

A re-evaluation of the system  $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  is presently under way and will be reported at a later date.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

## Surface Tension of Synthetic High Polymer Solutions<sup>1</sup>

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The equilibrium value and the rate of approach to equilibrium of the surface tension of relatively dilute solutions of a number of fractions of polystyrene in tetralin and polyvinyl alcohol in water have been measured by means of a pendant drop apparatus. Certain modifications of the apparatus allow us to study polymer solution drops without visible changes for periods exceeding 24 hours. As the molecular weight of the polystyrene fractions decreases the surface tension increment changes sign, as expected from theory, due to an entropy effect. This suggests in turn that molecular weight estimates obtained from surface tension measurements are sensitive to the low molecular weight tail of the molecular weight distribution curve. Certain effects due to the configuration of the polymer at the interface are noted. Both the polystyrene and the polyvinyl alcohol solutions exhibit a dependence of the surface tension on the age of the solution drop surface. The magnitude of this relaxation time and some factors which affect it are discussed.

### Introduction

Previous measurements<sup>5-7</sup> of the surface tension (S.T.) of solutions of synthetic macromolecules have been carried out on aqueous solutions of surface active high polymers whose monomers are themselves surface active.

A recently developed statistical mechanical theory<sup>8</sup> of the S.T. increment,  $\Delta\gamma$  ( $\Delta\gamma = \text{S.T. of the solution} - \text{S.T. of the solvent}$ ), of a dilute solution of a linear high polymer leads us to expect that  $\Delta\gamma$  could be positive as well as negative. For a sufficiently dilute solution  $\Delta\gamma$  is given by the sum of a negative term describing the tendency of the polymer molecule to be adsorbed at the solution interface due to attractive forces between the interface and the polymer segments and a positive activity term. The latter results from the larger configurational entropy available to a chain present in the bulk of the solution over that present in the interface region. Thus<sup>8</sup>

$$\frac{\Delta\gamma}{c} = \left(\frac{kT}{A_0}\right) \left[ \frac{\zeta\nu}{t} - K_{\text{ads}} \right] + O(c) \quad (1)$$

where  $t$  is the degree of polymerization of the chain polymer,  $\nu$  the average number of anchor segments per chain deposited in the interface,  $K_{\text{ads}}$  is in effect the surface adsorption isotherm equilibrium constant,  $A_0$  is the ideal area occupied by a deposited anchor segment and  $\zeta$  is a proportionality constant depending on the units of  $c$  if the latter is expressed in weight of polymer per unit volume of solution. In particular if the polymer chain is Gaussianly coiled,  $K_{\text{ads}}$  is proportional to a weakly increasing function of the molecular weight of the polymer,

(1) Supported in part by the Office of Ordnance Research, U. S. Army.

(2) Presented in part at the 132nd meeting of the American Chemical Society, New York City, September, 1957.

(3) Bell Telephone Laboratories, Murray Hill, N. J.

(4) Based on the Master's Thesis of S. Al-Madfaï, University of Southern California.

(5) A. Couper and D. D. Eley, *J. Polymer Sci.*, **3**, 345 (1948).

(6) A. Katchalsky and I. Miller, *J. Phys. Chem.*, **55**, 1182 (1951).

(7) C. Capitani and G. Righi, *Comp. rend.*, 27<sup>o</sup> Congr. intern. chim. ind. Bruxelles 1954, 3; *Industrie chim. belge*, **20**, Spec. No. 691, 695 (1955).

(8) H. L. Frisch and R. Simha, *J. Chem. Phys.*, **27**, 702 (1957).

$M$ ,  $f(M)$  (this increase is less than linear in  $M$ ) and  $\nu$  is proportional to  $M^{1/2}$  so that at constant temperature

$$\frac{\Delta\gamma}{c} = AM^{-1/2} - Bf(M) + O(c) \quad (2)$$

with  $A$  and  $B$  constants.

