the known rate of chain initiation by reaction of two styrene molecules. Thus, for the experiment containing 47.2 mole % styrene, the calculated rate would be 0.63 × 10^{-6} m./l./sec. compared with the actual observed value of 0.168 × 10^{-6}. Unless the diethyl fumarate contains some inhibitor which survives rather vigorous purification techniques, such a result is very difficult to interpret; perhaps some process such as six-membered ring formation between a biradical chain containing two styrenes and one fumarate (arising from the addition of fumarate to the initial two styrene unit biradical) is involved. A similar mechanism has been suggested for the Diels–Alder reaction, and for the formation of four-membered rings when certain monomers are heated alone[8] or when tetrafluoroethylene is heated with other olefins.[9]

TABLE II

RATES OF THERMAL COPOLYMERIZATION OF STYRENE AND DIETHYL FUMARATE AT 60°

Mole % styrene	Time, hr.	Yield, g./l.	Rate × 10^6, m./l./sec.
100	...	...	2.15[a]
85	161	40.2	0.60
68	161	36.8	.52
47.2	161	12.4	.168
26.1	141	2.22	.033
0	497	1.06	.003

[a] Av. value from R. A. Gregg and F. R. Mayo, THIS JOURNAL 70, 2373 (1948).

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[8] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); *cf.* footnote (27).

[9] D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949).

PASSAIC, N. J.

RECEIVED NOVEMBER 22, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Electrolytic Properties of Aqueous Solutions of Polyvinylpyridine Neutralized with Hydroiodic Acid

BY FREDERICK T. WALL, JOHN J. ONDREJCIN[1] AND MARIKA PIKRAMENOU

Solutions of polyvinylpyridine partially neutralized with hydrogen iodide have been electrolyzed between a silver–silver iodide cathode and a platinum anode in a transference cell separated into anode and cathode compartments by a coarse sintered glass frit. I^{131}, a radioactive isotope of iodine, was initially added as a tracer so that the net movement of the iodide ions could be determined by use of data obtained with a Geiger counter. Hydrogen ion concentrations and electrical conductivities were also measured.

A number of significant quantities were calculated using basic electrochemical equations. These included the transference number of the polyion, the equivalents of polymer transported per faraday of electricity passed through the cell, the fraction of iodide ions associated with the polyanions, and the over-all degree of ionization of the polymer. From 30 to 60% of the iodine is found to move with the cations.

Introduction

When a polymeric electrolyte is dissolved in water, it will generally ionize to some extent as any ordinary electrolyte might be expected to do. However, if the degree of polymerization is large, the per cent. of ionization appears to be small, even for salts whose monomer counterparts would be completely ionized. This apparent incomplete ionization of polymeric salts can be attributed to the very high charges that arise if appreciable ionization occurs. Such high charges give rise to ionic potential energies so great that complete ionization is energetically unfavorable.

Earlier work[2] on polyacrylic acid neutralized with sodium hydroxide showed that anywhere from 30–70% of the sodium ions might be bound to the polyanion depending upon the concentrations involved. The present investigation was carried out to learn something about the behavior of polymeric bases neutralized with a monobasic acid. For this purpose we chose the polymer of 2-vinylpyridine and hydroiodic acid. The experiments were carried out with the expectation that many of the iodide ions would be bound to the polycation and accordingly would appear to move to the cathode in an electrolysis experiment. To follow the movement of iodide it was found expedient to employ radioactive iodine, I^{131}, as a tracer.

Theory

Huizenga, Grieger and Wall[2] have already considered some of the theoretical aspects relating to electrical transference of polymeric electrolytes. Among other things, they were concerned with the effect of exchange of ions between a free state and a state in which they were bound to the polymeric ion. They showed mathematically that unless the rate of exchange is infinitely great, transference numbers cannot be simply obtained by tracer techniques unless the tracer is uniformly distributed throughout the anode and cathode compartments at the beginning of an electrolysis experiment. They further showed experimentally that in solutions of sodium polyacrylate, the rate of exchange of sodium ions between free and bound states was measurably finite. Accordingly, in our experiments dealing with polyvinylpyridinium iodide, we assumed, to be on the safe side, that the rate of exchange of iodide ions is likewise finite. Consequently all ordinary transference experiments were made with tracer uniformly distributed throughout the cell at the beginning of the experiment.

