

THE EFFECT OF SURFACTANTS ON ABSORPTION UNDER CONDITIONS OF HEAT PUMPS AND REFRIGERATORS

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Abstract

Experimental results on steam absorption by an immobile layer of water solution of lithium bromide with additions of surfactant (n-octanol) are presented. The profiles of adsorbate (water) temperature and concentration in the solution layer at different moments are presented for the first time. These results are compared with the similar ones, obtained without surfactant. Generation of convection in the near-surface layer is proved by video recording and thermal visual measurements of the moving interface temperature.

A possibility to use published information on interfacial tension for modeling of heat and mass transfer under conditions of heat pump absorber operation is analyzed. The method for calculation of interfacial tension gradients and Marangoni numbers is suggested.

KEYWORDS

Absorption; heat pump; heat and mass transfer; analytic solutions; diffusion, solution, surfactant.

INTRODUCTION

Vapor absorption by salt solutions, accompanied by release of heat, is widely applied in heat pumps and absorption refrigerating machines. More often, the process of absorption occurs on the films of solution, flowing over the surfaces of heat release. Therefore, most papers are dealt with the studies of film absorption.

Modern demands to development of high-efficient apparatuses stimulate the search for new methods of transfer intensification in absorbers. One of the methods for intensification of absorption is introduction of surfactants into solution, which provides generation of small-scale surface convection and, as a sequence, heat and mass transfer intensification. However, in experiments on surfactant effect on intensity of film absorption, it is difficult to separate contributions of the main flow and convection, caused by surface tension gradients, into heat and mass transfer. In this case, it is convenient to study vapor absorption by immobile layer of solution, when the forced flow is excluded. Theoretical and experimental data on local heat and mass transfer characteristics at absorption by immobile solution layer without surfactant was presented earlier [1, 2]. Then this data is used for comparison with results obtained in a presence of surfactant. In [3], this comparison is made only for one integral characteristic (the mass of absorbed substance changing in time).

EXPERIMENTAL RESULTS

Experiments on steam absorption by immobile layer of aqueous LiBr solution with additions of n-octanol (as a surfactant) were carried out to determine the surfactant effect on local characteristics of heat and mass transfer and to reveal the mechanism of this effect.

These studies were carried out using the setup and methods described in [2].

Results of eight experimental series performed under similar initial conditions and differing only by duration from 30 min. to 15 h. are presented. Experiments were carried out for two values of surfactant concentration (100 и 400 ppm).

Profiles of temperature and concentrations of the absorbed substance (water) within the solution layer were obtained for different moments of time together with a change in the mass of absorbed substance.

For lower concentration of n-octanol (100 ppm), the character of temperature and concentration profiles scarcely differs from similar profiles, obtained for solutions without surfactants. The typical temperature profiles at different moments of time are shown in Fig. 1. According to the figure, the

profile is very concave at absorption beginning, and with time it becomes more flat, and in 1000 seconds, it becomes linear (Fig. 1, a). Then, this profile stays linear during the whole experiment with a temperature, decreasing near the surface (Fig. 1, b). The temperature near the bottom is almost constant.

