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NATIONAL BUREAU OF STANDARDS REPORT

7448

THE ELECTROPHORETIC MOBILITY OF ASPHALTENES IN NITROMETHANE

by

James R. Wright and Richard R. Minesinger



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Organic Building Materials Section
Building Research Division

Sponsored by

National Bureau of Standards

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ABSTRACT

The microscope method of electrophoresis was employed to determine the electrophoretic mobility of asphaltenes in a nonaqueous system. Nitromethane was used as the suspending liquid. The electrophoretic mobilities of asphaltenes from 24 air-blown asphalts were measured by this method. All asphaltenes were found to bear a positive electrical charge, although the magnitude of charge varied as denoted by different electrophoretic mobilities. The presence of an electrical charge on asphaltenes supports the colloid theory of asphalt.

1. INTRODUCTION

The colloidal nature of asphalt was first recognized by Nellensteyn [1]^{1/}, who proposed that asphalt contains three principal fractions; (a) the medium or disperse phase (oils), (b) the lyophile part or protective bodies (resins), and (c) the lyophobe part (asphaltenes) which he believed to be elementary carbon. While many investigators accept Nellensteyn's colloid theory of asphalt, the elementary carbon nucleus concept has been abandoned [2]. Instead, the asphaltenes, which were shown by elemental analysis to contain C, H, N, O, and S [3], are considered to be dispersed in the continuous oil phase, with the dispersion being maintained by the resins [4].

Many factors have been cited in the literature to prove that asphalt is a colloidal system. Pfeiffer and Saal [5] proposed that the dispersed phase consists of asphaltenes complexed with high molecular weight components of the maltenes (oils and resins). They called this complex an asphaltene micelle. The continuous phase, or intermicellar phase, consists of the low molecular weight constituents of the maltenes. The asphaltenes are peptized to different degrees due to the aromatics and resins content of the maltene phase. Eilers [6] refers to a number of cases which showed that the rheological behavior of most asphalts is that of a colloidal dispersion. In the same paper, this author presents data on the voluminosity of asphaltenes in solutions, which he cites as proof of the colloidal properties of asphalt.

^{1/}

Numbers in brackets refer to literature references at the end of this report.

In an investigation of crude oils by ultra-centrifuging, at 80,000 times gravity, Eldib, et al [7] found that the material which moved to the bottom of the tube was colloidal in nature and was rich in asphaltenes. Swanson [4] has shown by dielectric constant experiments that asphaltenes are not homogeneous, and are polar in character. Csanyi and Bassi [8] found that the conductivity of a benzene-methanol solution was increased significantly by the addition of asphaltenes.

While many references may be cited which attest to the colloidal nature of asphalt, direct experimental evidence to support this theory is limited. For example, in the literature there is little experimental proof, by a direct method of measurement, that asphaltenes are electrically charged. However, if asphalt is truly a colloidal system, the dispersed phase (asphaltenes) probably would carry an electrical charge because one of the basic properties of colloidal particles is that they move in an electric field, i.e. exhibit electrophoresis [9, 10].

The purpose of the present work was to determine by a method of direct observation, microelectrophoresis, what charge, if any, was present on asphaltenes. Since it was not possible to disperse asphaltenes in water, the adaptation of the microelectrophoresis method [11] to a suitable nonaqueous system was an important part of the research.

2. APPARATUS, MATERIALS, AND PROCEDURES

2.1 Electrophoretic Mobility Apparatus

2.1.1 Description of the Apparatus

The glass cell used for the electrophoretic mobility measurements was of the Northrup-Kunitz type [12]^{2/}. This is a rectangular-type cell with dimensions of 4.5 cm between the platinum electrodes, 1.25 cm wide, and 0.056 cm deep. The cell was mounted on a specially designed lucite base which was positioned on the microscope stage by machined positioning pegs. This insured using the same part of the cell for every sample, and eliminated the problems of vibration and support due to the rubber connections as observed by Thompson [13].

^{2/}

Obtained from A. H. Thomas Company, Philadelphia, Pennsylvania.

Reversible zinc electrodes were placed in the end vessels and connected in series through a reversing switch to direct current power supply (0 - 300 volts). Saturated ZnSO_4 was used as the electrolyte. A Spencer microscope with a 30X eyepiece containing a cross-hatch graticle and both 10X and 20X objectives, was used for observing particle movement. The source of illumination was a detached microscope lamp, with a heat filter, focused on a reflecting mirror. This minimized temperature changes in the cell while measuring particle movement. Figure 1 is a schematic drawing of the electrophoresis apparatus.

