# Application of a Theory of Polymer Solutions to the Cloud Points of Nonionic Detergents

## J. GOLDFARB AND L. SEPULVEDA

*Department of Physical Chemistry, Faculty of Chemistry and Pharmacy, Universidad de Chile, Santiago, Chile*

The influence of the concentration of nonionic detergents on the cloud point of their aqueous solutions is discussed using Huggins' theory of polymer solutions. The treatment is exemplified by applying the theory to the phase diagrams obtained with detergents of varying polyethyleneoxide chain length. Under some simplifying assumptions, the activity coefficients of the water and the interaction parameters are calculated. From the same equations a relationship between cloud point and detergent concentration is obtained. Values for the enthalpic and entropic terms included in the interaction parameters are calculated for one detergent-water system for which vapor pressure data are available.

## INTRODUCTION

The so-called clouding of aqueous solutions of nonionic detergents has been receiving considerable attention in recent years; the temperature at which clouding occurs (cloud point) has been extensively studied in connection with the chemical structure of the detergent, the properties of the corresponding micelles, and the influence of added cosolutes (1–3 and references included). Most studies have been conducted, however, with reference to a single, usually dilute, concentration of detergent. Regarding the influence of the detergent concentration on the cloud point, it has been said that the curves obtained when the cloud points are plotted as a function of detergent concentration correspond to binary phase diagrams with lower consolute temperatures (4, 5); if this is the case, thermodynamic data from homogeneous solutions may then be used to examine the cloud points of a particular system (4, 5).

The phase diagrams obtained with aqueous nonionic detergents are as a rule highly un-symmetrical, with one branch nearly coincident with the temperature axis. Highly unsymmetrical phase diagrams are also found in solutions of polymers of very high molecular weight (6); this may not be a mere coincidence since the kinetic units of the solute in a detergent solution near the cloud point will consist of micelles of molecular weights as high as those of the polymers showing similar phase diagrams. With these analogies in mind, it appeared of interest to discuss the phase diagrams of aqueous nonionic detergents along the lines of the theories of polymer solutions. In this context the present work represents an attempt to apply the equations of Huggins' theory of polymer solutions (7) to a number of phase diagrams obtained with mixtures of octylphenylpoly-oxyethylene ethers using water as the solvent. The same treatment can be applied in principle to any other type of nonionic detergents showing similar miscibility behavior.

## EXPERIMENTAL

The octylphenylpolyoxyethylene ethers used were supplied by Rohm and Haas Co.,

Philadelphia (Tritons, Reg. Mark). Prior to use, solutions of these detergents were heated up to temperatures well above the cloud point and the aqueous phase was discarded; this procedure was repeated several times so as to eliminate traces of poly-ethyleneglycols that might be present in the samples (8). From the detergents supplied, various mixtures were prepared so as to obtain small mutual differences in the number of EO units in the hydrophilic chain. The average number of EO units for each mixture was calculated from elementary analysis performed in a Perkin Elmer automatic analyzer type 240. The samples selected had 7.3, 7.6, 8.0, 8.8, 9.6, and 12–13 EO units per molecule (the range in the last number reflects the difficulty in drying the sample). For a number of solutions of these samples in water at various concentrations the cloud points were determined visually, the temperatures for the appearance and disappearance of turbidities being within ±0.1° C.

In the following discussion, weight fractions are taken as equivalent to volume fractions calculated from the specific volumes of the pure compounds; both fractions differ
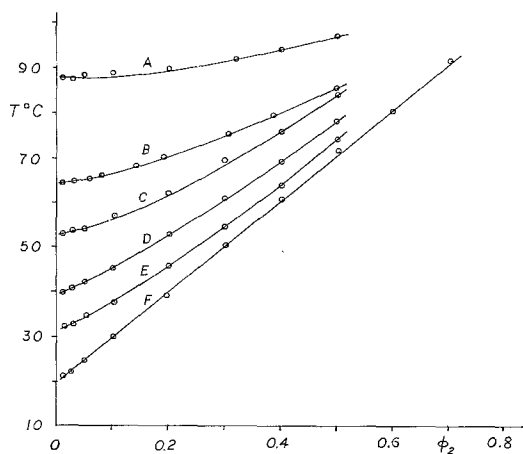


FIG. 1. Cloud points of nonionic detergent solutions as a function of volume fraction of detergent. Average number $n$ of EO units per molecule: Curve $A$: 12.5; $B$: 9.6; $C$: 8.8; $D$: 8.0; $E$: 7.7; and $F$: 7.3.

very little since the densities of the detergents used are very similar to the density of water.