Briefly the experiments consisted of electrolyzing aqueous solutions of poly-2-vinylpyridine neutralized to varying degrees by hydrogen iodide to which some iodide tracer had been added. Since poly-2-vinylpyridine is water soluble as a basic salt in the presence of 31% or more of the equivalent amount of hydrogen iodide, the transference studies

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[1] Firestone Tire and Rubber Company Fellow 1949–1950.

[2] J. R. Huizenga, P. F. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636 (1950).

were made over a range beginning at 31% neutralization.

To measure the final concentrations of the iodide ion (to be compared to the initial uniform concentration), the radioactivities of the anode and cathode solutions were determined. The increase in equivalents of iodide ion (p) brought about by transference into the cathode compartment is given by

$$p = \frac{rV_aV_c(C_c - C_a)}{1000\,(V_cC_c + V_aC_a)} \qquad (1)$$

where r is the concentration of the acid in equivalents per liter, V_c and V_a the volumes of the cathode and anode compartments in milliliters, C_c the radioactive counts per minute per unit volume of the cathode solution and C_a the corresponding quantity for the anode solution.

The solutions of polyvinylpyridinium iodide were electrolyzed using a silver–silver iodide cathode and a platinum anode, the reaction at the former being the reduction of silver iodide to metallic silver and iodide ion. Taking this fact into account, the net change in weight, g, of the cathode compartment is given in grams by

$$g = q(105.1 + r/C_p) + 127(p + n_e) \qquad (2)$$

where q is the equivalents of polymer moved into the cathode compartment, C_p the equivalent concentration of the polymer (thus making r/C_p the fraction of polymer neutralized), and n_e the faradays passed through the cell; 105.1 and 127 represent the molecular weight of 2-vinylpyridine and the atomic weight of iodine, respectively.

If α represents the degree of ionization of the polymeric solute, the equation for electroneutrality is

$$\alpha C_p + C_H = C_{OH} + rf \qquad (3)$$

where C_H is the hydrogen ion concentration, C_{OH} the hydroxyl ion concentration, and f the fraction of free iodide ions. The product rf obviously equals the iodide ion concentration.

Defining the transference number of the polyion, t_p as the fraction of the charge carried, we have

$$t_p = q\alpha/n_e \qquad (4)$$

Eliminating α from equations (3) and (4), the equation for the transference number becomes

$$t_p = q(C_{OH} + rf - C_H)/n_eC_p \qquad (5)$$

Now the transference number can also be defined as a ratio of specific conductances

$$t_p = K_p/K \qquad (6)$$

where K_p and K are, respectively, the specific conductances of the polyion and of the solution, corrected for the solvent. But

$$K_p = K - K_{OH} - K_H - K_I \qquad (7)$$

where the subscripts have the significance previously indicated. To evaluate K_I, K_H and K_{OH} we employ the familiar equations for equivalent conductances such as (for iodide)

$$K_I = \Lambda_I C_I/1000 \qquad (8)$$

The values (at 25°) for the equivalent conductances of iodide, hydroxyl and hydrogen ions are taken as 76.85, 198 and 350, respectively; although these values are for infinite dilution, they are sufficiently accurate for our purposes. Since C_I is the same as the product rf, equation (6) can be written as

$$t_p = (K - K_{OH} - K_H)/K - \Lambda_I rf/1000K \qquad (9)$$

Equating equations (9) and (5), then solving for the fraction of free iodide ions, we obtain

$$f = \frac{(K - K_{OH} - K_H) - qK/C_pn_e\,(C_{OH} - C_H)}{rqK/C_pn_e + \Lambda_I r/1000} \qquad (10)$$

where q, the equivalents of polymer gained by the cathode compartment can be obtained from equation (2).

