

Phase Partition of Acrylonitrile (AN) in Vinylidene Chloride (VDC)/Water System and Its Effect on VDC-AN Copolymer Composition

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Abstract Phase partition of acrylonitrile in the vinylidene chloride/water system at different temperature and under pressure was studied. A calculation method for average VDC-AN copolymer composition with AN phase partition considered was proposed. The calculated results are in good agreement with the experimental data nearly the entire conversion range. VDC-AN copolymer with narrower composition distribution can be prepared in the suspension process and interpreted with dynamic equilibrium of AN between the oil and water phases continuously.

Keywords vinylidene chloride, acrylonitrile, suspension copolymerization, phase partition, copolymer composition

1 INTRODUCTION

Copolymer composition is a key subject in copolymerization, since it will affect the physico-mechanical properties and thus the end-use properties of the copolymer. The kinetic behavior of suspension polymerization is similar to that of bulk polymerization. A monomer droplet in the suspension system may be regarded as a small individual reactor. The copolymer composition may be theoretically calculated from monomer feed composition and reactivity ratio and the latter will also affect the copolymer composition distribution^[1]. Usually, the calculated composition for suspension copolymerization from the reactivity ratio measured in a bulk process will give less errors if a practically water-insoluble comonomer pair is used. However, great deviation will occur from the suspension copolymerization of water-insoluble monomer with considerably water-soluble comonomer, since the actual comonomer content in the reaction region will be lower than the feed composition due to its partition between the monomer phase and aqueous phase. The vinylidene chloride (VDC)/acrylonitrile (AN)/water system is such a case.

Marker *et al.*^[2] studied the theoretical composition of VDC-AN copolymer in the emulsion process under atmosphere with AN solubility in water corrected. However, there is no report on the theoretical calculation of VDC/AN suspension copolymerization. The main objective of this work is to study firstly the phase partition of AN in the VDC/water system at different temperature and under pressure, then to predict the average VDC-AN copolymer composition with variable feed ratio over the full conversion range in the suspension copolymerization.

2 EXPERIMENTAL

VDC and AN were distilled before use. VDC-AN copolymer was prepared with a 200 ml stainless

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steel vessel in the suspension copolymerization process. Lauryl peroxide (LPO) was used as initiator, and hydroxy-propyl methyl cellulose (HPMC, K100M) and methyl cellulose (MC, A4M) from Dow Chemical Corporation as dispersants. Acetone semicarbazone (ATSC) was used as inhibitor of polymerization.

Conversion was measured by the weighting method. AN content in the copolymer was calculated from the nitrogen content determined by a Carlo Erba 1106 element analyzer.

The procedure for measuring phase partition of AN in the VDC/water system at room temperature under atmospheric pressure was as follows: The refractive index of a series of AN aqueous solution with known concentration was first measured by an Abbe refractometer for establishing a calibration curve. Thereafter, the refractive index of the aqueous phase from VDC/AN/water system was measured, and the AN concentration was read out from the calibration curve. The AN content in the oil (VDC monomer) phase was then calculated from the difference between the AN feed content and that in the aqueous phase by material balance. Phase partition of AN under pressure was evaluated from the copolymer composition at low conversion (< 10%).

3 RESULTS AND DISCUSSION

3.1 Phase partition of AN in VDC/water system

AN and water constitute a partially miscible system with a considerable AN solubility in water^[3]. On the other hand, AN is also miscible with a lot of monomers, such as VDC. Thus, certain partition of AN between water and monomer (oil) phases in the VDC/AN suspension copolymerization system will take place. AN partition in these two phases at temperature lower than the boiling point of VDC (31.8 °C) under atmospheric condition was shown in Fig. 1.

