BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 685—694 (1966)

Colloid Chemical Studies of Phase Diagrams of Binary Polyoxyethylene Nonylphenyl Ether - Water Systems

By Kazutoshi KENJO

Takahashi Toyodo Co., Ltd., Shinogawa-machi, Shinjuku-ku, Tokyo

(Received June 26, 1965)

Colloid chemical studies of the phase diagrams of binary systems of aqueous polyoxyethylene nonylphenyl ethers with different degrees of the polymerization of ethylene oxide, *n*, have been undertaken. The phase diagrams obtained have been divided into the heterogeneous region 1, existing in the range of temperature higher than cloud points; the homogeneous phase region II; the heterogeneous region III, existing below the II region; and the solid phase region IV. The II region contains a gel-like hardening region. The III region has been further divided into two sub-regions, on the higher and lower concentration sides; these subregions contain one hardening region each. The molecular and micellar structure models of these hardening regions have been presented. An unusual zone has been found in the phase diagram of the system for $n=7.5$; its state has also been discussed. Further, the mechanisms of the phase separation and phase inversion have been proposed, and three different types distinguished for the phase separation at the cloud point. A functional relationship has been found between the cloud point, the water content of an aqueous solution at the cloud point (the water affinity), and the *n* value. A linear relation has also been found between the solidification points of 100% surfactants and the ethylene oxide contents of the surfactants.

Owing to their stability against hydrolysis, heavy metal ions and pH change, and their rapid progress in chemical synthesis, the non-ionic surfactants are finding wide use in various industries. However, as for their chemical nature and fundamental properties, relatively few studies have been reported compared with the studies of the ionic surfactants.[1-4]

The present author has previously studied[5] ternary systems consisting of decaoxyethylene nonylphenyl ether, essential oils and water, and found some unusual phenomena, such as the existence of two cloud points in the same system, a discontinuity in the curve of the cloud point vs. the concentration, and a gel-like hardening.

The first phenomenon is very similar to the so-called "double cloud point" already reported,[6] which afterwards turned out to be due to the presence of impurities.[7] However, it is worth studying the phenomena in further detail since they have much to do with the practice of surfactant application. To facilitate the understanding of the phenomena shown by the ternary systems, it is pertinent first to get much information about the more simple binary systems, composed of the nonionic surfactants and water. As for such studies of binary systems, we have a few, but only a few reports, on, for instance, a possible phase diagram,[8,9] on the viscosity,[10-12] on the gel formation,[1,10,11,13] and especially on concentrated systems, for the variation of viscoelastic properties with the temperature,[14] the concentration,[15] and the frequency.[16]

Under such circumstances, the present author has taken up a binary system of aqueous nonionic surfactants of the polyoxyethylene nonylphenyl ether type, which are now widely used in practice, at temperatures ranging between −10°C and 100°C, constructed phase diagrams, and made colloid chemical studies by observing the change in the diagrams with the change in the degree of polymerization of ethylene oxide.

Materials

Polyoxyethylene nonylphenyl ether (abbreviation; NP-*n*, *n* being the degree of the polymerization of

---

1) N. Schönfeldt, "Oberflächenaktive Anlagerungs Produkte des Äthylenoxyds," Wissenschaftliche Verlagsges, Stuttgart (1959), pp. 100, 102.

2) T. Nakagawa, K. Shinoda, "Colloidal Surfactants," Academic Press, New York and London (1963), p. 97.

3) P. Becher, Fourth International Congress of Surface Activity, B/IV 20 (1964).

4) R. A. Hudson and B. A. Pethica, ibid., B/IV 21 (1964).

5) K. Kenjo, Unpublished.

6) C. D. Weston, *Hexagon Digest*, No. 13, 3 (1953).

7) T. Sagano, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **84**, 520 (1963).

8) R. R. Balmbra, J. S. Clunie, J. M. Corkill and J. F. Goodman, *Trans. Faraday Soc.*, **58**, 1661 (1962).

9) B. A. Mulley and A. D. Metcalf, *J. Colloid Sci.*, **19**, 501 (1964).

10) K. Boedeker, *Kolloid-Z.*, **94**, 161 (1941).

11) L. Marcou, *Teintex*, **17**, 421 (1952).

12) G. Böhme and R. Heusch, *Fette, Seifen, Anstrich Mittel*, **62**, 87 (1960).

13) H. L. Greenwald and G. L. Brown, *J. Phys. Chem.*, **58**, 825 (1954).

14) S. Kuroiwa, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **63**, 2065 (1960).

15) S. Kuroiwa, ibid., **63**, 1384 (1960).

16) S. Kuroiwa, ibid., **65**, 2032 (1962).

ethylene oxide) made by Nikko Chemicals and polyethylene glycol (abbreviation; PEG-*n'*, *n'* being the mean molecular weight) made by Sanyo Kasei were used after drying to a constant weight at 105°C. Some of their properties are shown in Table I. The NP-8.5 P in Table I was a sample derived from NP-7.5 by extracting it repeatedly, first with *n*-hexane at room temperature and then with water at temperatures higher than the cloud point. Thus, from 20 g. of NP-7.5, there were obtained 14.5 g. of a non-ionic agent, 5.1 g. of a *n*-hexane-soluble matter, and 0.2 g. of a hot water-soluble matter. Here, NP-8.5P denotes that the substance is purified from NP-7.5; the degree of the polymerization of ethylene oxide was found from its hydroxyl value to be about 8.5.

