

A Study of Particle Initiation in Vinyl Chloride Emulsion Polymerization Using Response Surface Experimentation*

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INTRODUCTION

Emulsion polymerization of systems in which latex particles are originated in micelles has been studied by a number of investigators. Smith¹ has quantitatively treated the chain initiation and kinetics of styrene emulsion polymerization, and has presented evidence that the number of particles is a function of the concentration of surface active material, catalyst, and the temperature of polymerization. It is generally accepted that soap micelles provide the loci for initiation of polymer particles in polymerizing emulsions when the initial soap content in the aqueous phase exceeds the critical micelle concentration.

Brass and Roe² and Wintgen and Neveling³ have demonstrated that there is extensive initiation of particles at subcritical soap concentrations in persulfate-catalyzed styrene systems. Particle initiation in this emulsifier range is extensive and strongly dependent on the soap concentration.

Although vinyl chloride emulsion polymerization has been covered extensively in the patent literature, only a few published investigations have treated the initiation and mechanism of vinyl chloride emulsion polymerization, for instance, the work of the German investigators Jacobi⁴ and Bier and Kramer.⁵

The purpose of this investigation was to determine the number of particles initiated in a vinyl chloride emulsion system with the use of a sodium bisulfite potassium persulfate catalyst system at subcritical emulsifier concentrations. The effects of the redox catalyst system and commercial sodium lauryl sulfate emulsifier on particle initiation were determined by response surface experimentation.

Response Surface Experimentation

Response-surface analysis assumes that the dependent variable can be expressed as a power

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series expansion in terms of the independent variables. Under this assumption the Taylor series expansion may be used. The overall experiment is designed in such a way as to give efficient estimates of the coefficients in this expansion.

Originally, response-surface designs were developed where the objective of the experiment was to arrive at an optimum set of conditions for some operating criterion. This optimum seeking is described by Davies.⁶

Besides the rather restricted objective of optimizing some dependent variable, experiments of this type are also ideally suited to laboratory research in which the objective is to study the effects of continuous variables. In this investigation the effect of the independent continuous variables—potassium persulfate, sodium bisulfite, and emulsifier concentrations—on particle initiation in vinyl chloride emulsion polymerization was determined. The number of particles initiated per milliliter of water phase was chosen as the dependent variable.

One of the basic designs that could be used for investigating this system by response-surface methods is the three-factor composite design, developed by G. E. Box, which has been described by Davies⁶ and is illustrated in Figure 1. Fifteen experimental conditions are designated as circles in Figure 1.

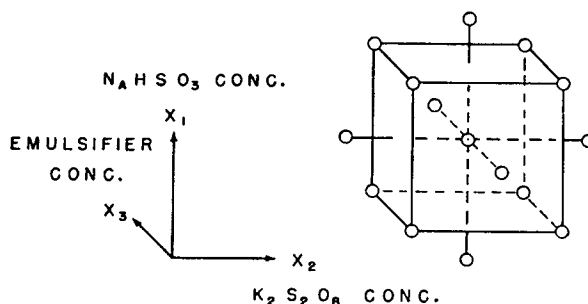


Fig. 1. A three-factor composite design.

In this investigation, a simplified modification of this design was used to obtain a series of latices whose particles could be measured easily by electron microscopy. The independent variables were each varied over three levels by moving the axial points into the face of the cube. At these fifteen points the number of particles was determined experimentally. Using Taylor's polynomial expansion, eq. (1), as a mathematical model to describe the experimental data, coefficients were calculated by regression analysis by a least squares method.

$$\hat{Y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

\hat{Y} , as defined in eq. (1), is called the response. The symbol over the Y (colloquially, Y hat) indicates that the calculated Y is an estimate of the true value of Y . How close \hat{Y} is to Y depends on how reliably the experiment is conducted and how closely the equation describes the true situation.

One attractive advantage of response-surface experimentation is the ease of extending an investigation. In this study a fourth level of sodium bisulfite was added to the original design.

EXPERIMENTAL PROCEDURE

The polymerization recipe was:

Water	55.0 ml.
Vinyl chloride	5.25 g.
NaHCO ₃	0.0634 M
NaHSO ₃	5, 10, 20, and 30 (mole/55 ml H ₂ O) × 10 ⁻⁵
K ₂ S ₂ O ₈	1, 2, and 5 (mole/55 ml H ₂ O) × 10 ⁻⁵
Sodium lauryl sulfate	0.0026, 0.0036, and 0.0051% (based on H ₂ O)

In the course of polymerization work it was found convenient to express the concentration of catalyst and reducing agent in terms of the number of moles in the water charge.