Fig. 1 shows that the temperature presents slight influence on AN partition in a narrow temperature range between 20 and 30 °C under the atmospheric condition, and the phase partition data can be fitted in a single curve for simplicity. The AN phase partition reported by Marker *et al.*^[2] approaches our observations. Marker proposed an equation for AN phase partition at 32.8 °C as follows

$$[(Av/V)/(Aw/W)][0.075 - Aw/W] = 0.060 + 7.6Aw/W \quad (1)$$

where Av and Aw are mass of AN in oil (VDC) and water phase, and V and W are mass of VDC and water respectively. The partition coefficient of AN between water and VDC phases increases with the increase of AN content as shown in Fig. 1.

However, VDC copolymerization is generally carried out under pressure at temperature (45—60 °C) higher than its boiling point (31.8 °C). The refractometry is not easily applied to determine the AN phase partition under pressure because of difficulty in sampling. Therefore, a new method was used in this work. The composition of copolymer made with various VDC/AN feed ratios at conversion below 10% was determined by elemental analysis. Then, the initial composition of monomer phase may be computed from the copolymer composition by Mayo-Lewis equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] r_2 [M_2] + [M_1]} \quad (2)$$

and the difference between the AN content in the feed and the calculated AN content in the monomer phase is that in the aqueous phase. The reactivity ratio of VDC/AN determined by bulk copolymerization ($r_1 = 0.37$, $r_2 = 0.91$)^[4] is used for the computation. AN phase partition thus obtained under pressure is also shown in Fig. 1.

From Fig. 1, it is seen that the solubility of AN in water at higher temperature and under pressure is higher than that at room temperature and under atmospheric condition. Curve fitting of the data at 60 °C and under 0.11 MPa in Fig. 1 leads to

$$w_{ao} = -0.008 - 0.158w_{aw} + 0.244w_{aw}^2 \quad (3)$$

where w_{ao} and w_{aw} are mass percentage of AN in oil and water phases respectively. Relationship between the real initial composition of the oil phase and the feed composition at different water/oil ratio is calculated with Eq. (3) and presented in Fig. 2. It shows that the greater the water/oil ratio, the larger the difference between real initial composition and feed composition, and thus the greater effect of AN solubility in water on copolymer composition will be caused.

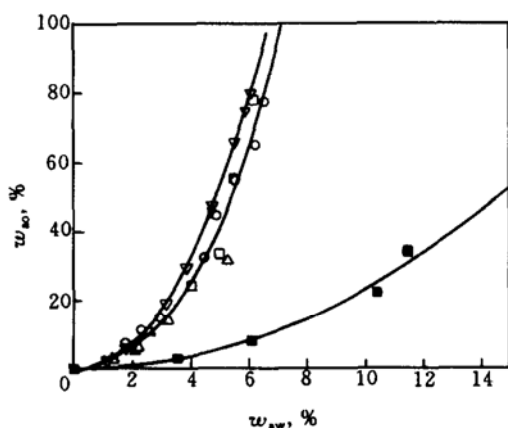


Figure 1 AN partition between water and oil phases at different temperature

□ 20 °C, atmosphere; ○ 25 °C, atmosphere;
△ 30 °C, atmosphere; ▽ Marker; ■ 60 °C, 0.11 MPa

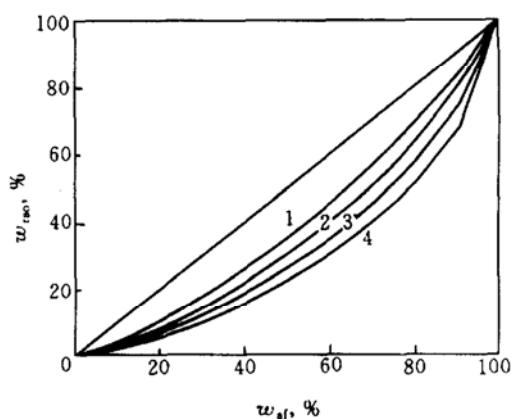


Figure 2 Relationship between real initial composition of oil phase and feed composition at different water/oil ratio ($T = 60, ^\circ\text{C}$) (water/oil ratio: 1—1.5:1; 2—2.0:1; 3—2.5:1; 4—3.0:1)

3.2 Correction of AN solubility in water for VDC-AN copolymer composition

The initial VDC-AN copolymer compositions may be estimated with using AN phase partition data as illustrated in Table 1.

