

**EFFECT OF SURFACTANT ADDED IN SMALL AMOUNTS
ON NONISOTHERMAL ABSORPTION:
AN EXPERIMENTAL STUDY**

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Results of an experimental study of water-vapor absorption by a stagnant layer of the aqueous solution of LiBr with admixed octanol, used as a surfactant, are described. Time dependences of temperature at various heights of the layer, time dependences of absorbed mass, and temperature and concentration profiles at various times are reported. A comparison with experimental data for surfactant-free solutions reveals an enhanced action of octanol on water-vapor absorption and an increase in the absorbent surface temperature at the initial stage of the process.

Key words: *absorption, heat and mass transfer, diffusion, solution, surfactant.*

Introduction. Heat- and mass-transfer intensification in advanced manufacturing technologies based on the absorption phenomenon is an important problem in developing heat exchangers for chemical industry and also for cold or heat production with the help of absorption heat pumps. Apart from design-related intensification approaches, there are methods based on the use of additives that do not affect the final product. For instance, the use of surfactants offers much promise in power engineering. Various compounds, including high-molecular spirits, are used as absorption-enhancement surfactants. The most effective surfactant for the aqueous solution of lithium bromide (LiBr) is *n*-octanol. Studying the action of *n*-octanol, Kashiwagi et al. [1] and Hozawa et al. [2] found that Marangoni convection develops during absorption of water vapor by LiBr aqueous solutions, presumably due to surfactant islands (microdroplets) present on the surface of the absorbent. The mass-transfer study of [3], based on measurements of the changes in mass of the absorbed substance, proved surfactants to be effective agents enhancing absorption at the initial stage of the process. Observations of the solution surface performed with the help of an IR camera [4] revealed emergence and development of temperature inhomogeneity of a cellular type already during the first ten seconds of the process.

In all the above-mentioned studies, attempts were made to deeper penetrate into the mechanism of the Marangoni convection during absorption; yet, the data obtained were insufficient to provide a more detailed description of the absorption process accompanied by intense heat generation at the interface between the phases. The models of combined heat and mass transfer proposed in [5, 6] ignore the mechanism responsible for origination of convective flows. A comparison of these models with the data obtained in a complex experimental study of water-vapor absorption by surfactant-free aqueous solutions of LiBr [7, 8] revealed differences (within 20%) only at high absorption times. In terms of heat transfer, the experimental and calculated results are in good agreement (the temperature profiles coincide within tenths fractions of a degree).

P–T– ξ -Dependence. The models mentioned above require detailed information on equilibrium concentrations, temperatures, and pressures. Therefore, it becomes necessary to study the effect of surfactants added in small amounts on the *P–T– ξ -dependence*.

Such studies were performed by the relative statistical method [9]. The basic part of the experimental setup was two piezometers placed in a thermostat. One of the two piezometers contained the aqueous solution of LiBr, and the other piezometer contained the same solution with addition of the surfactant.

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The piezometers were cylindrical glass flasks 80 cm³ in volume; the flasks were connected to different arms of a differential pressure transducer. The solution temperature in the flasks was measured by thermocouples encapsulated into capillary stainless-steel tubes 1.3 mm in diameter; the tubes prevented the adverse effect of the LiBr solution on the thermocouple material. Each thermocouple was subjected to an independent calibration test so that to allow temperature measurements within $\pm 0.1^\circ\text{C}$. The entire system was evacuated by a pump.

To measure the gas-pressure difference above the lithium bromide solution, we used a highly sensitive ‘‘Sapfir 22-MT’’ differential pressure transducer (model 2420) whose maximum allowed error was 0.5% of the measurement limit (2.5 kPa), i.e., ± 12 Pa. The signals from the thermocouples and pressure transducer were registered by a personal computer coupled with a 12-digit analog-to-digital converter.

