BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3722—3728 (1970)

Sound Velocity in Polyoxyethylene(6)laurylether Aqueous Solution

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(Received June 20, 1970)

The sound velocity and density of polyoxyethylene(6)lauryether and its aqueous solutions are measured, and the adiabatic compressibility is computed from these results. The virtual sound velocity was calculated in ideal mixtures by using Kudriavtsev's formula, and above 33°C for ideal suspensions by the use of the equation of Urick and Ament for dispersed systems. Some deviations in the experimental velocity from the calculated value are ascribed to the interaction energy of mixing. This energy, or the heat of the hydration of a nonionic surfactant, is obtained as a function of the temperature. The diagrams of the density, sound velocity, and adiabatic compressibility *vs.* the temperature at various concentrations always exhibit a common crossing point, nearly at the cloud point. It may thus be concluded that the measurements of the sound velocity and density give a new method for determining the cloud point.

The dissolved state and the properties of ionic surfactants in aqueous solutions have been studied with ultrasonics by Yasunaga *et al.*[1,2] and by Shigehara,[3–5] but so far no study of the dissolved state and properties of nonionic surfactants in aqueous

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[1] T. Yasunaga, H. Oguri and M. Miura, *J. Colloid Interfac. Sci.*, **23**, 352 (1967).

[2] T. Yasunaga, S. Fujii and M. Miura, *6th Inter. Congr. Acoust.*, **V**, J-61 (1968).

[3] K. Shigehara, This Bulletin, **38**, 1700 (1965).

[4] K. Shigehara, *ibid.*, **39**, 2332 (1966).

[5] K. Shigehara, *ibid.*, **39**, 2643 (1966).

solutions using ultrasonics has been reported.

In the present study, we adopted polyoxyethlene-(6)laurylether as the nonionic surfactant and measured its sound velocity in aqueous solutions.

The experimental data were compared with the results of the thermodynamical calculation of sound velocity using the Lennard-Jones potential. The heat of the hydration of the nonionic surfactant was estimated from deviation of the sound velocity from that of an ideal solution.

It is known that a nonionic surfactant in an aqueous solution suddenly turns cloudy white at a specified temperature called the cloud point (in our specimen, at 33°C). The curve of the difference in sound velocity between solvent and solution plotted against the temperature shows a sharp turn at nearly this temperature.

Solutions of a surfactant with a distribution of molecular weight exhibit a second transition temperature, the double cloud point (at 42°C for our specimen), above which two separated phases appear.

In the temperature range below 33°C, we computed the heat of hydration from the deviation of the experimental sound velocity from the ideal-solution sound velocity, as obtained by Kudriavtsev's formula.[6] In the 33—42°C temperature range, the present system becomes a dispersive system, or an emulsion. The sound velocity for emulsion or suspension is different from that of an ideal solution of the same composition, also in the absence of the heat of hydration. The ideal value of the sound velocity in this temperature range (33—42°C) was computed by Urick and Ament's formula;[7] we obtained the heat of hydration from the deviation of the experimental velocity from this ideal suspension value.

Experimental

Material. Polyoxyethylene(6)laurylether. The $C_{12}H_{25}O(C_2H_4O)_6H$ sample is a commercial product[*1] and is used without further purification. The surfactant has its cloud point and double cloud point at 33°C and 42°C respectively.

Apparatus. The sound velocity is measured with a variable-path ultrasonic interferometer with a 1/1000 mm reading and a frequency of 5 MHz. The density measurements are made by means of an Ostwald-type pycnometer to an accuracy higher than 1 part in 10^4. The temperature-regulated water in a thermostat of ± 0.05°C is circulated in the mantle surrounding the cell by means of a circulation pump. The overall accuracy of velocity measurement is ± 0.3 m/sec.

