops on the water surface

A drop of C_8F_{18} or DBP (or benzene) has a lens shape on the water surface and does not move. But if a C_8F_{18} drop of volume about 0.1 cm^3 and a similar DBP (or benzene) drop

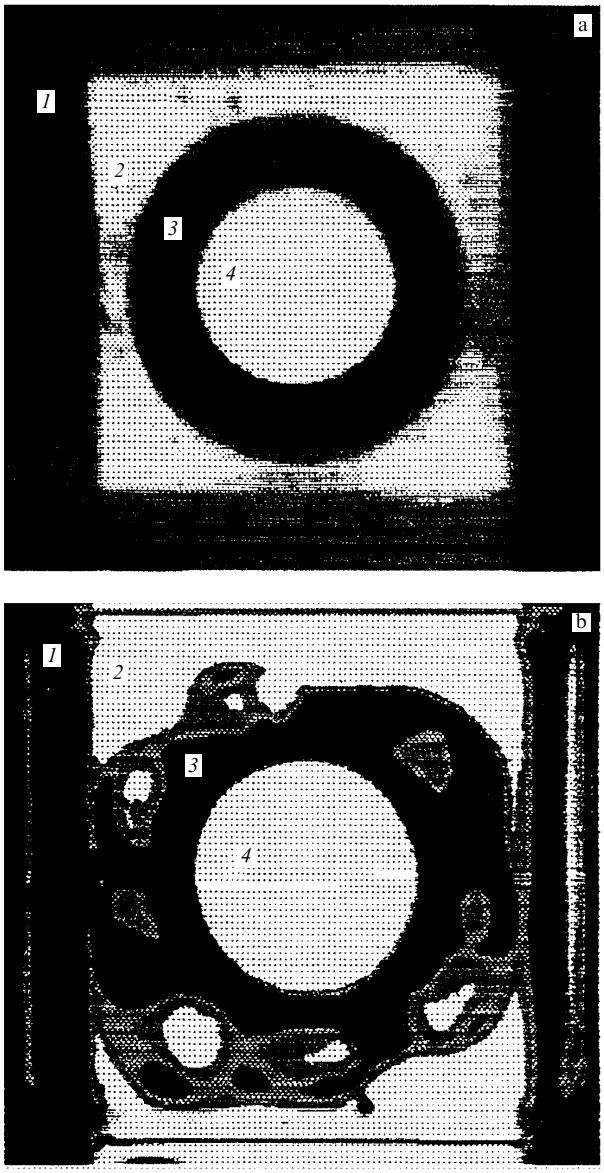

Figure 2. Top view of the ispalator containing three liquids in a closed (a) and open (b) container with chaotic surface waves repeatedly generated due to concentration capillary instability: *1* — container walls; *2* — water adjacent to the walls; *3* — colored DBP ring; *4* — free surface of C_8F_{18}.

interpose at a distance of 3 – 4 cm on the water surface in a wide open container, these drops of chemically inert fluids start moving closer together and interact intensively within a few minutes. This complicated physical process is similar to the behavior of living organisms with a trembling tremor of convergence, fusion and separation, with the ejection of films and formation of new drops till one of the liquids evaporates completely. A piece of ice on the water surface decelerates or absolutely terminates the interactions between the drops.

2.4 Vortex ring

It is interesting to carry out an experiment in an ispalator without water. In this case there are only two fluids in the container, i.e. C_8F_{18} and a ring of another fluid (for example, ethanol, 2-propanol, kerosene, glycerine, ether, benzene, CCl_4, DBP, DMP, oil, or dioxane) above it. In an open container the liquid ring (or torus) above the C_8F_{18} starts rotating perpetually in the vertical plane as a vortex. Neutral tracer particles added to the liquid for observation show that in the upper layer of the ring they move with velocity 1 – 10 cm s^{-1} radially from the central free zone to the walls. Then with a lower velocity they go down to the level of the fluorocarbon liquid, come back again to the central zone radially and rise up. Such a rotation of the ring in a hermetic container with a trap above the liquids, which is cooled by a fraction of a degree due to evaporating ordinary water, has continued for several years in our experiments, with the rate of vapor condensation on the trap being about 2 – 4 drops per hour. The estimated power required to maintain the rotation of the ring is about 10^{-5} W.

2.5 Liquid curtain

In the ispalator with a rotating ring a portion of the fluid in the form of a thin film rises along the container walls to a height of 2 – 30 mm above the fluid and there forms a ring of liquid drops. These drops are small for ethanol and DBP (their diameter is several tenths of millimeter) and form at a height of several millimeters. Benzene, kerosene, and 2-propanol drops are large, about half a centimeter in diameter; they form at a height of several centimeters and then go down along the walls similarly to the folds of a liquid curtain. Below, near the ring these drops change their position and height every second as if dancing in the flow of the film moving upward on the wall (and above the drops). Sometimes the drops come in contact with the liquid surface, partially merge with it and then set up on their own again. In essence, the films, waves, and drops, which were observed in the first experiment (see Section 2.2) with DBP on the water, in the case under discussion consist of the liquid of the ring and occur on the container walls.

If, upon stirring, the curtain of drops on the container walls is washed by liquid C_8F_{18}, the rotation of the ring ceases and the whole of the curtain starts going slowly down to the liquid ring (benzene, kerosene, ethanol – ether mixture). Several wedge-shaped fronts (with vertex angles about 20 – 80°) are formed at the upper boundary of the curtain, which descend with a velocity of 0.5 – 1 cm s^{-1} and move down the main portion of the curtain liquid. During this motion a narrow liquid bend of width 0.5 – 1 mm is formed at the vertical bisectrix of each angle, then this bend runs upward and evaporates. Within 3 – 5 s after complete dropping of the curtain and resumption of the ring rotation (which does not start at once over the whole body of the ring, but first only in a narrow region of width 1 – 2 mm near the walls, and then within 2 – 3 s extends to the whole of the ring), flat finger-like formations of width 1 – 2 mm start springing up all over from the liquid near the walls (the approximate rate of growth is 1 cm s^{-1}). At a height of 5 – 15 mm these fingers become thicker at the tops, merge with their neighbors, and give off drops, which move down and thus restore the earlier fallen curtain on the walls. The complete resumption of the curtain requires about half a minute. Such dropping and rising of the curtain can be observed repeatedly after each washing of the container walls. The curtain of lowering drops results from the fact that the velocity of upward transport of the liquid with a moving film exceeds the rate of liquid evaporation from the walls.

When the liquid in the ring is colored, the drops on the walls are also colored, and a colored ring of dry dye is gradually formed at the upper boundary of the liquid curtain. Dye molecules are carried upward from the rotating

ring by the moving film due to the action of capillary forces. The rotation of the ethanol ring terminates after the addition of 40% water. The water behaves differently; it does not rotate in the ring. The rotation of the water ring starts if we add a little soap, but the rotation rate is two orders less than that for ethanol and makes up 0.2 – 0.3 mm s^{-1}. The rotation rate of dimethyl sulfoxide (DMSO) is also so low.

The rotation rate of the ethanol ring increases as ether is added (10 – 50% by volume). On the C_8F_{18} surface, a pure ether (as well as benzene, kerosene, and 2-propanol) ring rotates at the maximum rate. Ether mixes with C_8F_{18} partially, pentane mixes completely, and benzene, ethanol, DBP, kerosene, and 2-propanol mix with C_8F_{18} to only a small extent. The liquids mix better with C_8F_{18} as the temperature rises, and if the temperature subsequently decreases the transparent C_8F_{18} layer gets muddy for several minutes (due to decreased mixing). Nonlinear $C_{10}F_{18}$ molecules with a ring-like structure are virtually not detected to mix with ether, DBP, and pentane.

2.6 Drops from the trap

As indicated above, condensed vapors in the form of drops return to liquids in a hermetic container with a cool trap of diameter about 1.5 cm, which is located at the center of the container at a height of 1 – 1.5 cm above liquids. Due to the long-term stable conditions of cooling, we can estimate the amount and composition of the liquid drops condensed at the trap and closing the chain of substance rotation in the ispalator upon moving downward. Visual estimates of the amount and composition of these drops falling from the trap demonstrate that the thickness of the film evaporating and condensed in drops does not exceed several nanometers at the maximum width of the moving front of 10 cm and a linear velocity of about 10 cm s^{-1}. In this case the molecules of C_8F_{18} can lie on the film surface as a continuous monomolecular layer. To increase the rate of vapor condensation in our experiments we cooled the ispalator trap with snow or ice.

