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Quantitative Structure-Property Relationship on Prediction of Surface Tension of Nonionic Surfactants

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Abstract: A quantitative structure-property relationship (QSPR) study has been made for the prediction of the surface tension of nonionic surfactants in aqueous solution. The regressed model includes a topological descriptor, the Kier & Hall index of zero order (*KH0*) of the hydrophobic segment of surfactant and a quantum chemical one, the heat of formation (ΔH_f) of surfactant molecules. The established general QSPR between the surface tension and the descriptors produces a correlation coefficient of multiple determination, r^2 =0.9877, for 30 studied nonionic surfactants.

Keywords: Quantitative structure-property relationship, surface tension, nonionic surfactants.

When a surfactant is solved into a solvent, it will adsorb onto the surface of the solution and reduce the surface free energy to a marked degree. The surface free energy, which is the minimum amount of work required to create that surface, is usually measured by surface tension. The minimum of surface tension γ^0 is the most useful key for characterizing the activity of surfactant. It is well known that γ^0 is determined by the molecular structure of surfactant, *i.e.*, the contributions from both the size of the hydrophobic domain (tail) and the size of the hydrophilic domain (head) of surfactant. Quantitatively, the measurement of γ^0 for a wide range of surfactants under different solvent conditions has been taken very accurately. Besides, some empirical relationships based on the data of experiment between the structural features of surfactants and γ^0 have been developed for surfactants[1,2]. However, there is no report on the investigation of the relations between surface tension and the motion state as well as the motion level of electrons in the surfactant molecules with the quantum chemistry method.

The present work is based on the observed values of γ^0 using the total energy E_T, the heat of formation ΔH_f , the ionization potential E_I, the energy of the lowest unoccupied orbit E_{LUMO} as well as the dipole moment D of the surfactant molecules, which are computed with the semi-empirical molecular orbital method, and the zero order Kier & Hall index $KH0$ of the hydrophobic fragment of the molecules as

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descriptors, to establish the QSPR between γ^0 and these descriptors for the nonionic surfactants.

Data and Methodology

The data set of γ^0 was chosen to contain only the most commonly used nonionic surfactants so that they can give more reliable observed values for study. The major source of these γ^0 values was mainly gotten from Rosen's textbook[1]. Additional values for $C_{12}H_{25}[(OC_2H_4)_m(OC_3H_6)_nOH]$ (m = 3, 4, 5 and n= 4, 5, 6) were obtained from our unpublished data.

Before the calculation, the molecular structures were optimized with MNDO-PM3 software. All the computation was carried out on a PIII 766 PC computer with the MNDO -MOPAC7.0 software.

The topological descriptor $KH0$, which represents the size of the hydrophobic segment and contains group contributions from all nonhydrogen atoms in the fragment, is defined as[3]

$$KH0 = \sum_{i=1}^{N} (\delta_i^v)^{-1/2} \qquad \text{where} \quad \delta_i^v = \frac{Z_i^v - H_i}{Z_i - Z_i^v - 1} \tag{1}$$

Here Z_i is the total number of electrons in the i th atom, Z_i^v is the number of valance electrons, and H_i is the number of hydrogen directly attached to the i th atom. Valence contributions are summed for all the atoms in the fragment, with the exception of the hydrogen atoms ($N = N_{\text{total}} - N_{\text{H}}$). The divisions of hydrophobic and hydrophilic segments of the nonionic surfactants and the values of KH0 as well as the quantitative chemical descriptors are listed in **Table 1**.

Results and Discussion

The regression on γ^0 with each quantitative chemical descriptor for the 30 studied nonionic surfactants shows that γ^0 has no regular dependence on E_{I}, E_{LUMO} and D, but linearly depends on ΔH_f and E_{T}. The regression equations are

$$\gamma^0 = 18.44 - 0.00902\,\Delta H_f \qquad (R = -0.9760,\ s^2 = 1.074) \tag{2}$$

$$\gamma^0 = 18.85 - 0.002211 E_{\text{T}} \qquad (R = -0.9572,\ s^2 = 1.436) \tag{3}$$

Here R is the correlation coefficient and s^2 is the standard error that measures the model error. These results mean that the reduction of surface energy of solution of surfactants does not exchange the electronic motion level and the dipole moment of surfactants. They also imply that this reduction mainly depends on the exchange of hydrogen bonds owing to the formation of the hydrogen bonds between surfactants and solvents. The variation of γ^0 *vs.* ΔH_f or E_{T} in **Table 2** for different oxyethyl group numbers with fixed hydrophobic segments gives further proofs of this conclusion.

