

The Effect of the Gamma-Ray Irradiation on Interfacial Electrical Properties of Polypropylene Fibres

Shizuo UEDA*, Shiro ISHIDA**, Akira WATANABE+
and Fukuju TSUJI**

(Department of Agricultural Chemistry, Faculty of Agriculture, Kyoto University*,
The Nippon Oils and Fats Company, Ltd.**, Gotoh+ and Koizumi**
Laboratories, Institute for Chemical Research, Kyoto University)

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The zeta potential of polypropylene fibers in contact with surface active agent solutions was measured by streaming potential method, and the free energies of adsorption and numbers of available sites were calculated. It was found that the interfacial electrical behaviour of these fibres is strongly influenced by the gamma-ray irradiation in air or water. The infra-red absorption spectra were also examined, which showed, in agreement with the results mentioned above, that negatively dissociating groups are formed by the exposure of fibres to the gamma-ray irradiation.

1. INTRODUCTION

Among many synthetic fibres as the materials for textiles, fabrics etc., the polypropylene fibre is one of the most promising ones not only from the economical point of view but also by the superiority in its physical as well as chemical properties to other fibres. These are the low density, low hygroscopy, high mechanical strength, high resistance against chemicals, the feasibility to spinning with other fibres etc., and are mainly ascribed to its chemical structure, the linear saturated hydrocarbon without cross-linking, having methyl groups in the isotactic configuration. However, this very structure at the same time gives rise to the difficulty in dyeing. Although quite a few experiments have been made in order to improve this drawback^{1,2)} none of them can be said to be satisfactory. The present work was undertaken in order to see whether it is possible to use successfully the gamma-ray irradiation for it³⁾. Since dyeing properties of fibres in general are intimately related to the interaction between dye molecules and the fibre surface⁴⁾, one of the fundamental methods of studying is afforded by the interfacial electrical properties of fibres^{5,6,7,8,9)}. We, therefore, measured the streaming potential produced at the interface between the fibres and cationic surface active agent solutions, examining how the zeta potential was influenced by the exposure to the gamma-ray irradiation of the polypropylene fibres.

* 上田 静男, ** 石田 祀朗
+ 渡辺 昌, ++ 辻 福寿

2. EXPERIMENTAL

1. Materials

The polypropylene fibres employed were prepared by the Mitsubishi Rayon Co. Ltd. The gamma-ray irradiation was carried out by the 2,000 C Co-60 gamma-ray irradiation facility of the Institute for Chemical Research, Kyoto University^{10,11}. The polypropylene fibres treated under various conditions will be denoted as follows :

PO fibres ; unexposed to the gamma-ray irradiation,

PA fibres ; exposed to the gamma-ray irradiation in air at

PA1 ; 1.0×10^6 r, PA2 ; 4.1×10^7 r and PA3 ; 7.0×10^7 r.

PW fibres ; exposed to the gamma-ray irradiation in distilled water, at

PW1 ; 1.0×10^6 r, PW2 ; 4.1×10^7 r and PW3 ; 7.0×10^7 r.

Ordinary distilled water was passed through a column of ion exchange resins and redistilled from an all Pyrex apparatus ; this gave water of specific conductivity 1.6×10^{-6} ohm⁻¹ cm⁻¹, which was used for all experiments.

The potassium chloride used as the supporting electrolyte for the streaming potential measurements¹² was of analytical grade. The cationic surface active agents used¹³ were dodecyl (DPC) and cetylpyridinium chloride (CPC).

2. Measurements of the Zeta-Potential by the Streaming Potential Method

Aliquots of surface active agent solutions were forced to pass through a

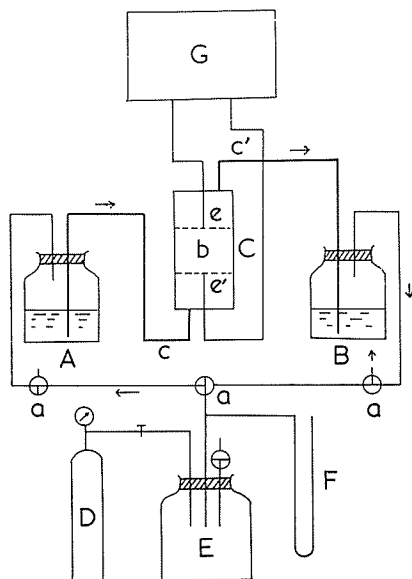


Fig. 1. The measurements of streaming potentials. A, B, Reservoirs for test solutions ; C, cell ; D, nitrogen bomb ; E, gas trap ; F, manometer ; a, three-way cocks ; b, fibre packings ; c, solution inlet ; c', solution outlet ; e, e', perforated platinum electrodes.

