cooling in an ice bath, 0.2 ml. of 1.5% 4-hydroxybiphenyl (in 2 to 4% NaOH) was added to the mixture. This was reacted at 30 to 37° for 30 min. and then heated at 100° for 90 sec. to dissolve excess 4-hydroxybiphenyl. After cooling, this was used for quantitative colorimetry at 580 m $\mu$ . Under this condition, the coexistence of ca. fifty times of serine to minimum quantity (0.06  $\mu$ mole per tube) of threonine for quantitative analysis has no effect.

## Result

Obtained results were shown in Table I. From this table, it is obvious that threonine exists in brain lipid of mouse and rat in the same quantity but it is not detected in brain lipid of guinea pig and rabbit. Although a question "In what type threonine exists as lipid?" is not clear, this seemed to be interesting from the viewpoint of comparative biochemistry.

Table I. Contents of Threonine, Serine, Ethanolamine and Choline in Brain Lipid of Mouse, Rat, Guinea-pig and Rabbit

	Threonine	Serine	Ethanolamine	Choline
	(μ moles per 10 μ moles of lipid-)			
Mouse	$0.040 \pm 0.002$	$1.0 \pm 0.09$	$3.4 \pm 0.40$	$4.3 \pm 0.29$
Rat	$0.041 \pm 0.003$	$1.1 \pm 0.12$	$3.1 \pm 0.28$	$4.1 \pm 0.32$
Guinea-pig	none	$1.3 \pm 0.09$	$3.1 \pm 0.30$	$4.1 \pm 0.27$
Rabbit	"	$1.5 \pm 0.013$	$3.3 \pm 0.32$	$4.0 \pm 0.30$

## Summary

Quantitative analysis of threonine in brain lipid of various animals was performed and it was found that brain lipid of mouse and rat containes 0.04  $\mu mole$  of threonine per 10  $\mu moles$  of lipid-P, while that of guinea-pig and rabbit does not contain threonine at all.

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Yuriko Kato: Formation of a Micelle-like Structure in Aqueous Solution of 1,4-Hexanediol.

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In the previous paper<sup>1)</sup> it was reported that physical constants were measured of aqueous solution of fourteen kinds of glycols of different number of carbon atoms, from propanediol to dodecanediol. The following results were obtained.

These experimental results show that glycols with hydroxyls on either terminal ends or in 1, 2-positions were considered to form a micelle-like structure. Glycols with one hydroxyl at a terminal end and the other in a median position also forms a micelle-like structure but those having both hydroxyls in median positions and none at the terminal position do not form such a structure.

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<sup>1)</sup> Y. Kato: This Bulletin, 10, 771 (1962).

In this paper, the aqueous solution of 1,4-hexanediol was examined as the suplimental example of glycol with one hydroxyl at a terminal end and the other in a median position.

1,4-Hexanediol was obtained by the route shown in Chart 1.

Physical constants, such as the surface tension, possible solubilization of pigments, refractive index, were measured of the aqueous solution of 1,4-hexanediol. The determination method was same as reported previously.<sup>1)</sup>

The relationship between surface tension and concentration is shown in Figs. 1 and 2, and the break point was observed at  $0.19\,M$ .

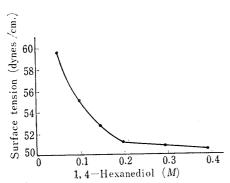


Fig. 1. Surface Tension of 1,4-Hexanediol Solution at 24°

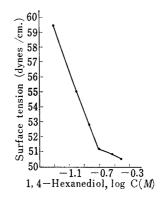


Fig. 2. Surface Tension at  $24^{\circ}$ , against  $\log C(M)$  1,4-Hexanediol

In pigment solubilization, absorbance, E, was plotted against the concentration, C, as shown in Fig. 3, and the amount of the dye solubilized increased markedly form  $0.20\,M$ 

In Fig. 4, the difference between the refractive index of the aqueous solution of 1,4-hexanediol and that of  $H_2O$  is plotted against the concentration and the crossing of the two lines,  $0.19\,M$ .