TABLE I. PROPERTIES OF MATERIALS USED

Material	Hydroxyl value	Solidification point, °C
NP-5	125	
NP-7.5	103	−11.8
NP-8.5	93.0	−1.8
NP-10	87.1	7.3
NP-12.5	76.8	14.0
NP-15	70.0	19.0
NP-18	58.3	25.2
NP-20	53.4	31.6
NP-25	45.9	35.0
NP-30	34.0	37.0
NP-50	25.8	43.5
PEG-1000	110	35.0
PEG-2000	54.5	47.2
NP-8.5P	94.5	−9.0

Experimental

Turbidity and Viscoelasticity Measurement.—Aqueous solutions or heterogeneous mixtures of water and non-ionic surfactants were taken in test tubes; the contents were heated to 100°C, and then cooled gradually. The change in the turbidity and viscoelastic appearance up to the solidification of the system was observed visually for rising and falling temperatures. The cooling curve was further constructed, and from it the solidification point was obtained.

Thus, the temperatures showing abrupt changes in turbidity and viscoelastic properties were plotted against the concentration of surfactant; the phase diagrams consisting of different dispersion states were thus obtained

The Observation of the Phase Separation.—The appearance of phase separation was visually observed for NP-7.5-surfactant solutions of 6, 8, 15, 33, 42 and 57% concentrations at varying temperatures (±0.2°C), and the volume fraction of the lower phase separated was measured.

Notations of the States of the System.—The turbid states were divided into five patterns, of the following increasing order of turbidity, on the phase diagrams:

transparent ░, half-transparent ░,
slightly turbid ▒, turbid ▒,
strongly turbid ▓

Here "half-tranaparent" corresponded to a TiO_2 (R-820 TiO_2, made by Ishihara Sangyo) aqueous dispersion below 0.0015%, "slightly turbid" to 0.0015—0.005%, "turbid" to 0.005—0.02%, and "strongly turbid" to above 0.02%-by-weight TiO_2.

The viscous states were divided into four gradations of "liquid" (S_1), "slightly viscous" (S_2), "viscous" (S_3) and "heavily viscous" (S_4) in the order of increasing viscosity. Here, S_1, S_2, S_3 and S_4 corresponded approximately to the viscosities below 0.5, 0.5—3, 3—12 and 12—50 poises respectively.

The hardened states were divided into four gradations of "weak paste" (P_1), "paste" (P_2), "strong paste" (P_3) and "rigid paste" (P_4) in the order of increasing consistency; they were qualitatively detected by the flow resistance of the paste. The "weak paste" was distinguished from the "heavily viscous" liquid in that the former did not deform perceptibly for at least ten seconds when the test tube used was kept horizontal. Here P_1, P_2, P_3 and P_4 corresponded approximately to 100—200, 200—600, 600—2000 and above 2000 poises respectively.

The Curves of the Diagrams.—CP-curve: cloud point curve; TP-curve; the curve of transparent points dividing the upper transparent and lower turbid regions; SP-curve: solidification point curve, and HP-curve: hardening point curve.

Results

Phase Diagrams.—The phase diagrams of NP-5 to NP-50 are shown in Figs. 1 to 11, and those of PEG·1000, PEG·2000 and NP-8.5P, in Figs. 12 to 14.

Symbols used in Figs. 1—14.

Regions
I: Region of two phase system
II: Region of homogeneous phase system
IV: Region of solid phase
R_{TP_1}, R_{TP_2}: Region of microheterogeneous system
R_{HP_1}, R_{HP_2}, R_{HP_3}: Region of hardening system
Ru: Unusual zone

Curves
SP: Solidification point curve
CP: Cloud point curve
TP_1, TP_2: Transparent point curve
HP_1, HP_2, HP_3: Hardening point curve
FP: Freezing point curve
T_I: Line of phase inversion

States of systems
Viscosity: Liquid (S_1), slightly viscous (S_2), viscous (S_3), and heavily viscous (S_4).

Consistency: Weak paste (P_1), paste (P_2), strong paste (P_3), and rigid paste (P_4)

Turbidity: Transparent ░

half-transparent ░

slightly turbid ▒

turbid ▓

strongly turbid █

//////////: Part of region showing fluorescence near minimum of CP-curve.

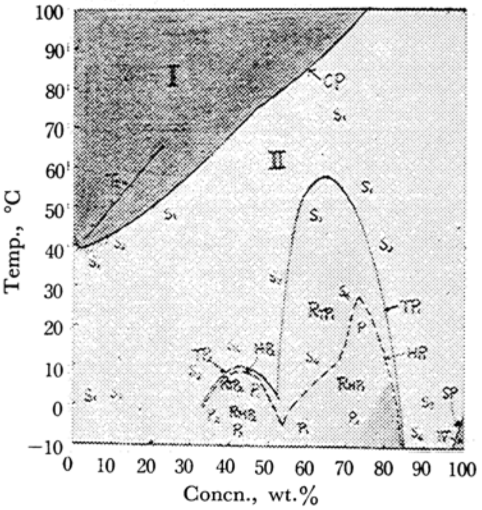

Fig. 3. Phase diagram of NP-8.5 - water system.

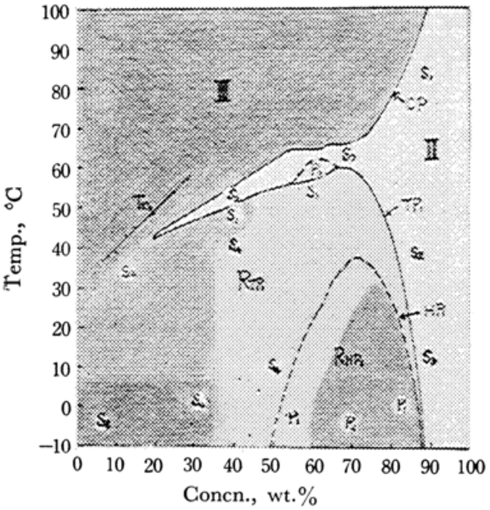

Fig. 1. Phase diagram of NP-5 - water system.

