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A desorption calorimetric method for use at high water activities

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Abstract

This paper presents a microcalorimetric technique to simultaneously measure water activity and enthalpy of mixing (differential heat of sorption) as functions of composition at high water activities. The instrument consists of a sorption vessel in a double twin microcalorimeter. A sample at high water activity is placed in one chamber of the vessel and an unsaturated salt solution is injected into another chamber. A tube connects the chambers and diffusion will cause the water in the sample to be desorbed and condensed in the salt solution. As the rate of diffusion is high when the sample is at high water activity it is possible to make detailed studies of phenomena taking place at high water activity. The method has been tested on the system dimethyldodecylamine oxide (DDAO)–water.

Keywords: Sorption calorimetry; Desorption; Water activity; Enthalpy of mixing; Differential heat of sorption; Surfactants

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1. Introduction

Investigations of interactions of different materials and substances with water are of great importance for thermodynamics, material science, biology and pharmaceutics. One of the techniques that can be used for such studies is the sorption calorimetry developed by Wadsö and co-workers [1,2]. This method, which works in absorption mode, can be used not only for investigating sorption itself, but also for studies of properties of mixing of various substances with water, where sorption is used as a method for scanning water content. Several systems have been studied with this absorption method: surfactants [3], lipids [4], cellulose [5] and other materials [5,6]. It is a powerful method as one can measure water activity and enthalpy of mixing as functions of composition in one experiment, which provides a rather complete thermodynamic description of interactions in aqueous systems. However, a substantial limitation of the method has previously been the difficulty in obtaining reliable results at higher water contents, where the activity of water is above 0.95. One should mention that systems with high water contents are of great importance in such applied areas as biophysics, biochemistry and pharmaceutics. Many interactions and transitions in biologically important systems occur at water activities close to 1.00. Such transitions are normally difficult to study as it is difficult to accurately generate relative humidities close to saturation, e.g., with saturated salt solutions and automated sorption balances. In this paper we describe a desorption method (based on the original absorption method [1,2]) for studies of systems with very high water activities.

2. Description of the method

2.1. The original absorption method

The original method of sorption calorimetry developed by Wadsö and co-workers has been used in several different versions with different cell geometries and different evaluation procedures (see for example [1,2,7]). Here we will briefly describe the instrument and the procedure, as they were used for the absorption measurements presented in this paper.

The instrument consists of a sorption cell and a specially designed double twin microcalorimeter. The sorption cell consists of two chambers—the vaporization chamber and the sorption chamber—connected by a tube (Fig. 1a). The diameter and length of the diffusion tube are 5.5 and 53 mm, respectively. Before an experiment a dry sample is placed

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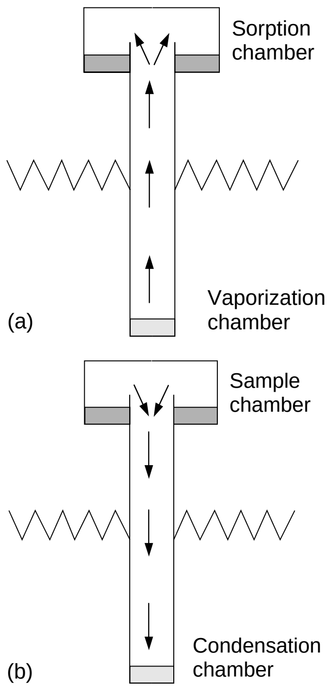

Fig. 1. Schematic descriptions of absorption (a) and desorption (b) experiments.

in the sorption chamber. Then the cell is placed in the double twin microcalorimeter [1,7] that has two channels that can separately measure heat released or absorbed in the two chambers of the cell. When the calorimetric signals from both channels have come to the baselines after a few hours, water is injected into the vaporization chamber, where it evaporates, diffuses through the tube and is absorbed by the studied sample in the sorption chamber. During the first minutes after an injection the measured thermal power is disturbed by the injection, heat of wetting and the initial vaporization. To correct for this the results of the first 5 min of the vaporization measurement are substituted with simulated (ideal) data [2]. From the measured thermal powers from the two chambers, one can calculate the mass of evaporated water (and therefore the water content of the sample), the activity of water and also the partial molar enthalpy of mixing of water [2,3]. The rate of the whole process in the calorimetric cell is normally determined by the difference of water activities (relative humidities) between the two chambers: the higher the activity difference, the higher the vapor flow in the tube. When an experiment starts the difference in activities of water between the two chambers is high; in the vaporization chamber the water activity is 1.00, and in the sorption chamber it is low, often close to 0. During the experiment the activity of water in the vaporization chamber does not change, while in the sorption chamber it increases. At the end of the experiment, at high water content in the sample, the water activity can reach high values (above 0.95) and then the rate of mass transfer between the chambers is low. Therefore, the thermal powers measured by the calorimeter are low and the uncertainties in the measured parameters (especially enthalpy of mixing) are high. Another problem is that if the rate of mass transfer is low, the experiment can take too much time—many days or even weeks—before the required water content is reached.