$\Delta\gamma$  is thus negative for a polymer-solvent system for which the term due to adsorption predominates. Such would be expected to be the case for a system consisting of a polymer with a highly lyophobic carbon backbone chain to which are regularly attached lyophilic functional groups particularly if the monomer segments are themselves surface active. This appears to be the case with the aqueous solutions of polyethylene glycols and the polyvinyl alcohol solutions studied by us. If on the other hand the attractive energetic interactions between the solution interface and the polymer segments are sufficiently weak, one expects that, although very high molecular weight fractions would possibly still be surface active (since adsorption is favored by large values of  $M$  under ideal conditions),<sup>8</sup> the entropy effect giving rise to the positive activity term would make  $\Delta\gamma$  positive below a certain value of  $M$ .

In order to observe this effect we chose to investigate the S.T. of fractions of polystyrene (PSt.), a typical hydrocarbon polymer, in tetralin a "good" hydrocarbon, non-aqueous solvent. Tetralin was chosen as the solvent because it has a relatively low vapor pressure at 25° and because it is a relatively "good" (in the sense of polymer solution theory) solvent for PSt. thus decreasing the tendency of the PSt. molecules to be adsorbed at the interface.<sup>8</sup> Styrene monomer in tetralin is surface active. Tentatively this is thought by us to be due to the double bond present in the monomer but absent in the polymer.

For the sake of comparison, we measured also the S.T. of two fractions of polyvinyl alcohol (PVA) in water in the same concentration range as used for the PSt.-tetralin. PVA in water was expected to be moderately surface active. The hydrocarbon backbone of PVA is hydrophobic while the hydroxyl groups are hydrophilic; more-

over the "monomer" (acetaldehyde or ethanol) is somewhat surface active in water.

The reported<sup>5-7</sup> relaxation in time of the apparent S.T. suggested that a static method be employed to study the S.T. The pendant drop method<sup>9,10</sup> was chosen since it allows one to measure the S.T. on a single surface which could be observed for considerable periods of time and on which the attainment of equilibrium could be suitably tested.<sup>11</sup> Other advantages of this method are<sup>10</sup> that it is an absolute method which is independent of the contact angle and which requires only small amounts of the solution for a measurement. The principle of the method is that under the action of S.T. and the force of gravity a drop, suspended from a capillary, assumes the shape of a surface of revolution whose radius of curvature depends only on the S.T. of the liquid,  $\gamma$ , its density (corrected for buoyancy in air)  $D$  and the gravitational acceleration  $g$ . In practice, it is easier to measure the shape factor  $S$  rather than the radius of curvature.<sup>10</sup>  $1/S$  is the ratio of the equatorial drop diameter  $d_e$  to the drop diameter at a plane intersection  $d_s$  taken at a distance  $d_e$  from the vertex of the drop.<sup>10</sup> From available tables<sup>12</sup> a quantity  $1/H$  as a function of  $S$  can be found. The S.T. is then calculated according to the relation

$$\gamma = \frac{1}{H} d_e^2 Dg \quad (3)$$

By means of such a pendant drop apparatus built by us both equilibrium values and the rate of approach to equilibrium of the S.T. of the polymer solutions could be determined. Drops of solution could be conveniently suspended without visible change for periods upward of 24 hours; however, in general, a period of less than 2 hours was needed to obtain the equilibrium S.T.

### Experimental

The pendant drop apparatus which was used to produce and photograph the drops is shown in Figs. 1 and 2 and is a modification of the one used by Andreas, Hauser and Tucker.<sup>9</sup> It consists essentially of a roughly parallel light beam source (Fig. 1C), the thermostated drop producing apparatus and cell in which the drop is suspended (Fig. 1D) and a microcamera (Fig. 1M). These are mounted on an optical bench (Fig. 1B) which is in turn placed on vibration absorbent rubber pads (Fig. 1A).

