Heat and mass transfer intensification at steam absorption by surfactant additives

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ABSTRACT

The mechanisms of surfactant admixture effect on heat and mass transfer were studied experimentally at steam absorption by a salt solution at operation of the heat pump absorber. Steam absorption by initially immobile water solution of lithium bromide with additives of n-octanol with concentrations of 25–400 ppm (both lower and higher than the solubility limit) was studied. Thermograms of a layer surface, moving during absorption, were obtained by thermal imaging equipment. Data on surface tension of lithium bromide solution with small additives of n-octanol was analyzed.

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1. Introduction

An absorber is an important component of the absorption heat pump and refrigerating machine. The following working system, applied by these devices, is considered to be the most efficient: water solution of lithium bromide (LiBr) – steam. Steam absorption at falling films of solution (film absorption) over the tube surface is the most common. Specific properties of lithium bromide solution are the reason for application of expensive materials for absorber tubes. A decrease in the number of tubes, and hence, reduction of metal content and absorber cost are possible at the expense of new methods for heat and mass transfer intensification at absorption.

One of these methods is addition of surfactants into solution, which lead to generation of small-scale surface convection and following heat and mass transfer intensification. However, in experiments studying the effect of surfactants on film absorption intensity, it is difficult to divide contributions of the main flow and surface convection into heat and mass transfer. In this case steam absorption by an immobile solution layer with excluded forced flow is an object, convenient for investigation. Previously, theoretical and experimental data on the local characteristics of heat and mass transfer at absorption by an immobile layer of solution without surfactants were presented [1,2]. Then, this data will be used as the standard for comparison with data, obtained in the presence of surfactants. In [3,4], this comparison was made only for one integral characteristic (for a change in the mass of absorbed substance in time).

2. Experimental setup and measurement methods

Experiments on steam absorption by initially immobile layer of water solution of lithium bromide with additives of n-octanol with concentrations of 25–400 ppm (both lower and higher than the solubility limit) were carried out to obtain data on surfactant effect on the local characteristics of heat and mass transfer and to understand the mechanism of this effect. At first, these experiments were carried out at the setup, described in detail in [1], then, they were performed at the setup with modernized absorber (Fig. 1).

At setup [1], a stainless steel cylindrical vessel of the 165-mm diameter and 87-mm length was used as the absorber. The temperature inside the layer was measured by thermocouples. Five thermocouples in protective covers in the form of capillary tubes of the 1-mm diameter were introduced into the absorbent layer through the lateral walls of absorber. They were located over the radius with a shift relative to each other in the horizontal plane of 36° with the step of 5 mm over the height. The lower capillary was near the bottom, and the upper one was at the height of 20 mm. Concentrated solution of LiBr was poured into the absorber (0.855 ± 0.025 kg) to cover the upper thermocouple with the liquid layer of 0.2–0.5 mm.

Thermocouples were made of copper and constantan wires with diameters 0.16 and 0.1 mm, correspondingly. Individual calibration allowed temperature measurements with an error of not more than 0.1 °C.

To get information about distribution of solution concentration over the layer, sampling from different layer levels was made. Tubes with the diameter of 2 mm with closed ends and 0.8-mm holes, drilled on the lateral surface, were used as the samplers. Sampling tubes were located to take solution from the given level, and their holes were directed upward. This location provided minimal solution mixing at its layer-by-layer drain.

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Nomenclature

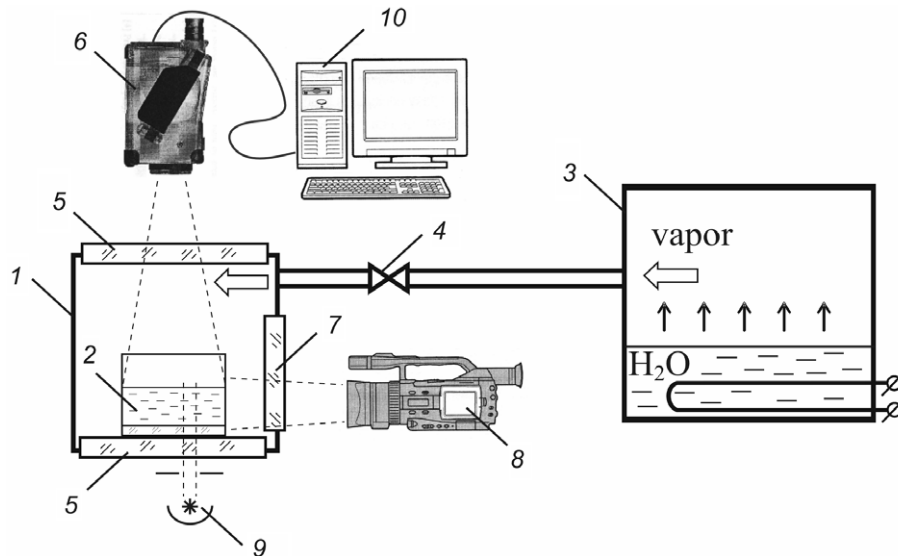|			
C	water concentration in solution (mass fraction) (%)	*Greek symbol*	
C^1	concentration of lithium bromide in solution (%)	σ	surface tension (N m^{-1})
C_{sur}	surfactant concentration (ppm)		
T	temperature (°C)		
t	time (s)		

Fig. 1. Experimental setup: (1) vacuum chamber, (2) bath, (3) vapor generator, (4) valve, (5) observation windows, (6) infrared (IR) chamber, (7) infrared glass, (8) video camera, (9) light knife and (10) personal computer.