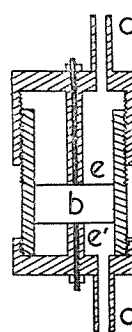


Fig. 2. The cell for streaming potential measurements. The notations are the same as in figure 1.

column of fibres, and the streaming potential was measured as a function of the applied pressure. The block diagram of the experimental device is given in Fig. 1. The cylindrical cell C consisted of polyacryl resin and of inner radius 20 mm, see Fig. 2. The electrodes e and e' were perforated platinum discs of radius 20 mm and set at a distance of ca. 10 mm¹²⁾. The solutions always contained 1×10^{-4} M KCl as the supporting electrolyte in addition to the surface active agents. 400 mg of polypropylene fibres, 5 mm long and well separated, were packed in the space b between the electrodes in Fig. 2, and were thoroughly washed by the solution under test and then dipped in the solution for 30 hours. Preliminary experiments showed that this time was sufficient for the adsorption equilibrium to be established.

The ζ -potential was calculated from the slope of the streaming potential E as a function of the applied pressure P , by using the Helmholtz equation⁷⁾, viz.

$$\zeta = (4\pi\eta/D)(E/P)\lambda \quad (1)$$

where η is the viscosity, D the dielectric constant and λ the specific conductivity of the solution under test, respectively. Fig. 3 shows typical examples of E vs. P relations. It is clear that a good linearity holds over the whole pressure range examined, giving a consistent value of ζ for each case.

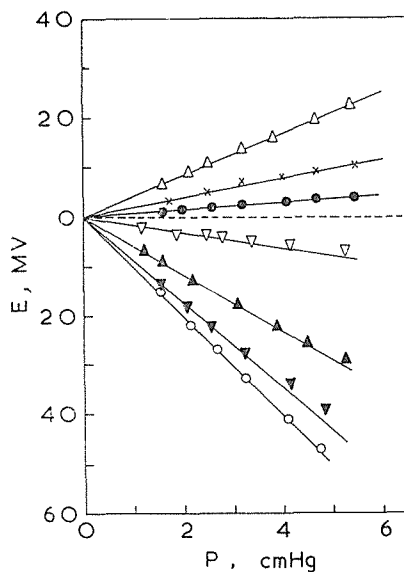


Fig. 3. E vs. P for PW3 fibres in contact with 10^{-4} M KCl solutions containing CPC at various concentrations:

○, 10^{-7} ; ▼, 10^{-6} ; ▲, 2.5×10^{-6} ; ▽, 5×10^{-6} ; △, 10^{-4} ; ×, 5×10^{-4} ;
●, 5×10^{-3} M.

Measurements of specific conductivities were carried out by employing the Yanagimoto ac. bridge, type MY-7. The critical micelle concentrations for surface active agent solutions containing 10^{-4} M KCl as the supporting electrolyte were obtained experimentally from points of discontinuity of specific conductance vs. surface active agent concentration plottings.

3. Measurements of the Infra-red Absorption

Infra-red absorption spectra of polypropylene fibres were taken by using the Nippon Bunko D.S. 301 Infra-red Spectro-photometer.

3. RESULTS

1. ζ vs. $\log c$ Curves for PO Fibres

Fig. 4 shows ζ vs. $\log c$ curves for PO fibres in contact with DPC and CPC solutions. It is noticed in the case of DPC solutions that the negative ζ value of about -0.5 mV for $c=0$ changes gradually in the positive direction with increasing c , the zero point of charge c_0 occurring at $c_0=4.57 \times 10^{-6}$ M. The curve shows a sharp increase in slope at $c \cong 5 \times 10^{-4}$ M, a maximum at $c \cong 10^{-3}$ M and then decreasing tendency at c higher than this.

