International Journal of Pharmaceutics, 1 (1978) 275–280

DIELECTRIC PROPERTIES OF POLYOXYETHYLENE-POLYOXYPROPYLENE GLYCOLS

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(Received January 13th, 1978)
(Accepted February 15th, 1978)

SUMMARY

Dielectric constants of several series of polyethylene-polypropylene glycols of the general formula $H(C_2H_4O)_n(C_3H_6O)_m$ were determined. The dielectric constants at fixed m is linearly related to the percentage of polyethylene glycol in the molecule. At fixed polyethylene glycol content, the dielectric constant decreases slightly with increasing molecular weight, but the dipole moments of the molecules are unaltered within experimentational error.

INTRODUCTION

The polyoxyethylene-polyoxypropylene glycols are substances that have gained considerable application in pharmaceutics in the twenty some odd years since their commercial introduction. They are used primarily as solvents, cosolvents and plasticizers. Although there have been some reports in the literature that they form micelles in aqueous systems, their solvent properties could well be due to their dielectric constant effects (Paruta, 1967; Paruta and Irani, 1965, 1966; Paruta and Sheth, 1966; Lordi et al., 1964). For this reason and in line with the general desirability of categorization of solvents and surfactants (Hildebrand and Scott, 1964; Gorman and Hall, 1963; Rebagay and Deluca, 1976), the study to follow reports the dielectric constants of a series of polyoxy-

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TABLE 1

APPROXIMATE VALUES OF n, m AND M FOR VARIOUS POLYOXYETHYLENE-POLYXYPROPYLENE GLYCOLS

Letter designation	Molecular weight of C_3H_6O- portion	m [b]	"Percent" C_2H_4O	Molecular weight of C_2H_4O- portion	n [b]	Total molecular weight, M
L61 [a]	1750	23	10	194	4	1944
L62	1750	23	20	438	10	2188
L63	1750	23	30	750	17	2500
L64	1750	23	40	1167	27	2917
P65 [a]	1750	23	50	1750	40	3500
F68 [a]	1750	23	80	7000	159	8750
L81	2250	30	10	250	6	2500
P84 [a]	2250	30	40	1500	34	3750
P85	2250	30	50	2250	51	4500
F87	2250	30	70	5250	119	7500
F88	2250	30	80	9000	205	11250
L101	3250	43	10	361	8	3611
P103	3250	43	30	1393	32	4643
P105	3250	43	50	3250	74	6500
F108	3250	43	80	13000	296	16250
L31	950	13	10	106	2	1056
L61	1750	23	10	194	4	1944
L81	2250	30	10	250	6	2500
L101	3250	43	10	361	8	3611
L121	4000	53	10	444	10	4444

[a] F denotes 'solid', P denotes 'pasty' and L denotes 'liquid' consistencies at 25°C.
[b] Molecular weight of C_3H_6O- is 76 and of C_2H_4O- is 44.

ethylene-polyoxypropylene glycols of the general formula:

$$HO-[OC_2H_4]_{n/2}[OC_3H_6]_m[OC_2H_4]_{n/2}-H$$

where n and m characterize the molecule. In the course of description the individual molecular contributions to the dielectric constants will be evaluated.

MATERIALS AND METHODS

The polyoxyethylene-polyoxypropylene glycols are known commercially as Pluronics *. Their compositions are listed in Table 1. The series of polyoxyethylene-polyoxypropylene glycols tested here were the complete series available from supplier *.

The samples were dehydrated at 60°C, and in all cases showed no change in dielectric constant upon further drying at 60 and 105°C. The dielectric constants were determined

* Supplier Ugine Kuhlman. 3 Rue Collange, 92 Levallois-Perret, France.

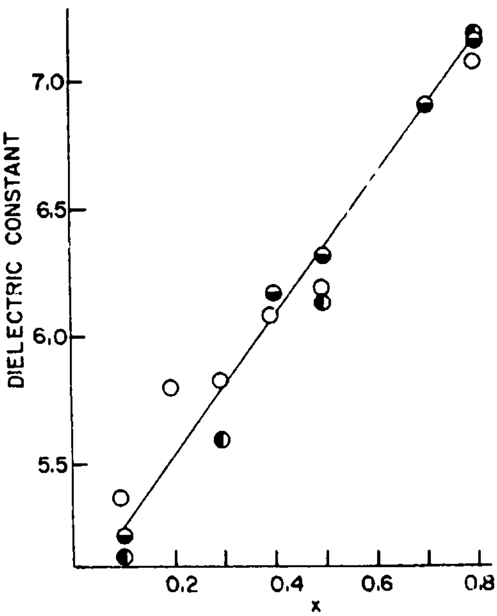

Fig. 1. Dielectric constant of polyoxyethylene-polyoxypropylene glycols of the series L61–68 (○), L81–88 (◒) and L101–108 (◐) as a function of the percent polyoxyethylene. The line shown is for the L81–88 series (Eqn. 1).

using an oscillating circuit, variable frequency apparatus with a thermostated cell (Q-meter *). The temperature used was 25.0 ± 0.1°C and 60.06 ± 0.2°C. The frequency used was 1500 kHz. Each measurement was carried out on four different samples, and the results averaged. The standard deviation of the dielectric constants obtained was of the order 0.05, and hence the coefficient of variation is less than 1%.

Density measurements were carried out pycnometrically (Carstensen, 1977).