Table 1 Correction for estimating initial VDC-AN copolymer composition ($w_{AN,0} = 17.19\%$)

	$w_{AN,1}, \%$	$w_{AN,2}, \%$	$w_{AN,3}, \%$	$w_{AN,4}, \%$
	30.01	24.70	23.67	16.15
Absolute error, %	+12.82	+7.51	+6.48	-1.04

polymerization conditions: $T = 60\text{ }^\circ\text{C}$; water/oil ratio=2 : 1, VDC/AN feed mass ratio=80 : 20.

It can be seen that the calculated initial composition of VDC-AN copolymer without any correction of AN solubility in water will deviate considerably from experimental data, and that the deviation may be reduced greatly after the AN solubility in water considered. Among all the alternative correction methods, the best is the correction by AN phase partition under pressure. Thus, the composition of VDC-AN copolymer prepared in a suspension process at higher temperature and under pressure may be calculated more accurately after the correction due to AN phase partition.

3.3 Effect of conversion on VDC-AN copolymer composition

The average composition of VDC-AN copolymer at the same feed mass ratio (VDC/AN=80:20) was determined at various conversion and plotted in Fig. 3. It shows that the actual average composition of VDC-AN copolymer observed is rather constant over the full conversion range. The copolymer composition calculated without and with AN phase partition is also plotted in Fig. 3 for comparison. The calculated results are obtained by numerical integration of Eq. (2) and the detailed description is in Ref. [1]. It may be seen that there is great difference between the observed and calculated copolymer compositions without correction by AN phase partition (curve 1), especially in the earlier stage of suspension copolymerization. Curve 2 is obtained with correction of AN solubility in water only in the initial stage of copolymerization. In this case, the difference between the observed and calculated copolymer composition is small at low conversion only, since AN is more active and is consumed more rapidly than VDC. Actually, AN dissolved in the water phase is continuously transferred back into the oil phase to regain equilibrium when AN in the oil phase is consumed during copolymerization. Therefore, VDC-AN copolymer composition should be further corrected by accounting for the dynamic equilibrium of AN phase partition, and this leads to curve 3 in Fig. 3 with further reduced error. Though VDC-AN copolymer is not soluble in AN at all, it can be swelled with a certain amount of AN^[5]. Thus, there is also partition between copolymer and monomer phases. We presumed simply the partition coefficient between these two phases is constant and suggest the following empirical equation by least square regression

$$w_{ap} = 3.0w_{ao} \quad (4)$$

where w_{ap} represents mass percentage of AN in polymer phase. The copolymer composition calculated by Eqs. (3) and (4) is found in good agreement with the experimental data over the full range of conversion, as shown by curve 4 in Fig. 3. From the above discussion and analysis, it seems that the water phase acts just as an AN reservoir, which supplies continuously AN to the oil phase for establishing equilibrium during the copolymerization process. It makes easier the preparation of copolymer with uniform composition over the entire process of copolymerization.

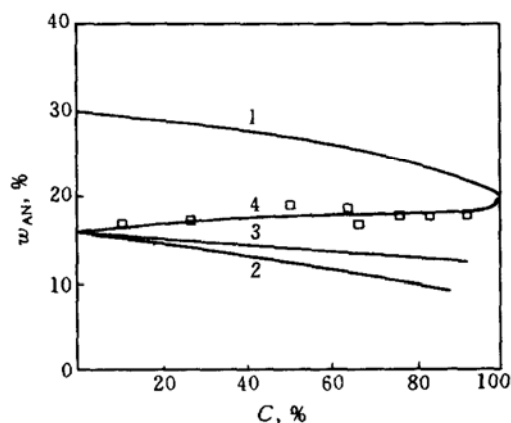


Figure 3 Comparison of VDC-AN copolymer composition observed with that calculated at different conversion

