Surface properties of binary and ternary solutions studied through precision measurements

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Abstract. The paper deals with the surface properties of aqueous two- and three-component organic solutions (water-acetone; water-1,4-Dioxane; water-acetone-1,4-Dioxane). A modern installation, K-100 tensiometer, was used to measure equilibrium surface or interfacial tension, contact angle, etc. The du Noüy ring and the Wilhelmy plate methods were used to measure the surface tension. It shows that the surface tension isotherms for a ternary system do not contain any features uncharacteristic of the surface tension isotherms for lateral binaries. The findings made it easy to specify the adsorption of surface-active agents in water. It shows that the nature of the ternary adsorption isotherms qualitatively coincides with the binary adsorption isotherms, which leads to the conclusion that, once used together as surfactants, organic substances (acetone and 1,4-Dioxane) in water does not enhance the surface activity of each other.

1. Introduction

Experimental and theoretical studies into the surface properties of binary and multicomponent organic solutions today remain an urgent scientific issue [1–4]. Interest towards these systems is caused by their wide use in many technological processes, and by the area of scientific problems being surface thermodynamics, colloidal chemistry, etc. Current modern technologies and complementary new approaches require the expansion of existing knowledge in the field of interfaces. In order to achieve these goals, reliable experimental data on the surface tension of these systems are required. This has contributed to a constantly growing interest towards theoretical and experimental studies into the effect of various surfactants on the surface properties [5, 6].

Thus, the paper aims to study the surface properties of aqueous organic solutions through precision methods.

To achieve this goal, the following tasks were set and solved:
1. To consider experimental methods based on the K-100 installation.
2. To explore the technique for measuring surface tension on the tensiometer K-100.
3. To experimentally determine the surface tension in ternary systems (water-acetone- acetone) and lateral binaries.
4. To calculate adsorption based the resulting experimental data.

An automatic K-100 tensiometer was used designed for versatile use in various fields of science and industry [7]. The software includes the latest research methods for surface tension, interfacial tension and contact angle.

Specifications and field of application of the K-100 tensiometer include measurement range of surface and interfacial tension – –1...1000 mN/m, resolution – 0.01 N/m, temperature range – –10...130 °C.

The measurement procedure on this tensiometer is fully automated and has a modular design. Measurement methods are divided into several groups, each of which has its own software (the device cannot work without a computer) and needs its own set of accessories available.

The functionality of the K-100 tensiometer enables precision measurements of surface tension and interfacial tension, critical micelle concentration (CMC), wetting angle of solids, fibers and powders. In addition, the installation determines the density of liquids and solids, as well as the sedimentation rate of dispersions.

2. Materials and methods

Contaminated samples can produce a very large measurement error once surface tension is measured with this tensiometer. Therefore, a sample must be carefully prepared and the air in the room must be free of dust. Sometimes it becomes necessary to filter the sample through a microfilter before taking a measurement.

Ring measurements can be performed on liquids for which the density is known. For most of the known liquids, there is a density-dependent temperature correction [8]. If the density of the system is not known, then it can be determined directly using the K100 tensiometer and a related module before taking the main measurements.

2.1 Automated surface tension measurements by the du Noüy ring method

Surface tension measurements by the du Noüy ring method follow a standard procedure that is replicated in the standard ADVANCE application. The automation details can be adapted to some specific conditions, but the general procedure cannot be altered.

**General Procedure for du Noüy ring Measurement:**
1. The force is zeroed, the container is filled with the liquid, a wire ring is above the surface.
2. The ring hits the surface and is pushed through the surface.
3. The ring breaks the surface and is lifted through the surface.
4. The force is actually measured. The stage is gradually lowered to pull up a meniscus of the ring. The approximate maximum force is reached. The meniscus stretches a little further, and then the stage is lifted to determine the exact maximum force and the corresponding height of the lamella on the way back.
5. It is necessary to move the stage downward to remove a measuring element and the container.

2.2 Automated surface tension measurements by the Wilhelmy plate method

Surface tension measurements using the Wilhelmy plate method follow a standard procedure that is recreated in the ADVANCE application. The automation details can be adapted to specific conditions, but the general procedure cannot be altered.

Typically, an automation program provides several surface tension values until the system reaches equilibrium. Generally, a default standard deviation is used as a stabilization criterion to automatically continue the measurement until equilibrium is reached.

**General Procedure for Wilhelmy plate Measurement:**
1. The force is zeroed, the container is filled with the liquid, the plate/rod is attached to a balance.
2. The plate/rod becomes immersed in water for wetting and then leaves the water.
3. The force is actually measured. The force is measured over time as long as the plate/rod touches the surface, and the surface tension is calculated based on the force required to raise the plate
4. It is necessary to move the stage downward to remove a measuring element and the container.