Particle movement was measured by an electric timer^{3/} which could be read directly to 0.01 second. The timer was equipped with a microsecond delay switch which completed the circuit when held closed manually. This permitted the operator to time the movement of a given particle with two motions instead of four as would be required with a stopwatch.

The microscope, electrophoresis cell, and auxiliary cells were mounted on plywood. This in turn was supported by cork and sponge rubber. These precautions eliminated ordinary building vibrations. The entire apparatus was used in an air-conditioned laboratory.

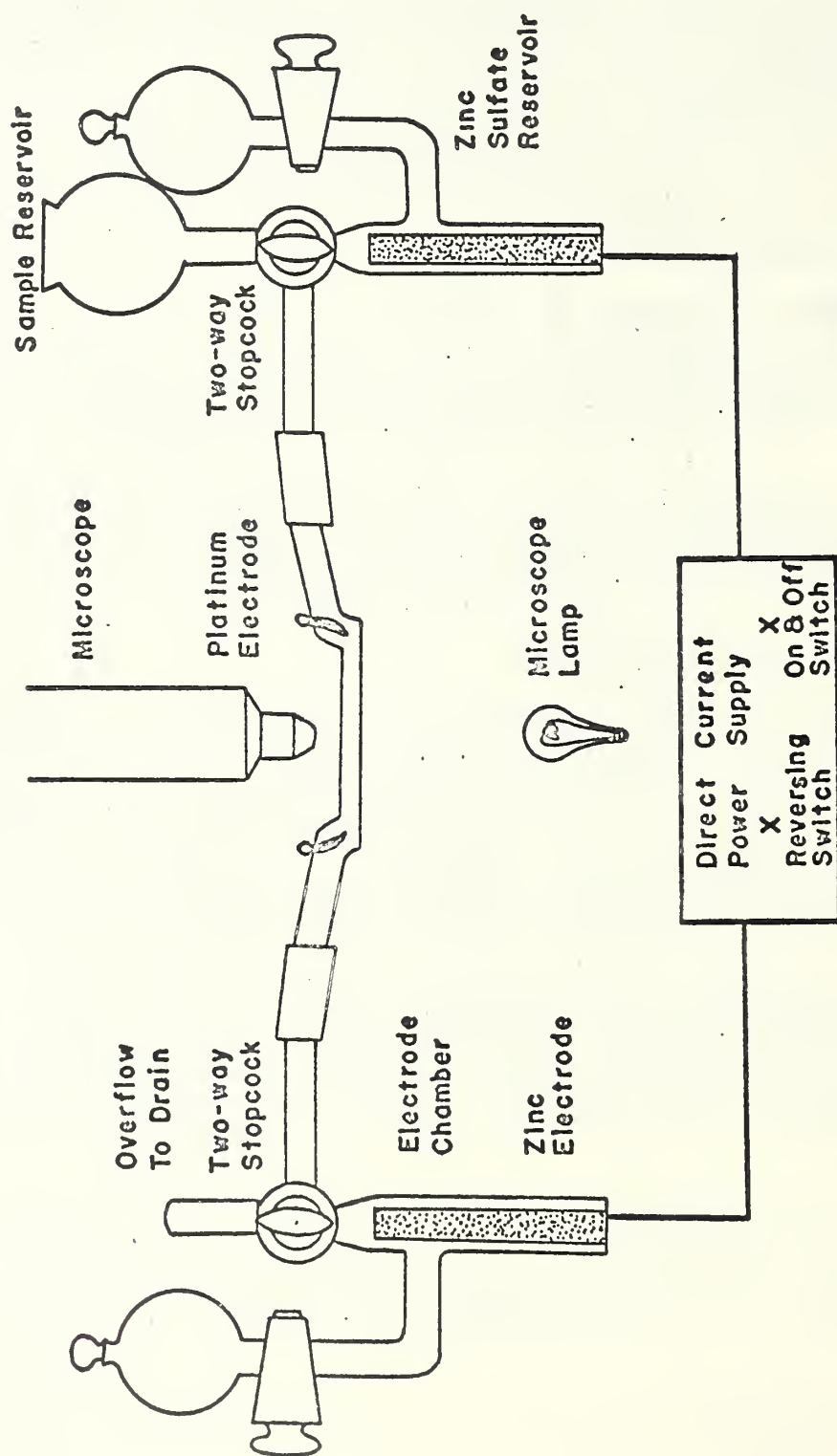
2.1.2 Calibration of the Apparatus

The ratio of applied EMF to the potential difference between the platinum electrodes in the electrophoresis cell was determined by the means of a quadrant electrometer.^{4/} The applied voltage was measured by a volt-ohm meter attached directly to the terminals of the zinc electrodes. This eliminated any error due to voltage drop between the power supply and the zinc electrodes. (Subsequently, a calibration curve was made for the voltage applied by the power supply and that obtained at the zinc electrodes. Applied voltages used in calculating particle mobility were taken from this curve).

Potentials ranging from 40 to 175 volts were applied at the zinc electrodes and the potential difference between the platinum electrodes was measured. Twenty measurements were made in each direction. An average value was used to calculate the ratio of applied voltage to the potential difference between the platinum electrodes. The value obtained was 5.86.

^{3/} Obtained from the Standard Electric Time Company, Springfield, Mass.

^{4/} Method described in "Directions for Use for Cataphoresis Apparatus No. 2873" furnished by A. H. Thomas Company, Philadelphia, Pa.



ELECTROPHORESIS APPARATUS

FIGURE 1. SCHEMATIC DIAGRAM OF ELECTROPHORETIC MOBILITY APPARATUS.

The cell depth was measured with the microscope. Dry asphaltenes, 1 - 5 μ diameter, were sifted into the cell before assembly and used as focusing points on the top inside and bottom inside of the cell. The cell depth, as measured by the microscope fine adjustment screw, was 565 μ . However, as pointed out by Thompson [13], the apparent depth of the cell when filled with water, for example, is less because of refraction by the contents unless a water-immersion objective is employed. The apparent depth of the present cell when filled with water was 424 μ which agrees well with the value of 423 μ as calculated by the method of Northrup [14]. Apparent depths were determined experimentally for the organic liquids used in measuring asphaltene mobility. Top and bottom stationary levels were 0.211 and 0.789 times the measured cell-depth values, respectively [13].