The polymerization was carried out in six-ounce, crown-cap bottles which were rotated end-over-end at 60 rpm in a constant temperature bath thermostated at 52.5 ± 0.5°C.

The salts were reagent grade, and the sodium lauryl sulfate was a commercial grade obtained from du Pont. Solutions of these materials were made prior to charging. The vinyl chloride monomer was a commercial grade (99.9% purity)

which had been washed with caustic solution to remove inhibitors.

The following charging procedure was used.

1. The water, emulsifier, buffer, sodium bisulfite, and potassium persulfate solutions were added in that order to the bottle.

2. A 100% excess of vinyl chloride monomer was added to the bottle and allowed to boil off to remove the oxygen from the vapor space.

3. The bottles were then capped in a hand-capping press with aluminum foil-lined caps with a cork gasket. Immediately after capping, the bottles were placed in an ice bath and later introduced into the polymerization bath.

4. After polymerizing for 60–75 minutes, the bottles were removed from the water bath and vented immediately. The yield of polymer was determined after venting to a constant weight.

Electron micrographs were made by mounting the latices on a carbon-coated collodion substrate over a standard 200 mesh copper grid. One hundred particles were measured on narrow distributions and up to 200 particles for broader distributions. The measurements were made by a Greenough microscope using a calibrated mechanical stage. From these diameters, the average volume diameter was calculated and used with the polymer yield to determine the number of particles per milliliter of water. The following expression was used:

$$Y = \frac{6W \times 10^{12}}{\rho(d_v)^3(55.0)} \quad (2)$$

where Y is the number of particles initiated per milliliter of water, W is the weight of polymer in grams, ρ is the density of polymer (1.403 at 25°C.), and d_v is the average volume diameter in microns.

The standard deviation of each particle size distribution was calculated according to

$$\sigma = \left(\frac{\sum X^2 - \frac{(\sum X)^2}{n}}{n - 1} \right)^{1/2} \quad (3)$$

where X is an individual measurement and n is the number of measurements.

RESULTS

1. Experimental Results and Regression Equation

The experimental results for the eight corner points in Figure 1 illustrating the effect of sodium bisulfite, potassium persulfate, and emulsifier concentrations on the number of particles initiated per milliliter of water are shown in Table I. By the use of Taylor's polynomial expansion to de-

TABLE I
 Experimental Conditions and Results

[NaHSO ₃], mole × 10 ⁵	[K ₂ S ₂ O ₈], mole × 10 ⁵	Emulsifier, % × 10 ⁴	Polymer wt., g.	$d_p \pm \sigma$, microns	Y observed, × 10 ⁻¹³	\hat{Y} , calculated × 10 ⁻¹³
5	1	26	0.30	0.09 ± 0.016	1.019	1.146
5	5	26	0.27	0.09 ± 0.008	0.918	0.795
5	1	51	0.38	0.11 ± 0.009	4.360	3.591
5	5	51	3.12	0.11 ± 0.012	5.610	5.035
30	1	26	1.83	0.10 ± 0.006	4.530	3.838
30	5	26	5.10	0.17 ± 0.010	2.460	2.893
30	1	51	1.47	0.09 ± 0.008	4.990	3.571
30	5	51	4.53	0.13 ± 0.016	5.100	4.421

scribe the experimental data, a regression equation was derived as described previously. The calculations were performed on an IBM 702 computer. The regression equation obtained was:

$$\hat{Y}_c = -2.1899 + 0.2357X_1 - 0.5630X_2 + 0.1058X_3 - 0.0059X_1X_2 - 0.0045X_1X_3 + 0.0187X_2X_3 \quad (4)$$

where $\hat{Y}_c = \hat{Y} \times 10^{-13}$, $X_1 = 10^5 \times$ moles of NaHSO₃/55 ml. water, $X_2 = 10^5 \times$ moles of K₂S₂O₈/55 ml. water, and $X_3 = 10^4 \times$ grams emulsifier/100 ml. water.

The 95% confidence limits for \hat{Y}_c were ± 1.88 . The variance was equal to 0.8826, while the correlation coefficient squared was equal to 0.6460. This means that approximately 65% of the dependence of \hat{Y} on the independent variables can be accounted for. The other 35% was due to uncontrolled variables or to experimental error.

