

Abstracts of the Papers Published in Other Journals by the Staff Members of the Institute from January to June, 1968

Nuclear Chemistry

Quasi-Free α - α Scattering in Be⁹ and C¹² at 37MeV. T. Yanabu, S. Yamashita, K. Hosono, S. Matsuki, T. Tanabe, K. Takimoto, Y. Ôkuma, K. Ogino, S. Okumura, and R. Ishiwari. *J. Phys. Soc. Japan*, **24**, 667 (1968).—Energy and angular correlations between two alpha particles from the Be⁹(α , 2 α)He⁵ and C¹²(α , 2 α)Be⁸ reactions were investigated. The incident alpha particle energies were 32.3 MeV and 37.4 MeV for Be⁹ and 37.4 MeV for C¹². It is concluded that the quasi-free scattering of incident alpha particles from alpha clusters in Be⁹ is the main process of the (α , 2 α) reaction on Be⁹. There remains some ambiguity for the mechanism of the (α , 2 α) reaction on C¹² to be explained as a simple quasi-free scattering process.

Disintegration of Li⁷ and Li⁶ by 29.4 MeV Alpha-Particles. S. Matsuki. *J. Phys. Soc. Japan*, **24**, 1203 (1968).—The Li⁷+ α → α + α + t and the Li⁶+ α → α + α + d reactions were studied with 29.4 MeV alpha-particles by detecting various pairs of final particles in coincidence. In the two-dimensional coincidence spectra, several resonances corresponding to the excited states of Li⁷, Li⁶ and Be⁸ were observed. When the resonances overlap each other, enhancement of the cross section seems to occur.

Decay correlations for the 4.63 MeV and 6.56 MeV states of Li⁷ and for the 2.18 MeV state of Li⁶ were measured in and out of the reaction plane. Strong azimuthal anisotropy with respect to the direction of the recoil nucleus was found. DWBA calculations of the decay correlations are in fairly good agreement with the experimental results, and the spin-parities of the 4.63 MeV and the 6.56 MeV states of Li⁷ are assigned to be 7/2⁻ and 5/2⁻, respectively.

Slight difference between the yields of particles emitted to opposite directions in the rest frame of the 4.63 MeV state of Li⁷ was found. The Moment method analysis suggests that this difference is mainly due to the effect of the background non-resonant waves.

Analytical Chemistry

Chemical Studies on the Seaweeds(23). Molybdenum Content in Seaweeds. T. Yamamoto, T. Fujita, T. Shigematsu and M. Ishibashi. *Records of Oceanographic Works in Japan*, **9**, 209 (1968).—The molybdenum contents of 74 seaweeds of 34 species and 4 limnetic weeds of 4 species were determined. Butylacetate extracts of the molybdenum-dithiol complex were subjected to the spectrophotometric determinations. The molybdenum content varies in the range of 0.03–1.16 ppm with on average of 0.33 ppm in the dry seaweeds.

The Coprecipitation and Spectrophotometric Determination of Iron as 8-Hydroxyquinolate. T. Shigematsu, M. Matsui, M. Munakata and T.

Sumida. *Bull. Chem. Soc. Japan*, **41**, 609 (1968).—The coprecipitation and spectrophotometric method, which is likened to the solvent extraction and spectrophotometric method, was applied to the following system for the first time; ferric ion was coprecipitated as 8-hydroxyquinolate with an organic coprecipitant, and was determined spectrophotometrically after the precipitate was dissolved with an organic solvent. The effect of the ligand concentration on the pH *vs.* absorbance curve in the present method was apparently similar to that for solvent extraction. A nearly constant absorbance was obtained above pH 4 at a ligand concentration of 4×10^{-3} M. Over 100 mg of *o*-phenylphenol, an almost quantitative coprecipitation was obtained, though the absorbance decreased gradually as the coprecipitant was increased. The effect of diverse ions was also examined. Titanium(IV), vanadium(V) and molybdenum(VI) interfered considerably, while others have little effect on the absorbance. The method was applied to the determination of trace amounts of iron in natural waters and reagent grade sodium chloride.

Gas Chromatography of Rare Earth Chelates of Pivaloyltrifluoroacetone. T. Shigematsu, M. Matsui and K. Utsunomiya. *Bull. Chem. Soc. Japan*, **41**, 763 (1968).—The gas chromatography of rare earth chelates of a new β -diketone, pivaloyltrifluoroacetone(PTA) was investigated. The trifluoromethyl group enhances the volatility of these chelates and the *t*-butyl one show the shielding effect to weaken the intermolecular bonding. By these effects, rare earth, Sc and Y PTA chelates were eluted in the gas phase. The elution order of elution is the same with that of increasing ionic radius of the central metal.

On the Trace Components in Sea Water. A Review. T. Shigematsu. *Bull. Soc. Sea Water Sci.*, **21**, 221 (1968), in Japanese.—Of trace elements in sea water, the amount, the state and the behavior are very interesting subject from the stand-point of biological, geochemical and oceanographical investigations.

This paper reviews the analytical method such as activation analysis, isotope dilution, atomic absorption, light absorption, fluorometry, polarography, flame photometry *etc.*, and presents the published data for the amounts of 58 elements and some organic materials in sea water.

Yttrium and Rare Earth Elements in Sea Water. T. Shigematsu. *Bull. Soc. Sea Water Sci.*, **21**, 241 (1968), in Japanese.—The author conducted a study on the absorption behavior of yttrium and rare earth elements in sea water. These elements adsorbed themselves to glass or polyethylene and to suspended particles from the solution of pH 5 to 8. Sample water, therefore, should be kept acidic (pH < 3) after sampling.