The light source (a Cenco optical bench illuminator) could be used continuously or flashed by connecting it to a flash unit (Hardwood Econoflash Model 111). A removable thermostated jacket (Fig. 1J) with a thermometer (Fig. 1I), plastic door and two circular side openings for the light path surrounds the cell chamber (Fig. 1E,F) and the drop forming device (Fig. 1H). Within the cell chamber are placed the optical Pyrex glass absorption cell (Fig. 1F) (Fig. 2B) (19.5 mm. o.w., 25 o.h., a 25 mm. optical path and a neck 10 mm. high) surrounded by the (internal) thermostated metallic jacket (Fig. 1E) (Fig. 2A) that is grooved so that light can pass through the cell. The cell mouth is closed by a serum bottle rubber cap (Fig. 2C). In order to introduce the hypodermic needle (Fig. 2E) from which the

(9) J. A. Andreas, E. A. Hauser and W. B. Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

(10) R. S. Burdon, "Surface Tension and the Spreading of Liquids," Cambridge at the University Press, 1949.

(11) The volume of the drop can be changed without affecting any other constraints on the system.

(12) D. O. Niederhauser and F. E. Bartell, in "Fundamental Research on Occurrence and Recovery of Petroleum," published by the American Petroleum Institute, Baltimore, Maryland, 1948-1949, p. 114-146.

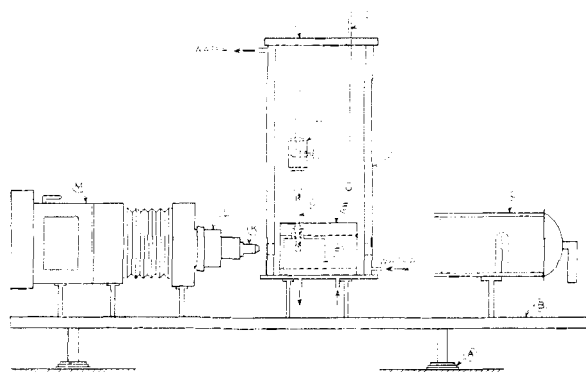


Fig. 1.—The pendant drop surface tension apparatus.

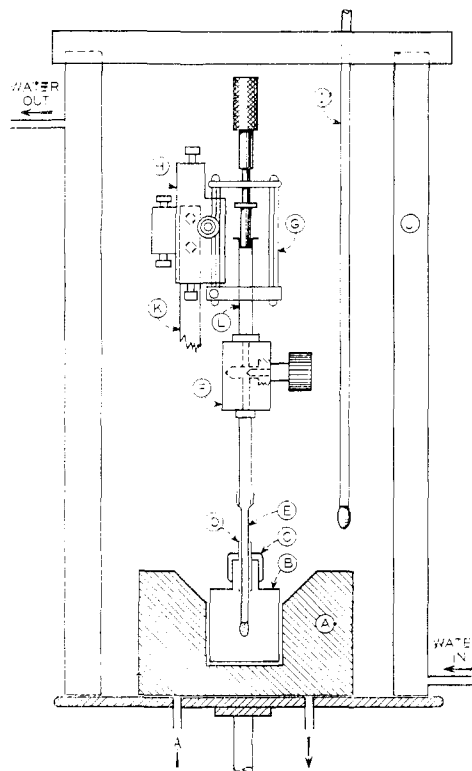


Fig. 2.—The drop producing device and the cell chamber.

pendant drop is suspended, a sharp edged stainless steel capillary (Fig. 2D) is used to pierce the rubber cap, the needle is then passed through it into the cell; the capillary is then withdrawn allowing the rubber cap to seal the needle in the now again closed cell. Water is pumped from a thermostated bath through both the internal (Fig. 2A) and external (Fig. 2J) thermostated jackets which maintain within the cell and cell chamber a temperature of  $25 \pm 0.1^\circ$ .

The drop forming device consists of a microburet (Fig. 2L) with a Teflon-glass needle valve (Fig. 2F) equipped with a glass tip made to fit a standard hypodermic needle joint. The tips of the hypodermic needles used are cut and ground carefully with an oil stone perpendicular to the vertical axis. The microburet is mounted on a metal holder (Fig. 2G) which is clamped to a microscope stage (Fig. 2H), which can move vertically and horizontally, and which in turn is screwed to a metal stand (Fig. 2K) which is attached to the optical bench.

