

unrestricted Hartree-Fock wavefunctions that $(8\pi/3)\gamma_e\gamma_n\psi^2(0)$ should be negative for atomic oxygen,¹² the second solution was preferred. Moreover, the value 426 Mc/sec for $\gamma_e\gamma_n\langle r^{-3} \rangle_s$, which corresponds to a value of $\langle r^{-3} \rangle_s$ of 3.97×10^{25} cm⁻³, agrees well with other estimates of this quantity. Harvey's estimate,¹¹ based on the hyperfine structure of the ¹⁷O, ³P level, was 3.46×10^{25} cm⁻³; the EPR spectra of O₂⁻ trapped in alkali halides¹³ yielded a mean value of 3.76×10^{25} cm⁻³;

the value calculated from Roothaan's Hartree-Fock wavefunction¹⁴ was 3.36×10^{25} cm⁻³; and finally, the value determined¹⁵ from Herman and Skillman's wavefunction was 3.93×10^{25} cm⁻³.

ACKNOWLEDGMENT

We thank Dr. J. Rolfe for the loan of the electrolysis apparatus and for growing various KCl and KBr crystals for us.

¹² N. Bessis, H. Lefebvre-Brion, and C. M. Moser, *Phys. Rev.* **128**, 213 (1962).

¹³ H. R. Zeller, R. T. Shuey, and W. Känzig, *J. Phys. Radium* **28**, 81 (1967).

¹⁴ E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1962).

¹⁵ C. M. Hurd and P. Coodin, *J. Phys. Chem. Solids* **28**, 523 (1967).

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Molecular Beams of Macroions

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By means of electro-spraying a dilute polymer solution into an evaporation chamber, negative macroions can be produced and a molecular beam formed by sampling the gaseous mixture of macroions, solvent, and nitrogen molecules with a nozzle-skimmer system of the Kantrowitz-Gray type. The macroion current can be detected by a Faraday cage after the light ions have been repelled from the beam by negative voltages on a repeller grid. Theoretical repeller voltages which best agree with the observed are those calculated by assuming a macroion velocity within 2% of the estimated supersonic beam velocity of 743 m sec⁻¹. Polystyrene macroions of 51 000 weight-average amu tend to form dimers and trimers in the beam while larger polystyrene macroions of 411 000 weight-average amu appear mostly to be multiply charged single species. The results demonstrate that definite mass/charge states can be formed by the electro-spray technique, that a considerable monochromatization of macroion velocities in the beam takes place, and that the macroions become highly concentrated relative to low-molecular-weight solvent and nitrogen ions during the transit time in the supersonic beam.

INTRODUCTION

It has never been possible to obtain intact gas-phase macromolecules by evaporation inasmuch as the vapor pressure of a high polymer such as polyethylene of 14 000 amu can be calculated to have a room temperature value of only 10^{-480} atm. On heating a macromolecule it always degrades before it evaporates. It occurred to one of us¹ that it might be possible to produce intact gas-phase macroions, if only momentarily, by electro-spraying a dilute solution into an evaporation chamber containing nitrogen, and by allowing the volatile solvent to evaporate from the tiny drops so produced. The residual macroions would then be suspended in

the gas phase in a mixture of solvent and nitrogen molecules.

Richardson² produced intact individual macromolecules on a mica-backed film of evaporated carbon by spraying a dilute solution of a high polymer onto the carbon and by allowing the solvent to evaporate. The solvent wetted the carbon and spread out, thereby separating the macromolecules and, after evaporation of the solvent, leaving them as single solid entities on the carbon surface where they could be shadowed and photographed in an electron microscope. O'Konski and Doyle³ were able to produce uniform aerosols of polystyrene having particle sizes in the range 0.1-1 μ by evaporating a mist produced by a Vaponefrin nebulizer.

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¹ M. Dole, Preprints, Intern. Symp. Macromol. Chem., Tokyo, Japan **6**, 132 (1966).

² M. J. Richardson, *Nature* **198**, 252 (1963); *Proc. Roy. Soc. (London)* **A279**, 50 (1964).

³ C. T. O'Konski and G. J. Doyle, *Anal. Chem.* **27**, 696 (1955).

Beeman and Neher⁴ have also used a Vaponefrin nebulizer to obtain beam currents of the order of 10^{-14} A using lysozyme and hemoglobin as the solute macromolecules. Other work along the line of suspending macromolecules in the gas phase by a spray-evaporation technique is that of Hutchinson and Montagu-Pollock⁵ who used a Vaponefrin atomizer in an attempt to prepare gas-phase DNA molecules and pleuropneumonia-like organisms. There have been many papers published on electrically charged droplets, a recent one, for example, is that of Pfeifer and Hendricks.⁶ However, all of this work, as far as we are aware, was done using nonvolatile liquids, and, therefore, not applicable to the results of this research.

By using an electrospray it was thought¹ that the drops on evaporation of the solvent would become electrically unstable and break down into smaller drops until possibly drops containing only one macromolecule per drop would result. On further evaporation of the solvent it was hoped to obtain electrically charged intact gas-phase macromolecules. It was thought that the charged drops would repel each other electrostatically and so prevent aggregation. It was also believed that the macroions so formed would be in a vibrationally unexcited state and so not fragment. Some preliminary results indicating the actual production of gas-phase macroions with definite mass/charge states have already been published.⁷ It is the purpose of this paper to give the details of this work as well as to present additional data and conclusions.

