constant giving the total number of sites of adsorbed molecules in a monolayer per unit area of the solution surface when no interaction between the adsorbed molecules exists, and a is another surface chemical constant relating to the adsorption energy of the solute molecule on the solution surface. The values of n and  $\alpha$  determined from the experimental data are given in Table 1.

11. Statistical Study on Calculation for the Calorific Value of Coal Wataru FUNASAKA, Chikao YOKOKAWA and Tsugio KOJIMA

## (Kodama Laboratory)

The accurate calorific value of coal is measured by Bomb-Calorimeter, which requires the expensive apparatus and troublesome process.

However, the calorific value of coal is much more simply calculated from the results of the proximate analysis. The present paper describes the statistical study of the degree of appropriety of the following eight formulae of calculation, those of Gmelin, Arai, Kôsaka, Nakamura, Lenoble, Goutal, Kent, and Schmit. When the coal of 3000–8000 Cal/kg. was tested, the best result in accuracy and precision was obtained by Gmelin's equation, and the Arai's followed. If the correlation is modified by using the regression line, the precision of the Arai's is improved.

12. Studies on the Sorption of Emulsifiers in the Emulsion-polymerisation

## Seizo OKAMURA and Takuhiko MOTOYAMA

## (Sakurada Laboratory)

In the emulsion-polymerisation of vinyl compounds, emulsifier plays roles of (1) the solubilizer of monomers into the micelle of emulsifier, (2) the locus of polymerisation and (3) the protector of the surface of polymer particles. These three roles have been already studied. For instances, the first has been pointed out by W. Harkins (*J. Am. Chem. Soc.*, 69, 1428 (1947)) and recently discussed in some details about different monomers by present authors (delivered at the Meeting of the Division of colloid chemistry in the Chemical Society in Japan, held at Fukuoka in Oct. 1952). The second has been researched by W. V. Smith (*J. Chem. Phys.* 16, 592, (1948); *J. Am. Chem. Soc.*, 70, 3695 (1948); 71, 4077 (1949)). And finally on the third point, we have assumed simply without any accurate determinations that emulsifier would be adsorbed in the surface of particles.

In the present paper the amount of emulsifiers sorbed in the surface of polymer particles was determined quantitatively and discussed on the relationships between properties of polymers formed and the amount of adsorption. After polymerizing vinylacetate in emulsion state, the emulsion obtained was centrifuged into two parts. The upper transparent liquor was analysed by colloidal titration method, i.e. anionic emulsifier analysed by cationic standard detergent and vs. Nonionic detergents were estimated by the titration method developed by Oliver (Nature, 164, 242, 1949).

The polymers precipitated were weighed and the amount of adsorption pro weight of polymer was calculated (Table 1).

		· · · · · · · · · · · · · · · · · · ·	Vinylacetate 8cd 1 at 60°C. for 5		ammonium
The Amount	The Amount	The Ame	ount of Emulsifi	ers Sorbed	Conversinn
of Emulsifiers	of Emulsifiers	by th	ne Surface of par	rticles	of
used	remained in water phase			() () () () () ()	Emuls.polym
(g.)	(g.)	(g.)	(g./g polymer)	(Mole/Mole polymer)	(%)
Na-laurylsul	lfate	4			, : <sup>,</sup> :
0.0101	0.0000	0.0101			
0.0303	0.0072	0.0231	0.0033	0.0010	95.9
0.0475	0.0201	0.0274	0.0038	0.0011	96.7
0.107	0.083	0.024	0.0034	0.0010	96.0
Polyethylene	glycollauryleth	er (P = 2)	2) Degree of Po	lym. = 6	
0.287	0.002	0.285			
0.486	0.110	0.386	0.052	0.011	92.7
0.721	0.331	0.390	0.053	0.011	91.7
1.103	0.706	0.397	0.055	0.012	90.2
Polyethylene	glycollauryletl	her $(P = 2$	2) Degree of Po	olym. $= 22$	
0.312	0.000	0.312			
0.470	0.095	0.375	0.051	0.005	92.1
0.964	0.594	0.370	0.051	0.005	91.2
• •	••••	•	5) Degree of Po	plym. = 45	
0.194	0.000	0.194			
0.597	0.196	0.401	0.054	0.0030	92.8
0.896	0.507	0.389	0.053	0.0029	91.9
1.333	0.718	0.415	0.057	0.0031	90.2
•	onocetylammon		e		
0.383	0.000	0.383			
0.588	0.011	0.577	0.079	0.026	91.2
1.032	0.432	0.600	0.083	0.027	90.3
1.281	0.701	0.580	0.082	0.027	89.0

Table 1. Sorption of emulsifiers on the surface of emulsion particles.