The absorber was modernized to eliminate the effect of metal wall temperature on temperature distribution over the layer surface during absorption. The modernized setup consists of vacuum chamber 1, bath with lithium bromide solution (LiBr) 2, steam generator 3, and valve for steam supply 4. Vacuum chamber 1 was made as a stainless steel cylinder of the 180-mm diameter and 90-mm height, equipped by one lateral observation window and two windows from the top and from the bottom.

The initial concentration of LiBr in experiments was 58%. The solution was poured into a round bath with the bottom diameter of 70 mm and thickness of 15 mm. An optic glass was the bottom. The height of poured solution was 20 mm. Bath walls were made of a thin (40 μm) transparent film.

The temperature of the moving interface of LiBr solution was measured distantly and without contact through upper window 5 by modern IR camera 6 – thermal imager NEC 7102WX. The registered range of IR radiation was 8–14 μm. Radiation from the surface of lithium bromide solution passed through window 7 to the objective of the IR camera. Glass, made of LiF, with the diameter of 140 mm and thickness of 20 mm was IR radiolucent. Video recording, observation, control and measurements of the layer level were performed through observation window 6. Recording was made by video camera 8 Canon XM2; for this purpose small marks were introduced into solution, and they were illuminated by flat light knife 9 through the lower observation window, made of optic glass.

The experimental setup was equipped by the automated system for data gathering and maintenance of the required conditions together with the system for PC result treatment 10.

Steam was generated by a vessel of 20 l volume with the heaters for water evaporation from LiBr solution, located on the vessel bottom. Absorption started after opening valve 5 and steam supply to vacuum chamber 1. The steam pressure in the vacuum chamber was kept of about 2 kPa. The computer control of generator power source allowed us to keep the pressure constant in the system with the accuracy of ± 5 Pa. This made possible to use the steam generator as a barostat, controlled by a differential membrane low-limit pressure sensor.

Two standard emitters were located within the viewing field to calibrate the IR camera. One of these emitters was heated and another was not. These emitters were made as the copper cylinders with the diameter of 10 mm and height of 10 mm. One of these emitters contained a microheater. The emitting surfaces of the cylinders were blackened by lamp black. Their temperature was measured by the calked thermocouples.

Long thermostating during 12 h at least provided a constant temperature of layer and absence of convective flows in the liquid before the experiment.

3. Experimental results

More than 20 experimental series with duration from 30 min to 20 h were carried out under the conditions, similar to operation of heat pumps and refrigerating machines.

After this research, we have obtained profiles of temperature and absorbed substance (water) concentration within the layer at different moments of time.

Temperature profiles measured by thermocouples at different moments of time for *n*-octanol concentration (100 ppm) are shown in Fig. 2. By the character they slightly differ from the similar profiles, obtained for solution without surfactants. At absorption beginning the temperature profile is concave; in 1000 s it becomes
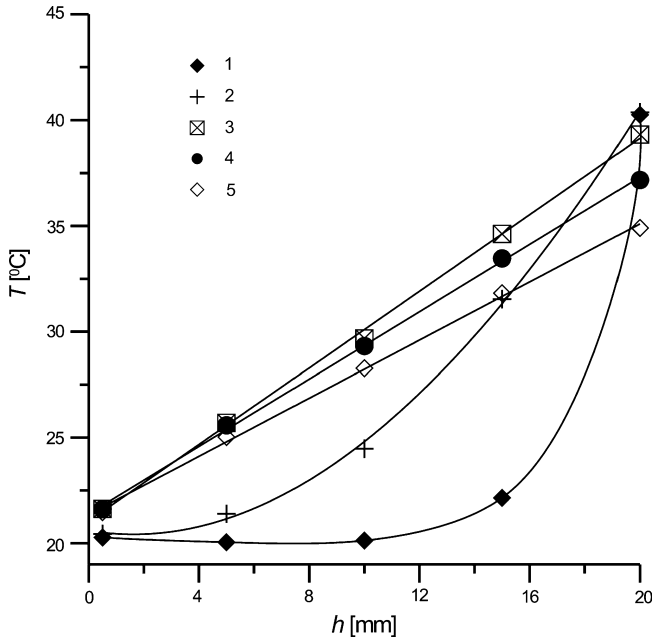
Fig. 2. Temperature profiles $t = 21.4$ (1), 204 (2), 1019 (3), 2020 (4), and 3715 s (5).

linear and stays linear during the whole experiment. The temperature near the layer surface does not change for short times, and then it decreases. The temperature near the bottom is almost constant.

