CCLXXXVI. PHYSICAL CHEMISTRY OF LIPOIDS.

III. RELATIONS BETWEEN THE IODINE VALUE OF MONOPHOSPHATIDES AND THEIR REACTIONS TO NEUTRAL SALTS.

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It has been reported in a previous communication [Spiegel-Adolf, 1932, 1] that, contrary to the Hofmeister series, colloidal solutions of egg-lecithin show a greater decrease in viscosity on addition of bromides than on addition of chlorides, iodides and thiocyanates. These results combined with more recent interferometric studies [Spiegel-Adolf, 1932, 2] were explained as due to reaction of molecular bromine with the unsaturated groups of the lecithin molecules. The experiments to be reported here were started with the aim of verifying this theory. As the number of unsaturated groups can be measured by their power to add iodine, determinations of the iodine value for the material under physico-chemical investigation were started.

These experiments of Spiegel-Adolf [1932, 1, 2] had been made on egg-lecithin (Merck). Therefore we first determined the iodine value in a colloidal solution of egg-lecithin, as we could not find references to the iodine value of colloidal lecithin. In order to exclude the factor of ageing [Spiegel-Adolf, 1932, 1], a two months-old lecithin sol was used, made in the way previously [Spiegel-Adolf, 1932, 2] described. The determinations of the iodine value were made according to Hübl [1924], after the lecithin had been precipitated by a mixture of CaCl_2 , MgCl_2 and HCl .

The result was an iodine value of 41. Levene and Rolf [1926] obtained 47 as the iodine value for a lecithin made from egg-yolk by precipitation with a cadmium salt.

In order to test further the supposed relation between iodine value and reactions to bromides different ways were tried of modifying the iodine value.

1. Irradiation by ultraviolet light is known to decrease the iodine value of lecithin. By exposing samples of 1 % lecithin sol in quartz tubes for 4 hours at a distance of 40 cm. to the irradiation of a mercury quartz lamp (Hanovia, 220 V, D.C.), it was possible to reduce the iodine value in another sample from 35 to 30. The viscosity showed a slight increase, thus confirming findings of Nagata [1930].

A shorter period of irradiation has a lowering influence on the viscosity of the lecithin sol. But whilst with the non-irradiated sample, as has been previously shown [Spiegel-Adolf, 1932, 1], bromide caused a sharper decline of the viscosity than did chloride, the difference disappeared completely with the irradiated sample. Table I shows the values for a typical experiment.

Table I.

Salt	Viscosity (measured in sec./5)			Iodine value
	None	KCl	KBr	
Non-irradiated lecithin	1261	1075	1069	35
Irradiated lecithin	1276	1090	1090	30
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2. A sample of egg-lecithin was iodinated to its maximum capacity, as for the determination of the iodine value. The chloroform was removed by evaporation, and the lecithin was washed till any increase in conductance of the wash water had disappeared. In a preliminary test it was ascertained that no further iodine could be added, the iodine value having become zero. It was possible to make a colloidal solution of this preparation, the viscosity of which was very low. The depressing effects of KCl and KBr were practically identical. Yet a higher concentration of KCl caused a still lower viscosity, showing that the lack of a specific effect of bromides on this sol was not due to the fact that the viscosity had already reached its lowest limit (Table II).

Table II. *Viscosity of iodinated lecithin sol.*

	Salt content			
	None	0.05N KCl	0.05N KBr	0.1 N KCl
Iodinated lecithin	869	863	864	859
Water	858	—	—	—

3. Two samples of lecithin and kephalin from human brains were available which had been oxidised in a non-evacuated desiccator. Their iodine values were 23 and 22.5 respectively. Levene and Rolf [1927] had found for brain lecithin an iodine value of 61. The reactions of colloidal solutions of these preparations with different salts as to viscosity and refractivity are summarised in Tables III and IV.

Table III.

	Viscosity (measured in secs./5)	Interferometric units		
		Measured	Calculated	Difference
0.5 % kephalin + 0.05N KCl	899	354	358	4
0.5 % kephalin + 0.05N KBr	900	407	412	5

Table IV.

Final kephalin concentration 1 %, final salt concentration 0.05N. For interferometric measurements diluted with distilled water 4 times.

Salt	Viscosity			Interferometric units		
	I	II	III	Measured	Calculated	Difference
	I	I	I	I	I	I
None	1062	1054	1014	109	—	—
KCl	1000	1012	975	141	141	0
KBr	1000	—	—	157	157	0
KI	1007	1021	—	195	194	-1
KCNS	1030	1046	1007	181	179	-2
KI + I ₂	—	1078	—	—	—	—

These results show no special effect of bromides either on viscosity or on refractivity, but they do show the validity of the Hofmeister series. Yet only the reaction of human brain lecithin can be used as further confirmation of the above-mentioned theory. Only lecithin sol shows a further drop in viscosity on addition of a mixture of KI + I₂ as does the egg-lecithin sol (Table V); kephalin sol, on the contrary, shows an absolute rise in viscosity.

As both lecithin and kephalin contain unsaturated fatty acids, the difference in their behaviours may be sought in their different degrees of hydration. In view of the recently suggested use of thiocyanates in brain diseases the figures should

Table V.

Final lecithin concentration 0.5 %, final salt concentration 0.05 *N*. For interferometric measurements 5 times diluted with distilled water.

Salt	Viscosity		Interferometric units		
	I	II	Measured I	Calculated I	Difference I
None	936	—	—	—	—
KCl	889	882	84	85	1
KBr	887	—	96	97	1
KI	—	880	—	—	—
KCNS	—	882	—	—	—
KI + I ₂	879	—	191	196	5

suggest some caution. The substitution of thiocyanates for chlorides may be followed by a swelling of the brain in which kephalin prevails quantitatively over lecithin [Singer, 1926].

SUMMARY.

The experiments reported were made in order to test the previously assumed relation between the number of non-saturated groups in lecithin sol and its specific reaction to bromides. Therefore determinations of the iodine value were made on various samples of normal, irradiated and iodinated egg-lecithin, and on spontaneously oxidised human lecithin sol and kephalin sol. In the same samples the changes in viscosity and refraction upon addition of various salts were observed. A marked parallelism between a decrease of the iodine value and the disappearance of a specific effect of bromides was found.

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