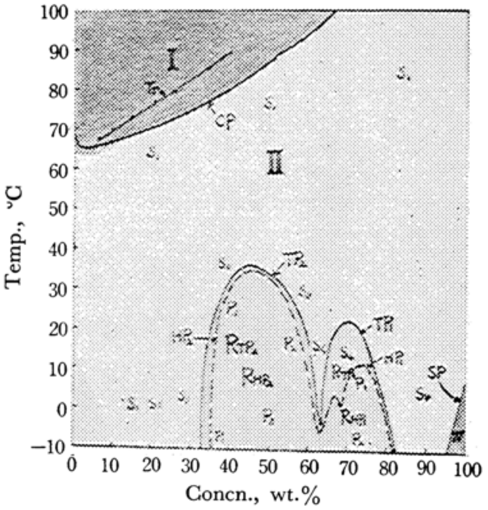

Fig. 4. Phase diagram of NP-10 - water system.

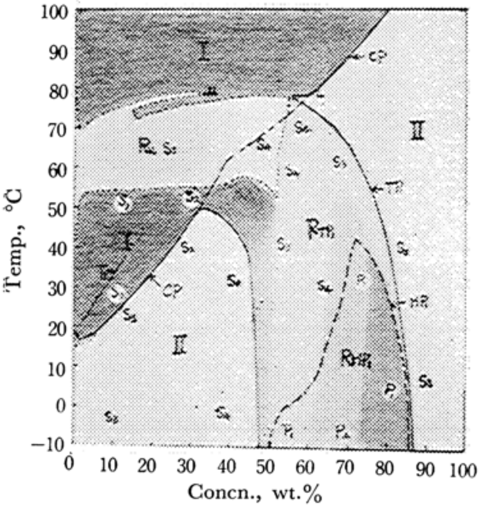

Fig. 2. Phase diagram of NP-7.5 - water system.

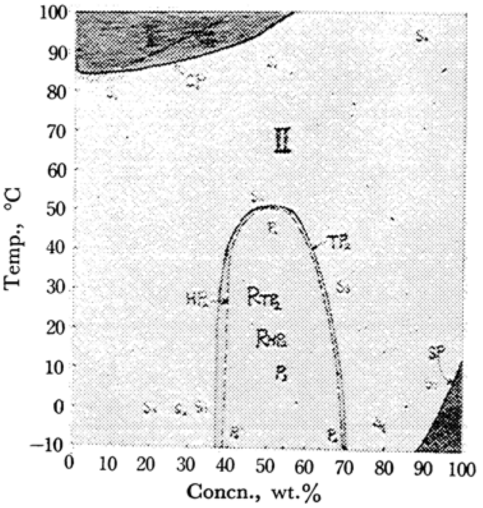

Fig. 5. Phase diagram of NP-12.5 - water system.

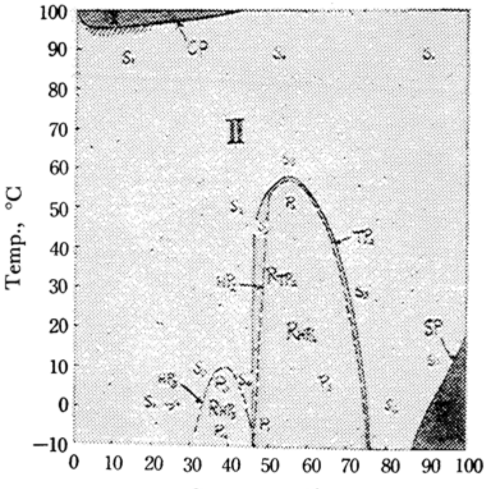

Fig. 6. Phase diagram of NP-15 - water system.

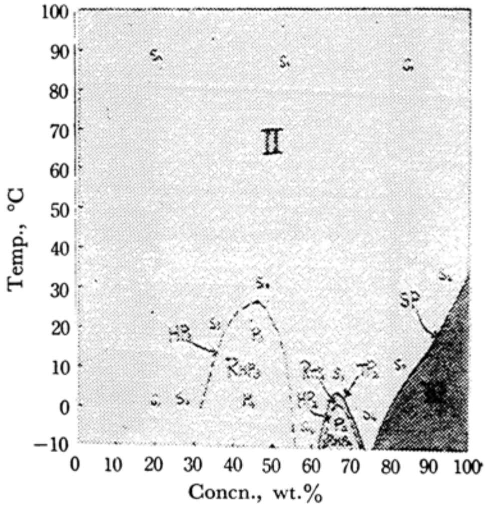

Fig. 9. Phase diagram of NP-25 - water system.

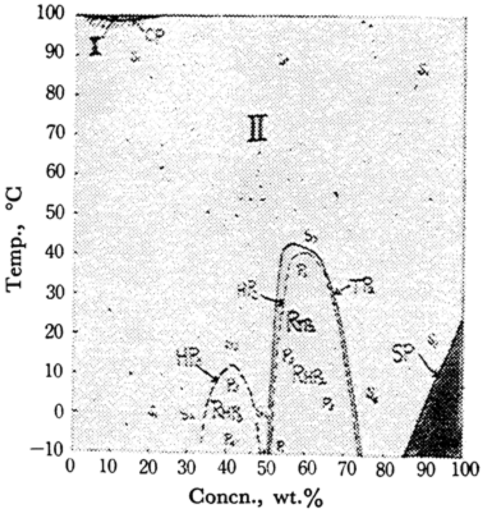

Fig. 7. Phase diagram of NP-18 - water system.