The composition of the drops also has some peculiarities. All the drops are colorless, but due to the different volatility of the compounds they have different compositions, which result in their different behavior later. A cool C_8F_{18} drop fallen from the trap to the free C_8F_{18} surface merges with the bulk liquid and disappears. But a drop containing fluid of the ring, upon falling on C_8F_{18} moves sideways and then merges with the ring fluid. However, sometimes the ethanol drop on the free surface of C_8F_{18} does not move instantaneously to the ring but, on the contrary, shifts to the center of the container as a ball of diameter 2.5 – 3 mm and without wetting depresses the C_8F_{18} surface giving it an arclike form, and lies there practically fully in sight of the observer as an ideal sphere for 3 – 15 s. Some motion is observed on the drop surface; when it ceases the drop sharply changes its shape. The surface tension of the ball decreases dramatically, its height diminishes but the diameter increases to 4 – 5 mm, and the drop half immerses into the C_8F_{18} and then rapidly moves sideways from the center to the ring and merges with it. It seems that the falling ethanol drop is sometimes covered with C_8F_{18} film, but the difference in temperatures and the separating gas layer under the drop do not allow the molecules of C_8F_{18} to merge with the bulk C_8F_{18} liquid immediately.

2.7 Drops on a continuous layer

When a cool C_8F_{18} drop falls from the trap onto the continuous benzene layer, it partially remains on the benzene surface as a flat-convex lens or a sagging drop of diameter 4 – 5 mm, incessantly changing its shape and size, and immediately giving off a flow on the benzene surface. Tracer particles in the benzene run over the benzene surface from the C_8F_{18} drop to the walls, then move down nearly to the bottom of the benzene layer and return to the C_8F_{18} drop. Near the spot external boundary they rise and move to the walls again. Within its lifetime (1 – 3 min), the diameter of the C_8F_{18} spot varies periodically from 5 to 20 mm, oscillating with a period of 5 – 15 s. The fall of a new cool C_8F_{18} drop from the trap onto the benzene surface immediately causes a decrease in the diameter of the C_8F_{18} spot to 5 mm followed by its expansion. Under equal conditions of trap cooling, the dust particles travel across the surface of the continuous benzene layer with the rates that are twice as large as those in the rotating benzene ring.

2.8 Rotation in a continuous layer

The following experiment demonstrates that liquids can rotate in the absence of a C_8F_{18} drop on the surface. In this case, as in the first experiment (see Section 2.2), an open container of diameter 3 – 6 cm and height 4 – 6 cm is filled with C_8F_{18}, the height of the fluorocarbon layer being 5 – 15 mm, and with kerosene (benzene, 2-propanol), the height of the continuous layer being 1.5 – 2 mm. To follow the process we added small tracer particles of wood ash or cotton filaments into the kerosene.

A permanent flow arises in the kerosene layer without any C_8F_{18} on its surface. The flow runs over the surface from the center of the container to the walls, then lowers near the walls to the C_8F_{18} level and moves back to the center of the container along this level where, in a small region of diameter about 1 – 2 mm, it rises to the surface and then repeats the motion. The flow rate is about 2 – 10 cm s^{-1}. In essence, the tracer particles move as in a rotating ring, but this ring degenerates: its internal diameter reduces to zero. The rotation in the continuous layer is made possible due to the delivery of C_8F_{18} molecules onto the kerosene surface, which takes place owing to the low solubility of C_8F_{18} in kerosene. The times of solution and evaporation of the C_8F_{18} molecules are equal to the period of rotation and do not exceed 3 – 5 s. Ordinary kerosene drops are seen on the walls as a curtain (as in the case of the rotating ring). In a container of diameter 5 – 10 cm, several centers of elevation arise in the kerosene layer, which move along the surface, merge and are generated again. A similar rotation is observed in a continuous layer above C_8F_{18} in the case of the mixture of ethanol and 20 – 50% of ether. Such a rotation does not take place in a continuous layer of pure ethanol above a bulk fluorocarbon liquid.

2.9 The heating effect

Minor heating leads to a decrease in the surface tension of the liquid in the presence of C_8F_{18} molecules. Under equilibrium conditions (in a hermetic container without any cooling), a fluorocarbon drop of diameter 3 – 5 mm can lie on a continuous kerosene layer for many hours. But even the lightest breath or touching the walls with a finger causes the drop to react, immediately shifting 1 – 1.5 cm away from the contact point. When we focus an image of an incandescent lamp on the drop at rest (for example, a lamp of power 50 W is placed at a distance of 1 – 2 m from the container and the lens used has diameter 3 – 5 cm), the drop immediately enlarges two or three times, gives off films at the boundaries and tends to move away from the heating point.

2.10 Preliminary conclusions

Based on these data we can make a preliminary conclusion about the nature of the above-described phenomena. In all the experiments we observe the motion of liquid films under the action of various forces of surface tension. In the middle of the container near the free region this tension is less than near the walls. The motion over the liquid surfaces, caused by various surface tensions, is named the Marangoni effect [13] after its discoverer, who described it more than hundred years ago, although at a later time an earlier description of this phenomenon was found in Thompson's heritage.

The effect of surface tension forces is easily observable in a visual school test with a toy paper ship on water. A piece of soap on the stern sets the toy-ship in motion. A decrease in the surface tension of water under the action of surfactants similar to soap makes the toy-ship move until the soap covers all the water surface in the container with a monomolecular layer; after that the toy paper ship stops for the absence of moving forces. However, in ispalators a similar motion is permanent, i.e. a difference in the surface tensions between various regions of one and the same liquid is created naturally and perpetually maintained in the container without any special power consumption.

The experimentally examined oscillations and rotations of many liquids and the rising of their films along the walls can be explained if we assume that the fluorocarbon compounds play the role of surface active substances which poorly dissolve in liquids, but presumably dissolve well in their surface layers and then easily leave them. In what follows we will discuss the correctness of this assumption, and now we describe some other experiments confirming the validity of this conclusion.

2.11 Gas motion

Using smoke, we can follow the motion of gas above the rotating ring. Near the surface of the ethanol ring in a layer of a fraction of a millimeter in thickness, the gas moves similarly to a liquid, from the center to the walls. Then the gas elevates through several millimeters and radially returns to the central zone where it moves down and then again runs to the walls. Such rotation of the gas above the ring and its upward motion only near the walls demonstrate that most of the fluoride molecules evaporate not from the free surface in the center of the container but from the walls, where these molecules are brought by a liquid film with a velocity exceeding the rate of diffusion of these molecules through the gas in the direction opposite to the free zone.

2.12 The influence of the wall substance

The influence of the composition of container walls on the rotation of a liquid ring is revealed in an experiment where a fragment of a glass wall in the angular sector 45 – 180° is covered with a Teflon film over the whole height of the container. After shaking the container, the ring can hold its shape, and in this case the rotation resumes only in the sectors which are not covered with Teflon. But often in practice the liquid of the ring wets Teflon poorly, and after shaking it tends to leave the sector covered with Teflon. Liquid C_8F_{18} wets Teflon well, therefore, the free zone of C_8F_{18} shifts from the center to the covered sector and contacts the Teflon. In this case the ring transforms into a horseshoe or a semiring and the liquid rotates with the same velocity as before in the sectors free of Teflon. The liquid rings in an aluminium container rotate with a velocity lower than that in a glass container, but a Teflon coating has the same effect on the ring as in the glass container. Additional cooling of a sector of the container by ice from outside increases the size of drops and decreases the rotation rate of the ring in this sector.

2.13 Evaporation from the walls

If we put a funnel-like cap with a central hole of diameter 10 mm on an open container, the distance between the hole and the free surface of the fluoride liquid being 1 – 2 mm, then the rotation of the ring terminates. The latter suggests that it is just the evaporation from the walls that is important for the rotation. This fact also accounts for the resumption of the ring rotation in the experiments with the liquid curtain (see Section 2.5), when the rotation starts initially in a narrow zone near the walls, from whence the film (found on the ring) containing fluorocarbon molecules extends over the walls for evaporation.

