was passed the specific conductivity increased again with increasing hydrogen ion concentration.

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Solubility of Acrylonitrile in Aqueous Bases and Alkali Salts

ELIAS KLEIN, J. W. WEAVER, AND BEVERLY G. WEBRE
Southern Regional Research Laboratory, New Orleans, La.

During a study of the reaction in which cotton cellulose was cyanoethylated with acrylonitrile using aqueous alkali bases as catalysts, the solubility of acrylonitrile in aqueous systems was required. Since the liquid phase associated most intimately with the cotton cellulose during the reaction is a dilute aqueous solution of sodium hydroxide or other base, the solubility of the acrylonitrile in this phase was believed to be a determining factor in both the rate of the reaction and the extent of cyanoethylation at equilibrium. The solubility of acrylonitrile in water has been reported for various temperatures (*1*), but no solubility data for acrylonitrile in various alkali and saline solutions could be found.

MATERIALS USED

The acrylonitrile was of commercial grade, containing 0.8% of water. In order to facilitate reading of the interface with aqueous layers the acrylonitrile was colored with 0.005% Celliton Fast Red GGA Ex. Conc. (Pr. 236). (Pr. 236 refers to the prototype dye number listed in the AATCC Yearbook for 1955.) All alkali hydroxides and salts were of reagent grade, except Naxonate G, a commercially available mixture of xylene sulfonates.

PROCEDURE

Because acrylonitrile reacts with water in the presence of bases, it was necessary to use a solubility determination procedure not based on equilibrium measurements. The measurements were carried out at 25° ±1° C. in an air bath. The techniques employed are essentially those reported by Booth and Everson (*2*) in their study of hydrotropic salts. In the procedure adopted, 45 ml. of various concentrations of alkali bases were weighed into stoppered, graduated sulfonation bottles (ASTM D 875-46T); a measured volume of acrylonitrile was then added rapidly, and the bottles were sealed and tumbled end over end. Thirty minutes after the addition of acrylonitrile the tumbling was stopped and the volume remaining was read on the graduated scale of the bottle. Thereafter readings were taken every 15 minutes until the residual acrylonitrile was less than 1.0 ml.

The change in the volume of acrylonitrile was due to two causes. The first, a rapid change complete in less than 30 minutes, was due to the solution of the acrylonitrile in the aqueous phase. The second, and slower change, was due to the hydration of acrylonitrile to ethylene cyanohydrin. As the aqueous phase was saturated with respect to acrylonitrile during the entire measurement period, and the base concentration remained essentially unchanged, the rate of acrylonitrile hydration was evidently zero order. A plot of the volume of acrylonitrile remaining *vs.* time was found to be linear. Extrapolation of this plot to zero time permitted a correction to be made for the loss of acrylonitrile due to reaction, and yielded the volume of acrylonitrile dissolved in the aqueous phase. Use of the density of the acrylonitrile and the known weight of water in the flask allowed calculation of the molality of acrylonitrile in the aqueous phase.

When both alkali bases and salts were present simultaneously, the same procedure was followed. The aqueous base was weighed into the flasks, and weights of the salt calculated to give a constant molality of salt solution were added.

When the solubility of acrylonitrile was determined in salt solutions alone, the previous method was not necessary. Weighed amounts of salt solutions were placed in the flasks and increments of acrylonitrile were added until a second phase persisted. The solutions were tumbled for 30 minutes between additions of acrylonitrile.