The cross-hatch graticle in the microscope eyepiece was calibrated with a stage micrometer. Each square was 50 μ across at 300X and 22 μ across at 600X.

The direction of positive particle velocity was determined for the apparatus assembled as shown schematically in Figure 1. The cell was filled with a dilute oil/water cationic emulsion. With the reversing switch in the "up" position, the particles, as viewed through the microscope, moved from left to right. Thus, positive velocity or the presence of a positive particle charge was shown by left to right movement in the apparatus. These results were verified by the migration of cationic and anionic asphalt emulsions, respectively.

As a final check on the present microelectrophoresis apparatus, a cell-depth profile was made with a dilute cationic o/w type asphalt emulsion. Particle velocity measurements were made at each eighth of the cell depth. A plot of particle velocity versus cell depth resulted in a parabolic curve. According to Thompson [13], this indicated that only electrophoretic effects are being observed.

2.2 Materials

2.2.1 Asphaltenes

The asphaltenes used in this research were obtained from twenty-four air-blown roofing asphalts. The properties of the asphalts were previously described by Greenfield and Wright [15] and Wright and Campbell [16]. The asphaltenes were separated from the maltenes by the method of Kleinschmidt [17], i.e. by extracting the maltenes with n-pentane.

Normally, in the separation of asphaltenes from n-pentane, each asphalt is digested for a fixed period of time. It seemed likely that if the degree of association of asphaltenes and maltenes varied among asphalts, the degree of separation would vary also for a given time of pentane digestion. To check this possibility, asphaltenes from four asphalts of different accelerated weathering durabilities were soxhlet extracted with n-pentane for eight hours at which time the extracting liquid was essentially colorless. Evaporation of the pentane resulted in maltenes amounting to 5.8 to 10.2% by weight of the original asphaltenes. These results showed that "purification" of the asphaltenes was necessary before attempting to measure electrophoretic mobility.

