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ADIABATIC COMPRESSIBILITY OF AQUEOUS SOLUTIONS OF POLYOLS

According to experimental data on the density of polyol solutions and the propagation velocity of ultrasonic waves in them, the adiabatic compressibilities of the aqueous solutions of erythritol, xylitol, sorbitol, and mannitol are calculated. For all examined solutions, the temperature dependence of the adiabatic compressibility is found to pass through a minimum. As the polyol concentration in water increases, the minimum of the adiabatic compressibility shifts toward lower temperatures. The temperature values corresponding to the minimum of the molar adiabatic compressibility are calculated. The concentration dependences of this parameter are shown to be linear. The presence of a special point for the studied aqueous solutions of polyols is established.

Keywords: adiabatic compressibility, polyols, aqueous solutions.

1. Introduction

During the last two decades, the study of critical phenomena in liquid systems obtained a new impetus and acquired a qualitatively new meaning [1–4]. This progress is associated with the study of systems that are characterized by a behavior typical of continuous phase transitions. Such systems include, first of all, water [5, 6], where the liquid-to-liquid transition was discovered [7–9], and aqueous solutions, in particular, of alcohols [10–14].

The properties of liquid systems in the vicinity of their singular points are researched using various methods [15–20], in particular, acoustic spectroscopy [21–23].

Polyols (sugar alcohols) and their aqueous solutions became widely used in emergency medicine (they form the basis of plasma substitutes), as well as in the pharmaceutical (drug excipients) and food (natural sugar substitutes and dietary nutrition supplements) industries. They are also needed in a number of chemical productions. Therefore, such researches are necessary and important.

The aim of this work was to study the temperature and concentration dependences of the adiabatic compressibility in the aqueous solutions of polyols.

2. Research Methods and Objects

The adiabatic compressibility β_S of a solution can be calculated using the known Newton–Laplace relation [23]

$$\beta_S = (\rho c^2)^{-1} \tag{1}$$

on the basis of the data for the density ρ and the propagation velocity c of sound vibrations in the exam-

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ined system. In order to calculate the adiabatic compressibility β_S according to formula (1), experimental studies of the density of polyol solutions and the sound propagation velocity in them were performed.

The solutions were prepared from doubly distilled water and various polyols of the chemically pure grade. The weighing was performed on an analytical balance with an error of $\pm 2 \times 10^{-4}$ g. Solutions of the following polyols and with the following concentrations were studied: erythritol (1, 5, 15, 25, 30, and 35 wt.%), xylitol (5, 10, 20, 30, 40, 50, and 60 wt.%), sorbitol (5, 10, 20, 30, 40, 60, and 70 wt.%), and mannitol (1, 3, 10, 15, and 20 wt.%).

The densities of the solutions were determined with the help of a two-capillary pycnometer. The ultrasound velocity in the liquid systems was measured by means of the pulse-phase method at a frequency of 15 MHz. The measurements were performed in a temperature interval of 283–353 K under atmospheric pressure. The specimens were thermostated with the help of a circulating liquid thermostat with an error of ±0.1°C. The relative measurement errors were 0.05% for the density and 0.5% for the ultrasound velocity.

3. Experimental Results

In Fig. 1, the temperature dependences of the ultrasound propagation velocity in the aqueous solutions of xylitol are plotted. Analogously to all other examined polyol solutions, the temperature dependences of the ultrasound velocity for the xylitol solutions with the concentrations far from the saturation demonstrate a maximum, which shifts toward low temperatures, as the content of non-aqueous component increases. In the xylitol and sorbitol solutions with concentrations higher than 40 wt.%, the maximum of ultrasound velocity in the studied temperature interval disappears, and this parameter decreases monotonically, as the temperature grows.

The increase of the polyol content in the solutions gives rise to the growth of the propagation velocity of sound waves in them. An example of the concentration dependence of the sound velocity is shown in Fig. 2. In the solutions with polyol contents up to 20 wt.%, the velocity growth is almost linear, as the concentration increases. In the polyol solutions with concentrations higher than 20 wt.%, deviations from the linearity are observed.