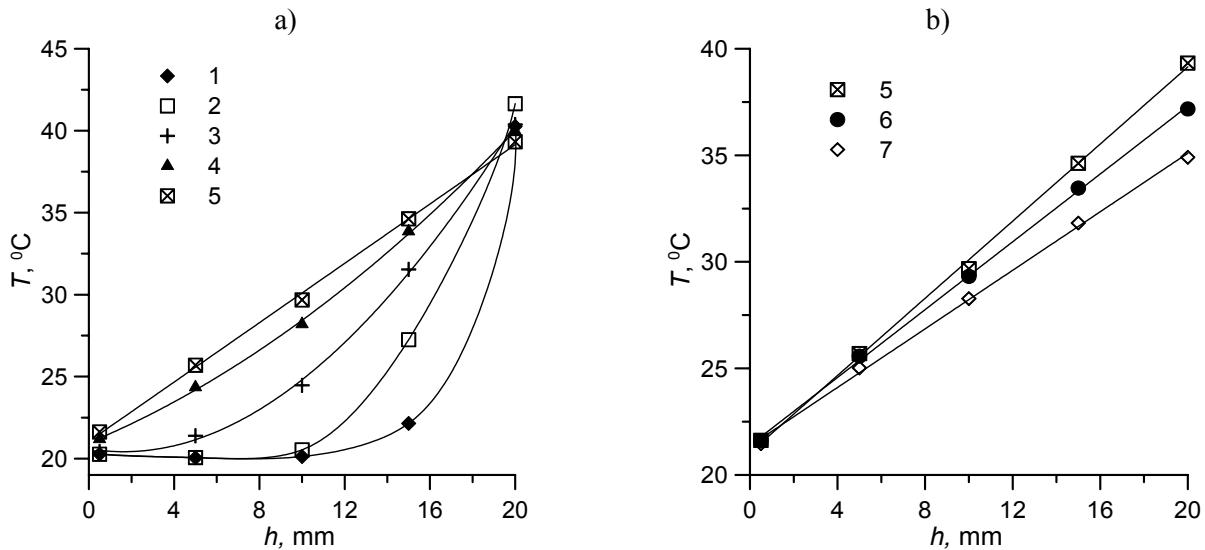


Fig. 1. Temperature profiles $t = 21.4$ (1), 60.4 (2), 204 (3), 515 (4), 1019 (5), 2020 (6), and 3715 sec (7): (a) profile evolving from a heavily concave to a linear form; (b) linear profile

Profiles of solution concentration are shown in Fig. 2. Concentration distribution in the layer of LiBr also changes from the more concave to the less concave profile. Concentration near the bottom during first 14000 seconds stays constant, and then it starts growing. This is connected with spreading of a diffusion layer towards the bottom.

The quantitative comparison with similar results obtained without surfactants demonstrates that a surfactant in solution provides a temperature increase at all levels of the layer (Fig. 3) and decreases water concentration near the layer surface (Fig. 2).

At n-octanol concentration of 400 ppm, which is higher than the solubility limit of a given surfactant in solution, the profile of water concentration changes significantly. Profiles of water concentration in solution are compared simultaneously in Fig. 4 for different concentrations of n-octanol. Such a change in the profile of adsorbate concentration leads to an increase in average concentration over the layer thickness and in adsorbate mass, despite a decrease in water concentration near the interface. A lower content of n-octanol in solution (100 ppm) does not change significantly the profile of adsorbate concentration; however, in this case we can observe some acceleration of absorption. A change in adsorbate mass with time is shown in Fig. 5 with and without surfactant.

Generation of convection was registered by video and photo in the near-surface layer for every surfactant concentration.

According to analysis of recent publications, most authors (for instance, [4-6]) refer improvement of mass transfer at absorption by solutions with surfactants to generation of convection, caused by the gradients of interfacial tension, near the interface. Different mechanisms of interfacial non-uniformity development on the surface are considered. In particular, there is a hypothesis about “islands” or “spots” of pure surfactant with a lower surface tension coefficient, appearing on the interface.

These “islands” were found out in experiments with n-octanol concentration of 400 ppm.

To explain intensification of absorption at concentrations below the solubility limit, we have suggested another hypothesis connected with possible stratification of liquid into fractions with different concentration of surfactant. This should also provide development of temperature non-uniformity and appearance of unstable interface. To check this hypothesis, additional investigations should be performed.

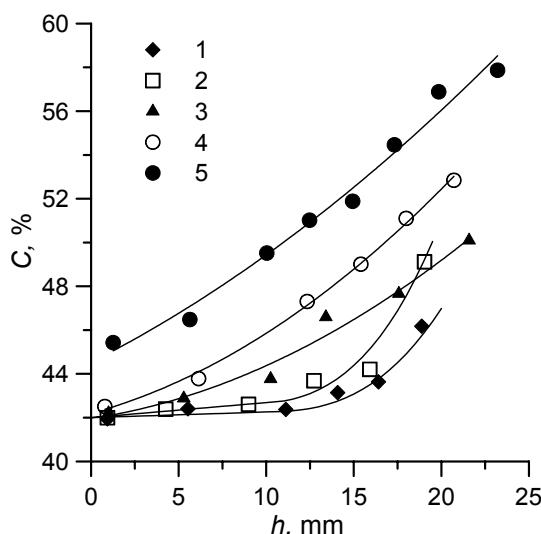


Fig. 2. Concentration profiles for $t = 1800$ (1), 3700 (2), 7200 (3), 14400 (4), and 54300 sec (5)