The microcamera consists of a microscope objective with a magnification  $\times 12$  (Fig. 1K) attached to a synchronized shutter (Fig. 1L, Alpha No. 4) with a focusing mount at whose end is attached a Bausch and Lomb type adapter

(Fig. 1M) and to this in turn a Land type Polaroid camera. The visual screen of the adapter is used for careful focusing. A traveling microscope, which reads to  $10^{-3}$  cm., is used to measure all drop and needle dimensions from the photographs. The actual magnification power was determined experimentally by comparing the actual diameter of the needle with that in the photographs.

Before each run with a given polymer solution the closed cell volume is saturated with solvent vapors by suspending a drop of the polymer solution to be studied inside the cell until evaporation ceases. The drop is then sucked up. A drop of proper size<sup>12</sup> is formed from a fresh polymer solution and after focusing, the drop is photographed at various time intervals.  $\gamma$  is found according to the relation expressed in equation 3. The S.T. values are plotted as functions of the time and the equilibrium S.T. is taken as the horizontal asymptote of this curve.

The apparatus and procedure were tested by measuring the S.T. of the liquids water and tetralin whose surface tensions at  $25.0 \pm 0.1^\circ$  were found to be 72.0 dyne/cm. and 35.30 dyne/cm. as compared with the values in the literature of 72.00 and 35.26 dyne/cm., respectively. The reproducibility of the measurements was tested and the maximum deviation for the PVA-H<sub>2</sub>O solutions was found to be  $\pm 0.3$  dyne/cm. while that of the equilibrium S.T. of the PSt-tetralin solutions was about  $\pm 0.1$  dyne/cm. (see Fig. 3).<sup>13</sup>

Two kinds of PSt. fractions were used: two medium broad fractions<sup>14</sup> possessing weight average molecular weights,  $M_w$  (determined by light scattering) of  $6 \times 10^4$  and  $1.5 \times 10^6$  and four samples of terminated polymers<sup>15</sup> supplied by Professor M. Szwarc which had viscosity average molecular weights of  $1.6 \times 10^4$ ,  $2.5 \times 10^4$ ,  $4 \times 10^4$  and  $8.7 \times 10^4$ . Two relatively crude fractions of PVA were obtained by fractionating a sample of 88% hydrolyzed polyvinyl acetate (Lemol 22-88, Lot 91-RL<sup>16</sup>) according to the procedure of Scherer.<sup>17</sup> Their viscosity average degrees of polymerization were found to be 2600 and 1700 from the measurement of the intrinsic viscosity of their aqueous solutions at  $25 \pm 0.1^\circ$  using the intrinsic viscosity-degree of polymerization relation proposed by Nakajima and Furutata.<sup>18</sup> The styrene-tetralin solution was made up from styrene vacuum distilled (under nitrogen) containing less than 0.01% polymer. The solution was made and its S.T. measured within the same hour. The solvents used in this work were distilled water and sodium dried tetralin, b.p. 207.9°.

## Results

The equilibrium S.T. increments of the 1 g./100 ml. aqueous solutions of PVA at  $25.0 \pm 0.1^\circ$  were found to be  $-20.2$  and  $-22.5$  dyne/cm. for the fractions whose viscosity average degrees of polymerization were 1700 and 2600, respectively.

The equilibrium S.T. increments of the PSt-tetralin solutions are shown in Table I (the last significant figure of any entry is underlined). The lower limit of the concentration interval chosen was fixed by the fact that below it  $\Delta\gamma$  for these solutions becomes equal to or less than the averaged order of precision of these measurements of 0.05-0.1 dyne/cm.

Within experimental error  $\Delta\gamma$  is roughly directly

(13) Further information on the procedure and results obtained can be found in the thesis of Mr. S. Al-Madfal for the M.S. degree in Chemical Engineering, University of Southern California.

(14) Kindly supplied by the Research Department, Dow Chemical Co., these have been further characterized elsewhere, see H. L. Frisch and S. J. Yeh, *J. Polymer Sci.*, **20**, 431 (1956).

