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INFRARED SPECTROSCOPIC INVESTIGATION OF PROPYLENE OXIDE – ETHYLENE OXIDE POLYMERS[*]

G. MESZLÉNYI[1], M. SIPOS[2], É. JUHÁSZ[1], M. ERŐSS-LELKES[1] and GY. POSZMIK[1]
[1]Research and Development Company for the Organic Chemical Industry
1428 Budapest, POB 41, Hungary
[2]National Institute for Hospital and Medical Engineering
1525 Budapest, POB 32, Hungary

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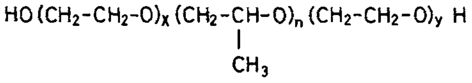
The surfactant properties of the title polymers depend on the total and relative number of the propylene oxide (PO) and ethylene oxide (EO) groups.

These numbers were determined by IR spectroscopy on the basis of the symmetrical bending vibration of the methyl group and the wagging vibration of the methylene group applying the Beer – Lambert law.

Some interesting absorption characteristics of the polymers have been revealed.

Introduction

Propylene oxide – ethylene oxide copolymers (PO/EO copolymers) have, similarly to other surfactants, two main parts; a hydrophobic moiety (here the polypropyleneglycol chain) and the hydrophilic part (here the polyethyleneglycol) (Fig. 1).



$$HO(CH_2\text{-}CH_2\text{-}O)_x(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}O)_n(CH_2\text{-}CH_2\text{-}O)_y\,H$$

x + y = numbers of the EO groups
n = numbers of the PO groups

Fig. 1. General formula of PO/EO copolymers

The absolute and relative quantity of PO and EO groups determine the applicabilities of the members of this group of surfactants. Details are given in Ref. [1].

Formerly conventional analytical methods have been used for the determination of the PO and EO units in PO/EO copolymers [2], [3]. Kotzschmar applied oxidation and subsequent gravimetric and titrimetric determination [3]. His method is accurate but time-consuming and laborious.

Among the instrumental analytical methods pyrolysis gas chromatography was used earlier for solving the task [4].

Recently infrared spectroscopy has been introduced for this purpose. Spanish researchers determined the EO content of p-nonylphenol-polyethylene-glycol ether by estimating the intensity changes of certain bands in the IR spectrum [5].

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In our work IR spectroscopy proved to be suitable for determining the PO/EO ratio and, with the knowledge of the molecular mass of a given substance, the absolute number of PO or EO units can be calculated.

Experimental

A PERKIN—ELMER 783 IR spectrophotometer, employing 1.0 mm calcium fluoride sealed liquid cells, and spectroscopic grade tetrachloromethane as solvent were used. For our examinations eight samples of PO/EO copolymers whose chemical compositions were known, were available (see Table I). The concentrations of the prepared solutions were 10 mg/cm^3. The accuracy of the weighing was 0.1 mg. The spectra were recorded between 1600 – 1300 cm^{-1} with compensation of the solvent. The absorbances were calculated by the base-line method.

Table I

Summary of the measured results

$\frac{PO}{EO}$	$\frac{A_{1375}}{A_{1350}}$	PO	EO	M	$A_{1cm}^{1\%}(1375)$	$A_{1cm}^{1\%}(1350)$	$\varepsilon(1375)$	$\varepsilon(1350)$
0.19	0.70	16.4	86.4	4700	1.70	2.44	800	1160
0.32	1.01	35.3	108.7	6600	2.35	2.32	1550	1585
0.76	1.86	16.4	21.6	1900	3.79	2.06	720	388
1.14	2.05	20.7	18.2	2000	4.22	2.04	844	412
1.77	2.53	20.7	11.7	1714	4.93	1.95	845	334
3.04	3.05	20.7	6.8	1500	5.70	1.87	855	281
6.83	3.53	69.0	10.1	4444	6.22	1.78	2862	791
6.86	3.62	30.2	4.4	1944	6.44	1.76	1209	342

Observation of the two IR spectra shown in Fig. 2 reveals why the absorptions of the bands at 1375 cm^{-1} and 1350 cm^{-1} were selected. The two peaks result from the symmetrical bending vibration of the methyl group (1375 cm^{-1}: $\delta_s CH_3$) and the wagging vibration of methylene group (1350 cm^{-1}: $\gamma_s CH_2$).