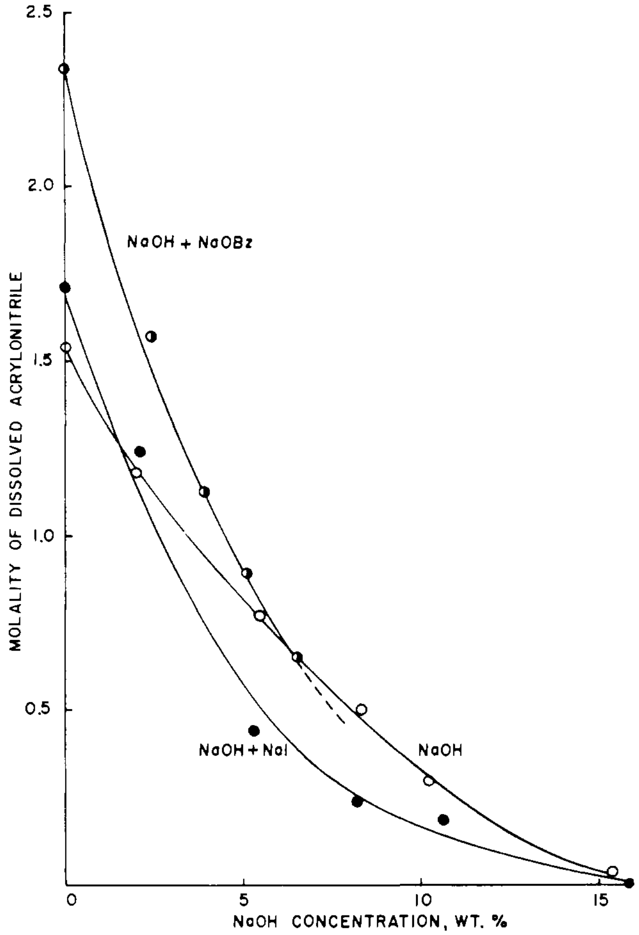

Figure 1. Solubility of acrylonitrile in aqueous sodium hydroxide, aqueous sodium hydroxide and sodium benzoate (1.5 molal), and aqueous sodium hydroxide and sodium iodide (2.0 molal) at 25° C.

The determination of the ternary solubility diagram of sodium iodide, water, and acrylonitrile required a combination of methods. Phase boundary *AC* (Figure 5) was determined by weighing sodium iodide solutions into the sulfonation bottles and adding increments of acrylonitrile until the second phase persisted after tumbling. Phase boundary *DE* was determined by weighing acrylonitrile into graduated oil centrifuge tubes and adding aqueous sodium iodide solutions until an aqueous layer separated. The refractive indices of all the saturated solutions were determined with an Abbé refractometer; these data were later used for establishing the direction of the tie lines. Point *F*, representing the solubility of sodium iodide in the acrylonitrile, was determined using the method of Vaughn and Nutting (*4*). The point is not quite on the sodium iodide-acrylonitrile base line, because of the presence of 0.8% of water in the acrylonitrile, and a trace of water in the sodium iodide.

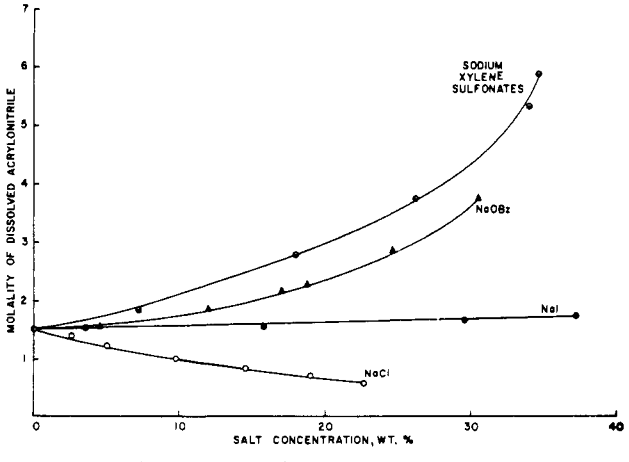

Figure 2. Solubility of acrylonitrile in various concentrations of sodium chloride, sodium iodide, sodium benzoate, and sodium xylene sulfonates at 25° C.

RESULTS AND DISCUSSION

Figure 1 shows the solubility of acrylonitrile, expressed as moles of acrylonitrile per 1000 grams of water, as a function of the weight per cent of sodium hydroxide in the solution. If the solubility of acrylonitrile is plotted against the square root of the sodium hydroxide molality, the relationship is linear. Addition of hydrotropic salts (*3*)—i.e., salts which increase the solubility of organic solutes in water, such as sodium iodide or sodium benzoate—increases the solubility of acrylonitrile in the sodium hydroxide solutions. This increase in solubility, however, holds only over a limited range of sodium hydroxide concentrations. With sodium iodide, the hydrotropic effect prevails up to 1.8% sodium hydroxide concentration; with sodium benzoate the effect extends to 6.5%. Above these base concentrations the salt effect becomes additive and the acrylonitrile is "salted out" more rapidly than if only the base were present.