The temperature of water in the thermostat, controlled with the help of a personal computer, was maintained in the experiments within a given range with an error of $\pm 0.05^\circ\text{C}$. This temperature was measured by a mercury thermometer with a scale factor of 0.1°C .

We experimentally examined the influence of octanol additives from 0.01 to 0.1% of the absorbent mass, on the vapor pressure above a 60-% solution of LiBr in water in the temperature range from 20 to 50°C . Only for the concentration of 0.1% and temperature $T = 50^\circ\text{C}$ was an insignificant, within the measurement accuracy, excessive vapor pressure above the surface of the solution with the admixed surfactant observed.

Experimental Results. The experimental setup and procedure used to experimentally study water-vapor absorption in the presence of the surfactant was described in detail in [8]. Octanol dissolved in water (0.01% of the absorbent mass) was added to a strong ($\xi > 60\%$) aqueous solution of LiBr; subsequently, the parameter ξ was accurately brought to its final value of $58.0 \pm 0.1\%$.

Eight experimental series were performed, which differed only in the total test duration (from 30 minutes to 15 hours) were performed. The absorbent-layer thickness in all tests was $h_0 = (20.0 \pm 0.1)$ mm; the initial temperature of the solution T_0 and the absorbent-bottom temperature T_w were maintained equal to 20.4°C , the absorption pressure was $P = (1970 \pm 10)$ Pa, and the mass concentration of LiBr in the solution was $\xi = 58\%$. Under such conditions, the thermophysical properties of the solution had the following values (see [10]):

Thermal diffusivity a , m ² /sec	$1.3 \cdot 10^{-7}$
Kinematic viscosity ν , m ² /sec	$4.12 \cdot 10^{-6}$
Diffusivity D , m ² /sec	$1.27 \cdot 10^{-9}$
Thermal conductivity λ , W/(m · °C)	0.415
Specific heat c_p , J/(kg · °C)	1980
Density ρ , kg/m	1680
Dynamic viscosity μ , kg/(m · sec)	$6.94 \cdot 10^{-3}$
Absorption heat r_a , J/kg	$2.72 \cdot 10^6$

The equilibrium state at the interface between the two phases can be fairly accurately described by a second-order polynomial; for $P = 1970$ Pa, the polynomial is

$$T_s = 180.5 - 414.66C_s + 267.6C_s^2. \quad (1)$$

The temperature and concentration profiles in the LiBr solution were measured in the present experiments. Figure 1 shows the typical temperature profiles at various times. It follows from the Fig. 1 that, initially, the temperature profile is heavily concave. With time, it become less concave and becomes linear after 1000 sec (Fig. 1a). Later, the profile remains linear during the remaining test time, while the surface temperature decreases (Fig. 1b). The temperature at the bottom remains practically unchanged.

The concentration profiles in the solution are shown in Fig. 2. The concentration profile in the LiBr layer also changes from a more concave to a less concave form. During the first 14,000 seconds, the concentration near the bottom remains unchanged and then starts increasing, presumably due to diffusion-layer extension to the bottom.

The time evolution of temperature at various heights from the bottom is illustrated in Fig. 3. To demonstrate the surfactant action on heat and mass transfer more clearly, similar data previously reported for the pure (surfactant-free) solution [8] are also plotted by dashed curves. Figure 3 also shows the surface temperature T_s in the octanol-free absorbent; this temperature was obtained by IR imaging (solid curves). Initially, the surface temperature in the solution with the admixed surfactant increases more rapidly than in the surfactant-free solution and reaches values 1°C greater than the surface temperature of the surfactant-free solution. The maximum values were observed approximately 60 sec after the process was initiated. Over this period, visual observations reveal convective flows developing in the surface layer. The faster growth of temperature is also observed at other levels.