2.2. *The new desorption method*

The new desorption method presented here uses the same equipment as the original absorption method described above; it is only a modification of the procedure that improves the ability to study processes at high water activities. Instead of running a measurement in absorption towards an activity of 1.00, we start with a humid sample and run it in desorption towards a lower activity. We will then get high rates of mass transfer when the sample is close to activity 1.00 and this gives higher signals and thus a better measurement.

To run a desorption measurement one needs an aqueous system with low water activity instead of water. This system will then not be a source of water but instead a water vapor sink and water will not be absorbed on the studied sample, but instead desorbed from it (Fig. 1b). The chamber with the aqueous system will no longer be a vaporization chamber, but instead a condensation chamber. The other chamber will be called sample chamber.

The ideal system used as a water sink in the condensation chamber should have the following properties:

- Low and constant water activity (water activity should not be dependent on amount of absorbed water);
- Constant heat of sorption of water;
- It should not react with the material of the calorimetric cell;
- It should not contain volatile components other then water.

Drying agents considered for this purpose meet only some of these criteria. For example, molecular sieves have very low and rather stable water activity, but we have observed that the heat of sorption of water on molecular sieves changes significantly during an experiment. In order to meet the criteria of constant activity and enthalpy one could use heterogeneous aqueous systems, in which the thermodynamic parameters of coexisting phases do not change during addition of water, the only change, taking place is the change of masses of the phases. A good example of such a system is a saturated salt solution in equilibrium with the salt. However, because of the small diameter of the injection needle it is impossible to inject a mixture of salt and its saturated solution into condensation chamber. Another possibility would be to load the saturated salt solution into the condensation chamber before the experiment, close the tube connecting the two chambers by a valve and, after achieving thermal equilibrium, to open the valve. However, in practice it is difficult to make a vapor tight valve that does not mechanically and thermally disturb the sensitive microcalorimeter when it is opened. Even very small amounts of vapor leaking through a valve can cause substantial baseline shift.

We have found that an unsaturated salt solution as a vapor sink is the best alternative. One advantage of this choice is that it is easy to start an experiment—the procedure is similar to that used in the original absorption calorimetric method. While in the absorption experiments water is injected into vaporization chamber, in the desorption experiments unsaturated salt solution is injected into the condensation chamber. Note that it is physically the same chamber having different functions in absorption and desorption experiments.

A disadvantage with the use of an unsaturated salt solution is that its water activity and enthalpy of mixing can change during an experiment. Below we will show how the effects of such changes can be taken into account.

The particular salt chosen for the present experiments was magnesium nitrate. The activities of water in its solutions are relatively low—about 0.53 near the saturation point at 25 °C [8,9]. Some solutions of halide salts—like $MgCl_2$ and LiCl—have even lower water activity, but they are corrosive to the material of the calorimetric cell (stainless steel).

The process of condensation of water vapor into an unsaturated magnesium nitrate solution can be considered as consisting of two steps: condensation of water vapor into pure liquid water and mixing of pure liquid water with salt solution (dilution). Therefore, the enthalpy of condensation into a salt solution consists of two terms: enthalpy of condensation of pure water and enthalpy of mixing:

$$H^{\mathrm{cond,salt}} = H^{\mathrm{cond,water}} + H^{\mathrm{mix}} \tag{1}$$

For salt solutions the absolute value of enthalpy of condensation of pure water is much higher than the enthalpy of mixing (see Section 3). We will use the following notations: P^{samp}: thermal power released in the sample chamber, P^{cond}: thermal power released in the condensation chamber, $H_{\mathrm{w}}^{\mathrm{cond}}$: enthalpy of condensation of water vapor into unsaturated salt solution calculated per mole of vapor. The amount of water n_{w} condensed per unit of time in the condensation chamber (the flow rate) can be calculated from the measured thermal power of condensation:

$$\frac{\mathrm{d}n_{\mathrm{w}}}{\mathrm{d}t} = \frac{P^{\mathrm{cond}}}{H_{\mathrm{w}}^{\mathrm{cond}}} \tag{2}$$

