phenylmagnesium bromide has been shown to yield 3-phenylcyclohexan-3-ol-1-one, 3-phenyl-Δ^2-cyclohexenone and 1,3-diphenylcyclohexadiene-1,3. A mechanism by which the latter substance could be formed is discussed.

2. The syntheses of 3-phenyl-Δ^2-cyclohexenone from the ethyl enol ether of dihydroresorcinol and of 1,3-diphenylcyclohexadiene-1,3 from 3-phenyl-Δ^2-cyclohexenone, are reported.

3. 3-Phenylphenol and *m*-terphenyl are conveniently prepared by the catalytic dehydrogenation, using palladized charcoal, of 3-phenyl-Δ^2-cyclohexenone and 1,3-diphenylcyclohexadiene-1,3, respectively.

COLLEGE PARK, MARYLAND RECEIVED JANUARY 28, 1948

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Partition of Acrylonitrile between Styrene and Water

BY WENDELL V. SMITH

A satisfactory discussion of the emulsion copolymerization of styrene and acrylonitrile requires a knowledge of the partition of the acrylonitrile between the water phase and the oil phase, since acrylonitrile is appreciably water soluble. Fordyce and Chapin[1] have compared the composition of the copolymer of styrene and acrylonitrile obtained in emulsion polymerization with that obtained in bulk polymerization and have found the emulsion copolymer to be consistently richer in styrene by a small amount than the bulk polymer produced from the same initial monomer composition. They have suggested that this difference may be due solely to the decrease in acrylonitrile content of the oil phase resulting from the water solubility of the acrylonitrile. The present investigation, which provides the data necessary to test this suggestion, has been carried out primarily to aid in discussing the emulsion copolymerization of these two monomers.

Under the conditions employed in emulsion polymerization, the ternary system, styrene–acrylonitrile–water, can be described sufficiently by specifying the compositions of two liquid phases, one of which may be called the aqueous phase, and the other the oil phase. A good approximation may be made by neglecting the solubility of styrene in the aqueous phase, also a fair approximation is obtained by neglecting the solubility of water in the oil phase (this is a good approximation when the oil phase is rich in styrene but becomes progressively less satisfactory as the acrylonitrile content of the oil phase increases).

Suppose that the system consists of

a volumes acrylonitrile
s volumes styrene
w volumes water

At equilibrium the oil phase will contain practically all the styrene and a_s volumes of acrylonitrile while the water phase will contain practically all the water and a_w volumes of acrylonitrile, where

$$a = a_s + a_w \qquad (1)$$

It is convenient to define a partition coefficient, α, by the relation

$$\alpha = \frac{a_s}{a_s + s} \cdot \frac{a_w + w}{a_w} \qquad (2)$$

Experimentally this partition coefficient may be determined by equilibrating a styrene–acrylonitrile solution of known composition with water and determining the resulting change in acrylonitrile content of the oil phase. If this change in acrylonitrile content is represented by

$$\Delta A = \frac{a}{a + s} - \frac{a_s}{a_s + s}$$

and if the equilibrium acrylonitrile content of the oil phase is represented by

$$A_s = a_s/a_s + s$$

then equations 1 and 2 give

$$\alpha = A_s\left[1 + \left(\frac{w}{a + s}\right)\frac{(1 - A_s)}{\Delta A}\right] \qquad (3)$$

After having determined α it is then possible to reverse the calculation and obtain the equilibrium composition of any mixture of water and oil phase. This may be done by rearranging equation 3 to obtain the quadratic

$$A_s^2 - [R(\alpha - s/a + s) + 1]A_s + R\alpha a/a + s = 0 \qquad (4)$$

where $R = (a + s)/(a + s + w)$. The most convenient method of solving equation 4 for A_s is by successive approximation. Since the first term is small, a first approximation for A_s may be obtained by neglecting A_s^2 and estimating α from Fig. 1 and an estimated value of A_s. From this first approximation a new value of α may be obtained from Fig. 1 and the small correction due to the first term may be calculated. Then a second approximation for A_s may be calculated from equation 4. This may be continued to give any degree of approximation warranted by the experimental work.

One other problem which is treated in the experimental section is that of calculating the acrylonitrile content of a water solution by equilibrating the water solution with styrene and determining A_s, the equilibrium acrylonitrile content of the

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[1] Reid G. Fordyce and Earl C. Chapin, THIS JOURNAL, 69, 581 (1947).