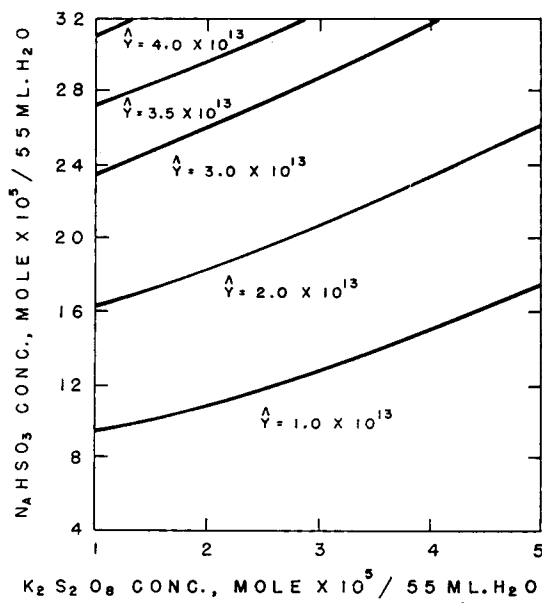


Fig. 2. Particle initiation at 0.002% emulsifier concentration.

2. Estimated Number of Particles Initiated at Various Emulsifier Concentrations

From eq. (4), the responses Y were calculated at emulsifier concentrations of 0.002, 0.003, 0.004, and 0.005% based on the weight of water and are shown in Figures 2, 3, 4, and 5, respectively. These figures were prepared by connecting points of constant value of the dependent variable, the number of particles initiated per milliliter of water, in planes defined as X_3 (the emulsifier concentration) equal to a constant.

3. Critical Micelle Concentration of Sodium Lauryl Sulfate

The critical micelle concentration (CMC) of sodium lauryl sulfate in a vinyl chloride emulsion system was determined by the absorption method of Maron.⁷ The small amounts of polymer obtained in bottle polymerizations (4-5 grams) were not sufficient to make use of this technique.

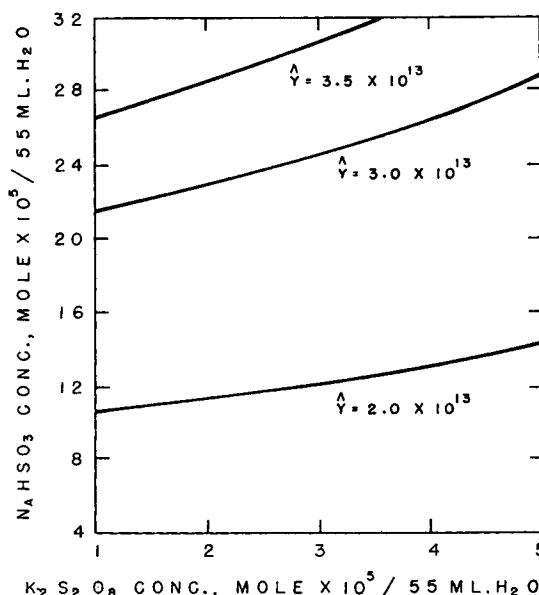


Fig. 3. Particle initiation at 0.003% emulsifier concentration.

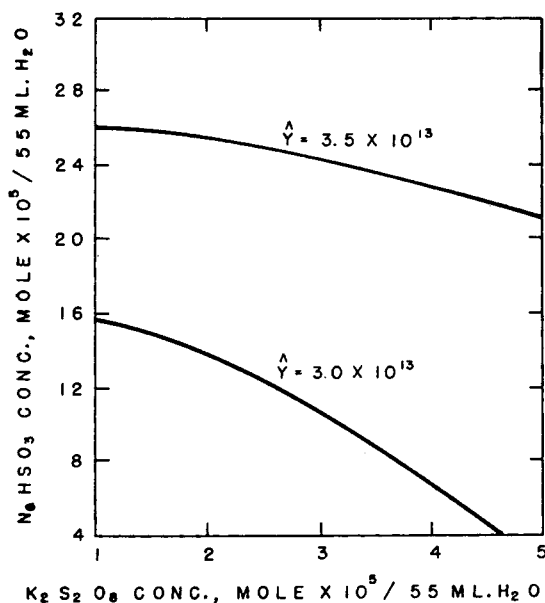


Fig. 4. Particle initiation at 0.004% emulsifier concentration.