Theoretical

The sound velocity in binary liquid mixtures has been thermodynamically calculated by Kudriavtsev.[6] It is assumed that, in an ideal mixture, the internal energy, E, and the volume, V, are additive;

$$E = x_1E_1 + (1-x_1)E_2 \tag{1}$$

$$V = x_1V_1 + (1-x_1)V_2 \tag{2}$$

where the suffixes 1 and 2 refer to the first and second components of the mixture respectively, and where x_1 is the mole fraction of the first component. By differentiating Eq. (1) twice with respect to the volume at a constant entropy, S, and noting that

$$\left(\frac{\partial^2 E}{\partial V^2}\right)_S = \frac{MC^2}{V^2} \tag{3}$$

where C is the sound velocity, and M, the molecular weight, we obtain this expression for the sound velocity in the mixture:

$$C^2 = x_1\frac{M_1}{\bar{M}}C_1^2 + (1-x_1)\frac{M_2}{\bar{M}}C_2^2 \tag{4}$$

Here, C_1 and C_2 are, respectively, the sound velocities in the first and second components, M_1 and M_2 are the molecular weights of the two components, and $\bar{M}$ is the average molecular weight:

$$\bar{M} = x_1M_1 + (1-x_1)M_2 \tag{5}$$

The Eq. (4) obtained by Kudriavtsev is only approximate, because the thermodynamic relation (3) gives the result more exactly:

$$MC^2 = \frac{E}{\chi'} \tag{6}$$

χ' is dependent on each liquid (and also somewhat on the temperature), as obtained by Nomoto,[8] though the range of χ' for various liquids is not very wide ($\chi' \fallingdotseq 0.2-0.3$). Therefore, we have, in place of Eq. (4), more exactly:

$$C^2 = x_1\frac{M_1}{\bar{M}}\frac{\chi}{\chi_1}C_1^2 + (1-x_1)\frac{M_2}{\bar{M}}\frac{\chi}{\chi_2}C_2^2 \tag{7}$$

Experimentally, however, Kudriavtsev's relation (4) is known to be quite valid for many liquid mixtures, and we use it below to represent the sound velocity in ideal mixtures.

Assuming the Lennard-Jones potential for the intermolecular potential of the liquids, we obtain:

$$\Phi(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \tag{8}$$

Here, r is the intermolecular distance. The A and B quantities are functions of the temperature, but at a constant temperature they are constants

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[6] B. Kudriavtsev, *Soviet Physics Acoustics*, **2**, 36 (1956).

[7] R. Urick and W. Ament, *J. Acoust. Soc. Amer.*, **21**, 115 (1948).

[*1] Products of Nippon Surfactant Industr. Inc., Tokyo.

[8] O. Nomoto, *J. Phys. Soc. Jap.*, **18**, 1526 (1963).

characteristic of the specified liquid. We can also write Eq. (8) in terms of the molar volume, V, as:

$$\Phi(V)=\frac{A_0}{V^4}-\frac{B_0}{V^2} \tag{9}$$

The deviation from ideal behavior expressed in Eq. (1) may be accounted for by taking into account the interaction energy of mixing ΔE_{12}:

$$E=x_1E_1+(1-x_1)E_2+\Delta E_{12} \tag{10}$$

If we assume that the internal energy of molecular interaction between the components of the mixture also obeys Eq. (9), then from Eq. (10) we can find:

$$C^2=x_1\frac{M_1}{M}C_1^2+(1-x_1)\frac{M_2}{M}C_2^2+2\times 4\gamma\Delta E_0 \tag{11}$$

where γ is the ratio of the specific heats. If we use for ΔE_0 the heat of hydration, L (cal/solution 1 g), then we have, as the sound velocity in mixtures, the expression:

$$C^2=x_1\frac{M_1}{M}C_1^2+(1-x_1)\frac{M_2}{M}C_2^2+3.35\times 10^8L \tag{12}$$

In the temperature range from the cloud point to the double cloud point, we have emulsions. Urick and Ament[7)] obtained the propagation constant in a medium containing numerous small spherical particles. In our notations, their expression takes the form:

$$\left(\frac{C_2}{C_s}\right)^2=\{1+\alpha(\beta_1-\beta_2)/\beta_2\}\{1+3\alpha\sigma/(2\sigma+3)\} \tag{13}$$

Here, C_2 and C_s are the sound velocities in the solvent water and in the dispersive system respectively. β_1 and β_2 are the adiabatic compressibilities of the surfactant and the solvent respectively, and $\sigma=(\rho_1-\rho_2)/\rho_2$, with ρ_1 and ρ_2 the densities of the surfactant and the solvent, and α, the volume fraction of the surfactant. We use Eq. (13) in place of Eq. (4) and use:

$$C^2=C_s^2+3.35\times 10^8L \tag{14}$$

to represent the deviation from an ideal emulsion in this temperature range.