In a closed container, when the equilibrium vapor pressure is settled over the whole volume of the container, the rotation of the ring terminates. In an open container (or in a hermetic one with a trap), where the vapor density is different at various heights, a constant difference in surface tensions of liquids arises, which causes the rotation of the ring or the propagation of waves across the surface. After evaporation of fluoride molecules, the surface tension of the liquid increases, the liquid assembles in drops and returns to the ring due to their weight. This effect resembles the so-called 'wine tears' described in the scientific literature [14, 15], which are formed on the walls of a cup with strong wine when alcohol evaporates from the solution; the only difference is that in our case we are dealing with torrents of tears, rather than individual ones. The similarity to another type of tears will be considered below.

2.14 Vapor effects on the particles on the surface

The influence of C_8F_{18} vapors on the surface tension is clearly demonstrated in the following experiment. We fill the container with kerosene (turpentine, DBP) and apply ash particles over the kerosene layer to mark it. If we bring a needle wetted with a liquid C_8F_{18} into the container, the distance between the needle and the kerosene surface being 5 – 10 mm, and move the needle over the kerosene, then the ash particles quickly run away from the needle due to the decreased surface tension of kerosene under the needle till it produces a small amount of C_8F_{18} vapor. A decreased velocity of recession is observed when the needle is wetted with a liquid $C_{10}F_{18}$ (an increased velocity will be considered in Section 5.3).

2.15 Drop descent in vapor

A decrease in the surface tension of liquids under the action of fluorocarbon vapor is also clearly demonstrated in an inverted experiment. The container is filled with a liquid C_8F_{18} and a needle with a drop of benzene (or ethanol, DBP, kerosene, 2-propanol) at its point end is slowly lowered into the container. In the air this drop is firmly attached to the needle and does not come off even with considerable acceleration. But in the container at a height of about 1 cm above liquid C_8F_{18}, where the density of heavy vapors is 20 Torr at 20 °C, the drop comes off the needle because of the surface tension reduction. We can see that the drop reversibly (and fast) changes its shape as the needle is put in or taken out of the container with C_8F_{18} vapor.

Table 1. Reduction (in %) of the surface tension of some liquids in fluorocarbon vapors.

No. from Ref. [16]	Vapor	Liquids							
		Ethanol	2-propanol	Benzene	DMP	DBP	Kerosene	CCl_4	Ether
670 (685)	C_6F_{14}	10	12	19	25	20	18	22	26
549 (560)	C_8F_{18}	7	10	12	17	20	16	20	16
546 (567)	$C_{10}F_{18}$	< 3	7	6	11	6	4	7	16

3. Measurements of surface tension in vapors by the drop method

3.1 Results of measuring the surface tension of liquids

The above-described qualitative experiments suggest a simple way to measure a decrease in the surface tension of liquids in an atmosphere of various fluorocarbon vapors. The number of benzene (ethanol, DBP, 2-propanol, kerosene, etc.) drops falling from a pipette of a certain volume increases by tens of percent when the pipette end is lowered into a container with C_8F_{18} vapor as compared to the number of drops falling in the air. The reduction of the surface tension of liquids estimated with an accuracy up to 3% is listed in Table 1 (as a percent of the initial value) and was estimated by an increase in the number of the drops of these liquids in fluorocarbon vapors. The first column lists the corresponding numbers of the fluorocarbons as they are given in PiM firm catalogue of 1998 (in parentheses the corresponding numbers from the catalogue of 2000) [16] where some properties of the compounds are also described. The saturation vapor pressure of perfluorodecaline $C_{10}F_{18}$ is about 3 Torr at room temperature, while that of perfluorohexane C_6F_{14} is about 150 Torr [8].

3.2 Changes in DBP surface tension versus the density of C_8F_{18} vapor

Figure 3 plots the dependence of a decrease in the DBP surface tension on the density of C_8F_{18} vapor in air at 20 °C. Starting from the initial value of 33 dyn cm^{-1}, the surface tension approximately decreases by a third at the saturation vapor pressure of C_8F_{18}. For a further increase in vapor pressure (and the elevation of temperature), the surface tension of liquids decreases insufficiently. Thus, as the density of C_8F_{18} vapors increases 30 times from 20 to 600 Torr (at 97 °C), the surface tension of DBP heated up to the same temperature decreases from 20 to 40%. Although the molecular structures of C_8F_{18} and C_6F_{14} are similar, the pressure of saturated C_6F_{14} vapor is 7-fold higher than that of C_8F_{18}, but as is seen from Table 1, it does not lead to a pronounced decrease in the surface tension of liquids.

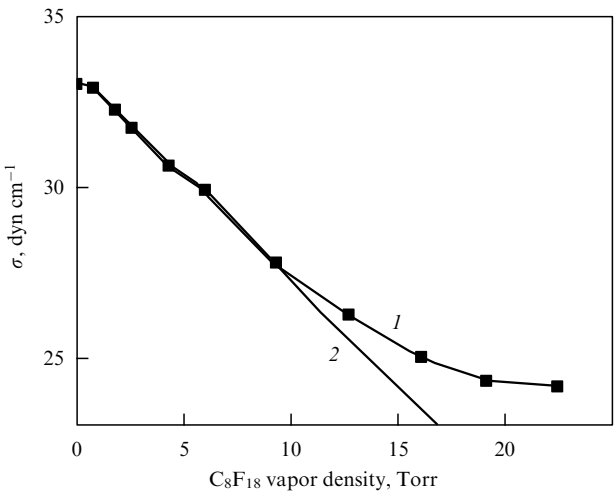

Figure 3. Reduction of DBP surface tension versus C_8F_{18} vapor density in air above the liquid at room temperature: *1* — experimental data; *2* — a linear approximation of the dependence at low pressures.

3.3 Break up of the DBP jet into drops

We can judge the dynamics and the rate of change in the surface tension of a fresh liquid after its contact with vapor observing the jet of DBP freely issuing from a pipette. In air, a jet of about 1 mm in diameter breaks up into drops at a distance of nearly 5 cm from the lower end. In air with saturated C_8F_{18} vapor, the same jet breaks up into drops at a distance of 15 cm. Without dwelling on the details of this complicated process [17, 18], we can conclude from the initial velocity of the jet at the pipette end (equal to 1 m s^{-1}) that changes in the surface tension of fresh DBP inserted into C_8F_{18} vapor take less than 0.1 s.

4. Conclusions and paradoxes

4.1 Fluorocarbon compounds as surfactants

Thus, the results of our experiments demonstrate that fluorocarbon compounds in the gas phase show the properties of surfactants and even at low concentrations significantly reduce the surface tension of organic and inorganic liquids [3, 4]. ***The diversity of the interactions, motions and rotations observed is based on the reduction of the surface tension of liquids, in response to changes in the density of fluorocarbon vapor above the liquid.***

This conclusion about the surface activity of fluorocarbon compounds seems convincing and indubitable, however, it sharply contradicts some conventional views, and hence is rather paradoxical.

The first (*physical*) *paradox* lies in the fact that, according to conventional views, *no* inert gases above liquids under a pressure less than several hundreds of atmospheres have an effect on the surface tension of liquids due to their low density [19]. This statement is based on the physical fact that surface tension arises from resulting interactions between many molecules. Gas can considerably influence the surface tension of liquids when its density is close to that of the liquid. For example, to reduce the surface tension of cyclohexane by 25%, a pressure of hydrogen of about 300 atm is required [20]. This commonly accepted rule has had no exclusions so far. But here we see that an absolutely inert fluorocarbon gas decreases the surface tension of various liquids by the same 20 – 30% even at a pressure of hundredths of an atmosphere (i.e. by 4 orders less than required according to the conventional rule). How can this be the case?

The second (*chemical*) *paradox*. All known surfactants have a polar structure and *necessarily* include hydrophilic and

hydrophobic end groups [21–24], such that the former prefer to be in liquids, while the latter are pushed out of it. As a result, surfactant molecules concentrate in the surface layer. Fluorocarbons do not have such end groups: they are symmetrical nonpolar molecules. How can they be surfactants?

The third (*thermodynamic*) *paradox*. When a cool trap contains ice, the temperature of the container walls is usually 2–3 °C less than that of the liquids. Hence, fluorocarbon molecules transfer with the film from a warmer region at the bottom of the container to a cooler one on the container walls for *evaporation* (see Section 2.11), i.e. they move in the direction opposite to that in ordinary thermal tubes. The absence of a temperature gradient typical of heat engines demonstrates that the motion in the ispalator is set up by a mechanism different from that in a Carnot cycle. It is also evident that this motion is caused by the difference in the concentration of fluoride molecules and, in principle, can occur under evaporation in *isothermic* conditions, too. Note that the development of an engine capable of working under isothermic conditions is an important problem of modern science [25].

