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Measurement of Surface Tension in Aqueous Polymerizing Systems

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ABSTRACT

Surface tension measurements on a polymerizing system can yield information concerning concentration changes of surface-active species present in the system. Such measurements have hitherto been performed under conditions more or less remote from those obtaining during the actual polymerization. The use of a twin-capillary dilatometer permits, in principle, the simultaneous determination of both conversion and surface tension as a function of time. The design of such a dilatometer is described, the precautions associated with its use examined, and its application to the monitoring of the surface tension of various polymerizing systems discussed.

INTRODUCTION

The presence (or formation) of surface-active species is of paramount importance in the interpretation of the observed kinetics of polymerization. It is therefore highly desirable to be able to monitor the surface tension of a polymerizing system.

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Changes in the surface tension of polymerizing systems (both in emulsion and in aqueous solution) have been reported by a number of workers [1-5]. The surface tension measurements have generally been performed on samples taken from the reaction mixture after separation of most of the monomer phase (if appropriate). The measurements have thus been carried out under conditions differing appreciably from those obtaining during the actual polymerization, and may not be truly representative of the changes occurring in the system.

Of the many techniques available for the measurement of surface tension, the method of differential capillary rise is most readily adapted for the present purpose (although a pendent-drop technique is also currently under consideration). Dilatometry offers a convenient means of monitoring the extent of reaction, and the addition of a second capillary to the dilatometer permits the simultaneous measurement of the surface tension of the system.

EXPERIMENTAL

Apparatus

The design of the dilatometer is shown in Fig. 1. The volume of the dilatometer was calculated from the mass of distilled water required to fill the apparatus from tap A to the top of the narrower capillary. The diameters of the capillaries were determined with the aid of mercury. The positions of the liquid levels in the capillaries were measured to ± 0.001 cm with the aid of a cathetometer. The dilatometer was immersed in a glass tank (100 dm^3 capacity) containing distilled water maintained at 50.00 ± 0.02°C by means of a Haake E52 temperature regulator.

Materials

All solutions were prepared in boiled-out doubly distilled water.

Potassium peroxydisulfate (B.D.H. Ltd.) was recrystallized from water. Analysis by means of $Fe^{2+}/KMnO_4$ [6] showed the purity of the recrystallized material to be 99.9 ± 0.3%.

Acrylonitrile (B.D.H. Ltd.) was distilled at atmospheric pressure. The fraction boiling at 77°C was collected and stored in a brown glass bottle.

Styrene (Ajax Chemicals) was freshly distilled before use (bp 40.6°C/16 torr).

Sodium oleate was prepared by the slow addition of alcoholic sodium hydroxide solution to a solution of freshly distilled oleic acid in ethanol. The crude soap was recrystallized from ethanol, dried, and extracted for 70 h with anhydrous ether. The purified material was stored under vacuum.

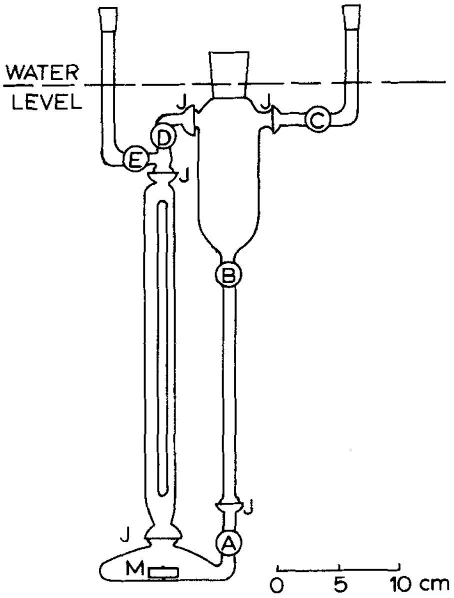

FIG. 1. The twin-capillary dilatometer. A-E: Teflon taps. J: Greaseless ball-joints. M: Magnetic stirring bar.