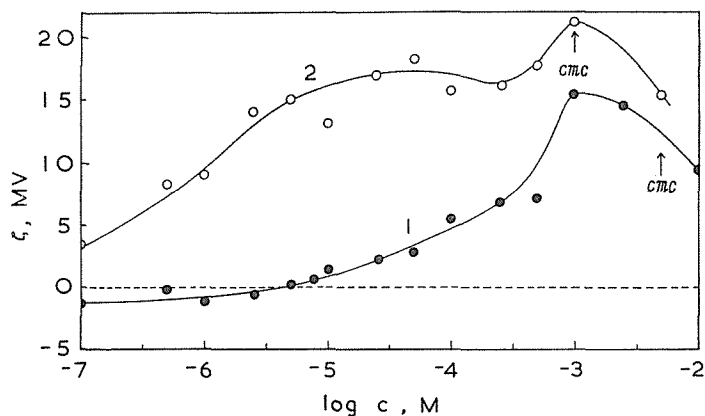


Fig. 4. ζ vs. $\log c$ for PO fibres. ●, DPC; ○, CPC.

In the case of CPC solutions, on the other hand, the initial negative ζ value of -0.5 mV for $c=0$ has already increased to a positive value of ca. $+3.5$ mV at the c value as low as 10^{-7} M, and then increases to a saturation value of ca. 17 mV. The occurrence of another sharp maximum at ca. 10^{-3} M is well defined. At concentrations higher than this the ζ value decreases with increasing c , a tendency which is observed also by the DPC solutions.

2. ζ vs. $\log c$ Curves for PA Fibres

The results for DPC solutions are given in Fig. 5 and 6, respectively. The general shape of curves is more or less the same as that for curves in Fig. 4. However, the effect of the gamma-ray irradiation on the shape of curves is apparent; this is characterized by the shift of curves in the negative direction of the zeta, *i.e.* the ordinate, axis as a whole. It is also noticed that the stronger the irradiation, the stronger the effect is.

A somewhat different behaviour is observed for the PA3 fibre in contact with CPC solutions as compared with other curves for PA fibres. This is the plateau observed over the concentration range from ca. 10^{-6} to 5×10^{-5} M with $\zeta \cong +4$ mV, indicating the completion of the monolayer adsorption. At concentrations higher

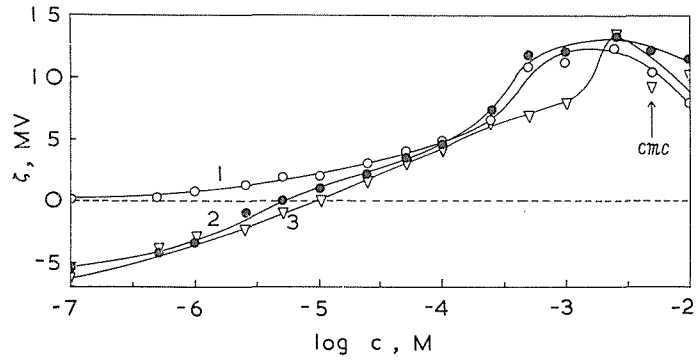


Fig. 5. ζ vs. $\log c$ for DPC solutions. \circ , PA1; \bullet , PA2; \triangle , PA3.

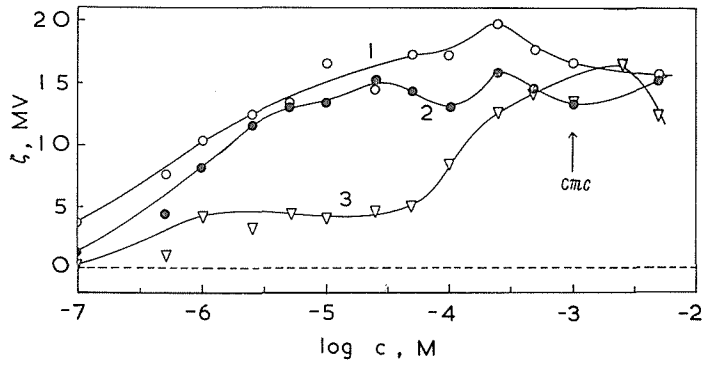


Fig. 6. ζ vs. $\log c$ for CPC solutions. \circ , PA1; \bullet , PA2; ∇ , PA3.