A polyvinyl chloride latex was made in larger equipment after the recipe shown previously at highest sodium bisulfite and potassium persulfate concentrations. Surface tension titrations were carried out at various polymer concentrations at 25°C. While these measurements were made at temperatures some 27°C. lower than polymerization temperatures, it is not likely that the values for CMC are significantly different.⁸

In Figure 6, C (grams of added sodium lauryl sulfate required to attain the CMC) is plotted vs. m (the polymer content of the latex at the CMC) in accordance with the equation

$$C = S_a m + C_f \quad (5)$$

where S_a is the concentration of emulsifier adsorbed per gram of polymer and C_f , the intercept on the ordinate axis, is the CMC of emulsifier in the latex. C_f is equal to 0.0093% with 95% confidence limits of $\pm 0.0012\%$.

DISCUSSION

In emulsion polymerization in which the monomer is solubilized in micelles, the number of primary particles initiated is established by the number of micelles present at the start of polymerization.⁹ Although the general features of micellized systems are well known and have been reported extensively in the literature, very little has been published about nonmicellized systems. Brass and Roe² and Wintgen and Neveling³ have demonstrated that there is extensive initiation of particles at subcritical emulsifier con-

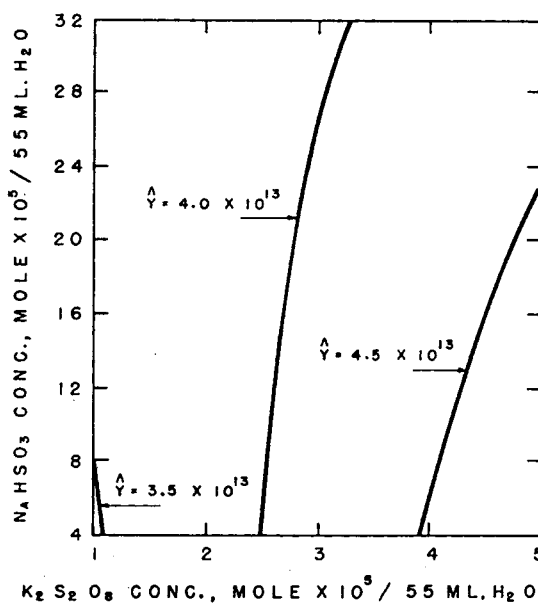


Fig. 5. Particle initiation at 0.005% emulsifier concentration.

centrations and that this is strongly dependent upon the emulsifier concentration.

In this work, the maximum emulsifier concentration investigated was 0.005%, while the critical micelle concentration of this emulsifier (sodium lauryl sulfate), as obtained by the absorption method of Maron, was 0.0093% with 95% confidence limits of $\pm 0.0012\%$. This is shown in the plot in Figure 6.

It can be seen in Figures 2, 3, and 4 that the emulsifier concentration at subcritical levels has a rather strong effect on the initiation of particles. This effect is more predominant at lower sodium bisulfite concentrations. At the 0.002% level of emulsifier the sodium bisulfite concentration has a predominant effect on particle initiation which then lessens as the emulsifier concentration is increased to 0.003 and 0.004%. At the highest emulsifier concentration, 0.005%, there is an apparent sudden change in the initiation mechanism. The bisulfite effect on particle initiation no longer exists. In Figure 5 the lines representing constant particle initiation of 4.0×10^{13} and 4.5×10^{13} particles/ml. water are nearly vertical.

In this system, the potassium persulfate concentration has a much smaller effect than the concentration of either the emulsifier or sodium bisulfite on particle initiation. There is a noticeable trend toward increased particle initiation as the emulsifier concentrations are increased, particularly at the 0.004 and 0.005% emulsifier levels.

The value of the square of the correlation coefficient (R^2) for the regression eq. (4) was

