

CCA-1283

YU ISSN 0011-1643

UDC 541.182

Original Scientific Paper

Micelle Formation by Tritons in Aqueous Solutions*

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Received November 11, 1979

The critical micellar concentrations and the mass-average micellar molecular masses of non-ionic surfactants, i. e. the members of the homologous series of *t*-octyl-phenoxy-polyethoxy-ethanols: Triton X-114, Triton X-100, Triton X-305, Triton X-405, and Triton X-705 have been determined by means of light scattering and other methods at 298 K. Variations in aggregation number from 6 to 220 (or micellar molecular mass from 19,000 to 120,000) have been found, depending on the length of monomeric molecule. These quantities, as well as c.m.c./mol dm⁻³, decrease with the increasing length of the hydrophilic part of the molecule, as has already been reported for other non-ionic surfactants.

INTRODUCTION

In order to study the mechanism of stabilization and the flocculation process in the case of interaction between a non-ionic surface active agent (NSAA) and a hydrophobic sol., we collected some experimental data on the micelle formation in aqueous solutions of Tritons, non-ionic surfactants of the octylphenoxyethanol (OPE) series, which were used as NSAA in our previous investigations^{1,2}. In the present paper, the following surfactants were investigated: Triton X-114, Triton X-100, Triton X-305, Triton X-405, and Triton X-705. They all have the same hydrophobic part of the molecule (*t*-octylphenyl group) but have different hydrophilic parts (an average of 7.5, 10, 30, 40 and 70 oxyethylene units per molecule).

Since Debye³ proved that the light scattering method is very sensitive for detecting the onset of micelle formation, many authors have used that method to determine the micellar molecular mass and the aggregation number of different non-ionic surfactants^{4,6-12}. Both the critical micellar concentration and the micellar molecular mass of Triton X-100 was determined first by Kushner and Hubbard^{4,5}, and since then its micellar characteristics have been reported many times¹³⁻¹⁷. However, other Tritons have not been studied quite so extensively and as far as we know their micellar properties have not been compared and discussed in the literature.

* Presented at the 6th Meeting of Chemists of Croatia, Zagreb, February 1979. Contribution No 222. of the Department of Physical Chemistry.

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In the present paper an attempt was made to evaluate and compare both the micellar molecular mass and the aggregation number of different Tritons, on the basis of light scattering data.

EXPERIMENTAL

Materials

The viscous 70% w/v liquids of Triton X-114, Triton X-100, and Triton X-405, as well as 100% w/v viscous liquids of Triton X-305 and Triton X-705, were obtained from Rohm and Haas Co, Philadelphia, U.S.A. Concentrated stock solutions of Tritons were prepared by weighing and diluting with dust-free doubly distilled water and dilute solutions were always freshly prepared volumetrically. The Rayleigh ratio of pure water which was used was calculated to be about $1.04 \times 10^{-6} \text{ cm}^{-1}$ and its dissymmetry was about 1.06.

Methods

Light scattering measurements were made using a Brice-Phoenix Model 2000 Light Scattering Photometer, Phoenix Precision Instrument Co., Philadelphia, U.S.A. The apparatus was checked as described earlier¹⁸. The measurements were performed at room temperature using 546 nm wavelength light. Polaroid sheets were used for polarization measurements. Scattered light was measured in the angular range of 30° to 135° using a cylindrical cell (Phoenix Catalog No C-105). The cell was cleaned with freshly distilled acetone.

The total Rayleigh ratios, R_u , were obtained experimentally by utilizing Brice's working standard method¹⁹. The absolute values of these ratios were calculated from an expression given by Kratochvil and Smart²⁰. Kratochvil²¹ reflection correction was applied. The dissymmetries, z , were calculated from the absolute values for the $R_u(45)$ and $R_u(135)$ ratios. To remove the effect of multiple scattering at finite concentration the measured values of dissymmetry were extrapolated to zero concentration. The Rayleigh ratio of the system at the critical micellar concentration c.m.c., (denoted as c_0), was subtracted from the solution ratio in each case to obtain the 'excess' scattering ratio for the systems above c.m.c. The precision of the calculated R_u values is estimated to be about 7%. In order to test the optical anisotropy of micellar solutions, the polarization ratios $D_u(90) = H_u(90)/V_u(90)$ were determined. In all cases the $D_u(90)$ values were low and the Cabannes correction factors were near unity. So, the influence of the anisotropic scattering upon the R_u ratios was within the experimental error.