Other quantities of interest are the degree of ionization of the polymer, (α), the ratio, (β), of the number of bound iodide ions to the degree of polymerization, the equivalent conductance per degree of ionization of the polymer, (Λ_p), and the "rational mobility" (ω_p). These are given by

$$\alpha = i/s = (C_{OH} + rf - C_H)/C_p \qquad (11)$$

$$\beta = j/s = (r/C_p)(1 - f) \qquad (12)$$

$$\Lambda_p = 1000K_p/\alpha C_p \qquad (13)$$

$$\omega_p = 6.51 \times 10^6\,\Lambda_p/(\alpha s) \qquad (14)$$

where i is the number of positive charges on the polyion, j the number of bound iodide ions and s the degree of polymerization. A more complete discussion of these quantities can be found in an earlier paper.[2]

Experimental

Apparatus and Procedure.—The transference cell shown in Fig. 1 consisted of a horizontal glass tube 26 cm. long and 20 mm. in diameter separated into anode and cathode portions by a coarse sintered glass partition. Vertical glass tubes 12 mm. in diameter were sealed 3.5 cm. from each end of the horizontal section to serve both as filling tubes and as openings for insertion of the electrodes. Glass tubing (5 mm.) sealed vertically to the underside of the cell provided a means for draining the compartments of the cell at the completion of a run. The anode draining tube was about 3 cm. longer than the cathode to help localize the triiodide solution formed at the platinum anode as electrolysis progressed.

The circuit consisted of the transference cell, a gas coulometer using dilute sulfuric acid, a variable resistance and a milliammeter, all in series. Since each run was timed with a stopwatch, the number of faradays passed through the cell could be computed both by ampere–time product and the volume of gas evolved by the coulometer. The two values usually agreed within 2%.

Solute weight changes in the cathode compartment were determined by evaporation of 20-ml. aliquot portions of the initial and final cathode solutions. Some decomposition of the poly-2-vinylpyridinium salt took place during the evaporation but this weight change was corrected by assuming the weight loss of the solute from the final cathode solution was in the same ratio as that of the original solution whose composition was known.

The volumes of the compartments were obtained by weighing the cell filled with water thermostated at 25°. The cathode and anode were found to have volumes of 52.0 and 53.6 ml., respectively.

Transference runs were made while the cell was immersed in a constant temperature bath controlled to 25 ± 0.1°.

Electrodes.—The anode was merely a coil of platinum wire sealed into a 6 mm. glass tube, which was filled with mercury to establish contact with the wire.

The silver–silver iodide cathode was prepared in a manner similar to that employed by Jones.[3] The platinum wire was cleaned in aqua regia and then silver plated in a solution of potassium silver cyanide using a current density of 0.08 milliampere per square millimeter. Silver oxide was prepared by precipitation from silver nitrate with barium hydroxide which had been allowed to stand overnight until the barium carbonate had precipitated. After washing the

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(3) G. Jones, THIS JOURNAL, **37**, 752 (1915).

silver oxide free of barium and nitrate ions. small portions of the brown oxide were placed on the wire electrode and heated in a flame. The silver oxide decomposed at 400–500° leaving a coarse spongy coat of silver. By electrolyzing in a 3% potassium iodide solution for two hours at the same current density as before, an adherent coat of silver iodide was formed. The electrodes were stored in a dark place because of their light sensitivity.

Conductance and *p*H Measurements.—The measurements of conductance and *p*H were carried out in the same manner as described in an earlier work on the transference properties of polyacrylates.[2]

Radioactive Counting Measurements.—The radioactive iodine solutions were counted with a scaling unit Model 163 equipped with a Model T1 dual timer, manufactured by the Nuclear Instrument Corporation.

The self-quenching counter consisted of a Geiger tube, a variable stabilized high voltage supply, and, since the counting rate was too great for a mechanical register, a scaling circuit in conjunction with an amplifier and an electric timer.

Twenty-five-milliliter portions of active solution were pipetted into a thin wall annular glass cell which fitted around the Geiger tube and rested on a small wooden frame in a vertical position. The operating curve for the Model 10-A, Mark 1, beta counter tube with a 30 mg./sq. cm. window was obtained from the Radiation Counter Laboratories; for this apparatus the plateau of the counting region was at 900 volts.

The cell was cleaned by placing it in a hot sulfuric–nitric acid mixture for one-half hour. This assured reasonable reproducibility of background count which was found to be 38 to 40 counts per minute. While the background count was measured, the cell contained distilled water.

A sufficient number of counts were taken to ensure probable error of about 1–2%. The counts observed usually varied from 1000 to 1500 per minute so it was not necessary to introduce coincidence correction especially since the most significant quantity involved in the calculation indicated by equation (1) is a difference of counts.