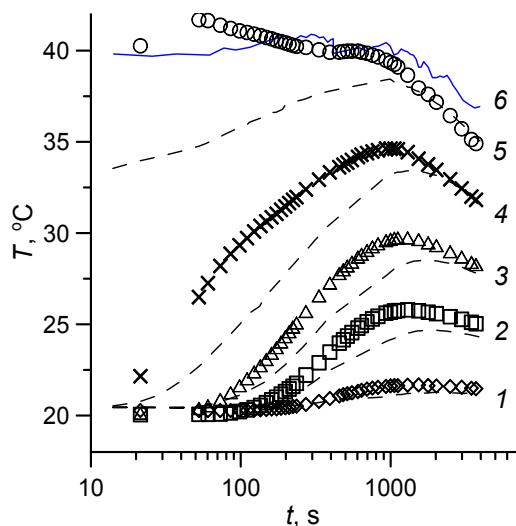


Fig. 3. Temperature versus time at distances from the bottom: $h = 0.5$ (1), 5 (2), 10 (3), 15 (4), and 20 mm (5); curve 6 refer to surface temperature for the surfactant-free solution; the points are the experimental data for the solution with the admixed surfactant; curves refer to data for the surfactant-free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

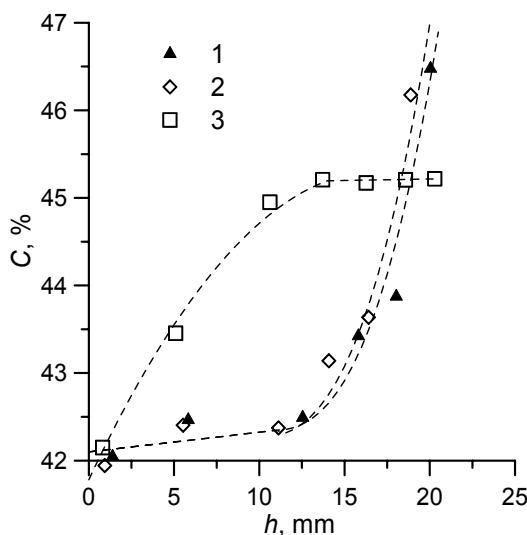


Fig. 4. Concentration profiles:
1 – data for the surfactant-free solution, 2 – $C_{sur} = 100$ ppm, 3 – $C_{sur} = 400$ ppm

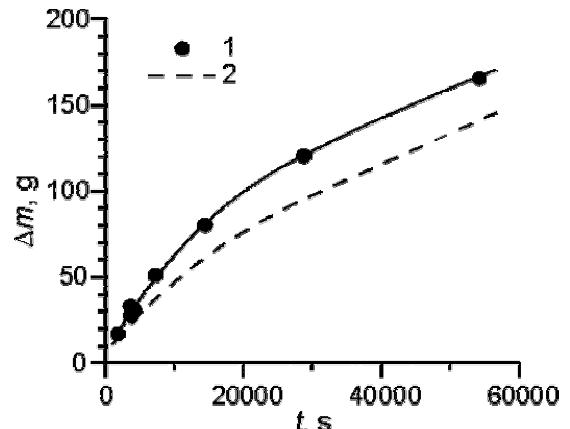


Fig. 5. Changes in absorbed-substance mass versus time:
1) data for the solution with the admixed surfactant; 2) data for the surfactant-free solution