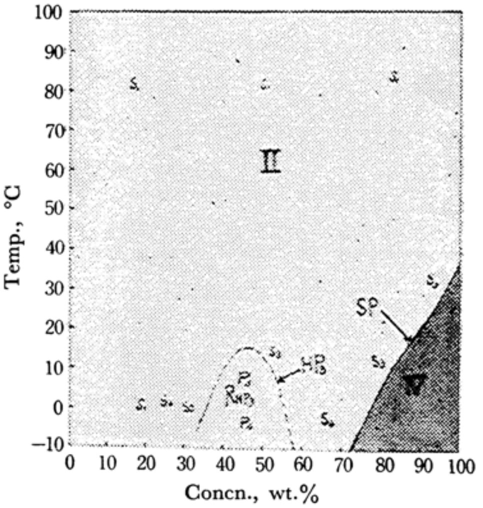

Fig. 10. Phase diagram of NP-30 - water system.

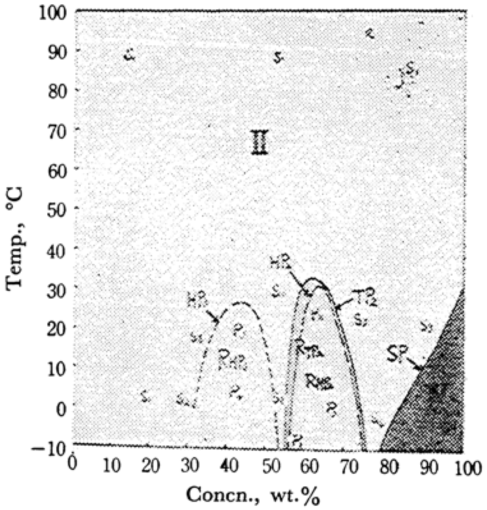

Fig. 8. Phase diagram of NP-20 - water system.

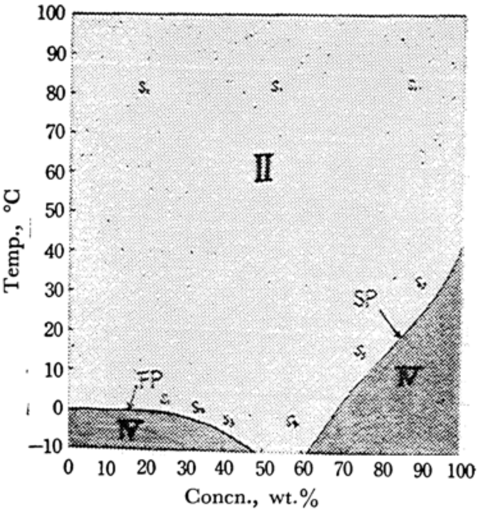

Fig. 11. Phase diagram of NP-50 - water system.

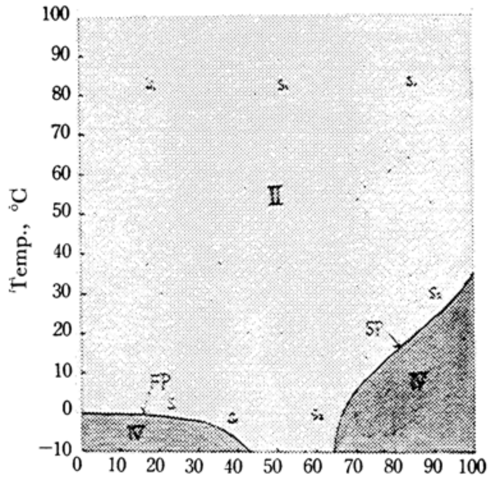

Fig. 12. Phase diagram of PEG-1000 - water system.

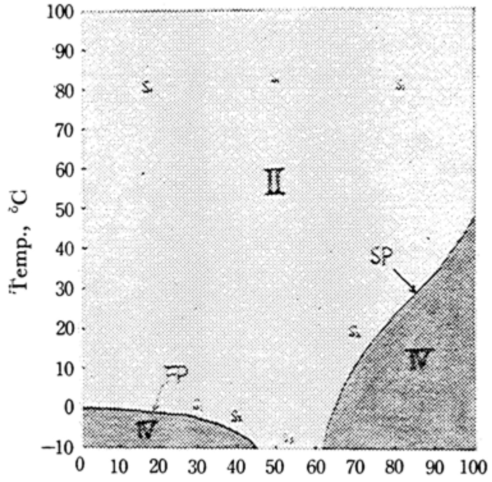

Fig. 13. Phase diagram of PEG-2000 - water system.

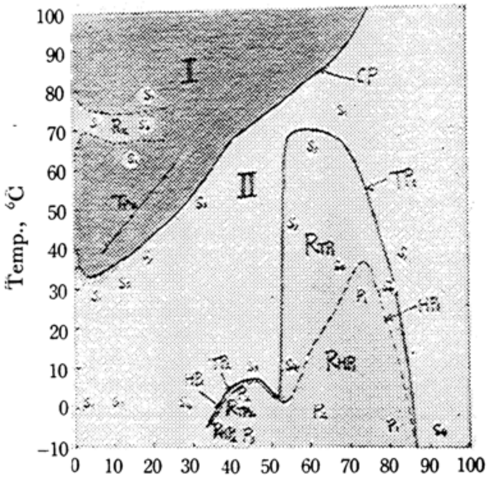

Fig. 14. Phase diagram of NP-8.5P - water system.

All the phase diagrams obtained were divided into four regions: I (a two-phase system existing above the CP-curve), II (a homogeneous phase system), III(a microheterogeneous or dispersed system below the TP-cruve) and IV (a solid phase system). For *n* values above 15, there was a region of clear paste, R_{TP_3}. The III region was further divided into two sub-regions, R_{TP} , and R_{TP_2}. containing R_{TP_1} and R_{TP_2} paste regions respectively, The phase diagram of PEG-2000 ($n\doteqdot 45$) system resembled that of the NP-50 system, but at lower temperatures the former system was much less biscous than the latter; at −20°C it remained in S_3 states, while the NP-50 system hardened at this temperature and in a concentration of about 52%.