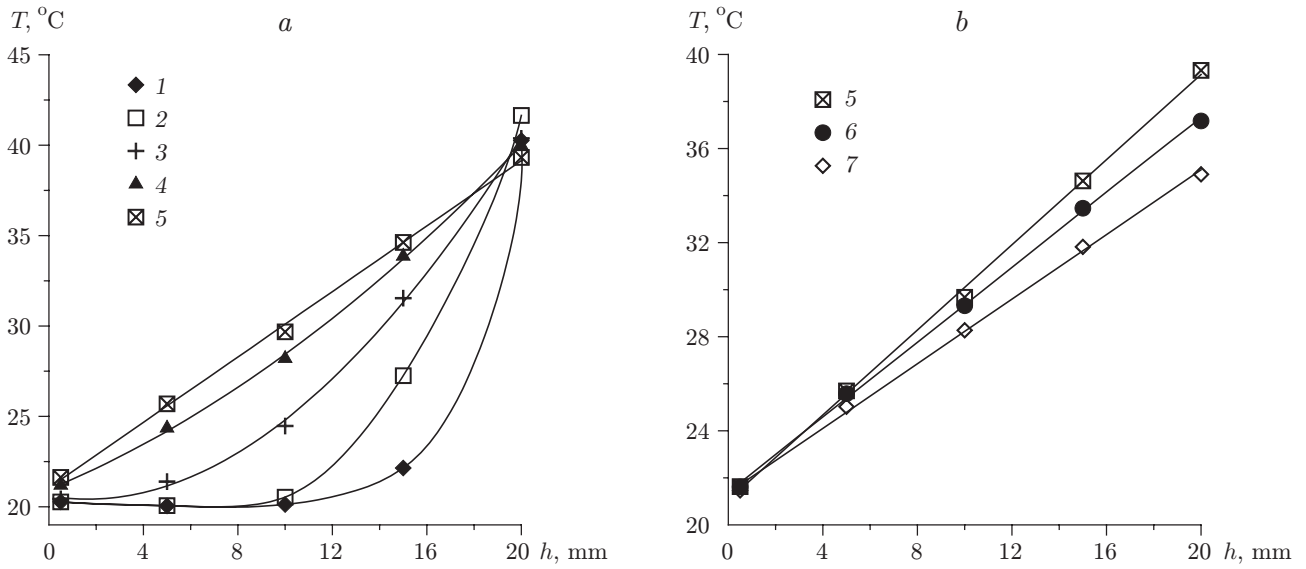


Fig. 1. Temperature profiles at $t = 21.4$ (1), 60.4 (2), 204 (3), 515 (4), 1019 (5), 2020 (6), and 3715 sec (7): (a) profile evolving from a heavily concave to a linear form; (b) linear profile.

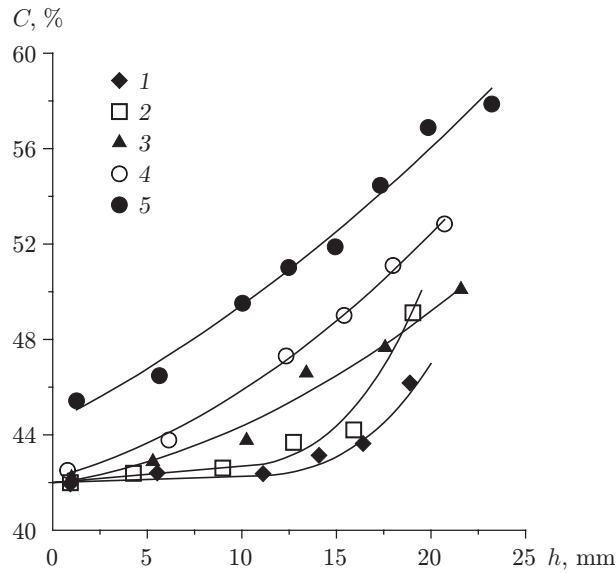


Fig. 2. Concentration profiles at $t = 1800$ (1), 3700 (2), 7200 (3), $14,400$ (4), and $54,300$ sec (5).