PRINCIPLES OF THE EXPERIMENT

Size of Drops Required

It is necessary to consider the size of a drop of solution such that the drop would contain on the average only one macromolecule. Calculations demonstrate that at 0.01 wt % concentrations and for molecular weights of 10^4 or more (smaller molecules are not usually considered to be macromolecules) drops of 0.1μ in diameter would be sufficiently small so that they would not contain more than one macromolecule per drop. However, drops made by liquid atomization are usually $1-5 \mu$ in diameter or larger.

The Electrospray Method

Hines⁸ and Tilney and Peabody⁹ have discussed the physics of the electrospray method of producing

charged liquid drops. Electrical fields at the tip of the liquid orifice (a hypodermic needle in our case) should be of the order of magnitude of $40\,000 \text{ V cm}^{-1}$ and the liquid should have an electrical conductivity in the range $10^{-9}-10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$. The number of unit charges per drop may run as high as 6×10^6 for a drop 34μ in radius.⁸ As the solvent evaporates and the drop shrinks, the drop becomes unstable (Lord Rayleigh¹⁰) when α equals 4 where

$$\alpha = q^2 / (3V\gamma\epsilon), \quad (1)$$

in which q is the charge on the drop, V its volume, γ its surface tension, and ϵ its dielectric constant. Ryce and Patriarche¹¹ have shown that the most stable state is obtained if a drop having α equal to 4 breaks down into four equal drops. It is necessary, of course, that the charges remain on the drop as the drop evaporates. This condition should be satisfied until the electric force of repulsion between the charges exceeds the attractive force due to polarization of the liquid by the charges.

Another consideration in the case of negatively charged drops is the electron affinity of the gas molecules; the higher their affinities the greater the tendency of the evaporating solvent molecules to evaporate as charged rather than neutral molecules. In this connection it is interesting to consider the data published by Bouby, Figuet-Fayard, and Abgrall¹² on the frequency of attachment of thermal electrons by organic vapors. In units of $\text{second}^{-1} \cdot \text{torr}^{-1}$, benzene and acetone have the value 1.5×10^8 and 0.4×10^8 , respectively, and are listed as compounds having weak coefficients of attachment. In the case of compounds containing chlorine or conjugated ketonic groups such as biacetyl or glyoxal the coefficients are of the order of magnitude 10^8-10^{10} . Using polystyrene as the macromolecular solute and a mixed benzene-acetone solvent, we did not expect the solvent molecules to strip completely electrons from either the drop or the polystyrene molecules.

The Problem of Solvent Evaporation

If the dilute polymer solution is electrosprayed into a vacuum, the drops would not evaporate within the required fraction of a second because of the strong evaporative cooling of the drop. The temperature T to which the residual drop falls from its initial temperature T_0 , assuming no transfer of heat to the drop, is given by the equation

$$T - T_0 = (\Delta H_v / C_p) \ln x, \quad (2)$$

where x is the fraction of the drop remaining at temperature T , ΔH_v is the heat of vaporization of the

⁴ W. W. Beeman (private communication). See also E. Neher, M.S. thesis, University of Wisconsin, 1967.

⁵ F. Hutchinson (private communication).

⁶ R. J. Pfeifer and C. D. Hendricks, *Phys. Fluids* **10**, 2149 (1967).

⁷ M. Dole, R. L. Hines, L. L. Mack, R. C. Mobley, L. D. Ferguson, and M. B. Alice, *Macromol.* **1**, 96 (1968).

⁸ R. L. Hines, *J. Appl. Phys.* **37**, 2730 (1966).

⁹ R. Tilney and H. W. Peabody, *Brit. J. Appl. Phys.* **4**, S51 (1953).

¹⁰ Lord Rayleigh, *Phil. Mag.* **14**, 184 (1882).

¹¹ S. A. Ryce and D. A. Patriarche, *Can. J. Phys.* **43**, 2192 (1965); see also J. W. Cahn, *Phys. Fluids* **5**, 1963 (1962).

¹² L. Bouby, F. Figuet-Fayard, and H. Abgrall, *Compt. Rend.* **261**, 4059 (1965).

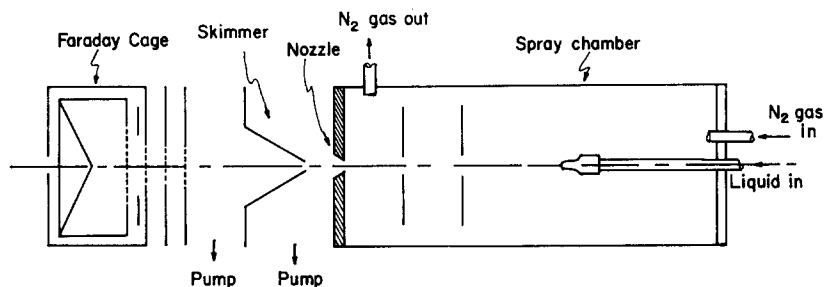


FIG. 1. Schematic diagram of apparatus (macromass spectrometer: inlet system test assembly) for the production and detection of macroions.

liquid, and C_p the heat capacity of the liquid. Equation (2) is based on the assumption of a uniform drop temperature within the drop and of ΔH_v and C_p constant with temperature. When half of the drop has evaporated, x equal to 0.5, the drop in temperature for benzene as solvent would be 160° . Obviously heat must be transferred to the drop to maintain a high rate of evaporation. In the work described below this was done by evaporating the drop in flowing nitrogen gas at atmospheric pressure.