Results and Discussion

We studied the behavior of sound velocity in dilute aqueous solutions of polyoxyethylene(6)-laurylether (a commercial product). The phase diagram of this purified surfactant + water system was previously studied by Balmbra *et al.*[9)]

Figures 1—4 show the sound velocity as functions of the temperature for solutions with various concentrations of the nonionic surfactant. The experimental values and computations for ideal solutions by Eq. (4) and for an ideal emulsion by Eq. (12) are shown. The difference between the observed sound velocity and the ideal-solution (or -emulsion) velocity increases with an increase in the concentration. The emulsion velocity (C_s) is somewhat lower than the ideal solution velocity, though the difference is rather small.

As L represents the heat of hydration per gram of solution (p wt%), the heat of mixing L_M per mole of the solute becomes:

$$L_M=\frac{ML}{1000\left(\frac{p}{100}\right)}\ \text{(kcal/mol)} \tag{15}$$

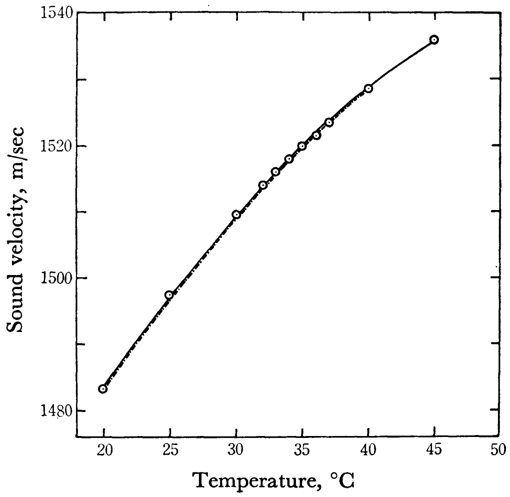

Fig. 1. Sound velocity as function of temperature for 0.5 g/100 cm³ water-solution.
—·—· computation with Eq. (4)
-------- computation with Eq. (12)
—⊙— observed values

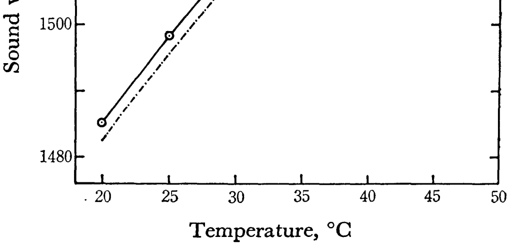

Fig. 2. Sound velocity as function of temperature for 3 g/100 cm³ water-solution.
—·—· computation with Eq. (4)
-------- computation with Eq. (12)
—⊙— observed values

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9) R. Balmbra, J. Clunie, J. Cokill and J. Goodman, *Trans. Faraday Soc.*, **58**, 1661 (1962).

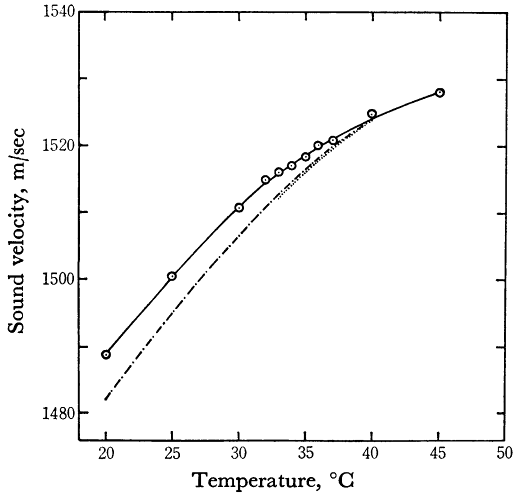


Fig. 2. Sound velocity as function of temperature for 5 g/100 cm³ water-solution.
—·—· computation with Eq. (4)
-------- computation with Eq. (12)
—⊙— observed values

