marked discontinuities throughout a wide range of concentration.

Acknowledgment—The authors wish to thank Dr. E. Gonick for the hexanolamine oleate from which the solutions were made.

Summary

1. Transparent aqueous systems of hexanolamine oleate have been examined by X-ray diffraction over the wide range of concentration from 30 to 92% soap. The more dilute systems exhibit a water halo. All exhibit a well-marked halo with the Bragg spacing of 4.5 to 4.6 Å., as well as a long spacing often in two orders.

2. This confirms similar results from Germany and this country, which have uniformly been interpreted as proving the presence of lamellar micelles in aqueous solutions of colloidal electrolytes.

3. The lamellar micelles consist of alternate layers of soap and of water. The soap molecules are packed side by side (giving rise to the side spacing) and end to end, the long spacings being due to the alternate layers of water and soap.

4. The long spacing increased approximately linearly over the range of systems studied, some of which were fluid and isotropic, others fluid and anisotropic and others semi-solid and anisotropic. Hence throughout the aqueous systems the essential structure of the primary micelle appears to be maintained and the variations in properties caused by changing relations of these micelles to each other.

STANFORD UNIVERSITY CALIF. RECEIVED MAY 14, 1945

[CONTRIBUTION FROM THE POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Copolymerization of Styrene and Allyl Chloride

BY TURNER ALFREY AND JOHN G. HARRISON, JR.

It is well known that allyl halides exhibit markedly lower polymerization reactivities than do vinyl halides and many other substituted ethylene derivatives, such as styrene. This low polymerization tendency may be the result of a low rate of activation, a low rate of propagation, or a high rate of chain termination.

A number of investigators[1,2,3] have demonstrated that copolymerization experiments make it possible to isolate the chain propagation step, and determine quantitatively the relative rates at which different monomers add to a specific free radical chain end. This investigation of the system styrene–allyl chloride leads to the conclusion that allyl chloride exhibits a very low relative rate of addition to a growing free radical chain of either type.

Both Lewis and Mayo[1] and Alfrey and Goldfinger[2] arrived independently at the following equation, which relates the chemical composition of a copolymer with that of the monomer mixture from which it is formed.

$$\frac{b}{a} = \alpha\cdot\frac{B}{A}\,\frac{\beta B + A}{\alpha B + A}$$

where

b/a = the molar ratio of the monomer units in the copolymer,

B and A = molar concentrations of the unpolymerized monomers,

α = the ratio of the respective rate constants for addition of monomer B and A, respectively, to type A radical; *i. e.*, k_2^{ab}/k_2^{aa}

and

β = the ratio of the respective rate constants for addition of monomer B and A, respectively, to type B radical; *i. e.*, k_2^{bb}/k_2^{ba}

In this investigation styrene has been selected as monomer A and allyl chloride as monomer B.

Experimental

Reagents.—Styrene, pure grade, from the Dow Chemical Co. was shaken with four successive portions of 10% sodium hydroxide solution and four portions of distilled water, dried with calcium chloride and distilled under 20-mm. pressure. Allyl chloride, b. p. 44.9° (from the Shell Chemical Division of the Shell Union Oil Corporation) was stated to be 99% pure, the impurities being by spectrographic evidence 1-chloro-1-propene (b. p. *cis*- 32–32.2° and *trans*- 36.7°) and isopropyl chloride, b. p. 36.5°. The lower boiling points of the impurities indicated that no purification beyond a very careful fractionation was necessary. An efficient column with a reflux ratio of 3:1 was used, the first and last 10% being rejected.

Procedure and Results.—The copolymerization equation discussed above is in the differential form and has been integrated by Lewis and Mayo. In this work, however, the degree of conversion was small, and the relative concentrations of the unreacted monomers did not essentially change throughout the reaction, as will be shown in Table I. Therefore, the differential form of the equation was quite satisfactory, particularly when average, rather than initial, monomer ratios were used.