□ observed; — calculated

- 1—without considering AN solubility in water; 2—with only the initial composition of oil phase corrected;
 3—with correction of AN phase equilibrium between water and oil phases;
 4—with correction of AN phase partition among water, oil and polymer phases

3.4 Effect of feed ratio on VDC-AN copolymer composition

The average composition of VDC-AN copolymer can be calculated by Eqs. (3) and (4) with the correction of AN phase partition among water, monomer and polymer phases. The comparison of copolymer composition determined and calculated at different feed ratios in Table 2 shows smaller difference and the maximum absolute error is only $\pm 3\%$. Because the partition coefficient of Eq. (4) is obtained from VDC/AN (80:20) suspension copolymerization, the above method proposed for predicting VDC-AN copolymer composition is more suitable for those systems with VDC as the major monomer.

Table 2 VDC-AN copolymer composition made with different feed ratio*

VDC/AN feed mass ratio	C , %	$w_{AN,o}$, %	$w_{AN,c}$, %	Absolute error, %
94.2/5.8	65	5.97	3.61	-2.36
86/14	49.2	10.23	11.65	1.42
81/19	57.3	15.87	16.75	0.88
73.2/26.8	66.4	21.25	24.27	3.02
64.6/35.4	79.7	29.99	32.45	2.46
55/45	88.1	41.81	40.84	-0.97
44/56	92.3	53.0	52.90	-0.10

*polymerization conditions: $T=70^{\circ}\text{C}$, water/oil ratio=2:1, time=10 h; reactivity ratios used $r_1=0.37$, $r_2=0.91$.

4 CONCLUSIONS

Phase partition coefficient of AN between VDC and water phases increases with increase of AN content. The solubility of AN in water phase at higher temperature and under pressure is higher than that at room temperature and under atmospheric condition. VDC-AN copolymer with narrower composition distribution can be prepared in the suspension process due to the dynamic equilibrium and continuous transfer of AN from water phase to monomer phase. Average copolymer composition can be calculated more accurately when AN phase partition among water, monomer and polymer phases is considered.

NOMENCLATURE

- A_v mass of AN in oil (VDC) phase, g
- A_w mass of AN in water phase, g
- C conversion, %
- $[M_1]$ concentration of monomer 1, $\text{mol}\cdot\text{L}^{-1}$
- $[M_2]$ concentration of monomer 2, $\text{mol}\cdot\text{L}^{-1}$
- r_1, r_2 reactivity ratio
- V mass of VDC, g
- W mass of water, g
- w_{AN} copolymer composition represented by AN, %
- $w_{AN,c}$ copolymer composition calculated with AN phase partition in water, monomer and polymer phases considered, %
- $w_{AN,o}$ observed copolymer composition, %
- $w_{AN,0}$ initial percentage of AN in VDC-AN copolymer observed, %
- $w_{AN,1}$ initial percentage of AN in VDC-AN copolymer calculated without correction of AN solubility in water, %

$w_{AN,2}$	initial percentage of AN in VDC-AN copolymer calculated with correction of AN solubility in water by Eq. (1), %
$w_{AN,3}$	initial percentage of AN in VDC-AN copolymer corrected by AN phase partition under atmosphere, %
$w_{AN,4}$	initial percentage of AN in VDC-AN copolymer corrected by AN phase partition under pressure, %
w_{af}	mass percentage of AN in VDC/AN feed composition, %
w_{ao}	mass percentage of AN in oil phase, %
w_{ap}	AN mass percentage swelling in copolymer, %
w_{aw}	mass percentage of AN in water phase, %
w_{rao}	real initial mass percentage of AN in oil phase, %

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