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Publisher *Taylor & Francis*

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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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**To cite this Article** Iwunze, M. O.(2005) 'The determination of the effective dielectric constant of micelles and microemulsions', *Physics and Chemistry of Liquids*, 43: 2, 195 – 203

**To link to this Article:** DOI: 10.1080/00319100500038686

**URL:** <http://dx.doi.org/10.1080/00319100500038686>

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## The determination of the effective dielectric constant of micelles and microemulsions

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(Received 1 November 2004)

Pyridinium *N*-phenoxide betaine, commonly known as  $E_T(30)$  molecule, is used to probe the polarity of the cetyltrimethylammonium bromide (CTAB) micelle and the didodecyldimethylammonium bromide (DDAB) bicontinuous microemulsion systems. The observed  $E_T(30)$  values of these aggregated systems were observed to lie within those of the  $C_1$  through  $C_5$  alcohols, and have good correlation with their respective dielectric constants,  $\epsilon$ . The effective dielectric constant of the micelles and microemulsions were determined using the correlation obtained from the alcohols'  $E_T(30)$  values correlated with their corresponding dielectric constants. Generalized equations, usable for all micelles, irrespective of the type of surfactant was developed and the effective dielectric constant values obtained using the equation were in good agreement with the literature values. An equally satisfactory equation based on the ratio of surfactant and oil (S/O) for the bicontinuous microemulsion system was also developed.

*Keywords:*  $E_T(30)$ ; Dielectric constant; CTAB Surfactant; Micelles; Microemulsion

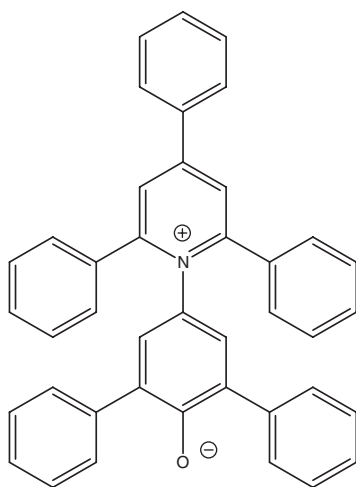
### 1. Introduction

Solvent polarity and its attendant dynamics influence the thermodynamics and kinetics of chemical/biological reactions. This is consistent with the modern theory of solvent systems. The properties that accord solvents such dynamics in reaction systems include the dielectric constants, static ( $\epsilon_s$ ) and optical ( $\epsilon_\infty$ ), as well as the viscosity,  $\eta$ . These properties are related to the solvent longitudinal relaxation time,  $\tau_L$ , ( $\tau_L = (\epsilon_\infty/\epsilon_s)\tau_D$ , where  $\tau_D = (4\pi/kT)\eta a^3$ ). This last solvent property,  $\tau_L$ , is known to correlate well with the reactants' barrier-crossing frequency,  $\nu_n$ . In *a* this relation *a* is the radius of solute or reactant embedded in the reaction medium. A good knowledge of these solvent dynamical properties is therefore essential in order to fully understand the mechanism to control and tailor such reactions to specific applications. For most common solvents, these dynamical properties are known and well documented in