The Problem of Molecular Aggregation

In order to obtain intact isolated macroions it is necessary that they not aggregate either during the evaporation of the solvent or after the solvent has all evaporated. Because of the enormously large van der Waals forces of attraction between macromolecules and because of their many internal degrees of freedom over which any energy of condensation can be rapidly dissipated, it is evident that two macromolecules colliding in the gas phase will most surely associate. However, if the macromolecules are charged, the electrostatic forces of repulsion will tend to keep them apart and prevent aggregation. A simple calculation will illustrate this point. Consider two polyethylene molecules each of molecular weight 10^6 , and having a unit charge. Assuming the molecules to be coiled up into a dense sphere of unit density (a gas phase is the worst possible solvent for a macromolecule) then the electrostatic repulsive potential energy at moment of contact would be (assuming a dielectric constant of 2) 0.048 eV. This is to be compared with a thermal energy ($\frac{3}{2}RT$) at room temperature of about 0.039 eV. Smaller singly charged macromolecules of 51 000 molecular weight and unit charge would have a repulsive potential of 0.13 eV. Particles with multiple charges would, of

course, have even higher repulsive potentials. Coulombic repulsive potentials fall off much more slowly with distance than do the van der Waals attractive potentials. However, collisions against the Coulombic repulsion are quite probable; hence we might expect some aggregation to occur.

Sampling of the Gas by the Nozzle-Skimmer System

To sample the gas and to produce a molecular beam of macroions we have made use of a nozzle-skimmer system of the type first described theoretically by Kantrowitz and Grey.¹³ Anderson, Andres, and Fenn¹⁴ have recently reviewed the subject of supersonic nozzle beams. The supersonic nozzle and skimmer system has the following advantages: (1) It involves a two-stage reduction of pressure so that one can work at much higher pressures in the source chamber. (2) The intensity of the final beam is greater by a factor of 11 or more over that of a conventional oven beam.¹³ (3)

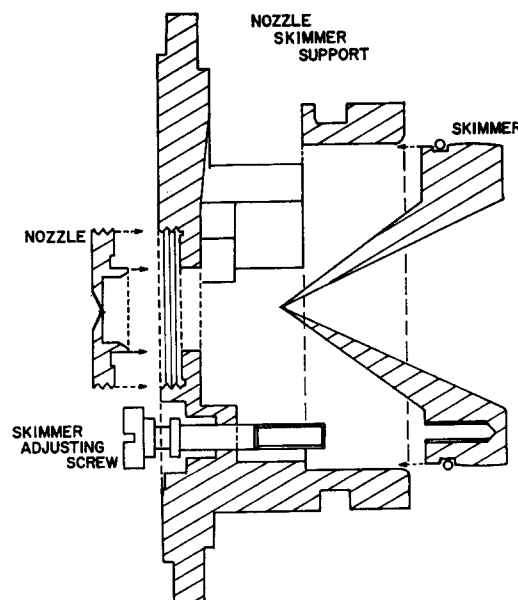


FIG. 2. The nozzle and skimmer system.

TABLE I. Theoretical repeller voltages for ions of unit charge and different masses.

Ion	Atomic mass units	V_R (V)
N_2	28	0.08
C_6H_6	78	0.2
Polystyrene	51 000	146
Polystyrene	411 000	1173

¹³ A. Kantrowitz and J. Grey, *Rev. Sci. Instr.* **22**, 328 (1951).
¹⁴ J. B. Anderson, R. P. Andres, and J. B. Fenn, *Molecular Beams*, J. Ross, Ed. (Interscience Publishers, Inc., New York, 1966), Chap. 8, p. 275.

With seeded beams (beams of mixed gases) the heavier molecules tend to become more concentrated in the beam. (4) Considerable velocity monochromatization occurs.

Under the conditions of the nozzle-skimmer system used by us, the temperature T of the beam at the entrance to the skimmer is given by the equation¹⁵

$$T/T_0 = [1 + (\gamma - 1)M^2/2]^{-1}, \quad (3)$$

where T_0 is the temperature of the gas in the source chamber, γ is the ratio of the specific heat at constant pressure to that at constant volume, and M is the Mach number of the jet at the entrance to the skimmer. It is interesting to point out that according to Eq. (3) in the case of the isentropic expansion of a gas of very high molecular weight, whose γ would be practically unity, there would be very little drop of temperature. However, in our case in which the gas was about 99% by volume nitrogen, we can safely take γ equal to that for nitrogen which is 1.40 at room temperature. With a Mach number of 7.5, T is calculated to be the very low value of 24.5°K. This is the translational temperature; in the case of a large macromolecule with many internal degrees of freedom, it is unknown at the present time to what extent vibrational and torsional relaxation occurs. In the case of argon gas, the low temperatures attained in supersonic beams promote cluster formation and clusters up to Ar_{20}

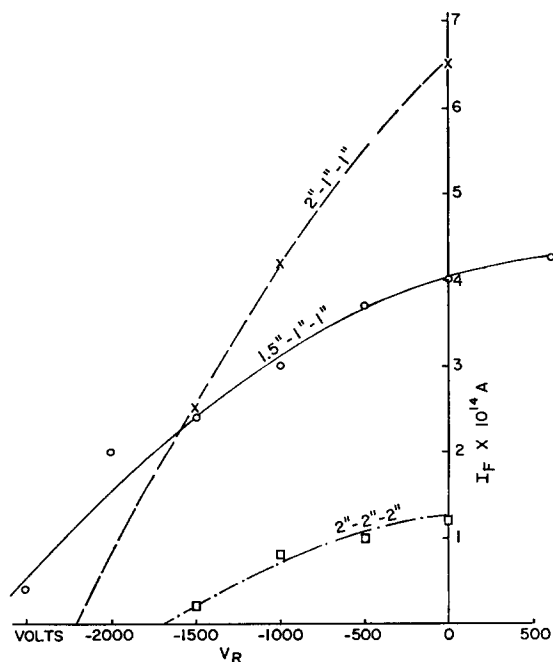


FIG. 3. First current-voltage curves obtained with the solvent alone (no macromolecular solute).