Subsequently the asphaltenes from all 24 asphalts were "purified" by the following procedure: The particle size of the asphaltenes was reduced to a maximum of ca 10 μ by pulverizing in a Wiley Mill (Laboratory Intermediate Model, 60 mesh screen). Five grams of the pulverized asphaltenes were soxhlet extracted with 400 ml of n-pentane for 8 hours. The extracted asphaltenes were vacuum dried for 19 hours at 35°C and 10 mm (Hg) pressure. All extractions were made with Phillips Pure-Grade n-pentane. A gas chromatograph of this product showed 99.88% n-pentane. The only impurity was iso-pentane.

The pulverized asphaltenes remained finely divided after extraction, and were easily dispersed in the organic suspending liquid for electrophoretic mobility measurements.

2.2.2 Dispersion Medium for Asphaltenes

Since asphaltenes cannot be wet by or dispersed in water, it was necessary to use a non-aqueous system for electrophoretic mobility determinations. The factors to be considered in selecting a non-aqueous suspending liquid are suggested by the Helmholtz-Smoluchowski equation [11], which is:

$$u = \frac{e\zeta E}{4\pi \eta}$$

where: u = electrophoretic mobility
 e = dielectric constant of the suspension
 ζ = zeta potential
 E = voltage drop between the platinum electrodes
 η = viscosity of the suspending liquid

In addition to these factors, it was desirable that the asphaltenes be insoluble or sparingly soluble in the organic suspending liquid.

Van der Minne and Hermanie [18] in their extensive research on electrophoretic mobility in non-aqueous systems have shown that a suspending medium must have a minimum dielectric constant in the range of 10 to 15 in order to measure particle mobility normally and in the same way as in aqueous systems. Preliminary experiments in this laboratory with a series of alcohols as suspending liquids, showed that a viscosity of 2.8 centipoises at 25°C represented the maximum, if high applied potentials were to be avoided. With these limits as guides, i.e. $\epsilon_{\min} = 14$ and $\eta_{\max} = 2.8$ centipoise, the International Critical Tables^{5/} were reviewed for organic compounds which were potential suspending liquids for asphaltenes. A total of 82 compounds was found.

The compounds were screened with respect to toxicity, volatility, availability, etc., and reduced to 20 in number. These were procured in the highest purity commercial grades and evaluated as suspending liquids for asphaltenes. N, N-Dimethylacetamide and N, N-Dimethylformamide were also included. The compounds are listed in Table 1.

A spectrographic method was used to measure the relative solubility of the asphaltenes in each suspending liquid. Ten milligrams of asphaltenes were dissolved in 100 ml of chloroform, and the absorbance measured in the 400 to 600 m μ range with a Beckman DU Spectrophotometer. Thus, the absorbances in all of the organic liquids evaluated were relative to those in chloroform.

Ten milligrams of asphaltenes were mixed with 10.0 ml of each of the 22 compounds being evaluated, and allowed to stand overnight. In most cases the asphaltenes settle to the bottom of the container. Where asphaltenes were observed to be suspended, they were removed by filtration. Absorbances were determined and the percent asphaltenes dissolved, relative to chloroform, was calculated for each liquid. The results are given in Table 1. Liquids dissolving more than 6.0% asphaltenes were eliminated from further consideration.

^{5/} Dielectric constant data from Volume VI; Viscosity data from Volume VII of the International Critical Tables, respectively.

TABLE 1. COMPOUNDS EVALUATED AS SUSPENDING LIQUIDS
FOR ASPHALTENES

<u>No.</u>	<u>Name</u>	<u>Dielectric Constant</u> (20°C)	<u>Viscosity</u> (centipoise @20°C)	<u>Asphaltene Solubility</u> (%) ^{a/}
1	Propionitrile	27.7	0.41 ^{f/}	1.03
2	n - Propyl nitrate	14.2 ^{d/}	---	10.8
3	N, N - Dimethylacetamide	---	---	10.3
4	iso - Butyronitrile	20.8 ^{b/}	---	1.68
5	Propionaldehyde	18.9 ^{c/}	0.41	6.0
6	Nitroethane	30.0 ^{d/}	---	2.06
7	Nitrobenzene	36.0	2.03	60.0
8	Acetonitrile	38.8	0.36	0.22
9	2 - Propanol	26	2.22 ^{g/}	1.41
10	Cyclohexanone	18.3	2.30 ^{c/}	55.0
11	Methanol	33.7	0.59	0.26
12	N, N - Dimethylformamide	---	---	2.55
13	2 - Butanone	18.5	0.43	9.4
14	Ethanol	25.9	1.7	0.87
15	Nitromethane	39.4	0.62 ^{f/}	0.24
16	Mesityl oxide	15.4	---	17.0
17	2 - Chloroethanol	25.8 ^{b/}	---	0.69
18	α - Toluntrile	18.3	---	3.5
19	Ethyl cyanoacetate	27.7 ^{e/}	---	0.16
20	2, 4 - Pentanedione	23.1	---	5.1
21	Citraconic anhydride	40.3	---	2.6
22	O - Nitroanisole	24.2	---	7.1