As a result of fluorometric determination, sea water was found to contain about $\sim 0.15 \mu\text{g/l}$ of yttrium, and above a half of the content was concerned with suspended matter.

Lanthanum and europium were determined by neutron activation, and the results were $\sim 0.04 \mu\text{g La/l}$ and $\sim 0.002 \mu\text{g Eu/l}$.

Physical Chemistry

The Counterion Binding at Oil-Water Interfaces. Akira Watanabe,

Mutsuo Matsumoto, Hisako Tamai and Rempei Gotoh. *Nippon Kagaku Zasshi*, **89**, 454 (1968), in Japanese.—The interfacial tension of oil-water interfaces between the oil phase containing an ionic surface active agent and the aqueous phase containing an inorganic electrolyte changed with the applied potential. From these studies, some information was obtained concerning the structure of electrical double layers, as well as the interaction between the surface active ion and counter ions at the oil-water interface. In the present paper, the specific adsorption of lecithin and its interaction with counter ions were studied by using this method. Lecithin is an amphielectrolyte and it was found that the dissociation of this material at the oil-water interface was governed by the pH of the water side of the interface. Over the region of acidic side of the isoelectric point, this material showed the surface activity, which was characteristic of the cationic type, at the oil-water interface and that of the anionic type over the opposite region. Over the pH region near the isoelectric point, the interfacial tension was independent of the applied potential. This isoelectric point was found to almost coincide with the bulk value measured by the turbidity method. The effect of inorganic electrolytes on the isoelectric point was extremely specific, but was not very much influenced by the concentration. Moreover, the cationic sequence of the binding with lecithin at the interface agreed with that obtained by other methods in the literature.

Cinematographic Observation of Crystallization Process of Amorphous Titanium Dioxide Films. Makoto Shiojiri, Hiroshi Morikawa and Eiji Suito. *J. Electron Microscopy*, **17**, 1 (1968).—Continuous electron microscopic observation was carried out cinematographically on the crystal nucleation and growth process during crystallization of amorphous titanium dioxide films. The films were crystallized by irradiation of an electron beam, and changed into rutile and anatase. Formation of small angle grain boundaries and twinning were also observed in the growing anatase crystals. The generation mechanisms of the boundaries and twin crystals which were proposed in a previous paper (*J. Phys. Soc. Japan*, **21**, 335 (1966)) are confirmed by these observations.

Elastic and Plastic Deformation of Colloid Gold. Hiroshi Kiho, Saiyu Maruyama and Natsu Uyeda. *J. Electron Microscopy*, **17**, 113 (1968).—Deformation in very thin crystal has been studied on lamellar crystals of colloid gold, of about 100Å in thickness and with (111) orientation, grown in dislocations.

Prominent elastic bending is often seen. From the estimation of the curvature, it is concluded that the crystals are capable of being deformed elastically as far as the theoretical strength.

At the beginning of plastic deformation, {111} twins are formed mechanically, their thickness determined from the subsidiary maxima of diffraction twin spots being several ten Ångströms. As the deformation proceeds, thickening of twins occurs. {111} slip is also observed.

The n-Donor Complex Formation and Polymorphic Transformation of Zinc Phthalocyanine in Organic Suspension Media. Takashi Kobayashi, Natsu Uyeda and Eiji Suito. *J. Phys. Chem.*, **72**, 2446 (1968).—The polymorphic transformation process of zinc phthalocyanine dispersed in various organic suspension media was studied by x-ray diffraction, differential thermal analysis, and infrared absorption spectroscopy. Strong n-donor solvents, such as heterocyclic and normal amines,

dioxane, and dimethyl sulfoxide, were found to form stoichiometric molecular compounds with zinc phthalocyanine in the solid phase. The compositions were determined by weight-loss measurements and from the thermal behavior of the addition compounds as observed by DTA analysis and x-ray diffraction. The decomposition temperature ranged from 70 to 240°, above which the crystallites were converted into the β form. Solvents other than n-donors caused the α form to undergo an ordinary transformation into the β form. The process was found to be consecutive and two different new polymorphs (χ and θ) appeared as the intermediate phases, depending upon whether the suspension media consisted of electron donors or electron acceptors. The infrared absorption spectra assigned to the fundamental bands of the adduct molecules showed large shifts toward higher frequencies, which suggested that the coordination in the complexes could be interpreted in terms of a charge transfer mechanism.

Relation between particle size and packing properties of powder.

Masafumi Arakawa. *Journal of the Japan Society of Powder and Powder Metallurgy*, **15**, 55 (1968).—The relation between particle size and packing properties of powder were studied by various experiments as follows:

The effect of particle size on the apparent density of powder, the porosity change based upon mixing of fine powders having different size and the attractive force between powder particles were measured. Furthermore, the packing state of blistered polystyrene sphere was observed.

These results suggested that the packing properties of powder will be determined by the balance of particle weight and attractive force at contact point of each particles.

The Flow Property of Powder in Vibrating State.

Masafumi Arakawa, Misao Nishino and Eiji Suito. *J. Soc. Material Sci. Japan*, **17**, 545 (1968), in Japanese.—The viscosity of powder was measured with the rotational viscometer in a vibrating state. In this experiment, the outer cylinder of Stomer viscometer was tightly connected to the vibrator which had constant frequency (120_{cps}), and the amplitude was varied by changing the voltage applied to the vibrator. The α -alumina powders with several kinds of particles sizes were used as samples.