METHOD OF MARANGONI NUMBERS DETERMINATION

Attempts to study instability and to model the transfer processes at absorption by solutions with surfactants were made in [3-5]. It was necessary to get information about dependencies of interface tension on determining parameters at absorption, particularly, in absorbers of heat pumps and refrigerators. In this case, we should consider the system liquid solution – vapor, where the interface is in equilibrium at a constant pressure of vapor, and this is one of the features of absorber operation in the heat pumps and refrigerating machines. Mostly, the system, where aqueous LiBr solution is the liquid phase and steam is the gaseous phase, is considered. As a rule, this system is used in experiments, including those on investigation of surfactant effect on absorption intensity. Various spirits are used as the additives. Unfortunately, there is no data on interface tension for such a system

under conditions of phase equilibrium and constant vapor pressure. Therefore, to study interface stability and heat and mass transfer at steam absorption by aqueous LiBr solution, available data on the surface tension (i.e., data, obtained for the system with the air gaseous phase, containing water vapor) is used. (According to [7], terms “interfacial” and “surface” tension are related only to the system with the air gaseous phase). The problem of application of data on the surface tension under the considered conditions requires preliminary analysis of data, obtained for the system with aqueous LiBr solution without surfactant.

This data [8-10] is usually shown in the form of tables or diagrams, describing dependency of surface tension on two independent variables: lithium bromide concentration in solution (or water) and temperature. The partial pressure of vapors in the gaseous phase is not shown. Since these results were obtained for the system in equilibrium, the partial pressure of vapor may be correlated with every pair values of temperature and concentration, using knowing dependencies $P = F(C, T)$, which describe the state of equilibrium.

The values of partial pressure together with data [10] on surface tension are shown in Table 1. Here, the partial pressure is calculated by equilibrium dependencies, presented in [12].

Table 1. The surface tension of lithium bromide solution and partial pressure of the vapor versus temperature and concentration of the solution

$C, \%$	Values σ , mH/m; P , kPa					
	$T = 20^\circ\text{C}$	$T = 30^\circ\text{C}$	$T = 40^\circ\text{C}$	$T = 50^\circ\text{C}$	$T = 60^\circ\text{C}$	$T = 70^\circ\text{C}$
40	$\sigma = 94.4$ $P = 0.18$	$\sigma = 93.7$ $P = 0.35$	$\sigma = 92.8$ $P = 0.67$	$\sigma = 91.5$ $P = 1.22$	$\sigma = 90.6$ $P = 2.21$	$\sigma = 89.9$ $P = 3.58$
50	$\sigma = 88.1$ $P = 0.59$	$\sigma = 86.6$ $P = 1.11$	$\sigma = 85.8$ $P = 2.00$	$\sigma = 84.8$ $P = 3.46$	$\sigma = 83.8$ $P = 5.76$	$\sigma = 82.7$ $P = 9.29$
60	$\sigma = 83.3$ $P = 1.13$	$\sigma = 82.2$ $P = 2.38$	$\sigma = 81.0$ $P = 4.23$	$\sigma = 79.9$ $P = 7.23$	$\sigma = 78.5$ $P = 11.9$	$\sigma = 77.3$ $P = 18.9$
70	$\sigma = 80.2$ $P = 1.54$	$\sigma = 78.8$ $P = 3.42$	$\sigma = 76.9$ $P = 6.92$	$\sigma = 75.5$ $P = 13.2$	$\sigma = 74.1$ $P = 23.7$	$\sigma = 72.4$ $P = 40.7$

Since at absorption during heat pump operation, the gaseous phase contains pure steam, the total pressure of vapor coincides with the partial pressure, and data presented can be used for determination of interfacial tension. However, there arises the question, how this data can be used for determination of interfacial tension gradients and Marangoni numbers, if the vapor pressure is kept constant, i.e., it is set.

In [3-5], for analytical studies, particularly, for determination of Marangoni numbers, two derivatives of surface tension are used: $\partial\sigma/\partial T$ for every concentration (for every line of the table) and $\partial\sigma/\partial C$ for every temperature (for every column of the table). Thus, these derivatives are determined by dependencies $\sigma = \sigma(T, C)$, corresponding to Table 1 or similar data with pressure (T, C), varying for every pair. Apparently, these derivatives can not characterize the state of interface at a constant vapor pressure.