The fourth (*theoretical*) *paradox*. To resolve all the above mentioned paradoxes, a conclusion is made which, in essence, is also paradoxical. According to this conclusion, fluorocarbon molecules become surface active only when they collide with the liquid surface and form *pair complexes* on it with molecules of various liquids (as they do with oxygen or CO_2 molecules in the artificial blood, where the binding energies are equal to 0.1–0.2 eV [26, 27]). The molecules of liquids can bind only to one end of a fluorocarbon molecule, namely, to CF_3 groups, since we know that the Teflon surface where these groups are few in number, is not wetted by the liquids. In this complex a molecule of the liquid plays the role of a hydrophilic group and remains in the liquid, while the long chain of a fluoride molecule plays the role of a hydrophobic group of the complex and is pushed out of the liquid. Occupying the liquid surface, the fluoride molecules decrease its surface tension, the latter depending on the degree of surface occupation [28].

However, these surface active complexes (SAC) are not very stable. Judging from the collision frequency of fluorocarbon molecules with the liquid surface at a vapor pressure of 10 Torr, at which the dependence of the surface tension on the vapor density begins to show a nonlinear character and the decrease in surface tension is saturated (see Fig. 3), these complexes exist for fractions of a microsecond (10^{-7} s). This lifetime is determined by the complex strength. Thus, for ethers it seems to be shorter, since as the volatility of the compounds increases (see Table 1), a saturation in the decrease of its surface tension is detected even in $C_{10}F_{18}$ vapor. For some compounds described below, this lifetime is considerably longer. The decrease in the surface tension is determined by the total density of such complexes on the liquid surface, where they are in dynamic equilibrium. This density easily and virtually immediately changes depending on the vapor pressure in the adjacent layer. To our knowledge, such thermodynamically unstable SACs with nonpolar fluorocarbons have not been found or considered so far, but the effects observed in ispalators require their existence.

The proper surface tension of fluorocarbons at the air boundary is usually about 12–14 dyn cm^{-1} [8]. At the boundary with some other liquids (except for water and DMSO) this surface tension is nearly twice less according to our measurements. For liquids in contact with fluorocarbon vapor, i.e. partially covered from above with a layer of complexes with fluorocarbon molecules, this surface tension is higher. This difference in surface tensions is responsible for the upward motion of films from the low boundary of the ring and to the container walls, thus causing permanent rotation of the liquid rings.

And, finally, a *paradox of obviousness*. Fluorocarbon compounds are not found in nature [29, 30], and mankind started dealing with them together with other fluoride compounds half a century ago, after the Manhattan project on the atomic bomb. Thus, for half a century thousands of people all over the world have been dealing with the production of a huge amount of fluorocarbons, which are used, sunk, mixed, and investigated every day. Why has this effect, which stands out visible to the naked eye in an open glass, required so many years to be discovered?

4.2 Vapor action and problems

Among the other main changes in the properties of liquids in an atmosphere of fluorocarbon vapor the following are noteworthy. The velocity of rising of the boundary of liquid DBP along a thin-layer chromatographic plate decreases approximately by 23% when saturated C_8F_{18} vapor is present in the ambient air. This fact is in agreement with the 20% decrease in DBP surface tension. The velocity of rising of the boundary of water along the same plate decreases several times in an atmosphere of air and saturated 509 compound vapor (Table 2). The amplitude of oscillations of rising air bubbles from side to side in liquid, which was of concern to Leonardo da Vinci as far back as 500 years ago [31, 32], decreases several times in kerosene and DBP, when the bubbles contain saturated C_8F_{18} vapor.

Of practical interest is a reduction of the surface tension of various engine oils in an atmosphere of air and saturated fluorocarbon vapor. This decrease results from the formation of a permanent layer of fluorocarbon complexes on the oil surface. Besides, fluoride vapor here plays the role of an unusual modifier of lubricants [3]. Our measurements show that such dynamic fluorination of the oil surfaces in mechanical devices through their contact with fluorocarbon vapor considerably decreases the friction coefficient in lubricated mechanical units. For example, if we put an ordinary wrist watch into a glass containing C_8F_{18} vapor, then in approximately 10 s the maximum angular amplitude of oscillations of watch's pendulum will regularly increase by 10–30%, while the watch remains in the glass. When we take the watch out, the maximum amplitude of oscillations will return to the initial value in 10 s. The peculiarity of gas modifiers of lubricants is in the fact that they make possible a permanent restoration of the fluorinated surface damaged by friction both due to contact with fluorocarbon vapor and the displacement of the fluorocarbon layer with decreased surface tension to damaged surface regions with high surface tension (as in ispalators).

Volatile fluoride surfactants insoluble in water hold considerable promise for industry, particularly for a new method of drying semiconductors. The method is aimed to eliminate liquid water films from intermediate products by using high gradients of surface tension in a gas medium above the washing bath. With this method, ultraclean surfaces of semiconductor wafers can be produced by slow lifting them with velocity 1 mm s^{-1} from deionized water at the final stage of their wet treatment.

Table 2. Reduction (in %) of the surface tension of liquids in organofluoric vapors.

No. from Ref. [16]	Vapor	Liquids			
		Ethanol	DBP	Water	Kerosene
480 (493)	$(CF_3)_2CFCF=CFCF_3$	22	36	33	23
575 (586)	$H(CF_2)_4CH_2OH$	2	2	33	0
746 (765)	$HCF_2CF_2CH_2OH$	2	3	15	1
324 (328)	$H(CF_2)_6CH_2OH$	3	2	43	0
461 (474)	$CF_3CFHCF_2CH_2OH$	2	4	30	3
399 (412)	$CF_3CF_2CF_2CH_2OH$	2	9	59	2
483 (655)	$CF_3CF_2CH_2OH$	5	12	46	5
891 (910)	CF_3CH_2OH	6	13	66	5
478 (491)	$(CF_3)_2CHOH$	19	16	30	5
509 (521)	$(CF_3)_3COH$	24	21	78	7
954 (976)	$C_6F_{15}N$	10	28	36	24
382 (395)	$C_{11}F_{20}$	4	8	19	2
383 (396)	$C_9F_{20}O$	5	20	19	10
482 (495)	C_9F_{18}	6	21	30	9
558 (569)	C_4F_8 (1 atm)	9	18	11	12
113 (110)	C_6F_5Br	2	6	18	1
198 (196)	C_6F_5Cl	2	8	21	2
455 (468)	C_6F_6	4	13	23	3
651 (665)	$C_6F_5CF_3$	2	10	19	6
673 (690)	$C_6H_2F_4$	3	7	19	3
592 (607)	C_6F_5H	2	5	29	4
148 (147)	CF_3Br (1 atm)	4	14	0	3
452 (465)	$H(CF_2)_8CH_2OH$	—	—	60	—
338 (342)	$H(CF_2)_{10}CH_2OH$ (75 °C)	—	17	52	—

Chemically inert fluorocarbon gaseous additives can also be used in medicine (pulmonology) to reduce the surface tension of liquid films coating the lungs in certain respiratory diseases.

It is interesting from the practical and theoretical points of view to investigate changes in radial flows in the rings of stationary ispalators (see Section 2.4), when the container in the ispalator acquires additional rotation around its axis. This may be used to model the complicated dynamics of monsoons on the Earth.

Of interest is the question of why the addition of 40% water to ethanol terminates the ring rotation. In this case the surface tension of the mixture increases only slightly from 23 to 28 dyn cm^{-1} [33], while the density of ethanol molecules on the surface of the mixture virtually does not change. However, there is evidence [33] that the CH_3 end groups of methyl alcohol molecules, inclined to the methyl – air interface, change their angle of inclination from 40° to 16° (with reference to the vertical dropped onto the surface) as the water concentration in the mixture increases. Perhaps, similar changes in the orientations of ethyl end groups C_2H_5 and a simultaneous decrease in the surface density of ethanol molecules diminish the rate of formation of fluorocarbon complexes and terminate the rotation.