The quantitative comparison with similar results, obtained without surfactants, demonstrated that surfactants increase the temperature at all layer levels, including the moving layer surface. In Fig. 3 layer surface temperatures, measured by the thermal imager, are shown by curves 6 (without surfactants) and 7 (with surfactants). If we assume that the interface is in the state of thermodynamic equilibrium and surfactants do not effect this
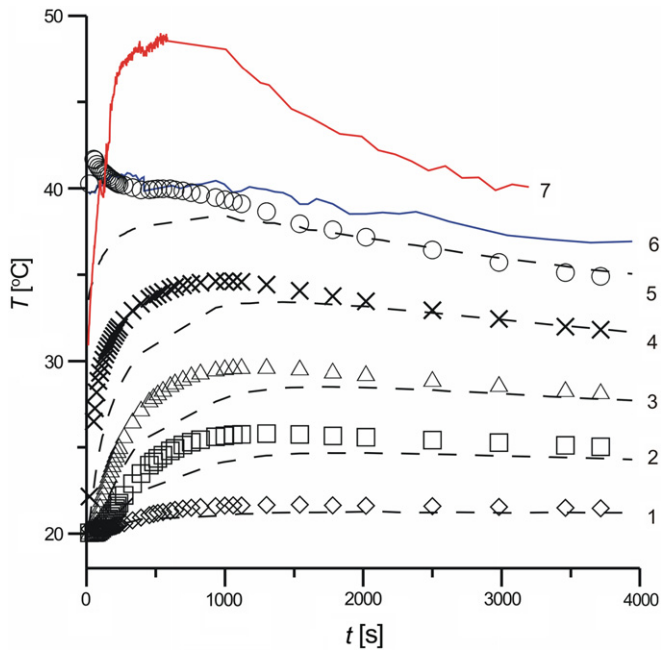
state, an increase in the layer surface temperature at a fixed steam pressure corresponds (e.g., see data on thermodynamic equilibrium in the system: water solution of lithium bromide – steam [5]) to a decrease in water concentration near the layer surface (to the rise of salt concentration).

This is also proved by measurements of water concentration profile in solution with and without surfactants. Profiles of water concentration in solution are compared in Fig. 4 at the same moment of time without surfactants and for *n*-octanol concentration of 400 ppm, what is higher than the solubility limit of this surfactant. In this case, the profile of water concentration changes significantly in the presence of surfactant, what provides an increase in the average concentration over the layer thickness and a growth of absorbed substance mass, despite a reduction of water concentration near the interface.

The qualitative pattern of surfactant effect on a change in interface temperature and average layer temperature during absorption is shown in Fig. 5. It can be noted that the surfactant presence increases the surface temperature and the average layer temperature, and the initial period ($t_{0sur} < t_0$), when the surface temperature is kept constant, decreases. The similar situation is shown in Fig. 6 for concentration of the absorbed substance, average over the layer, and for concentration near the interface. In the presence of surfactant, average concentration in the layer is higher than concentration in solution without surfactant, whereas, surface concentration of the absorbed substance in solution with surfactant is less than concentration in solution with surfactant. The typical dependence between concentration of the absorbed substance and temperature in the state of thermodynamic equilibrium is shown in Fig. 7 for the given steam pressure. An arrow indicates the direction of temperature and concentration changes at the interface during absorption.

Generation of convection in the near-surface layer was registered by video and photo recording at introduction of a surfactant into solution.

Thermograms of the moving layer surface were obtained for different time moments by thermal imaging equipment. Some
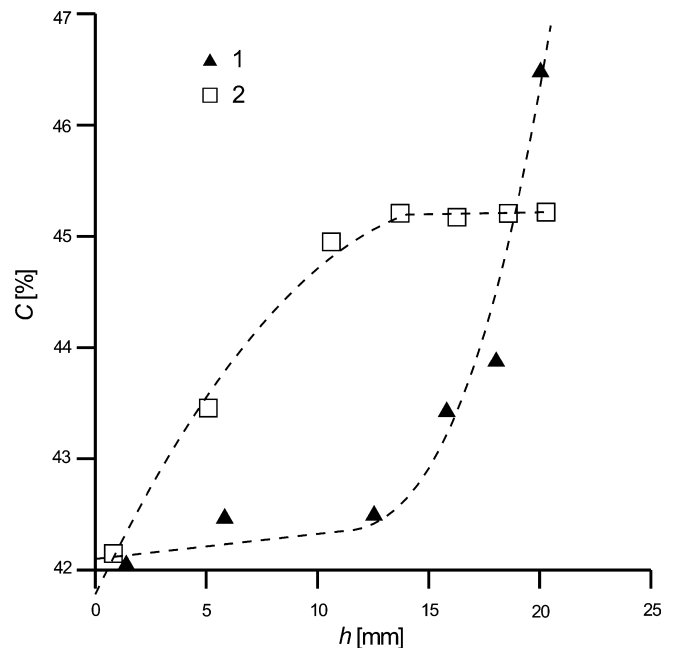