The flow curves, obtained for powders of various particle sizes under different amplitudes and temperatures, were found to be similar to one of non-Newtonian liquids. When the amplitude decreased, each powder behaved like a continuous solid.

The apparent viscosity was obtained from these flow curves in relation to the different amplitudes and particle sizes. At a constant rate of shear and large amplitude, the apparent viscosity decreased with decrease in particle size. When the amplitude was sufficiently small, the apparent viscosity reached its minimum at a definite particle size. It was considered that in the fine powders their coagulated secondary particles moved as flowing units, and that these coagulated particles were broken into primary particles with increase of amplitude.

The Porosity Change Based upon Mixing of Fine Powders Having Different Sizes. Masafumi Arakawa and Eiji Suito. *J. Soc. Materials Sci. Japan*, **17**, 642 (1968), in Japanese.—The packing models such as those devised by Hudson and Horsfield and ordinarily used for mixed powders of different sizes are not applicable

to fine powders in which the force of interaction between the powder particles can not be neglected.

The change of porosity based upon mixing powders having different particle size, was measured. The porosity increased rapidly by addition of small amount of fine powders. However, the porosity seemed to remain constant within certain range of further addition of fine powders. But it increased again when more amount of fine powders were added beyond this range.

The mechanism of this process can be explained by a simple assumption that cohesion of small particles to larger ones increased their points of contact. And the relation between the weight fraction of the small particles added and the increase ratio of porosity of powder bed in every mixed powder was obtained as

$$\frac{W_s}{f(\varepsilon) \times (W_0 - W_s)} = \alpha + \beta \frac{W_s}{W_0}$$

where W_s is the weight of added powder, W_0 is that of total powder mixed and ε is the porosity. The constant β was related to the equilibrium porosity, but the meaning of the constant α was not yet known.

The State of Trimethyloctadecylammonium · Steramide Complexes Adsorbed on Bentonite. Tsunoru Yoshida, Masafumi Arakawa and Eiji Suito. *Kogyo Kagaku Zasshi*, **71**, 820 (1968), in Japanese.—The complexes of trimethyloctadecylammonium · steramide (TMODA · SA) and trimethyloctadecylammonium (TMODA) with bentonite were studied by x-ray diffraction and differential thermal analysis (DTA).

(TMODA)-bentonite shows stepwise increments of 4Å in basal spacing with increasing organic contents. (TMODA · SA)-bentonite shows mixed layer structures in which basal spacing were 19Å and 12.5Å at contents of 90 meq-(TMODA · SA)/100g-clay and 19Å, 15.5Å and 12.5Å at organic contents of 150 meq-(TMODA · SA)/100g-clay.

The DTA curves of (TMODA · SA)-bentonite show two endothermic peaks at 60°C and 78°C, but TMODA-bentonite has no DTA peak at those temperature ranges.

From the interpretation of peak area of the DTA peaks, it was concluded that SA and TMODA or TMODA-chloride adsorbed on the external surface of bentonite have made two-dimensional order structure.

Calcium Carbonate as a Powdered Material. Eiji Suito. *Gypsum & Lime*, No. **94**, 87 (1968), in Japanese.—Review.

Electron Microscopic Studies on Inorganic Materials. Eiji Suito. *Ceramics*, **3**, 443 (1968), in Japanese.—Review.

Inorganic Chemistry

Preparation of Thin Films of BaTiO₃ Glass-Ceramics and Their Dielectric Properties. T. Kokubo, C. Kung and M. Tashiro. *Yogyo Kyokai Shi*, **76**, 89 (1968).—A method of preparation, dielectric properties and microstructure are dealt with for the BaTiO₃ glass-ceramic films thinner than 100μ.

Glass-ceramic films of 50 to 100 μ in thickness were prepared from glasses of the system BaO·TiO₂-Al₂O₃-SiO₂ by a method which comprises squeezing the glass melts by the two drums of solid cast iron rotating in mutual contact and subjecting the produced glass films to heat treatments.

The dielectric constant of the resulting glass-ceramic film increased with increasing content of BaO·TiO₂ component in original glass. With BaO·TiO₂ content kept constant, it reached a maximum when the Al₂O₃/SiO₂ mole ratio was 35/65. By controlling the composition the present method gave a glass-ceramic film having dielectric constant of 500 and $\tan \delta$ of 0.03 (at 10⁶ c/s).

Generally, the dielectric constant of the film as studied in the present work was about a half of that of the bulk sample for a given composition. The rather critical thickness below which the dielectric constant of the film tends to become noticeably low was about 200 μ . The low value of the dielectric constant of the thinner films was attributed to the preferred orientation of hexacelsian crystals precipitated near the surface of the specimens.

The Shift of the Spin Flip Temperature of α -Fe₂O₃ Fine Particles. Naoichi Yamamoto. *J. Phys. Soc. Japan*, **24**, 23 (1968).—The particle size dependences of the spin flip transition temperature (Morin temperature) and of the lattice constant of α -Fe₂O₃ were studied experimentally. With decreasing particle size, it was found that the Morin temperature shifts downwards and crystal lattice expands both in *a*- and *c*-axis directions. As the origin of the Morin temperature shift, the change of the dipolar magnetic field due to the lattice dilatation was considered. Experimental values were compared to the theoretical calculation of Artmann and a qualitative agreement was obtained.

