EVAPORATION OF EMULSION DROPS IN STILL AIR

V. I. Blinov and V. V. Dobrynina

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The results of a study of the evaporation of benzene, toluene, xylene, and butyl benzene emulsions in water are presented. An explanation is given of the kinetics involved in the evaporation of such emulsion drops in still air.

A review of the results of studies concerning the evaporation of liquid drops is given in the nomograph by Fuks [1].

Until not so long ago the evaporation of drops of individual liquids was studied under various conditions and only recently have there appeared articles dealing with the evaporation of drops of binary solutions [2, 3], while the evaporation of emulsions often used in practice has, to the author's knowledge, received no consideration at all. We have attempted now to fill this gap. We have studied the evaporation of benzene, toluene, xylene, and butyl benzene drops in water emulsion in various concentrations and under various conditions.

The evaporation rates of such drops were measured with microweights consisting principally of an 18 cm long fine horizontal glass filament. Its one end was rigidly fastened while the other (free) end was bent into a hook. Around the latter was looped a short fine ($d = 20\ \mu$) glass filament with a 3 cm long straight extension. The free end of the latter was fused into a bead 1 mm in diameter. A drop specimen was placed on this bead. Evaporation of the drop caused the free end of the microweight filament to move. The displacement was measured under a horizontally mounted microscope with an ocular scale. The weights had been precalibrated. Their sensitivity was $2.1 \cdot 10^{-5}$ g per scale division, independent of the load and constant throughout the test time. The diameter of a drop was being measured simultaneously under another horizontally mounted microscope.

For measuring the temperature, a drop identical to the tested one was placed on the junction of a Constantan–manganin thermocouple in a separate apparatus. The thermocouple had been made up of gage 30 μ and 100 μ wires.

The initial diameter of the drops fluctuated between 1.7 and 2.0 mm.

The emulsions were prepared by the procedure described in [4]. A 5% solution of sodium oleate served as the emulsifier. The emulsions for these tests were stable. We studied emulsions containing 90, 80, 60, 40, and 20% of the dispersed substance.

First we studied the evaporation of drops of the individual emulsion components.

Results of Experiments with Individual Liquids. In Fig. 1 we show the results of some tests for benzene drops of similar dimensions. As can be seen here, the mass m of the drops decreased relatively slowly with time, while the temperature ϑ first rapidly decreased to a level at which it then remained constant until the end of the test. The same pattern was observed also in the evaporation of other liquids.

On the basis of an analysis of the test data, the evaporation rate of drops could be conveniently characterized by the ratio $\dot{m}/d$, which will be denoted by $\dot{\mu}$. It was also found that the change of $\dot{\mu}$, the diameter d, and the mass m with time could be satisfactorily described by the relation

$$z = z_0 - at + bt^2. \tag{1}$$

Here z represents any of the enumerated variables; z_0 is the initial value of z; and a, b are coefficients.

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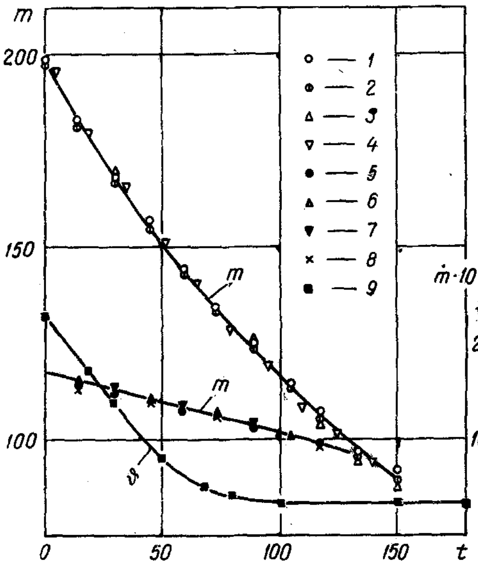