A peculiarity was noted in the region I of the NP-7.5 system, which was divided into two parts by an "unusual zone" (Fig. 2). In this unusual zone the system did not separate into macroscopic phases, even after prolonged standing.

Phase Separation.—The results for the phase-separation experiments in the case of a 6% aqueous solution of NP-7.5, for instance, showed that, at the temperatures slightly above 76°C and 28°C, the lower phase considered as the dispersed phase sedimented in the upper phase of the dispersion medium, while slightly below these temperatures the lower phase changed into the dispersion medium and the upper phase creamed up and separated from the lower one.

Therefore, 28°C and 76°C are considered to be the temperatures of the phase inversions in this system. The volume fraction of the lower phase after the complete separation into two layers and the time required for it are plotted against the temperature in Fig. 15.

Usually, the lower phase after complete separation became turbid when the temperature was slightly raised, while it suffered no change when the temperature was lowered. However, somewhat different features were seen near 76°C; namely, the

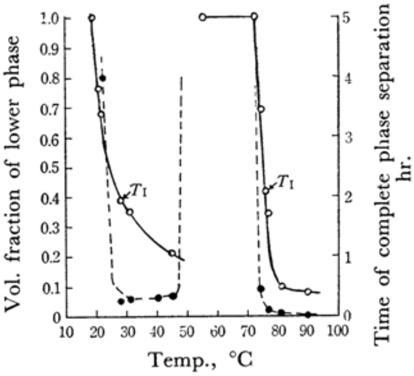

Fig. 15. Relative phase volume (solid line) and time of complete phase separation (broken line) vs. temperature for 6% aqueous solution of NP-7.5.

T_I indicates the temperature of phase inversion.

lower phase separated at 76°C, became transparent between 74.5°C and 76°C, and turbid below 74.5°C and above 76°C, while the upper phase suffered no change upon such a slight change of temperature. From these facts it follows that a narrow region, presumably belonging to the region II, may exist close to the upper limit of the unusual zone.

Calculating from the concentrations and the volume fractions of the lower phases, the concentration of NP-7.5 in the upper phase was found to be almost zero within the range of experimental errors for all cases; this can also be expected from the phase diagram (Fig. 2), and it is also in agreement with the result obtained by Nakagawa et al.[17] Figure 15 shows that there are two phase-inversion temperatures and that the volume fractions, of the lower phase at these two temperatures are nearly equal (0.42 and 0.39 respectively). This would mean that the volume ratio of the phase inversion is distinctly fixed for a given concentration of the surfactant. Results in the case of 8% and 15% solutions of NP-7.5 were similar to that of the 6% solution.

In the case of a 33% solution at 77.5°C, corresponding to the system in the narrow projected region I, the turbid liquid gradually turned into fluorescent heterogeneous state, but it did not separate into two phases, even after prolonged standing; this was presumably due to the small difference between the compositions of these two phases. In the case of a 42% solution at 79°C, the system rapidly separated into two phases, and the volume fraction of the lower phase was 0.35. From this result, the two phases separated are considered to have compositions corresponding to the U (33.3%) and L (60.5%) points in Fig. 2, the upper and the lower phases respectively. The upper phase, U, should then further separate very rapidly into two phases when the temperature is further raised slightly, since they are quite different in composition but are nearly equal in volume, while the lower phase, L, is expected to show only a slight turbidity. Such was actually proved to be the case. Thus it was confirmed that the point U in Fig. 2 is the extreme point of the narrow projection of the unusual zone, as is shown in Fig. 2. In the case of a 57% solution, the appearance of phases separated above the cloud point (78.5°C) was similar to that of the 6% solution, but below 77°C in the R_{TP_1} region the system did not separate into two phases, even after standing for 24 hr.

The temperatures of phase inversion obtained above were also plotted against the concentration in the phase diagrams, which can be expressed approximately by the following equation:

$$T_I = Ac + B \tag{1}$$

where T_I denotes the temperature of the phase inversion; and c, the concentration by weight % of the surfactants, and A and B are constants depending only on n. The values of A and B obtained are shown in Table II, while the straight lines obtained are indicated on the phase diagrams by the line T_I.

Table II. The values of A and B

Surfactant	A	B
NP-5	0.96	30.2
NP-7.5	1.48	18.4
NP-8.5	1.15	38.7
NP-10	0.69	62.3
NP-12.5	0.46	80.2
NP-8.5P	1.21	29.9

Discussion

Solidification Point.—The solidification points of 100% surfactants shown in Table I first rose markedly, and then gradually, with the increase in n. However, plotting the 100% solidification points, S, against the weight content, E, of ethylene oxide in a surfactant molecule (Fig. 16) gives:

$$S = 168E - 106 \tag{2}$$

where $E = 44n/(220+44n)$.

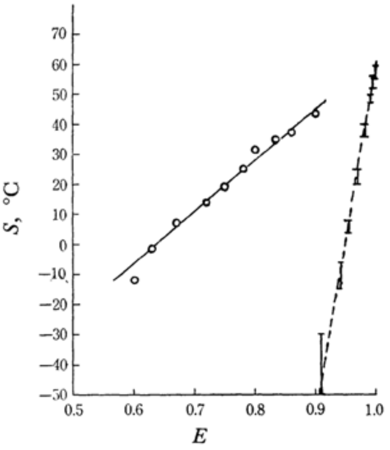

Fig. 16. Solidification point vs. weight content of ethylene oxide in NP-series (solid line) and PEG series (broken line).
S : Solidification point of 100% substances
E : Weight content of ethylene oxide in a molecule

The deviation of the solidification point of NP-7.5 from the straight line in Fig. 16 is considered to be due to its being a lower member.