Measurements of the differential refractive indices were taken using a Brice-Phoenix differential refractometer, Model BP-2000-V (Phoenix Precision Instruments-Virtis Co., N. Y., U.S.A.). All measurements were performed at a constant temperature of 298 K using 546 nm wavelength light. The instrument was calibrated with standard potassium chloride solutions on the basis of Kruijs's²² data. The errors were about 2%.

The UV light absorption measurements were performed at $\lambda_{\text{max}} = 276 \text{ nm}$ and path length 40 mm using a Pye Unicam SP 1800 spectrophotometer.

The surface tension of the Triton solutions was measured by the drop-weight method.

Viscosity measurements were performed at 298 K using capillary KPG-Ubbelohde viscometers, produced by Jena²³ Glasswerk Schott und Gen., Mainz, BDR.

The densities of the Triton solutions were determined with a pycnometer, and were close to unity over the whole range of concentration from 1×10^{-5} to $1 \times 10^{-2} \text{ mol/dm}^3$.

RESULTS

The c. m. c. data (c_0 in molar concentrations) of the investigated Triton aqueous solutions at room temperature are summarized in Table I. They are determined on the basis of several methods as: surface tension and pH (inflection point) (Figure 1.), differential refractometry (Figure 2a.), light scattering, UV spectrophotometry, and viscosity (Figure 3.). The total Rayleigh

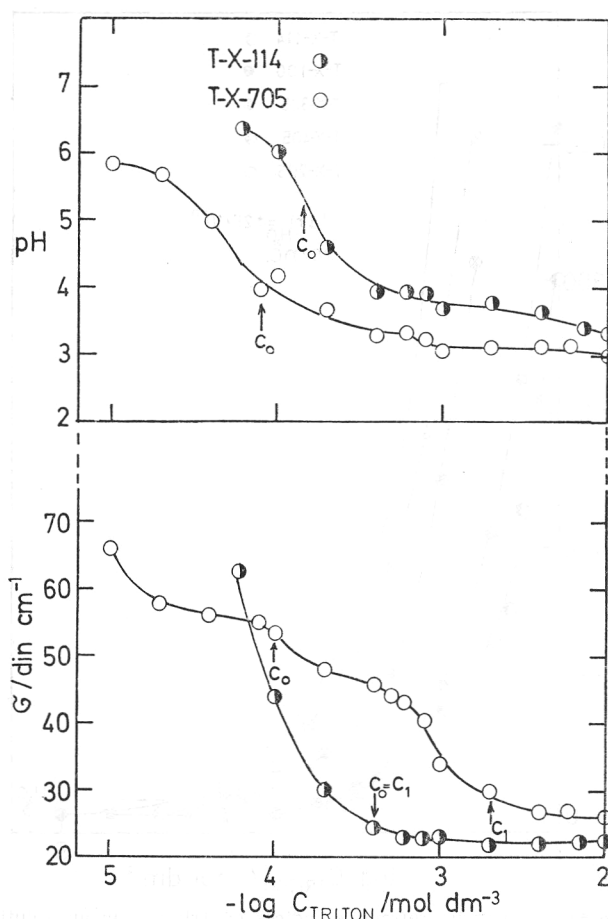


Figure 1. Surface tension and pH of Triton X-114 and Triton X-705 aqueous solutions

ratios at 90° , differential refractive indices (Δn) and relative viscosity (η_{rel}) of all Triton solutions did change only inappreciable with increasing concentration up to c_0 , while above c_0 a significant linear increase of these quantities was observed (Figure 4., Figure 2b., and Figure 3.). Consequently, η_{rel}/c values decrease with increasing concentration up to c_1 and remain almost constant above c_1 . At c_1 concentrations, which are about ten times higher than c_0 , micelles attain a generally constant size. Between c_0 and c_1 is the region of increased micellar size, (e.g. c_1 is about 4×10^{-3} mol/dm³ for Triton X-114 and about 8×10^{-4} mol/dm³ for Triton X-705). It is worth noting that a lower c_0 and c_1 value in mol/dm³ corresponds to a the Triton with higher chain length and vice versa (trend is opposite when c is expressed in g/cm³). The general dependence of Rayleigh ratios at 90° for Triton micelle concentrations above their c.m.c. values and corresponding dissymmetries are plotted in Figure 4. An almost symmetrical envelope of scattering intensities was observed for all solutions of the samples Triton X-114 and Triton X-100, indicating