The δ_s and γ_s denotations correspond to the symbol system introduced by Sohár, Holly and Varsányi [6]. The intensity and the absorptional position of the γ_s CH_2 vibrational band (1350 cm^{-1}) can be explained by the –I effect of the neighbouring oxygen atoms.

Table I presents the PO/EO and A_{1375}/A_{1350} ratios and the determined absorptivities as well as molar absorptivities at 1375 and 1350 cm^{-1}.

Results and discussion

Plotting the determined A_{1375}/A_{1350} against the PO/EO ratios a saturation curve is obtained (Fig. 3).

The shape of the curve can be explained by γ_s CH_2 band that characterizes both the polypropyleneglycol (PPG) and the polyethyleneglycol (PEG) units. The saturation value probably indicates the A_{1375}/A_{1350} rate for pure PPG, which is 3.9 – 4.0 based on our measurements.

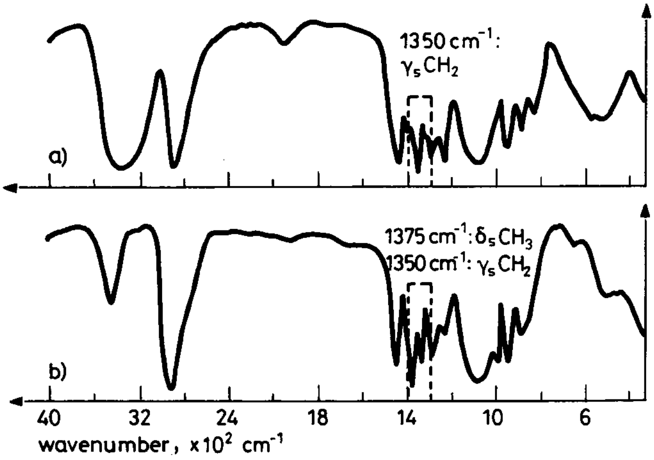

Fig. 2. The spectra of a polyethyleneglycol (a) and a PO/EO copolymer (b)

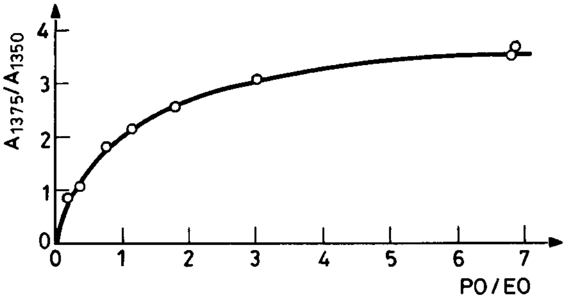

Fig. 3. Plot of A_{1375}/A_{1350} vs PO/EO

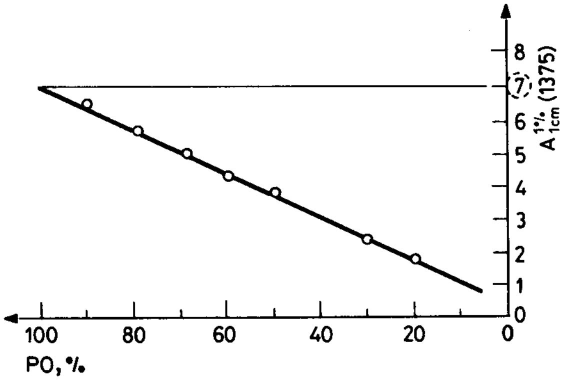

Fig. 4. Plot of $A^{1\%}_{1cm}$ (1375) vs PO(%)

The absorptivity at 1375 cm^{-1} for pure PPG can be calculated by means of the Beer — Lambert law. Fig. 4 depicts $A_{1cm}^{1\%}(1375)$ against the PO content in per cent.

As shown in Fig. 4 the absorptivity at 1375 cm^{-1} is a linear function of the PO content. Extrapolating the function to 100% PPG content we can estimate the value of $A_{1cm}^{1\%}(1375)$ in pure PPG. This value is 7.0.

For the determination of the absolute number of PO and EO units the knowledge of the molecular masses is necessary.

Determination of the molecular masses by measuring the OH stretching vibration at 3490 cm^{-1} is not possible owing to inherent association; at 3490 cm^{-1} the fundamental law is not valid. That is why we worked out a conventional analytical method based on the hydroxyl number determination to solve this problem.

The described relationships are well utilizable in practice. Our spectroscopic method is simple, requires no tedious sample manipulation; it is a useful tool in the analysis of tensides.

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