Epitaxial Growth of Nickel Ferrite on (111) and (110) Surface of MgO. Koichi Nagasawa, Yoshichika Bando and Toshio Takada. *Japan. J. Appl. Phys.*, **7**, 174 (1968).—This note reports on the preparation of a single crystal film of nickel ferrite on (111) and (110) surface of MgO in a closed system using HCl gas. Sintered material of nickel ferrite was loaded at one end of a silica tube and MgO single crystal having polished (111) or (110) surface at other end. After the tube was evacuated to 10⁻⁶ mmHg, 50 mmHg of HCl gas was admitted and the tube was sealed off. The temperature was 1030°C at the source part and 860°C at the substrate part. Nickel ferrite was transported away from the source part to the substrate part, and then film grew on the substrate. X-ray measurements and electron diffraction were made on the films removed from substrates. The nickel ferrite film on the (110) surface of MgO have surface of (110) plane and on the (111) surface of MgO have surface of (111) plane. It was concluded that the film was nickel ferrite and deposited epitaxially on the (110) and (111) plane of MgO.

Anomalous Behavior of Paramagnetic Susceptibility of TEMPAD Biradical. Akira Nakajima, Hiroaki Nishiguchi, and Yasuo Deguchi. *J. Phys. Soc. Japan*, **24**, 1175 (1968).—This note reports on the paramagnetic susceptibility of the TEMPAD biradical which indicates the anomalous deviation from the Curie-Weiss' law at low temperature, has a broad maximum at 16.5 \pm 0.5°K, and then drops rapidly below this temperature. This behavior suggests that there is a singlet-triplet equilibrium in a molecule. The theoretical value of χ_M of S-T equilibrium is

$$N_0 g^2 \beta^2 S(S+1) / kT [3 + \exp(\delta/kT)]$$

and from the experimental results the exchange parameter J is estimated to be -1.14×10^{-3} eV.

ESR Hyperfine structure in N-picryl-9-aminocarbazyl. Hiroshi Makino, Hiroaki Nishiguchi, Yasuo Deguchi and Hideo Takaki. *Tetrahedron Letters*, **No. 18**, 2267 (1968).—Electron spin resonance (ESR) hyperfine structure and three principal values of g -tensors of N-picryl-9-aminocarbazyl free radical have been measured. The observed spectrum in very dilute solution is analyzed by use of ESR simulator as follows,

$$\begin{array}{ll} \text{AN}(\alpha) = 11.1 \text{ Gauss,} & \text{AN}(\beta) = 6.0 \text{ Gauss,} \\ \text{AH} = 2.6 \text{ Gauss,} & \text{AN(pic)} = 0.4 \text{ Gauss,} \end{array}$$

where suffices N and H denote nitrogen nucleus and proton, respectively. On the other hand three principal values of g -tensors, $g_1=2.0022$, $g_2=2.0034$ and 2.0039 were estimated from the anisotropic ESR spectrum of the powder sample purified by the column-chromatographic method. The average value of the three ones was 2.0032 which agreed with the one in solution.

Organic Chemistry

The Synthesis of Methacrylic Esters by the Carboxylation Reaction of Methylacetylene. II. Catalytic Synthesis of Methyl Methacrylate using Nickel Carbonyl as the Catalyst. S. Kunichika, Y. Sakakibara and T. Nakamura. *Bull. Chem. Soc., Japan*, **41**, 390 (1968).—The catalytic synthesis of methyl methacrylate by the carboxylation reaction of methylacetylene using nickel carbonyl as a catalyst was studied under various conditions. The experimental results concerning the effects of the reaction conditions on the reaction rate, the stability (regeneration) of nickel carbonyl, and the product yields suggested the most desirable conditions for the synthesis. It was ascertained that, in the catalytic process, the pressure of carbon monoxide played a very important role; a high pressure gave a good regeneration of nickel carbonyl, *i.e.*, a high value of 95% in the so-called catalytic level, but the initial reaction rate decreased remarkably with an increase in the pressure, probably in reverse proportion to its second power, or more. A semicontinuous process was much better for the synthesis than a batch process. A good yield of 85% (based on the methylacetylene used) of the total of methyl methacrylate and methacrylic acid and a high catalytic level of 95% were obtained when the reaction was carried out semicontinuously in the presence of methacrylic acid and water at a total pressure of 13 atm (initial charge of carbon monoxide at room temp.: 4 atm) at 130°C. A mechanism for the catalytic reaction was proposed to account for the experimental results.

Syntheses of 2-Aryl-3H-quinazolinone-(4) and 3-Aryl-2H-1, 2, 4-benzothiadiazine 1, 1-dioxide. Shigeo Tanimoto, Sumio Shimojo and Ryohei Oda. *Yūki Gōsei Kagaku Kyōkai Shi*, **26**, 151 (1968), in Japanese.—N-Phenylamines were condensed with *o*-aminobenzamide to obtain the following: 2-phenyl-3H-quinazolinone-(4) (Y=61%), 2-(*o*-tolyl)-3H-quinazolinone-(4) (Y=35%), 2-(*m*-tolyl)

-3H-quinazolinone-(4) (Y = 51%), 2-(*p*-tolyl)-3H-quinazolinone-(4) (Y = 61%), 2-benzyl-3H-quinazolinone-(4) (Y = 78%), 2-(α -naphthyl)-3H-quinazolinone-(4) (Y = 39%), 2-(β -naphthyl)-3H-quinazolinone-(4) (Y = 72%).