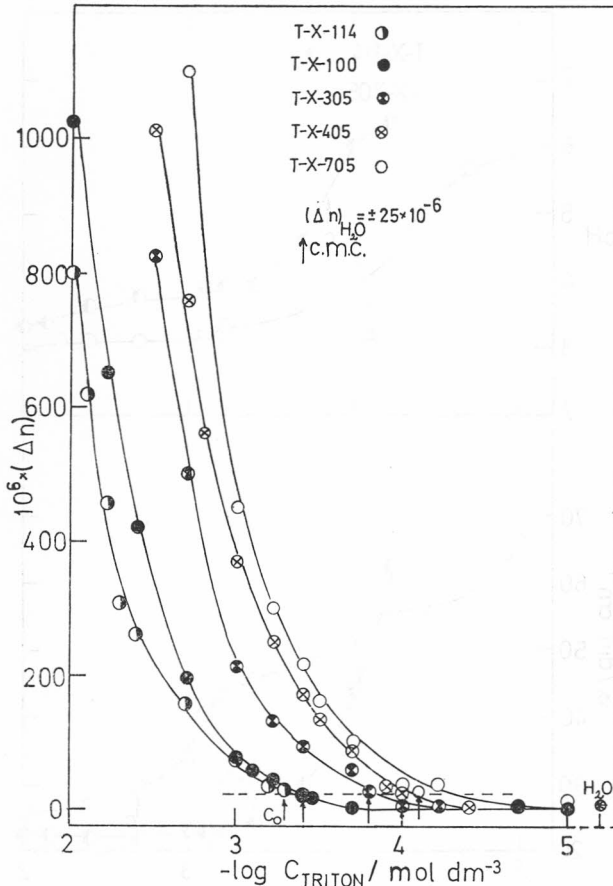


Figure 2a. Differential refractive indices of Triton aqueous solutions.

Rayleigh scatterers. In contrast, the dissymmetries for micellar solutions of all other Triton samples were found to be greater than unity, thus indicating an asymmetrical scattering envelope characteristic of Rayleigh-Debye scatterers. The feature of these plots is the rise and subsequent levelling off in dissymmetry as the NSAA concentration increases.

ANALYSIS OF THE RESULTS AND DISCUSSION

Generally, the mass-average relative molecular mass of micelles (molecular weight), M_{mic} , can be evaluated from light scattering data using the Debye equation 3 given here by a power series in concentration:

$$[K(c - c_0)(1 + \cos^2 \theta)]/R_u(\theta) = 1/M_{mic} P(\theta) + 2B(c - c_0) + 3D(c - c_0)^2 + \dots \quad (1)$$

with the usual symbols. In fairly dilute micellar solutions, the third term in Eq. (1) becomes negligible and, at $\theta = 90^\circ$ for optically isotropic particles, small in comparison with the wavelength (Rayleigh scatterers), Eq. (1) reduces to:

TABLE I

NSAA	C_0 (c.m.c./mol dm ⁻³) determined by:					$-\Delta G_{mic}^0$ (25°C)* kJ mol ⁻¹
	surface tension $\sigma = f(\log c)$	light scattering $R_u(90) = f(\log c)$	refractometry $\Delta n = f(\log c)$	UV-spectro-photometry $A = f(c)$	viscosity $\eta_{rel}/c = f(c)$	
T-X-114	4.0×10^{-4}	9.0×10^{-4}	4.0×10^{-4}		4.0×10^{-4}	19.4
T-X-100	3.0×10^{-4}	8.0×10^{-4}	3.0×10^{-4}	2.8×10^{-4}	3.0×10^{-4}	20.1
T-X-305	2.0×10^{-4}	4.0×10^{-4}	1.5×10^{-4}	1.5×10^{-4}		21.8
T-X-405		3.0×10^{-4}	1.0×10^{-4}	1.2×10^{-4}		22.8
T-X-705	1.0×10^{-4}	2.5×10^{-4}	0.8×10^{-4}		1.0×10^{-4}	23.4

* The change in Gibbs free energy of micellization was calculated using refractometric data for c.m.c.