In this case, the temperature and concentration should be dependent because equilibrium for every given pressure is determined by function $C = f_1(T)$ or $T = f_2(C)$. Then, interfacial tension will depend only on one variable T or C , and corresponding boundary condition at the interface and Marangoni number will include only one derivative $\partial\sigma/\partial T$ or $\partial\sigma/\partial C$. Hence, while studying absorption (in particular, for determination of Marangoni numbers) under conditions of heat pump or refrigerator operation, i.e., when there is the equilibrium at the interface and the vapor pressure is kept constant, we can not use function $\sigma = \sigma(T, C)$. Then, this dependency should be transformed into $\sigma = \sigma(P, C)$. For this purpose, approximation $\sigma = \sigma(T, C)$ can be applied simultaneously with function $T = T(C, P)$, describing phase equilibrium.

Results of such transformation with approximation of data on the surface tension, shown in [11] are presented in Table 2 and Fig. 6 for the temperature range of 10 - 80°C and water concentration of

35-60%. To describe thermodynamic equilibrium of the solution-vapor system, dependencies presented in [12] were used.

Table 2. The surface tension and equilibrium temperature of the solution into the system: aqueous lithium bromide solution – steam versus the solution concentration and steam pressure

C, %	Values σ , mH/m; T , °C						
	$P = 0.5$ kPa	$P = 1.0$ kPa	$P = 1.5$ kPa	$P = 2.0$ kPa	$P = 2.5$ kPa	$P = 3.0$ kPa	
40	$\sigma = 90.15$ $T = 35.29$	$\sigma = 88.98$ $T = 46.57$	$\sigma = 88.32$ $T = 53.61$	$\sigma = 87.86$ $T = 58.83$	$\sigma = 87.50$ $T = 63.00$	$\sigma = 87.21$ $T = 66.50$	
45	$\sigma = 88.08$ $T = 25.84$	$\sigma = 86.87$ $T = 36.85$	$\sigma = 86.17$ $T = 43.72$	$\sigma = 85.69$ $T = 48.81$	$\sigma = 85.32$ $T = 52.89$	$\sigma = 85.02$ $T = 56.31$	
50	$\sigma = 86.40$ $T = 17.43$	$\sigma = 85.12$ $T = 28.23$	$\sigma = 84.39$ $T = 34.98$	$\sigma = 83.88$ $T = 39.97$	$\sigma = 83.49$ $T = 43.97$	$\sigma = 83.17$ $T = 47.32$	
55	$\sigma = 84.84$ $T = 10.69$	$\sigma = 83.64$ $T = 21.21$	$\sigma = 82.88$ $T = 27.77$	$\sigma = 82.35$ $T = 32.63$	$\sigma = 81.94$ $T = 36.52$	$\sigma = 81.60$ $T = 39.78$	
60	$\sigma = 83.64$ $T = 6.26$	$\sigma = 82.31$ $T = 16.26$	$\sigma = 81.54$ $T = 22.51$	$\sigma = 81.00$ $T = 27.13$	$\sigma = 80.59$ $T = 30.83$	$\sigma = 80.25$ $T = 33.93$	