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most reference books. This is not so for aggregated systems, such as micelles and microemulsions, fluid systems that have come of age as microreactor systems. Several research workers have attempted the use of different molecular systems for the determination of the polarity of micelles of selected surfactants [1–7]. Such systems include the well-known Kosower's  $Z$ -value, which is based on the absorbance maximum of the charge transfer band transition spectrum of some pyridinium iodide systems [8,9]. However, the water solubility of these complexes make them quite unsuitable for probing the polarity of micellar systems whose interior (micellar core) is the effective reaction sphere with a polarity quite different from its bulk aqueous phase. In its stead, another empirical polarity parameter developed by Reichardt [10,11], pyridinium  $N$ -phenoxide betaine ( $E_T(30)$ ), whose structure is shown in figure 1, has been found suitable for probing the polarity of the micellar core. The preference for this compound stems from its slight solubility in water (solubility  $< 10^{-6}$  M) [12]. The  $E_T(30)$  molecule also exhibits quite a wide range of dipole moments between its ground and excited states [1,13]. Its excited state transition band is quite sensitive to changes in solvent polarity. It was therefore used to establish a spectroscopically derived empirical solvent polarity parameter [14,15]. Zachariasse and his coworkers [16] have used this system to evaluate the effective dielectric constant,  $\epsilon_f$ , of different micellar systems with satisfactory results. However, the study was carried out at a very narrow concentration range. Most of the studies were done at only one surfactant concentration of a micelle, microemulsion or liposomal system. The interior microviscosity and polarity of the aggregated systems is sensitive to the concentrations of their surfactant monomers. For this reason, we extended this study with respect to cetyltrimethylammonium bromide (CTAB) for concentrations ranging from 1.0 to 200.0 mM, and developed a correlational relationship between the micellar concentration and the effective dielectric constant. As shown in Zachariasse's work, *op. cit.*, the dielectric constant of most of the micelles of different surfactants do not differ significantly from one surfactant system



Pyridinium  $N$ -phenoxide betaine  $E_T(30)$

Figure 1. Structure of  $E_T(30)$  molecule.

to another. We therefore believe that the equation developed in this work will be usable for micelles, not only of cationic surfactants, but also micelles of other classes of surfactant. In addition, we present the result for the effective dielectric constant of the bicontinuous microemulsion system of didodecyldimethylammonium bromide–dodecane–water system.

## 2. Experimental

### 2.1. Materials

Reichardt's dye ( $E_T(30)$ ) of 90% purity and reagent grade dodecane were obtained from Aldrich Chemical Co. So were the *n*-butyl and *n*-propyl alcohols, which were of HPLC grade. Ethyl (absolute) and methyl (ACS certified grade) alcohols were obtained from Pharmco Chemicals. Cetyltrimethylammonium bromide and didodecyldimethylammonium bromide of 99% purity were obtained from Acros Chemicals. All chemicals were used as received.

### 2.2. Solution preparation

Unless otherwise specified, all solutions and their respective solvents contained  $2.0 \times 10^{-3}$  M  $E_T(30)$  molecule and the concentrations of CTAB varied from 1.0 to 200 mM. Bicontinuous microemulsions were prepared in accordance with the literature methodology [17–19]. In this work, the ratio of oil (dodecane) to water was kept constant at 2:1 while the percentage of DDAB varied from 16 to 40%. All aqueous solutions were prepared using triply distilled and deionized water from a Reagent Grade Water System obtained from Photronix.

### 2.3. Absorption measurement

All absorption measurements were made using the Cary spectrophotometer, model 1E, supplied by Varian Analytical Instruments. Measurements were made at room temperature,  $25 \pm 0.2^\circ\text{C}$ .

### 2.4. Treatment of data

The determination of the  $E_T(30)$  values for all solvents were obtained from equation (1), which was developed as per [1].

$$E_T(30), \text{kcal/mol} = hc/\lambda_{\text{max}} N_A = 28591/\lambda_{\text{max}}(\text{nm}) \quad (1)$$

In the above equation,  $h$  and  $c$  are the Planck's constant and the velocity of light in vacuum, respectively.  $\lambda_{\text{max}}$  is the wavelength maximum of the intramolecular charge transfer absorption band of Reichardt's dye and  $N_A$  is Avogadro's number. Since the charge transfer absorption spectrum of  $E_T(30)$  is solvent sensitive, its value in a normal alcohol series, varying from methanol to pentanol, were obtained and found to have a linear relationship when plotted against the respective dielectric constant,  $\epsilon$ ,

obtained from [20]. This observation is consistent with those of Zachariasse. The resulting regression equation is given in equation (2).

$$\varepsilon = (E_T(30) - 43.8115)/0.3381 \quad (2)$$

This equation was used for the determination of the effective dielectric constant,  $\varepsilon_f$ , of the surfactant systems studied in this work.