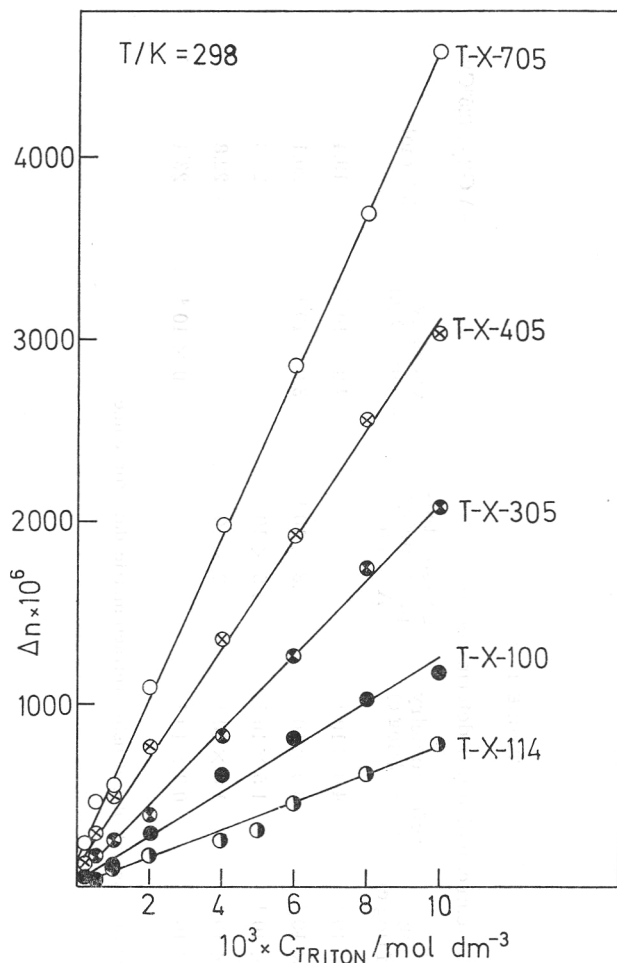


Figure 2b. Differential refractive indices of Triton aqueous solutions.

$$K(c - c_0)/R_u(90) = (1/M_{\text{mic}}) + 2B(c - c_0) \quad (2)$$

because the form factor $P(\theta) = 1$ in that case (see e. g. ref. 23.)

In Figure 5., in which the experimental results of Figure 4. and Figure 2b. have been used in order to plot $K(c - c_0)/R_u(90)$ as a function of micelle concentration, it is seen that we obtain straight lines above c_1 (within the accuracy of measurement) in accord with Eq. (2). The extrapolation to zero concentration was made, and the intercepts, $1/M_{\text{mic}}$, of the lines determined for the measured series were calculated by the least squares method. The slopes, $2B$, of these lines are almost equal to zero, and correspond to the second virial coefficients. According to the dissymmetry results, the micellar molecular mass of Triton X-114 and Triton X-100 was determined using Eq. (2), because z is near unity, and for the other Tritons Eq. (1) was used. In the latter case, the total Rayleigh ratios were measured at 90° and the