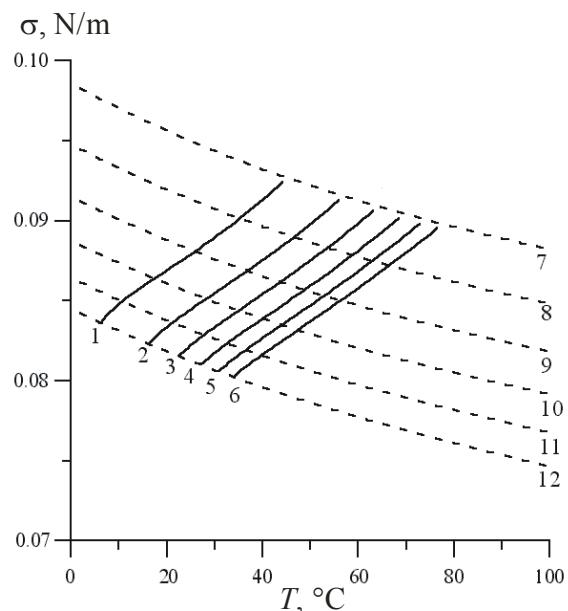


Fig. 6. Dependency of the surface tension of water solution of lithium bromide on temperature (°C) for different solution concentrations and steam pressures (1-6 – $P = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0$ kPa; 7-12 – $C = 0.35, 0.4, 0.45, 0.5, 0.55, 0.6$)

In case of solution with a surfactant, the situation becomes more complex because one more parameter is added (surfactant concentration). This parameter effects interface tension, and, generally speaking, phase equilibrium should change. However, the surfactant effect on equilibrium functions is not considered and discussed. Perhaps, in publications dealt with the properties of system: aqueous LiBr solution with surfactant – steam, there is no data on phase equilibrium of such a system.

If we assume that under the studied conditions, small additions of surfactant do not effect phase equilibrium, the interfacial tension at a constant vapor pressure should be determined by two parameters: the temperature (or concentration of one of the main solution components, connected with the temperature by the equilibrium condition) and surfactant concentration. In this case, Marangoni

numbers should be determined by two derivatives $\frac{\partial\sigma_p}{\partial T}$ and $\frac{\partial\sigma_p}{\partial C_{sur}}$. Subscript p here indicates that the

interfacial tension is considered at a constant pressure of vapor. The same derivatives should be included into the boundary conditions at modeling of transfer processes at absorption under the constant vapor pressure. However, like for solutions without surfactants, there is no data on dependencies between the interfacial tension and surfactant temperature and concentration at given vapor pressures.

Apparently, the available data on surface tension of aqueous LiBr solution with surfactant additions [4, 6, 10, 11] is insufficient for plotting accurate dependencies of σ on surfactant temperature and concentration at a given pressure of vapor (similar to Table 2), and for the following strict determination of interfacial tension gradients and Marangoni numbers. Thus, data on the surface tension of aqueous LiBr solution with two different additions is presented in [10] at a change in concentration of additions from 1 to 4000 ppm only for two values of temperature (25°C and 50°C) and one value of concentration (50%). Dependencies of surface tension on lithium bromide concentration at one temperature are presented in [4] for several concentrations of surfactant (octanol). Dependencies between surface tension and temperature at one value of lithium bromide concentration are also shown there. Dependencies of σ on concentration of two different surfactants are shown in [6] only for two values of temperature and two values of lithium bromide concentration. Similar dependencies are presented in [11] for one value of lithium bromide concentration and four values of solution temperature, etc.

The Marangoni numbers can be determined incorrectly, if there is no data on interfacial tension for the system: aqueous LiBr solution with surfactant additions – steam, at the given pressures of vapor.

Thus, in [6], [14] it is suggested to estimate the total Marangoni number for analysis of surfactant stability and intensifying effect

$$Ma = Ma_1 + Ma_2 + Ma_T,$$

$$\text{where in [6]} \quad Ma_1 = -\frac{\partial\sigma}{\partial\tilde{N}} \frac{\Delta\tilde{N} \cdot d}{\mu\nu}, \quad Ma_2 = \frac{\partial\sigma}{\partial\tilde{N}_{sur}} \frac{\Delta\tilde{N}_{sur} \cdot d}{\mu\nu}, \quad Ma_T = \frac{\partial\sigma}{\partial T} \frac{\Delta T \cdot d}{\mu\nu},$$

$$\text{and in [14]} \quad Ma_1 = \frac{\partial\sigma}{\partial\tilde{N}} \frac{\Delta\tilde{N} \cdot d}{\mu D}, \quad Ma_2 = -\frac{\partial\sigma}{\partial\tilde{N}_{sur}} \frac{\Delta\tilde{N}_{sur} \cdot d}{\mu D_{sur}}, \quad Ma_T = -\frac{\partial\sigma}{\partial T} \frac{\Delta T \cdot d}{\mu a}.$$

In [15], Ma_1, Ma_T is determined as in [6], and term Ma_2 is neglected at the estimate of the total Marangoni number.