General Procedure

All glassware was cleaned with chromic acid and rinsed with copious quantities of doubly distilled water. The dilatometer was dried by immersing it in the thermostat (generally at 50°C) and drawing filtered air through the apparatus. After being dried, the whole assembly was purged with oxygen-free nitrogen. The reaction mixture was admitted to the bulb of the dilatometer and stirred gently, care being taken to avoid foaming. The liquid was subsequently admitted to the capillaries. The liquid levels were then lowered slightly from their initial positions to facilitate adequate wetting of the capillary walls. The positions of the liquid levels in the capillaries were measured alternately at 0.5 min intervals.

Systems Studied

To check the performance of the apparatus, the surface tensions of distilled water, aqueous acrylonitrile (4% w/v), and aqueous sodium oleate (0.002 mol/dm^3) were measured.

Acrylonitrile Polymerization (50.00°C)

The reaction mixture consisted of 4% (w/v) aqueous acrylonitrile containing 0.001 mol/dm^3 $K_2S_2O_8$. The liquid was admitted to the capillaries either just before or immediately after the onset of polymerization (indicated by the development of turbidity in the dilatometer and filling vessel).

Polymerization of Styrene in Aqueous Solution

Two systems were studied: (i) 0.0021 mol/dm^3 styrene, 0.0148 mol/dm^3 $K_2S_2O_8$ at 50°C; (ii) 0.0043 mol/dm^3 styrene, 0.0148 mol/dm^3 $K_2S_2O_8$ at 70°C (cf. Ryabova et al. [5]). In System (ii), samples were also taken from the bulk solution during the reaction, quenched by the addition of hydroquinone and rapid cooling, and the surface tensions of the samples measured at 25°C, using the method of differential capillary rise.

Emulsion Polymerization of Styrene (50.00°C)

Styrene (5.17 g) was mixed with water (88.0 g) and sodium oleate (0.258 g), and the monomer emulsified at 50°C with the aid of an Ultra Turrax TP 18/2 homogenizer. After the foam had subsided, 5.00 cm^3 of $K_2S_2O_8$ solution (0.01145 mol/dm^3) was carefully mixed with the emulsion. The magnetic stirrer was then started and the dilatometer filled. Control experiments with initiator-free systems showed the amount of thermally initiated polymerization to be negligible.

Calculations

For approximately hemispherical menisci, a first approximation to the surface tension, $\gamma^{(1)}$, is given by

$$\gamma^{(1)} = \Delta\rho g r_w r_n (h_n - h_w)/2(r_w - r_n) \qquad (1)$$

where $\Delta\rho$ is the density difference across the interface and h denotes the position of the meniscus in a capillary of radius r. The subscripts n and w identify the narrow and the wide capillary, respectively. In our apparatus, $r_n = 0.02765$ cm and $r_w = 0.1575$ cm.

A more exact relationship is

$$\gamma = \Delta\rho g b_w b_n (h_n - h_w)/2(b_w - b_n) \qquad (2)$$

where b denotes the radius of curvature at the bottom of the meniscus. An iterative procedure may then be employed to obtain better approximations to γ [7,8]. The surface tensions reported herein were generally calculated with the aid of Eq. (1); the use of Eq. (2) would only reduce the values by about 0.6×10^{-3} N/m (0.6 dyn/cm).

The conversion of monomer to polymer was calculated from

$$\%\ \text{conversion} = (100\pi / w_m K_m)(r_w{}^2 \Delta h_w + r_n{}^2 \Delta h_n) \tag{3}$$

where w_m is the mass of monomer in the dilatometer, Δh represents the change in the liquid level in a capillary, and K_m is the specific contraction, i.e., the volume change per gram of polymer formed. The values of K_m used in this work were: acrylonitrile: 0.283 cm^3/g [9]; styrene: 0.188 cm^3/g [10].

The density of the acrylonitrile solution was determined with the aid of 100 cm^3 volumetric flasks, calibrated at the appropriate temperature. Other density values were taken from the literature [11a, 12].

RESULTS

The results of the preliminary surface tension measurements are shown in Table 1.