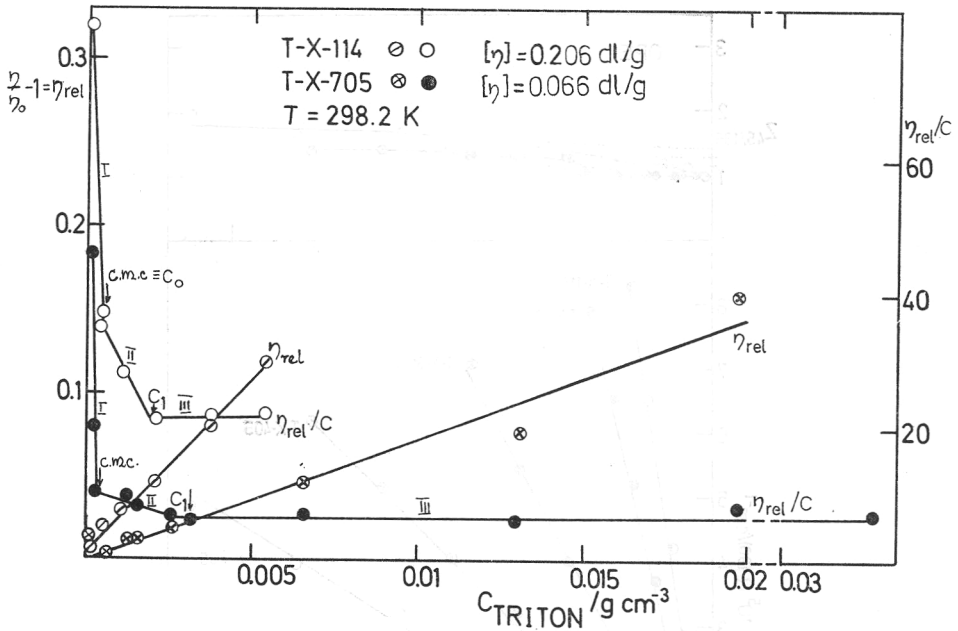


Figure 3. Relative viscosity of Triton X-114 and Triton X-705 aqueous solutions

experimentally determined M_{mic} were corrected with the $1/P(90)$ factor corresponding to a particular value of the dissymmetry²⁵. The extrapolation of dissymmetry to zero concentration was done as suggested by Debye and Anacker²⁶, i. e. taking into account the dissymmetries of those micellar solutions belonging to the concentration range where the micellar size does not increase with NSAA concentration. From the theoretical point of view, it is necessary to make some assumptions about the shape of the micelle before its micellar mass can be determined from Eq. (1) using $P(\theta)$ factors. Doty and Steiner²⁵ showed, however, that the numerical values of different $P(\theta)$ functions are practically coincident in the range where the dissymmetries are between 1.0 and 1.4., i. e. the correction factor does not depend on the particle shape. As is seen from Figure 4. Triton X-305, Triton X-405, and Triton X-705 the samples meet the above mentioned condition regarding their extrapolated dissymmetries. For instance, if $z = 1.45$ (Triton X-705, sample) the difference between the $1/P(90)$ values corresponding to the spherical and rod-like model of particles amounts to about 3%, which, when calculating the micellar mass by Eq. (1), leads to the same values within the experimental error. The $1/P(90)$ values were obtained by graphical interpolation from the data tabulated in paper Beattie and Booth's²⁷. It should be noted also, that Eq. (1) does not take into consideration the effect of a possible optical anisotropy of the scattering system. If the scattering system shows appreciable anisotropy the R_v values measured must be corrected appropriately (see e. g. ref. 24.) to obtain the

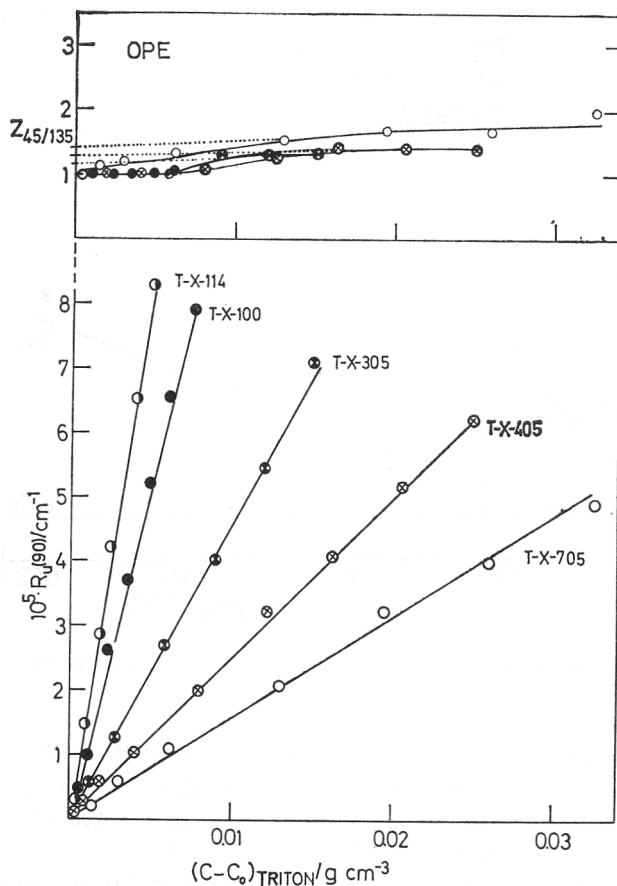


Figure 4. Total Rayleigh ratios at 90° of Triton aqueous solutions above c.m.c. and corresponding dissymmetries

true value of the micellar molecular mass. This is not necessary in our case as we mentioned in the experimental part. Consequently, the micellar molecular masses of Triton X-305, Triton X-405, and Triton X-705 were determined on the basis of measurements at 90° by the use of Eq. (1) and corrected with the corresponding $1/P(90)$ values for spheres. The choice of a spherical shape as a model of the micelle shape was preferred on the basis of data reported by several authors^{4,6,28}, although it is not essential because for low dissymmetries the correction factors are practically equal for any particle shape.