The results of the cloud points measured in the systems examined are shown in Fig. 1.

DISCUSSION

As stated in the Introduction, the phase diagrams of aqueous nonionic detergents will be examined from the point of view of polymer solution theories. According to Huggins (7), the chemical potential of the solvent in a solution containing a macromolecular solute will be given by:

$$\mu_1 = \mu_1^0 + RT$$
$$\cdot \left\{ \ln \phi_1 + \left( 1 - \frac{\bar{V}_1}{\bar{V}_2} \right) \phi_2 + \chi \phi_2^2 \right\}, \quad [1]$$

where the subscripts 1 and 2 refer to solvent and solute, respectively, $\mu_1^0$ being the molar free energy of pure solvent at temperature $T$, $\phi_i$ the volume fractions, $\bar{V}_i$ the partial molar volumes, and $\chi$ an "interaction parameter" which will be described below. Although Eq. [1] has been derived strictly only for solutions of linear macromolecules, it will be used here for the solvent in a micellar solution on the basis of the extended treatment given by Hildebrand (9). A similar approach has been used by Kuriyama (1).

If the curves of Fig. 1 are considered as binary phase diagrams, two liquid phases will be in equilibrium at any given temperature above the lower consolute point; that is, one phase made up of virtually pure solvent (henceforward to be called the aqueous phase) which on the scale of Fig. 1 appears coincident with the temperature axis and another phase containing appreciable amounts of detergent (henceforward to be called the concentrated phase). For the aqueous phase the chemical potential of the water may be taken as equal to $\mu_1^0$ without serious error. Either from spectrophotometric measurements (10) or from surface tension data (5), the volume fractions of detergent in the aqueous phase come to between $10^{-3}$ and $10^{-4}$. If it is assumed that Raoult's law

holds for these solvents at these concentrations (4), $(\mu_1 - \mu_1^0)/RT$ will be of the order of $10^{-4}$. Under that approximation and using the equilibrium condition of equality of chemical potentials of the solvent in both phases we obtain:

$$\ln \phi_1^c + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right)\phi_2^c + \chi^c(\phi_2^c)^2 = 0, \quad [2]$$

where the superscript $c$ refers to critical compositions, that is, those along the lines of phase separation for the concentrated phases of Fig. 1.

A further simplification is obtained by taking $(1 - \bar{V}_1/\bar{V}_2)$ as equal to one; this appears justified since the ratio of molar volumes: water/detergent micelles will be of the order of $10^{-4}$ or lower. Thus, for concentrations not too close to the consolute temperature ($\phi_2^c \geqq 0.03$ approximately), the following equations can be applied to the system:

$$\ln \phi_1^c + \phi_2^c + \chi^c(\phi_2^c)^2 = 0 \quad [3]$$

and

$$\ln \phi_1^c + \ln \gamma_1^c = 0, \quad [4]$$

where $\gamma_1^c$ is the activity coefficient of the water in the concentrated phase on a volume fraction basis. Then, values of $\chi^c$ and $\gamma_1^c$ can be easily calculated by inserting in Eqs. [3] and [4] the corresponding water volume fractions, these in turn being obtained from the phase diagrams. The advantage of having a set of phase diagrams with small mutual differences like those of Fig. 1 is that

it makes it possible to obtain values of $\chi^c$ and $\gamma_1^c$ for related systems at the same temperature. The results of the calculations are shown in Table I.

*The Interaction Parameter.* It appears of interest to attempt to express the values of $\chi^c$ shown in Table I in terms of the separate enthalpy and entropy contributions. This may be done, following Huggins (7), as follows:

The parameter $\chi$ of Eq. [1] may be taken as the sum of two separate terms, namely:

$$\chi = \chi_h + \chi_s, \quad [5]$$

where

$$\chi_h = \frac{\Delta \bar{H}_1}{RT\phi_2^2} \quad [6]$$

and

$$\chi_s = -\frac{1}{\phi_2^2}\frac{\Delta \bar{S}_1}{R}$$

$$-\frac{\ln \phi_1 + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right)\phi_2}{\phi_2^2}. \quad [7]$$

Here $\Delta \bar{H}_1$ and $\Delta \bar{S}_1$ stand for the partial molar enthalpy and entropy, respectively, of the solvent.