Materials and Reagents.—The 2-vinylpyridine used in this work was obtained from Reilly Tar and Chemical Corporation. The monomer was distilled through a 12-in. Vigreux column at 90–95° under 15–18 mm. pressure to remove inhibitor and solid impurities.

Several methods of polymerization[4,5] were tested, but the following recipe, which gave a 100% yield after two hours at 34°, was found to be the most satisfactory: 20.0 ml. of water, 10.0 g. of 2-vinylpyridine, 0.1 g. of benzoyl peroxide, 0.1 g. of ferrous ammonium sulfate, 0.1 g. of sodium pyrophosphate, 0.1 g. of sorbose, 0.5 g. of S. F. flakes.

The monomer charge, containing 200 g. of freshly distilled 2-vinylpyridine, was placed in a 32-oz. beverage bottle and capped. The bottle was clamped to a motor driven shaft located in a thermostated water-bath. In this way the liquid charge was agitated continuously until polymerization was complete.

The crude polymer was washed with water to remove excess soap and then treated with sufficient concentrated hydrochloric acid to ensure solution, simultaneously effecting partial purification. When the hydrochloride solution was dropped into an aqueous solution of sodium hydroxide the polymer precipitated in tacky curds. This conversion of hydrochloride to polymer was repeated several times, thus removing a large portion of the water soluble impurities.

The next step in obtaining pure polymer was the preparation of a methanol solution of poly-2-vinylpyridine hydrochloride and its precipitation by acetone. This was done by using a volume of concentrated hydrochloric acid five times that of the weight of the polymer and a volume of methanol ten times that of the acid. The resultant yellow solution was dropped into a volume of actone four times that of the methanol. The hydrochloride precipitated as a white, finely divided mass which could be filtered. It was observed that the hydrochloride was very hygroscopic and absorption of atmospheric water vapor resulted in a very sticky product; hence it was necessary to carry out the filtration in a nitrogen atmosphere. The dry salt obtained in this manner gave a Mohr chloride analysis of 25.3% HCl as compared to the theoretical 25.8%. The chloride salt is very soluble in water, and aqueous solutions as concentrated as 30% are easily prepared.

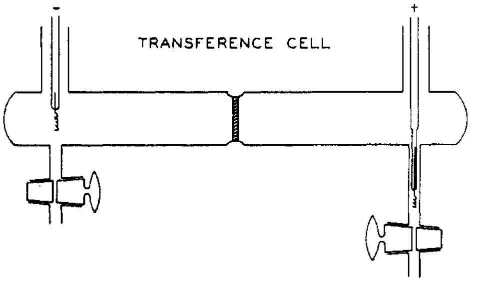

Fig. 1.—Transference cell.

To accomplish the final steps of purification, a water solution of the hydrochloride salt of the polymer obtained from the acetone precipitation was poured into an excess of sodium hydroxide. An 8–10% isopropyl alcohol solution of polymer was then prepared from the precipitate. This solution was held in a separatory funnel whose stem had been bent at right angles and whose tip had been drawn down to capillary size. The tip of the funnel was placed below the surface of some water (approximately five times the volume of the isopropyl alcohol solution) contained in a large beaker. A motor driven stirrer dipped into the beaker of water. As the isopropyl alcohol solution came into contact with the water, a fine filament of polymer formed and this was wrapped around the stirrer. This operation was designed to remove any sodium chloride and sodium hydroxide acquired by the polymer in the previous step. The resulting product was superficially dried and a 5% solution of polymer in *t*-butanol was prepared. Anhydrous sodium sulfate was added to the *t*-butyl alcohol to remove the remaining water. An erlenmeyer flask containing the solution was placed in a Dewar flask containing an alcohol–water mixture at approximately −10°, thus freezing the contents. The system was evacuated by a high vacuum pump equipped with a Dry Ice–acetone trap. After sublimation of the solvent the polymer remained a white, very light, foam-like structure.

