Conclusion

It is obvious from the above that eq. (8) is of better applicability than eq. (7) as it does not involve the term ΣD, the solution of which is difficult and has not been attempted. The entire derivation is based on the important assumption that interfacial polymerization is governed by the well-known distribution law. The only unknown in eq. (8) which makes a direct determination of the average polymer molecular weight difficult is the numerical value of n. n has been shown to be proportional to the catalyst concentration.[3] Hence for a monomer emulsion of constant catalyst concentration, undergoing polymerization at the interface for a definite time interval, the ratio of the average polymer molecular weight of the polymer coming out calculated from the equation proposed, assuming n equal to one, to that calculated from one of those already in vogue, will give the numerical value for n. If, for the same system, for a different time interval the calculated ratio is about the same, then the value of n can be assumed for subsequent determinations and the validity of the equation would be assured. Experimental work is in progress to test the applicability of the equation.

From the above analysis, it is considered probable that polymer formation in emulsion polymerization consists of discrete steps each of which represents: (a) interfacial adsorption of the emulsifying agent; (b) chain growth at the active centers; (c) termination of the chain and transfer of the active centers; (d) outward diffusion of the final polymer particle enveloped by a monomolecular layer of the emulsifying agent, into the aqueous phase.

THE SOLUBILITY OF SILVER PROPIONATE AND SILVER BUTYRATE IN AQUEOUS SODIUM NITRATE

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Solubilities of silver propionate and silver butyrate have been measured in aqueous silver nitrate solutions. The solubility increases with ionic strength as expected from normal activity coefficient behavior, but activity coefficients have not been calculated from the data in view of the uncertain degree of ionization of the salts. Techniques for the preparation of pure samples of these salts are described.

The effect of inert salts on the solubility of silver carboxylates can be interpreted[1] as due to a change in activity coefficients consistent with the theory of Debye and Hückel. However, electromotive force measurements have shown incomplete ionization in the case of the acetate,[2,3] chloroacetate,[4] and benzoate.[5,6] The quantitative interpretation of these measurements requires the estimate of the mean activity coefficient as a function of ionic strength based on solubility studies. With this in mind, measurements of the solubility of silver propionate and silver butyrate in sodium nitrate solutions were undertaken.

Materials and Experimental Method

Silver nitrate, sodium nitrate, sodium hydroxide and potassium thiocyanate were of reagent quality. The sodium nitrate was dried for two weeks at 175° and stored over magnesium perchlorate. Since the silver carboxylates are not available commercially and previous investigators[7-9] of these salts did not report adequate methods of preparation, the preparations will be given in some detail.

Silver Propionate.—Approximately 19 ml. of Eimer and Amend C.P. propionic acid was neutralized with 250 ml. of sodium hydroxide solution; 1 ml. of excess acid was added. To this was added slowly with vigorous stirring an equivalent amount of silver nitrate (44 g.) dissolved in 250 ml. of distilled water. The white precipitate was collected in a sintered Pyrex filter, washed twice with 100-ml. portions of water and twice with reagent grade methanol by removing the precipitate from the filter before each washing, and dried over magnesium perchlorate. All operations were carried out in dim illumination. Analysis of one preparation Ag, 59.65, 59.75, 59.47; second preparation 59.54, 59.74, 59.78; calcd. for $AgC_3H_5O_2$: Ag, 59.62.

Silver Butyrate.—Coleman and Bell C.P. butyric acid (23 ml.) was neutralized with 250 ml. of sodium hydroxide solution, then made slightly acid to litmus by addition of more acid. To this was added slowly in total darkness with vigorous stirring 44 g. of silver nitrate in 250 ml. of water. The precipitate was washed twice with 100-ml. portions of water and twice with 60-ml. portions of acetone and dried for two weeks over magnesium perchlorate. Samples prepared in this way were white and quite light stable, but precipitation with exposure to light, or washing with methanol, even in total darkness, gave dark products which dissolved with difficulty in dilute nitric acid and gave low silver analyses. Analysis of silver butyrate prepared as described showed Ag, 55.22, 55.52, 55.57 and 55.35; calcd. for $AgC_4H_7O_2$: Ag, 55.35.

Washing with water-miscible volatile solvents was used to effect reasonably rapid drying at room temperature, since silver salts of low molecular weight carboxylic acids sometimes decompose in the drying oven. Oven drying has been found satisfactory for the chloroacetate at 55°,[1] the benzoate at 120°,[5] the *t*-butylacetate at 110°[10] and the salts of several aromatic acids at 100–105°.[11]

Solubility Measurements.—A weighed portion of sodium nitrate and distilled water measured with a calibrated pipet were introduced into brown glass stoppered bottles along with an excess of the silver salt. The bottles were sealed