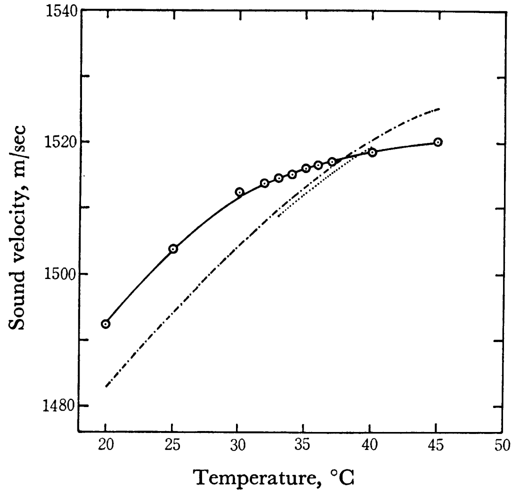
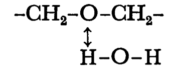


Fig. 4. Sound velocity as function of temperature for 10 g/100 cm³ water-solution.
—·—· computation with Eq. (4)
-------- computation with Eq. (12)
—⊙— observed values

In the temperature range betweem the two cloud points, both the values of L_M, these calculated by using $C_{cal}=C_{ideal}$ and $=C_s$, are as shown in Table 1. Each datum is the average of four determinations. It may be seen in Table 1 that the calculated energies from an ideal solution and from a dispersive solution are nearly equal. As is also to be seen from Table 1, the mixing is exothermic at lower temperatures, but it becomes endothermic at higher temperatures. As regards the sound velocity, we can see from Figs. 1—4 that C_{exp} is higher than C_{ideal} in the lower temperature range, while $C_{exp}<C_{cal}$ in the higher temperature range. From Table 1, it is also to be seen that the value of energy found is comparable to the energy for the breakdown of the hydrogen bond (3.4 kcal/mol[10]) between water molecules. According to Chwala and Martina,[11] in an aqueous solution of ethylene oxide derivatives a hydrogen bridge is formed between the ether-like combined oxygen atom and the water molecule as is illustrated below:

TABLE 1

Temperature °C	From Eq. (12) L_M kcal/mol	From Eq. (14) L_M kcal/mol	From Eq. (16) L_M kcal/mol
45	−1.77		
40	−0.29	+0.98	
37	0.66	1.20	
36	0.55	1.13	
35	1.30	2.19	
34	1.44	2.18	
33	2.23	2.56	
32	3.02		
25	4.09		
20	5.03		2.30



$$\begin{array}{c}\text{-CH}_2\text{-O-CH}_2\text{-}\\ \updownarrow \\ \text{H-O-H}\end{array}$$

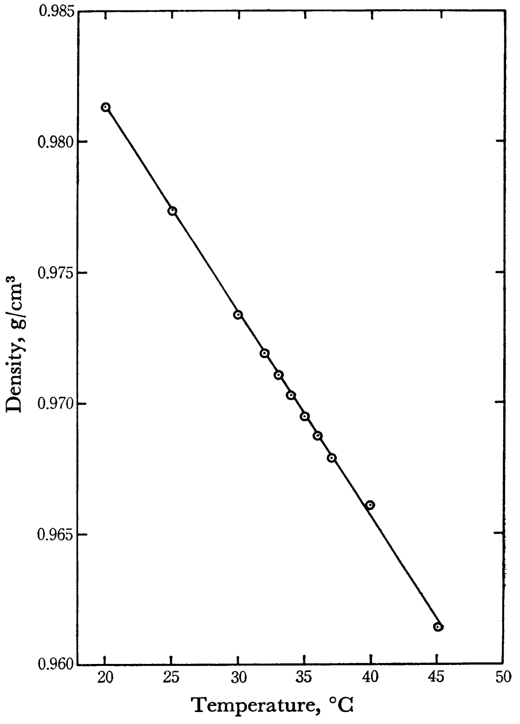


Fig. 5. Temperature dependence of density for surfactant.

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10) G. Pimentel and A. McClellan, "The Hydrogen Bond," Reinhold Publishing Corp., New York (1960), p. 363.