3. Calculation
To study the surface properties of aqueous organic solutions, the authors sought to explore the ternary water-acetone-1,4-Dioxane system and water-acetone and water-1,4-Dioxane lateral binaries. The Wilhelmy plate and du Noüy ring methods were used to ensure measurements. Based on the findings, the isotherms show the relations between the changes in concentration and the changes in the surface tension.

As shown by Fig. 1, the surface tension decreases intensively both in the binary acetone-water and 1,4-Dioxane-water systems and in the ternary acetone-1,4-Dioxane-water systems, with a small content of the added component (from 0 to 0.1 molar fractions of organic substances), i.e. organic substances show surface activity on water. A further increase in the proportion of adsorbate in the systems leads to a more monotonic decrease of the curve indicating the dependence of surface tension on molar fractions. The isotherms show that the highest activity of acetone and 1,4-Dioxane in water is found to be present in the range of up to 0.2 mole fractions.

![Figure 1. Isotherms for the surface tension in aqueous solutions: 1) acetone-1,4-Dioxane-water (1,4-Dioxane-acetone = 1:1); 2) water-1,4-Dioxane; 3) water-acetone at 293 K](image)

The resulting data suggest that the nature of the surface tension isotherms for the ternary system (1,4-Dioxane -acetone = 1:1) is due to the combined effect of organic components (1,4-Dioxane and acetone) on the liquid surface tension. In this case, as indicated by Fig. 1, this isotherm occupies an intermediate position between the isotherms for the dependence of concentrations on the binary surface tension. This situation gives reason to assert that the surface-active agents in this ternary system do not enhance the surface activity of each other.

Based on the experimental data, the authors performed the adsorption calculations (n-variant) according to Guggenheim and Adam [9]. The adsorption is calculated using the following formula:

\[
\Gamma_i^N = \frac{a_i(1-x_i)}{RT} \left( \frac{\partial \sigma}{\partial a_i} \right)_T,
\]
where \( x_i \) is molar fractions; \( a_i \) is thermodynamic activities of components; \( R \) is the universal gas constant, \( \Gamma_{i}^{N} \) is the adsorption.

The adsorption of acetone and dioxane is calculated based on the dependence of concentrations on the ternary surface tension \( X_{\text{acetone}}:X_{\text{dioxane}} = 1:1 \). The total adsorption of surfactants in water are shown in Fig. 2.

As can be seen from the data available, the adsorption of acetone and 1,4-Dioxane in the three-component system is positive. The adsorption of acetone and 1,4-Dioxane as the second component is also positive.

![Figure 2. Isotherm for adsorption in acetone-1,4-Dioxane-water at 293 K. 1 – adsorption of acetone in water-acetone system; 2 – adsorption of 1,4-Dioxane in water-1,4-Dioxane; 3 – adsorption of acetone and 1,4-Dioxane in ternary system X_{acetone}:X_{dioxane} = 1:1](image)

The resulting isotherms show that the adsorption isotherm for organic substances of the ternary system in shape and magnitude has similar values to the adsorption isotherms for acetone and 1,4-Dioxane in the linear binaries. It can be seen from the graphs that these curves have similar values in terms of the adsorption value.

4. Conclusion
The tensiometer used here as a precision device for studying the surface properties, bulk properties (density) and dispersed state of a substance, etc. made it possible to obtain reliable results on the dependence of changing concentrations on the surface tension in a ternary system and lateral binary aqueous organic solutions.

The experimental data (Fig. 1) confirm the conclusion, made earlier and based on the study of metal systems, that the surface tension isotherms for a three-component system do not contain any qualitative features in comparison with the values of the surface tension in lateral binaries of this three-component system [10].

As can be seen from the isotherm (Fig. 2), the adsorption value up to 0.6 mole fractions of the water-acetone-1,4-Dioxane system is positive. At concentrations in the range of 0.1-0.2 molar fractions of organic components in water, the adsorption sharply increases and reaches maximum values, followed by an intensive decrease, up to a concentration of 0.4 molar fractions. With a further increase in concentration, the equilibrium values of adsorption decrease more smoothly. This is
apparently due to the fact that the adsorption film at a given concentration is already filled with adsorbate and a further increase in the concentration of additional components (dioxane-acetone) does not cause an increase in the adsorbate concentration in the surface layer. As long as the concentration of additional components ranges from 0.6 molar fractions and above, the adsorption in the multicomponent system is zero.

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