Fig. 1

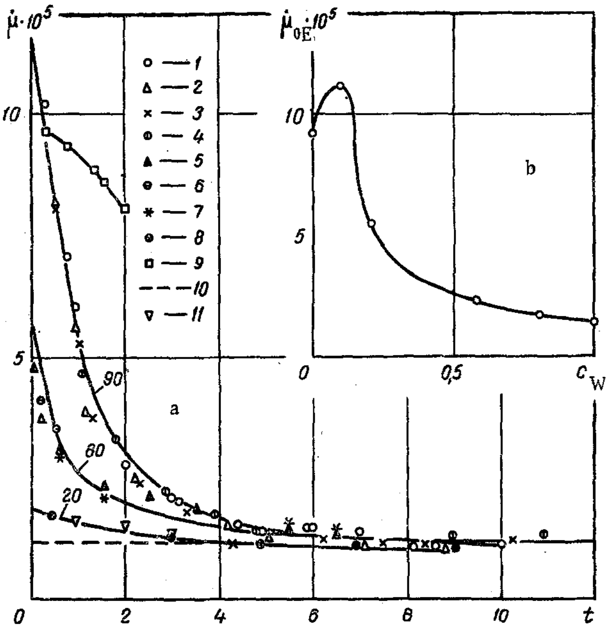

Fig. 2

Fig. 1. Mass m in arbitrary units (1-4), rate of change of mass $\dot{m}$ in g/cm · sec (5-8), and temperature ϑ, °C (9) as functions of time, during the evaporation of benzene.

Fig. 2. Evaporation rate $\dot{\mu}$ in g/cm · sec as a function of time: for emulsion drops containing 90% benzene (1-4), 80% benzene (5-7), 20% (8, 11); for benzene drops (9); and for water drops (10).

The temperature of benzene, toluene, xylene, water, and butyl benzene drops stabilized at 19, 9.5, 2.5, 9.0, and 1.0°C, respectively, below room temperature.

Results of Experiments with Emulsions. Table 1 gives the size distribution of 988 benzene particles in water emulsion. These data were obtained by an analysis of microphotographs. The second row in Table 1 indicates the number of particles having diameters between d and d + Δd.

It can be seen from Table 1 that the distribution curve had its peak near d = 1 μ and that the emulsions used in the tests contained particles the size of which varied within narrow limits.

The results agree closely with the data in [4].

On the basis of the material presented in [4], one may see that the distribution curves for toluene, xylene, and butyl benzene emulsions in water do not differ much from the one for benzene emulsion in water.

In Figs. 2, 3, and 4 we show some of the results on the evaporation of drops of benzene and butyl benzene emulsions in water. It can be seen here that the $\dot{\mu} = f(t)$ and $\vartheta = f(t)$ curves for these emulsions are markedly different from the corresponding curves for the pure substances.

It was found that the evaporation rate $\dot{\mu}$ of 90% benzene and 90% butyl benzene emulsions in water varied according to the relation:

$$\dot{\mu}_E = A \exp(-kt) + B, \tag{2}$$

where A is a coefficient and B is the maximum value of $\dot{\mu}$. For a benzene emulsion in water, B was equal to the value of $\dot{\mu}$ for pure water, while for a butyl benzene emulsion in water it was equal to $\dot{\mu}$ for pure butyl benzene.

The magnitude of $\dot{\mu}$ for the butyl benzene emulsions containing at least 20% of the latter increased first and then began to decrease according to Eq. (2). The period of time during which $\dot{\mu}$ first increased became longer as the water content in the emulsion increased.

According to the tests, the drops of toluene emulsion in water evaporated at a rate $\dot{\mu}$ which slowly decreased with time.

TABLE 1. Size Distribution of Benzene Particles in Emulsion

Range, μ	0–0,65	0,65–1,	1,3–1,95	1,95–2,6	2,6–4,0	4,0–6,6	6,6–10,6
Number of particles	180	328	286	148	56	28	12

The evaporation rate $\dot{\mu}$ for 80 and 90% xylene emulsions remained almost unchanged throughout the test, while for 40% xylene drops it first increased slightly and then slowly decreased.

The curves in Figs. 3 and 4 indicate that the temperature ϑ of the evaporating emulsion drops first decreased rapidly and then, having reached a certain minimum level, began to rise, tending to some upper limit. For emulsions with a high benzene content in water, $\vartheta_{\min}$ was close to the temperature at which the drops of pure benzene evaporated. This lowest temperature became higher for the other emulsions as c_W increased.

For butyl benzene emulsions in water ϑ reached the evaporation temperature of water drops, then remained almost constant throughout a time period which became longer as c_W increased, and finally increased, approaching the evaporation temperature of pure butyl benzene.

The temperature of toluene emulsion drops in water first decreased to a level below the evaporation temperatures of both components, then increased, and at the end of the test became higher than the temperature of water drops.