A series of copolymers with varying amounts of each component was prepared by heating the mixtures in sealed glass vessels immersed in a water-bath held at 70 ± 0.1°. Benzoyl peroxide (0.5%) was used as a catalyst. Polymerization was stopped at a low degree of conversion.

The "initial polymers" so obtained were purified by precipitating in methyl alcohol and reprecipitating from methyl ethyl ketone solution. The resulting powders were dried in a vacuum oven overnight at 50° and weighed. The polymers were microanalyzed in duplicate for chlorine

TABLE I

Conversion, %	Cl, %		Mole fraction allyl chloride Monomers Initial	Residual	Av.	Polymer	Rate of polymer production, % per min.	$[\eta]$
2.50	0.26	.25	0.15	0.15_7	0.15_4	0.007_5	0.081	0.43
2.80	0.39	.35	.30	$.31_6$	$.30_8$	$.010_9$	.061	.34
1.34	1.01	1.30	.50	$.51_1$	$.50_6$	$.033_6$	.036	.26
1.19	2.30	2.40	.70	$.72_0$	$.70_9$	$.067_8$	.019	.17
0.93	4.98	4.87	.85	$.87_0$	$.86_0$	$.139_3$	.0075	.10

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[1] Lewis and Mayo, THIS JOURNAL, **66**, 1594 (1944).

[2] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

[3] Alfrey and Merz, *Polymer Bulletin*, **1**, 86 (1945).

content and results are given below. The percent. conversion and the amount of each monomer converted to polymer were known, and the amount of each monomer in the residual monomer mixture was calculated. Intrinsic viscosities of the copolymers in toluene at 30° were also determined.

Discussion

In Fig. 1 the circles are drawn to show the experimental results. These results indicate that both α and β are extremely small in value; *i. e.*, allyl chloride monomer is much less reactive than styrene monomer as far as addition to either type of free radical chain end is concerned. As a result, the form of the composition curve is very much dominated by the constant α. The ratio β has an appreciable influence on only the extreme right-hand part of the curve, corresponding to very high mole fractions of allyl chloride in the monomer mixture. Theoretical curves were calculated using α values from 0.028 to 0.036, and β was arbitrarily set at zero. The curve which had the minimum sum of the squares of the deviations from the experimental results was that where $\alpha = 0.032$. The middle solid curve represents these values of α and β. The two other solid curves in Fig. 1 correspond to the values $\alpha = 0.028$ and $\alpha = 0.036$, again with $\beta = 0.0$. The best value of α would seem to lie between these two extremes; α can be said to be equal to 0.032 ± 0.004.

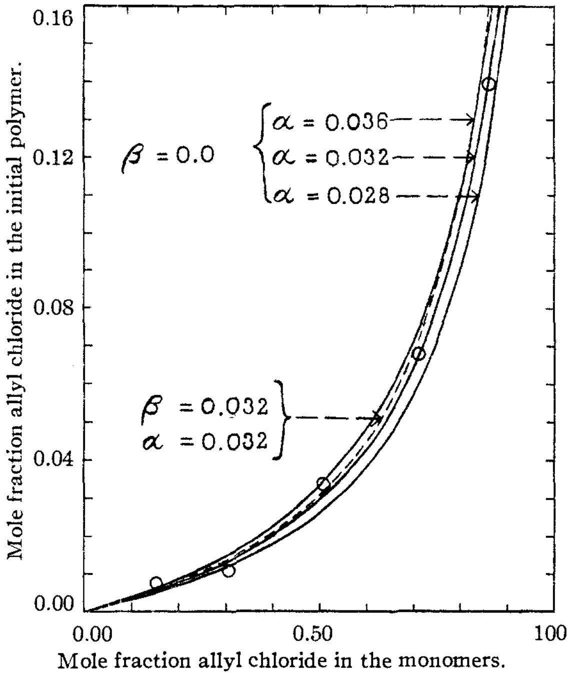

Fig. 1.—Copolymerization of allyl chloride–styrene.