### 3. Results and discussion

Figure 2 shows the  $E_T(30)$  absorption spectra for the first four alcohols used in this work. There is a noticeable bathochromic shift of the absorption band with an increase in the alcohol chain length. The wavelength at the maximum absorbance,  $\lambda_{\max}$ , for each of these alcohols including that of *n*-pentanol were used to obtain the respective  $E_T(30)$  values using equation (1). These values, which are listed in table 1, were plotted against

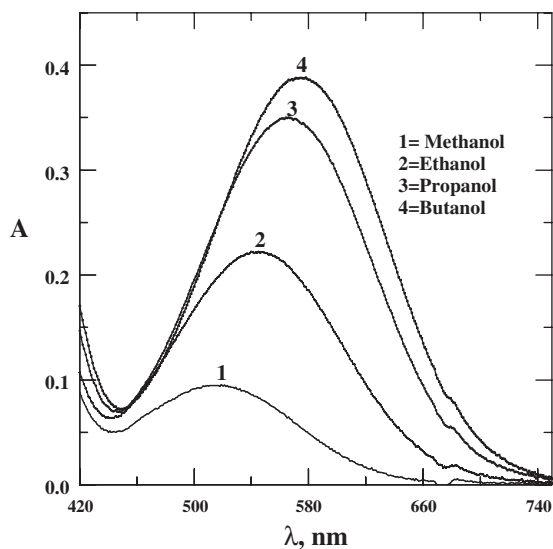


Figure 2. Absorption spectra of  $E_T(30)$  in  $C_1$ – $C_4$  alcohols.

Table 1. Wavelength maximum,  $E_T(30)$  values and dielectric constants of  $E_T(30)$  molecule in different alcohols.

Solvent	$\lambda_{\max}$ (nm)	$E_T(30)$ (kcal/mol)	$\varepsilon_f$
Methanol	519.0	55.09	33.613
Ethanol	545.0	52.46	24.852
Propanol	564.0	50.69	20.524
Butanol	578.0	49.46	17.332
Pentanol	583.0	49.04	15.13

the respective dielectric constant as shown in figure 3. This figure, which is seen to be quite linear with a regression coefficient of 0.9974, was used to develop equation (2).

### 3.1. Determination of the effective dielectric constant of micellar solutions

Table 2 lists the observed  $\lambda_{\max}$  and calculated  $E_T(30)$  values at different CTAB concentrations. As can be seen in this table, the determined  $E_T(30)$  values at all CTAB

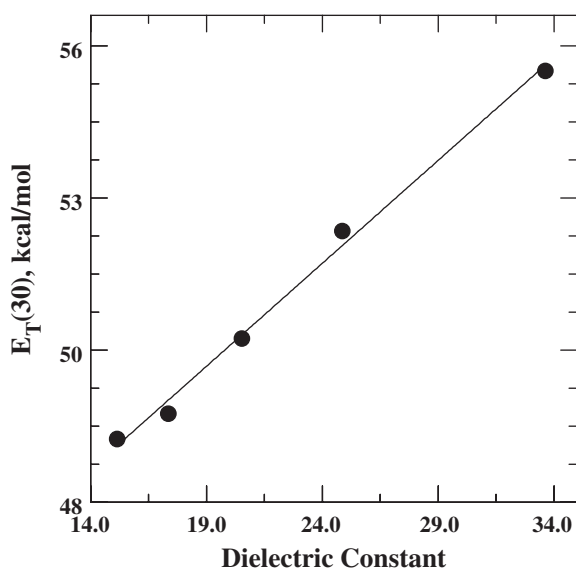


Figure 3. Plot of  $E_T(30)$  values versus the alcohols' dielectric constants.

Table 2. Maximum wavelength,  $E_T(30)$  values and calculated effective dielectric constants of  $E_T(30)$  molecule in different CTAB concentrations.