¹⁵ H. W. Liepmann and A. E. Puckett, *Introduction to the Aerodynamics of a Compressible Fluid* (John Wiley & Sons, Inc., New York, 1947), p. 25.

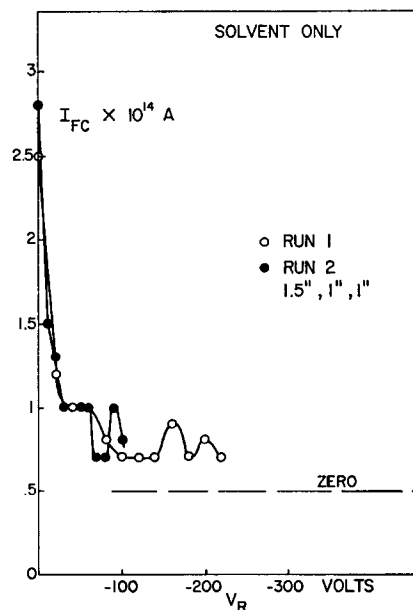


FIG. 4. Same as Fig. 3; spacings $1\frac{1}{2}$, 1, and 1 in. Data obtained two months after those of Fig. 3.

have been observed.¹⁶ On this basis clusters of macroions and solvent molecules might occur, but any lag of the vibration degrees of freedom in following the drop in translational temperature would impede cluster formation; in other words, the macromolecule would be "hot" internally while being "cold" translationally. The extent of vibrational relaxation is a very interesting problem which we hope to consider at a later date.

Another property of the supersonic nozzle beams of great importance in this work is the possibility of enhancement of the macromolecules in the beam by virtue of the so-called Mach focusing factor which is proportional¹⁷ to $(3 + \gamma M^2)$ although the accuracy of this proportionality factor has never been verified experimentally for mixtures. Inasmuch as M is inversely proportional to the velocity of sound which itself is inversely proportional to the square root of the molecular weight, M^2 is directly proportional to the molecular weight. In the case of macromolecules of 51 000 amu the Mach focusing factor is 1254-fold greater than that for the carrier gas, taking γ equal to unity for the macromolecule. Inasmuch as there are about 10^7 solvent molecules per macromolecule in the initial solution, it is obvious that any mechanism for the concentration of the macroions in the jet is extremely important.

In the discussion of our data that follows we have assumed that the velocity of the macroions in the supersonic jet is equal to that of the carrier gas. It is

¹⁶ F. T. Greene and T. A. Milne, *J. Chem. Phys.* **39**, 3150 (1963); F. T. Greene, J. Brewer, and T. A. Milne, *ibid.* **40**, 1488 (1964).

¹⁷ Reference 14, p. 312.

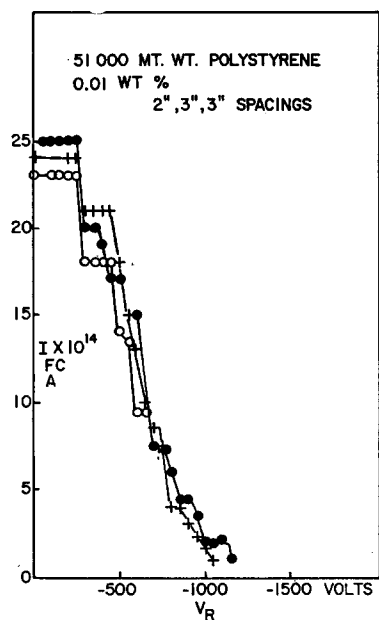


FIG. 5. Current-voltage curves for 0.01 wt% solution of 51 000 amu polystyrene.

interesting to calculate rather simply the number of head-on collisions between the swiftly moving nitrogen molecules and a macromolecule required to increase the macromolecule velocity from a negligible value in the forward, x , direction to a velocity equal to that of the carrier gas. Starting with the equations which come from the conservation of momentum, namely,

$$Av + Bu_{i-1} = Av_i + Bu_i \quad (4)$$

and

$$v_i = v + 2(s - v), \quad (5)$$

$$u_i = u_{i-1} + 2(s - u_{i-1}), \quad (6)$$

where v is the velocity of the carrier gas molecules (assumed to be constant) in the x direction before the collision, v_i the velocity after the i th collision, u_{i-1} and u_i similar velocities for the macromolecule, s the velocity of the combined bodies at the moment of collision, and A and B the masses of the solvent molecule and macromolecule, respectively, it is easy to show that

$$v + v_i = u_{i-1} + u_i. \quad (7)$$

From (4) and (7) we obtain

$$v_i = v \{ 1 - [2r(r-1)^{i-1}] / (1+r)^i \}, \quad (8)$$

where r is the ratio of the mass of the macromolecule to that of the carrier gas molecule and i the number of collisions. Letting Q represent the second term in the brackets, (8) may be rewritten

$$(v - v_i) / v = Q. \quad (9)$$

The number of collisions, i , required to bring the velocity of the macromolecule from rest to within the

ratio v_i/v of the carrier gas velocity can be calculated from the equation

$$i = \frac{\{\ln Q - \ln[2r/(r-1)]\}}{\ln[(r-1)/(r+1)]} \quad (10)$$

or when v_i approaches v ,

$$i = \frac{\ln Q}{\ln[(r-1)/(r+1)]},$$

or

$$i = -\frac{1}{2}r \ln Q \quad (11)$$

inasmuch as $\ln Q$ approaches $-\infty$ as v_i approaches v and $1 \gg 1/r$.

