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Determination of Solutions Density by the Dilatometric Titration Method

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Abstract—A new approach to the determination of solutions density based on dilatometric titration data was developed. The results of testing this method by the example of dilution of a sodium chloride solution are presented. The method allows density of solutions to be determined with a high accuracy ($\pm 1 \times 10^{-5}$ g cm^{-3}) in a wide concentration range in the course of a single experiment.

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One of the most important characteristics of liquid systems is their density. The knowledge of this value is necessary both from the academic point of view (for example, for studying structure of solutions depending on concentration and for calculating other physico-chemical properties) and for the development of various technological schemes. The main methods of the density determination are the areometric, bottle, hydrostatic balance, and magnetic float. A disadvantage of the areometric method, which is the most simple in application, is its low accuracy (about 10^{-3} g cm^{-3}); the bottle method is characterized by a slightly greater accuracy, but it is noticeably more difficult in execution. The hydrostatic balance and the magnetic float methods [1] are recognized as the most convenient and accurate methods, which are used, in particular, in various automatic densimeters [2, 3]. At the same time all the specified methods are methods of "separate tests," i.e. methods based on experiments with separate samples of a liquid. Yet solution of many problems requires the knowledge of density of solutions in a wide range of components concentrations both in binary and in multicomponent systems. In this case the use of the above-mentioned methods appears rather labor- and time-consuming; furthermore, at such approach to density determination the probability of an error in the analysis of separate samples is rather high (especially at low concentrations), which can break perceptual unity of a solution density dependence on concentration. The specified conditions point to the necessity of the development of a fundamentally new "continuous" method of density determination allowing a determination of solutions density in a wide concentration range in the course of a single experiment. In this work we offer dilatometric titration as such a method.

Unlike densitometric methods considered above, dilatometry is a direct method of measuring volume properties of solutions. The dilatometric technique has undergone a long evolution: from elementary dilatometers allowing determination of volume variations only in separate solution samples up to modern precision dilatometers-testators, which make it possible to obtain experimental data on volume properties in a wide range of concentrations by a single titration [4, 5].

The detailed description of a dilatometer-testator used in the present work is given in [6]; the schematic diagram of the device is presented in Fig. 1. The device consists of two chambers, upper *1* and lower *2* separated from each other by piston *3* and connected to one another by a narrow tube *4*. Both chambers are filled with solutions under study; a thin graduated capillary *5* is brought to a lower chamber of the device. During the experiment the piston is displaced upwards by means of a special mechanical provision, a part of the solution passes through connecting tube *4* from the upper chamber in the lower chamber, and as a result solutions are mixed with each other, and, generally, a total volume of solutions is changed (the change can

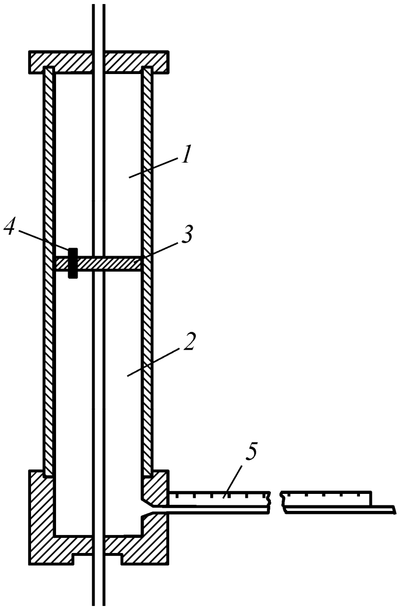

Fig. 1. Schematic diagram of a dilatometer-titrator. (*1*) upper chamber, (*2*) lower chamber, (*3*) piston, (*4*) connecting tube, and (*5*) graduated capillary.

be calculated from a displacement of a meniscus in capillary *5*). The construction of the device makes it possible to vary the piston position continuously (by small steps); in this connection this experiment was named "dilatometric titration." The resulting dependence of the change of the total volume of the solution on the volume of solutions passed in a lower chamber (or on the concentration of a solution in the lower chamber) is rather informative for the physicochemical analysis of multicomponent systems, in particular, for the determination of regions of domination of various chemical processes [7–10].