The appearance of a colored ring of dry dye on the container walls together with the fact that liquid curtains of different fluids rise to different heights lead us to conclude that as a ring consisting of a mixture of fluids rotates, the fluoride complexes of these fluids, rising up the container walls to different heights, result in a spatial separation of the regions where these fluids evaporate (as in the case with thin-film chromatographic separation). An example of direct separation of substances in ispalators will be given in Section 7.2.

If the rotating ring itself consists of a mixture of selected liquids near their demixing point, then the homogeneous mixture is carried by the film from the container center to the walls, evaporates, and permanently separates. In the process one liquid is released as drops, which return to the central zone.

In a hermetic ispalator, the form of liquid structures and the dynamic behavior of ring oscillations and rotations are rather sensitive to a decrease (or increase) of gravity or the availability of the ispalator rotation with a constant velocity around its vertical axis.

The detailed description of processes occurring in ispalators is justified by the large number of surprising effects observed there.

5. Extension of the range of substances used in experiments

5.1 Fluoride compounds

Of interest is the search for other fluoride and nonfluoride compounds, which in the gas phase can generate similar unstable active complexes at interfaces (of liquids or melts) as well as an estimate of the limiting efficiency of mechanical energy transformation realized in ispalators.

For this purpose we consider the data of Table 2, which lists the values of reduction of the surface tension of liquids in saturated vapors of other organofluoric compounds. These data are obtained at room temperature by the same drop method.

Note that some organofluoric compounds listed in Table 2 (the first column of the table indicates their numbers in accordance with the PiM catalogue [16]) are chemically active, have a smell, some of them mix well with the test liquids and require a more careful treatment than the inert compounds presented in Table 1. In view of the low volatility of the crystal compound 338, experiments with its saturated vapors were carried out at 75 °C, while some experiments described below were carried out at room temperature. The data listed in Table 2 allow us to follow the tendencies in the

influence of the chemical structure of molecules on a reduction of surface tension of liquids.

5.2 Toy-ships on water

As is seen from Table 2, the vapor of compound 509 boiling at 44–45 °C [16] sharply reduces the surface tension of water from 72 to 16 dyn cm^{-1}. This compound is well soluble in water but evaporates fast. Thus, a thin polyethylene bag of size 0.5×1 cm^2 with a hole in the corner, containing a drop of compound 509, circulates over the water surface in an open container of diameter 8 cm with velocity 10 cm s^{-1} for 20 minutes, i.e. much faster and longer than a toy paper ship with an ordinary nonvolatile soap. The motion does not take place due to the reactive force, since the moving ship does not generate frontal waves: the water surface before the ship is perfectly smooth and undisturbed. Since the ship can circulate fast around its axis, the surface density of complexes containing water and compound 509 is not saturated at room temperature and a pressure of about 400 Torr, i.e. the lifetime of the complexes does not exceed several nanoseconds. Compound 461 is less soluble in water and less effectively reduces the surface tension of water, therefore a toy polyethylene ship with a drop of compound 461 runs by water with a velocity of about 7 cm s^{-1}. Figure 4 plots the dependence of the surface tension of water on the density of 461 vapor in the air above the water at room temperature. Compound 480 virtually does not mix with kerosene.

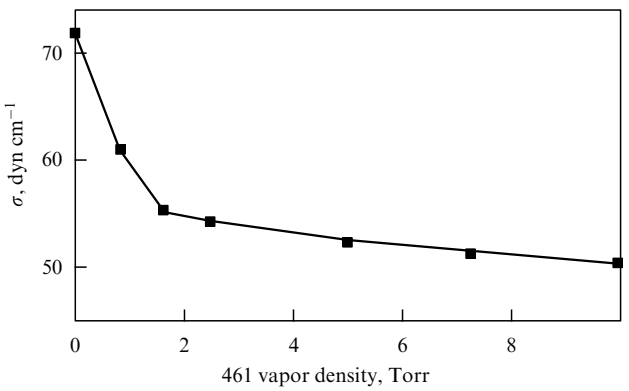

Figure 4. Lowering of the surface tension of water at room temperature as a function of the vapor density of compound 461 above it.

5.3 Choppiness of water caused by compound 509 vapor

If we hold a small open container with the liquid compound 509 above a wide water surface (as in the experiments described in Section 2.14), then the 509 molecules evaporating and moving down collide with the water surface and initiate noticeable choppiness of water, depression of its surface and fast gusty recession of fragments of the water upper layer and dust particles with velocity 10–50 cm s^{-1} away from the point of vapor contact.

5.4 Trembling drop

The evaporation of compound 509 dissolved in water is accompanied by sharp changes in the surface tension of the water. This is observed in the following experiment. A drop can hang for hours at the end of a pipette containing 0.5–0.8 cm^3 of water with dissolved compound 509 (about 2% of the water volume). Every 5 s it winces strongly as if it is trembling at strong gusts of wind trying to tear it off and alters its height by 0.5 mm at a frequency 5–10 Hz. As new 509 molecules enter the drop from the pipette, the dust particles inside the drop start rotating. The presence of compound 509 in the drop enhances its twisting and trembling due to the Marangoni effect. The enhancement is more pronounced than in the experiments with a methanol drop [35].

6. Crystal 338 and camphor

6.1 Crystal 338 on water

At room temperature, compound 338 (as well as compound 452 with a similar structure) is a solid crystalline substance without smell. The pressure of its saturated vapor is about 0.015 Torr. Its chemical structure, typical of the investigated series of molecules, as well as its low volatility did not lead us to expect that this substance would show any unusual properties. But the results of our experiments appeared to be rather surprising. Crystal 338 is heavier than water but is not wetted by it. If we put the crystal on a water surface carefully, it can float. We were surprised to find that in our experiments the crystal permanently moved and rotated slowly on the water surface of a wide open container of diameter 20–30 cm for hours and weeks with a velocity of about 1 mm s^{-1}. The moving crystal pushed away tracer particles reposing on the water surface and slightly diminished in size. Such wandering of a heavy fluoride sample over water immediately reminds us of no, not Christ, but another thoroughly described phenomenon of motion and twisting of light camphor grains ($C_{10}H_{16}O$) and relative compounds of camphor acid and borneol ($C_{10}H_{18}O$) [7] on the surface of water with a faster velocity of about 3 cm s^{-1} for tens of minutes till they completely disappear. The enigmatic behavior of these particles has been investigated and considered for more than a hundred years [36] up to the present time [37, 38].

Notice that there is no direct similarity in the chemical composition of camphor and crystal 338 nor are they similar in structure. The camphor molecule is solid [7], camphor crystals sublimate and have a smell at room temperature, they are lighter than water and slightly water-soluble. At the same time, the similar behavior of these substances on the surface of water suggests that the physical causes of their surface motion may be analogous. As is indicated by the surrounding dust particles, the crystals give off films (complexes) on the water surface, which subsequently disappear. The molecules of films around the crystals reduce the water surface tension to 57 dyn cm^{-1} for the camphor sample [37], and even greater for crystal 338. A drop of soapy water completely terminates the motion of the camphor crystal.

The behavior of camphor has already been explained by its similarity to soap: both the substances reduce water surface tension around the sample. However, neither camphor evaporation nor the vapor effects have been considered so far. The pressure of saturated camphor vapor is about 0.18 Torr at room temperature and 12 Torr at 80 °C. The vapor effects are usually neglected because of low vapor density. Our tests demonstrated that experiments with a running camphor sample at room temperature can be carried out even in a closed container with a small air volume (about several cm^3, a test without air will be described in Section 6.7) and a large water volume (greater than 100 cm^3). In these experiments, the camphor sample rotates and runs over the water surface for tens of minutes, gradually decreasing the

velocity from 3 to 1 cm s^{-1}, when the air is saturated with camphor vapor and the film molecules can only move to the water and dissolve there. Raising the water temperature or shaking lead to an increased velocity of the camphor motion. But there is a significant peculiarity, which is not pointed out in the scientific literature. This motion accelerates considerably anew when we open the container once again and the camphor starts evaporating into the air.