The micellar molecular masses are recorded in Table II and refer to the micellar species of approximately constant size. The number of NSAA monomers in micelle i.e. aggregation numbers (\bar{N}) are listed in Table II also. The last two columns contain the corrected micellar molecular masses and the corresponding aggregation numbers.

TABLE II

NSAA	X	M_{NSAA}	$\frac{dn/dc}{cm^3 g^{-1}}$	K	\bar{M}_{mic}	\bar{N}	\bar{M}_{mic}^*	\bar{N}^*
T-X-114	7.5	536	0.138	1.25×10^{-7}	1.2×10^5	220		
T-X-100	10	628	0.134	1.17×10^{-7}	8.9×10^4	142		
T-X-305	30	1526	0.131	1.13×10^{-7}	3.9×10^4	26	4.5×10^4	30
T-X-405	40	2066	0.125	1.03×10^{-7}	2.2×10^4	10—11	2.6×10^4	12—13
T-X-705	70	3286	0.134	1.17×10^{-7}	1.5×10^4	4—5	1.9×10^4	6

* Corrected for the disymmetries; the corresponding $1/P(90)$ values for spheres were used.

In our present work the marked decrease in micellar molecular masses with lengthening the NSAA molecule is evident. This is a phenomenon generally observed with micellar solutions of NSAA^{6,28,29}. Our results in Table II.