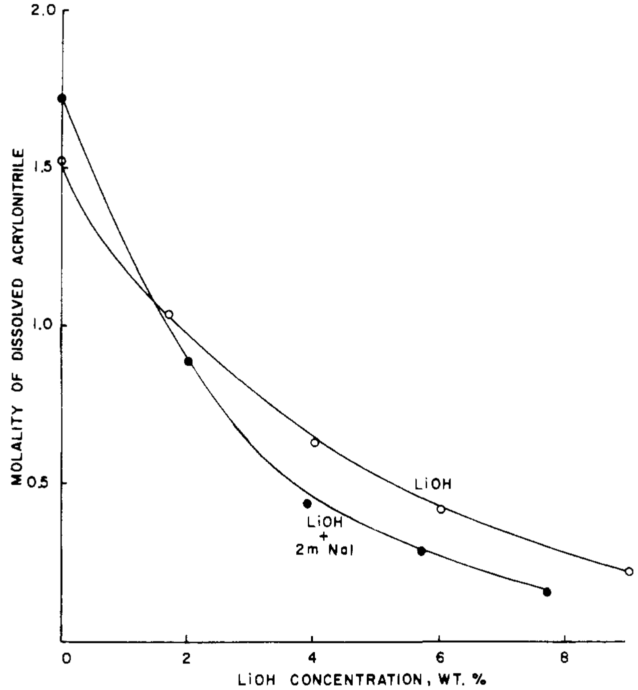

Figure 3. Solubility of acrylonitrile in aqueous lithium hydroxide, and aqueous lithium hydroxide and sodium iodide (2.0 molal) at 25° C.

The hydrotropic effect of several salts on the solubility of acrylonitrile in water can be seen from Figure 2. The solubility of acrylonitrile, given in molal units, is plotted against the weight per cent of the salts in the aqueous solutions. Sodium chloride is also shown, to illustrate the salting out effect. Of the three hydrotropic salts shown, the mixed sodium xylene sulfonates are the most efficacious. While the data for the latter compounds are not

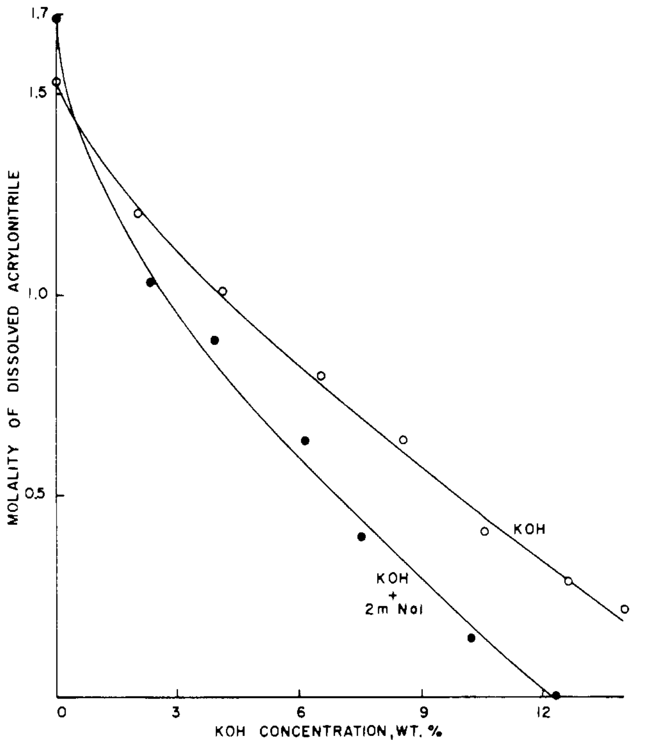

Figure 4. Solubility of acrylonitrile in aqueous potassium hydroxide, and aqueous potassium hydroxide and sodium iodide (2.0 molal) at 25° C.

shown here, they increase the solubility of acrylonitrile in aqueous sodium hydroxide, when the sodium hydroxide concentrations are below 9%.

Other salts which showed hydrotropic effects with acrylonitrile were potassium iodide, sodium salycilate, and potassium thiocyanate. No hydrotropic effects were shown by the sodium salts of 1,3,6-naphthalenetrisulfonic acid, 1,5-naphthalenedisulfonic acid, and sulfosalycilic acid (data not shown here).