RESULTS AND DISCUSSION

The dielectric constants (y) are linearly related to the percent of polyoxyethylene in the molecule. Fig. 1 demonstrates this; here the data are plotted as function of the fraction, x (rather than the percentage). The measurements were carried out at 60°C because some of the compounds in the series are solid (Table 1). The least squares fits for the 3 series with m = 23, 30 and 43 and their correlation coefficients (r) are

$$(m = 23) \quad y = 5.11 + 2.52x \quad (r = 0.96) \tag{1}$$

$$(m = 30) \quad y = 4.98 + 2.71x \quad (r = 0.99) \tag{2A}$$

$$(m = 43) \quad y = 4.77 + 2.90x \quad (r = 0.99) \tag{2B}$$

* Ferisol, 18 Av. Paul-Vaillant-Couturier, 78 Trappes, France. Model: Q-Mètre, type M803 A, with liquid cell CS 601 (thermostated).

TABLE 2

DIELECTRIC CONSTANTS AT 25°C AND 60°C (FIG. 2)

Designation	T°K	Dielectric constant, y	Density (g/cm^3) ρ [a]	Molecular weight, M	Dipole moment (Debye)
L31	298	6.37	1.009 ± 0.005	1056	2.5
L61	–	5.71	–	1944	2.3
L81	–	5.52	–	2500	2.5
L101	–	5.37	–	3611	2.1
L121		5.31	–	4444	2.4
L31	333	5.83	0.990 ± 0.004	1056	
L61	–	5.38	–	1944	
L81	–	5.22	–	2500	
L101	–	5.13	–	3611	
L121	–	5.07	-	4444	

[a] The density within a series remains unaltered. The density figures are the average of the individual measurements followed by 95% confidence limits on the average.

The slopes of the two lines are not significantly different. It is noted that the position of the line does not depend much on the length of the C_3H_6O-chain, but it does depend on it, since the intercepts in Eqns. 1 and 2 differ significantly. To demonstrate this on a systematic basis, a series of experiments were carried out with glycols all containing 10% polyoxyethylene, i.e. all of a composition * $H-(C_2H_4O)_{0.19m}(C_3H_6O)_mOH$. These are all liquid at 25°C, and this allows comparison of data at 25°C with data at 60°C, which in turn allows estimation of dipole moments.

The data are shown in Table 2. It is apparent that they obey an equation of the type:

$$[y - y_\infty] = [y_0 - y_\infty]\, e^{-\alpha M} \tag{3}$$

M is here the molecular weight of the polyoxyethylene-polyoxypropylene glycol and α is a series dependent constant. A logarithmic form of Eqn. 3 is used for the data in Fig. 2. The value of y_∞ is a least squares fit value obtained by iteration, and it is the dielectric constant of the molecule without the terminal H and OH groups, i.e. of $-(C_2H_4O)_{0.19m}(C_3H_6O)_m-$. The least squares fit values are 5.0 at 60°C and 5.24 at 25°C.

One can determine the induced molar polarization, P, of the data in Fig. 2 via the equation

$$P = \frac{y-1}{y+2}\frac{M}{\rho} \tag{4}$$

* For each 76 g of C_3H_6O there is a total of 76/0.9 = 84.4 g of compound, i.e. 8.44 g = 8.44/44 = 0.19 moles of C_2H_4O-.

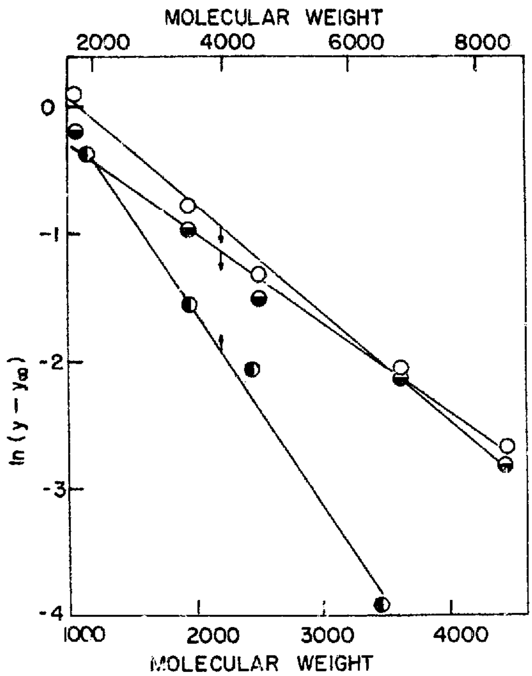

Fig. 2. Dielectric constants of the series L31–121 at 25°C (○, $y_\infty = 5.24$), and 60°C (◒, $y_\infty = 5.0$), as well as the series 35–105 at 60°C (◐, $y_\infty = 6.1$). The least squares parameters are L31–121 at 25°C (○): $\ln[y - y_\infty] = 0.914 - 0.0008M$ ($r^2 = 0.995$). L31–121 at 60°C (◒): $\ln[y - y_\infty] = -0.0007M + 0.439$ ($r^2 = 0.985$) and L35–105 at 60°C: $\ln[y - y_\infty] = -0.0008M + 1.124$ ($r^2 = 0.988$). M denotes molecular weight and r correlation coefficient.

where ρ is the density (g/cm^3). The dependence of P on the absolute temperature, T, is given by (Maron and Prutton, 1968)

$$P(T_1) - P(T_2) = B\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (5)$$

where

$$B = (4\pi N\mu^2)/(9k) \quad (6)$$

k is here Boltzmann's constant and μ the molecular dipole moment in c-g-s units. These latter are shown in Table 2 in Debye units (i.e. 10^{18} times c-g-s units). It is seen that they are all of the same order of magnitude and apparently independent of molecular weight.

ACKNOWLEDGEMENT

The authors are indebted to Dr. T.T. Luong, Laboratoire Pharmuka, Gennevilliers, for technical advice and assistance in this study.

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