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Factors Influencing Liquid Membrane Mass Transfer

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Abstract

An improved design of a liquid membrane diffusion column was developed which enabled the measurement of a concentration difference of surfactant between liquid membranes and the solutions used to form them. The previously proposed model for liquid membrane diffusion which assumed that the films were of the order of a few molecules thick was not consistent with the data observed using a specially designed diffusion column. A bimodal droplet distribution was measured for a typical emulsion, and the influence of the liquid constituent of the membrane on the permeation rate was investigated. No statistically significant difference in permeation rates was noted when different liquids were used to form the membranes.

INTRODUCTION

Although the use of liquid membranes in a separation device was proposed by Li (*1*) in 1966, his work attracted very little attention until the publication in 1970 of two additional papers describing the details of the process as well as several observations about the underlying mechanisms (*2*, *3*). To date, the information relating to liquid membranes presented in the literature has been sufficient to create an interest in potential applications of this technique; however, the underlying mechanisms have not been adequately explained, and sufficient information is not available to allow an evaluation of its commercial potential.

Previous investigators have proposed three principal methods to obtain diffusion and selectivity data for liquid membrane systems. The first of these methods measures the transfer rate across the membrane due to the passage of a succession of droplets through a solvent in a diffusion column. The second method increases the overall permeation rate by producing a large surface area for transfer by employing an emulsion. The last method, which requires the simplest experimental apparatus, makes measurements on a single stationary droplet in order to collect the desired permeation data. The advantages of each of these various techniques have been described elsewhere; however, it should be pointed out that the potential industrial applications of liquid membrane separations are believed to require the use of emulsion systems.

EXPERIMENTAL PROGRAM

After considering the results of previous investigators concerning liquid membrane transport, it was decided that a liquid membrane diffusion column similar to that described by Li (*2*) would be a useful experimental tool to obtain permeation data. Careful measurements concerning the passage of droplets through such a device offered the possibility of independent calculation of the external mass transfer coefficient for the droplet and thus the isolation of the effects of membrane permeation.

A number of attempts were made to evaluate the permeation rates from a diffusion column similar to those described by previous investigators. In these experiments the droplet phase was benzene while the solvent phase was a mixture of carbon tetrachloride and 2,2,4-trimethyl pentane which had a density of 0.95 g/cc. This particular solvent–droplet system was selected in order to permit the concentration changes to be measured with a gas chromotograph. The surfactants used to form the membranes were saponin, dodecyl sodium sulfate, and sodium lauryl sulfate.

Minimum breakage of the droplets during passage through the solvent phase was observed when the solution charged to the surfactant reservoir contained 0.035 wt % sodium dodecyl sulfate in water. Even under the best of conditions, the breakage during passage through the column was found to be too extensive to obtain permeation rate data. This conclusion seems consistent with the findings of Li who observed that up to 30 % of the droplets broke up in a similar column.

After operating the liquid membrane diffusion column over an extended period of time, it was observed that the collisions between the rising benzene droplets and the falling spent membranes which were returning to the bottom of the column was the principal cause for the high level of droplet break up. In an attempt to eliminate this difficulty, a new top was designed for the column which allowed the membrane fluid to flow through a separate return leg to the surfactant reservoir. This improved design, which is illustrated in Figs. 1 and 2, includes a weir which serves the particularly important function of preventing the spent membranes from falling down the column.

In general the operation of this redesigned column was a vast improvement over the older model; however, the fraction of the droplets that broke up was still large enough to preclude the collection of meaningful permeation data. As was the case with the previous model, there appeared to be an optimum surfactant concentration which minimized droplet break up. If the concentration of the surfactant was too dilute, the membrane around the droplet would be weak and unstable. If the concentration of the surfactant was too great, a tough interface developed between the surfactant reservoir and the solvent phase which precluded the passage of single droplets and only allowed penetration by clusters of droplets. For membranes composed of dodecyl sodium sulfates and water, minimum droplet break up occurred in a 0.035-wt % surfactant solution where benzene was used as the droplet phase. As shown by the break up data reported in Table 1, the breakage of benzene droplets was as low as 0.2 % at this surfactant level. However, droplet break up was normally much higher.