CTAB concentration (M)	$\lambda_{\max}$ (nm)	$E_T$ (kcal/mol)	$\epsilon_f$
0.001	530.0	53.94	29.72
0.003	533.63	53.58	28.90
0.005	533.82	53.56	28.58
0.007	535.53	53.39	28.07
0.01	536.19	53.32	27.89
0.02	537.92	53.15	27.38
0.03	539.03	53.04	27.06
0.04	539.43	53.0	26.94
0.05	539.94	52.95	26.79
0.06	540.35	52.91	26.68
0.07	540.86	52.86	26.53
0.08	541.39	52.81	26.38
0.09	541.73	52.78	26.28
0.10	542.08	52.74	26.18
0.13	542.77	52.67	26.07
0.148	543.12	52.64	25.98
0.20	544.0	52.56	25.76

concentrations are all within those determined for the alcohols (cf. table 1). This fact lends some credibility to the use of equation (2), which is due to the alcohols, for the estimation of the  $\varepsilon_f$  of the CTAB solutions. The  $\varepsilon_f$  values thus determined are also shown in table 2. There is a subtle change of  $\varepsilon_f$  values with increasing CTAB concentration. This observation in table 2, which is consistent with Zachariasse's observation, reflects a decrease in the polarity of the micellar pseudophase, which is sensed by the  $E_T(30)$  molecule.

### 3.2. Correlation of $\varepsilon_f$ with CTAB concentration

It was necessary to derive correlational parameters that will make for easy accessibility of  $\varepsilon_f$  values at all CTAB concentrations. To this end, a correlation of the observed  $\varepsilon_f$  values was made with the CTAB concentrations. These data fit a logarithmic format given in equation (3).

$$\log \varepsilon_f = 1.3914 - 0.0273 \log [\text{CTAB}] \quad (3)$$

with a correlation coefficient of 0.9993. To avoid excessive data clustering, selected data were used to plot the log of  $\varepsilon_f$  as a function of log [CTAB] in accordance with this equation. The resulting plot is shown in figure 4. It is believed that equation (3) will be applicable for the determination of  $\varepsilon_f$  for most surfactants irrespective of their kind, that is, anionic and cationic surfactants alike. This conclusion was based on the  $E_T(30)$  and  $\varepsilon_f$  values listed in table 1 of [16]. In order to demonstrate the applicability of this equation to different types of surfactant, selected surfactants, their concentrations and their  $\varepsilon_f$  values from reference [16] are listed in table 3 and compared with calculated values using equation (3). There is a satisfactory agreement between calculated and experimental values, within limits of experimental uncertainty. The value of 27 listed for Triton X-100 may be low when compared with a value of 30

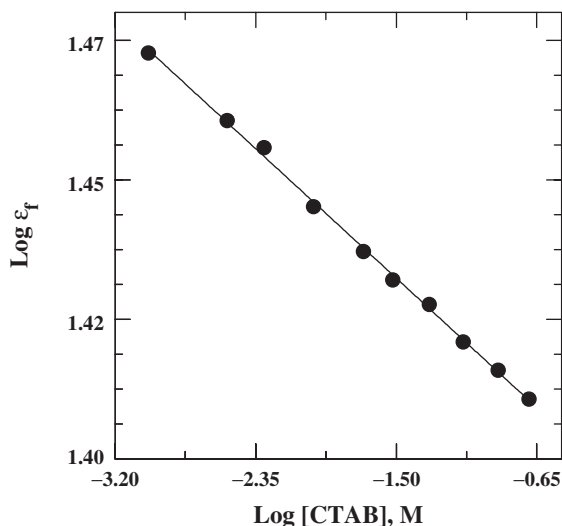


Figure 4. Plot of the log of effective dielectric constant versus the log of CTAB concentrations.

Table 3. Comparison of the calculated and observed effective dielectric constants of E<sub>T</sub>(30) molecules in different surfactant media.

Surfactant	Concentration	$\epsilon_f(\text{calc})$	$\epsilon_f(\text{obsd})^*$	% Error
Brij 35	0.09	26.30	27.0	+2.6
C12EO	0.01	27.92	27.0	-3.4
CTAB	0.01	27.92	28.0	0.29
	0.05	26.73	27.0	+1.0
Triton X-100	0.004	28.63	27.0 <sup>#</sup>	-6.0

\*Values taken from [16].