Analogous reactions of N-phenylamidines with *o*-aminobenzenesulfamide gave the following: 3-phenyl-2H-1,2,4-benzothiadiazine

1,1-dioxide(Y=44%), 3-(*m*-tolyl)-2H-1,2,4-benzothiadiazine
 1,1-dioxide(Y=43%), 3-(*p*-tolyl)-2H-1,2,4-benzothiadiazine
 1,1-dioxide(Y=26%), 3-(α -naphthyl)-2H-1,2,4-benzothiadiazine
 1,1-dioxide(Y=33%), 3-(β -naphthyl)-2H-1,2,4-benzothiadiazine 1,1-dioxide
 (Y=36%)

Similarly, the following compounds were obtained using N-phenylamidines and 3,4-diaminotoluene: 5-methyl-2-phenylbenzimidazole (Y=87%), 5-methyl-2-(*m*-tolyl)-benzimidazole (Y=49%), 5-methyl-2-(*p*-tolyl)-benzimidazole (Y=73%), 2-benzyl-5-methylbenzimidazole (Y=82%), 5-methyl-2-(α -naphthyl) benzimidazole (Y=41%).

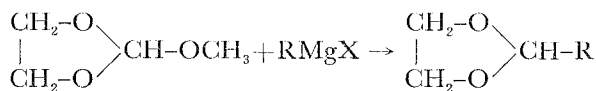
Syntheses and Reactions of β -Chlorovinyl Sulfones. Shigeo Tanimoto, Tadamasu Kurosaki and Ryohei Oda. *Yuki Gosei Kagaku Kyokai Shi*, **26**, 361 (1968), in Japanese.— β -Chlorovinyl ketones are known to be very reactive toward nucleophilic substitution.


In the present study, β -chlorovinyl sulfones were synthesized and their reactions investigated. Thus, condensation of arylsulfonyl chloride with vinyl chloride followed by dehydrochlorination with the aid of triethylamine gave the following; β -chlorovinyl-*p*-tolyl sulfone (3a) (mp 43~47°C), β -chlorovinyl-2,4-dimethylphenyl sulfone (3b) (bp 135~142°C/0.12 mmHg), β -chlorovinyl-2,5-dimethylphenyl sulfone (3c) (mp 99.5~102.5°C), and 4,4'-bis-(β -chlorovinylsulfonyl)-phenoxybenzene (3d) (mp 127~132°C). All those β -chlorovinyl sulfones were *trans*-isomers.

The reactions of (3a) with Bisphenol-A or cyclohexylamine, (3b) with methanol, and (3d) with diethylamine were studied. (3d) was also condensed with hexamethylenediamine, ethylenediamine, and Bisphenol-A to obtain polymers with intrinsic viscosities of 0.20 dl.g⁻¹ (dimethylformamide, 30°C), 0.16 dl.g⁻¹ (dimethylformamide, 30°C), and 0.09 dl.g⁻¹ (dioxan, 30°C), respectively.

Reactions of 2-Methoxy-1,3-dioxolane with Grignard Reagents. Shigeo Tanimoto, Sumio Shimojo and Ryohei Oda. *Yuki Gosei Kagaku Kyokai Shi*, **26**, 435 (1968), in Japanese.—The possibility that 2-alkoxy-1,3-dioxolane might be attacked by nucleophilic reagent to form 2-substituted-1,3-dioxolane prompted us to conduct this set of studies.

Thus, 2-methoxy-1,3-dioxolane was treated with Grignard reagents and heated to form the corresponding 2-alkyl- or 2-aryl-1,3-dioxolanes, as follows:



R = C₆H₅ (24% yield), *o*-CH₃C₆H₄ (39%), *m*-CH₃C₆H₄ (16%), *p*-CH₃C₆H₄ (19%), *p*-ClC₆H₄ (9%), *o*-CH₃OC₆H₄ (15%), *m*-CH₃OC₆H₄ (15%), *p*-CH₃OC₆H₄ (9%), *n*-C₃H₇ (10%), *n*-C₄H₉ (13%), CH₂=CH--(6%).

Similarly, *p*-vinylphenylmagnesium chloride gave 2-(*p*-vinylphenyl)-1,3-dioxolane (VPD). This was bulk polymerized by 2,2'-azobisisobutyronitrile to give a polymer with intrinsic viscosity of 0.18 dl.g⁻¹ in dioxane at 30°C. Possible initial processes of the radical polymerization and the simultaneous crosslinking reactions of VPD were discussed based on the infrared spectra of the product polymers.

Syntheses of Some Bi-functional Compounds from Dimethyl Terephthalate. Sumio Shimojo, Shigeo Tanimoto, Masaya Okano and Ryohei Oda. *Yuki Gosei Kagaku Kyokai Shi*, **26**, 490 (1968), in Japanese.—Upon treatment of dimethyl terephthalate with methylsulfinylcarbanion in DMSO, a solution of the carbanion of 1,4-bis(methylsulfinyl acetyl) benzene (2) was obtained. When the solution was treated with an aqueous acid, compound (2) underwent Pummerer rearrangement to yield *p*-phenylenediglyoxal bis(methylhemimercaptal) (8), which gave *p*-phenylenediglyoxal (9) on hydrolysis. *p*-Phenylenediglycolic acid (10) was also prepared from (8). Reduction of (2) with zinc dust and acetic acid gave *p*-diacetylbenzene (3) and this was converted to a bisepoxy compound, 1,4-bis(1',2'-epoxyisopropyl) benzene (7), by the action of a sulfonium methylide. The bis-(Mannich base), 1,4-bis(β -N,N-dimethylaminopropionyl) benzene dihydrochloride (5) derived from (3), formaldehyde, and dimethylamine hydrochloride gave a bispyrazoline by condensation with phenylhydrazine.