Integrating Eq. (2) we get the amount of water condensed in the condensation chamber as a function of time:

$$n_{\mathrm{w}} = \frac{\int P^{\mathrm{cond}}\,\mathrm{d}t}{H_{\mathrm{w}}^{\mathrm{cond}}} \tag{3}$$

The diffusional flow rate is proportional to the difference in activity between the chambers (Fick's first law). It is also proportional to the thermal power of condensation (Eq. (2)). We can therefore write the following relation for the activity of water in the sample chamber:

$$a_{\mathrm{w}}^{\mathrm{samp}} = a_{\mathrm{w}}^{\mathrm{cond}} + \frac{P^{\mathrm{cond}}}{P^{\mathrm{cond,max}}}(1 - a_{\mathrm{w}}^{\mathrm{cond}}) \tag{4}$$

Here $a_{\mathrm{w}}^{\mathrm{samp}}$ and $a_{\mathrm{w}}^{\mathrm{cond}}$ are the activities of water in the sample and condensation chambers, respectively, $P^{\mathrm{cond,\,max}}$ is the highest possible thermal power of condensation (for a particular salt solution and geometry of the calorimetric cell), corresponding to the situation when there is pure liquid water in the sample chamber.

Some of the water desorbed from the sample is not condensed in the condensation chamber but remains in the vapor phase in the cell. This needs to be taken into account in the calculation of the water content in the sample. For the calculation we use the water activity in the sample chamber calculated using Eq. (4), the perfect gas law, and assume that the effective activity of water in the diffusion tube is the mean value of water activities in the two chambers (this is a good approximation as the activity changes linearly for steady-state diffusion in a tube):

$$n_{\mathrm{w}}^{\mathrm{vap}} = \frac{p_{\mathrm{w}}^{0}}{RT}\left(a_{\mathrm{w}}^{\mathrm{samp}}V^{\mathrm{samp}} + \frac{a_{\mathrm{w}}^{\mathrm{samp}} + a_{\mathrm{w}}^{\mathrm{cond}}}{2}V^{\mathrm{tube}}\right) \tag{5}$$

where V^{samp} and V^{tube} are the volumes of sample chamber and the tube, respectively. Subtracting the amount of water calculated using Eq. (5) from the one calculated using Eq. (3) gives the water content in the sample. This correction is in the order of 1% of the calculated moisture content.

In order to derive an expression for the enthalpy of sorption of water into the sample, we combine Eq. (2) and an analogous equation for the sorption chamber. As a result one gets the partial molar enthalpy of sorption of water:

$$H_{\mathrm{w}}^{\mathrm{sorp}} = \frac{H_{\mathrm{w}}^{\mathrm{cond}}P^{\mathrm{samp}}}{P^{\mathrm{cond}}} \tag{6}$$

Here the enthalpy of sorption corresponds to the heat of transfer of water from vapor phase to a solid or liquid sample. As well as in the case of enthalpy of condensation of water into a salt solution, the enthalpy of sorption consists of two contributions: enthalpy of condensation of pure water and enthalpy of mixing of water with the substance of the sample. The enthalpy of condensation of pure water is highly exothermic and is not a function of properties of studied system. The enthalpy of mixing is usually much lower in absolute value. Therefore, the value of enthalpy of sorption is normally highly exothermic and is not sensitive to the molecular interactions in the sample. The enthalpy of mixing reflects the properties of hydration of a studied substance in a better way. Therefore, we have here used the partial molar enthalpy of mixing of water for characterizing the thermal properties of aqueous systems:

$$H_{\mathrm{w}}^{\mathrm{mix}} = H_{\mathrm{w}}^{\mathrm{vap}} - H_{\mathrm{w}}^{\mathrm{cond}}\frac{P^{\mathrm{samp}}}{P^{\mathrm{cond}}} \tag{7}$$

Here $H_{\mathrm{w}}^{\mathrm{vap}}$ is the enthalpy of vaporization of pure water. Many authors, e.g. [10], instead of "partial molar enthalpy of mixing of water" use the expression "differential heat/enthalpy of sorption". Here we use the former term as it reflects the physical nature of the process, but not the technical details of the experiment, as the latter one does.