A similar linear relation (Fig. 16) is obtained for polyethylene glycol homologues (F-4772 of the Union Carbide Chemical Co., U. S. A.) as follows:

$$S = 1200E - 1139.5 \tag{3}$$

---

[17] T. Nakagawa, K. Tori, *Kolloid-Z.*, **168**, 132 (1960).

where S denotes the solidification point of 100% polyethylene glycol, and E, the weight content of ethylene oxide calculated from $44n/(18+44n)$.

Equations 2 and 3 indicate that the solidification is affected mainly by the polyoxyethylene chain and that the solidification point rises linearly with the ethylene oxide content of the molecule. The larger the weight of the part of the molecule to which ethylene oxides are attached, the smaller the slope of the straight line which may result, presumably because of their stronger resistance against the solidification.

It may be seen from the phase diagrams obtained that the smaller the n value of the surfactants, the greater the slope of the SP curves near 100% surfactants becomes, and that the slopes near 100% are smaller for PEG systems than for NP systems. This is because the weight fraction of the polyoxyethylene chain mainly responsible for solidification becomes smaller with the decrease in n for the NP series and is smaller for the surfactant than for polyethylene glycol possessing an approximately equal n value for an equal solute concentration.

Recently, Iino et al.[18] measured the solidification points of polyoxyethylene fatty acid esters, the fatty acid radical of C_6—C_8 chain length and the polyoxyethylene of $n=2$—30 mol. ethylene oxide. If the solidification points they obtained are plotted against the ethylene oxide content in the esters given above, linear relations are obtained for the esters of fatty acids of C_6 and C_8 possessing polyoxyethylene chains longer than the one corresponding to the minimum point, but not for those of fatty acids above C_{10}. This again confirms the above solidification effect of polyoxyethylene, while too long a fatty acid chain interferes with, and causes anomalies in, solidification.

Cloud Point.—In Fig. 17 the minima of CP-curves, CP_m, and the corresponding concentration, m, are plotted against n, the latter being linear, as is shown. The CP_m and m values NP-8.5P, which are shown by circles in the figure, correspond approximately to those of $n=8$ and $n=11.5$ respectively. Thus it is shown that the removal of lesser hydrophilic compounds such as the lower homologues results in a little increase in CP_m but a large increase in m when expressed in terms of n.

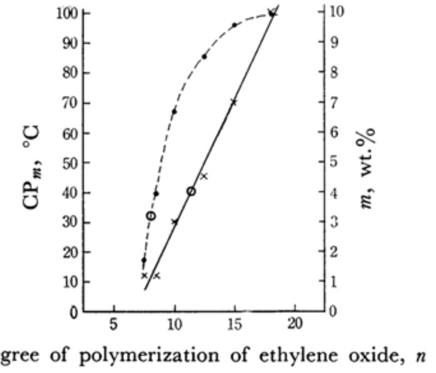

Fig. 17. Change of temperature (●: CP_m) and concentration (×: m) of minimum in CP-curve with n.
Circles indicate the value for NP-8.5 P.

Such minima of CP curves in relatively dilute solutions were also found for the series of polyoxyethylene isooctylphenyl ethers.[19]

Phase Separation and Phase Inversion.—The heterogeneous system above the CP curve (Fig. 18) is composed of an upper layer of water or a dilute aqueous solution and a lower layer of a surfactant-rich solution. The line MN in the figure shows the line of the phase inversion.

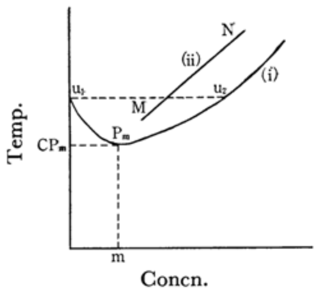

Fig. 18. CP-curve (i) and line of phase inversion (ii).

The heterogeneous region left to the line MN forms an emulsion of the surfactant-in-water type, while the heterogeneous region to the right of the line MN forms the opposite type of emulsion. The line MN passes through the minimum point P_m of the CP curve. Therefore, the heterogeneous system with a surfactant concentration larger than that of the point P_m shows the phase inversion phenomena when the system above the line MN is cooled, while the heterogeneous system with a concentration less than that of P_m shows no indication of a phase inversion under similar treatment. The clouding behavior of the heterogeneous system at the cloud point when heated also differs according as the concentration is below that of P_m, between P_m and U_2 in Fig. 18 (namely, the lowest possible concentration at which pure water separates at the cloud point), and above U_2. The results of the experiments showed that the first system separated minute droplets of a relatively-concentrated surfactant solution; the second, a dilute aqueous solution, and the third, pure water. The first case mentioned above is in agreement with the findings of Nakagawa et al.[20] that very large micelles

---

[18] S. Iino, K. Tagawa and N. Oba, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 2047 (1962).

[19] M. Aoki and Y. Iwayama, *J. Pharm. Soc. Japan*, **79**, 516 (1959).

[20] T. Nakagawa, K. Kuriyama and H. Inoue, Symposium on Colloid Chem., (Chem. Soc. Japan) 12th symposium, p. 29 (1959).

suddenly appear at the cloud point.

Shinoda et al.[21] have regarded the cloud point as the temperature of the pseudo-phase inversion in veiew of the fact that the micelle formation is a phenomenon similar to a phase separation and because it is considered that, upon being heated, the systems of aqueous non-ionic detergent are altered from a detergent-in-water type to a water-in-detergent type at the cloud point. As has been mentioned above, not the region II below the CP curve but the region I above the CP curve is regarded in the present study as a dispersion or a heterogeneous system in the usual sense, one in which phase inversion occurs. Thus, the concept of the phase inversion is different in the present study from the concept of pseudo-phase inversion of Shinoda et al.