The hydroiodic acid used in this research was prepared by dilution of concentrated acid of specific gravity 1.50 and standardized against sodium hydroxide solutions prepared according to the method of Pierce and Haenisch.[6] The basic solution was standardized against potassium acid phthalate and hydrazine sulfate.[7]

The water used for preparing the final solutions was redistilled over potassium permanganate and had a specific conductance of 2×10^{-6} ohm^{-1} cm.$^{-1}$ at 25°. The iodine tracer was obtained from Oak Ridge, Tennessee, in carrier free sodium bisulfite solution.

Results and Discussion

***p*H Effects on the Polymeric Ion.**—Poly-2-vinylpyridine is a very weak base. As hydrogen ions are added, the polymer builds up a positive charge which tends to uncoil the molecule and to resist attraction of additional hydrogen ions.[8] The *p*H as a function of the degree of neutralization for a polymer of normality 0.0250 *N* is shown in Fig. 2 and given, together with other quantities of interest, in Table I.

Association and Transport of the Iodide and Polymer Ions.—The gain in equivalents of iodide ion in the cathode compartment was determined by measuring the radioactivities of the anode and cathode compartments followed by calculation using equation (1). In contrast to sodium polyacrylate solutions, for which the net flow of sodium

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[4] R. H. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948).

[5] F. T. Wall and T. J. Swoboda, THIS JOURNAL, **71**, 919 (1949).

[6] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1943.

[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947.

[8] F. T. Wall and E. H. deButts, Jr., *J. Chem. Phys.*, **17**, 1330 (1949).

Table I

C_p	100 r/C_p	10^3K ohms^{-1} cm.$^{-1}$	pH	-10^4p equiv.	10^4q equiv.	q/n_e
0.0250 N	31.0	0.505	3.91	0.9572	3.706	1.268
	40.0	.685	3.49	.8008	2.683	0.923
	50.0	.993	3.20	.6306	1.928	.574
	60.0	1.417	2.96	.5140	1.377	.413
	70.0	1.918	2.70	.4580	0.966	.300
	80.0	2.518	2.41	.5376	.862	.259
	90.0	3.14	2.27	.4323	.582	.174
0.0500 N	31.0	0.881	4.15	1.2104	3.345	1.095
	40.0	1.109	3.54	1.0512	2.246	0.782
	50.0	1.463	3.21	1.0475	3.391	1.061
	60.0	2.088	2.88	0.8691	2.717	0.814
	70.0	2.921	2.42	.5371	1.367	.278
	80.0	4.011	2.26	.4871	1.180	.354
	90.0	5.05	2.10	.3760	0.725	.217
0.0750 N	31.0	1.244	4.22	1.672	3.994	1.203
	40.0	1.523	3.64	1.253	2.116	1.191
	50.0	1.907	3.21	1.419	3.796	1.201
	60.0	2.624	2.80	0.388	2.298	0.689
	80.0	5.10	2.13	0.442	0.727	0.218

ion was observed in both directions depending on concentration and degree of neutralization, the net flow of iodide ion in solutions of poly-2-vinylpyridine and hydroiodic acid was always toward the anode, in our experiments, even at relatively high concentrations. This behavior may be characteristic of the basic polymer, but it can also be attributed to a low degree of polymerization which would cut down the tendency to hold the counter ions. It is our belief that the vinylpyridine polymer which we used had a lower degree of polymerization than did the polyacrylate, so it should not associate as large a fraction of available free ions as the polyacrylate.

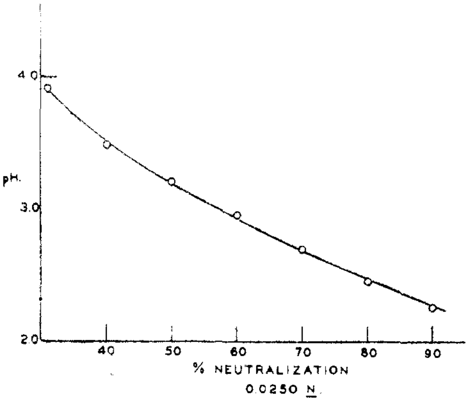

Fig. 2.—pH of polyvinylpyridine as function of degree of neutralization with hydroiodic acid (C = 0.0250 N).