On the other hand, $\chi$ may also be written (7) as the sum of a temperature-dependent and a temperature-independent term, that is:

$$\chi = a_x + \frac{b_x}{T}, \quad [8]$$

where

$$a_x = \frac{-\ln \phi_1 - \phi_2}{\phi_2^2} - \psi_a \quad [9]$$

TABLE I

ACTIVITY COEFFICIENTS AND INTERACTION PARAMETERS FOR WATER IN NONIONIC DETERGENTS

| $n$ | 7.3 | | | 7.7 | | | 8.0 | | | 8.8 | | | 9.6 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $t(°C)$ | $\phi_1^c$ | $\gamma_1^c$ | $\chi^c$ | $\phi_1^c$ | $\gamma_1^c$ | $\chi^c$ | $\phi_1^c$ | $\gamma_1^c$ | $\chi^c$ | $\phi_1^c$ | $\gamma_1^c$ | $\chi^c$ | $\phi_1^c$ | $\gamma_1^c$ | $\chi^c$ |
| 55 | 0.66 | 1.5 | 0.65 | 0.70 | 1.4 | 0.63 | 0.77 | 1.30 | 0.59 | 0.96 | 1.05 | | | | |
| 65 | 0.57 | 1.8 | 0.71 | 0.60 | 1.7 | 0.69 | 0.64 | 1.55 | 0.66 | 0.76 | 1.31 | 0.59 | 0.98 | 1.02 | (0.50) |
| 75 | 0.46 | 2.2 | 0.81 | 0.50 | 2.0 | 0.79 | 0.54 | 1.85 | 0.74 | 0.61 | 1.64 | 0.69 | 0.71 | 1.40 | 0.62 |

*Note:* $n$ is the average number of EO units per molecule (see Experimental Part) $\phi_1^c$, $\gamma_1^c$, and $\chi^c$ as defined by Eqs. [3] and [4].

and

$$\psi_a = \psi_a{}^0 + \psi_a{}'\phi_2 + \psi_a{}''\phi_2{}^2 + \cdots ; \quad [10]$$

$b_x$ can also be expressed as a power series of $\phi_2$, namely:

$$b_x = b_x{}^0 + b_x{}'\phi_2 + b_x{}''\phi_2{}^2 + \cdots . \quad [11]$$

In the treatment below, the parameters of Eq. [8] will be used in preference to those of Eq. [5] because $a_x$ is defined in [8] to be temperature independent. In Eq. [5] $\chi_s$ may vary with temperature, thus making it more difficult to use this equation.

*A Relation between Cloud Point and Detergent Concentration.* The dependence found experimentally between the concentration of detergent and the temperature at which phase separation takes place can be accounted for on the basis of the equations just developed as follows:

Comparison between the parameter $\chi^c$ as defined in Eq. [3] and $\chi$ as defined in Eqs. [8] and [9], that is,

$$\chi^c = \frac{-\ln \phi_1{}^c - \phi_2{}^c}{\phi_2{}^{2c}}, \quad [3']$$

$$\chi = \frac{-\ln \phi_1 - \phi_2}{\phi_2{}^2} - \psi_a + \frac{b_x}{T}, \quad [8']$$

shows that for $\chi$ to become equal to $\chi^c$, it is required that $\psi_a$ be equal to $b_x/T$. This will take place at a particular temperature $(T^c)$ given by:

$$T^c = \frac{b_x}{\psi_a}$$

which by means of Eqs. [10] and [11] becomes:

$$T^c = \frac{b_x{}^0 + b_x{}'\phi_2{}^c + b_x{}''\phi_2{}^{2c} + \cdots}{\psi_a{}^0 + \psi_a{}'\phi_2{}^c + \psi_a{}''\phi_2{}^{2c} + \cdots}, \quad [12]$$

giving the desired relation between cloud point and detergent concentration. By adjusting the parameters of Eq. [12] it should be possible to fit the right branches of the various phase diagrams of Fig. 1. However, this type of calculation would be of value only when the number of parameters involved is small. Hence, it appears convenient to attempt to find, from [12], equations that may account for the main features of the phase diagrams in terms of the minimum number of adjustable parameters.