(15) R. Waack, A. Rembaum, J. D. Coompers and M. Szwarc, *THIS JOURNAL*, **79**, 2026 (1957).

(16) Kindly supplied by the Monomer Department, Chemical Division of the Borden Co.

(17) P. C. Scherer, "Study of the Relation of Molecular Weight Distribution Curves to Mechanical Properties," Progress Report No. 3, Project 235-01-185, 1952, Virginia Polytechnic Institute.

(18) A. Nakajima and K. Furutata, *Chem. High Polymers*, **6**, 460 (1949).

TABLE I  
SURFACE TENSION INCREMENTS OF POLYSTYRENE IN TETRALIN SOLUTIONS AT  $25.0 \pm 0.1^\circ$

Concn. (g./100 ml.), $M$	$\Delta\gamma$ , dyne/cm.			Source	
	1	0.75	0.5		
$1.5 \times 10^6$	<u>-1.04</u>	....	<u>-0.54</u>	$\sim -0.4$	Dow
$8.7 \times 10^4$	( <u>-0.54</u> )	....	( <u>-0.14</u> )	....	Szwarc
$6 \times 10^4$	<u>-0.74</u>	....	<u>-0.39</u>	$\sim -0.3$	Dow
$4 \times 10^4$	<u>-0.34</u>	....	<u>-0.14</u>	....	Szwarc
$2.5 \times 10^4$	<u>+0.26</u>	<u>+0.16</u>	<u>+0.06</u>	....	Szwarc
$1.6 \times 10^4$	<u>+0.46</u>	<u>+0.21</u>	<u>+0.11</u>	....	Szwarc

proportional to  $c$  in this concentration range (see equation 5 below).

Some typical apparent  $\Delta\gamma$  versus surface aging time curves for the above solutions are shown in Fig. 3, 4 and 5. Since the  $\Delta\gamma$  values remain, within experimental error, unchanged after 120 minutes these plots are terminated at about that time value.

The equilibrium S.T. increment at  $25.0 \pm 0.1^\circ$  of a 1.58 g./100 ml. solution of styrene in tetralin was  $-0.60$  dyne/cm. The equilibrium S.T. of pure styrene at the same temperature was 30.35 dyne/cm., which is lower than that of tetralin.

## Discussion

As expected PVA in water is moderately surface active. The degree of surface activity increases slightly with increasing  $M$ . This agrees with the findings of Couper and Eley,<sup>5</sup> on polyethylene glycols in water. They concluded that considerable deposition of the polymer at the interface occurs from the fact that the apparent surface area of the deposited monolayer was proportional to the intrinsic viscosity of their solutions.

In comparison with the above measurements the  $\Delta\gamma$  of the PSt-tetralin solution show considerable qualitative differences as would be expected from theory.<sup>8</sup> Even at the highest  $M$  (which exceeds that of both PVA fractions)  $\Delta\gamma$  is comparatively weakly negative. We have no lyophilic and lyophobic parts of the macromolecule as in the case of PVA or polyethylene glycols in water and presumably the forces responsible for the adsorption of the high molecular weight fractions are weak dispersion forces. Again as  $M$  is decreased we find that the surface activity of the PSt. in tetralin decreases until at  $M$  ca.  $3 \times 10^4$  the positive activity term reverses the sign of  $\Delta\gamma$ . If we take the initial slope of the  $\Delta\gamma$  versus  $c$  curves,  $\Omega$  (in 100 ml./sec.<sup>2</sup>), to be given by that of the 0.5 g./100 ml. solutions, *i.e.*

$$\Omega = (\Delta\gamma/c)_{c \rightarrow 0} = (\Delta\gamma/c)_{c=0.5\%} = \Omega_{exp} \quad (4)$$

we find that the molecular weight dependence of the data is fitted by the following relation suggested by theory<sup>4</sup> for a Gaussian coil

$$\Omega = 1.4 \times 10^2 M^{-1/2} - 0.21 \log_{10} M \quad (5)$$

Equation 5 agrees exactly with equation 2 if  $f(M)$  is taken to be  $\log_{10} M$ . The constant coefficients  $A$  and  $B$  of equation 2 or 5 have been obtained by a least squares fit of the data rejecting the anomalous result for  $M = 8.7 \times 10^4$ . Equation 5 reproduces the data to within an average de-