The above-mentioned dependence can be applied also to the determination of solutions density. We designate the initial density of a solution in the lower chamber (before mixing) as ρ_{lo} and the density of a solution in the lower chamber after mixing as ρ_{l}. In this case Eqs. (1), (2) will be valid.

$$\rho_{\mathrm{lo}} = m_{\mathrm{lo}}/V_{\mathrm{lo}}, \tag{1}$$

$$\rho_{\mathrm{l}} = m_{\mathrm{l}}/(V_{\mathrm{lo}} + V_{\mathrm{add}} + \Delta V). \tag{2}$$

Here V_{lo} is the initial volume of the lower chamber, V_{add} is the volume of solution passed from the upper chamber into the lower chamber owing to the piston displacement, and ΔV is the change of the total volume on mixing. The values of V_{lo} and V_{add} can be determined from data of the dilatometer calibration. The value of ΔV can be calculated from the displacement of a meniscus in the capillary (ΔS, cm) [Eq. (3)].

$$\Delta V = V_{\mathrm{1cm}}\, \Delta S. \tag{3}$$

Here V_{1cm} is the volume of solution corresponding to 1 cm of the capillary.

The weight of a solution in a lower chamber after mixture is calculated by Eq. (4).

$$m_{\mathrm{b}} = m_{\mathrm{lo}} + m_{\mathrm{add}} = \rho_{\mathrm{lo}} V_{\mathrm{lo}} + \rho_{\mathrm{up}} V_{\mathrm{add}}. \tag{4}$$

Here m_{add} is the weight of a solution passed from the upper chamber into the lower owing to the piston displacement; ρ_{up} is the density of a solution in the upper chamber.

Substituting Eq. (4) in Eq. (2), we obtain the following Eq. (5) for calculating the ρ_{up} value.

$$P_{\mathrm{l}} = (\rho_{\mathrm{lo}} V_{\mathrm{lo}} + \rho_{\mathrm{up}} V_{\mathrm{add}})/(V_{\mathrm{lo}} + V_{\mathrm{add}} + \Delta V). \tag{5}$$

Knowing V_{add} and initial concentration of a solute (solutes), we can calculate the concentration of solution in the lower chamber at any moment of the titration. When a solution of substance A is diluted by water (a study of binary systems) or by a solution free from substance A (ternary or multicomponent systems) relations (6), (7) are valid.

$$\omega_{\mathrm{lo}} = m_{\mathrm{A}}/m_{\mathrm{lo}}, \tag{6}$$

$$\omega_{\mathrm{l}} = m_{\mathrm{A}}/m_{l}. \tag{7}$$

Here m_A is the weight of a solute and ω, its weight fraction. Substituting Eq. (4) in Eq. (7) and expressing m_{A} through Eqs. (6) and (1), we obtain expression (8).

$$\Omega_{\mathrm{l}} = \omega_{\mathrm{lo}}[(\rho_{\mathrm{lo}} V_{\mathrm{lo}})/(\rho_{\mathrm{lo}} V_{\mathrm{lo}} + \rho_{\mathrm{up}} V_{\mathrm{add}})]. \tag{8}$$

Thus, for a known density of initial solutions in the both chambers (ρ_{lo} and ρ_{up}) we can determine the dependence of the density of a solution in a lower chamber on its concentration by Eqs. (5) and (8). In the case of a solution dilution by water the knowledge of only the solution density in the lower chamber ρ_{lo} is required, as the density of pure water of 0.997048 g cm^{-3} at 25°C is known [11]. The range of concentrations of solutions, for which it is possible to obtain such dependence, is defined first of all by a ratio of volumes of the lower and upper chambers. This range can be rather wide. If the volume of the upper chamber exceeds that of the lower chamber, a repeated dilatometric experiment with "reversion" of solutions (when a solution, which was in the upper chamber in the previous experiment, is placed in the lower chamber and wise versa) allows measuring density of solutions in the whole range of concentrations under study.

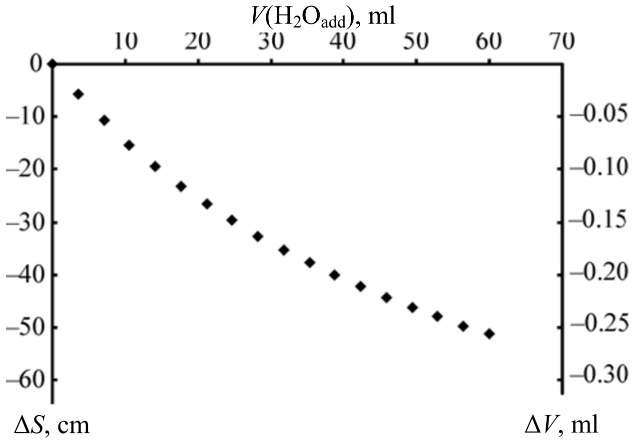

Fig. 2. Dependence of a meniscus displacement ΔS in the capillary and a total volume variation ΔV on the volume of added water at a dilution of a NaCl solution (ω 20%).