Only an infinite number of hits will make u_i equal to v (assuming all the incident carrier gas molecules to have the same velocity v , which is not strictly true); nevertheless we can calculate i for v_i being within 2% of v ; that is when Q equals 0.02. For r equal to 51 000/28 in the case of the experiment using polystyrene of 51 000 amu and nitrogen as the carrier gas, i is calculated to be 3560 hits.

The above treatment assumes perfectly elastic collisions between the carrier-gas molecules and the macromolecules; if completely inelastic collisions occur, i.e., if the impinging molecule is momentarily adsorbed and then re-emitted at random with a velocity equal to that of the macromolecule, the average momentum transfer per collision can be expressed by the equation

$$(v-u)dm = Mdu, \quad (12)$$

where dm and M are the masses of the light and heavy molecules, respectively. Treating the incoming stream of nitrogen as continuous,

$$\int_0^m dm = M \int_0^u \frac{du}{v-u}$$

or

$$m = M \ln[v/(v-u)], \quad (13)$$

where m is the total mass of the carrier-gas molecules that have collided with the macromolecules. In this treatment

$$i = (m/dm) = (M/dm) \ln[v/(v-u)]$$

or

$$i = -r \ln Q. \quad (14)$$

Letting Q again equal 0.02, i is calculated to be 7120 collisions for the 51 000-amu polystyrene-nitrogen mixture or just twice the number for the perfectly elastic collision case. These two calculations for the inelastic and elastic collision cases demonstrate the order of magnitude of collisions required to accelerate the macromolecule to within 98% of the velocity of the carrier-gas stream. These collision numbers are reasonable.

Identification of the Macroions

In order to distinguish between macroions and low-molecular-weight solvent or nitrogen-gas ions, in the absence of a macromass spectrometer we have adopted a Faraday cage arrangement preceded by a repeller-grid. In the absence of any repelling voltage on the grid, the current to the Faraday cage will be that due to all ions collected irrespective of mass. By gradually increasing the repelling voltage on the grid it was hoped to screen out the low-molecular-weight ions and so detect any macroions that might be present in the supersonic jet. It was assumed that the electric repulsive energy would be exactly equal to the kinetic energy of the ions when the current of the latter dropped to zero. For supersonic velocities of 743 m sec^{-1} the repelling voltages for different masses at unit charge are given in Table I. From Table I one can see the sharp jump in the required repeller voltages in passing from a solvent ion to a macroion; hence it should be possible to screen out readily all of the low-molecular-weight ions.

EXPERIMENTAL

Materials

The solvent for the electro spray solution consisted of 3 parts by volume of benzene and 2 of acetone. The latter was added to bring the electrical conductivity to $7.4 \times 10^{-9} \text{ cm}^{-1} \cdot \Omega^{-1}$. The mixture had a density of 0.827 g cm^{-3} . Two fractionated samples of polystyrene were used; one of 51 000 weight-average molecular weight and a ratio of weight average to number average equal to 1.06. The second sample had a weight average molecular weight of 411 000 and a weight to number average ratio of 1.10. The samples came from the ArRo Laboratories, Inc., Joliet, Illinois. The solutions were always about 0.01 wt % total of polymer.

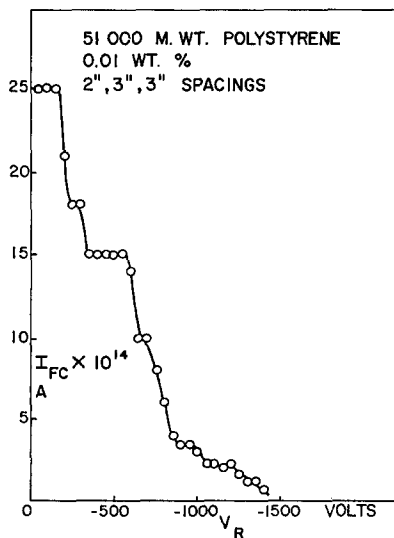


FIG. 6. Same as Fig. 5.

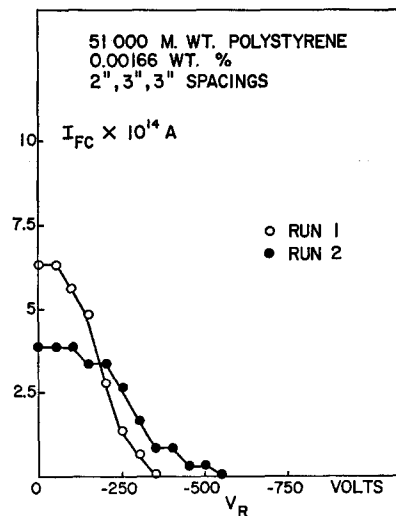


FIG. 7. Same as Figs. 5 and 6 but with the solution diluted to $\frac{1}{6}$ of the original concentration.

Hypodermic Needle

To form the electro spray the solution flowed through a hypodermic needle, 29 gauge, with a sharply bevelled tip and an inside and outside diameter of 8 and 16 mils, respectively. The needle was supported in an horizontal position with the tip on the lower side.