Although within experimental error $\beta = 0.0$, altering the value of β from 0.0 to 0.032 yields a theoretical curve which fits the experimental data only slightly less well. This is shown by the broken line in Fig. 1 where both β and α were chosen to be equal to 0.032. This variation in β is just at the limit of experimental error.

It is interesting to compare the behavior of allyl chloride as exhibited in this investigation with that of maleic anhydride[4] and maleic esters,[5] both of which exhibit a specific reluctance to add to *themselves* in the growing chain but add to styrene free radicals quite readily. The present investigation does not prove that allyl chloride has such a specific reluctance, and indeed, the fact that allyl chloride does polymerize alone indicates that β cannot completely vanish.

Probably the most precise statement of findings would be: "For the system styrene (A)–allyl chloride (B), the rate constant ratio α equals 0.032 ± 0.004. This indicates that allyl chloride monomer adds to a styrene free radical only about 0.032 times as fast as styrene monomer adds. The ratio β is also very small, lying between 0.0 and 0.032, thus indicating that allyl chloride adds to an allyl chloride radical very slowly as compared to the rate of styrene addition to the allyl chloride radical."

The data presented in Table I show that the over-all rate of polymerization decreases with increasing allyl chloride content. Furthermore, the intrinsic viscosity $[\eta]$ of the copolymer decreases regularly with increasing allyl chloride content. The $[\eta]$ values in Table I represent lim $(\eta_{sp}/c)_{c\to 0}$, where c is expressed in grams of solute per 100 ml. of solution. While no actual molecular weight determinations were made, it seems safe to conclude that increasing concentrations of allyl chloride in the monomer mixture result in decreasing polymerization degrees.

Taken together, these results suggest the conclusion that a low rate of chain propagation is one contributing factor to the low over-all rates and the low polymerization degrees characteristic of allyl chloride. It must be recognized, however, that this investigation tells nothing at all about the relative reactivities of allyl chloride *free radicals* as compared with styrene free radicals, but only fixes the relative reactivities of allyl chloride *monomer* and styrene *monomer* with a given free radical. The rates of the various chain propagation reactions would be influenced by any differing reactivities of the radicals as well as by the relative reactivities of the monomers. Since the demonstrated low reactivity of the allyl chloride monomer might be compensated by a higher reactivity of the allyl chloride radical, no conclusion can be drawn as to the relative rates of propagation in pure styrene and pure allyl chloride.

Summary

Mixtures of styrene and allyl chloride have been found to copolymerize; the rate of polymerization and the polymerization degree of the co-

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[4] Alfrey and Lavin, THIS JOURNAL, 67, 2044 (1945).

[5] Alfrey, Merz and Mark, *J. Polymer Research*, 1, 37 (1946).

polymer decrease regularly with increasing concentrations of allyl chloride. In this copolymerization reaction, allyl chloride monomer adds to styrene free radical or to allyl chloride free radical much more slowly than does styrene monomer.

BROOKLYN, N. Y. RECEIVED OCTOBER 26, 1945

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Properties of the Electrical Double Layer at a Mercury Surface. II. The Effect of Frequency on the Capacity and Resistance of Ideal Polarized Electrodes[1]

BY DAVID C. GRAHAME

The nature of the interaction of ionized substances with metallic surfaces is most effectively studied by investigation of the interfacial tension and electrical capacity of such surfaces. In the first paper of this series,[2] hereafter called Paper I, a method was presented for the determination of the electrical capacity of mercury–solution interfaces with a precision not previously attained. In that method the capacity of the surface of an expanding mercury droplet in contact with an aqueous solution was measured by means of an impedance bridge operating with an alternating current having a frequency of 1000 cycles. It was found that the values obtained were in agreement with values calculated from the corresponding electrocapillary curves obtained by Gouy[3] in 1903.