The foregoing experimental results have shown that a comparatively sudden change occurs in a aqueous solution of 1,4-hexanediol at the concentration of  $0.19\sim0.20\,M$  and

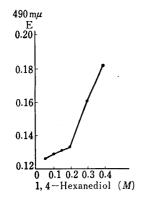


Fig. 3. Solubilization of Sudan III by 1,4-Hexanediol Solution

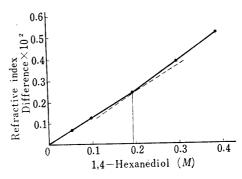


Fig. 4. Refractive Index Increment of 1,4-Hexanediol Solution plotted as Function of Concentration

this fact indicates that a phenomenon similar to the formation of micelle at the critical concentration is present in a aqueous solution of 1,4-hexanediol.

An additional example was obtained, which substantiate assumption that glycols with one hydroxyl at a terminal end and the other in a median position forms a micelle-like structure.

## Experimental

## Synthesis of 1,4-Hexanediol

3-Methoxycarbonylpropionyl Chloride (I)—Obtained by a known method.2)

Methyl 4-Oxohexanoate (II)—Following the method for obtaining methyl 4-oxo-7-methyloctanoate.<sup>3)</sup> Grignard reagent prepared from 2.7 g. of Mg turnings and 17.5 g. of EtI in 60 ml. of dry Et<sub>2</sub>O, then cooled in an ice bath, 9.8 g. of dry CdCl<sub>2</sub> has been added, the ice bath was removed and the mixture was stirred for 5 min. and then heated under reflux with stirring for an additional 45 min. Et<sub>2</sub>O was distilled off, 35 ml. of dry benzene was added to the residue, the mixture was dissolved with warming. After cooling, 12 g. of I in 15 ml. of dry benzene were added at the rate that the mixture maintained gentle reflux. After the addition, the mixture was stirred and heated under reflux for an additional 1 hr. The reaction mixture was cooled in an ice bath and decomposed in the usual way by the addition of 60 ml. of ice and H<sub>2</sub>O, 70 ml. of 20% H<sub>2</sub>SO<sub>4</sub>. This solution was extracted with benzene, and combined benzene solution was washed successively with H<sub>2</sub>O, 10% Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, and was dried over anhyd. Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the residue was distilled under reduced pressure to collect 6 g. (52.2%) of a liquid, b.p<sub>20</sub> 95°. IR  $\nu_{max}^{captl·}$  cm<sup>-1</sup>: ca. 1740 (C=O, broad). semicarbazone<sup>4)</sup>: m.p. 142°. Anal. Calcd. for C<sub>8</sub>H<sub>15</sub>O<sub>3</sub>N<sub>3</sub>: C, 47.75; H, 7.51. Found: C, 47.76; H, H, 7.34.

1,4-Hexanediol (III)—4.0 g. of  $\Pi$  was reduced with 2.6 g. of LiAlH<sub>4</sub> by a known method.<sup>5)</sup> 1.7 g. of  $\Pi$ , b.p<sub>30</sub> 138~139° (reported b.p<sub>13</sub> 127.5~127.7°, <sup>6)</sup> was obtained as a colorless viscous liquid. Yield, 52%. IR  $\nu_{\text{max}}^{\text{caphl}}$  cm<sup>-1</sup>: ca. 3400 (OH, broad), 1052 (C-O).

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<sup>2)</sup> Organic Syntheses Coll. Voll., III p. 169 (1955).

<sup>3)</sup> Ibid., Vol., III, p. 601 (1955).

<sup>4)</sup> H. T. Taylor: J. Chem. Soc., 4, 3924 (1958).

<sup>5)</sup> E. Von Rudloff: Can. J. Chem., 36, 486 (1958).

<sup>6)</sup> C. Glacet: Compt. rend., 218, 283 (1944).