sition from the first excited singlet to the ground triplet state

$$D^* \longrightarrow D'$$

is greatly enhanced by the paramagnetic ion. Presumably the probability of the radiative transition

$$D' \longrightarrow D + h\nu'$$

likewise is increased. The present results demonstrate that the non-radiative transition

$$D' \longrightarrow D$$

similarly is enhanced. At room temperature in fluid solvents, the non-radiative transition is dominant; but, at low temperatures in rigid solutions, the radiative transition (phosphorescence) is relatively important. The non-radiative process appears to be strongly dependent upon either the temperature or the viscosity of the medium, while the radiative transition is probably largely independent of these factors.

We were likewise unable to observe any transient spectral changes when aqueous solutions of hemoglobin, oxyhemoglobin or the bacteriochlorophyll–protein complex were used.

In an attempt to confirm Gibson's interesting results[15] we made a few measurements using carboxyhemoglobin in water, in the presence and in the absence of air. A flash of light induced in these solutions a short-lived increase in absorption at wave lengths between 400 and 455 mμ. The half duration of this transient was roughly 250 μsec. That this change was due to the same photochemical intermediates as were studied by Gibson is improbable; the present data are insufficient to resolve this doubt.

[15] Q. Gibson, *J. Physiol.* (*London*), **134**, 123 (1956).

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

Surface Tension of Synthetic High Polymer Solutions. II[1]

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The equilibrium value and the rate of approach to equilibrium of the surface tension of purified block copolymers of polyethylene oxide and polyoxypropylene in tetralin have been measured. As in the polystyrene–tetralin system,[3] the surface tension increment of relatively dilute solutions changes sign from minus to plus as the molecular weight of the polymer solute decreases. Further surface tension measurements are reported on a mixture of a high and low molecular weight polystyrene fraction in tetralin which have individually been studied[3] previously and on polyvinyl alcohol fractions in water (in particular one foam fractionated sample).

Introduction

In a previous communication[3] we described the use of a modified pendant drop apparatus for the investigation of the equilibrium value and the rate of approach to equilibrium of the surface tension (s.t.) of polymer solutions and reported s.t. data on a number of polystyrene (PSt) fractions in tetralin. The s.t. increment (*i.e.*, s.t. of the solution − s.t. of the solvent) of the PSt solutions changes sign as the molecular weight of the polymer solute decreases, as expected from theory,[4] due to an entropy effect. This in turn suggested[3] that s.t. measurements on a solution of polydisperse polymer sample may be sensitive to the low molecular weight tail of the molecular weight distribution.

We report here the results of s.t. measurements on tetralin solutions of purified block copolymers obtained by condensing ethylene oxide (EO) on a polyoxypropylene base (PO) to form polymers whose structure is believed to be $HO-(C_2H_4O)_x-(C_3H_6O)_y-(C_2H_4O)_z-H$ (POEO).[5] Like the PSt–tetralin solutions,[3] the POEO–tetralin solution s.t. increments change sign (from minus to plus) as the molecular weight ($\bar{M}$) of the polymer solute decreases. To test the sensitivity of a s.t. measurement to the presence of lower molecular weight polymer the s.t. of a mixture of two PSt fractions ($\bar{M} = 1.6 \times 10^4$, 8.7×10^4) in tetralin has been found.

Experimental

All s.t. measurements were carried out at 25 ± 0.1° using the pendant drop apparatus whose construction and operation were described elsewhere.[3]

Three POEO samples were studied; these were highly purified Pluronic (surfactant type) L31, L61 and L81[5] whose characteristics are listed

Sample	EO/PO ratio	$\bar{M}$ (Chem.)	Cloud pt., °C., 10% sol.	Ash content, %
POEO-L31	0.18	1070	29	0.01
POEO-L61	.15	2045	17	Nil
POEO-L81	.18	2470	15	Nil

The two PSt fractions and two polyvinyl alcohol (PVA) fractions used have been characterized previously.[3] One of the PVA fractions having a viscosity average degree of polymerization of 1700 was further foam fractionated. 250 ml. of a 1 g./100 ml. aqueous solution of this PVA was placed in a beaker and nitrogen was bubbled through the solution by means of a gas dispersing tube. The rate of flow of nitrogen was adjusted so that half of the polymer solution was foamed out over a period of about two hours. After all the foam had been removed, the remaining PVA solution was transferred to a weighed beaker and dried at 65 ± 10° to constant weight. The resultant PVA film was partially redissolved in water to a known volume of solution. The portion of the film remaining in the beaker was dried again to constant weight. A 0.804 g./100 ml. aqueous PVA solution was thus obtained having a viscosity number

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[1] Supported by the Office of Ordnance Research, U. S. Army.

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[3] H. L. Frisch and S. Al-Madfai, THIS JOURNAL, **80**, 3561 (1958).

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

[5] We are indebted to Dr. D. R. Jackson and Dr. K. C. Frisch of the Research Department of the Wyandotte Chemical Corporation for supplying us with these purified polymers.