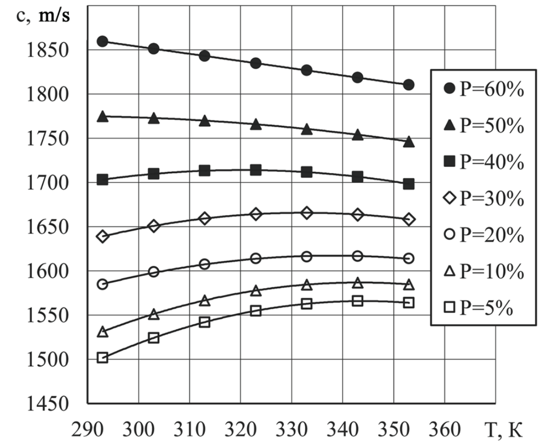

Fig. 1. Temperature dependences of the ultrasound propagation velocity in aqueous xylitol solutions

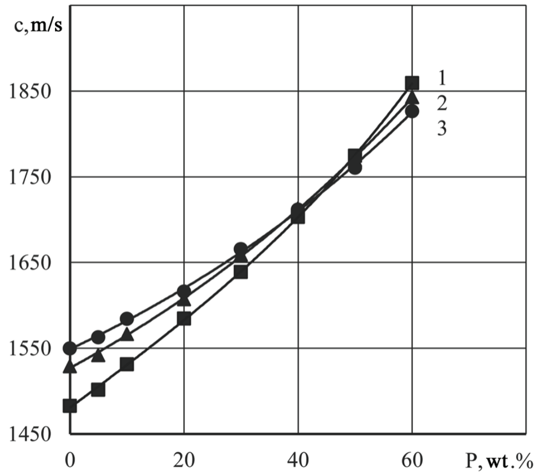

Fig. 2. Concentration dependences of the sound propagation velocity in aqueous sorbitol solutions at various temperatures: 293 (*1*), 313 (*2*), and 333 K (*3*)

From the results of our experiments, it follows that the densities of the aqueous solutions of erythritol, xylitol, sorbitol, and mannitol non-monotonically decrease with the increasing temperature and increase with the increasing polyol content.

Characteristic temperature dependences of the adiabatic compressibility of the aqueous solutions of studied polyols, which were calculated according to formula (1), are shown in Figs. 3 and 4. As one can see from those figures, the adiabatic compressibility of the solutions passes through a minimum, when the temperature changes, and this minimum shifts toward lower temperatures, as the concentra-

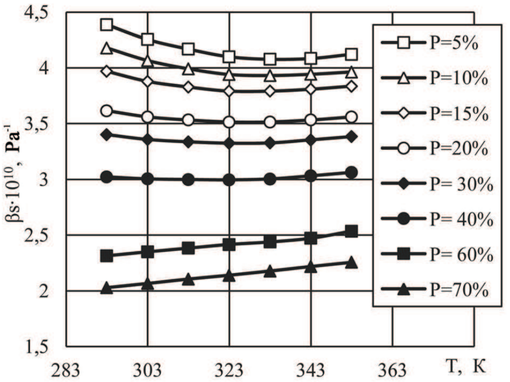

Fig. 3. Temperature dependences of the adiabatic compressibility for aqueous sorbitol solutions with various concentrations

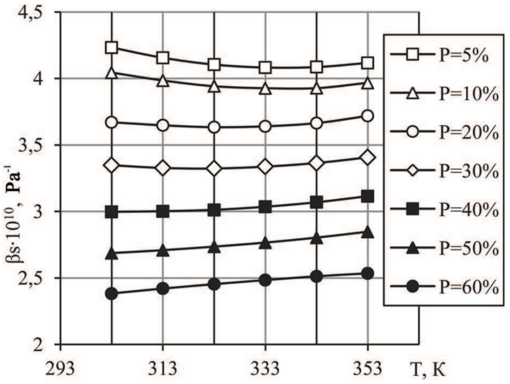

Fig. 4. Temperature dependences of the adiabatic compressibility for aqueous xylitol solutions with various concentrations