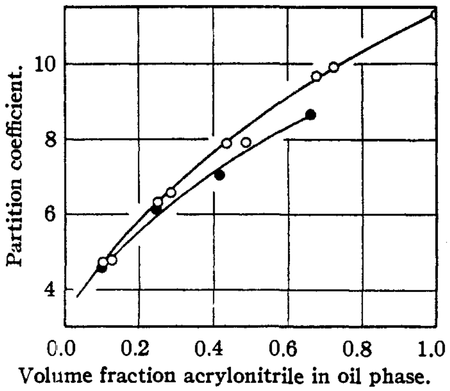

Fig. 1.—Partition coefficient of acrylonitrile between styrene–acrylonitrile solutions and water: 26°, ○; 60°, ●.

styrene solution. In this problem s, $a + w$ and A_s are measured, α is known from the relation between α and A_s, and it is desired to calculate $a/(a + w)$. This is done from equations 1 and 2 giving as a result

$$\frac{a}{a+w} = \left(\frac{s}{a+w}\right)\left(\frac{A_s}{1-A_s}\right)\left(1-\frac{A_s}{\alpha}\right)+\frac{A_s}{\alpha} \qquad (5)$$

Experimental

The compositions of all the styrene–acrylonitrile solutions used in the partition experiments were obtained from refractive index measurements. The relationship between refractive index and composition was established by making styrene–acrylonitrile solutions of known compositions, saturating them with water by adding a very slight excess of water and measuring the refractive indices with an Abbe refractometer. The results used to establish the relationship are given in Table I.

TABLE I

REFRACTIVE INDICES OF STYRENE–ACRYLONITRILE SOLUTIONS SATURATED WITH WATER

A_s	0.00	0.20	0.40	0.60	0.80	1.00
n^{20}_D	1.5460	1.5167	1.4852	1.4536	1.4220	1.3912

The solutions were made from measured volumes of each ingredient and the above volume fractions of acrylonitrile, A_s, are based on the assumption that the volumes are additive.

The results indicate substantially a linear relationship between refractive index and volume fraction. All compositions were obtained by linear interpolation of the data in Table I.

The partition coefficients were determined by shaking styrene–acrylonitrile solutions with water and determining the refractive indices of the solutions at equilibrium. The initial compositions of the solutions and the initial volume of water and solutions were known. It was found that equilibrium was established rapidly (*i. e.*, in less than one-half hour at room temperature) as judged by constancy of the refractive index. The results are given in Table II.

The second column gives the ratio of the initial volume of aqueous to oil phase. The third and fourth columns give the volume fractions of acrylonitrile in the initial and equilibrated oil phases, respectively; they were obtained from the measured refractive indices and the data of Table I. The partition coefficients, α, in the last column were calculated from the other values using equation 3. The data obtained at 60° are considerably more uncertain than those at 26°. While the solutions and water were only allowed to remain at 60° for twenty minutes, there was evidence that polymer was present at the end. Also the boundaries in the refractometer were quite fuzzy on the samples which had been equilibrated with water at 60°; this was probably due to the formation of a cloudy suspension of water when the styrene solution was cooled down to 20° for making the refractive index measurement. Table II shows that the partition coefficient, α, is a function of the equilibrium acrylonitrile content.

TABLE II

PARTITION COEFFICIENTS OF ACRYLONITRILE BETWEEN STYRENE AND WATER

Temp., °C.	$\frac{w}{a+s}$	$\frac{a}{a+s}$	A_s	α
26	3	0.197	0.125	4.73
26	3	.379	.281	6.55
26	3	.586	.485	7.90
26	3	.788	.723	9.95
26	5	.200	.101	4.67
26	5	.400	.247	6.32
26	5	.600	.434	7.84
26	5	.800	.679	9.68
60	5	.200	.100	4.6
60	5	.400	.243	6.1
60	5	.600	.416	7.0
60	5	.800	.660	8.7

To extend the investigation to even higher acrylonitrile contents, the limiting value of the partition coefficient as the styrene approaches zero was determined from the water solubility of acrylonitrile. This was done first by making use of the above determined partition coefficients. Water was saturated with acrylonitrile by shaking with an excess and allowing it to stand in contact with the acrylonitrile overnight in a separatory funnel. The saturated water was then withdrawn and shaken with styrene, then the refractive index of the styrene layer determined. The results are given in Table III.

TABLE III

WATER SOLUBILITY OF ACRYLONITRILE FROM EQUILIBRIUM WITH STYRENE AT 25°

$\frac{w}{a+s}$	A_s	α	$\frac{a}{a+w}$
10	0.310	6.9	0.0878
5	.213	5.9	.0882

The water solubilities (volume fraction of acrylonitrile, $a/a + w$) given in the above table were calculated from equation 5, using values of α given by Fig. 1.

In order to verify this calculated water solubility and at the same time to get an independent check on our values for the partition coefficients, α, a direct determination of the solubility was made. It was found that 9.2 cc. of acrylonitrile in a total of 100 cc. of water solution gave a single homogeneous phase at 27°, while 9.4 cc. gave a very small amount of a second phase which would not dissolve. Thus, the direct determination gives the solubility as between 9.2 and 9.4%. This is in satisfactory agreement with the value calculated from the equilibration with styrene and thus serves as an independent check on the partition coefficients. Taking the water solubility to be 0.088 (volume fraction) the limiting "partition coefficient" for 0% styrene is 11.3; this neglects the effect of the solubility of water in the acrylonitrile which may give a 10% error in α.