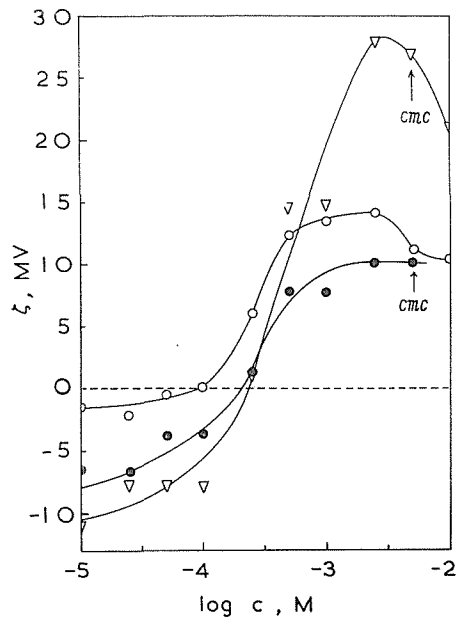


Fig. 7. ζ vs. $\log c$ for DPC solutions. \circ , PW1; \bullet , PW2; ∇ , PW3.

than this the ζ value starts to increase with increasing inclination; this appears to be due to the adsorption at different kind of sites or the polylayer adsorption at the same kind of adsorption sites, see later.

3. ζ vs. $\log c$ Curves for PW Fibres

The results are shown in Fig. 7 and 8 for DPC and CPC solutions, respectively. Although the effect is qualitatively the same as that given in the last section, the effect is much stronger than the latter. It is also observed that the zero points of charge shift to higher c values for PW fibres than for the PO for PA fibres. Among all experiments carried out in the present study the highest ζ value is attained by the PW3 fibre in contact with DPC solutions. It is noticed that the slope of curves DPC is extremely large over the concentration range from ca. 10^{-4} to 10^{-3} M.

In contrast to the fact that zero points of charge are lower than 10^{-7} M for PO or PA fibres in contact with CPC solutions, see sections 2 and 3, the reversal of charge occurs at c values higher than 10^{-7} M for the case shown in Fig. 8. The first monolayer adsorption appears to be complete at $\zeta \cong +10$ mV. It must be pointed out in this connexion that the completion of the monolayer adsorption is observed only in the case of the CPC for the PW fibres.

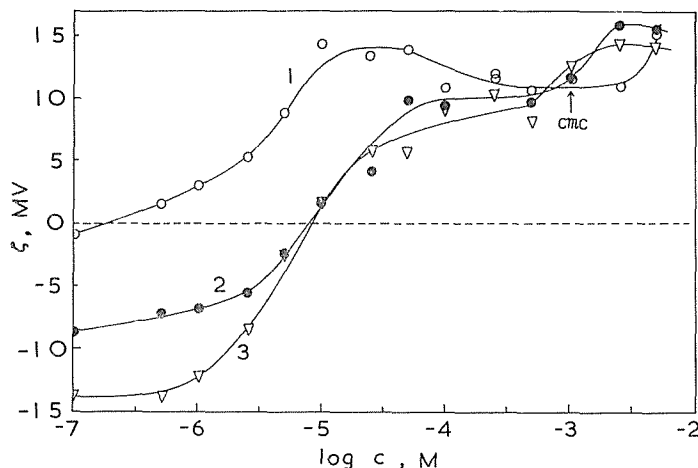


Fig. 8. ζ vs. $\log c$ for CPC solutions. \circ , PW1; \bullet , PW2; ∇ , PW3.

4. Infra-red Spectra

The infra-red spectra for PO, PA3 and PW3 fibres are shown in Fig. 9.

We shall first consider the case of PA3 fibre, curve B, as compared with the PO fibre, curve A. The increase in absorption at $3,200\text{ cm}^{-1}$ indicates the formation of OH groups by oxidation, while the absorption at $3,400$ and $3,555\text{ cm}^{-1}$ are due to hydroperoxide groups, since they disappear by treating this fibre in boiling water. The formation of carbonyl groups by oxidation is shown by the absorption at $1,708\text{ cm}^{-1}$ for R-COOH and that at $1,780\text{ cm}^{-1}$ for $>\text{C}=\text{O}$ groups. The presence of a wide absorption band over the range $3,000$ to $2,900\text{ cm}^{-1}$ for the CH stretching indicates the occurrence of the chemical change at

the methylene groups. The heights of the absorption bands at 997 and 965 cm^{-1} , which are considerably different from each other for the PO fibre, become almost the same for the PA3 fibre, indicating the decrease in the degree of crystallinity by the gamma-ray irradiation in air. Hence, in the case of the gamma-ray treatment in air, the presence of the oxygen prevents the formation of cross-linkage and thus oxidative degradation is the main reaction taking place.