Even at the reduced breakage levels, meaningful permeation data was not obtained from the improved diffusion column. However, the design did permit the investigation of surfactant concentration effects in the liquid membranes. With the addition of the surfactant return leg to the column, it was possible to obtain a sample of the membrane material as it returned to the surfactant reservoir. Therefore, any differences in concentration between the surfactant solution and the membrane films could be detected.

Since visual observations of the column suggested that a difference in membrane surfactant concentration and bulk surfactant concentration might exist, a 0.1 % surfactant solution and a 0.95 g/cc solvent phase composed of carbon tetrachloride and 2,2,4-trimethyl pentane were charged to the column. Pure benzene was bubbled through the column as the droplet phase. The column was operated for approximately 2 hr, then a 25-ml sample of surfactant solution was removed from the return leg. This solution and a similar sample of the surfactant solution charged to the column were evaporated to dryness and weighed. The results of these comparisons, which were made using surfactant solutions of sodium dodecyl sulfate and sodium lauryl sulfate, are reported in Table 2. It is interesting to note that

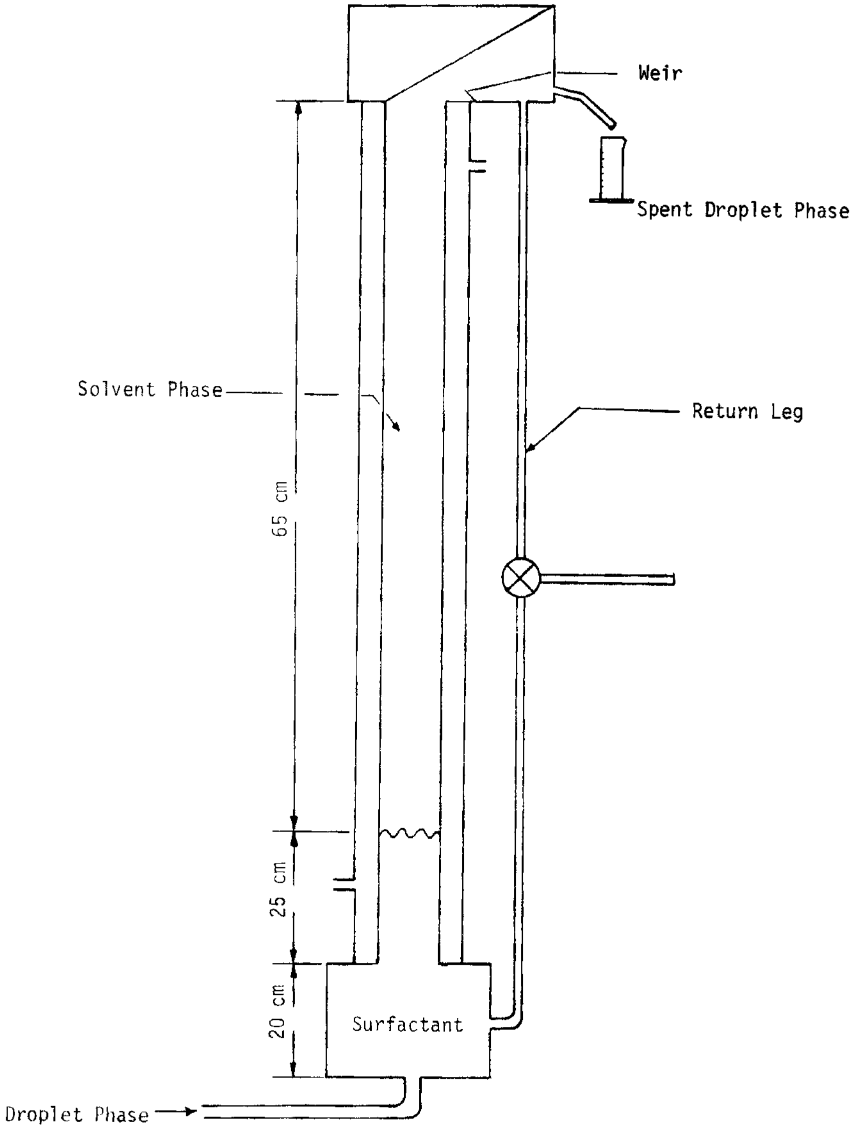

FIG. 1. Liquid membrane diffusion column with separate leg for returning broken membranes.