Evaporation Chamber

The evaporation chamber was about 12 cm in diameter and 70 cm long. It was made of a plastic film with a zipper opening to make it easy to clean the needle tip. A plate of Teflon served to support the film on one end as well as the needle system, the nitrogen-gas inlet, and the supports for the brass collimating plates, see Fig. 1. The supports consisted of brass rods inside cylinders of Teflon. The distance between the collimating plates and the needle and nozzle could easily be changed. Most of the results described below were obtained with a separation of 2 in. between needle and first plate, and 3 in. between the plates and between the second plate and the nozzle. The collimating orifice in each plate was a circular hole 1 cm in diameter.

Gas and Solution Flow Rates

Nitrogen gas at room temperature and atmospheric pressure flowed through the chamber at velocities that varied from 4.8–14.7 liters min^{-1} . The solution liquid flow rate was $0.3 \pm 0.1 \text{ cm}^3 \text{ min}^{-1}$. On the average the vapor of the mixed solvent constituted about 1% of the total gas system after complete evaporation of the solvent. The solution pressure head at the needle was 35 ± 7 torr. The shape of the spray consisted of a stream about 0.125 in. long which broke up into a fine, systematic cone-shaped spray which did not visibly wet the first collimating plate.

TABLE II. Summary of data for solutions of polystyrene.

Stopping voltages (neg. volts)	Frequency out of 16 experiments	Molecules/charge	Theoretical stopping voltages for $v_0 = 743$ m sec ⁻¹		
			1.02 v_0	v_0	0.90 v_0
51 000 Molecular weight					
150-200	3	1	149	146	132
250-275	9	5/3	248	243	219
300-350	6	2	297	291	263
350-400	3	5/2	371	364	329
450-475	8	3	446	437	394
500-525	5	7/2	520	510	460
550-600	3	4	594	582	525
750-800	5	5	743	728	655
850-900	3	6	891	874	787
411 000 Molecular weight					
7 Experiments					
200-250	2	$\frac{1}{5}$	250	235	212
350-400	5	$\frac{1}{3}$	400	392	354
600-650	5	$\frac{1}{2}$	600	588	531
900-925	3	$\frac{3}{4}$	897	881	793
1000-1050	3	$\frac{5}{6}$	999	979	881
411 000 and 51 000 Mixed solution					
2 Experiments					
100-125	1	$\frac{3}{4}$	111	109	98
250-300	2	2	297	291	263
450-475	1	3	446	437	394
550-600	2	4	594	582	525
700-725	1	5	743	728	655
850-875	1	6	891	874	789

The Nozzle-Skimmer System

Figure 2 illustrates the nozzle and skimmer. The nozzle and skimmer apertures were both 0.004 in. in diameter and the separation of the apertures was 0.030 in. The distance from the skimmer aperture to the first grid of the Faraday cage was 2.94 in. The cone angle of the skimmer was 62° on the outside and 50° on the inside as recommended by Kantrowitz and Grey.¹³

The Pumping System

The Kantrowitz-Grey nozzle-skimmer system¹³ makes possible the reduction in pressure from atmospheric to about 10⁻⁴ torr through a two-stage pumping system as illustrated in Fig. 1. The nozzle chamber was pumped by a mechanical pump of 425 liters min⁻¹ capacity while the skimmer chamber was pumped by a cold trapped diffusion pump backed by a 140-liter min⁻¹ mechanical pump. The effective pumping speed of this latter combination at the skimmer chamber was somewhat over 100 liters sec⁻¹. When the pressure in the evaporation chamber was atmospheric the pressure in

the nozzle chamber was 0.13 torr and in the skimmer chamber 1×10⁻⁴ torr.

The Faraday Cage and Grids

Figure 1 illustrates the Faraday cage and grid system. The first grid met by the molecular beam was at ground potential; on the second, potentials up to ±3 kV could be established. The cage was mounted on a Teflon rod for insulation.

Electrical Components

The high voltage on the needle varied between 0 and 30 kV. The operating needle voltage was usually 10 kV negative with -3 kV on the first collimating plate and -1.4 kV on the second. Current to the first collimating plate could be measured; it usually was about 0.2 μA, but when a corona discharge occurred, it was much greater than this. The current to the Faraday cage was of the order of magnitude of 10⁻¹⁴ A and was measured by means of a Victoreen vibrating-reed

electrometer whose long response time, about 20 sec, was helpful in smoothing out current fluctuations so that a reasonably accurate average value with an uncertainty of about $\pm 10\%$ could be measured. The repeller grid voltages came from a Fluke power supply and the molecular beam of ions was scanned by increasing the repeller voltages in units of 50 V. Because of instability of the spray it was not possible to scan in any smaller voltage increments.

The system was first tested with no spray and only air ions produced by a voltage of -15 kV on the needle. The current of 3×10^{-14} A to the Faraday cage was easily stopped by -10 V on the retarder grid or by putting a paper shield over but not touching the nozzle inlet to the vacuum system. After reversing all potentials, the same results were obtained with positive ions. These tests clearly showed that air ions generated at atmospheric pressure could be converted into a molecular beam by the supersonic nozzle and skimmer system and detected in a Faraday cage.

General Operation and Behavior of the Spray

The best results were obtained with a low liquid flow rate and a voltage on the hypodermic needle slightly below that which would produce a corona discharge. Under these conditions the current to the first collimating plate was less than $0.2 \mu\text{A}$. On corona formation the current rose to $25 \mu\text{A}$ and it was usually observed that a whisker formation of a black deposit had formed. The tiny whiskers were brittle and could easily be removed from the needle. It was noticed that after several minutes of operation the spray sometimes became unstable and corona discharge occurred. The instability may have been due to a slow charge build-up on the Teflon rods supporting the collimating plates and the needle system. When the corona discharge occurred, it could always be detected because the current to the Faraday cage dropped to zero.