The temperature–time curves for xylene emulsion drops in water converged with the corresponding curves for butyl benzene emulsion drops in water. The lowest temperature in the given case was close to the temperature of water drops.

The trend of the curves of $\dot{\mu}$ and ϑ versus time t for the emulsions is clear evidence that the relative contents of the emulsions changed with time.

The test curves shown here may be useful for determining the evaporation rates of the emulsion components. The formulas needed for calculations can be derived from the laws of conservation. Obviously, for a quasistationary process

$$L_1\dot{m}_1 + L_2\dot{m}_2 = \alpha s(\vartheta_a - \vartheta) = \pi\lambda\,\mathrm{Nu}\,(\vartheta_a - \vartheta)\,d$$

and

$$\dot{m}_E = \dot{m}_1 + \dot{m}_2,$$

where subscripts E, 1, and 2 refer to an emulsion, its first, and its second component, respectively. It follows from these relations that

$$\dot{\mu}_1 = \frac{\pi\lambda\,\mathrm{Nu}\,(\vartheta_a - \vartheta) - L_2\dot{\mu}_E}{L_1 - L_2}; \quad \dot{\mu}_2 = \dot{\mu}_E - \dot{\mu}_1. \tag{3}$$

The value of Nu can be calculated according to the formula in [7]:

$$\mathrm{Nu} = 2 + 0.6\,\mathrm{Gr}^{1/4}\,\mathrm{Pr}^{1/3}. \tag{4}$$

The calculated results for $\dot{\mu}$ (g/cm · sec) are given in Table 2 for benzene emulsions in water and in Fig. 4c for butyl benzene emulsions.

As can be seen, the value of $\dot{\mu}_B$ for emulsion drops containing 90% benzene was initially close to the value of $\dot{\mu}$ for a drop of pure benzene and then decreased considerably. The value of $\dot{\mu}_B$ for the 40% benzene emulsion was all the time lower than for pure benzene. It was found that $\dot{\mu}_B$ varied with time in the same manner as $\dot{\mu}_E$. During the evaporation of the 90% benzene emulsion, $\dot{\mu}_W$ increased rapidly approaching the value of $\dot{\mu}$ for a drop of pure water. During the evaporation of the 40% benzene emulsion, $\dot{\mu}_W$ remained almost constant and almost equal to $\dot{\mu}$ for a drop of water.

The curves in Fig. 4c indicate that the evaporation rate $\dot{\mu}_W$ of the 90% butyl benzene emulsion decreased in the same manner as $\dot{\mu}_B$. The evaporation rate $\dot{\mu}_W$ of the emulsion containing 40% water initially remained constant and then began to decrease exponentially. The evaporation rate $\dot{\mu}_{BB}$ increased in both cases, approaching the value of $\dot{\mu}$ for a drop of pure butyl benzene.

An analysis of the material relating to the 90, 80, and 40% toluene emulsions indicates that in each case $\dot{\mu}_T$ increased slowly with time according to a relation analogous to (2). The evaporation rate $\dot{\mu}_T$ of