^{a/} Based on solubility in chloroform as 100%.

^{b/} 24°C.

^{c/} 17°C.

^{d/} 18°C.

^{e/} 21°C.

^{f/} 25°C.

^{g/} 22°C.

The remaining compounds were evaluated as suspending liquids for asphaltenes in the apparatus described previously. Mixtures of 70 mg of asphaltenes and 70 gm of each liquid were made and the preliminary mobility rates determined. A number of compounds were not satisfactory due to high viscosity, excessive settlement, low mobility rates, etc. Nitromethane was selected as the best suspending liquid for asphaltenes ($e = 39.4$, asphaltene solubility = 0.24%). Eastman Spectro Grade nitromethane was fractionated through a packed Whitmore-Fenske column. The infrared spectrum of the fractionated product was compared with that of API Scan, Serial No. 1751.

2.3 Procedure for Electrophoretic Mobility Measurements

The asphaltene samples were prepared by dispersing 70 mg of asphaltenes in 70 grams of nitromethane (0.10% concentration), and the mixture allowed to stand about 30 minutes. The apparatus was adjusted to top stationary level position, and the electrophoresis cell filled with nitromethane, care being taken to avoid the presence of air bubbles. The asphaltene suspension was poured into the sample reservoir and a portion of it introduced into the electrophoresis cell. The stopcocks were turned to the ZnSO_4 - Zn junctions and the asphaltene particles checked to insure that no movement or drift was taking place under zero potential.

Sufficient potential was applied to the zinc electrodes to produce particle movement of such a velocity as to eliminate any diagonal drift (usually not less than 75 volts). Particles of about 5μ diameter were selected for mobility rate measurements over a distance range of 50 to 150μ , and their movements timed.

The field was reversed about every 30 seconds to prevent electrode polarization [19]. The potential was reduced to zero when readings were not being made. Fresh samples of asphaltenes were introduced into the electrophoresis cell periodically or when too few particles were in focus for the desired number of readings. When the readings for a given sample were completed, the asphaltene suspension was drained from the system.

The apparatus was prepared for the next sample by flushing with chloroform (to dissolve residual asphaltenes), methanol, and nitromethane. The ZnSO_4 -Zn electrode compartment was always inspected for gas bubbles which could be removed by the addition of electrolyte from the ZnSO_4 reservoir. The presence of any gas in this chamber sometimes caused drift of the particles with no applied potential; presumably due to unequal pressures in the closed system.

For each asphaltene sample, 20 to 30 particle velocity readings were made in each direction. A single average time value was used to calculate the electrophoretic mobility (u) by the following equation:

$$u = \frac{D}{t} \cdot \frac{r}{V} \cdot d$$

where:

- D = distance particle travels during timing period
- t = time required to travel distance D
- r = ratio applied potential to potential difference between the platinum electrodes
- V = voltage applied to zinc electrodes
- d = distance between the platinum electrodes

By this equation, electrophoretic mobilities are expressed in $\mu/\text{sec}/\text{volt}/\text{cm}$. In the apparatus used in the present work, $r = 5.86$ and $d = 3.25 \text{ cm}$.

3. RESULTS

Electrophoretic mobility measurements were made on asphaltenes from 24 asphalts. The number of samples measured for asphaltenes from each asphalt range from one to three. The results are presented in Table 2.

In Table 3 the electrophoretic mobility data on asphaltenes from six asphalts are compared to various properties of the original asphalts. Comparisons are made with accelerated weathering durability, carbonyl index, filtration time, solubility parameter and asphaltene content [15].