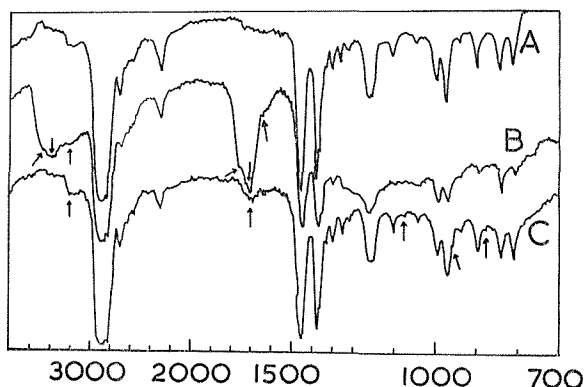


Fig. 9. Infra-red spectra. A, PO fibre; B, PA3 fibre; C, PW3 fibre.

The PW fibre shows absorptions at 1,075 and 3,200 cm^{-1} for the secondary alcohol group ($>\text{CHOH}$). The absorption at 960 cm^{-1} is attributed to the formation of transvinylidene radicals ($\text{RCH}=\text{CHR}'$), and that at 885 cm^{-1} to the formation of vinylidene radicals ($>\text{C}=\text{CH}_2$). It is therefore concluded that, in the absence of oxygen the formation of cross-linkages predominates and hence the degree of crystallinity does not change so much. This is shown by the conservation of the shape of the double absorption at 997 and 965 cm^{-1} . Due to the presence of the solvent, *i.e.* water, the formation of secondary alcoholic OH groups is also noticed, but the amount formed is smaller than in the case of the PA fibre. The formation of a small amount of carboxyl groups can also be noticed.

4. DISCUSSION

1. Adsorption Behaviours of DPC and CPC at Lower Concentrations

The general shape of experimental ζ *vs.* $\log c$ curves, showing the increase in ζ value in the positive direction by the addition of cationic surface active agents, is explained by the adsorption of these agents on the fibre surface. It is then possible to express these curves in terms of the theory proposed by the present authors¹²⁾. According to this theory, the ζ value of a plane surface in contact with a surface active agent solution is given as a function of the concentration c by

$$\zeta = [c_i / (c + c_i)]^{1/2} [\zeta^* + k_1 k_2 c / (1 + k_2 c)] \quad (2)$$

$$k_1 = (2\pi \cdot 1000 kT / Dc_i N)^{1/2} N_1 \quad (3)$$

and

$$k_2 = \exp(-\overline{\Delta G}/kT)/55.6 \quad (4)$$

where ζ^* is the ζ value for $c=0$; c_i is the molar concentration of the supporting electrolyte, which is 10^{-4} in the present case; k is the Boltzmann constant; T is the absolute temperature; N is the Avogadro number; N_1 is the number of adsorption sites per cm^2 ; and $\overline{\Delta G}$ is the electrochemical free energy adsorption of the cationic surface active agent, assumed to be uni-univalent electrolyte. Equation (2) was derived under the assumption that ζ is sufficiently small so that the so called Debye-Hückel approximation applies. If we assume in addition that the surface active agent concentration is very small, *i.e.* $c \ll c_i$, then we have

$$\zeta = \zeta^* + k_1 k_2 c / (1 + k_2 c) \quad (5)$$

and

$$d\zeta/d \log c = 2.303(\zeta - \zeta^*) + (\zeta - \zeta^*)/k_1 \quad (6)$$

at the zero point of charge, $\zeta=0$, this equation reduces to

$$(d\zeta/d \log c)_{\zeta=0} = -2.303*[1 + \zeta^*/k_1]. \quad (7)$$

Thus, N_1 can be estimated from the slope of ζ vs. $\log c$ curves by using equation (6) or (7), since k_1 values obtained therefrom are related to N_1 values by equation (3).

The electrochemical free energy of adsorption $\overline{\Delta G}$ is calculated by using equation (4) from k_2 , which is easily obtained from the zero point of charge $c=c_0$ by an equation

$$1/c_0 = -k_2[(k_1/\zeta^*) + 1] \quad (8)$$

This equation is derived from equation (5) by equating $\zeta=0$. It is also possible to obtain k_2 by

$$1/k_2 = c[k_1/(\zeta - \zeta^*) - 1] \quad (9)$$

This equation is used in the present calculation of $\overline{\Delta G}$, since the zero point of charge is very often lower than the lowest c value examined, *i.e.* 10^{-7}M , and hence the c_0 value obtained by extrapolation was not accurate. It is also important to state that for PO fibres in contact with DPC solutions the c_0 value and the slope $d\zeta/d \log c$ at the zero point of charge are so small that sufficient accuracy is not expected in order to work out k_1 value. The k_1 value obtained for CPC solutions was therefore used instead.