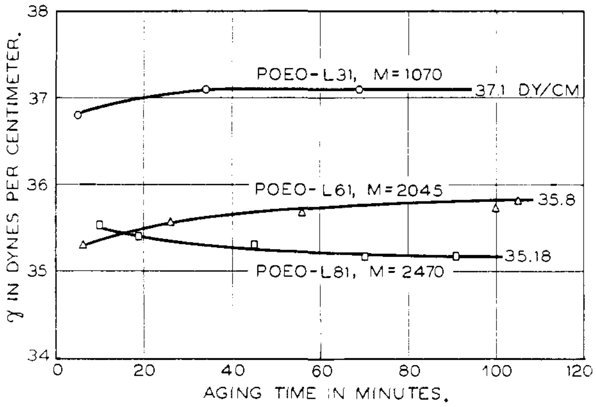

Fig. 1.—The surface tension of 1% POEO in tetralin as a function of time.

(25 ± 0.1°) of 0.971. This corresponds to a viscosity average degree of polymerization (D.P.) of 2010.[6]

The solvents used were distilled water and sodium dried tetralin, b.p. 207.9°, equilibrium s.t. of 35.*30* dynes/cm.

Results[7]

The experimental error in the s.t. measurements of the tetralin solutions is believed not to exceed ±0.1 dyne/cm. while the error in the s.t. measurements of the aqueous solutions is believed not to exceed ±0.3 dyne/cm. (The last significant figure of any entry is *italicized.*) The equilibrium s.t. increments ($\Delta\gamma$ in dyne/cm.) at 25 ± 0.1° of the polymer solutions are listed in Table I.

Table I

Surface Tension Increments of Polymer Solutions at 25 ± 0.1°

——Concn. (g./100 ml.)—— Polymer	Solvent	1.0 $\Delta\gamma$	0.8 $\Delta\gamma$	0.5 $\Delta\gamma$	0.2 $\Delta\gamma$
POEO-L81 M = 2470	Tetralin	− 0.*1*	...	...	...
POEO-L61 M = 2045	Tetralin	+ 0.*5*	...	+ 0.*3*	...
POEO-L31 M = 1070	Tetralin	+ 1.*8*	...	+ 1.*6*	...
1:1 (by wt.) (Szwarc) PSt. Mixture $M = 8.7 \times 10^4$ and 1.6×10^4	Tetralin	+ 0.*2*	...	...	...
PVA D.P. = 2570	Water	−22.*5*	...	−19.*7*	−18.*3*
PVA D.P. = 1740	Water	−20.*2*	...	−17.*7*	−16.*5*
FOAM Fctd. PVA D.P. = 2010	Water	...	−16.*7*	...	...

Typical apparent $\Delta\gamma$ *versus* surface aging time curves for the POEO–tetralin system are shown in Fig. 1. The equilibrium s.t. of the PSt mixture in tetralin was attained in about 20–25 minutes and did not change thereafter.

Discussion

Polymers similar to the POEO samples studied are known to be moderately strongly surface active in water in the same concentrations as used in this study, *e.g.*, a 1 g./100 ml. aqueous solution of Pluronic L62 (EO/PO Ratio of 0.14, $M \sim 2500$) has an apparent s.t. (ring balance) of 35 dyne/cm. at 30°.[5] The completely different s.t. behavior in tetralin of these materials at least tentatively can be ascribed to the fact that the polyethylene oxide portion is not strongly lyophilic and the polyoxypropylene portion is not strongly lyophobic in this solvent as they are in water. Treating, in rough approximation, the 1 g./100 ml. POEO–tetralin solutions as a dilute solution of Gaussian random coils to which equations 2 and 4 of reference 3 apply we find, by a least squares fit, that

$$\Omega = \left(\frac{\Delta\gamma}{c}\right)_{c=1\%} = \mathit{1}.6 \times 10^2 M^{-1/2} - \mathit{1}.0 \log M \quad (1)$$

roughly reproduces the observed molecular weight dependence of the data, where c is the concentration (g./100 ml.). This corresponds to an ideal area per deposited anchor segment, A_0 (*cf.* equation 6 of reference 3), of 3.5×10^{-16} cm.^{2}, whose order of magnitude is not unreasonable.

As expected from theory[3,4] the s.t. increment of the 1 g./100 ml., 1:1 by weight, mixture of the (Szwarc) PSt of $M = 1.6 \times 10^4$ and 8.7×10^4 in tetralin is within the experimental error (±0.1 dyne/cm.) equal to the s.t. increments of the 0.5 g./100 ml. solution of the (Szwarc) PSt of $M = 1.6 \times 10^4$ of 0.1 ± 0.*1* dyne/cm. (and of the calculated value).[3]

The concentrations of the aqueous PVA solutions are still far from dilute as can be seen from the extrapolation to zero concentration of the data in Table I. This is also the case with aqueous solutions of other moderately surface active polymers such as the POEO, polyethylene glycols,[8] etc. Due to the non-ideality of these polymer solutions, the concentration dependence is expected to be quite complex.[4] The data in Table I are in agreement with the general conclusion[3,4] that $\Delta\gamma$ of a solution of a given surface active polymer is the more negative the larger M. The s.t. behavior of the foam fractionated PVA solution is anomalous. We are not able at this time to decide whether this is due to the presence of a surface active impurity (whose concentration is decreased by the foam fractionation), the selective removal by the foam fractionation of PVA possessing fewer than an average of 10% acetyl groups, etc.

In conclusion we wish to thank Professor K. J. Mysels for his interest and the guidance given to one of us (S.A.M.).

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[6] A. Nakajima and K. Furatata, *Chem. High Polymers*, **6**, 460 (1949).

[7] A complete tabulation of the experimental data is given in the Supplement to the M.S. thesis of S. Al-Madfai, University of Southern California.

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