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TABLE I

MOLAL SOLUBILITIES OF SILVER PROPIONATE AND SILVER BUTYRATE IN AQUEOUS SODIUM NITRATE AND DENSITY OF THE SATURATED SOLUTIONS

m_{NaNO_3}	$m_{Ag\ P}$	d	m_{NaNO_3}	$m_{Ag\ P}$	d	m_{NaNO_3}	$m_{Ag\ B}$	d
0.0000	0.04934	1.002	0.2902	0.05849	1.019	0.0000	0.02403	1.000
.0000	.04932	1.003	.3008	.05899	1.019	.0000	.02441	1.000
.0000	.04897	1.001	.3605	.06098	1.023	.0160	.02495	1.000
.0253	.05088	1.004	.3653	.06061	1.021	.0280	.02569	1.001
.0322	.05134	1.004	.4366	.06126	1.027	.0663	.02670	1.003
.0720	.05310	1.007	.5070	.06219	1.030	.0822	.02721	1.005
.0756	.05333	1.007	.5481	.06236	1.034	.1298	.02844	1.008
.0991	.05408	1.008	.5912	.06361	1.035	.1580	.02883	1.010
.1204	.05466	1.009	.6783	.06415	1.040	.1937	.02914	1.011
.1302	.05516	1.010	.6783	.06378	1.040	.2164	.02951	1.012
.1750	.05648	1.012	.7477	.06438	1.045	.3361	.03061	1.020
.1973	.05670	1.014	.7608	.06522	1.044	.4132	.03131	1.023
.2165	.05731	1.015	.9065	.06582	1.052	.5313	.03180	1.029
.2326	.05778	1.015	.9503	.06645	1.052	.6459	.03268	1.035
.2516	.05808	1.017	.9965	.06681	1.055	.6989	.03245	1.040
.2740	.05880	1.018	1.051	.06720	1.056	.8229	.03291	1.040
						.8818	.03356	1.048
						1.0395	.03422	1.055
						1.1349	.03436	1.066

with paraffin, immersed in a thermostated water-bath for at least two weeks at 25.00 ± 0.05°, and shaken frequently during the equilibration. After equilibration samples of the solution were removed by pipetting through a cotton filter, weighed and analyzed for silver.

Silver analyses were by the Volhard method using potassium thiocyanate which had been standardized against fused silver nitrate.[12]

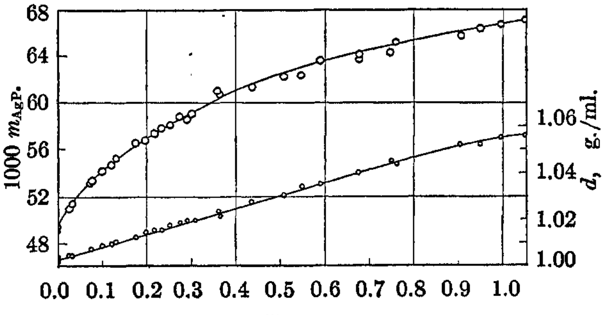

Fig. 1.—Solubility of silver propionate in aqueous sodium nitrate solutions and density of the saturated solutions.

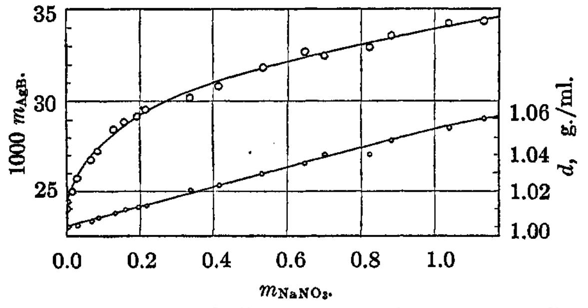

Fig. 2.—Solubility of silver butyrate in aqueous sodium nitrate solutions and density of the saturated solutions.

Discussion and Results

The dependence of the molal solubility of silver propionate and silver butyrate on molality of sodium nitrate is shown in Table I and Figs. 1 and 2. Also included are the densities of the saturated solutions calculated from the weights of the samples analyzed and the volume of water delivered by the sampling pipet.

It can be seen that the solubility increases with ionic strength at about the rate expected from the usual decrease in activity coefficients of the ions. While this increase could probably be fitted with an activity coefficient equation in the same manner as the data for silver acetate and silver chloroacetate,[1] in view of the very high probability that the silver salts are not completely ionized it appears futile at this time to carry out this analysis. If the ionization constants of these salts are about the same as that of silver acetate,[8] the saturated silver propionate solution in pure water is about 80% ionized and the butyrate 90%.

Our values for the solubility of silver propionate in pure water are almost 2% lower than those of Goldschmidt[8] and Knox and Will.[9] Previous measurements with silver butyrate have not been made at this temperature, but our value appears somewhat lower than what would be found by interpolation in the data collected by Seidell.[13] Since the literature values are quite old, it is possible that the differences are due to lack of temperature control or contamination of the silver salts with silver nitrate in the work of the early investigators. While our solubilities in Table I are given to four figures on the basis of precision of the analyses, inspection of the graphs shows that consistency of the results limits the reliability to three figures.

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