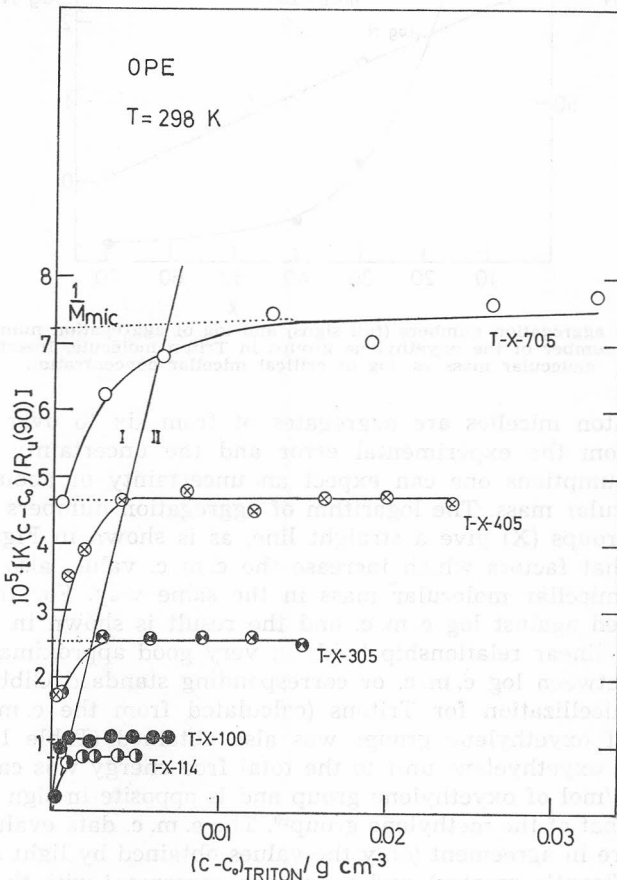


Figure 5. Debye plots for Tritons

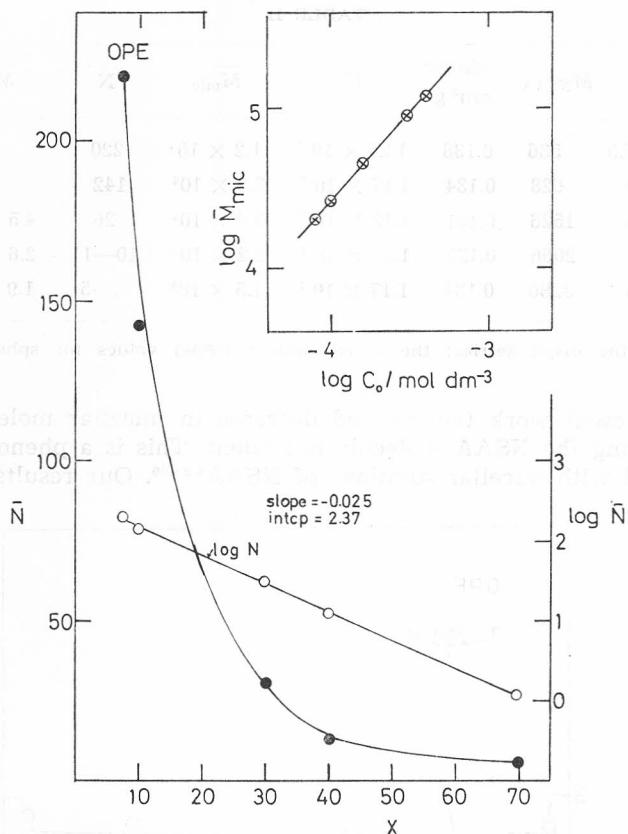


Figure 6. Average aggregation numbers (full signs) and log of aggregation numbers (open signs) as a function of number of the oxyethylene groups in Triton molecule. Insert: log of micellar molecular mass vs. log of critical micellar concentration

show that Triton micelles are aggregates of from six to over two hundred monomers. From the experimental error and the uncertainty of the above mentioned assumptions one can expect an uncertainty of about 10% in the micellar molecular mass. The logarithm of aggregation numbers vs number of oxyethylene groups (X) give a straight line, as is shown in Figure 6. It is to be expected that factors which increase the c. m. c. value, also influence the value of the micellar molecular mass in the same way. For this reason $\log M_{mic}$ are plotted against \log c. m. c. and the result is shown in upper part of Figure. 6. The linear relationship holds in very good approximation. A linear relationship between \log c. m. c. or corresponding standard Gibbs free energy changes on micellization for Tritons (calculated from the c. m. c. data) and the number of oxyethylene groups was also obtained (Table I.) The contribution of each oxyethylene unit to the total free energy was calculated to be about -0.1 kJ/mol of oxyethylene group and is opposite in sign and ten times smaller than that of the methylene group²⁹. The c. m. c. data evaluated by several methods are in agreement (only the values obtained by light scattering method are significantly greater), and are also in agreement with the results of others. Hertz and Barenholz¹⁵ have determined the c. m. c. of Triton X-100 in a

0.16 mol/dm³ K₃PO₄ buffer solution of pH = 6.5 and found it to be 0.1–0.2 mmol/dm³ with a corresponding $\Delta G_{\text{mic}}^0 = (-5.3) - (-4.9)$ kcal/mol. Kushner and Hubbard⁴ have determined the micellar molecular mass of Triton X-100 to be about 90.000 ($\bar{N} = 140$), which is in excellent agreement with our results.

In summary, we have investigated a series of Tritons, commercially prepared NSAA, using light scattering measurements and other methods and found that on increasing the ethyleneoxyde chain length of the OPE's from 7.5 to 70, the M_{mic} decreases by an order of magnitude, which is regular behaviour already observed.

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SAŽETAK**Formiranje micela tritona u vodenim otopinama***N. Stubičar i J. J. Petres*

Određene su kritične micelarne koncentracije i srednje masene molekularne mase neionskih tenzida tj. članova homologne serije t-oktil-fenoksi-polietoksi-etanola: Tritona X-114, Tritona X-100, Tritona X-305, Tritona X-405 i Tritona X-705, metodom raspršenja svjetlosti i drugim metodama na 298 K. Nađeno je da agregacijski broj varira od 6 do 220 (ili micelarna molarna masa od 19 000 do 120 000) ovisno o dužini molekule monomera. Oni se smanjuju s porastom dužine hidrofilnog dijela molekule, što je već bilo opaženo i kod drugih neionskih tenzida.

ZAVOD ZA FIZIČKU KEMIJU
PRIRODOSLOVNO-MATEMATIČKI FAKULTET
i
ZAVOD ZA IMUNOLOGIJU
ZAGREB

Prispjelo 11. studenoga 1979.