Since dependencies of surface tension on C, T, C_{sur} with a pressure, alternating for every pair (C, T), are used there for derivative determination, these Marangoni numbers can not serve as the criteria, which determine the interface state at a constant vapor pressure.

To determine the gradients of surface tension at a constant vapor pressure, it would be convenient to use the approximation dependencies of interfacial tension on temperature, solution concentration on surfactant concentration $\sigma = \sigma(T, C, \tilde{N}_{sur})$ simultaneously with the function, describing phase equilibrium. If we assume that a surfactant does not effect the equilibrium function, i.e., $P = P(C, T)$; then at $P = const$; $C = C(T)$; and $\sigma = \sigma(T, \tilde{N}_{sur})$. In this case, Marangoni numbers

should include only two derivatives $\frac{\partial\sigma_p}{\partial T}; \quad \frac{\partial\sigma_p}{\partial\tilde{N}_{sur}};$

$$Ma_2 = \frac{\partial\sigma_\delta}{\partial\tilde{N}_{sur}} \frac{\Delta\tilde{N}_{sur} \cdot d}{\mu D_{sur}}, \quad Ma_T = -\frac{\partial\sigma_\delta}{\partial T} \frac{\Delta T \cdot d}{\mu a}.$$

Unfortunately, the experimental data, available now, is insufficient for accurate approximation dependencies of the surface tension of solutions with surfactants. There is the dependency in [6],

which approximates experimental data on the surface tension of aqueous LiBr solution for two different surfactants: 2-methyl-1-pentanol and octafluorine-1-pentanol.

This dependency takes the form

$$\ln \sigma = \ln(A_0 + A_1 T) + (A_2 + A_3 T) \ln C_{sur}.$$

Coefficients A_0, A_1, A_2, A_3 are the constants for the given surfactant and given concentration of LiBr, presented only for two values of LiBr concentration (60% and 50%). Coefficients presented in [6] for solution with octafluorine-1-pentanol does not correspond to experimental data, shown in the same paper. Therefore, it was attempted to calculate $\frac{\partial \sigma_p}{\partial T}$ only for 2-methyl-1-pentanol. To describe thermodynamic equilibrium of the solution – vapor system, we used the dependency from [12], which does not consider the presence of surfactant in solution.

Calculation results on temperature components of interfacial tension gradients are presented in Fig. 7 for the system: aqueous LiBr solution with 2-methyl-1-pentanol as a surfactant – steam. Tangents of straight line inclination (— and - · -) to axis T are the sought temperature components of the gradient at two values of vapor pressure and two values of surfactant concentration. Since coefficients A_0, A_1, A_2, A_3 are available only for two values of lithium bromide concentration (60% and 50%), the sought derivatives can be determined via a straight-line connection of two points, whose coordinates on the temperature axis correspond to the equilibrium temperature values at these two concentrations. Apparently, the accuracy of this calculation can not be high.

It seems that this example of calculation and other arguments presented are sufficient to prove the necessity of additional experimental studies on determination of interfacial tension under equilibrium conditions for the system: water solution of lithium bromide with a surfactant – water vapor at a fixed pressure of vapor. The surfactant effect on phase equilibrium should be also studied.