Fig. 3. Temperature vs. time at distances from the bottom: $h = 0.5$ (1), 5 (2), 10 (3), 15 (4), and 20 mm (5); curve 6 refer to surface temperature for the surfactant-free solution; curve 7 refer to surface temperature for the surfactant; the points are the experimental data for the solution with the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

Fig. 4. Concentration profiles: (1) data for the surfactant-free solution, (2) $C_{sur} = 400$ ppm.
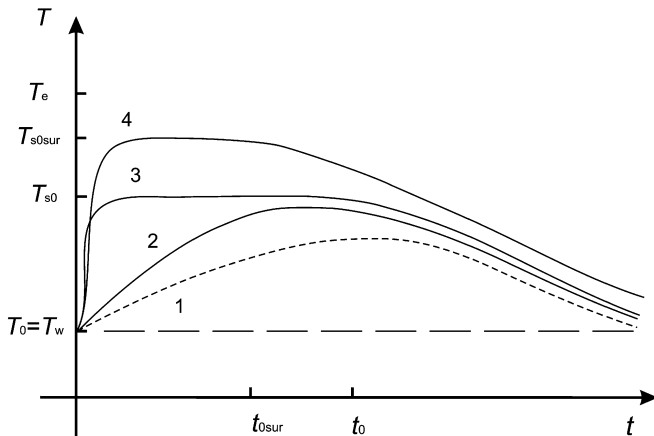
Fig. 5. The qualitative pattern of surfactant effect on a change in interface temperature and average layer temperature during absorption: (1) average layer temperature without surfactant, (2) average layer temperature with surfactant, (3) interface temperature without surfactant and (4) interface temperature without surfactant.
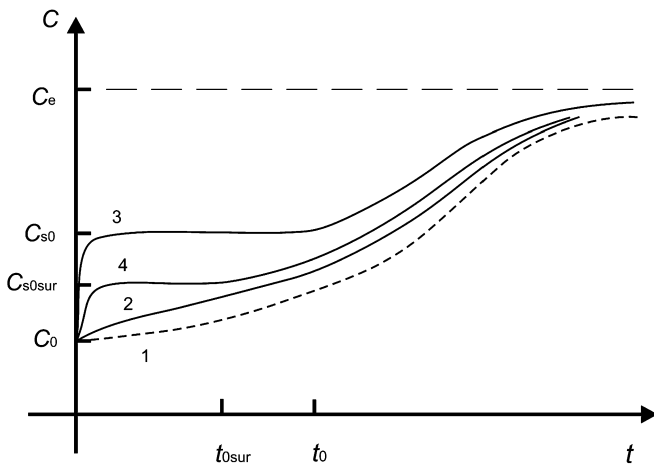

Fig. 6. The qualitative pattern of surfactant effect on a change in concentration of the absorbed substance average over the layer, and for concentration near the interface: (1) average layer concentration without surfactant, (2) average layer concentration with surfactant, (3) concentration near the interface without surfactant and (4) concentration near the interface with surfactant.

thermograms are shown in Fig. 8. Temperature nonuniformity, typical for convective cells, was registered in the obtained thermograms for all surfactant concentrations. Time dependences of maximal, minimal and average interface temperatures, proving the above nonuniformity, are shown in Fig. 9.

According to thermal imaging measurements of temperature of the moving layer surface for surfactant concentrations below the solubility limit (25–100 ppm), even very small admixtures of surfactants increase the average surface temperature in comparison with the temperature without surfactants. At that, according to the diagram of thermodynamic equilibrium, for the fixed steam pressure a higher salt (LiBr) concentration on the surface corresponds to a higher temperature (Fig. 10). Therefore, experimental confirmation for the hypothesis about "surface salting out" [3,4], probably causing near-surface convection at introduction of surfactants with concentrations below the solubility limit, was firstly obtained.

Previously, the mechanism of intensifying effect of surfactants was considered only as the hypotheses. Thus, it was assumed in [3,6] that for surfactant concentrations above the solubility limit, surface convection may be caused by "island" of not dissolved sur-
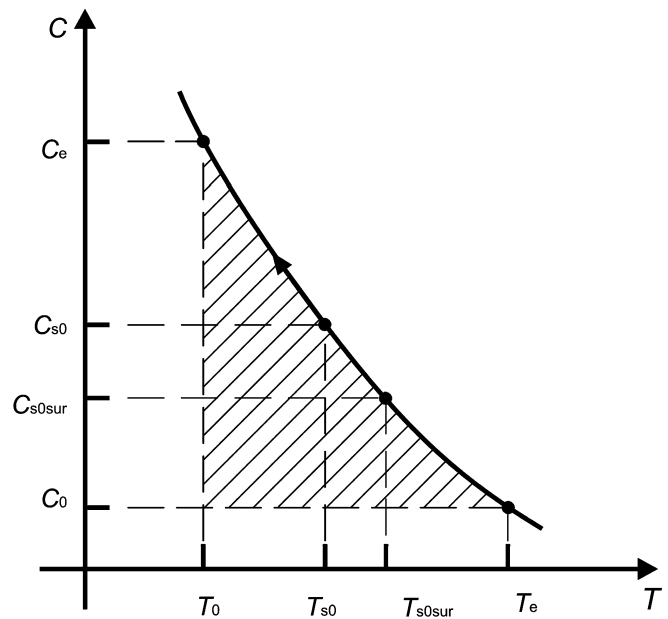