Other investigators,[4-8] working with stationary polarized mercury surfaces, have reported that the capacity of such surfaces depends upon the frequency of the alternating potential used for the measurement, although no two workers have agreed concerning the magnitude of the effect. It is apparent that no reliable conclusions can be drawn from measurements of the capacity of the double layer so long as a fairly large unexplained frequency effect persists in the measurements. In the present paper we shall describe the results of measurements made in an effort to ascertain as certainly as possible the cause of the frequency dependence reported by other workers. In our own measurements the effect was finally eliminated by very careful design, but it was not very large even in the original relatively crude apparatus. This was due to the use of a dropping mercury electrode, which automatically overcomes most of the major difficulties associated with this work.

It is possible in principle to obtain all of the significant thermodynamic properties of mercury–solution interfaces by measurements of the interfacial tension,[9,10] but as a practical matter the precision required in such measurements for the calculation of the differential capacity is so great that direct measurement of this quantity is generally to be preferred. In addition, measurements of differential capacity and resistance under non-equilibrium conditions give information not derivable from the electrocapillary curves and reveal interesting and important properties of the surfaces studied. For example, it will be shown in a paper to follow that the slow step in the discharge of hydrogen ions on a mercury surface can be identified with the reaction

$$H_3O^+ + e^- \longrightarrow H + H_2O$$

Experimental

Many forms of apparatus were tried and used. One of the best is shown in Fig. 1. B is a fully shielded R.C.A. beat frequency oscillator with its neon indicator removed to eliminate a slight electrical disturbance. S and S′ are carbon resistors of approximately equal resistance, used to reduce the voltage input to the bridge to a suitable value. T is a General Radio shielded bridge transformer with the shield of the secondary not grounded, a vital point. This transformer has spacers between the primary and secondary which serve to isolate the source of alternating potential. R_s, R_2 and R_3 are Leeds and Northrup A-C resistance boxes, their types 4750, 4748 and 4631, respectively. C_s is a mica capacitor decade of total capacity 1.1 microfarads adjustable in steps of 0.0001 microfarads. A is a two-stage high-gain amplifier connected to an oscillo-

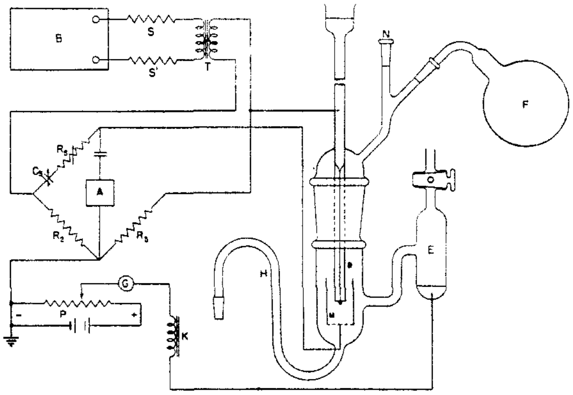

Fig. 1.—Experimental arrangement for the measurement of the capacity of the electrical double layer between mercury and conducting solutions.

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[1] Supported by a grant from the Penrose Fund of the American Philosophical Society.

(2) D. C. Grahame, THIS JOURNAL, **63**, 1207 (1941).

(3) G. Gouy, *Ann. chim. phys.*, [7] **29**, 145 (1903).

(4) M. Wien, *Ann. Phys.*, [2] **58**, 37 (1896); [4] **8**, 372 (1902).

(5) P. Schönherr, *ibid.*, [4] **6**, 116 (1901).

(6) F. Kruger, *Z. physik. Chem.*, **45**, 1 (1903).

(7) N. Thon, *Compt. rend.*, **198**, 1219 (1934); **200**, 54 (1935).

(8) T. Borissowa and M. Proskurnin, *Acta Physicochim. U. R. S. S.*, **12**, 371 (1940).

(9) F. O. Koenig, *J. Phys. Chem.*, **38**, 111, 339 (1934).

(10) D. C. Grahame and R. B. Whitney, THIS JOURNAL, **64**, 1548 (1942).