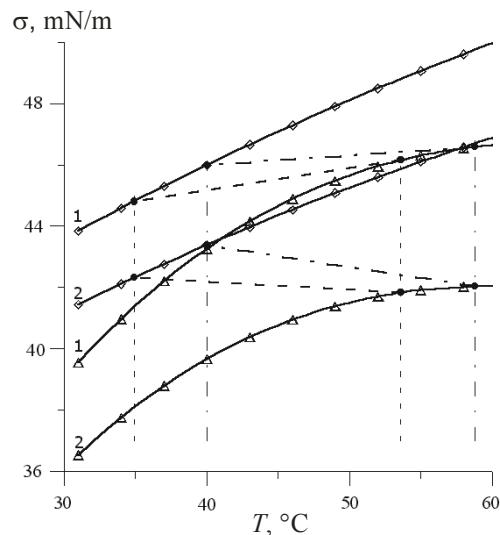


Fig. 7. Example determination of temperature gradients of surface tension for two concentrations of surfactant (1 – $C_{sur} = 1000$ ppm; 2 – $C_{sur} = 1500$ ppm) and two steam pressures (straight lines — correspond to $P = 1.5$ kPa; lines - · - $P = 2$ kPa); (\diamond – $C = 50\%$; Δ – $C = 60\%$)

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References

1. Nakoryakov V.E., Grigoryeva N.I., Bufetov N.S., Dekhtyar R.A., Marchuk I.V. Vapor absorption by immobile solution layer // *Int. J. Heat and Mass Transfer.* 2004. Vol. 47. Pp. 1525-1533.
2. Nakoryakov V.E., Bufetov N.S., Grigoryeva N.I., Dekhtyar R.A. Heat and mass transfer at vapor absorption by an immobile layer of solution // *J. of Applied Mechanics and Technical Physics.* 2003. Vol. 44. Pp. 111-118.
3. Hozawa N., Inoue M., Sato J., Imaishi T. Marangoni convection during steam absorption into aqueous LiBr solution with surfactant // *J. of Chemical Engineering of Japan.* 1991. Vol. 24. Pp. 209-214.
4. Ji W., Setterwall F. Effect of heat transfer additives on the instabilities of an adsorbing falling film // *Chemical Engineering Science.* 1995. Vol. 50. Pp. 3077-3097.
5. Daiguji H., Hihara E., Saito T. Mechanism of absorption enhancement by surfactant // *Int. J. Heat Mass Transfer.* 1997. Vol. 40. Pp. 1743-1752.
6. Glebov D., Setterwall F., Gustafson M. The estimate of mass transfer intensification at introduction of surfactants on the basis of a new semi-empirical method // *Theoretical Foundations of Chemical Engineering.* 2002. Vol. 36. Pp. 481-486.
7. *Hand-Book on Heat Exchangers* / English transl. edited by O.G. Martynenko et al., Moscow, Energoatomizdat, 1987.
8. Gruzdev V.A., Kiselev E.Ya. Experimental investigation of the surface tension of electrolyte water solutions // *Investigation of thermal-physical properties of solutions and melts.* Coll. of scientific papers. Novosibirsk. 1974. Pp. 37-52.
9. Lower H. *Thermodynamische und physikalische eigenschaften der wassrigen lithium bromide-lösung*, PhD. thesis, Karlsruhe, 1960.
10. Yao W., Bjurström H., Setterwall F. Surface Tension of Lithium Bromide Solutions with Heat-Transfer Additives // *J. of Chemical and Engineering Data.* 1991. Vol. 36. Pp. 96-98.
11. Zyukanov V.M., Baranenko A.V., Orekhov I.I. Surface tension of aqueous LiBr solution with surfactants / *Refrigerating Machines and Thermotransformers.* Leningrad. 1984. Pp. 3-7.
12. Lowell A. McNeely Thermodynamic properties of aqueous solutions of lithium bromide // *ASHRAE Trans.* 1979. Vol. 85. Pp. 413-434.
13. Dolotov A.G., Pyatko V.Yu. The calculation methods for thermodynamic and thermophysical properties of aqueous LiBr solution at electronic digital computer // *Refrigerating Machines and Thermotransformers.* Leningrad. 1985. Pp. 60-66.
14. Kim K.J., Berman N.S., Wood B.D. Absorption of Water into LiBr Solutions with 2-Ethil-1-Hexanol // *AICHE Journal.* 1996. Vol. 42. Pp. 884-888.
15. Fujita I., Hihara E. Surface tension- driven instability of thin liquid film of Li Br aqueous solution absorbing water vapor // *Proceedings of the Int. Sorption Heat Pump Conf., Munich, Germany.* 1999. Pp. 367-373.