Fig. 7. The typical dependence between concentration of the absorbed substance and temperature in the state of thermodynamic equilibrium.

factant with a lower surface tension than the ambient solution has. The generated gradients of surface tension are considered as the convection reason (Marangoni effect).

Actually, for *n*-octanol concentration of 400 ppm, these "island" were revealed and recorded in the experiments (Fig. 11).

4. Analysis of data on surface tension and thermodynamic equilibrium

When interpreting the experimental results, obtained particularly at confirmation of the "salting out" hypothesis, we used the assumption that for small surfactant additives relationship, describing thermodynamic equilibrium of the interface, does not change.

Application of this assumption is connected with a full absence of data, required for description of thermal equilibrium in the following system: water solution of lithium bromide with surfactants – steam with additives of volatile surfactant. In the presence of surfactant in solution and in steam, the total number of parameters and independent variables increases, and strictly speaking, relationships, describing thermodynamic equilibrium of this complex system, should change. However, in papers dealt with surfactant effect on steam absorption, this is not considered and discussed. Thermodynamic equilibrium in [3,4,6,7] is described without consideration of surfactants.

In this case, for the two-phase system, consisting of two-component solution (without surfactant) and single-component gas (vapor) phase, including only one component of solution, only two parameters can be independent by the phase rule, and for the constant vapor pressure only one parameter can be arbitrary. Therefore, concentration and temperature of solution are not the independent variables. So, the relationship, connecting concentration of one of the main components of solution (water or lithium bromide) with the temperature, is used as the function, describing thermodynamic equilibrium. In mathematic modeling this function is considered liner for simplicity. It is evident that a lack of accurate data on thermodynamic equilibrium of the considered system impedes full understanding of the mechanisms of surfactant intensifying effect.
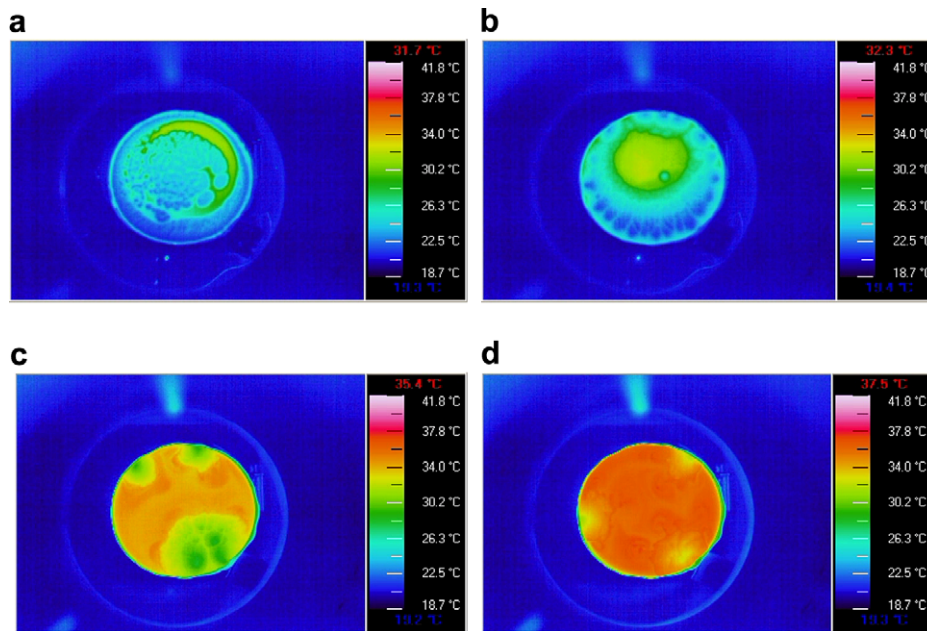
Fig. 8. Thermograms of the moving layer surface: (a) 1 s, (b) 10 s, (c) 60 s and (d) 120 s.
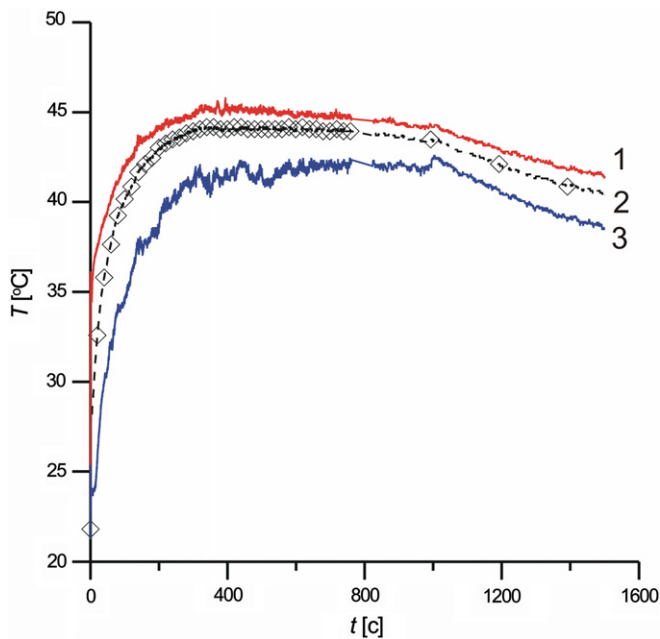