The simplest case is that of the lower homolog studied $(n = 7.3)$, for which the straight-line relationship shown in Fig. 1 may be represented in terms of only three parameters, namely:

$$T^c = \frac{b_x{}^0 + b_x{}'\phi_2{}^c}{\psi_a{}^0}. \quad [13]$$

Applying [13] to the experimental data we obtain the following ratios: $b_x{}^0/\psi_a{}^0 = 292$; $b_x{}'/\psi_a{}^0 = 109$; and $b_x{}^0/b_x{}' = 2.7$. Furthermore, since both the intercepts and slopes are positive, it is concluded that the three parameters involved must have the same sign.

As the EO chain increases, the slopes of the curves of Fig. 1 are seen to decrease with decreasing $\phi_2{}^c$; this behavior may be reproduced by including in Eq. [13] an additional term $\psi_a{}'\phi_2{}^c$ with $\psi_a{}'$ opposite in sign to $\psi_a{}^0$. For the highest homologs in Fig. 1, the slopes are very close to zero for low detergent concentrations. To reproduce this behavior it is necessary to add three additional terms to Eq. [13], namely, $b_x{}''\phi_2{}^2$, $\psi_a{}'\phi_2$, and $\psi_a{}''\phi_2{}^2$, but then to work with an equation of six adjustable parameters is of no practical value.

The fact that at a given volume fraction the cloud point is seen to increase when the EO chain increases may be accounted for by postulating a decrease in $\psi_a{}^0$ when the chain length increases, together with a constancy or a slight decrease in $b_x$. As discussed later, this behavior is consistent with experimental evidence for this and related systems.

*Discussion of Data from Homogeneous Solutions.* The values of $\chi^c$ discussed in the preceding sections may be compared with the values of the interaction parameter $\chi$ calculated for homogeneous one-phase systems of the same composition. Values of $\chi$ for

aqueous detergent solutions may be obtained from water activities calculated from the measured partial vapor pressures of water of the solutions.

In Eq. [1], the term within the brackets on the right-hand side of the equation is equal to the logarithm of the water activity $a_1$; therefore $\chi$ will be given by:

$$\chi = \left(\ln \frac{a_1}{\phi_1} - \phi_2\right)\frac{1}{\phi_2{}^2}, \qquad [14]$$

from which $\chi$ may be calculated if $a_1$ and $\phi_1$ are known. The values of $\chi$ thus calculated using the vapor pressure data obtained previously (5) for aqueous solutions of Triton X-114 at 40°C, are presented in Fig. 2 as a function of detergent concentration, The values of $\chi^c$ calculated from [3'] are plotted in the same figure. It may be observed that the values of $\chi$ all lie below the $\chi^c$ line; this is to be expected since for homogeneous solutions $\mu_1 < \mu_1{}^0$ and in order to attain phase separation $\mu_1$ must become equal to $\mu_1{}^0$. Hence at a given $\phi_2$, $\chi$ must increase, thereby increasing $\mu_1$ until it reaches the critical value $\chi^c$ necessary to satisfy Eq. [3']. At constant $\phi_2$, $\chi$ will increase with temperature if $b_x < 0$ because $a_x$ has been defined as temperature independent, as can be seen

in Eq. [8]. The difference between $\chi$ and $\chi^c$ at a given temperature and volume fraction is simply $-\psi_a + b_x/T$ according to Eqs. [3'] and [8']. If it is assumed that the functional form of $\psi_a$ and $b_x$ is the same at lower temperatures as that used in Eq. [13] (which describes the cloud point–concentration relationship) the difference between $\chi$ and $\chi^c$ will be given by a linear relation in $\phi_2$, namely:

$$\chi - \chi^c = \frac{b_x{}^0}{T} + \frac{b_x{}'}{T}\phi_2 - \psi_a{}^0. \qquad [15]$$

By calculating the differences between $\chi$ and $\chi^c$ from the data shown in Fig. 2 and plotting them as a function of $\phi_2$, an approximately linear relation is obtained. From the slope of this line $b_x{}'$ comes out $-50$; from this value the values of the other parameters can be calculated using the parameter ratios obtained above from the phase diagrams. The values obtained are $-0.46$ for $\psi_a{}^0$ and $-135$ for $b_x{}^0$.

For values of $\phi_2$ smaller than 0.2 the system becomes a two-phase one. At that volume fraction the $\chi$ line must intersect the $\chi^c$ line and the $\chi$ line in Fig. 2 has been extrapolated accordingly (dotted region). In this region $\chi$ values cannot be obtained from vapor pressure data (5) and the extrapolation may be used to estimate approximate values up to the critical composition at that temperature.