Water Affinity.—In the case of the concentration range above the minimum m of the CP curve, when a system has reached the CP curve by the repeated addition of water to the surfactant at a certain temperature, the system became turbid because of the deposit of a slight excess of water. Therefore, we call the weight ratio, x, of water to surfactant at the cloud point the "water affinity" of the surfactant at that temperature. By plotting the logarithm of the water affinity against the cloud point, as in Fig. 19, a linear relation is found between them in the surfactant-rich region of the CP curve measured; this is shown by the following general equation:

$$\log x = \log X + K\,(100-t) \qquad (4)$$

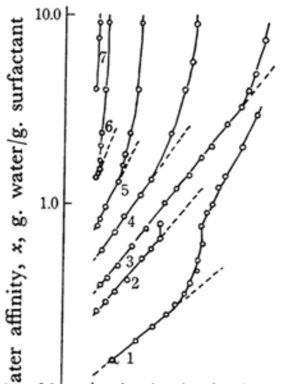

Fig. 19. Relation between the water affinity and cloud point.

1 NP-5 4 NP-10 7 NP-18
2 NP-7.5 5 NP-12.5
3 NP-8.5 6 NP-15

where t represents the cloud point; X, the water affinity of the surfactant at 100°C, and K, a constant. In Eq. 4, the constants, X and K, are found to be expressed as a function of n, as is shown by the following equations:

$$\log X = \log 0.0320 + 0.117n \qquad (5)$$

$$K = 0.00257n \quad (n<12.5) \qquad (6)$$

From Eqs. 4, 5 and 6 we obtain for $n<12.5$, and $t\approx 100°\mathrm{C}$:

$$\log x = \log 0.0320 + 0.117n + 0.00257n\,(100-t) \qquad (7)$$

The Transparent Point, the Hardening Point and Their Regions.—In the hardening region, the molar ratio of water to ethylene oxide units in a surfactant is considered to be more significant than the concentration. Thus, for instance, the relationship of such a molar ratio for three hardening regions and n at 20°C is as is shown in Fig. 20. This figure shows that every surfactant of the NP-n series possesses no, one or two hardening regions, according to the variation in n value.

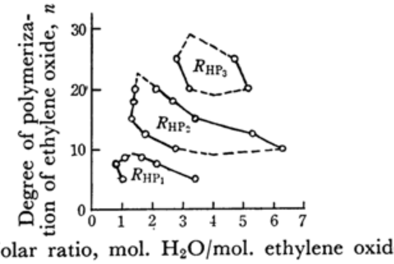

Fig. 20. Relation between n and molar ratio of water to ethylene oxide unit in surfactants in each hardening region at 20°C.
Broken lines indicate the ranges presumed from diagrams.

The relation between n and the nature of the hardening regions at various temperatures is shown in Table III.

The maxima of the viscosity of the aqueous solutions of non-ionic surfactants have been reported,[10] and the gel formation of such systems have also been found.[11-13,15] The systems showed a single concentration region in most cases, but the existence of two concentration regions of gel formation was reported in a few special cases.[1,12] Thus, for instance, Schönfeldt[1] measured the viscosity of the aqueous solutions of the NP-n series and found a single gel region for each surfactant in the range of n between 8.0 and 36.0, with two exceptions (the n values of 9.0 and 17.2 showed two gel regions each).

Comparing our hardening regions (in Table III) with those of Schönfeldt, the hardening regions of his $n=9.0$ value correspond to our R_{HP_1} and R_{HP_2} regions, while those of his $n=17.2$ value correspond to our R_{HP_2} and R_{HP_3} regions.

Several explanations have been given for the maximum of the viscosity versus the concentration

---

[21] K. Shinoda and H. Arai, *J. Phys. Chem.*, **68**, 3485 (1964).

TABLE III. THE RANGES OF n FOR VARIOUS HARDENING REGIONS AND TEMPERATURE

Number of hardening regions	0	1			2	
Type of hardening regions		R_{HP_1}	R_{HP_2}	R_{HP_3}	R_{HP_1} and R_{HP_2}	R_{HP_2} and R_{HP_3}
5°C	>37.0	5.0—8.0	11.0—13.5	24.0—37.0	8.0—11.0	13.5—24.0
15°C	>31.5	5.0—9.0	9.0—18.5	23.0—31.5	9.0— 9.5	18.5—23.0
20°C	>29.0	5.0—9.0	9.3—19.0	22.5—29.0	9.0— 9.3	19.0—22.5
25°C	9.0— 9.3, >28.0	5.0—9.0	9.3—19.3	22.0—28.0	—	19.3—22.0
35°C	8.0—10.0, >19.5	5.0—8.0	10.0—19.0	—	—	—

curve and for the gel formation: (1) the interlocking of incompletely-hydrated surfactant molecules to form a network,[5] (2) a phenomenon resembling the phase inversion in the emulsion consisting of water as one phase, and hydrated surfactants assumed to be composed of one water molecule per ether linkage as another phase,[12] and (3) the immobilization of the water in the network by the entanglement of the hydrophilic groups of surfactants because of their spacious properties.[15] Kuroiwa[15] has further suggested that the decrease in viscoelasticity at the higher concentrations is produced by the formation of inverse micelles in the system.

However, these explanations can not well be applied to the system showing two or more maxima in viscoelastic properties, as was found in the present NP-8.5, 10, 15, 18, 20, and 25 systems.

The phenomena observed in the present experiments may, however, be appropriately explained as follows.