Figures 3 and 4 show the solubility of acrylonitrile in aqueous lithium and potassium hydroxide, respectively, and in the same solutions made 2.0 molal with respect to sodium iodide. In the case of lithium hydroxide the point at which the hydrotropic effect ceases to function is 1.5%; in that of potassium hydroxide the corresponding point is at 0.4%. A comparison of the solubility of acrylonitrile in the three alkali hydroxides shows that the salting out effect, due to the bases alone, is strongest with lithium hydroxide and weakest with potassium hydroxide. This comparison is valid, also, when the concentrations are compared on a molality basis.

A comparison of Figures 1 and 2 indicates that the concentration of sodium hyrdoxide at which hydrotropy ceases depends on the efficacy of the hydrotropic salt. This suggests that the greater the hydrotropic effect of the salt in water, the greater will be the range of base concentration over which the effect will prevail.

Figure 5 depicts the ternary solubility diagram of sodium iodide, water, and acrylonitrile. This system was investigated with the hope that it might shed some light on the mechanism by which the increased solubility of acrylonitrile was obtained. Sodium iodide was chosen as the salt because of its ease of handling and the simplicity of the hydrate diagram. Line *AC* designates the solubility of acrylonitrile in water with increasing sodium iodide concentrations. The area enclosed by *ACB* and the base lines represents a homogeneous solution of the three components. Line *BC* delineates the solubility of sodium iodide in water containing increasing amounts of acrylonitrile. Line *DE* delineates the solubility of water in acrylonitrile with increasing sodium iodide content of the organic phase. Line *EF* shows the solubility of sodium iodide in acrylonitrile containing varying amounts of water.

An initial composition falling in the area *E*-*F*-sodium iodide vertex separates into two phases: a solid sodium iodide phase and an acrylonitrile phase saturated with sodium iodide. An initial composition falling in the area *E*-*C*-*G*-sodium iodide separates into three phases consisting of NaI or $NaI.H_2O$, an aqueous phase of composition *C*, and an organic phase of composition *E*. The position of the phase transition between anhydrous sodium iodide and its monohydrate was not determined because of the experimental difficulties involved. However, when acrylonitrile was added to a mixture of sodium iodide and water having a composition lying along segment *BG*, the first appearance of an organic phase occurred at a composition lying on line *GC*; this indicates that saturated aqueous solutions of composition *BC* are in equilibrium with $NaI.H_2O$ despite the presence of acrylonitrile in the aqueous phase.

Phase boundaries *AC* and *DE* show that acrylonitrile is salted into water due to the presence of sodium iodide, but that water is salted out of acrylonitrile by the presence of sodium iodide.

CONCLUSIONS

The solubility of acrylonitrile in water is decreased by the presence of alkali bases. This lower solubility can be compensated for in dilute base solutions by the addition of hydrotropic salts, such as sodium iodide, sodium benzoate, and sodium xylenesulfonate.

The range of base concentrations over which a given hydrotropic salt can exert its influence appears to be proportional to its hydrotropic effectiveness in the absence of the base.

There appears to be no definite method for predicting whether or not a given salt will have hydrotropic effect on solutions of acrylonitrile. However, a small but finite solubility of the salt in acrylonitrile appears to be required. The converse of this statement is not necessarily true: Dioxane is soluble in acrylonitrile, but its addition, in

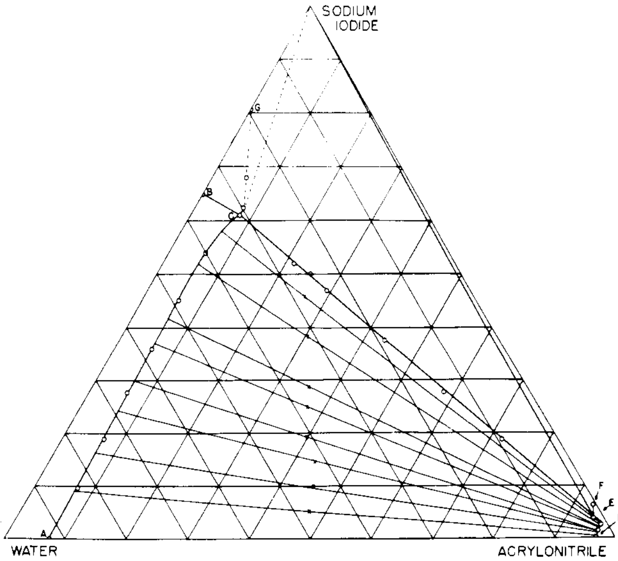

Figure 5. Ternary solubility diagram of sodium iodide, water, and acrylonitrile at 25° C., weight per cent

amounts up to 10%, to a saturated aqueous solution of acrylonitrile will cause the separation of an acrylonitrile phase.