Most values of k_1 and k_2 were obtained at zero points of charge c_0 , but in some cases, especially for PW fibres in contact with DPC solutions, the calculations were made on the basis of data for $c=5 \times 10^{-6}\text{M}$. This is due to the fact that a sharp increase in $d\zeta/d \log c$ near c_0 indicates the occurrence of the second adsorption at such a low c value. We have, therefore, chosen the c value lower than c_0 at which only the first monolayer adsorption appears to be taking place. While, for PA fibres in contact with CPC solutions, the zero points of charge are lower than all concentrations examined, and hence the data for an arbitrarily chosen c value, *i.e.* $5 \times 10^{-7}\text{M}$, were adopted for the estimation of k_1 and k_2 . It can be seen in Fig. 6 that no second adsorption is taking place at this concentration.

Table 1. The adsorption characteristics of cationic surface active agents on polypropylene fibres.

Surface active agents Fibres	DPC		CPC	
	N_1 (cm ⁻²)	$-\Delta G$ (cal/mole)	N_1 (cm ⁻²)	$-\Delta G$ (cal/mole)
PO	(3.55 × 10 ¹²) ⁺	(7,830) ⁺	3.55 × 10 ¹²	11,100
PA1	0.59 × 10 ¹²	9,920	3.04 × 10 ¹²	11,400
PA2	1.97 × 10 ¹²	9,860	4.03 × 10 ¹²	11,500
PA3	2.89 × 10 ¹²	9,820	3.85 × 10 ¹²	11,800
PW1	1.70 × 10 ¹²	8,710	1.89 × 10 ¹²	11,900
PW2	2.72 × 10 ¹²	8,290	5.52 × 10 ¹²	9,340
PW3	2.87 × 10 ¹²	8,240	8.26 × 10 ¹²	9,120

⁺ Values estimated by using the k_1 value for the CPC.

The values of N_1 and $\Delta \bar{G}$ thus obtained are summarized in Table 1. The electrochemical free energy of adsorption $\Delta \bar{G}$ is related to the chemical free energy of adsorption ΔG by

$$\Delta \bar{G} = ze\psi + \Delta G \quad (10)$$

where ψ is the electrostatic potential of the adsorption layer. Since $\psi \cong \zeta \cong 0$ at or near the zero point of charge we can write

$$\Delta \bar{G} = \Delta G \quad (11)$$

It is clearly observed in Table 1 that the effect of the gamma-ray irradiation is to increase the number of adsorption sites for DPC and CPC, thus indicating the formation of new adsorption sites. This effect is more marked in the case where the irradiation is performed in water than in air.

In view of the fact that ΔG values are different for PW fibres and for PO or PA fibres, the difference being from 1 to 1.5 kcal/mole, for both the DPC and CPC solutions, the adsorption sites appear to be different for these two sets of fibres. This is also verified by the fact that the ζ^* value, *i.e.* the ζ potential in the absence of surface active agents, shifts to the negative direction by the exposure to the gamma-ray irradiation, as is shown in Table 2. This indicates that some sort of negatively dissociating groups are formed by this treatment, thus making the surface charge of fibres more negative than the original one.

Table 2. The change in ζ^* values.

Fibre	ζ^* (mV)
PO	-0.55
PA1	0.00
PA2	-4.96
PA3	-8.29
PW1	-5.13
PW2	-10.8
PW3	-13.8

The formation of such groups increases with increasing radiation doses.

The absolute values of ΔG in Table 1 are comparable to those obtained for other kinds of interfaces. Thus, ΔG values of DPC and CPC for negative silver iodide sols are 9,450 and 11,300 cal/mole¹⁶⁾, and for Pyrex glass diaphragms 7,810 and 9,570 cal/mole, respectively¹⁶⁾. The difference of about 2 kcal/mole in Table 1 for the increase in the hydrocarbon chain length from C12 to C16, that is ca. 500 cal/mole for each CH₂ group, is a reasonable value^{12, 13, 14, 15, 16)}.