During the next 200 sec, the surface temperature slightly decreases; afterwards, it remains constant in the time interval from 250 to 700 sec and coincides with the surface temperature in the surfactant-free solution. As it follows from Fig. 3, the thermal layer reaches the bottom by that time, and the upper layers start experiencing the effect of heat withdrawal through the bottom part of the absorber. From this time on, both the surface temperature and the mean temperature in the solution start decreasing, and the temperature profiles in the solution with and without the surfactant become almost coincident. Such a behavior of temperature can be consistently explained, at least qualitatively, by convection that first develops and then gradually decays in the surface layer. This phenomenon was previously reported in [2–4] and was visually observed in the present study.

According to [5, 6], the initial temperature and concentration at the solution surface for $v = 0$ can be found by solving the system of equations

$$T_0 - T_s = \frac{r_a}{c_p} \sqrt{\frac{D}{a}} (C_0 - C_s), \quad T_s = f(C_s).$$

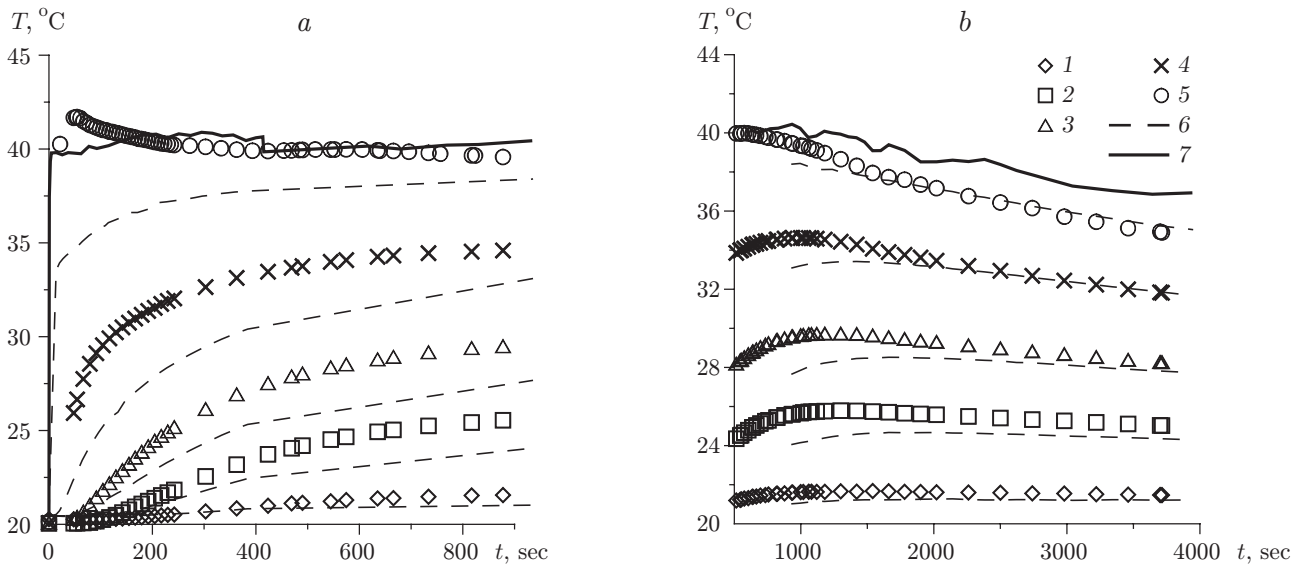


Fig. 3. Temperature versus time at distances from the bottom for short (a) and long (b) time intervals: $h = 0.5$ m (1), 5 (2), 10 (3), 15 (4), 20 mm (5); the points are the experimental data for the solution with the admixed surfactant; curves 6 refer to the data for the surfactant-free solution and curve 7 refer to the surface temperature.