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Viscosities of Fluorinated Methyl Bromides and Chlorides

JOHN F. REED AND B. S. RABINOVITCH
Department of Chemistry, Loyola University, Chicago, Ill., and
Department of Chemistry, University of Washington, Seattle, Wash.

In studying the chemical reactions of the fluorinated methyl chlorides and bromides with sodium vapor, it was necessary to obtain the viscosities of these halides. Very few data on the viscosities of these compounds are recorded; the values that exist have been obtained by independent measurements and provide no opportunity for internal comparison or consistency.

EXPERIMENTAL

The fluorinated chloro compounds were obtained from the Kinetic Chemicals Division, E. I. du Pont de Nemours & Co. Methyl chloride and bromide were Eastman Kodak white label products. The fluorinated bromo compounds were all synthesized by using the Hunsdiecker degradation of the silver or sodium salt of the corresponding carboxylic acid by bromine. All compounds were distilled several times on a low temperature fractionating column and only the middle fractions of constant boiling range were employed. Mass spectral patterns were obtained for all compounds and showed the absence of appreciable impurities.

The coefficient of viscosity was determined by allowing the specimen gas to flow from a 2-liter bulb through a uniform glass capillary at room temperature into an evacuated borosilicate glass trap refrigerated by liquid nitrogen. The initial and final pressures in the bulb were measured, as well as the elapsed time. The collected condensate was transferred to a tared evacuated gas bulb and weighed. Samples were 100 to 300 mg. and required collection times were 1 to 3 hours. The pressures in the large bulb were 2 to 15 cm. and no correction for slip was necessary. Three to seven determinations were made on each sample. The maximum error was in the weighing, which had a precision within 1%.

RESULTS

The procedure was calibrated using methyl chloride, for which the value of the absolute viscosity of Benning and Markwood (*1*) was adopted. All measurements were adjusted to 25 ° C., using temperature coefficients of 0.3 and 0.6 micropoise per degree for the chlorides and bromides, respectively, based on the methyl compounds. These corrections were of the order of magnitude of the probable error of a single measurement. The results are given in Table I, with literature values.

Table I. Viscosities and Molecular Diameters of Gases

Compound	η, Exptl. (25 °C.),[a] Micropoises	η Lit. (25 °C.), Micropoises	Diameter, A.
CH_3Cl	[107.9 (0.1)]	107.9 (*1*)	5.55
CFH_2Cl	113.1 (0.7)	...	5.85
CF_2HCl	...	129.2 (*1*)	5.81
CF_3Cl	139.6 (0.7)	...	5.85
CH_3Br	134.8 (0.1)	135.2 (2)	5.81
CFH_2Br	129.1 (0.4)	...	6.20
CF_2HBr	140.4 (0.1)	...	6.18
CF_3Br	151.2 (0.2)	...	6.15

[a] Probable error of average given in parentheses.

DISCUSSION

The coefficient of viscosity increases gradually with increase in the number of fluorine atoms in the molecule for the chlorides, although a minimum occurs in the bromide series. This may be considered a consequence of the relative increase in molecular mass and molecular diameter, on passing down the two series.

In view of the general lack of transport quantities of gases, one or more of these quantities must often be estimated. When insufficient data are available for correlations based on structural features, the kinetic theory of gases is often used. However, even in the latter case, a structural parameter, such as a collision diameter, is necessary. The collision diameter of each of these molecules was calculated from the viscosity coefficient on the basis of the hard, elastic sphere approximation (Table I). Substitution of one fluorine atom in the molecule results in an increase in diameter, and successive substitutions of fluorine cause no further increment. This behavior is consistent with the view of the simple, hard sphere model.

ACKNOWLEDGMENT

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