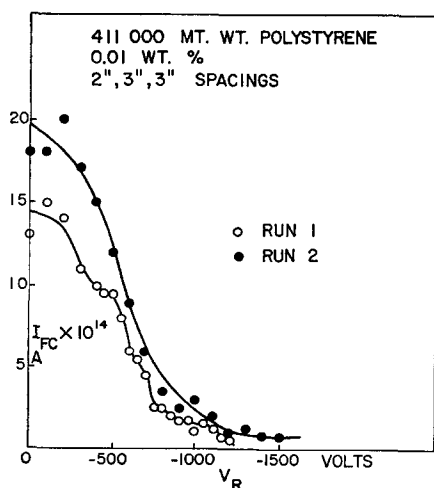


FIG. 8. Same as Fig. 5, but for 411 000 amu PS.

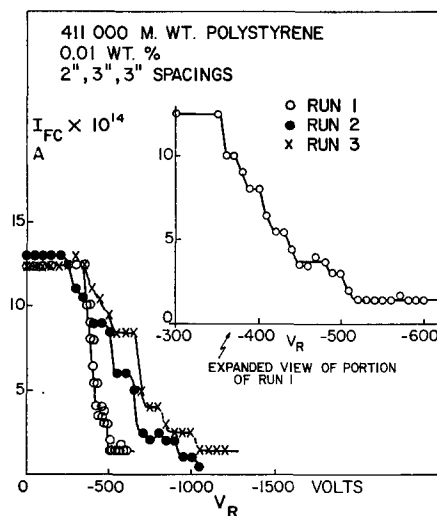


FIG. 9. Same as Fig. 8. Insert shows an expanded plot of the data of Curve 1.

RESULTS

Pure Solvent

In order to identify the current due to macroions it was first necessary to investigate the currents to the Faraday cage when pure solvent alone was being sprayed. Figure 3 illustrates the first results obtained; the Faraday cage currents in units of 10^{-14} A are plotted as a function of the repeller voltage for the following distances between needle and first plate, first and second plates, and second plate and nozzle, respectively, namely 2, 2, and 2 in.; 1.5, 1, and 1 in.; and 2, 1, and 1 in. Although it was originally expected that a small repeller voltage would prevent all solvent ions from reaching the Faraday cage, much to our surprise voltages as high as -2000 V or more were required to bring the currents to zero. This may have been due to incomplete evaporation of all drops, or to cluster or polymer formation in the spray. Increasing the distances involved reduced the over-all current and also the repeller voltage required to attain the state of zero current. Assuming unit charge, the radius of a droplet requiring a stopping voltage of -1500 V can be calculated to be 0.001μ . At longer distances between needle and nozzle one would expect the evaporation to be more complete.

In contrast to the data of Fig. 3, the results plotted in Fig. 4 represent more nearly the ideal behavior. Here the current dropped to 1×10^{-14} A or less with the application of 20 V negative retarding potential. The initial negative slope of the curve was very steep. At greater distances of separation the current should have been even smaller and, indeed, rather negligible in light of the data on the macromolecular solutions to be described below. The data of Fig. 4 were obtained several months after those of Fig. 3 when considerably more experience in the operation of the spray had been obtained.

TABLE III. Normalized percentage of macroion current due to separate species.

51 000 amu Solution		411 000 amu Solution		Mixed solution	
Molecules/charge state	% current	Molecules/charge state	% current	Molecules/charge ^a state	% current
1	8.4	$\frac{1}{5}$	25.4	$\frac{3}{4}$	8.2
5/3	8.7	$\frac{1}{3}$	34.8	2	25.4
2	19.2	$\frac{1}{2}$	22.5	3	15.6
5/2	7.9	$\frac{3}{4}$	11.7	4	15.6
3	18.3	$\frac{5}{6}$	5.6	5	18.8
7/2	13.8			6	16.4
4	9.6				
5	8.3				
6	5.8				

^a In the case of the mixed solution, the molecules/charge states were calculated for the 51 000 amu PS.

Solution of 51 000 Molecular Wt Polystyrene

Using a 0.01 wt % solution of polystyrene (PS) of weight-average molecular weight, 51 000, the data of Fig. 5 were obtained. One notices first of all an order of magnitude increase in the Faraday cage current over that of the pure solvent shown in Figs. 3 and 4. Second, in contrast to the pure solvent curves, definite plateaus are immediately evident. The reproducibility of the voltage of the sudden decrease in current is quite good for several of the plateaus. The first drop of current occurred at about 250 V which is 100 V greater than expected for a simple monomolecular species of unit charge. Other curves were obtained, however (Fig. 6), in which the initial drop in current did occur at the predicted voltage of 150 V (Table I). To attempt to increase the number of monomeric macroions in the beam, the concentration of the solution was reduced to one-sixth of its initial concentration. The macroion current was considerably reduced, Fig. 7, and the first dropoff in current did occur closer to the theoretical voltage of 146 V.

In Table II the results of 16 current-voltage curves are summarized. The first column gives the voltage range at which the dropoff in the current occurred; the second column, the number of times out of 16 curves that particular break in the curve was observed; the third column, the number of molecules of the PS per unit charge for which the theoretical stopping voltages of Columns 3, 4, and 5 were calculated. It will be noted that best agreement with the data was obtained for a theoretical velocity of the macroion equal to $1.02v_0$ where v_0 is the calculated velocity of the supersonic jet at the entrance to the skimmer.