As the concentration of a surfactant is increased at a constant temperature, the micelles increase, while, at a certain concentration, depending upon the n and on the temperature, the system hardens because of the network composed of micelles and water acting as adhesives between micelles by means of hydrogen bonding with polyoxyethylene groups of the surfaces of micelles and by means of the immobilization of the aqueous solution with a monomolecular dispersion. The ability of water to act as an adhesive is considered to have an optimum range of compositon depending on the temperature, the n value, and the nature of the surfactant molecule. As is clear from such an explanation, this hardening region should be the one appearing in the region II; it is considered to correspond to R_{HP_3} or R_{HP_2}.

On a further increase in the concentration, micelles further increase in number, but the water molecules combining them become insufficient; accordingly, each individual micelle is rendered relatively free in motion. This state coincides with the part of the region II, between two hardening region in the phase diagrams.

A further increase in the concentration results in the approach of micelles more closly, and the inverse micelles appear with a saturated aqueous phase inside. The region of the concentartion where such an iversion of micelle type occurs and where both types of micelles coexist is considered to correspond to another hardening region, R_{HP_2} or R_{HP_1}. The systems of these hardening regions are more or less turbid because they are mixtures of two phases. The smaller the value of n becomes, the greater the difference between the two types of micelles may be expected to grow because of the more hydrophobic property of the surfactant. This results in the increasing turbidity and the decreasing viscosity of the system in R_{HP}. On the contrary, the system of the surfactant with a larger n value is considered to be somewhat similar in structure between the two phases. This hardening system would be something like the lamellar structure of micelles with sandwiched water;[22] therefore, it results in a much less turbid and more rigid state, as in R_{HP_2}.

Upon the further addition of the surfactant, the system eventually turns into a single-phase system composed of the inverse micelle type or the surfactant, with water dissolved in it, which is transparent and low in viscosity.

The above explanation of the two maxima of viscoelasticity in the nonionic surfactant-water system coincides approximately with those suggested by Kuroiwa[15] for the hardening region in the lower concentration and by Greenwald et al.[13] for the hardening region in the higher concentration. In the former mechanism of the hardening, of course, the polyoxyethylene group must be long enough to exhibit an effective adhesive field for hydration. The adequate chain length is considered to correspond to $n=22$ for R_{HP_3} and $n=15$ for R_{HP_2} in the NP-n series.

The appearance of the R_{TP_1} and R_{TP_2} regions is explained somewhat similarly to that of R_{HP_1} but all the regions, except for R_{HP}, were out of the range of the suitable ratio between water and surfactant for the hardening or the higher temparature range, showing no hardening due to the reduced hydration. The fact that R_{TP_1} had quite a wide range at temperatures higher than R_{HP_1} can be explained by the fact that the system of this region contains relatively little water and appears

---

[22] S. S. Marsden and J. W. McBain, ibid., **52**, 110 (1948).

only in the case of surfactant with a low *n* value. Therefore, it should be cooled to a temperature sufficiently low in order for hydrogen bonding to harden the system.

Unusual Zone.—Sugano[7] found an unusual zone such as is shown in Fig. 2 above the cloud point in the aqueous solution of crude hexaoxyethylene lauryl ether. He ascribed the appearance of this phenomenon to such impurities as the higher alcohols or non-ionic surfactants of a low hydrophilic property. Since his unusual zone indicated an unusually high viscosity and a double refraction, he concluded that the zone was similar to the liquid crystalline state formed when amphiphilic compounds were added to the aqueous solution of ionic surfactants.[23] It has been further referred to the G-phase obtained by Winsor[24] and to the optical anisotropic state found in concentrated solutions of sodium laurate and hexanolamine oleate.[25]

If the unusual zone found in the present study is considered to be the liquid crystalline state, this zone can well be explained as that formed by the extension of the R_{TP_1} region in the direction of higher temperatures and lower concentrations, as may be seen from its contact with R_{TP_1}, which is considered to be optically anisotropic.[8] This also explains the discontinuity in the CP cruve.

If the unusual zone appears because of the existence of R_{TP_1}, it would not appear in any aqueous system of the surfactant with an *n* value above 12.5, but in fact it may appear even in such a system because of the possible transition of R_{TP_2} into R_{TP_1} by the addition of the lower homologues, as in the change of the NP-8.5P to the NP-7.5 system.

Although the NP-5 system (Fig. 1) seems not to show the unusual zone, it shows considerable anomalies below a 70% surfactant solution. The narrow transparent zone is somewhat similar to the narrow transparent part of the unusual zone of the NP-7.5 system (Fig. 2). The slopes of the CP curve below 70% of a surfactant and the slopes of the line of the phase inversion were smaller than those of NP-7.5. Further, the transparent hardening region found above the TP_1 curve is simialr to the part at the highest concentration of the unusual zone in the NP-7.5 system. In veiw of these points, the NP-5 system below 70% of the surfactant may be considered to show an unusual zone except for the region I.

The author wishes to express his deep gratitude to Professor Tsunetaka Sasaki of Tokyo Metropolitan University for his valuable advice and for his inspection of this report; to Mr. Tsunetaro Matsumoto, Manager of the Laboratory of Takahashi Toyodo Co., Ltd., for his encouragement throughout this investigation, and to the President of the Takahashi Toyodo Co., Ltd., for permission to publish this research. He is also grateful to Miss Sadako Usui for her aid in preparing this paper.

---

[23] A. J. Hyde, D. M. Langbudge and A. S. C. Lawrence, *Discussions Faraday Soc.*, **18**, 239 (1954).

[24] P. A. Winsor, *J. Phys. Chem.*, **56**, 391 (1952).

[25] E. Gonick and J. W. McBain, *J. Am. Chem. Soc.*, **68**, 683 (1946).