The pattern outlined here for nonionic detergents of varying hydrophilic chain length appears to contradict the idea that the increasing cloud points obtained are a result of increased hydration of the molecules (12). If hydration is related to the corresponding heats of solution in water, greater hydration will imply a lower and negative heat of solution; this would not be in agreement with the data obtained for the corresponding polymers (11) since $\chi_h{}^0$ appears to decrease with increasing chain length in polyethylene glycols. However, the correlation between hydration and heats of solution is by no means unambiguous, as discussed elsewhere
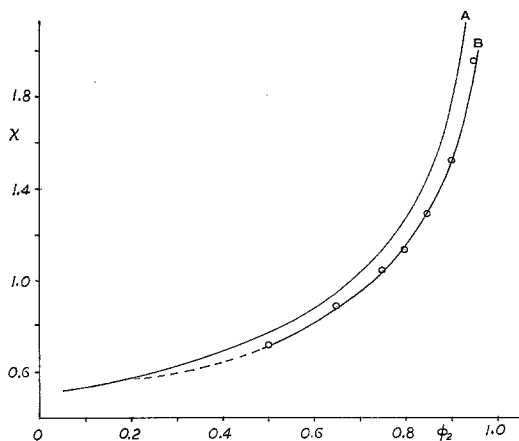


FIG. 2. Interaction parameters as a function of detergent volume fraction. Curve $A$: $\chi^c$ calculated from Eq. [3]. Curve $B$: $\chi$ calculated from Eq. [14] using the vapor pressure of water in mixtures with Triton X-114 at 40°C (cf. reference 5).

(13). Values of hydration of detergent molecules obtained by other methods (14) show irregular variations with chain length.

On the other hand, the idea that phase separation in this type of detergent and in the corresponding polyethylene glycols is largely controlled by the entropic contributions to the chemical potentials (4, 5, 15) is in agreement with the signs and magnitudes of the $\psi_a$ parameters obtained here which are directly related to the entropy of the systems as stated by Eqs. [6] and [9]. On going from one homolog to the next, a decreasing value of the $\psi_a$ parameter would imply smaller deviations from the ideal entropy of mixing on a volume fraction basis and hence miscibility in a more extended range of temperature and compositions. However, since $\psi_a$ is not strictly equal to $\chi_s$, further improvements of the theory would be necessary in order to be able to calculate one from the other.

## REFERENCES

1. KURIYAMA, K., *Kolloid-Z.uZ. polymere* **181**, 144 (1962).

2. ELWORTHY, P. H., AND MACFARLANE, C. B., *J. Pharm. Pharmacol.* **17**, 65 (1965).

3. ARAI, H., *J. Colloid Sci.* **23**, 348 (1967).

4. CLUNIE, J. S., CORKILL, J. M., GOODMAN, J. F., SYMONS, P. C., AND TATE, J. R., *Trans. Faraday Soc.* **63**, 2839 (1967).

5. SEPULVEDA, L., AND MACRITCHIE, F., *J. Colloid and Interface Sci.* **28**, 19 (1968).

6. HERMANS, J. J., In H. R. Kruyt, ed., "Colloid Science," Vol. 11, pp. 77, 78. Elsevier, Amsterdan, 1949.

7. HUGGINS, M. L., *J. Am. Chem. Soc.* **86**, 3535 (1964).

8. SHINODA, K., AND NAGAKAWA, T. "Colloidal Surfactants," pp. 167. Academic Press, New York, 1963.

9. HILDEBRAND, J. H., AND SCOTT, R. "The Solubility of Nonelectrolytes," pp. 109. Dover, New York, 1964.

10. DOREN, A., AND GOLDFARB, J., Unpublished results.

11. KAGEMOTO, A., MURAKAMI, S., AND FUJSHIRE, R., *Makromol. Chem.* **105**, 154 (1967).

12. SCHICK, M. J., *J. Colloid Sci.* **17**, 810 (1962).

13. GOLDGARB, J., AND RODRIGUEZ, S., *Makromol. Chem.* **116**, 96 (1968).

14. SCHOTT, H., *J. Colloid Sci.* **24**, 193 (1967).

15. MALCOLM, G. N., AND ROWLINSON, J. S., *Trans. Faraday Soc.* **53**, 921 (1957).