11) A. Chwala and A. Martina, *Melliand Textilber.*, **18**, 992 (1937).

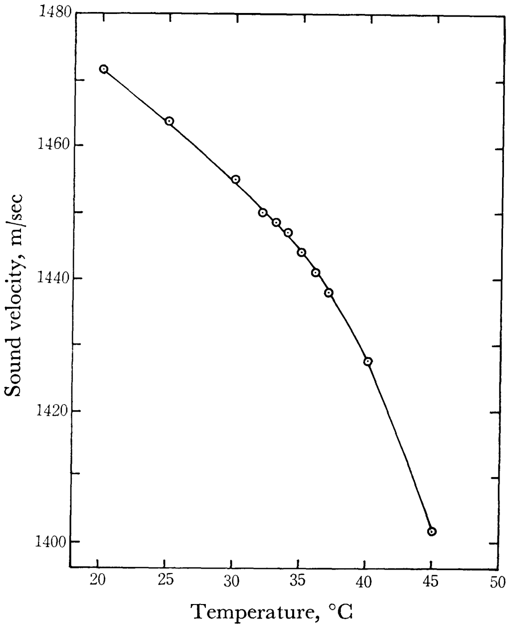

Fig. 6. Temperature dependence of sound velocity for surfactant.

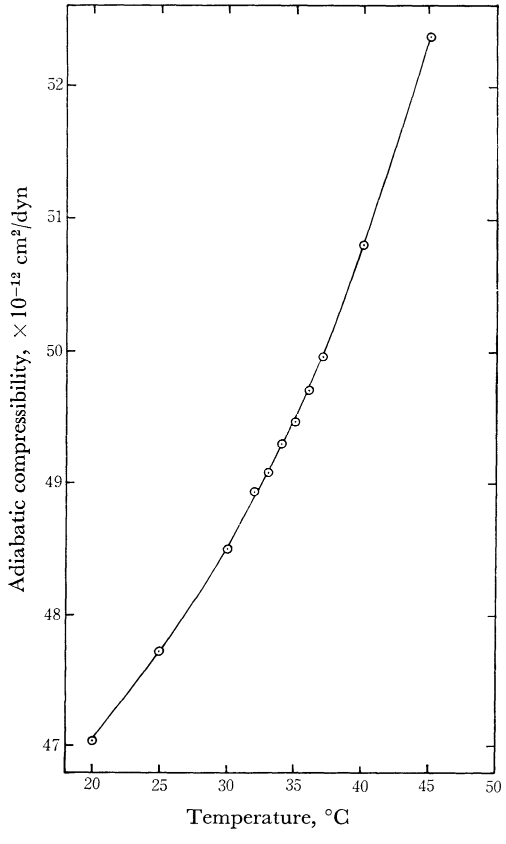

Fig. 7. Temperature dependence of adiabatic compressibility for surfactant.

At temperatures above the cloud point, dehydration phenomena of the nonionic surfactant may be expected in forming the emulsions.

As the value of the heat of hydration decreases with an increase in the temperature, it may be inferred that the cloud point phenomenon does not take place abruptly at a specified temperature, but that the phase separation takes place gradually in the temperature range slightly below the cloud point. Our sample being a high polymer, it may have a distribution of molecular weights, and the gradual-phase separation may thus be attributed to the distribution of molecular weights. This makes it difficult to analyse the dissolved state and the properties of the solution. If we can get a substance with a narrow distribution of molecular weight by the method of solvent extraction, molecular distillation or particular synthesis, we may be able to clarify the relationship between the heat of hydration and the phase separation.