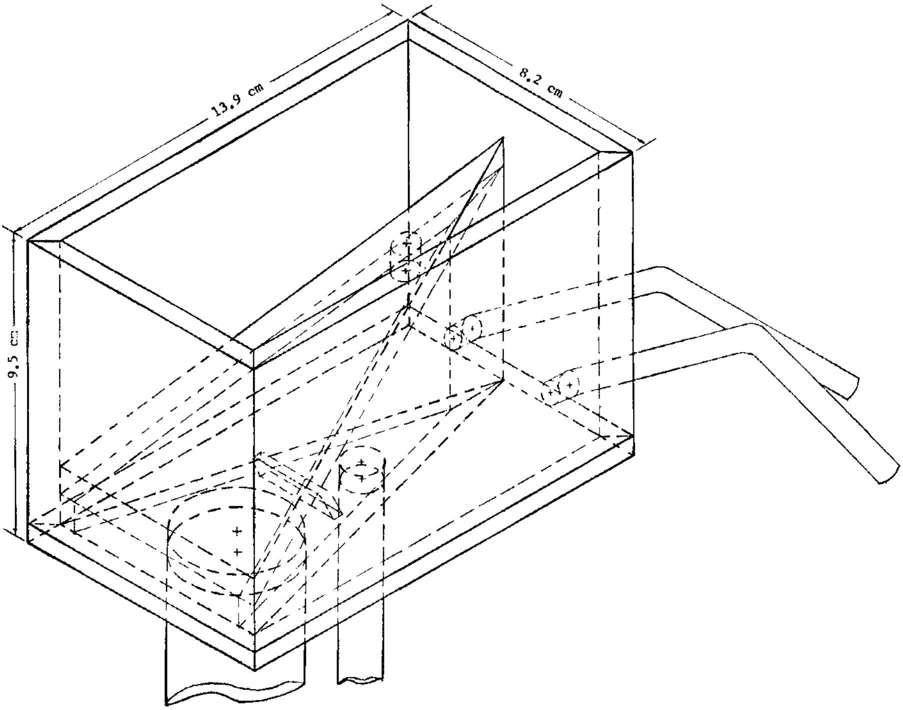

FIG. 2. Droplet overflow device for liquid membrane diffusion column designed to allow spent membranes to return to surfactant reservoirs.

TABLE 1

Summary of Droplet Breakup in the Improved Diffusion Column[a]

Surfactant	Percent breakage
Dodecyl sodium sulfate	0.2
Tween 80	18
Tween 80	19
Tween 40	40
Tween 40	50
Tween 20	8
Tween 20	12
Tween 20	3.5

[a] Concentration of surfactant: 0.035 wt%. Droplet fluid: benzene. Solvent: carbon tetrachloride and iso-octane.

TABLE 2

Increase in Concentration of Surfactant in Membrane as Compared to Bulk Surfactant Solution

Surfactant	Bulk concentration	Film concentration	Percent increase
Dodecyl sodium sulfate	0.100	0.130	30.0
Dodecyl sodium sulfate	0.104	0.128	24.0
Sodium lauryl sulfate	0.089	0.137	54.3

the surfactant concentration in the membranes was over 25% greater than the concentration in the solution charged to the column for both of the solutions investigated.

Later in this discussion it will be shown that the thickness of liquid membranes is rather large. Since this concentration increase was observed over the range of the entire membrane, the effect cannot be attributed to simple surface adsorption such as that classically dealt with in surface chemistry.

The improved design of the top of the diffusion column also permitted the measurement of the flow rate of spent membrane solution in the return leg to the reservoir. Since the rate of formation of droplets and their diameter was known, an estimate of the thickness of the average membrane could be calculated. The calculated film thickness was found to be of the order of 0.005 cm. There is a considerable potential for error in this value, since the experiments were not conducted in such a manner to control accurately the droplet rate and there was a considerable amount of droplet break up. The data is, however, easily accurate within an order of magnitude, therefore it was concluded that in the diffusion column the film thicknesses were of the same order of magnitude as the droplet sizes reported in emulsion systems.

The estimate of a film thickness for liquid membranes of approximately 0.005 cm was not in agreement with the previously reported literature which indicated that liquid membranes were only a few molecules thick (*2*). The calculated film thickness would represent something of the order of 10^5 molecules, which is a rather large number. It is suspected that the film thickness might vary from system to system and depend upon the hydrodynamics of droplet formation, its rise through the surfactant, and the variation of rate of transfer from the surfactant phase to the solvent phase.