As shown in Table 1, the sorption of detergents was observed to reach some saturated constant values. By the electronmicroscopic determination, the size of emulsion particles was found to decrease by increasing concentration of detergents in these saturated range. Therefore, in emulsion polymerisation of vinylacetate these detergents seem to be not only sorbed in the surface but also soluble into the polymer particles. Table 2 shows some results of same experiments on the other vinyl compounds. Methylacrylate behaves similarly to vinylacetate, but methylmethacrylate, acrylonitrile and styrene show no saturation. In the cases of latter three monomers, the detergents would be adsorbed around the emulsion particles as reported already by various authors.

0.0381 0.0600 0.0762 0.1210 0.0100 0.0167	(g.) 0.0381 0.0521 0.0536 0.0550 0.0067 0.0127 0.0284 0.0601	Sorbed (g./g. polymer) 0.0053 0.0072 0.0074 0.0076 0.0018 0.0018 0.0040 0.0087	radius of particles (µ) precipitated during polymerisation 0.1 0.067
0.0381 0.0600 0.0762 0.1210 0.0100 0.0167 0.0334 0.0675	0.0381 0.0521 0.0536 0.0550 0.0067 0.0127 0.0284 0.0601	0.0053 0.0072 0.0074 0.0076 0.00097 0.0018 0.0040	precipitated, during 0.1
0.0600 0.0762 0.1210 0.0100 0.0167 0.0334 0.0675	0.0521 0.0536 0.0550 0.0067 0.0127 0.0284	0. 0072 0. 0074 0. 0076 0. 00097 0. 0018	precipitated, during polymerisation 0.1
0.0762 0.1210 0.0100 0.0167 0.0334 0.0675	0. 0536 0. 0550 0. 0067 0. 0127 0. 0284 0. 0601	0.0074 0.0076 0.00097 0.0018 0.0040	precipitated, during polymerisation 0.1
0. 1210 0. 0100 0. 0167 0. 0334 0. 0675	0.0550 0.0067 0.0127 0.0284 0.0601	0.0076 0.00097 0.0018 0.0040	precipitated during polymerisation 0.1
0.0100 0.0167 0.0334 0.0675	0.0067 0.0127 0.0284 0.0601	0.00097 0.0018 0.0040	<pre>polymerisation 0.1 POCOLO </pre>
0.0167 0.0334 0.0675	0.0127 0.0284 0.0601	0.0018 0.0040	<pre>polymerisation 0.1 POCOLO </pre>
0.0334 0.0675	0.0284 0.0601	· · · · · · · · · · · · · · · · · · ·	<b>0:1</b> 1000.0
0.0675	0.0601		
		<b>0.0087</b>	0.067
0.1670	سيشتر والانجار المراجع		
	0.1555	0.0224	aa <b>0: 053</b>
0.7002	0.6540	0.0895	0.033 mind and a
1.166	0.8645	0.1182	$(m_{1}, \dots, m_{2}) \in M^{2}(O, X)$
0.0668	0.0000	<b>0</b>	precipitated during
0.1002	0.0000	1941.C	polymerisation
0.2188	0.1986	0.0276	0.15 datates
0.3660	0.2510	0.0349	<b>0.1</b> - the state of the star
0. 6250	0.4060	0.0563	0.07
A	1 N 2		200.asri
	0.2188 0.3660 0.6250	0.2188         0.1986           0.3660         0.2510           0.6250         0.4060	0. 2188         0. 1986         0. 0276           0. 3660         0. 2510         0. 0349           0. 6250         0. 4060         0. 0563

Table 2. Sorption of Na-laurylsulfate on polymer particles. (Polymerisation recipes are the same as in Table 1).

 On the Lethal Effect of the Powder of Silicon Carbide to Adults of the Azuki Bean Weevil, Callosobruchus chinensis L., with Special Reference to the Relation between Lethal Effect and Particle Size

Sumio NAGASAWA

(Takei Laboratory)

It has been known for few years that the silicon carbide powder has a lethal effect to some stored grain weevils and that fine particle is more effective than the