Table 1 The values of descriptors, the observed (25℃) and the calculated logarithm of *cmc* for linear alkyl polyethylene oxide and *p*,*t*-octylphenyl polyethylene oxide

Structure (Hydrophobic seg.[Hydrophilic seg.])	E/eV	H/kJ.mol^{-1}	KH0	$\gamma_{ob.}$ /mN.m^{-1}	$\gamma_{cal.}$ /mN.m^{-1}	Temp./°C
$C_6H_{13}[(OC_2H_4)_6OH]$	-4775	-1299	4.54	32.0	31.5	25
$C_{10}H_{21}[(OC_2H_4)_6OH]$	-5373	-1390	7.36	30.0	31.8	25
$C_{10}H_{21}[(OC_2H_4)_8OH]$	-6557	-1714	7.36	35.6	35.2	25
$C_{12}H_{25}[(OC_2H_4)_3OH]$	-3895	-950.8	8.78	27.9	27.2	25
$C_{12}H_{25}[(OC_2H_4)_4OH]$	-4487	-1112	8.78	28.6	28.7	25
$C_{12}H_{25}[(OC_2H_4)_5OH]$	-5080	-1274	8.78	30.5	30.3	25
$C_{12}H_{25}[(OC_2H_4)_6OH]$	-5672	-1436	8.78	31.0	31.8	25
$C_{12}H_{25}[(OC_2H_4)_7OH]$	-6264	-1597	8.78	33.7	33.4	25
$C_{12}H_{25}[(OC_2H_4)_8OH]$	-6856	-1759	8.78	34.8	34.9	25
$C_{12}H_{25}[(OC_2H_4)_9OH]$	-7449	-1921	8.78	36.0	36.4	25
$C_{12}H_{25}[(OC_2H_4)_{12}OH]$	-9225	-2413	8.78	40.0	41.1	25
$C_{13}H_{27}[(OC_2H_4)_8OH]$	-7006	-1782	9.49	35.3	34.7	25
$C_{14}H_{29}[(OC_2H_4)_8OH]$	-7155	-1804	10.19	34.0	34.5	25
$C_{15}H_{31}[(OC_2H_4)_8OH]$	-7305	-1827	10.9	34.6	34.4	25
$C_{16}H_{33}[(OC_2H_4)_6OH]$	-6270	-1527	11.61	32.0	31.7	25
$C_{16}H_{33}[(OC_2H_4)_7OH]$	-6862	-1688	11.61	33.0	32.9	25
$C_{16}H_{33}[(OC_2H_4)_9OH]$	-8047	-2012	11.61	36.0	35.4	23
$C_{16}H_{33}[(OC_2H_4)_{12}OH]$	-9823	-2504	11.61	39.0	39.1	23
$C_{12}H_{25}[(OC_2H_4)_3(OC_3H_6)_6OH]$	-8346	-2057	8.78	38.8	37.8	25
$C_{12}H_{25}[(OC_2H_4)_4(OC_3H_6)_5OH]$	-8197	-2035	8.78	38.7	37.6	25
$C_{12}H_{25}[(OC_2H_4)_5(OC_3H_6)_4OH]$	-8047	-2012	8.78	38.5	37.4	25
p-t-$C_8H_{17}C_6H_4[(OC_2H_4)_7OH]$	-6438	-1396	10.02	30.0	31.1	25
p-t-$C_8H_{17}C_6H_4[(OC_2H_4)_8OH]$	-7030	-1558	10.02	32.0	32.5	25
p-t-$C_8H_{17}C_6H_4[(OC_2H_4)_9OH]$	-7622	-1720	10.02	33.5	33.9	25
p-t-$C_8H_{17}C_6H_4[(OC_2H_4)_{10}OH]$	-8215	-1881	10.02	35.0	35.3	25
$C_8H_{17}[CHOHCH_2OH]$	-2113	-585.9	5.95	23.4	23.1	25
$C_8H_{17}[CHOHCH_2CH_2OH]$	-2263	-605.9	5.95	23.6	23.3	25
$C_{10}H_{21}[CHOHCH_2OH]$	-2412	-631.3	7.36	22.7	23.0	25
$C_{10}H_{21}[CHOHCH_2CH_2OH]$	-2562	-650.6	7.36	23.7	24.1	25
$C_{12}H_{25}[CHOHCH_2CH_2OH]$	-2861	-696.1	8.78	26.5	24.8	25