Solution of 411 000 Molecular Wt Polystyrene

The first results obtained with a 0.01 wt % solution of PS of 411 000 amu are illustrated in Fig. 8. The magnitude of the current at zero repeller voltage was surprisingly high considering the fact that at 0.01%, the number of macromolecules per cubic centimeter of

solution was only approximately $\frac{1}{6}$ that of the solution of 51 000 amu PS. One of the curves of Fig. 8 was the first curve observed in which the existence of plateaus was suggested. Other typical curves for the 411 000-amu solution are illustrated in Fig. 9. Table II also summarizes the data for the 411 000-amu solutions.

Mixed Solution

Data for one of the current voltage curves obtained in the case of the 0.005 wt % 51 000 and 0.005 wt % 411 000-amu PS have already been published.⁷ Results for the two curves obtained are summarized in Table II.

Table III gives the average percentage decreases in the current at the stopping voltages listed.

INTERPRETATION OF THE DATA

If the Mach number of the supersonic beam is known, i.e., the ratio of the jet velocity to the velocity of sound, then the speed of sound, a , under the conditions of the jet can be calculated from the following equation,¹⁵ assuming a to be the same in our nitrogen-vapor mixture as in air (the average molecular weights are almost identical):

$$a = a_0 [1 + (\gamma - 1)M^2/2]^{-1/2}, \quad (15)$$

where a_0 is the speed of sound at 760 torr and 25°C, 347 m sec⁻¹. The Mach number was estimated to be 7.5 from the curves of Owen and Thornhill¹⁸ for our nozzle diameter and nozzle-skimmer separation. Taking γ to be 1.4, a was calculated to be 99 m sec⁻¹ and v_0 , the jet velocity at the skimmer, to be 743 m sec⁻¹. Referring to Table II it will be seen that the jet velocity which best agrees with the velocity calculated from the stopping voltages is 758 m sec⁻¹ or only 2% greater than the theoretically expected velocity. Thus we come to the conclusion that the velocity of the macroions is that of the jet; this conclusion is well within the experi-

¹⁸ P. L. Owen and C. K. Thornhill, Aeronautical Res. Council Reports and Memoranda, No. 2616, 1948, Fig. 2.

mental uncertainties. In this connection it is interesting to point out that Abuaf, Anderson, Andres, Fenn, and Miller¹⁹ recently demonstrated that in a 1% xenon-99% hydrogen mixture expanding from an 0.051-cm orifice at 1980°K the xenon velocity approached that of the hydrogen as the pressure increased from 10-100 torr and became equal to it at still higher pressures.

Another observation that can be made is that there has been a remarkable monochromatization of macroion velocities in the jet. If this were not so, then we could expect that the sharp breaks in the current would not be nearly so sharp as they appear to be.

It is also interesting to observe that whereas in the case of the 51 000-amu PS solute the tendency is for singly charged dimers, trimers, etc., to exist in the beam, in the case of the 411 000-amu species, the tendency is to have multiply charged monomers, see Tables II or III. The most abundant species in the 51 000 case is the dimer whereas in the 411 000 case it is the triply charged monomer (although in the latter case the doubly and triply charged species are almost equally abundant). Of course, it should be realized that our data can give only ratios of mass/charge as in any mass spectrometric analysis. The surface of the macroion, assuming a spherically shaped entity, is proportional to (molecular wt)^{2/3}; hence the ratio of surfaces of the 411 000 and 51 000 macromolecules is equal to 8.0^{2/3}, approximately, or to 4.0. If the residual charges on the macroions are proportional to the surface area, then we might expect the 411 000 PS molecules to have four times the charge of a 51 000 PS molecule. In the case of the 51 000 dimer, and the 411 000 monomer, the ratio of surfaces is 2.5. As mentioned above, the doubly and triply charged 411 000 monomers are about equally abundant. Thus it would appear that to a first approximation the charges which remain on the macroion in the evolution of the charged drops are proportional to the surface area. Once again it should be remarked that we cannot distinguish between a doubly charged dimer and a singly charged monomer. By monomers in this paper, we mean single macromolecules, and by dimers, we mean two single macromolecules bound together by van der Waals forces.

The flat plateaus followed by the sharp drops in

current over a small voltage range are difficult to understand. Although fractionated polymers were used, the fractionation was not perfect, M_w/M_n equal to 1.06 in the 51 000 case and to 1.10 in the 411 000 case. Assuming either a Schulz-Zimm or a Wesslau distribution,²⁰ one can calculate the expected shape of the decrease in the current-voltage curve due to the molecular weight spread. Curves more like those of Fig. 7 are obtained. Whether or not additional fractionation occurs in our spray-nozzle-skimmer system is difficult to say at this beginning stage of our research. At any rate the flat plateaus are a rather remarkable phenomenon of the experiment.

To conclude, the data presented here demonstrate rather conclusively, we believe, that distinct macroions of definite mass-charge states can be produced in the gaseous state by the electrospray technique. Furthermore, these macroions can be concentrated in a supersonic jet and detected in a Faraday cage after small-molecular-weight ions have been repelled from the jet by suitable repeller voltages. We have yet much to learn, however, about the properties of the spray and of the macroions produced. The data obtained to date suggest numerous additional researches which we hope to carry out in the future.

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¹⁹ N. Abuaf, J. B. Anderson, R. P. Andres, J. B. Fenn, and D. R. Miller, Proc. Intern. Symp. Rarefied Gas Dyn. 5th 2, 1317 (1967).

²⁰ O. Saito, H. Y. Kang, and M. Dole, J. Chem. Phys. 46, 3607 (1967).