Synthesis of Polyquinacridonequinone. Sumio Shimojo, Shigeo Tanimoto, Masaya Okano and Ryohei Oda. *Kobunshi Kagaku*, **25**, 16 (1968), in Japanese.—Polyquinacridonequinone was prepared by the condensation of hydroquinone and benzidine-3,3'-dicarboxylic acid in the presence of ammonium vanadate and sodium chlorate and subsequent heating in concentrated sulfuric acid.

Similarly, it was obtained from hydroquinone-2,5-dicarboxylic acid and a diamine such as benzidine, 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenylether.

Their preparations and physical properties such as thermal stabilities, solubilities in various solvent and inherent viscosity are described.

In comparison with other polymers which have good thermal stability, it was observed that polyquinacridonequinone had the most excellent thermal stability.

Partial Asymmetric Synthesis in the Simmons-Smith Reaction I. S. Sawada, K. Takehana and Y. Inouye. *J. Org. Chem.*, **33**, 1767 (1968).—Partial asymmetric synthesis of cyclopropanes was obtained by reaction of the Simmons-Smith reagent with (–)-menthyl esters of α , β - and β , γ -unsaturated carboxylic acids. The steric course was interpreted as proceeding through an intermediate complex in which the Simmons-Smith reagent coordinates with ester carbonyl oxygen and the double bond in a twisted cisoidal conformation. Evidence for an effective coordination of the Simmons-Smith reagent with ester carbonyl oxygen was provided by the Simmons-Smith reaction with 2-cyclohexenyl acetate, leading exclusively to *cis*-2-bicyclo[4,1,0] heptanol.

Partial Asymmetric Synthesis in the Simmons-Smith Reaction. II. S. Sawada, J. Oda and Y. Inouye. *J. Org. Chem.*, **33**, 2141 (1968).—The Simmons-Smith reaction of achiral olefins in the presence of (–)-(R)-menthol under the

standardized conditions afforded the corresponding cyclopropanes with optical activity and of the same configurational series, (*R*)- and (*R*:*R*)-configurations unexceptionally. This provides one with a useful means of determining the absolute configuration of cyclopropanes in general.

Solvent Effect in a Partial Asymmetric Synthesis. I. Y. Inouye, S. Inamasu, M. Horiike, M. Ohno and H.M. Walborsky. *Tetrahedron*, **24**, 2907 (1968).—The *cis/trans* ratio as well as *trans*-(-)-(*R*:*R*)/(+)-(*S*:*S*) ratio of cyclopropane products in the NaH-catalyzed Michael type condensations of (-)-menthyl chloropropionate with methyl methacrylate, conducted in media of varying dielectric constant, unequivocally showed the dependence of stereoselectivity of the reaction on solvent polarity. The stereochemical outcome was explicable in terms of electrostatic stabilization and non-bonded repulsive interactions in the postulated transition state conformations stabilized by orbital overlap and charge delocalization in the rate- and therefore, stereochemical-determining cyclization step. The solvent effect was also correlated fairly well in quantitative terms by the Kirkwood-Onsager theory.

7-Bromo-6-hydroxy-quinoline. Eiichi Fujita. *Synthetic Method of Organic Compounds (Yūki Kagobutsu Gōseiho)*, **18**, 26 (1968), in Japanese.—2,6-Dibromo-4-nitrophenol, glycerol and conc. phosphoric acid were mixed and to the mixture was slowly added conc. sulfuric acid under cooling and stirring. Then, the mixture was heated at 150~160° for 3 hr. After cooling, the solid mixture was extracted with 5% hydrochloric acid.

The extract was treated as usual to give 7-bromo-6-hydroxy-quinoline as colorless needles.

The yield was about 60%. This method is a very convenient for synthesis of the titled compound.

Terpenoids. VII. The Structure and Absolute Configuration of Nodosin, a New Diterpenoid from *Isodon* Species. Eiichi Fujita, Tetsuro Fujita and Masayuki Shibuya. *Chem. Pharm. Bull. Tokyo*, **16**, 509, (1968).—Nodosin, a new diterpenoid isolated from *Isodon trichocarpus* KUDO and *I. japonicus* HARA, was converted into a keto lactone acetal *via* several steps of reactions. The conversion made it possible to propose the gross structure for nodosin.

The remaining hydroxy group proved to be located at C-11 of enmein skeleton and its absolute configuration was also established. Thus, the structure and absolute configuration of nodosin were completely elucidated.

Polymer Chemistry

Statistical Chain Dimensions of Poly(vinyl acetal)-Type Molecules. Hisayuki Matsuda and Hiroshi Inagaki. *J. Macromol. Sci.-Chem.*, **A2** (1), 191 (1968).—Acetalization of poly(vinyl alcohol) molecules results in acetal ring formation between two successive hydroxyl groups. This will dominate the chain stiffness of poly(vinyl acetal) in different ways, depending on the stereospecificity of poly(vinyl alcohol) used as the starting material. The present paper first deals with calculations of statistical dimensions of hypothetical poly(vinyl acetal) chains with a 100%

degree of substitution and different stereospecificities (isotacticity and syndiotacticity). The calculations are essentially identical with those made by Wall and Markovitz, but recent stereochemical knowledges of the acetal ring and poly(vinyl alcohol) are taken into account. The results show that the chain dimension of poly(vinyl acetal) chain derived from isotactic poly(vinyl alcohol) is much larger than that of poly(vinyl acetal) derived from the syndiotactic one. The treatment used above is extended to more realistic chains that have any degree of stereoregularity and of substitution. As has been anticipated intuitively, it is ascertained that the chain dimensions increase with increase in the degree of substitution for each stereospecificity.