After experiencing limited success with a diffusion column and after evaluating the other methods available for measuring mass transfer across liquid membranes, a single droplet apparatus similar to that described by Li was assembled (*3*). Prior to conducting experiments on this apparatus, the solvent phase that was to be transferred across the membrane interface was first analyzed using a gas chromotograph. The device was then filled with 325 ml of surfactant and 25 ml of solvent phase. In order to insure that the droplet would remain stationary, the solvent phase was adjusted to a density very near that of the droplet phase using a mixture of 2,2,4-trimethyl pentane and carbon tetrachloride. A droplet of the material under consideration was then injected into the surfactant reservoir where it acquired a membrane coating prior to rising into the solvent phase where the permeation rate was monitored. A 10-μl sample of the solvent was taken at periodic intervals, and analyzed. At the termination of a run, the droplet was broken and the solvent analyzed to determine the amount of material that was originally in the droplet phase. As a check, the initial size of the droplet was also measured with a cathetometer.

CALCULATIONAL PROCEDURE

In order to develop an expression from which a mass transfer coefficient could be calculated for the sample droplet exponents, it was necessary to consider the change in the surface area of the droplet as a function of time. This was done by first assuming that the mass transfer could be expressed by a relation of the form

$$N_A = k_A \Delta C_A \tag{1}$$

(symbols are defined in a list at the end of the text). Equation (1) may also be rewritten as

$$d\mathcal{M}_A/dt = k_A \Delta C_A S \tag{2}$$

If the concentration of Component A is negligible in the solvent phase, then

$$\Delta C_A \simeq (C_{A_{\text{droplet}}} - 0)$$

or

$$\Delta C_A \simeq C_{A(\text{droplet})}$$

If only a pure component droplet phase is being used in the experiment, then

$$\Delta C_A \simeq C_A{}^*$$

Now it is noted that

$$\mathscr{M}_A = (V_0 - V_{TA})C_A^*$$

and thus Eq. (2) may be approximated as

$$\frac{-d(V_0 - V_{TA})C_A^*}{dt} = k_A C_A^* S \tag{3}$$

Now for the experiments conducted during this study, the pure component concentration is a constant, therefore

$$\frac{-d(V_0 - V_{TA})}{dt} = k_A S$$

If at this point we consider the geometry of a sphere:

$$S = \pi D^2 \qquad \text{and} \qquad V = (1/6)\pi D^3 \tag{4}$$

Equating the above quantities,

$$V = (V_0 - V_{TA}) = (1/6)\pi D^3$$

or

$$D = \left[\frac{6}{\pi}(V_0 - V_{TA})\right]^{1/3} \tag{5}$$

Replacing D in Eq. (4) with Eq. (5) yields

$$S = \pi\left[\frac{6}{\pi}(V_0 - V_{TA})\right]^{2/3} \tag{6}$$

If Eq. (6) is substituted into Eq. (3), then

$$-d(V_0 - V_{TA}) = k\pi\left[\frac{6}{\pi}(V_0 - V_{TA})\right]^{2/3} dt$$

or

$$\frac{-d(V_0 - V_{TA})}{(V_0 - V_{TA})^{2/3}} = k\pi\left(\frac{6}{\pi}\right)^{2/3} dt$$

This may be integrated to obtain

$$-\int_{V_{TA(1)}}^{V_{TA(2)}} \frac{d(V_0 - V_{TA})}{(V_0 - V_{TA})^{2/3}} = k\pi\int_{t_1}^{t_2}\left(\frac{6}{\pi}\right)^{2/3} dt$$

or

$$3[(V_0 - V_{TA(1)})^{1/3} - (V_0 - V_{TA(2)})^{1/3}] = k\pi\left(\frac{6}{\pi}\right)^{2/3}(t_2 - t_1)$$

Solving for the mass transfer coefficient:

$$k = \frac{0.62035[(V_0 - V_{\mathrm{TA}(1)})^{1/3} - (V_0 - V_{\mathrm{TA}(2)})^{1/3}]}{t_2 - t_1} \tag{7}$$

Equation (7) may be used to calculate the mass transfer coefficient associated with Eq. (1) for permeation across a liquid membrane based on analytical data collected using a pure component in the single droplet apparatus.