The last column of Table I gives q/n_e where q is the equivalents of polymer moved and n_e the faradays of electricity passed through the cell. This is similar, but not identical, to the transference number which is properly defined as the fraction of the current carried by the ion. In general, q/n_e decreases monotonically with increasing neutralization. Except for the lowest degrees of neutralization, this is similar to the behavior observed for polyacrylic acid.[2]

Transference Numbers and Related Quantities.—In Table II are given data on polymer transference number, polymer charge and bound iodine for various degrees of neutralization at different concentrations. It will be noted as illustrated in Fig. 3 that the transference number of the polymer ion generally decreases with increasing neutralization. This is readily understandable, for increasing acidity permits a greater portion of the cell current to be carried by iodide ions.

Table II

C_p	100 r/C_p	10^3K_p ohm^{-1} cm.$^{-1}$	$1 - f$	t_p	i/s	j/s
0.0250 N	31.0	0.112	0.414	0.223	0.176	0.128
	40.0	.135	.433	.197	.226	.173
	50.0	.175	.378	.176	.285	.189
	60.0	.221	.297	.156	.378	.178
	70.0	.272	.297	.142	.452	.208
	80.0	.284	.433	.113	.298	.346
	90.0	.276	.432	.088	.296	.388
0.0500 N	31.0	0.171	0.425	0.194	0.171	0.132
	40.0	.182	.463	.164	.209	.185
	50.0	.336	.540	.230	.218	.270
	60.0	.495	.510	.237	.267	.306
	70.0	.295	.519	.101	.260	.363
	80.0	.441	.463	.110	.319	.370
	90.0	.384	.489	.076	.301	.440
0.0750 N	31.0	0.250	0.455	0.201	0.167	0.141
	40.0	.341	.522	.224	.188	.209
	50.0	.415	.618	.218	.182	.309
	60.0	.469	.536	.179	.257	.321
	80.0	.290	.544	.079	.266	.364

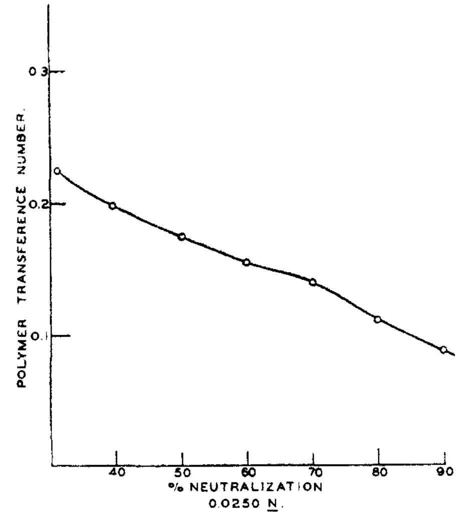

Fig. 3.—Transference number of polymer as function of degree of neutralization.

It will also be noted that the degree of ionization, or charge fraction (i/s), of the polymer increases with increasing per cent. of neutralization. This behavior is also one which would normally be expected. The fraction, j/s, of amine sites in the polymer occupied by iodine, likewise increases with neutralization as might be predicted. The fraction of bound iodine, $1 - f$, is roughly constant in the neighborhood of 0.4 to 0.5. This approximate constancy is interesting although no simple quantitative explanation is forthcoming.

The equivalent conductance (per fraction ionized) of the polymer, Λ_p, was found to fluctuate in the neighborhood of approximately 25 ohm^{-1} cm.^{2} equiv.$^{-1}$ for the experimental concentrations and neutralizations investigated. The product of "rational mobility," ω_p, and s, the degree of polymerization, for a 0.0250 N solution averages about 1.8×10^{-8} cm. per sec. per dyne.

URBANA, ILLINOIS RECEIVED DECEMBER 11, 1950

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Thermal Analysis of the System Sodium Stearate–Cetane

BY F. H. STROSS AND S. T. ABRAMS

The phase behavior of anhydrous sodium stearate in various hydrocarbons reported in the literature does not present a consistent picture, possibly because of the presence of traces of water. An attempt has been made to obtain a phase diagram of carefully prepared and rigorously dried sodium stearate and cetane by means of differential thermal analysis, supplemented by some visual observations under polarized light. This diagram indicates that there is no appreciable interaction between soap and medium below about 140°. At higher temperatures, however, the transition temperatures of the soap are depressed by the addition of solvent, but the depression is constant over most of the concentration range studied. No phase islands have been found by the techniques used. Approximate measurements of the latent heats were made and the summed molal latent heats for sodium stearate and the summed partial molal latent heats for the soap in the solvent were found to amount to about 10,700 g. calories.