The Determination of Molecular Weight Distributions of Macromolecules by Velocity Ultracentrifugation Method; Dependence of the Sedimentation Coefficient on the Concentration and Pressure (Rotor Speed) in Θ Solvent Systems. Nobuo Donkai and Tadao Kotaka. *Kogyo Kagaku Zasshi*, **71**, 545 (1968) in Japanese.—The sedimentation behavior of polystyrene-cyclohexane system at the Θ -temperature (35°C) was studied with an emphasis on examining the effects of pressure as well as the concentration dependence to establish a method for determination of molecular weight distribution.

It is found that the boundary position of a schlieren pattern may be approximated by the peak position instead of using the second moment, and that the "best fit" method is most appropriate for estimating zero-time-correction.

The effect of pressure on sedimentation coefficient, s , becomes significant when the rotor speeds, ω , is above 50,000 r.p.m. and the correction is made by using Fujita's equation. The pressure dependence parameter, μ , is estimated as 10^{-9} $\mu=1.2\sim 2.0$.

The dependence of s on the concentration is not negligible even in the Θ condition. Moreover, in the experiments at a finite concentration and at different speed, ω , the value of s corrected for the pressure effect is still dependent on ω , *i.e.*, s is smaller at higher speeds. The limiting sedimentation coefficient (value of s extrapolated to zero-concentration and 1 atm), is independent of ω within an experimental error, while the concentration dependence coefficient, k_s , depends slightly on ω .

The Determination of Molecular Weight Distributions for Macromolecules by Velocity Ultracentrifugation Method: Single Concentration Method in Θ Solvent Systems and Comparison with Other Methods. Nobuo Donkai and Tadao Kotaka. *Kogyo Kagaku Zasshi*, **71**, 879 (1968) in Japanese.—The method for estimating molecular weight distributions from sedimentation transport experiments in Θ solvent system (polystyrene-cyclohexane at 35°C) was studied with several polystyrenes of narrow and broad distributions. The procedures for making a correction for the pressure effect on sedimentation boundary were investigated in detail. Since the sedimentation coefficient S^0 depends on the concentration even in the Θ condition, the correction for the concentration-dependent effects is also necessary.

The value of concentration-dependence coefficient k_s at a given rotor speed ω was found proportional to the limiting sedimentation coefficient S^0 as predicted by Pyun and Fixman. However, the value of k_s corrected for the pressure effect by use Fujita's equation still depended slightly on ω ; *i.e.*, $k_s=3.7 \times 10^{11} S^0$, $3.2 \times 10^{11} S^0$

and $3.0 \times 10^{11} S_0^\circ$ at $\omega = 59,780, 42,040,$ and $29,500$ rpm, respectively. For deducing the distribution of S_0° from data of a single sedimentation run, the empirical relations of k_s vs. S_0° together with $S_c^\circ = S_0^\circ(1 - k_s c^\circ)$ were employed. The applicability of the "single concentration method" is discussed in detail.

The results of the single concentration method were compared with those from elution chromatography and also from gel permeation chromatography (GPC). The GPC method gave somewhat broader distributions than other methods especially for samples with high molecular weights (*e.g.*, $> 5 \times 10^5$) and/or with narrow distributions.

Dilute Solution Properties of Styrene-Methyl Methacrylate Random Copolymers. Tadao Kotaka, Yoji Murakami, and Hiroshi Inagaki. *J. Phys. Chem.*, **72**, 829 (1968).—The results of an extensive study on dilute solution properties of three series of styrenemethyl methacrylate random copolymers are described. The copolymers are prepared by a free radical polymerization method (conversion = less than 10%) and subsequently fractionated by use of a butanone-diisopropyl ether system. The characterization of the fractions is made by combustion analysis, by osmometry, and by light-scattering methods. The θ temperatures for the copolymers are determined as the temperatures at which the osmotic second virial coefficient $A^2 = 0$ in cyclohexanol and 2-ethoxyethanol. Measurements of intrinsic viscosity, $[\eta]$, under the θ conditions show that $[\eta]_\theta$ is proportional to $M^{1/2}$ (M , the molecular weight) in the copolymer solutions. Measurements of $[\eta]$ are also made in toluene, 1-chloro-*n*-butane, and diethyl malonate, which have typically different solvent powers toward the parent homopolymers. All the $[\eta]$, A_2 , and M data are examined on the basis of the current excluded volume theories. Then the short-range and the long-range interaction parameters, A and B , are estimated for each copolymer-solvent pair, and their dependences on the monomer composition are examined in relation with those of the parent homopolymers. It is found that the values of $A^2 = (\langle S^2 \rangle_0 / M)$, with $\langle S^2 \rangle_0$ being the unperturbed mean-square molecular radius, are larger than the simple composition averages of those of the parent homopolymers. The parameter B shows the presence of repulsive interactions between the unlike monomer units.