It has long been found that the motion of camphor is associated with a reduction of water surface tension around the sample, but only recently did the researchers relate the mechanism underlying this phenomenon to sublimation [37], assuming that a decrease in water surface tension is caused by evaporation of film camphor molecules into the air. The authors of Ref. [38] pay attention to the diffusion of camphor derivatives in water. Consideration of the sublimation effect in an effort to explain the permanent motion of camphor across the surface of water points to the question of whether the water surface tension depends on the pressure of camphor vapor above it. But the authors of Refs [37, 38] do not discuss this dependence nor do they consider the dynamics of the rate of dissolving the film molecules as the camphor sample runs in a closed container. Physically, the effect of camphor vapor on the surface tension is similar to that in the above-described mechanism of the motion of liquid films in ispalators [3,4]. The similarity is also made clear when we compare the peculiarities of the motion of camphor and compound 338 described above.

6.2 Motion of crystal 338

In a closed container, crystals of fluoride compound 338 terminate their motion across the water surface within 10 – 20 min, but in 4 – 6 min after opening the container they resume their motion, which will grow faster as the temperature of the water increases. The crystal 338 reduces on water and is surrounded by an invisible but rigid film of radius 1 – 10 cm; the crystal is frozen in this film as if in ice and moves in the direction in which the film size is shorter. The film can be detected with a needle or a rod applied to the water around the crystal from any side. The contact between the needle and the film edge immediately results in crystal motion, changing its velocity. Inserting the needle into the film, we can *draw* the crystal over the water surface behind the needle, which indicates that the film is rather rigid. The film is little sensitive to changes in air flows above it, but it can be eliminated from the water surface, for example, by putting paper into water near the grain 338. We will see at once that the velocity of the sample motion will increase several times. (In the case of camphor, the film radius probed by a needle does not exceed 3 – 7 mm.) Crystal 452 has similar properties on the water surface. A drop of soapy water virtually does not effect the motion of 338 and 452 crystals, because the water surface tension reduces by half around the crystals, i.e. more than is caused by soap.

6.3 Interactions between camphor and 338 crystals on a water surface

When at room temperature we place in the same container a 338 (or 452) crystal sample on a water surface at a distance 1 – 10 cm from a camphor crystal, the camphor sample instantaneously terminates its fast motion, while the fluoride sample starts moving. The camphor sample *resumes* its motion only 5 – 15 min after removing a 338 crystal and 2 – 4 min after removing a 452 crystal. This indicates that the surface lifetime of complexes containing water and the 338 or 452 molecules is much longer than that of complexes containing camphor and water and being formed around a camphor crystal.

A drop of 509 compound lowered on the water surface near a camphor grain casts it away but does not terminate the grain motion due to the short lifetime of complexes including water and compound 509. When the temperature of water is higher than 40 °C, the camphor and 338 crystals rotate intensively on the water surface in close proximity but without getting in the way of each other. This fact testifies to a substantial decrease in the lifetime of corresponding camphor and 338 complexes on water with rising temperature.

In contrast to the liquid 324 sample which partially dissolves in water, 452 and 338 crystals virtually do not dissolve; neither do they possess flavor or smell. The 338 crystal terminates its motion over the water surface in the presence of a 452 sample. Figure 5 plots the dependence of the water surface tension on the density of 452 and 324 vapors above the water at room temperature. For 452 vapor, the decrease in the surface tension of water is saturated at about hundredths of torrs, which, with regard to the frequency of collisions with the water surface, corresponds to an approximate lifetime of the 452 + water complexes of 10^{-4} s.

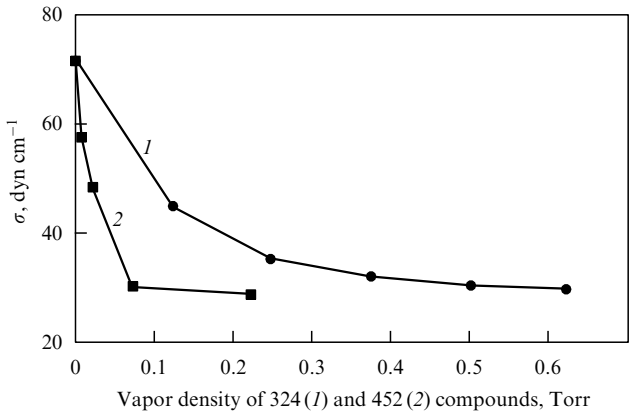

Figure 5. Dependence of water surface tension on the density of vapor above the water at room temperature: line *1* — compound 324, and line *2* — compound 452.

A water jet of diameter 1 mm issuing down from a pipette breaks down into drops in the air at a distance 6 – 6.5 cm from the outlet, and at a distance 14 – 15 cm when saturated 324 vapor is in the air.

6.4 Camphor 'tears'

When a camphor crystal is deposited on a thin water layer (about 3 mm thick) at the bottom of a high conical wine glass, it disturbs the boundary of the water film with camphor molecules, which lifts up along the wine-glass walls through 0.7 – 1.0 cm with velocity about 1 cm s^{-1} and forms a continuous water board at that height. This board incessantly releases water drops in the same manner as was described in the experiments with the liquid curtain in the ispalators. As in the case with ispalators, air flows increase evaporation and enhance formation of the drops. By analogy with wine 'tears' these drops could be referred to as camphor 'tears'.

6.5 Tears caused by a 338 crystal

When a 338 crystal is put on water in a wine glass, a film lifts up through 1.5 – 2.0 cm in fractions of a second and forms a water board at that height. This board releases occasional water drops, which move down along the glass walls. Air flow virtually does not effect the intensity of the drop formation.

6.6 Similarity between camphor films and those in an ispalator

To complete the analogy with ispalators, we note that the reduction of the water surface tension measured by the drop method at room temperature in saturated camphor vapor is about 5%. Dust particles on pure water surface start moving when a camphor sample is placed at a distance of 2 – 5 mm above the surface. When the camphor sample is deposited at the bottom of a conical wine glass on a fresh water layer of thickness of about 3 mm, the dust particles in water near the camphor grain run away across the water surface from the camphor to the glass walls with a high velocity of 5 – 20 cm s^{-1}. Near the walls they move down through 2 – 3 mm, and travel at this level back to the sample with a lower velocity. Near the sample they rise, i.e. behave just as in ispalators (see, for example, Section 2.7).

The discovered analogy in the behavior of these chemically different substances leads us to conclude that the physical causes for their motion are identical and related to the formation of unstable surface active complexes, whose density depends on their vapor pressure and ability to be dissolved in liquids. By analogy with the behavior of compounds 338 and 452 on water, one would expect that at low temperatures crystals of other fluorocarbons should behave similarly on the surfaces of cooled but not frozen liquids.

6.7 Camphor on an irregular water surface and under water

Of interest is the behavior of a camphor sample on an irregular water surface in a wide closed ispalator of diameter 8 cm (like that depicted in Fig. 1). Some grains of camphor are put in this ispalator on C_8F_{18} surface (at the water ring) instead of DBP substance. As noted above, the fresh water ring above C_8F_{18} is motionless, but the inserted camphor grains come into contact with water and circulate along the perimeter of the free zone for tens of minutes. They produce transparent C_8F_{18} films which intensively move upward, are assembled on the water surface into sagging drops of diameter 5 – 8 mm, and slide down over the water surface back to the free zone. In 1 – 2 min, the rate of issuing films on the water surface slows down and then the process goes on less intensively till the camphor crystals disappear completely, and the films moving to the free zone do not contain large drops. The mechanism of drop formation is rather simple. The camphor sample gives off a film of its molecules on the water surface above which, as films of many other substances described in the foregoing, complexes with C_8F_{18} molecules are formed. These complexes decrease the surface tension of the film, accelerate the film motion, and at high velocity the film carries away liquid C_8F_{18} from the free zone to the water. During the film motion over the water surface, the camphor molecules are detached from complexes and run off into the water. Remaining C_8F_{18} molecules, which cannot evaporate, form drops and slide down to the free zone. As the film velocity decreases, the number of these molecules also decreases and large drops are no longer formed. This indicates that the films are produced (initially, more intensively) as long as camphor molecules are dissolved in water, i.e. while the water is saturated with camphor molecules. With regard to the solution of camphor molecules, we refer to such a unit as a 'solventor'.

If we put an additional 338 crystal on the water surface, the film formation completely terminates, but it resumes 10 – 15 min after removing the sample 338 from the water surface. When we use a 338 sample instead of camphor, then C_8F_{18} films and C_8F_{18} drops are formed more intensively during the first minute, however the lifetime of 338 molecules on water is long and in several minutes the formation of the films and drops completely terminates. The process can be repeated if we remove the 338 film from the water with paper.