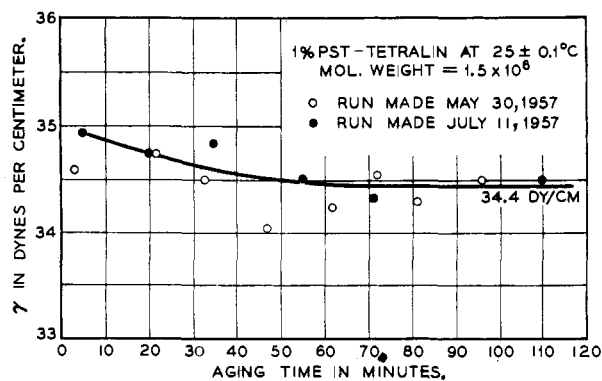


Fig. 3.—The surface tension of 1% polystyrene in tetralin as a function of time.

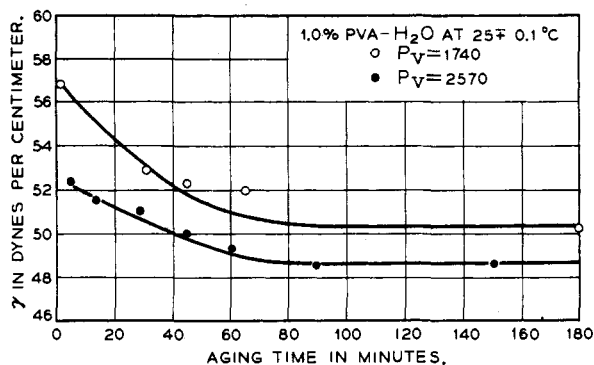


Fig. 4.—The surface tension of polyvinyl alcohol in water as a function of time.

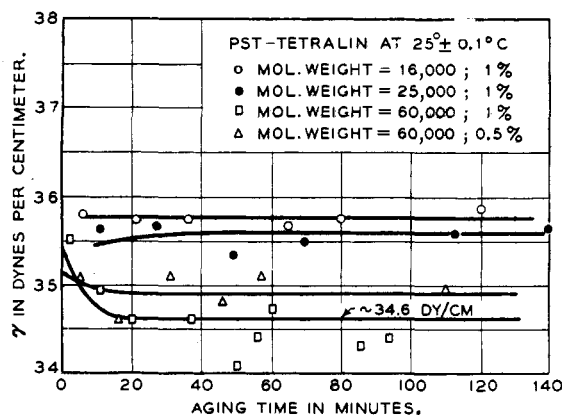


Fig. 5.—The surface tension of polystyrene in tetralin as a function of time.

variation of 20% which is of the same order of magnitude as the experimental reproducibility.

The additivity of surface free energies and equation 5 suggest that S.T. measurements are suitable for relative determinations of  $M$ . In suitable systems, e.g. PST-tetralin, an average  $M$  obtained from such measurements may be particularly sensitive to the low molecular weight tail of the molecular weight distribution function because of the entropy effect. In polydisperse mixtures the entropy factor may tend to disappear in too concentrated solutions.<sup>19</sup> In principle (cf. equation 1),

(19) We are indebted to Prof. K. J. Mysels for this observation.

such measurements also can tell us something about the configuration of the polymer at the interface since  $\nu$  varies depending on whether the polymer is completely deposited or not as well as the degree of flexibility or coiling of the polymer chain.<sup>8</sup> While our measurements are too few in number and insufficiently precise to do this in any reproach-free manner, they do suggest that the polymer is roughly a three-dimensional Gaussian coil at the interface. From the value of  $A$  in equation 5 we can estimate  $A_0$  of PSt. at the solution interface. Taking<sup>8</sup>  $\nu \sim t^{1/2}$  we find

$$A_0 \approx \frac{kTm_0}{100M_0^{1/2}d_0A} = 4 \times 10^{-16} \text{ cm.}^2 \quad (6)$$

with  $m_0$  and  $d_0$  the molecular weight and density of tetralin and  $M_0$  the molecular weight of styrene.<sup>20</sup> Such an area is not unreasonable in view of the reported<sup>21</sup> length of a statistical segment in PSt., found from light scattering in toluene or cyclohexane solutions, of  $2.52 \times 10^{-8}$  cm.