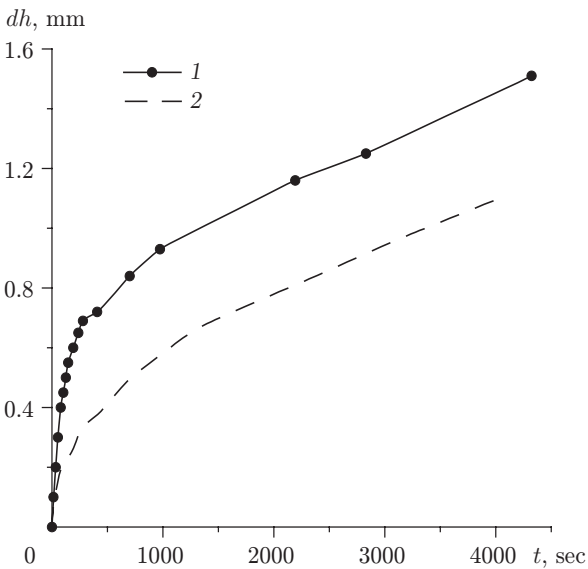


Fig. 4

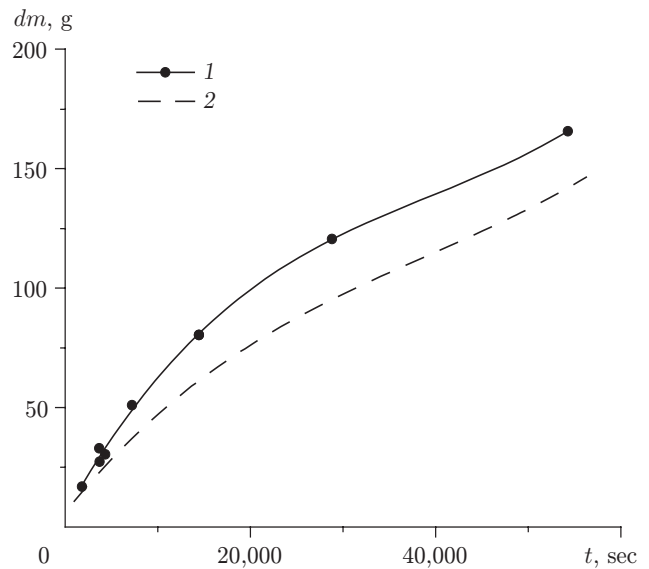


Fig. 5

Fig. 4. Absorbent-layer thickness versus time: data for the solution with the admixed surfactant (1) and data for the surfactant-free solution (2).

Fig. 5. Changes in absorbed-substance mass versus time: data for the solution with the admixed surfactant (1) and data for the surfactant-free solution (2).

Here, the temperature T_s is found by formula (1). We can see that the values of T_s and C_s depend only on the parameter $Le = D/a$.

Making allowance for a nonzero growth rate of the layer thickness ($v \neq 0$) complicates the determination of the concentration and temperature at the surface; yet, both quantities again depend only on the Lewis number. For instance, if there are no convective flows, the surface temperature is initially 40°C . The convective flows draw the effective values of a and D closer to each other, i.e., the Lewis number increases and tends to unity in the case of developed convection. Thus, the maximum temperature at the surface can reach 48°C for the initial parameters used.

The thickness of the LiBr solution layer was monitored throughout the whole experiment. Figure 4 shows the typical curve (curve 1) of the increase in the layer thickness for the solution with the admixed surfactant in comparison with the analogous curve for the surfactant-free absorbent. A faster increase of the layer thickness during the first 200 seconds for the solution with the admixed surfactant is evident; later, the rates become identical, and the distance between the curves remains approximately unchanged.

The total change in the mass of the absorbed substance was determined at the end of each test. The results shown in Fig. 5 also indicate the faster increase in the mass of the layer if the surfactant was added to the LiBr solution.

Thus, the data obtained in the present comprehensive study of water-vapor absorption by a stagnant solution of LiBr in water with admixed octanol (0.01 wt.%) show that the surfactant enhances absorption, simultaneously increasing the surface temperature of the solution layer in a restricted initial time interval.

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