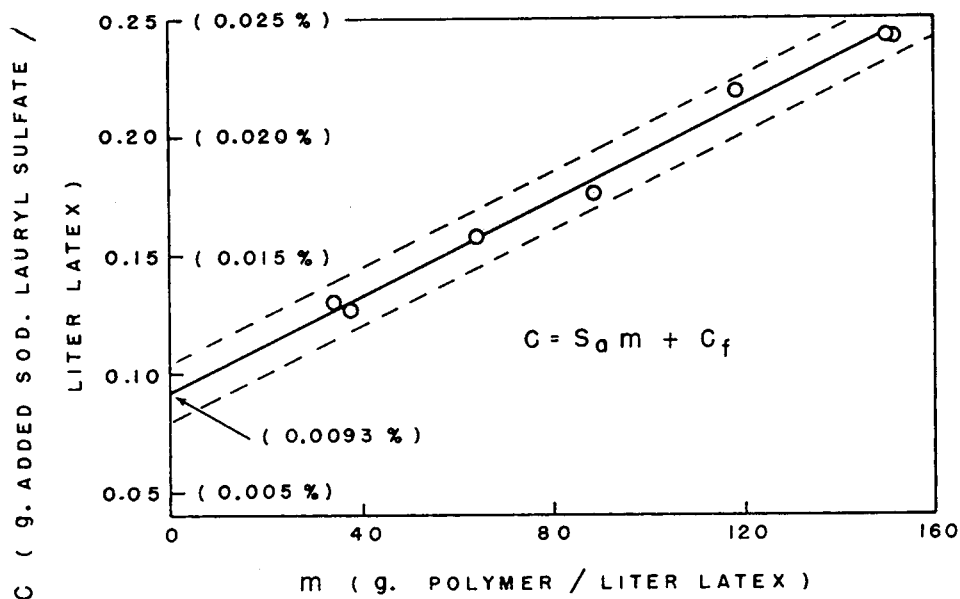


Fig. 6. Determination of the CMC value from extrapolation of surface tension soap titrations.

0.6460, which is admittedly lower than desired. A value of 1.000 would mean that the equation was a perfect fit for the experimental data. It is felt that this equation is adequate for a good approximation of this system and provides a good basis for subsequent investigations.

Even though an investigation into the kinetics and mechanisms of particle initiation of vinyl chloride emulsion polymerization was beyond the scope of this work, a few general statements can be made on the basis of the experimental data.

It is apparent from an investigation of the data that a sharp change in the mechanism of particle initiation takes place between the 0.004 and 0.005% emulsifier level. Up to the former point, particle initiation is predominantly in the water phase and is dependent upon the rate of free radical formation, as shown by the dependence of particle initiation on sodium bisulfite concentration. The particles initiated at the subcritical emulsifier concentrations are probably stabilized by the existence of surface-active end-groups of the sulfonate or sulfate type. The existence of surface-active endgroups in both redox systems and straight persulfate systems has been demonstrated by a number of investigators.^{5,10,11} It has also been shown by Whitby, Gross, et al.¹² that the relative particle size by light scattering of a potassium persulfate-sodium bisulfite-initiated styrene-methacrylonitrile system was decreased by increasing the catalyst concentration.

The dependence of particle initiation on emulsifier concentration at subcritical micelle concentration is very likely to be due to the slight

solubility of monomer in the water phase. The solubility of vinyl chloride in water at 20°C. has been given by Schildknecht¹³ as 0.09%. One could expect an increase in monomer solubility in the presence of small concentrations of emulsifier even below the CMC. The pressure involved in this vinyl chloride emulsion polymerization at 52.5°C. should also be responsible for some increased solubilization. The dependence of particle initiation on the emulsifier concentration in this work could be explained on the basis of such solubilization.

The shift in mechanism as shown at the 0.005% emulsifier level could very well indicate the appearance of a micellized system. Just as a sharp change in physical phenomena, such as surface tension, conductivity, or refractive index, is noticed at the critical micelle concentration (CMC), so do a sharp change and discontinuity in particle initiation occur in this system also. The emulsifier concentration almost completely controls particle initiation above the CMC. Since the CMC is an approximate range and since many of the methods cited in the literature¹⁴ for relatively pure systems are in disagreement, it is not unreasonable to find a difference between 0.005% obtained by the initiation method and $0.0093 \pm 0.0012\%$ by the soap adsorption method.

CONCLUSIONS

It has been shown that response-surface experimentation is a useful tool for investigating variables affecting particle initiation in a vinyl chloride emulsion system. In a bisulfite-persulfate redox

system, the number of particles initiated at subcritical emulsifier concentrations is dependent upon the emulsifier and sodium bisulfite concentrations and, to a lesser degree, upon the persulfate concentration. As the critical micelle concentration is approached, an apparent change in the initiation mechanism is observed. In this system, this change occurs at a concentration of 0.005% emulsifier, above which point the emulsifier concentration almost completely controls particle initiation. A regression equation has been developed which describes the number of particles initiated in this vinyl chloride emulsion system as a function of the independent variables studied.