Normal Stress Effect in Dilute Solutions of Poly-*n*-butyl Methacrylate in Chlorinated Diphenyl. Mikio Tamura, Michio Kurata, Kunihiro Osaki and Kanji Kajiwara. *Japan. J. Appl. Phys.*, **7**, 447 (1968).—Normal stresses and the shear stress in steady shear flow as well as the dynamic complex modulus are measured for dilute solutions of poly-*n*-butyl methacrylate in chlorinated diphenyl, in the range of concentration, 0.2~1.0 wt.% and of molecular weight, $5.21 \times 10^5 \sim 2.30 \times 10^6$. The secondary normal stress was negligibly small compared to the principal one when the rate of shear was low. The steady shear compliance was proportional to the number of polymer molecules in the solution and its magnitude was of the order predicted from the spring-beads model theories. A relatively strong tendency to non-Newtonian effect was observed for the solutions with relatively high concentrations, and the reduced plot which was successfully performed for polystyrene solutions failed in this case at high rate of shear.

Normal Stress Effect of Dilute Poly- α -methylstyrene Solutions—Phenomenological Aspect—Mikio Tamura, Michio Kurata, Kunihiro Osaki and Kazumasa Matsushita. *Nippon Kagaku Zasshi*, **89**, 469 (1968), in Japanese.—Normal stresses ($-\partial P/\partial \ln \tau$) and shear stresses σ_{12} of dilute solutions of monodisperse poly- α -methylstyrene were measured with a parallel plate rheogoniometer and a coaxial cylinder rheometer, respectively. Elastic recovery s_l of these solutions was evaluated from these data. In the systems of comparatively low-viscosity solvent, s_l was independent of the polymer concentrations v_2 and was proportional to σ_{12} , especially when v_2 was very small. Elastic recovery of the polymer molecules alone, s_l^* , was evaluated by excluding the contribution of solvent $\kappa\eta_s$ from σ_{12} . The elastic recovery s_l^* was proportional to $\sigma_{12}^* = \sigma_{12} - \kappa\eta_s$, the shear stress due to the polymer molecules alone, irrespective of v_2 or η_s of the solution.

Biochemistry

Effect of Dinitrophenylation on the Properties of G- and F-Actin.—B. R. Gerber and T. Ooi. *Biochim. Biophys. Acta*, **155**, 162 (1968).—Dinitrophenylation of G- and F-Actin carried out at a low temperature showed loss in polymerizability for G-Actin, but polymerizable G-Actin could be obtained from dialysis DNP-F-Actin against water. Chemical analysis of modified actins revealed the modification of lysine, histidine, and tyrosine residues. Comparison curves in loss of polymerizability with the numbers of residue modified suggests one tyrosine residue is directly responsible for polymerization of actin.

Crystals of Tropomyosin and Native Tropomyosin.—S. Higashi and T. Ooi. *J. Mol. Biol.*, **34**, 699 (1968).—Preliminary results obtained by electron microscopic observations on crystals of tropomyosin and native tropomyosin are reported. A rod-like proteins, tropomyosin, can be crystallized into three dimensional crystals in which molecules are arranged as networks of 200 Å spacing. Troponin, another component protein in addition to tropomyosin in native tropomyosin, locates on the middle of neighboring two sides of tetragons which constitute 200 Å network.

Occurrence of Arginine Racemase in Bacterial Extract.—Kenji Soda, Takamitsu Yorifuji and Koichi Ogata. *Amino Acid and Nucleic Acid*, **17**, 43 (1968), in Japanese.—*Pseudomonas graveolens* IFO 3460 could utilize D-arginine as a sole nitrogen source. The sonic extract of this bacteria possessed the activity to racemize D- and L-arginine. It was shown that the extract failed to catalyze transaminase reactions between D- or L- arginine and pyruvate or α -ketoglutarate, and that these keto acids had no effect on the reaction. Although the extract exhibited alanine racemase activity, these results exclude the possibility of racemization *via* the combined reactions of D- and L-amino acid transaminases and alanine racemase or another amino acid racemase, and allow to conclude that this racemization is catalyzed by a single enzyme racemizing arginine, *i.e.*, arginine racemase. The racemase activity of this organism was found to be elevated inducibly by the addition of L-arginine in the growth medium.

Protocatechuate 3,4-Dioxygenase. I. Crystallization and Characterization. H. Fujisawa and O. Hayaishi. *J. Biol. Chem.*, **243**, 2673 (1968).—A procedure

is described for the purification and crystallization of protocatechuate 3,4-dioxygenase from *p*-hydroxybenzoate-induced cells of *Pseudomonas aeruginosa*. Overall purification was about 30-fold, with 23% yield. Crystallization of the enzyme was achieved when it was incubated with a sulfhydryl reagent such as mercaptoethanol for over 1 week prior to the addition of ammonium sulfate. The crystalline enzyme was homogeneous as judged by ultracentrifugation, starch gel electrophoresis, and immunoelectrophoresis. The molecular weight was estimated to be approximately 700,000 and the molecular activity was calculated to be 45,500 at 24°. The enzyme had a deep red color with a broad absorption between 400 and 650 m μ , and contained about 7 g atoms of nonheme iron per mole of enzyme. Crystallization was also achieved by treating the enzyme with iodoacetamide prior to the addition of ammonium sulfate, or by dialyzing it against distilled water. Polymerization of the enzyme appeared to occur under certain conditions and to prevent the formation of crystals. The mode of polymerization and certain other properties of the crystalline enzyme are also reported.