<sup>#</sup> $\epsilon_f$  obtained in dioxane-water mixture and ethanol-water mixture is 30.

Table 4. Weight percent DDAB, E<sub>T</sub>(30) values and effective dielectric constants of E<sub>T</sub>(30) molecule in different surfactant to oil (S/O) ratios.

Wt % DDAB	S/O	$\lambda_{\text{max}}$ (nm)	E <sub>T</sub> (30) (kcal/mol)	$\epsilon_f$
16.0	0.28	547.94	52.18	24.76
25.0	0.50	551.55	51.84	23.75
34.0	0.77	558.76	51.17	21.77
38.0	0.92	561.0	50.96	21.15
40	1.0	562.37	50.84	20.79

obtained in both dioxane-water mixture and ethanol-water mixture [16]. If 30 is taken as the  $\epsilon_f$  of Triton X-100, then the error percentage reduces to 4.6 from the calculated value, which is certainly within an experimental uncertainty.

### 3.3. The case for bicontinuous microemulsion

The E<sub>T</sub>(30) values obtained in bicontinuous microemulsion systems were also observed to be within the range of those of the alcohols given in table 1 and also those due to the micelles of CTAB in table 2. Therefore, the  $\epsilon_f$  values of these emulsion systems were computed using equation (2). The respective  $\lambda_{\text{max}}$ , E<sub>T</sub>(30) and  $\epsilon_f$  values are listed in table 4. In this bicontinuous microemulsion system, which is a ternary system of oil-water-surfactant, the ratios of the surfactant to oil in weight percentage (S/O) are plotted against their  $\epsilon_f$  values. A linear plot was obtained (figure 5), with a correlation coefficient of 0.9955 and a regression equation (4).

$$\epsilon_f = 26.4243 - 5.7354 (S/O) \quad (4)$$

As per table 4, both the E<sub>T</sub>(30) and  $\epsilon_f$  values of the bicontinuous microemulsion systems are consistently lower than those observed for the micelles but are still within the range of those of alcohols, a justification for using the alcohol  $\epsilon$  system for the determinations given in the aforementioned table.

It may be safe to state that in all micelles and emulsion systems, equations (3) and (4) can be used generally for the determination of these aggregated systems.



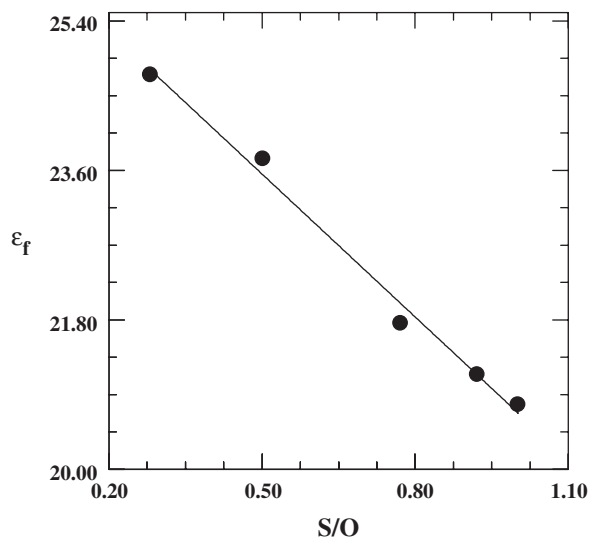


Figure 5. Plot of the effective dielectric constant of bicontinuous microemulsions versus surfactant to oil ratio.

#### 4. Conclusions

It has been shown in this work that the  $E_T(30)$  molecule is useful in the estimation of the effective dielectric constants of aggregated systems of surfactants (micelles and microemulsions). Generalized equations usable for the determination of this important micellar/microemulsion property were developed based on the alcohol system. This is consistent with that proposed by Zachariasse and coworkers. There was a satisfactory agreement between the calculated and experimental  $\epsilon_f$  values, within experimental limits, using the regression equations developed in this work.

#### Acknowledgement

The author is grateful to the EARDA program of Morgan State University for support of this work.

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