Physical Chemistry

1957

SovietRxiv

Fig. 1. Dependence of deformation on deformation time for glycerin of 100% concentration. 1—$P = 0.0002$; 2—$P = 0.0004$; 3—$P = 0.0006$; 4—$P = 0.0008$; 5 —$P = 0.002$ dyn/cm^2.

Figure 1: Fig. 1. Dependence of deformation on deformation time for glycerin of 100% concentration. 1—$P = 0.0002$; 2—$P = 0.0004$; 3—$P = 0.0006$; 4—$P = 0.0008$; 5—$P = 0.002$ dyn/cm^2.

Abstract

Full Text

Physical Chemistry

L. V. Khailenko

Investigation of the Kinetics of the Development of Shear Deformation in Aqueous Solutions of Glycerin, Sucrose, and Xylitol

(Presented by Academician P. A. Rehbinder, March 28, 1957)

In 1953 we showed (⌢1) that the flow curves $\varepsilon = \varphi(\tau, P)$ of hydrated glycerin do not correspond to a Newtonian liquid, but are analogous to rheograms of the flow of solutions of high-molecular compounds (⌢2). The presence of an elastic-viscous segment on the flow curve of glycerin was confirmed by the work of A. Korotkova and D. Sandomirskii, who in 1955 observed this effect in a study of glycerin on a Weiler-Rehbinder elastometer (⌢3).

In view of the unexpected nature of the results obtained, it was of interest to study in detail the rheological properties of glycerin and its aqueous solutions over as wide a range of concentrations as possible, as well as aqueous solutions of hydroxyl-containing compounds, since the hydroxyl group may determine the existence of the indicated anomaly in solutions through hydrogen bonding. Aqueous solutions of sucrose and of the pentahydric alcohol xylitol were chosen as the objects of investigation.

Fig. 1. Dependence of deformation on deformation time for glycerin of 100% concentration.
1—$P = 0.0002$; 2—$P = 0.0004$; 3—$P = 0.0006$; 4—$P = 0.0008$; 5—$P = 0.002$ dyn/cm^2.

The elastic-viscous properties of dry and hydrated glycerin, as well as of the above-mentioned solutions, were studied in the highly sensitive Shvedov elasto-viscometer, which makes it possible to experiment in the region of shear stresses from 0.0002 dyn/cm^2 and higher (^{1,}4).

Fig. 2

Figure 2: Fig. 2

The experiment showed that pure dry glycerin, under the given deformation regime, behaves as a true Newtonian liquid. The rheograms $\varepsilon = \varphi(\tau, P)$ are represented graphically by straight lines without recovery after removal of the load (Fig. 1). When glycerin is diluted with water, its elastic-viscous properties change sharply. Even a 95% solution possesses clearly expressed elasticity. With further dilution, the elastic-viscous constants increase, reaching a maximum in the 70% solution.

Figure 2 presents the curves $\varepsilon = \varphi(\tau, P)$ obtained for an 80% solution and typical for the glycerin-water system in the range of concentrations investigated.

The equilibrium modulus

$$E = \frac{P}{\varepsilon_m},$$

calculated from the corresponding curves $\varepsilon = \varphi(\tau, P)$, changes with the concentration of the solution as follows:

Concentration, %	80	70	60
E, dyn/cm^2	0.03	300.0	80.0

Rheograms $\varepsilon = \varphi(\tau, P)$ were recorded for an aqueous sucrose solution of 50% concentration at shear stresses from $P = 0.0002$ to $P = 0.002$ dyne/cm^2 (see Fig. 3).

The curves of the dependence of shear deformation on deformation time, shown in Fig. 3, indicate that this solution possesses the elasticity characteristic of solutions of high-molecular compounds and observed by us in the glycerin-water system.

Fig. 2. Dependence of deformation on deformation time for an 80% glycerin solution.
1 $-P = 0.0021$; 2 $-P = 0.0043$;
3 $-P = 0.0064$; 4 $-P = 0.0085$ dyne/cm^2

When the solution is heated to 100°, destruction of the continuous structural network responsible for the elastic-elastic properties of the system occurs, followed by restoration upon cooling of the solution to 20°.

Fig. 3. Dependence of deformation on deformation time for a 50% solution of sucrose in water.

Fig. 3

Figure 3: Fig. 3

Fig. 4. Dependence of deformation on deformation time for a 50% solution of xylitol in water. $1 - P = 0.0021$; $2 - P = 0.0043$; $3 - P = 0.0085$ dyne/cm^2.

Figure 4: Fig. 4. Dependence of deformation on deformation time for a 50% solution of xylitol in water. $1 - P = 0.0021$; $2 - P = 0.0043$; $3 - P = 0.0085$ dyne/cm^2.

$1 - P = 0.0002$;
$2 - P = 0.0004$; $3 - P = 0.0007$ dyne/cm^2

A 50% aqueous solution of xylitol was studied in the same way. Rheograms $\varepsilon = \varphi(\tau, P)$ were recorded at various shear stresses from $P = 0.002$ dyne/cm^2 to $P = 0.008$ dyne/cm^2 at a temperature of 20°.

In all cases, curves were obtained analogous to the curves obtained for aqueous solutions of glycerin and sucrose (Fig. 4).

From the data presented it follows that:

1. Concentrated aqueous solutions of glycerin, sucrose, and xylitol are not true Newtonian liquids, as was considered until recently, but possess the elasticity characteristic of solutions of high-molecular compounds.
2. The appearance in the investigated liquids of mechanically rigid and elastically viscous structures can be explained by the existence in these systems of hydrogen bonds forming long quasipolymeric macromolecules, for which a highly elastic time-dependent defor-

···formation, leading to the concept of an equilibrium or limiting modulus of elasticity.

3. The structures arising in the liquids under study are thixotropic, highly elastic, with small cohesive forces between the elements of the structure. Apparently, they occupy an intermediate position between the coagulation and condensation structures studied in modern colloid chemistry [5,6].

Fig. 4. Dependence of deformation on deformation time for a 50% solution of xylitol in water.
$1 - P = 0.0021$; $2 - P = 0.0043$; $3 - P = 0.0085$ dyne/cm^2.

4. The application of highly sensitive methods of viscometry, carried out by us with the aid of the Shvedov viscometer, makes it possible to study very subtle properties of intermolecular interaction, manifested in the present case in the existence of a mechanically rigid structural framework.

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Received
14 I 1957

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Note: Figure translations are in progress. See original paper for figures.