(a) Figure 2 shows the time-dependence of the surface tension of an aqueous acrylonitrile solution, as well as the changes in % conversion and in surface tension as a function of time.

(b) The surface tensions of aqueous styrene solutions (both 0.0021 and 0.0043 mol/dm^3) did not differ significantly from the surface

TABLE 1. Surface Tension Values

		$10^3\gamma$ (N/m)		
Substance	t (°C)	Eq. (1)	Eq. (2)	$10^3\gamma$ (N/m) (lit.)
Water	50.00	69.0	68.3	67.91 (11b)
Water	25.2	73.0	72.3	71.93 (11b)[a]
Sodium oleate (0.002 M)	28.7	26.6	26.0	24.29 (13)[b]
Acrylonitrile (4% w/v)	50.00	51.5		

[a] Interpolated value.
[b] At 20°C.

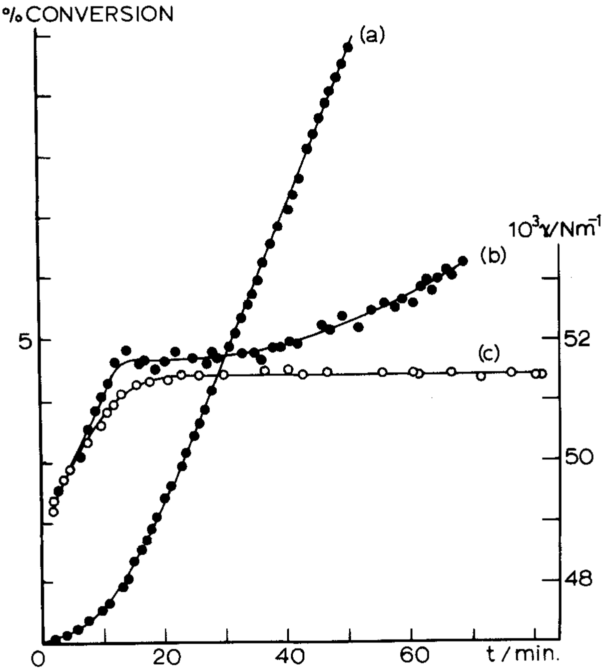

FIG. 2. Conversion and surface tension vs time for 4% (w/v) aqueous acrylonitrile: (a) conversion curve, (b) surface tension curve, (c) surface tension in the absence of initiator.

TABLE 2. Surface Tensions during the Aqueous-Phase Polymerization of Styrene

System	t (°C)	$10^3\gamma^{(1)}$ (N/m)	$10^3\gamma(H_2O)$ (N/m) (11b)
(i) All conversions	50	68.2	67.91
(ii) All conversions	70	65	64.4
(ii) Quenched samples	25	72	71.97

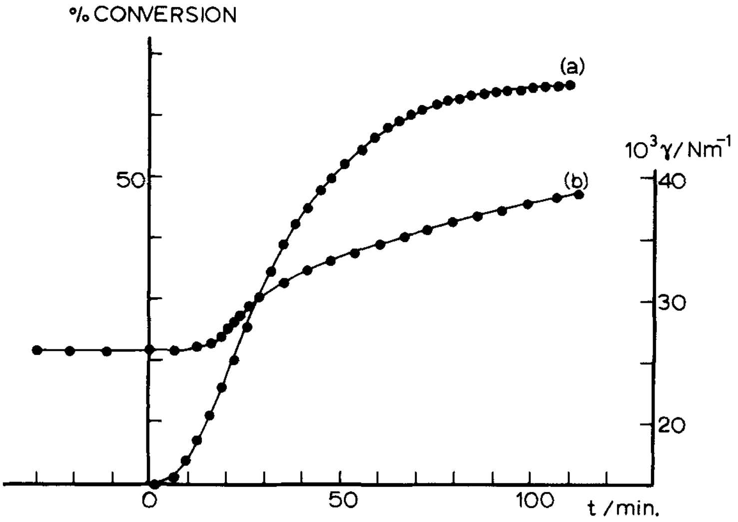

FIG. 3. Conversion and surface tension vs time for the emulsion polymerization of styrene: (a) conversion curve, (b) surface tension curve.

tension of water at the appropriate temperature. The decrease in surface tension during polymerization, reported by Ryabova et al. [5], was not observed. See Table 2.