The energy set free in the form of heat is measurable by the calorimetric method, but we obtained the heat of hydration from the deviation of the sound velocity from that of an ideal mixture instead of by calorimetric study. From their calorimetric measurements, Racz and Orban[12] give an empirical

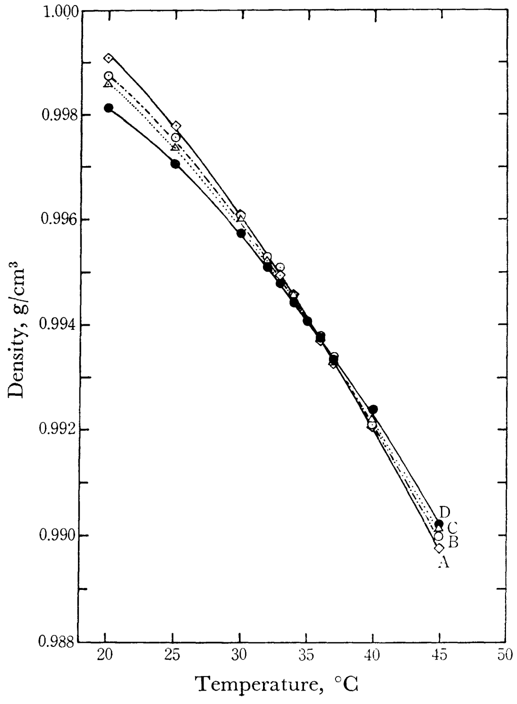

Fig. 8. Density as functions of temperature for various concentrations.

(A) 10g/100cm³ water
(B) 5g/100cm³ water
(C) 3g/100cm³ water
(D) 0. 5g/100cm³ water

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[12] I. Racz and E. Orban, *J. Colloid Sci.*, **20**, 99 (1965).

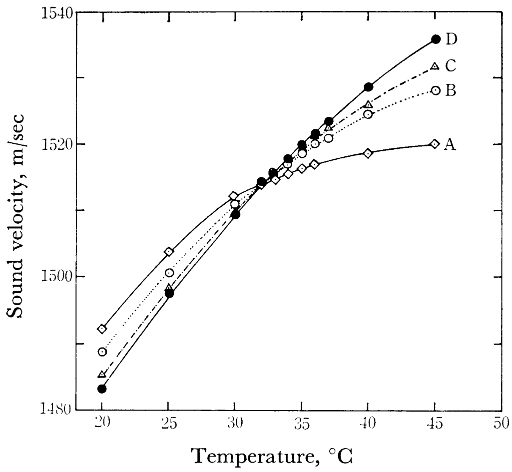

Fig. 9. Sound velocity as function of temperature for various concentrations.
(A) 10g/100cm^3 water
(B) 5g/100cm^3 water
(C) 3g/100cm^3 water
(D) 0. 5g/100cm^3 water

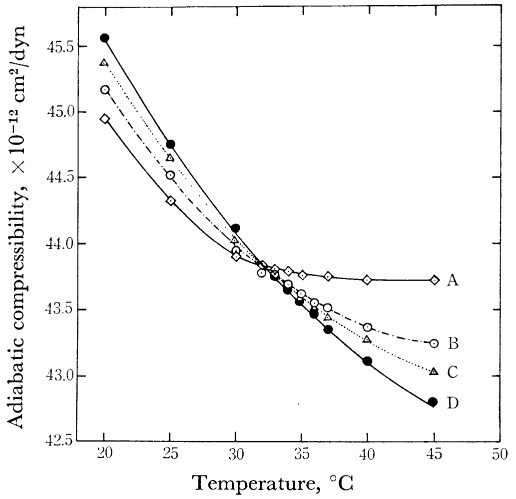

Fig. 10. Adiabatic compressibility as function of temperature for various concentrations.
(A) 10g/100cm^3 water
(B) 5g/100cm^3 water
(C) 3g/100cm^3 water
(D) 0. 5g/100cm^3 water

relation between the hydrophile lipophile balance (*HLB*) of a liquid nonionic surfactant and the heat of hydration (at the temperature of 20°C):

$$HLB = 0.42Q + 7.5 \qquad (16)$$

where Q=heat of hydration in cal/g surfactant. Using Eq. (16) for our specimen with HLB=9.6,[13] we obtain the energy of hydration, L_M, as 2.3 kcal/mol. Though the value of *HLB* in our specimen is in nearly the same range as that investigated by Racz and Orban, the samples are somewhat different in the two cases. The samples of Racz and Orban were Tweens.*[2] Therefore it is not certain