To demonstrate the ability of the method we have carried out experiments on dehydration of dimethyldodecylamine oxide (DDAO) at 25 °C. This particular surfactant was chosen because its phase behavior at high water content is known [11–13] and because in the binary system DDAO–water several phase transitions occur at medium water content and medium water activity, which allowed us to apply both absorption and desorption calorimetry and compare the results obtained using these two methods.

3. Experimental results

3.1. Calibration of the salt solution

As a system for the vapor sink for the condensation chamber we have chosen unsaturated solution of $Mg(NO_3)_2$. The solution used in our experiments had slightly higher water content than the saturated one. The exact composition of the solution does not need to be known as its properties (water activity and maximal thermal power of condensation) can be determined in a separate calibration experiment in which the solution is placed in the top (sample) chamber and water is injected into the bottom chamber (Fig. 1a). Since the absorption technique is applied in the calibration, the equations from [2,3] were used for evaluation of its results. For the solution used in the measurement described below the activity of water was $a_w = 0.534$ and the thermal power of condensation of water into the solution was $P^{cond} = -255\,\mu W$ (corresponding to the highest possible thermal power of condensation $P^{cond,\,max}$ in the desorption experiment).

Both the activity of water and the thermal power of condensation were not perfectly constant, but had significant slopes during the calibration experiment. To use correct values of those parameters in Eq. (4), one needs to take changes of a_w and $P^{cond,\,max}$ into account. Based on the results of the calibration experiment we assumed that the dependencies of these parameters are linear with respect to the mass of condensed water m_w (in g) during desorption experiments:

$$a_w = 0.534 + 3.45\,m_w \tag{8}$$

$$P_s = -2.55 \times 10^{-4} + 1.91 \times 10^{-3}\,m_w \tag{9}$$

Eqs. (8) and (9) are valid for the 200 μl volume of magnesium nitrate solution used in our desorption experiments.

The partial molar enthalpy of mixing of water H_w^{mix} is small for unsaturated magnesium nitrate solutions. Its value obtained in the sorption experiment was close to the uncertainty of the experiment. Therefore, we also used isothermal titration calorimetry to obtain a value of this parameter. With titration calorimetry one can obtain more accurate results than with the sorption calorimetric method. On the other hand, the sorption method is a more general technique as it can be used to study both liquids and solids and because it provides information about both activity and enthalpy. The partial molar enthalpy of mixing of water obtained from the titration measurement was $H_w^{mix} = -0.62\,kJ/mol$. This is much smaller than the enthalpy of vaporization of pure water $H_w^{vap} = 44.01\,kJ/mol$. Therefore, we do not take into account *the change* of enthalpy of mixing during an experiment. Enthalpy of condensation of water vapor into the salt solution is then $H_w^{cond} = -44.63\,kJ/mol$.

3.2. Desorption experiments

The calibrated solution of magnesium nitrate was used as a vapor sink in the desorption experiments. As a system for the desorption studies we used a DDAO solution. Of the three similar measurements made we here describe the results from one. The composition of the solution was 98.09 mol% (80.15 wt.%). The initial mass of the sample was 21.60 mg. At the beginning of the experiment the DDAO solution was equilibrated in the sample chamber until the calorimetric signals reached stable values (baselines). Then the injection of the magnesium nitrate solution into the condensation chamber was made. After about 2 days of measurement the signals came to new, slightly different, baselines. In the beginning of the experiment the activity of was very high—close to 1.00—and at the end of the experiment it was 0.59 (a part of the dependence composition–water activity is presented in Fig. 2). The partial molar enthalpy of mixing of water was slightly positive in the whole studied concentration range excluding the exothermal peak corresponding to the phase transition from hexagonal to cubic phase (Fig. 3a).

To compare the desorption results with data obtained using another technique we also made two experiments on DDAO using the original absorption method. Since the transition between cubic and hexagonal phases was observed in both absorption and desorption experiments, we have used it to compare the two techniques. In Table 1 the mean values

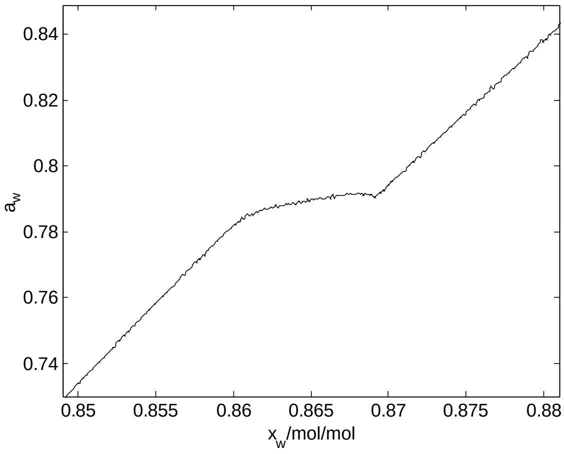

Fig. 2. Water activity in the binary system (DDAO–water) near the phase transition between cubic and hexagonal phases in the desorption experiment.