(c) Figure 3 reproduces the results obtained during the emulsion polymerization of styrene.

DISCUSSION

The low values for the calculated surface tensions in the first 10 to 15 min for both the polymerizing and initiator-free acrylonitrile systems are attributable to the (clearly visible) nonzero contact angle caused by initial adsorption of acrylonitrile vapor onto the glass walls prior to filling the capillaries. Once the liquid is in contact with the walls, reequilibration would be expected to occur. After a period of 20 min in the initiator-free acrylonitrile solution, the lowering of the liquid levels resulted in a contact angle visually indistinguishable from zero. In the polymerizing system the receding menisci helped to ensure the contact angle remained indistinguishable from zero after 12 min of polymerization. The subsequent rise in the surface tension of the polymerizing system is consistent with the reduction of the bulk concentration of acrylonitrile. There was no evidence of polymer deposition on the capillary walls.

For aqueous styrene (system ii), Ryabova et al. [5] reported that the surface tension decreased by about 15×10^{-3} N/m during the first 50 min of polymerization, and regarded the decrease as evidence for the formation of highly surface-active oligomers. All our measurements on the same system have consistently yielded a constant value of 65×10^{-3} N/m for the surface tension throughout the polymerization. This suggests that any surface-active species formed during the polymerization are present at a concentration far lower than that implied by Ryabova's results.

The fairly sharp increase in the surface tension of a polymerizing emulsion of styrene in water is in agreement with Harkins' observation [1, 2]. The rise does not appear to be the result of the oxidation of sodium oleate by the peroxydisulfate, as control experiments failed to detect a significant change in surface tension over a period of 20 h.

The possibility of "creaming" of the emulsion makes the relative positions of the conversion and surface tension curves (Fig. 3) uncertain, but the actual rise in the surface tension is unequivocal.

Several practical points also deserve mention:

1. Bubbles in the capillaries must be removed.
2. The use of Eqs. (1) and (2) requires that the contact angles be zero. Receding menisci help to ensure this.
3. Inhibition by atmospheric oxygen can be avoided by purging the apparatus with nitrogen.
4. Diffusion up the capillaries is slow and may make the surface region unrepresentative of the bulk. Test experiments on surface tension changes of soap solutions in the apparatus showed that "pumping" the liquid up and down in the capillaries provides adequate mixing. For the experiments reported here, this pumping was carried out only when the liquid was admitted to the capillaries.
5. Evaporation of volatile constituents from the interfacial region can be avoided by allowing the vapor spaces in the filling vessel and in the dilatometer to come to equilibrium prior to allowing the liquid to enter the capillaries.
6. The breaking of an emulsion in either capillary precludes meaningful surface tension measurements.
7. "Creaming" of emulsions will alter the density difference across the interface as well as changing the composition of the system with respect to the bulk.
8. Foam is best avoided. A small amount can be tolerated in the wide capillary.

SUMMARY AND CONCLUSIONS

There was no detectable decrease in the surface tension of initially homogeneous systems during polymerization. The surface tensions of aqueous styrene solutions remained constant for the duration of the reaction, and did not differ significantly from the surface tension of water at the same temperature. The rise in surface tension observed during the polymerization of an aqueous solution of acrylonitrile was consistent with the decrease of monomer concentration as a result of polymerization.

The rise in surface tension during the emulsion polymerization of styrene could not be attributed to the peroxydisulfate oxidation of sodium oleate, and was consistent with Harkins' observation.

Although a number of precautions are necessary in its use, the dilatometer described in the present work was found to be quite suitable for the simultaneous measurement of conversion and surface tension in aqueous polymerizing systems.

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