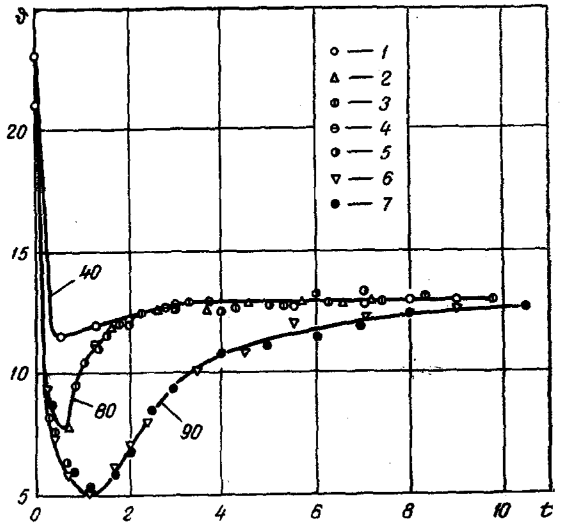

Fig. 3

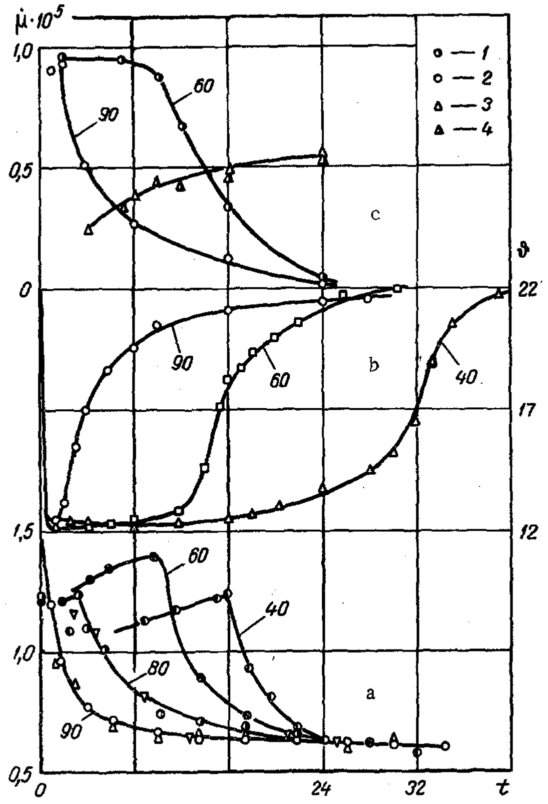

Fig. 4

Fig. 3. Temperature, as a function of time, of emulsion drops containing 40% (1), 80% (2-5), and 90% (6-7) benzene. The numbers next to the curves indicate the benzene content in the emulsions.

Fig. 4 Evaporation of butyl benzene emulsion drops in water: a) $\dot{\mu}$ as a function of time; b) temperature ϑ as a function of time; c) $\dot{\mu}_W$ (1, 2) and $\dot{\mu}_{BB}$ (3, 4) as functions of time. The numbers next to the curves indicate the butyl benzene content in the emulsions.

the first specimen remained close to the value of $\dot{\mu}$ for pure toluene, $\dot{\mu}_T$ of the second specimen remained approximately 1.5 times lower and $\dot{\mu}_T$ of the third specimen approximately 5-6 times lower than in the first case. The value of $\dot{\mu}_W$ remained almost constant throughout the test time for all specimens, but was higher for those with a higher water content. The evaporation rate was low for the first specimen and almost equal to $\dot{\mu}$ of pure water for the third specimen.

The evaporation rate $\dot{\mu}_X$ of the 90% xylene emulsion drops remained constant and almost equal to $\dot{\mu}$ of pure xylene, while $\dot{\mu}_W$ decreased with time toward zero. An opposite trend was observed in the evaporation of 40% xylene emulsions. Here $\dot{\mu}_W$ remained constant and equal to the evaporation rate of pure water, while $\dot{\mu}_X$ was small and decreased further with time. The value of $\dot{\mu}_X$ for the 80% xylene emulsion drops increased toward the value of $\dot{\mu}$ for pure xylene while $\dot{\mu}_W$ decreased.

Discussion of Results. The conclusion based on general concepts and on available data [5] is that the evaporation of drops of pure liquids in still air may be described by a relation analogous to that describing heat transfer by free convection [6] and expressed as

$$\mathrm{Sh} = \beta_n (\mathrm{Ar\,Sc})^n, \tag{5}$$

where β_n and n are parameters constant for a given range of values of Ar · Sc but different for different modes of free air flow, $0 \leq n \leq 1/3$.

Inserting the values of Sh, Ar, and Sc into (5), then expanding into series and retaining only the first terms, we easily arrive at Eq. (1).

"If liquids are mutually insoluble, then the vapor pressure of each component is equal to its vapor pressure as if it were alone, regardless of the amount of the other component present." Such assertions are to be found in studies on solutions. Since emulsions are mixtures of mutually insoluble liquids, one

TABLE 2. Evaporation Rates $\dot{\mu}_W$ and $\dot{\mu}_B$ for 90 and 40% Benzene Emulsion

Benzene	Time, min	0,25	0,5	1,0	2,0	4,0	5,0	7,0
90 %	$\dot{\mu}_W \cdot 10^5$	—	0,3	0,9	1,2	1,0	0,95	0,9
	$\dot{\mu}_B \cdot 10^5$	9,4	7,7	4,6	1,8	0,5	0,35	0,2
Benzene	Time, min	1	1,5	2,5	4,5	6,5	7,5	9,5
40 %	$\dot{\mu}_W \cdot 10^5$	1,0	0,97	0,98	0,95	0,98	0,96	0,93
	$\dot{\mu}_B \cdot 10^5$	1,15	1,18	1,0	0,75	0,50	0,49	0,42

would assume that their evaporation rate does not depend on the concentrations. The experimental material which we have reported here proves convincingly that this statement is not true. An idea of the dependence of $\dot{\mu}$ on the concentration is given by Fig. 2b.