From Figs. 3, 4 and 5 we see that the apparent relaxation times of the S.T. for typical 1 g./100 ml. solutions decrease in the order PVA-H<sub>2</sub>O, Dow Pst.-tetralin (except the sample whose  $\bar{M}_w = 1.5 \times 10^6$ ), Szwarc PSt.-tetralin. This is also the estimated order of these polymers in molecular and species homogeneity. In particular the Szwarc PSt. fractions besides being presumably relatively monodisperse are also relatively free of polymer isomers due to side reactions (branching, chain-transfer, etc.). The curvature of all curves is the expected one. The apparent S.T. of the 1 g./100 ml. PVA-H<sub>2</sub>O and Dow PSt.-tetralin solutions were found to vary with time according to the relation

$$\frac{\gamma(t) - \gamma(\infty)}{\gamma(0) - \gamma(\infty)} = \exp(-t/\tau) \quad (7)$$

where  $\gamma(\infty)$  is the equilibrium S.T.,  $\gamma(0) - \gamma(\infty)$  a constant and  $\tau$  the relaxation time. The  $\tau$  for the Dow PSt.-tetralin solutions were thus found to be 71.3 and 14 min. for the samples having  $\bar{M}_w$  of  $1.5 \times 10^6$  and  $6 \times 10^4$ , respectively, while the  $\tau$  of the PVA-H<sub>2</sub>O were 36.5 and 28.2 min. for the samples having viscosity average degrees of polymerization of 2570 and 1740, respectively.  $\tau$  varies directly with the square root of  $\bar{M}_w$  or the viscosity average degree of polymerization.<sup>22</sup>  $\tau$  appears to decrease with concentration.

The order of magnitude of these relaxation times is not inconsistent with the view that the relaxation of the S.T. is controlled by diffusion from (or into) the interface of the pendant drop. If this is the case the relaxation time should be of the order of magnitude of the diffusion time as calculated from the Einstein relation

$$t_D = R^2/6D \quad (8)$$

where  $R$  is the radius of the drop and  $D$  the diffu-

(20) Experimental fits of the data to eq. 1 with  $\nu = t$  (completely deposited chain) and  $\nu = 1$  (rigid chain sticking into the bulk of the solution) lead to  $A_0$  values of  $4 \times 10^{-16}$  and  $8 \times 10^{-16}$  cm.<sup>2</sup>, respectively.

(21) H. A. Stuart, "Die Physik der Hochpolymeren," Vol. II, Springer Verlag, Berlin, 1953, p. 655.

(22) E.g. for PVA-H<sub>2</sub>O:  $\tau_{2570}/\tau_{1740} = 1.29 \approx 1.26 = \sqrt{2570/1740}$  while for Dow PSt.-tetralin:  $\tau_{1.5 \times 10^6}/\tau_{6 \times 10^4} \times 10^4 = 5.09 \approx 5 = \sqrt{1.5 \times 10^6/6 \times 10^4}$ .

sion constant of the polymer. For a typical value of  $R$  of 0.1 cm. and taking  $t_D \approx \tau$ , we find for the Dow PSt. in tetralin with  $\bar{M}_w = 1.5 \times 10^6$  a value of  $D$  of  $4 \times 10^{-7}$  cm.<sup>2</sup>/sec. This compares, in order of magnitude at least, with a diffusion constant of  $1.06 \times 10^{-7}$  cm.<sup>2</sup>/sec. reported<sup>23</sup> for a PSt. fraction in toluene with a  $\bar{M}_{w,w}$  of  $1.1 \times 10^6$ .<sup>24</sup> Such a diffusion process is caused not by the presence of an initial concentration gradient but by a

(23) H. A. Stuart, ref. 21, p. 474.