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References

1. W. V. Smith, *J. Am. Chem. Soc.*, **70**, 3695 (1948); *ibid.*, **71**, 4077 (1949).
2. P. D. Brass and C. P. Roe, Paper presented at the 130th meeting of the American Chemical Society, Atlantic City, New Jersey, September 1956.
3. R. Wintgen and K. Neveling, *Kolloid-Z.*, **138**, 142 (1954); **124**, 141 (1951).
4. B. Jacobi, *Angew. Chem.*, **64**, 539 (1952).
5. G. Bier and H. Kramer, *Kunststoffe*, **46**, 498 (1956).
6. O. L. Davies, ed., *Design and Analysis of Industrial Experiments*, 1st Ed., Hafner, New York, 1954.
7. S. H. Maron, M. E. Elder, and I. N. Ulevitch, *J. Colloid Sci.*, **9**, 89 (1954); *ibid.*, **9**, 382 (1954).
8. H. B. Klevens, *J. Colloid Sci.*, **2**, 301 (1947).
9. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
10. W. Kern, *Angew. Chem.*, **61**, 471 (1949).
11. K. L. Perry and J. H. Peterson, *J. Am. Chem. Soc.*, **73**, 5195 (1951).
12. G. W. Whitby, M. D. Gross, J. R. Miller, and A. J. Costanza, *J. Polymer Sci.*, **16**, 549 (1955).
13. C. E. Schildknecht, *Vinyl and Related Polymers*, Wiley, New York, 1952, p. 395.
14. R. J. Williams, J. N. Phillips, and K. J. Mysels, *Trans. Faraday Soc.*, **51**, 728 (1955).

Synopsis

Vinyl chloride monomer was polymerized in an emulsion system in the presence of a redox catalyst and relatively low

concentrations of emulsifier. The effects of sodium bisulfite, potassium persulfate, and commercial sodium lauryl sulfate concentrations on particle initiation were determined by response-surface experimentation. A regression equation was developed which describes the number of particles per unit volume initiated in this vinyl chloride emulsion system. At subcritical emulsifier concentrations, the number of particles initiated was dependent primarily upon the emulsifier and sodium bisulfite concentrations and to a lesser degree upon the persulfate concentration. As the critical micelle concentration was approached, an apparent change in the particle initiation mechanism was observed, in that the sodium bisulfite concentration ceased to have an effect. In this system the change occurred at a concentration of 0.005% emulsifier.

Résumé

Le chlorure de vinyle a été polymérisé en émulsion avec un catalyseur redox et à des concentrations d'agent émulsionnant relativement faibles. L'influence de la concentration de persulfite de sodium, de persulfate de potasse et de sulfate lauryle de sodium sur le nombre de particules amorçées a été étudiée par la méthode des surfaces à réponse égales (surface response experimentation). Une équation de regression a été établie qui donne le nombre de particules amorçées par unité de volume dans ce système. A des concentrations d'agent émulsionnant inférieures à la concentration critique le nombre de particules amorçées dépendait d'avantage de la concentration de l'agent émulsionnant et de celle du bisulfite de sodium, que de la concentration de persulfate. En approchant une concentration de micelles critique, on observait un changement apparent dans le mécanisme d'amorçage des particules, la concentration de bisulfite de sodium n'entrant plus en jeu. Dans ce cas la concentration critique d'agent émulsionnant était de 0,005%.

Zusammenfassung

Die Emulsionspolymerization von Vinylchlorid bei niedriger Emulgatorkonzentration und unter Verwendung eines Redox-Katalysatorsystems ist behandelt. Mit Hilfe statistisch aufgestellter Experimente wurde der Einfluss der Menge an Natrium-laurylsulfat, Natrium-bisulfit und Kalium-persulfat auf die Teilchenzahl ermittelt. Eine Regressions-Gleichung wurde entwickelt welche die Teilchenzahl pro Volumeneinheit in diesem System zu beschreiben gestattet. Unterhalb der kritischen Mizellen-Konzentration des Emulgators ist die Anzahl der gebildeten Polymereteilchen hauptsächlich von der Emulgator- und Bisulfit-Menge und nur zu einem geringen Teil von der Persulfatkonzentration abhängig. Bei Annäherung an die kritische Konzentration des Emulgators ging der Einfluss der Natrium-bisulfit-Menge auf die Teilchenbildung verloren. Unter den benutzten Versuchsbedingungen trat dies bei einer Emulgatorkonzentration von 0,005% ein.

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