Li has suggested that the solubility of the diffusing substance in the liquid membrane might be the controlling parameter (*2*). However, during one of his experiments in which acetone replaced water as the carrier for the surfactant, the data appeared to cast some doubt on this assumption. To further investigate the possibility that solubility might be a controlling factor, it was decided to use a series of solvents in the place of water in the surfactant solution. Experimentally, this was extremely difficult since the membranes were not overly stable with carriers other than water and the droplets burst before any meaningful measurements could be made. This problem was resolved by making a solution of the new solvent with water and thereby retaining some of the stability associated with the water system. The data collected for membrane systems of methanol and dimethyl sulfoxide in water are summarized in Table 3.

A Student's *t*-test of the data for the various samples in Table 3 indicated that the observations did not support the assumption that the various

TABLE 3

Effect of Surfactant Carrier Solvent on Mass Transfer in Liquid Membrane Films

Carrier solvent	Surfactant* concentration (wt %)	Mean transfer coefficient (k) (cm/sec)	Number of observations	Standard deviation (cm/sec)
Water	1.0	6.44×10^{-5}	14	4.39×10^{-5}
Water	1.5	4.91×10^{-5}	4	2.74×10^{-5}
5% Dimethyl sulfoxide in water	1.0	5.25×10^{-5}	6	2.37×10^{-5}
15% Dimethyl sulfoxide in water	1.0	6.83×10^{-5}	5	2.38×10^{-5}
10% Methanol in water	1.0	7.68×10^{-5}	7	5.14×10^{-5}
20% Methonal in water	1.0	2.44×10^{-5}	3	2.18×10^{-5}
Water	0.5	4.10×10^{-5}	8	1.80×10^{-5}

[a] All experiments performed using sodium dodecyl sulfate as the surfactant.

solvents resulted in a different diffusion rate. This suggests the conclusion that there is very little difference between permeation rates observed for the various carriers when employing a common surfactant.

One additional method which was also briefly investigated was an emulsion system similar to that previously described by Li (*3*). The principal problem encountered when attempting to measure permeation rates in the emulsion system was the determination of the surface area due to the distribution of drop sizes.

In order to gain some insight into emulsion systems, some limited data on drop size distribution were obtained. An emulsion of 1% saponin in water with benzene was made using a high-speed mixer. When an emulsion of this type was formed, it was found that care must be taken in order to prevent the inclusion of air bubbles in the hydrocarbon-in-water emulsion. The best procedure to exclude air bubbles involved the use of a baffled vessel to prevent the mixer from forming a vortex and sucking air into the mixture. A dye was added to the benzene to provide phase contrast when observing the emulsion.

After the emulsion was formed it was photographed using a microscope. The equipment available for this procedure was not overly sophisticated. The microscope was an American Optical Spencer Model with a 100 to 1 magnification. A piece of 2-in. pipe was fitted over the eyepiece of the microscope and coupled to the body of a 35 mm camera. Photographs were made at speeds ranging from 1/50 of a second to approximately 3 sec. The film used for this procedure was Kodak pan ASA 32. Photographs were also taken of a 0.001-in. wire for use as a size standard. Each droplet on a photographic print of the emulsion was measured and compared against the size of the wire. A probability distribution curve of the droplets observed for the water–saponin–benzene emulsion was calculated, and it is included here as Fig. 3.

The bimodal distribution is somewhat surprising in that most previous work refers to a monomodal distribution (*4*). Bimodal distributions have, however, been reported in the literature although very few comments have been made about their properties (*5*).

At the present time the droplet distribution data from emulsions have not been used to measure permeation data, because the photographic procedure would not permit the measurement of droplet sizes much smaller than 0.0025 mm. It was found that the addition of glycerine, as suggested by Li (*3*), decreased the droplet size and made measurement difficult with the equipment available. An examination of the potential for application