2. The Adsorption Behaviours at Higher Concentrations

A sharp increase in ζ value over the concentration range from 10⁻⁴ to 10⁻³M indicates another adsorption mechanism which is taking place at higher c values. If we assume a second kind of adsorption sites, equation (2) is extended to include this mechanism as

$$\zeta = \left(\frac{c_t}{c+c'} \right)^{1/2} \left[\zeta^* + \frac{k_1 k_2 c}{1+k_2 c} + \frac{k_1' + k_2'}{1+k_2' c} \right] \quad (12)$$

However, the calculation of adsorption coefficients leads to a negative k_1' value, an improbable condition. It is therefore concluded that the adsorption at higher concentrations is not of the simple Langmuir type, but that some kind of poly-layer adsorption is taking place. It would probably be true that not only the hydrocarbon chain of the cationic surface active agent molecules adsorbed in the first layer provides the adsorption sites for the poly-layer adsorption, but also some parts of the polypropylene fibre chains show strong affinity to the hydrocarbon chain of the surfactant ions by the van der Waals attraction, since the hydrophilic ionic sites in the first layer are neutralized by the cationic surfactant and hence the hydrophobic character of this part increases. The concentration range, over which the poly-layer adsorption is taking place, is a little lower than the cmc of DPC and CPC, in 10⁻⁴M KCl solutions, *i.e.* 5×10⁻² and 10⁻²M, respectively.

3. Comparison with the Infra-red Adsorption Spectra

Among various groups formed by the gamma-ray irradiation, those which are especially related to the adsorption of cationic surface active agents are the alcoholic OH groups and carbonyl groups in the case of PA fibres, and the secondary alcohol groups in the case of PW fibres. Thus, the shift of ζ^* values in Table 2 can be explained by formation of these negatively dissociating groups on the fibre surface.

Values of N_1 in Table 1 decrease at first by a small dose of the gamma-ray irradiation, and then increase to higher values than those for PO fibres. Thus, seems probable that the N_1 value for PO fibres is for the adsorption due to the van der Waals attraction. However, for fibres exposed to a small amount of gamma-ray radiation, the hydrophobic character decreases with the formation of carbonyl or OH groups, thus giving rise to the decrease in the van der Waals attraction. But, negative adsorption sites of these groups are not sufficient in number in order for the decrease in N_1 values to be cancelled. With increasing radiation doses, however, the adsorption sites increase with increasing carbonyl

or hydroxyl groups formed.

5. CONCLUSION

The influence of the gamma-ray irradiation on interfacial electrical properties of polypropylene fibres was examined by measuring the electrokinetic zeta potentials of fibres in contact with various concentrations of cationic surface active agent solutions, containing 10^{-4} M KCl as the supporting electrolyte. The free energy of adsorption $-\Delta\bar{G}$ and the number of adsorption sites N_1 were estimated from ζ vs. $\log c$ curves thus obtained.

The ζ value of fibres in contact with solutions for $c=0$ becomes more negative by the gamma-ray irradiation, thus indicating the formation of negatively dissociating groups. Values of $\Delta\bar{G}$ of DPC and CPC at low concentrations were of the order of ca. 9 and 11 kcal/mole, respectively. It was observed in addition that ΔG values decrease with increasing the radiation doses, and moreover the ΔG value is smaller for fibres irradiated in water than in air. The N_1 value increased with increasing radiation energy, but it was smaller than that for untreated fibres at small values of the radiation energy.

These results were in good agreement with the results obtained by the infrared absorption spectra. In the case of irradiation in air, some oxidation takes place, thus giving rise to the formation of alcoholic OH, carbonyl and carboxyl groups. The gamma-ray irradiation in water gives rise to the formation of secondary alcoholic OH, a small amount of carboxyl groups and cross-linkages. It is supposed that the OH and COOH groups are responsible for the negative adsorption sites for cationic surface active agents. That is, the formation of these hydrophilic dissociating groups decreases the hydrophobic character of the hydrocarbon chains near-by, and thus weakening the van der Waals attraction. However, for sufficiently high radiation doses, the formation of dissociating groups predominates, thus increasing the adsorption of surface active agents.

Over a higher concentration range a sharp increase in the absolute value of ζ is observed. This would be explained by the polylayer adsorption of surfactant, due to the van der Waals attraction between surface active ions and hydrophobic chain of fibres and between the hydrophobic chains of surface active ions themselves. This occurs at surface active agent concentrations lower than the cmc.

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Interfacial Electrical Properties of Polypropylene Fibres

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