Although the regression on γ^0 with *KH0* does not show a clear regular dependence either, the combination of *KH0* with ΔH_f can further improve the value of the correlation coefficient and give the best regression equation among the multiple descriptor regression analysis as

$$\gamma^0 = 12.66-0.01529\,\Delta H_f +0.6310KH0+0.0006576\,\Delta H_f\,KH0$$

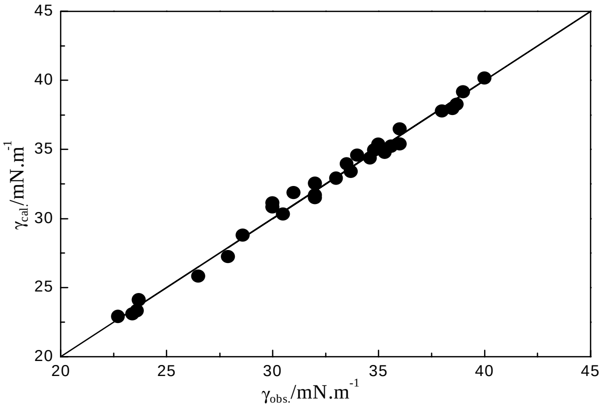
$$(R = -0.9877,\ s^2 = 0.7735)\ n = 30) \qquad (4)$$

Compared with Eq. (2), the absolute value of correlation coefficient in Eq. (4) increases slightly from 0.9760 to 0.9877. This result is consistent with the conclusion that the volume of hydrophobic segment of surfactants can only slightly affect the surface tension[2]. The calculated values ($\gamma^0_{cal.}$) from Eq.(4) and the observed ones ($\gamma^0_{obs.}$) are also listed in **Table 1** and the corresponding scatter plot is shown in **Figure 1**.

Table 2 The regression equation between γ^0 and E_T as well as ΔH_f of nonionic surfactants

Structures	Number of sample	Relationships between γ^0 and E_T	R_E	Relationships between γ^0 and ΔH_f	R_H
$C_{12}H_{25}[(OC_2H_4)_nOH]$	8	$18.40-0.002360E_T$	-0.9948	$19.42-0.008601\,\Delta H_f$	-0.9948
$C_{12}H_{25}[(OC_2H_4)_nOH]$	4	$19.42-0.002011E_T$	-0.9960	$20.87-0.007310\,\Delta H_f$	-0.9958
$C_8H_{17}C_6H_4[(OC_2H_4)_nOH]$	4	$12.21-0.002791E_T$	-0.9973	$15.91-0.001022\,\Delta H_f$	-0.9973
average slope		-0.002387		-0.005644	
average $\overline{R}$			-0.9960		-0.9960

Figure 1 Scatter plot of the calculated surface tension $\gamma_{cal.}$ *vs.* the observed surface tension $\gamma_{obs.}$ for 30 nonionic surfactants.



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References

1. M. J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd, John Wiley and Sons, New York, **1988**, pp.122-132.
2. G. X. Zhao *Physical Chemistry of Surfactants*, 1st, Peking University Press, Beijing, **1991**, 456-502.
3. P. D. T. Huibers, V. S. Lobanov, *et. al.*, *Langmuir*, **1996**, *12*, 462.

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