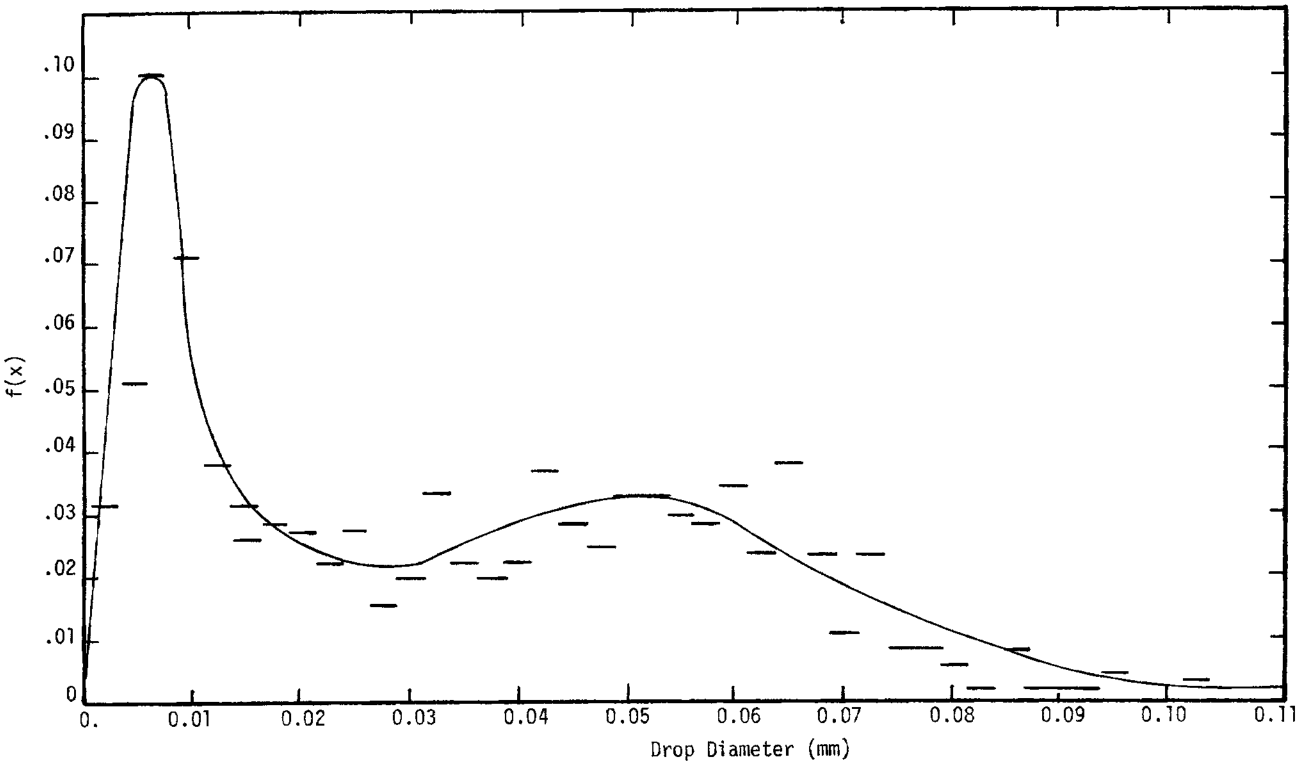

FIG. 3. Probability density function for benzene droplets in an aqueous 1% saponin solution.

of the emulsion technique will probably require a more extensive study using more sophisticated equipment.

CONCLUSIONS

Returning the recycle membranes to the surfactant reservoir by a path different from that of the diffusing droplets was found to drastically reduce the breakage of droplets in a liquid membrane diffusion column. The operation of a column with this modification allowed measurement of the surfactant concentration in the liquid membranes. From this measurement it was found that the liquid membranes had a higher surfactant concentration than the solution from which the membranes were formed. The liquid membrane thicknesses calculated from the observed accumulation rate in the return leg was found to be greater than those previously assumed. It was also observed that there was very little difference between the permeation rates of various solvent carriers for the surfactant in a liquid membrane diffusion column. Finally, the observed distribution of droplets in an emulsion was bimodal.

SYMBOLS

C_A	molar concentration of a Component A in a mixture
C_A^*	molar concentration of pure Component A
d	differential operator
D	diameter of a droplet
k_A	mass transfer coefficient of Component A
$\mathscr{M}_A$	moles of Component A in a droplet
N_A	molar flux of Component A
S	surface area of a droplet
t	time
V	volume of a droplet
V_0	volume of a droplet at time = 0
V_{TA}	volume transferred from a droplet

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