It is well known that the maximum concentration of a monodispersed emulsion consisting of undeformed drops is 74% [9]. Clearly, in our highly concentrated polydispersed emulsions the drops were densely distributed and were possibly deformed. Their fluidity was low. The drops of the dispersed phase were surrounded by thin water films not necessarily continuous around the drop surface.

Considering this, we can, to a first approximation, describe the emulsion evaporation process. Let us first consider the emulsion which contained 90% benzene. In the beginning, apparently, the film around the drop was not continuous. For this reason, the evaporation rate of water from this drop was low while the evaporation rate of benzene was high. The evaporation rate of benzene being almost nine times higher than that of water, the benzene content in the drop decreased rapidly. After some time, the water film closed up and became continuous, its thickness increased, and the evaporation rate of water became almost equal to that of benzene. Benzene vapor now diffused through the film, the evaporation rate of benzene became low and further decreased with time. In the case of the 80 and 40% benzene emulsions, the water film around the surface of drops was already continuous at the beginning and, therefore, the evaporation rate of benzene was reduced considerably, especially in the emulsions with the higher water content.

On the basis of these considerations, one may assume now that the rate of change of $\dot{\mu}$ with time is proportional to $\dot{\mu}$:

$$-\frac{d\dot{\mu}}{dt} = k\dot{\mu} + b. \tag{6}$$

From this, after integration, follows the relation which had earlier been established empirically.

Let us now consider the evaporation of 90% butyl benzene emulsion drops in water. In this case, apparently, the water film around the surface of the butyl benzene drops had not been continuous. With water evaporating much faster than butyl benzene, however, the surface of the water film contracted. Its evaporation rate decreased with time while that of butyl benzene increased. Relation (6) remained in force throughout the process.

When the butyl benzene concentration was less than 90%, the water film around the surface of an emulsion drop was continuous and its thickness increased with increasing water content. As a result of diffusion through the film, the evaporation of butyl benzene combined with the evaporation of the water film. With time, the thickness of the water film decreased and the evaporation rate of butyl benzene increased. Then, when the water concentration had dropped to a certain definite level, the film ceased to be continuous, its surface area decreased, and the emulsion continued to evaporate in the same manner as the 90% butyl benzene emulsion.

The water film around the surface of a 90% toluene emulsion drop was, apparently, also discontinuous; this was indicated by the relatively low evaporation rate of water from a drop. Since the evaporation rates of water and toluene expressed in moles/cm · sec are almost the same, however, the two components reached an "equilibrium" state. The evaporation rate of water from the emulsion did not change further, while $\dot{\mu}_T$ varied in the same manner as $\dot{\mu}$ for pure toluene.

Another pattern prevailed in the evaporation of the 40% emulsion. In this case the water film was continuous and, apparently, rather thin. Toluene vapors diffused through the film.

It is not difficult to explain the pattern observed in the evaporation of the xylene emulsions in water.

The interpretation given here agrees with the temperature data.

NOTATION

m	is the mass, g;
d	is the diameter, cm;
ϑ	is the temperature, °C;
$\dot{m}$	is the rate of change of mass, g/sec;
ϑ_a	is the ambient temperature, °C;
ϑ_{min}	is the lowest temperature of an emulsion drop, °C;
$\dot{\mu} = \dot{m}/d$	is the evaporation rate, g/cm · sec;
$\dot{\mu}_E$, $\dot{\mu}_B$, $\dot{\mu}_T$, $\dot{\mu}_X$, $\dot{\mu}_{BB}$, $\dot{\mu}_W$	are the evaporation rates $\dot{\mu}$ of an emulsion, of benzene, of toluene, of xylene, of butyl benzene, and of water, respectively;
Sh	is the Sherwood number;
Ar	is the Archimedes number;
Sc	is the Schmidt number;
Gr	is the Grashof number;
Nu	is the Nusselt number;
Pr	is the Prandtl number;
L	is the specific heat of evaporation;
λ	is the thermal conductivity of air;
c_W	is the percent volume content of water in an emulsion.

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