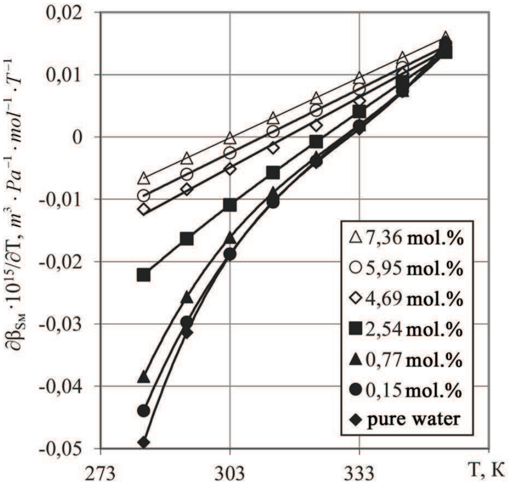

Fig. 5. Temperature dependences of the temperature coefficient of molar adiabatic compressibility for aqueous erythritol solutions with various concentrations

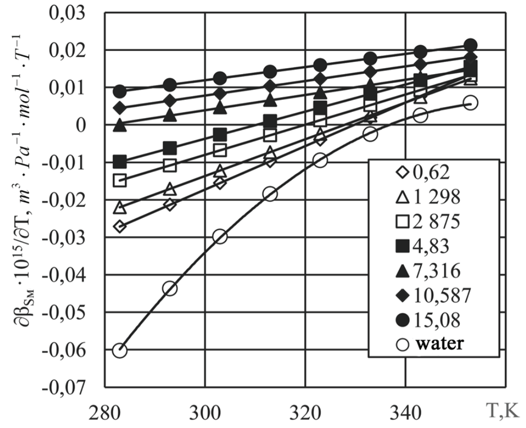

Fig. 6. Temperature dependences of the temperature coefficient of molar adiabatic compressibility for aqueous sorbitol solutions with various concentrations

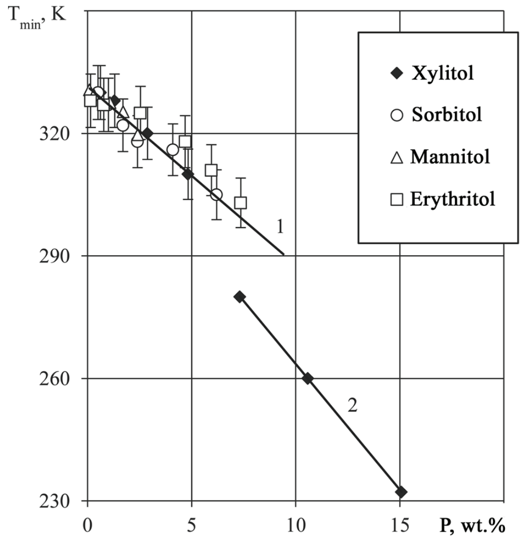

Fig. 7. Concentration dependences of the temperature of the molar adiabatic compressibility minima for aqueous solutions of various polyols

tion grows. In the solutions of polyols with concentrations higher than 40 wt.%, the minimum of the adiabatic compressibility disappears in the studied temperature interval, and this parameter increases linearly.

The isotherms of the concentration dependences of the adiabatic compressibility in the researched systems pass through a minimum and have intersection points, which gradually shift toward the region of lower contents of the non-aqueous component.