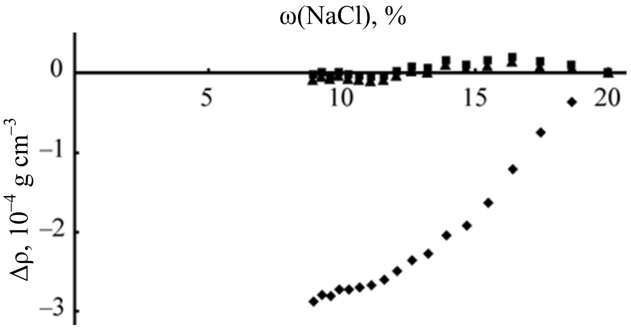

Fig. 3. Deviation of density values calculated from the data of dilatometric measurings from published data [14] (squares), [15] (rhombs), and [16] (triangles).

To test this method, we have fulfilled a dilatometric titration of a 20% NaCl solution by distilled water. The experimental conditions are described in the experimental part, and the results obtained are given in Fig. 2.

It is seen from this figure that the total volume decreases on the dilution of the NaCl solution. The found run of the dependence of volume variation is typical for solutions of electrolytes and is accounted for by strengthening electrostriction on the solution dilution, i.e. by water "compression" under the action of the electric field of ions [12, 13].

Analysis of references on the density of NaCl aqueous solutions of various concentrations has shown that the data of [14] have gained the greatest recognition, therefore we used them in the present work for comparison with the data of dilatometric measurings. For this purpose we also used the data of the handbook [15] and results of Hall [16], who has estimated the error of the density determination at 5×10^{-6} g cm^{-3}.

To analyze the correspondence between the dilatometric results and the published data, we have constructed approximating curves $\rho = f(\omega)$ according to [14–16] and interpolated these data to ω values found in the present experiments. As the ρ_{lo} values for three data sets ([14], [15], and [16]) have appeared somewhat different, we have fulfilled three series of calculations of $\rho = f(\omega)$ by Eqs. (5) and (8) and then calculated the deviation of the calculated density values from the corresponding interpolated published data. The results obtained are shown in Fig. 3. The comparison of the data on density obtained in the present work with the interpolated data of [14] is presented in the table.

As follows from the table and Fig. 3, the maximal deviation of density values calculated in the present work from the reference data [14] is 2×10^{-5} g cm^{-3}; deviations from the data of [16] do not exceed 1.5×10^{-5} g cm^{-3}. The root-mean-square deviation of the dilatometric titration data from the published data [14, 16] is 1×10^{-5} g cm^{-3}, i.e. it is comparable to the accuracy of the density determinations [14, 16], which allows us to recommend the dilatometric technique for the determination of solutions density.

Comparison of data on the density of NaCl aqueous solutions obtained by the dilatometric titration method with the published data [14].

ω, %	ρ, g cm^{-3}		ω, %	ρ, g cm^{-3}	
	[14]	this work		[14]	this work
8.916	1.06082	1.06081	12.618	1.08829	1.08829
9.217	1.06302	1.06302	13.229	1.09288	1.09289
9.538	1.06539	1.06538	13.901	1.09797	1.09798
9.883	1.06792	1.06792	14.645	1.10363	1.10364
10.253	1.07066	1.07066	15.474	1.10997	1.10998
10.652	1.07362	1.07361	16.402	1.11711	1.11713
11.084	1.07682	1.07682	17.448	1.12523	1.12524
11.552	1.08031	1.08030	18.637	1.13454	1.13455
12.062	1.08411	1.08411			

The data of the handbook [15] agree with the results of the dilatometric density determination much worse, the deviations monotonically increasing with solution dilution and reach a value of about 3×10^{-4} g cm^{-3} to the end of the titration. This fact points to insufficient accuracy of these data. Thus, dilatometric measurings can also allow a conclusion to be drawn on incorrectness and interior disagreement of one or other data set on density.

The results of the present work allow us a conclusion that the dilatometric titration method can be applied successfully to the determination of solutions density. A possibility of obtaining data on density in a wide concentration range in the course of a single experiment, a low probability of separate deviations, and also a high accuracy make this method rather promising for the determination of solutions density both in binary and multicomponent systems.

EXPERIMENTAL

The experiment was carried out using a precision dilatometers-testator [4, 6]. The initial volume of the lower chamber of the dilatometer V_{1o} was 42.00 cm^3. Diameter of the capillary was 0.8025 mm, the volume of solution V_{1cm} corresponding to 1 cm of the capillary length was 0.0050579 cm^3.

In the work we used sodium chloride of special-purity grade. Both NaCl solutions and distilled water were preliminarily degassed within 15 min in a vacuum desiccator under stirring. During the experiment the temperature was maintained at 25±0.01°C. Accurate maintaining temperature was reached by means of two sequentially connected ultrathermostats and an air thermostat, in which the dilatometer was placed.

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