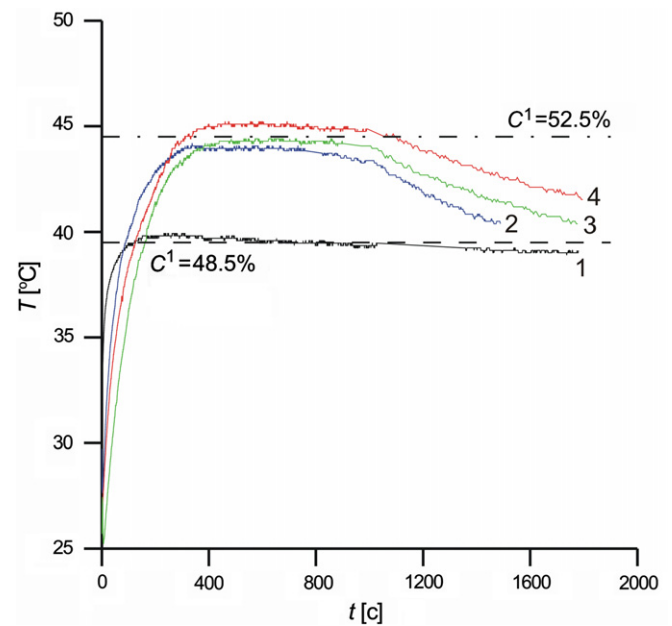**Fig. 9.** Time dependences of maximal (1), average (2) and minimal interface temperatures (3).

Fig. 10. Average temperature of interface for different surfactant concentrations: (1) without surfactant, (2) 25 ppm, (3) 50 ppm and (4) 75 ppm.

When studying the mechanisms of convection generation, estimating heat and mass transfer intensification by surfactant introduction and performing physical and mathematic modeling of transfer processes at absorption, it is necessary to have information on the surface tension in the system: water solution of LiBr with surfactants – pure steam (without air), under the operation conditions of corresponding devices. In particular, these data are required for calculation of interface tension gradients and Marangoni numbers, which determine one of the boundary conditions for the model of heart and mass transfer and are very important for the analysis of interface stability.

Since the surface tension is the property of interface in the state of thermodynamic equilibrium, for the constant vapor pressure, it

can be a function (except C_{sur}) of only one of two variables (C or T). It was found out that for the conditions of thermodynamic equilibrium of the interface at a constant vapor pressure there is almost no such information on the surface tension. There is a lack of data only on the surface tension of LiBr solution with some surfactant additives in the system, where air with steam acts as the gas phase. This data is usually presented as the table or graphic functions of three independent variables $\sigma = \sigma(C, T, C_{sur})$, where a certain partial pressure of vapor should correspond to each pair of values (C, T) by the condition of thermodynamic equilibrium. It is evident that for the given vapor pressure, when C and T are not independent variables, it is impossible to use this data directly. For the constant vapor pressure, it is necessary to convert dependence $\sigma = \sigma(C, T, C_{sur})$
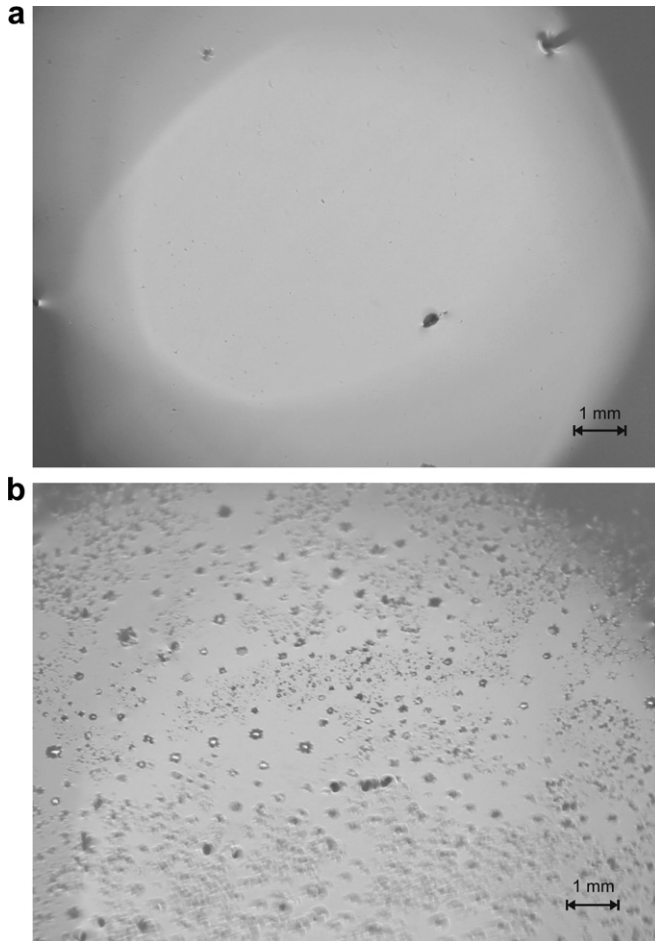
Fig. 12. Surface tension vs. concentration of LiBr at 25 °C with *n*-octanol concentration as parameter [8]: (○) without octanol; (□) 100 ppm; (△) 40 ppm; and (×) 500 ppm.