4. Discussion

The authors of work [24] came to the conclusion that, when studying aqueous solutions, it is more illustrative to analyze the behavior of the molar adiabatic compressibility $\beta_{S\mathrm{mol}}$, rather than the adiabatic compressibility β_S. The parameter $\beta_{S\mathrm{mol}}$ is determined by the formula

$$\beta_{S\mathrm{mol}} = \beta_S V_m, \tag{2}$$

where $V_m = M/\rho$ is the molar volume, and M the molar mass of the solution. This change can be explained by the fact that the value of the molar adiabatic compressibility is related to the same number of molecules. Therefore, for example, the temperature $T_{\min}$ corresponding to the minimum of the molar adiabatic compressibility may be more informative.

Note that, for aqueous solutions with known concentrations, the minima in the dependences of the adiabatic compressibility and molar adiabatic compressibility are observed at different temperatures. The minimum of the molar adiabatic compressibility is observed at a temperature lower by about 10–15 K than the corresponding temperature of the adiabatic compressibility minimum.

The values of $\beta_{S\mathrm{mol}}$ calculated using formula (2) were applied to determine the temperatures $T_{\min}$ corresponding to the minimum of the molar adiabatic compressibility. For a definite solution, the values $T_{\min}$ were determined by analyzing the dependences $\beta_{S\mathrm{mol}}(T)$ for the extremum. The calculations were performed using the software program "Advanced Grapher". The results of calculations are presented in Figs. 5 and 6, which show the dependences of $\partial\beta_{S\mathrm{mol}}/\partial T$ on T.

In Fig. 7, the dependences of the temperature $T_{\min}$ on the solute concentration are exhibited for various aqueous polyol solutions. The increase of the polyol content in water brings about a monotonic shift of the temperature of the molar adiabatic compressibility minimum toward low temperatures. For all examined solutions, to a determination error of $\pm(2\div3)\%$ for $T_{\min}$, the concentration dependences of $T_{\min}$ turned out grouped along the same line (Fig. 7, line *1*). Such a behavior of the concentration dependence of the temperatures of the molar adiabatic compressibility minima is observed for all investigated solutions up to concentrations of about 6–7 mol.%, with $T_{\min} = (305 \pm 6)$ K.

Xylitol and sorbitol can create aqueous solutions with concentrations higher than 7 mol.%. For those solutions with concentrations in an interval of 6–7 mol.%, the temperatures corresponding to the molar adiabatic compressibility minimum undergo a "jump-like" change to lower values (Fig. 7, line *2*).

The value obtained for the temperatures of the adiabatic compressibility minima, $T_{\min} = (305 \pm 6)$ K, agrees well with the temperatures of specific points in the aqueous solutions of propyl alcohols [3] and testifies to the presence of specific points in the aqueous polyol solutions.

5. Conclusions

1. Our research of the aqueous solutions of polyols with various concentrations has shown that the adiabatic compressibility of the examined systems passes through a minimum as the temperature changes.

2. The temperature $T_{\min}$ corresponding to the minimum of the molar adiabatic compressibility decreases linearly with the growth of polyol concentration in water.

3. The change in the slope (the cusp) of the dependence of the temperature corresponding to the minimum of the molar adiabatic compressibility on the concentration in the aqueous solutions of examined polyols near the special point of water (315 K) testifies to the presence of a special point in them.

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АДІАБАТИЧНА СТИСЛИВІСТЬ ВОДНИХ РОЗЧИНІВ ПОЛІОЛІВ

За експериментальними даними про густину і швидкість поширення ультразвукових хвиль проведено розрахунки адіабатичної стисливості у водних розчинах еритриту, ксиліту, сорбіту і маніту. Встановлено, що температурні залежності адіабатичної стисливості досліджених систем проходять через мінімуми. Зі збільшенням концентрації поліолу у воді мінімум адіабатичної стисливості зміщується у бік нижчих температур. Розраховано значення температур мінімумів молярної адіабатичної стисливості. Показано, що концентраційна залежність температур мінімуму молярної адіабатичної стисливості носить лінійний характер. Встановлено наявність особливої точки для досліджуваних водних розчинів поліолів.

Ключові слова: адіабатична стисливість, поліоли, водні розчини.