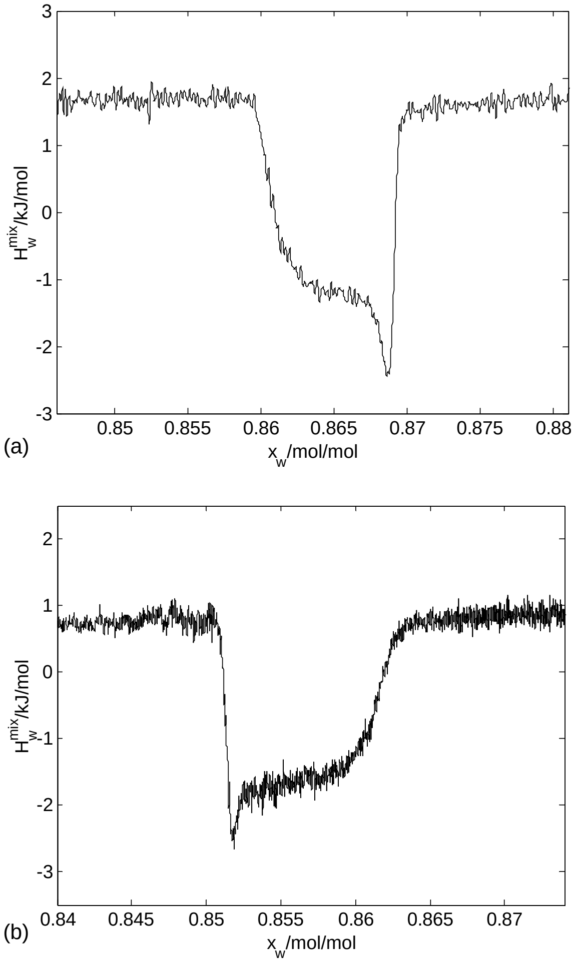

Fig. 3. Partial molar enthalpy of mixing of water in the binary system (DDAO–water) near the phase transition between cubic and hexagonal phases. (a) Desorption experiment and (b) absorption experiment.

of the parameters of the phase transition obtained using two methods are given. Mean values of compositions at which the transitions were observed differ by 1.6 mol%. Activities of water at the transition obtained using two methods were very similar. The values of the enthalpy of the transition obtained in the absorption and desorption experiments were also similar. The enthalpy of the transition was calculated as the area of the peak on the curve molar ratio (r) vs. partial molar enthalpy of mixing of water ($H_{\mathrm{w}}^{\mathrm{mix}}$). The level of $H_{\mathrm{w}}^{\mathrm{mix}}$ in the cubic phase was used as a baseline for the calculation:

$$\Delta H^{\text{cub–hex}} = \int_{\text{cub}}^{\text{hex}} H_{\mathrm{w}}^{\mathrm{mix}} - H_{\mathrm{w}}^{\mathrm{mix}}\,(\text{cub})\,\mathrm{d}r \tag{10}$$

$$r = \frac{n_{\mathrm{w}}}{n_{\mathrm{DDAO}}} \tag{11}$$

Table 1
Parameters (and their 80% confidence intervals) of the transition between cubic and hexagonal phases in DDAO–water system measured by absorption and desorption calorimetric methods

Parameter	Absorption	Desorption
x_{w} (mol%)	85.4 ± 0.9	87.0 ± 1.1
Δx_{w} (mol%)	0.83 ± 0.05	0.66 ± 0.10
a_{w}	0.790 ± 0.006	0.793 ± 0.003
$\Delta H^{\text{hex–cub}}$ (kJ/mol)	−1.3 ± 0.2	−1.41 ± 0.05

4. Discussion

The results given above show that the desorption calorimetric method works and can be used for studies of systems with high water activity, for example, surfactant systems with relatively high water content. Since both the absorption and the desorption methods are scanning methods (water content changes during the whole experiment) one should consider that a result may have been obtained at non-equilibrium conditions. In equilibrium the rate of the sorption process is determined only by diffusion of water vapor in the tube. In the non-equilibrium case the sorption/desorption of water to/from the sample makes the process slower. Then in an absorption experiment the observed activity will be higher than the true one, and in a desorption experiment it will be lower. Therefore, the consistency of the water activities obtained by the two methods is a good criterion of whether one has obtained equilibrium data. Since the activities of water of the considered phase transition obtained by the two methods are identical within the uncertainty of the experiment, then the experimental results are close to the equilibrium.