Fig. 13. Surface tension vs. temperature for 50% concentration of LiBr with *n*-octanol concentration as parameter [8]: (○) without octanol; (△) 10 ppm; (□) 40 ppm; (×) 80 ppm; and (+) 400 ppm.

Fig. 11. Pictures of solution surface: (a) without surfactant and (b) at surfactant concentration of 400 ppm.

into $\sigma = \sigma(C, C_{sur})$ or $\sigma_p = \sigma_p(T, C_{sur})$ substituting thermodynamic equilibrium condition $T = T(C)$ or $C = C(T)$, correspondingly.

According to analysis of data on the surface tension of lithium bromide solution with small additives of *n*-octanol, used in [6–8], these table and graphic data are insufficient for derivation of approximation dependence $\sigma = \sigma(C, T, C_{sur})$ and its following conversion into $\sigma = \sigma(C, C_{sur})$ or $\sigma_p = \sigma_p(T, C_{sur})$. Besides, these data conflict with results of other works. Thus, according to data in Figs. 12 and 13 [8] on lithium bromide solution with additives of *n*-octanol with concentration from 10 to 500 ppm, the surface tension increases with a rise of temperature and decreases with a rise of LiBr concentration in the solution. It is also obvious that dependences of surface tension differ significantly for different surfactant concentrations.

At the same time in [3,4,6] to determine the Marangoni number and set the boundary conditions, the fixed negative values of both derivatives $\frac{\partial\sigma}{\partial T} = -2.1 \times 10^{-4}$ N/mK; $\frac{\partial\sigma}{\partial C} = -6.4 \times 10^{-4}$ N/mwt.% are used for any surfactant concentrations below the solubility limit (in particular, for $C_{sur} = 10, 25, 65$ ppm).

It has been already noted in [9] that application of dependences $\sigma = \sigma(C, T, C_{sur})$ in [10–12] for determination of Marangoni number is incorrect. Derivatives $\frac{\partial\sigma}{\partial C}; \frac{\partial\sigma}{\partial T}$ themselves cannot determine the state of the interface under thermodynamic equilibrium in the system: solution – steam under the constant pressure. Therefore, Marangoni numbers, determined proportionally to these derivatives in [10–12], cannot be used as the criteria, determining the interface state under these conditions. In this case, Marangoni
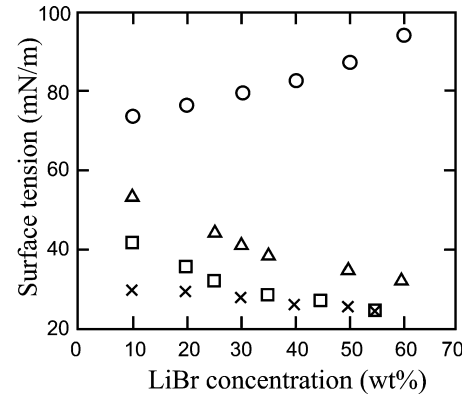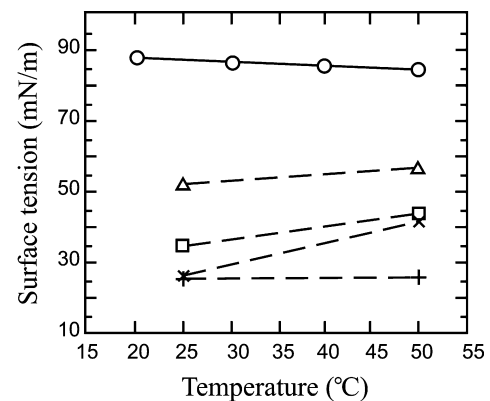
numbers should be determined by two derivatives $\frac{\partial\sigma_p}{\partial C}$ (or $\frac{\partial\sigma_p}{\partial T}$ and $\frac{\partial\sigma_p}{\partial C_{sur}}$.