(24) The  $M$  dependence of  $\tau$  (since  $\nu \approx 1/D$ ) is not inconsistent with the above.

gradient in chemical potential of the polymer in the drop.

**Acknowledgments.**—We are grateful to Dr. E. Fatt and his associates at the California Research Center for allowing us to study their pendant drop apparatus. Finally we wish to thank Prof. K. J. Mysels for many valuable suggestions and clarifying discussions in connection with the experimental work as well as for his interest in this problem.

LOS ANGELES, CAL.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## Displacement Reactions at the Sulfur Atom. I. An Interpretation of the Decomposition of Acidified Thiosulfate

BY ROBERT EARL DAVIS<sup>1</sup>

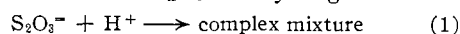
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The kinetic results of La Mer and co-workers on the decomposition of acidified sodium thiosulfate in dilute aqueous solution have been interpreted on a mechanistic basis. The initial rate of production of sulfur is given by the rate  $k(\text{Na}_2\text{S}_2\text{O}_3)^{3/2}(\text{HCl})^{1/2}$ . This rate expression has been explained using a series of nucleophilic displacement reactions at the sulfur atom. The proposed reactions fit the experimental data and the rate laws are derived. The production of various polythionic acids and hydrogen sulfide during the decomposition has been explained.

### Introduction

The decomposition of acidified sodium thiosulfate solutions has received intensive study<sup>2-12</sup> and has been important in the development of the physical chemistry of colloidal solutions.<sup>6-10</sup> The products of the reaction have been determined<sup>4-6,12</sup> and various kinetic investigations have been made,<sup>4-6,8,11,12</sup> but the results have remained essentially unexplained and difficult to interpret on a mechanistic basis.<sup>11</sup> Any proposed mechanism must be able to explain the products of the reaction, and the results of the kinetic studies: the reaction order and the effect of salts upon the rate.

**Products.**—The products of reaction 1 are sulfur dioxide, colloidal sulfur,  $\text{S}_8$ ,  $\text{S}_6$ , various polythionic acids of the formula  $\text{H}_2\text{S}_x\text{O}_6$  and hydrogen sulfide.



The nature of the products has been determined by Bassett and Durrant<sup>5</sup> and confirmed by other workers. Several forms of sulfur are produced in the reaction; much of the sulfur occurs as  $\text{S}_8$  and some as insoluble sulfur which is a polymeric form having long sulfur chains. Hexatomic sulfur,  $\text{S}_6$ , is produced in small yield from the decomposition of concentrated solutions of sodium thiosulfate and

hydrochloric acid in the cold.<sup>13,14</sup> This form has been characterized by molecular weight determinations, by its greater reactivity,<sup>14</sup> by its ultraviolet spectrum<sup>14,15</sup> and by X-ray diffraction patterns.<sup>16</sup> The production of the polythionic acids can be increased by the addition of varying amounts of arsenic trioxide<sup>17,18</sup> to the reaction mixture. The presence of hydrogen sulfide formed during the reaction escaped the attention of many of the early workers but has been detected in small amounts.<sup>5,19</sup> The yield of hydrogen sulfide has always been low; this would be expected because sulfur dioxide and hydrogen sulfide react in water, producing among other products sulfur.<sup>18,20</sup> The results of the radiochemical study of reaction 1 demonstrate that the two sulfur atoms of thiosulfate are not equivalent<sup>21</sup> and that during the preparation of thiosulfate and during the decomposition in acid the sulfur atoms maintain their identities and individualities.

(13) A. H. W. Aten, *Z. physik. Chem.*, **68**, 321 (1914).

(14) P. D. Bartlett and G. Meguerian, *THIS JOURNAL*, **78**, 3710 (1956).

(15) R. E. Whitfield, Thesis, Harvard University.

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