If the obtained data reflect the equilibrium situation, then the errors of the experiment have not physical but technical origins—uncertainties of calibration, of preparation of the sample etc. Here we will discuss some of them. The equations used for the calculation of thermodynamic parameters (Eqs. (2)–(7)) include several parameters that are determined by calibrations. The parameters are calibration coefficients of the two channels of the double twin calorimeter (needed to calculate the thermal powers), maximal thermal power of condensation $P^{\text{cond, max}}$, activity of water in the salt solution, and enthalpy of condensation of water in the salt solution. The last parameter consists of two terms (Eq. (1)) and if the enthalpy of mixing of water is determined using titration calorimetry, then the uncertainty of the $H_{\mathrm{w}}^{\mathrm{cond}}$ is small. If the enthalpy of mixing is measured by sorption calorimetry, then the uncertainty is higher, but still relatively low because the main contribution to the enthalpy of condensation into the salt solution comes from the enthalpy of condensation of pure water, which has a well-known value. Error in the determination of activity of water in the salt solution affects only the value of activity of water in sample (Eq. (4)), but does not affect the composition and enthalpy. Formally, $a_{\mathrm{w}}^{\mathrm{cond}}$ is included in Eq. (5), but the effect of its uncertainty is insignificant. The calibration coefficients of the calorimeter affect all the measured values, especially the partial molar enthalpy of mixing of water. The form of Eq. (7) requires that the ratio of two calibration coefficients of two channels should be precisely measured. The difference of the enthalpy levels in Fig. 3a and b probably arises from uncertainties of this ratio (note, however, that the enthalpy of the transition as determined by Eq. (10) is much less uncertain). It may be possible to decrease this uncertainty by the use of physico-chemical instead of electrical calibration.

Error in determination of mass and initial composition of the sample affects the results of measurements of compositions of phase transitions. In the present case with the cubic–hexagonal phase transition in the DDAO–water system the difference of the results obtained by the two different methods was about 1 mol% (or a couple of wt.%). In the experiment presented in Figs. 2 and 3b the initial mass of the sample was 21.60 mg, including 4.29 mg of DDAO. Since the masses are very small, their uncertainties can affect the composition results. The error is higher when the measured composition is far from the starting point—during the experiment the error of determination of mass of water is accumulating. Therefore, if accurate results about a particular phase transition are required, the sample should have an initial composition with a relatively small excess of water (but large enough to avoid influence of initial disturbances of experiment).

As was mentioned above, the baselines before and after the experiment had slightly different values. In the calculations we used the baselines registered after the experiment because their values were closer to the values of the baselines of the empty calorimetric cell. The reason for the difference in the baseline levels was in the very high water activity of the sample before the experiment. Since the water activity in the sample was close to that of pure water, some desorption occurred (though very slowly) even before the injection of the salt solution, as water vapor was adsorbed on the walls of the tube and the condensation chamber. As a result, the baselines were shifted—in the sample chamber a small endothermic and in the condensation chamber a small exothermic heat effect was observed. Because of this the formally measured value of the water activity was slightly higher than 1.00 at the start of the experiment. We therefore recommend that the baselines should be taken after a desorption experiment, or when this is impossible, the baselines of the empty cell should be used.

In the described experiment a larger amount of the solution of DDAO was prepared and then a part of it was used in the desorption experiment. This method of preparation can be used only for one-phase systems. If the initial sample is a two-phase system then one cannot know the exact composition of the aliquot because the amounts of the two phases in it can vary. In this case the solid (or liquid) substance should be mixed with water directly in the sample chamber. As a side effect of this procedure, one should equilibrate the mixture for longer time before the injection is made, because the system should come not only to thermal equilibrium, but also to diffusion equilibrium.

The method may have some limitations associated with its dynamic properties, for example, investigations of phase transitions in systems that require a long equilibration time (such as polymers) can be a problem.

In this paper we describe a desorption calorimetric method and the results of its first application for the study of a phase transition in an aqueous surfactant system. We believe that this method will be a useful tool for investigations of thermodynamic properties of surfactants, lipids, biological compounds and other substances at moderate and high water contents.

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