However, derivatives $\frac{\partial\sigma_p}{\partial C}$ and $\frac{\partial\sigma_p}{\partial T}$ can be expressed via $\frac{\partial\sigma}{\partial C}$ and $\frac{\partial\sigma}{\partial T}$.

$$\frac{\partial\sigma_p}{\partial C} = \frac{\partial\sigma}{\partial C} + \frac{\partial\sigma}{\partial T}\cdot\frac{\partial T}{\partial C}; \quad \frac{\partial\sigma_p}{\partial T} = \frac{\partial\sigma}{\partial T} + \frac{\partial\sigma}{\partial C}\cdot\frac{\partial C}{\partial T};$$

It is obvious that relationship $\frac{\partial\sigma_p}{\partial T} = \frac{\partial\sigma_p}{\partial C}\cdot\frac{\partial C}{\partial T}$ is satisfied; and if thermodynamic equilibrium is described by linear function $C = k_1 + k_2T(k_1, k_2$ are determined by the vapor pressure), then $\frac{\partial\sigma_p}{\partial T} = k_2\cdot\frac{\partial\sigma_p}{\partial C}$. Determination of Marangoni number proportionally to any of derivatives ($\frac{\partial\sigma_p}{\partial C}$ or $\frac{\partial\sigma_p}{\partial T}$) is equivalent.

5. Conclusions

According to the obtained experimental results, addition of surfactants into a solution at steam absorption generates surface convection even in the initially immobile layer. Generation of convection is connected with temperature nonuniformity at the interface.

Existence of surfactant "island" on the layer surface at surfactant concentrations above the solubility limit was proved experimentally. For concentrations below the solubility limit, the hypothesis of surface "salting out" was proved.

It is shown that for more detailed investigation of mechanisms, intensifying surfactant effect on steam absorption under the conditions of heat pump operation, data on the surface tension and thermodynamic equilibrium in the system: water solution of LiBr with

surfactant additives – steam with additives of volatile surfactant, are required. Available data on the surface tension of LiBr solution with small additives of *n*-octanol, obtained fro the system with the air gas phase are discrepant and insufficient for determination of Marangoni numbers and analysis of intensifying effect of surfactants under the operation conditions of heat pump absorber.

Acknowledgement

References

[1] V.E. Nakoryakov, N.I. Grigoryeva, N.S. Bufetov, R.A. Dekhtyar, I. V Marchuk, Vapor absorption by immobile solution layer, Int. J. Heat Mass Transfer 47 (6–7) (2004) 1525–1533.

[2] V.E. Nakoryakov, N.S. Bufetov, N.I. Grigoryeva, R.A. Dekhtyar, Heat and mass transfer at vapor absorption by an immobile layer of solution, J. Appl. Mech. Tech. Phys. 44 (2) (2003) 111–118.

[3] H. Daiguji, E. Hihara, T. Saito, Mechanism of absorption enhancement by surfactant, Int. J. Heat Mass Transfer 40 (8) (1997) 1743–1752.

[4] J. Castro, L. Leal, C.D. Perez-Segarra, P. Pozo, Numerical study of the enhancement produced in absorption processes using surfactants, Int. J. Heat Mass Transfer 47 (14–16) (2004) 3463–3476.

[5] A. McNeely Lowell, Thermodynamic properties of aqueous solutions of lithium bromide, ASHRAE Trans. 85 (1979) 413–434.

[6] N. Hozawa, M. Inoue, J. Sato, T. Imaishi, Marangoni convection during steam absorption into aqueous LiBr solution with surfactant, J. Chem. Eng. Jpn. 24 (2) (1991) 209–214.

[7] W. Ji, F. Setterwall, Effect of heat transfer additives on the instabilities of an adsorbing falling film, Chem. Eng. Sci. 50 (19) (1995) 3077–3097.

[8] W. Yao, H. Bjurström, F. Setterwall, Surface tension of lithium bromide solutions with heat – transfer additives, J. Chem. Eng. Data 36 (1) (1991) 96–98.

[9] N.I. Grigoryeva, About the methods for determination of Marangoni numbers at investigation of absorption under the conditions of heat pump operation, Theor. Foundat. Chem. Eng. 39 (6) (2005) 561–565.

[10] D. Glebov, F. Setterwall, M. Gustafsson, Estimate of mass transfer intensification at addition of surfactants on the basis of a new semi-empirical method, Theor. Foundat. Chem. Eng. 36 (5) (2002) 481–486.

[11] K.J. Kim, N.S. Berman, B.D. Wood, Absorption of water into LiBr solutions with 2-ethyl-1-hexanol, AIChE J. 42 (3) (1996) 884–888.

[12] I. Fujita, E. Hihara, Surface tension – driven instability of thin liquid film of Li Br aqueous solution absorbing water vapor, in: Proceedings of the International Sorption Heat Pump Conference, Munich, Germany, 1999, pp. 367–373.