The fact of long (tens of minutes) motion of camphor without evaporation, caused only by solution, is exhibited in an unusual experiment when the camphor crystal is put on a flat and wide (5 – 10 cm) water – C_8F_{18} interface or water – $C_{10}F_{18}$ interface under the water layer. In this case the crystal adheres to the fluoride liquid and does not float in water. It immediately starts rotating and moving under the water layer. As is seen from tracer dust particles, a film is formed around the crystal at the liquid interface, where camphor molecules can leave the film only in the water direction.

7. About the film structure

7.1 Monomolecular layer

Our data do not clarify the question about the detailed structure of films of complexes on liquids. However, it turned out that a substance similar to the 338 compound was investigated in the steady Langmuir – Blodgett films at air – water and hexane – water interfaces [39], which suggests that orientation and the surface structure of these compounds are similar to a fluoride molecular monolayer.

Monolayer structures of $F(CF_2)_{10}(CH_2)_2OH$ compound on a water surface were investigated in Ref. [39] by diffraction of X-rays from a synchrotron source with a wavelength of $\lambda = 0.0825 \pm 0.0002$ nm. This compound differs from compound 338 in that the latter has an additional CH_2 group and contains end fluorine in place of the end hydrogen. The results of Ref. [39] demonstrate that at room temperature heavy fluoride molecules at the water – air interface and even at the hexane – water interface self-organize and line up close to each other in the direction perpendicular to the interface, because the end fluoride groups are hydrophobic. These monolayers have the structure of close-packed solid two-dimensional crystals, which is stable at a temperature of up to 37.5 °C in hexane and at up to 58.8 °C in water. The ability of linear fluoride molecules to form dense monolayers with perpendicular molecular orientations seems to be typical of these substances, since even nonvolatile, nonpolar $F(CF_2)_{20}F$ compound exhibits this property on water [40]. Our data on ispalators show that such fluoride layers are not only typical of more simple volatile fluoride compounds on surfaces of various liquids, but they also cause a dynamically fast reduction of the surface tension of liquids with such monolayers. The thickness of the layers in question on the film is determined by monomolecular sizes as is the case with other effective surfactants [41]. The motion of the dense layer of fluoride molecules at the liquid interface is clearly demonstrated in the experiments presented below.

7.2 Flickering drops

An interesting type of new ispalator was produced with the use of the fluoride compound 452. A large amount of the compound is dissolved in ordinary turpentine with a specific density 0.88 – 0.9 g cm^{-3} and a surface tension of about 27 dyn cm^{-1} till the solution is saturated. Two immiscible liquids are formed in the solution, namely, a light upper phase (fraction) with a specific density 0.97 g cm^{-3} and surface tension decreased by 17% with respect to that in turpentine, and a heavy low fraction with density 1.44 g cm^{-3} and surface tension decreased by 25%. A drop containing the light fraction with a volume of about 0.1 – 0.2 cm^3 is deposited on a pure water surface in an open container of diameter exceeding 9 cm. (Similar experiments can be carried out with the heavy fraction of turpentine and with saturated solution of compound 452 in DBP, which does not evaporate over a day. Compound 452 melting at 50 °C on a hot water surface can also be used, but special measures are required to keep the drop on the water surface, so that it should not sink. For example, the drop can be put on the bottom of the container.)

As is known pure turpentine spreads over the water surface, forming a thin film. But in the case under consideration, despite an additional reduction of the surface tension of the solution containing compound 452, the drop on water takes the shape of a round lens of diameter 1 – 2 cm and thickness 0.4 – 0.8 cm with a sharp edge. When we remove from the water surface small droplets formed there during deposition of the solution, the perimeter of the main drop in the water plane begins to move, forming flickering protuberances, which *fluctuate* at a frequency of 1 – 10 Hz and amplitude of several tenths of a millimeter. The oscillations continue for hours and days. They present another type of ispalators, namely, flickering drops; the mechanism of their motion is described below.

The 452 molecules in the turpentine drop diffuse down to the water surface, forming a continuous layer there of molecules whose fluoride ends are oriented to the drop. The surface tension of the layer is low, and it extends from under the drop due to the high surface tension of the surrounding water. For many hours this layer moves from the turpentine drop with the same velocity as from the DBP drop. The lack of DBP molecules on the water surface (DBP virtually does not evaporate) suggests that the layer does not carry out solvent molecules to the water and hence it does not contain molecules of solvents.

When air flows above the container enhance or the water surface is purified, the drop momentary enlarges its diameter and may even break down into small droplets. In a closed container, the flickering motion terminates in 10 s. In an open container of diameter 4 cm, the flickering motion of a drop is faintly visible, and in a container of diameter 2.5 cm it is invisible.

The layer moves from the drop along the water surface with approximate initial velocity 0.5 cm s^{-1} (as judged from dust particles), then quickly slows down, travels 2 – 3 cm for 3 – 5 min, and evaporates. This provides a permanent extraction of the film from under the drop. Thus, a drop of solution lies not on the water, but on a film given off and expanding from under it and is poorly wetted by the drop. The film consists of closely packed 452 molecules (providing an example of separation of substances). Saving itself from being extended over the fluoric film, the drop incessantly draws in fluctuating protuberances, resulting in the flickering motion of the drop perimeter. Tracer dust particles in the drop move up from the drop bottom along the surface contacting with the water with a velocity of 3 – 5 mm s^{-1}. Near the water surface they change the direction of their motion and return to the center of the drop with considerable acceleration, and then slowly move down. Sometimes, dust particles adhering to the film are carried away by the film and leave the drop. The drop also blinks in the case when the saturated solution is diluted with turpentine but not more than twice. At a higher degree of dilution, the drop produces a film with less speed and the drop edges do not blink.

When we put a small drop of pure turpentine on the film moving away, it takes the shape of a lens, whose contours incessantly change. The drop draws in the surrounding film, adsorbs it, moves in the direction opposite to the film motion, and finally coalesces with the main drop. A small drop of saturated solution of 452 compound and turpentine shifts from the main drop by 1 cm and starts to blink, moving with the film to the walls of the container. Small drops contain a small number of 452 molecules, they run fast over water near the walls and then terminate their motion.

Using refractive light, we observed interference fringes of fast varying shape at the surface of the main drop near its edges; these fringes were caused by the evaporation of turpentine from the upper drop layer. A drop which has been flickering and evaporating for 24 hours may become heavier than water, change its shape, and sink into the water. Besides, turpentine changes gradually its viscosity and other properties in an air atmosphere.

If we add several drops of the heavy fraction to the main drop of the light fraction, then the heavy phase will dispose as an enveloping continuous layer between the light fraction and the water. Dust particles rotate in this layer in the same direction as in the drop, i.e. upward at the water interface and downward at the interface between the fractions. When the velocity of the film motion is high (0.5 cm s^{-1}), a portion of the flow of the heavy fraction at the edge of the drop is trapped by the flux of the light fraction and moves along the drop surface to its center, forming small (0.2 – 0.3 mm) droplets there looking like picturesque permanent rain. These small droplets move to the drop bottom as a prolonged (hour long) downpour and merge there with the coating of the heavy fraction. A sensitive microphone can probably detect the 'murmuring' sound produced by the edges of a flickering drop as it gives off a film onto water and the 'knock' of rain drops at the bottom.

A turpentine drop saturated with less volatile 338 compound flickers on the water for several seconds only, till the water surface is coated with the film. After that the flickering stops, since the lifetime of 338 molecules on water is long. If we remove the film with paper, the drop will blink again for a time. When the water surface is coated with the film anew, the drop again calms down and lies motionless. A drop with 452 compound deposited near the drop saturated with 338 compound goes on flickering.

The described method of producing fluoride films is similar to the procedure used in Ref. [39] for obtaining fluoride films on water surface from fluoride molecules with a similar structure. The only difference is that we did not use a diluted solution as in Ref. [39] but rather a saturated one, which enables us to see permanent issuing of the film from under the drop, its evaporation, and flickering of the drop edges with the naked eye.

Permanent pulling out of the film from under the drop, which is uniform in all directions, clarifies the mechanism of

the above-described spontaneous dancing of crystals over the water surface. A similar molecular film is produced under the crystals, too. But in this case, it arises on irregular surfaces of a floating-on-water crystal and due to great local gradients the film extracts from under the crystal with a different velocity in various directions. As a result, the crystal permanently moves changing the direction of its motion and turns from side to side.