In the study of grease-like systems it is most useful to have available the oil–soap phase diagram, so that the state of the system is known for any temperature and concentration desired. Such phase diagrams are difficult to construct because no single method known appears capable of a complete analysis of the behavior of the system. Some visual and microscopic observations of a typical system, namely, sodium stearate–cetane, have been referred to in a previous publication,[1] but these methods do not give complete and consistent diagrams which can be readily reproduced. The method of differential thermal analysis is attractive because it yields an objective record of any transition with a palpable latent heat, and because the latent heat itself can be determined with reasonable accuracy. This method has found widespread application in the study of clays, and has also recently been used in the study of soaps,[2] and soap–hydrocarbon mixtures.[3] The instability of many soaps in air at temperatures above about 150°, the large number of transitions below the melting point and other characteristics of soap–hydrocarbon systems make necessary more refined instruments for the thermal analysis than those used for clays, including high sensitivity and sealed calorimeters with good internal heat distribution. The object of this study, to contribute to the construction of the phase diagram mentioned, made necessary the design of appropriate equipment, which is briefly described in the following section.

Experimental

The demands of the problem were met by the construction of twin cylindrical calorimeters made of stainless steel, with a threaded closure fitted with a silicone rubber gasket; by means of this closure the atmosphere of the calorimeter could be replaced or evacuated, and the calorimeter then could be hermetically sealed. The favored calorimeter heat distributing system, of several tried, consisted of a flattened silver helix winding around the well and extending to the walls of the calorimeter. The maximum heat lag in a sample of grease was calculated to be about 0.5° at a heating rate of 2° per minute. The calorimeters were spaced symmetrically by means of glass and Mykroy spacers in a copper block, with a thermal barrier consisting of a 2 mm. air space around each calorimeter. The copper block which was used to provide uniform furnace temperature was heated at a constant rate in an air-bath at rates varying from 0.4 to 2.0° per minute. The dimensions of the calorimeters were 12 mm. dia. by 20 mm. height; with their closures they weighed between 9 and 10 g., and had a free capacity of about 2 ml.

The difference in temperature between the calorimeters was automatically recorded by means of a differential copper–constantan thermocouple connected to a Leeds and Northrup Type HS galvanometer operating a photopen deflection recorder. Periodically, the thermocouple-galvanometer circuit was manually disconnected and the temperature of either of the individual calorimeter thermojunctions was measured by means of a Leeds and Northrup Portable Precision Potentiometer. Figure 1 shows a typical thermogram of a mixture containing 34.9% sodium stearate. A thermogram of the pure soap is shown in Fig. 2. It was obtained by heating to 300° at a rate of 2°/min. immediately followed by cooling at a rate of 2°/min. in a new instrument that provided controlled cooling as well as heating.[4]

In a differential analysis run, soap sample and the inert sample are heated in the copper block; when the active sample undergoes a phase change, there arises between it and the inert sample a difference in temperature which is measured.

In a given system with a well-defined thermal path, in which the conductivity within the sample is large compared to that of the thermal barrier, the latent heat ΔH of the transition is

$$\Delta H = K \int_a^b (t_r - t_a)dz \tag{1}$$

t_r = temperature of the reference sample
t_a = temperature of the active sample
z = time
K = constant including conductivity and dimensions of the thermal path

provided that the quantity K is maintained adequately constant during the run. The integral is taken between two temperatures a and b at which the temperature difference $t_r - t_a$ is zero or negligible. The sensible heats of the two samples cancel if the heat capacities are equal. This condition is sufficiently well satisfied experimentally by adjusting the amount of samples used. Inadequate heat distribution within the calorimeter will cause distortion of the transition peaks with corresponding loss in characterization and accuracy in the latent heat values. It follows from equation

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[1] F. H. Stross and S. T. Abrams, THIS JOURNAL, **72**, 3309 (1950).

[2] R. D. Vold, *ibid.*, **63**, 2915 (1941).

[3] R. D. Vold and M. J. Vold, *J. Colloid Sci.*, **5**, 1 (1950).

[4] This instrument was constructed, and the curve was furnished by Mr. C. J. Penther of these Laboratories.