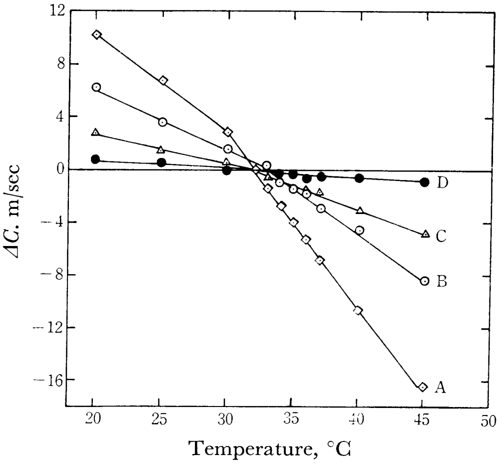

Fig. 11. The difference of sound velocity (ΔC) between solution and solvent as function of temperature in solutions of various concentrations.
(A) 10g/100cm^3 water
(B) 5g/100cm^3 water
(C) 3g/100cm^3 water
(D) 0. 5g/100cm^3 water

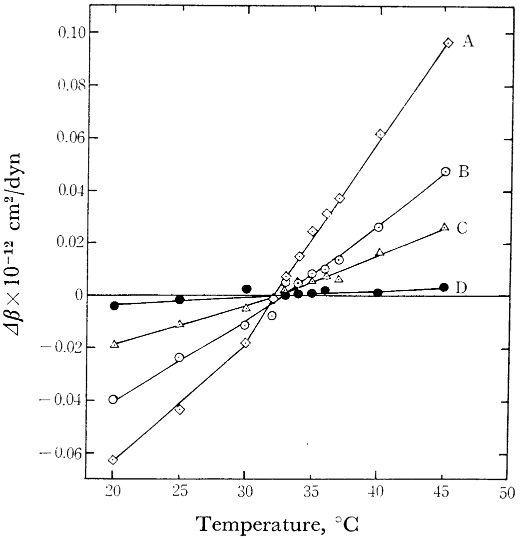

Fig. 12. The difference of adiabatic compressibility ($\Delta\beta$) between solution and solvent as function of temperature in solutions of various concentrations.
(A) 10g/100cm^3 water
(B) 5g/100cm^3 water
(C) 3g/100cm^3 water
(D) 0. 5g/100cm^3 water

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13) *Nikkol*, (1966), p. 23, Nippon Surfactant Industr. Inc., Tokyo.

*[2] Products of Atlas Chemical Industr. Inc., Wilmington Delaware.

whether this value of $L_M = 2.3$ kcal/mol is sufficiently accurate. We may thus conclude that the acoustically-determined energy of hydration for the nonionic surfactant is nearly in agreement with the calorimetric measurements.

Figures 5—7 show the temperature dependence of the sound velocity(C), density(ρ), and the adiabatic compressibility(β), respectively, for polyoxyethylene(6)laurylether. As is to be seen in Fig. 5, ρ plotted against T becomes a straight line, while we see from Figs. 6 and 7 that the curves of $C(T)$ and $\beta(T)$ have somewhat different slopes in different temperature ranges.

Figures 8—10 show the values of ρ, c, and β as functions of T for various concentrations. It may be seen that all of these curves intersect at one temperature, independent of the concentration. This temperature is about 32°C and is to be identified as the cloud point.

It is to be noticed that the sound velocity, the density, and the adiabatic compressibility are all independent of the concentration at the cloud point. We obtain the "acoustical cloud point" 32—33°C from Fig. 9; it coincides with the visual cloud point (33°C) within the range of experimental error.

Figures 11 and 12 show the difference in sound velocity (ΔC) and adiabatic compressibility ($\Delta\beta$) between the solution and the solvent as functions of the temperature in solutions of various concentrations. Each curve consists of two linear segments, with a turn at nearly 32—33°C. This break point, independent of the concentration of the surfactant, may reasonably be ascribed to the cloud point. The slopes per unit of concentration of ΔC–T curves and $\Delta\beta$–T curves are nearly constant above and below the cloud point respectively.

Mr. Noriaki Ohba of Nippon Surfactant Industr. Inc. has kindly supplied the surfactant sample for us. We express our sincere thanks to him in this place.