A 452 crystal of base about 20 mm^2 and width about 1 mm loses its mass on water with the rate 0.001 – 0.003 g h^{-1}, which is two or three times faster than the rate of evaporation of the dry crystal in the air. This crystal is virtually does not dissolve in the water. Molecules evaporate from the crystal surface in accordance with the volatility of their compounds. The surface of the film surrounding the crystal is several orders larger than the surface of the crystal itself, while the numbers of molecules evaporating from the crystal and the film are comparable, as is observed in the experiments. This fact suggests that the intensity of molecular evaporation from the crystal is two orders more intense than that from the unit film surface.

It is of interest to find a relation between the long lifetime (about a minute) of firm films on a water surface and the above-estimated short lifetime (10^{-4} s) of their constituent complexes and to reveal whether is it related to a special strength of two-dimensional monocrystal films on the water surface, when molecules are in a tight contact with each other (therefore the film is firm) and evaporate mainly from the film edges, where this attraction is weaker.

The described permanent stripping of the fluoride molecular layer off the drop is a process of separation. It is the reverse of the process of continuous coating, when a steady planar jet of paint falls onto a moving surface, wets it, and covers it with a continuous layer. In this case the velocity of the surface motion is limited [42]; at higher velocities the contacting wetting line is not flat but saw-tooth and air bubbles may be entrained into the liquid from the vertices of trailing saw-teeth.

A natural continuous reverse process of emanation of 452 molecules from solution onto the film, which takes place without special energy consumption and, to our knowledge, has been observed in experiments with drops for the first time, could be referred to as 'decoating' (i.e. removal of the coating). During this process a thin monomolecular contacting layer is stripped off the drop with the film and becomes nonwettable. The process of removal of the layer and the loss of wettability by the separating surfaces at high rate of separation, observed in the drops, is also accompanied by the formation of a saw-tooth discontacting line detected as the flickering motion and changes in the composition of the new surface of the drop formed after removal of the film at air interface, i.e. dynamic changes in the contacting angle. (The changes in the composition are caused by evaporation of turpentine into the air and subsurface transformations of disordered fluoride molecules on the surface layer of the solution.) The study of these processes could be useful to check the validity of the recently developed hydrodynamic theory of wettability, where the difference between the static and dynamic contacting angles is taken into account [43 – 45].

The computer programs developed, such as "Gaussian 98", should provide a better understanding of the effect of attachment of the negative charge to fluorine atoms of molecules, resulting in the attraction of the fluoride molecules in the layer. Calculations show [46] that the polarizability of linear molecules along the fluorocarbon chain is characterized by a dipole moment equal to 2 D. Complexes with organofluoric molecules, formed in ispalators, can probably be initial centers or nuclei of condensation in supersaturated vapors of various liquids.

8. Ispalators and Rayleigh – Marangoni – Bénard cells

The discovered similar physical behavior of chemically different substances shows that the ispalator can be produced with the use of various fluoride and organic compounds capable of forming unstable active complexes on liquid surfaces.

Of interest is the theoretical study of general properties of substances capable of forming SAC, and the search for SAC (for example, for liquid metals) as well as the investigation of peculiarities of evaporation of the layers consisting of unstable SAC from liquid surfaces. Properties of SAC, the dynamics of their formation, the times of their mutual orientation and coagulation of molecules onto SAC, as well as the binding energy of the molecules, lifetime and influence on liquid surface tension are yet to be understood.

The substantial influence of inert gases at low pressures on the hydrodynamics of liquids, which is observed in ispalators, allows us to estimate similar effects in self-organized one- or multilayered liquid Rayleigh – Marangoni – Bénard cells which are thoroughly described in the scientific literature [47 – 49]. Usually, the evaporation and condensation are not considered in these cells. According to our experiments, evaporation in a hermetic ispalator and the return of drops condensed in a cool trap into the liquid result in the fast motion of the films of these liquids over each other even in the case of a simple immiscible two-component liquid containing 30 – 70% of ethanol and 70 – 30% of kerosene with a common upper surface. This motion is accompanied by permanent wavy fluctuations at frequency of 1 – 5 oscillations per second and amplitude 2 – 5 mm at the interface, as in ispalators with fluorocarbons described above, but without the participation of active complexes of fluoride compounds. Therefore the pattern of motions and flows in the Rayleigh – Marangoni – Bénard cells may become even more complicated with due regard for the SAC and the presence of fluorocarbon vapor above the conventional cells. The adsorption of the vapor is different on the upper sections of liquid surfaces with different temperatures, which can result in the reduction of their surface tension.

9. Conclusions

We have completed the description of our main results. Compounds both containing and not containing fluorides used in our experiments are available and can be purchased, for example, from the PiM firm [16]. Simple experiments with ispalators, their complicated behavior, and the indicated paradoxes are not just scientifically curious, but can serve as an immediate guide for theorists and experimenters as well as practicians investigating volatile, regenerating fluorocarbon surfactants, which can penetrate deeply and with thermally stability at temperatures up to 400 °C (i.e. at the temperatures when usual surfactants are destroyed). These surfactants can be used as a volatile soap or gas modifiers of lubricants, an implantation for suppressing corrosion, for the flotation of

ores, as ingredients for oil extraction from pore rocks, volatile pesticides (terminating energetic metabolism of insects and bacteria), and for transport not only of oxygen but also of other useful compounds into the human organism.

The permanent rotation of rings in ispalators and interference fringes observed in refracted light near the free zone of fluorocarbon compounds on rotating liquids opens for research a unique opportunity to study for an endlessly long time the steady profiles of the dynamic boundary of extending fluorocarbon films on the running liquid surface (with no mass expenditure). The ring rotation can be used to pump and replace dye solutions in resonators [4].

A reader puzzled by the absence of formulas typical of physics articles, certainly, understands that great efforts are required to treat the mechanism of self-organized spontaneous oscillating excitations in ispalators at the atomic level with the use of quantum-mechanical terms and to develop a detailed mathematical model of the phenomena. The latter is a hydrodynamic problem with an open surface, in which account should be taken of the Marangoni effect, the motion of liquid films rising up the vertical walls, the mass and energy exchange between liquid and gas at varying surface tension. It is rather a difficult problem, comparable with the treatment of the global El Niño phenomenon, which also should take into consideration nonlinear Navier – Stokes equations, adsorption and desorption equations as well as equations for gas solution, motion of nano-sized films, film rising up the vertical walls [50], evaporating flows [51, 52], diffusion and gas transfer, chaotic interactions of several oscillators and the arising instabilities. Attention and participation of all the specialists of the so-called hydrodynamic culture [54] are required to overcome these difficulties as was done to develop the El Niño model [53].

In ispalators the experimental methods are more thoroughly developed than the theoretical ones, but ispalators are very convenient for the experimental examinations. These are simple open systems, which are not in thermal equilibrium, where spontaneous self-induced oscillations arise, and switching from wettability to nonwettability takes place due to changes in van der Waals forces of unstable complexes. Ispalators are a representative model for investigating the peculiarities of two-dimensional interface effects, based on the combination of the generalized Navier – Stokes equations and general nonlinear dissipative equations of synergetics, the reactive – diffusion Ginzburg – Landau equations with local order parameters for dynamic structures evolving in complex systems. It is also of interest to investigate the entropy of ispalators and the relative degree of ordering of such nonequilibrium systems [55, 56].

Being an open system, the ispalator is similar to lasers and other self-organized systems with nonequilibrium phase transitions, where the oscillating states are energetically more stable and have a threshold for generation. The difference is in the fact that the working ispalator does not require any special energy consumption as it is naturally excited during evaporation.

The discovery of ispalators exhibits that the parameters of liquids, which have always been considered constant or slowly varying (such as surface tension, wettability, nonwettability), independent of pressure and the type of inert gases above the liquids, are affected by SAC and *can vary under the influence of SAC in different container regions over fractions of a microsecond with no special power consumption*. It opens new fields of research in physics, chemistry, thermodynamics, synergetics and applications. This research field may be called the hydrodynamics of open systems containing SAC, or briefly SAC-hydrodynamics.

Ispalators are a convenient model to investigate the thermodynamics of self-organizing open systems with dissipative structures, using the term by I Prigogine [57, 58], and to check the theories currently developed for treating more complicated nonequilibrium systems including economic, social, and other open systems such as man and the arrangement of his thought.

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