As is to be expected, α varies with the composition of the equilibrium phases. In Fig. 1 α is plotted against the volume fraction of acrylonitrile in the hydrocarbon phase at equilibrium.

Discussion

The partition data given here make it possible to calculate the compositions of the oil phases used by Fordyce and Chapin[1] in their study of the emulsion copolymerization of styrene and acrylonitrile. In their work the value of R was 0.367 and the temperatures were 60 and 75°. The results of this calculation are given in Table IV.

TABLE IV

ACRYLONITRILE CONTENTS OF THE OIL PHASES PRESENT DURING THE EMULSION COPOLYMERIZATION STUDIES OF FORDYCE AND CHAPIN[1]

Initial mole %	8.24	9.36	14.86	17.90	18.83	24.93
Equilibrium mole %	5.76	6.63	10.9	13.4	14.1	19.4
Initial mole %	32.92	36.32	45.68	66.25	94.64	
Equilibrium mole %	26.5	29.7	38.9	60.5	93.6	

The values given for the initial mole %'s in the table are the acrylonitrile contents of the oil phases before adding to the emulsion while the values for the equilibrium mole %'s are the acrylonitrile contents of the oil phases present in the emulsions during the polymerization. These latter values were calculated from the initial values using equation 4 and values of the partition coefficient, α, given by Fig. 1.

Having calculated the compositions of the oil phases actually present during the emulsion copolymerizations, it is now possible to compare the compositions of copolymers produced in emulsion with those produced in bulk from oil phases of identical composition. The data of Fordyce and Chapin[1] so treated are shown in Fig. 2. It is seen that this correction of the compositions of the emulsion oil phases makes the emulsion and bulk copolymerization composition curves identical within the accuracy of the data. Thus, the suggestion of Fordyce and Chapin that the consistent difference which they found was due to the water solubility of the acrylonitrile is substantiated by this investigation.

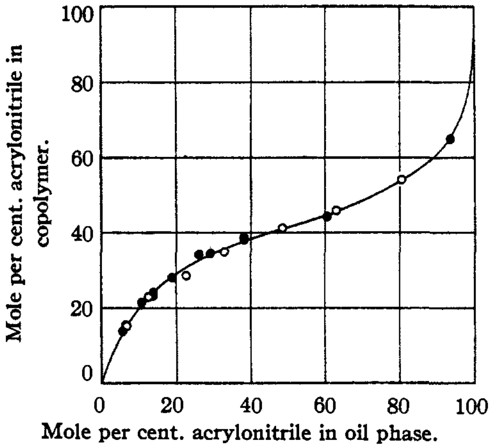

Fig. 2.—Monomer-polymer composition curve for styrene–acrylonitrile with correction for water solubility of the acrylonitrile: bulk polymerization, ○; emulsion polymerization, ●.

Summary

The compositions of styrene–acrylonitrile solutions in equilibrium with water–acrylonitrile solutions have been determined. These equilibrium compositions have been used to calculate the acrylonitrile contents of the oil phases present in the emulsion copolymerization experiments of Fordyce and Chapin. It is shown that when this is done the above authors' emulsion data are identical with their bulk polymerization data in regard to composition of polymer produced from a given oil phase.

PASSAIC, NEW JERSEY

RECEIVED JULY 12, 1947

[CONTRIBUTION FROM SCHOOL OF MINES AND METALLURGY, UNIVERSITY OF MISSOURI]

Some Equilibrium Relations in the System Magnesium Oxide–Sulfur Dioxide–Water (Acid Region) at Pressures below Atmospheric[1]

BY FRANK H. CONRAD AND DONAT B. BRICE

I. Introduction

This is a report of the study of the equilibrium $MgSO_3 \cdot 6H_2O$ + solution + vapor, in the system magnesium oxide–sulfur dioxide–water. It presents the pressure–composition relations at constant temperature (15 and 25°). The liquid phase of this system consists of a solution of the bisulfite of magnesium containing a small amount of the monosulfite. The vapor phase consists of SO_2 and water vapor.

These relations were desired because of the contemplated use of magnesia base cooking liquors in the "Sulfite Pulping Process" in place of calcium base liquor. Hatch[2] has pointed out that magnesia base liquor has the advantages: (a) the spent liquor may be used to recover both the magnesia and the sulfur dioxide; (b) heat is supplied to the process from the burning of the organic solids in the evaporated spent liquor; and perhaps most important; (c) the problem of disposing of the spent liquor is eliminated.

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[1] This paper is based on a Dissertation presented by Donat B. Brice in May, 1947, to the Faculty of the Graduate School of the School of Mines and Metallurgy, University of Missouri, Rolla, Missouri, in candidacy for the degree of Master of Science in Chemical Engineering.

[2] R. S. Hatch, *Paper Trade J.*, **122**, No. 11, 54-56 (March 14, 1946).