The statistical data on the electrophoretic mobility of asphaltenes from six asphalts are presented in Table 4. For each asphalt, three separate samples of asphaltenes in nitromethane were evaluated and the results reported. The data are presented as average time values in each direction, and a final mobility value in $\mu/\text{sec}/\text{volt}/\text{cm}$.

4. DISCUSSION

4.1 General

By subjecting a dispersion of asphaltenes in nitromethane to an electric field, as described previously, it was soon established that asphaltenes carry an electric charge. It was further established that this charge is of sufficient intensity to produce particle mobility by ordinary microelectrophoresis techniques.

TABLE 2. ELECTROPHORETIC MOBILITY DATA ON
ASPHALTENES FROM TWENTY-FOUR ASPHALTS

No.	Asphalt Source	Asphaltene Samples (number) ^{a/}	Asphaltene Migration Time ^{b/}			Electrophoretic Mobility $\mu/\text{sec}/\text{volt}/\text{cm}$
			Direction		Avg.	
			Left	Right		
1	Tia Juana	3	4.31	4.22	4.26	4.61
2	Tia Juana-Lago Colon	1	3.62	3.70	3.66	5.36
3	Calif. Coastal (catalyzed)	2	5.07	4.94	5.00	3.93
4	Talco-Hankins	1	5.10	5.10	5.10	3.85
5	Kansas-Indiana	1	5.01	4.51	4.75	4.13
6	Talco	2	5.12	5.04	5.08	3.86
7	Talco-Heidleberg	1	5.28	5.21	5.24	3.75
8	Talco	3	4.92	4.94	4.93	3.98
9	Calif. Coastal (fluxed)	2	4.41	4.34	4.38	4.48
10	Lagomar	3	4.24	4.35	4.30	4.56
11	Kansas-Lyons	1	3.80	3.81	3.80	5.16
12	Tia Juana Medium	1	4.43	4.34	4.38	4.48
13	Venezuela (fluxed)	1	5.38	4.67	5.02	3.91
14	Tia Juana C	1	3.76	3.81	3.78	5.19
15	Arkansas Blend	1	5.07	4.99	5.03	3.90
16	Ill-Kan-Okla	3	5.14	4.97	5.06	3.89
17	Venezuela-Mid East	1	6.17	5.87	6.02	3.26
18	Los Angeles Blend	1	5.04	4.34	4.69	4.18
19	Kansas A	1	5.07	4.39	4.73	4.15
20	Santa Maria	3	4.28	4.05	4.16	4.70
21	South Mountain	1	4.73	4.68	4.70	4.18
22	Lagunillas	1	5.07	4.93	5.00	3.93
23	Talco	1	5.01	4.72	4.87	4.03
24	Baxterville, La.	3	4.78	4.58	4.68	4.20

^{a/} Designates number of duplicate asphaltene-nitromethane dispersions used in average time values for each mobility direction.

^{b/} Seconds per 100 μ distance at 97 applied volts. Values reported for each direction are averages of 20 readings per sample.

TABLE 3. COMPARISON OF THE ELECTROPHORETIC MOBILITY OF ASPHALTENES TO VARIOUS PROPERTIES OF THE ORIGINAL ASPHALTS^{a/}

Asphalt No.	Electrophoretic Mobility ^{b/} (μ /sec/volt/cm)	Durability (days ^{c/})	Carbonyl Index (ΔA)	Filtration Time (seconds)	Critical Solubility Parameter	Asphaltene Content (%)
20	4.70	52	0.225	150	8.08	41.6
1	4.60	54	0.066	203	7.85	42.0
10	4.56	59	0.058	305	7.97	38.7
24	4.20	48	0.061	284	7.99	38.9
8	3.98	46	0.064	216	7.90	45.0
16	3.89	93	0.038	642	7.73	39.8

a/ Source: S. H. Greenfeld and J. R. Wright, "A Study of Several Methods for Predicting the Durability of Roofing Asphalts," Materials and Standards Research (in press).

b/ The values given here are averages of those shown in Table 2.

c/ ASTM D 529-59%, Tentative Recommended Practice for Accelerated Weathering of Bituminous Materials.

TABLE 4. STATISTICAL DATA ON THE ELECTROPHORETIC MOBILITY OF ASPHALTENES

No.	Asphalt Source	Asphaltene Sample	Asphaltene Migration Time ^{a/}					Electrophoretic Mobility $\mu/\text{sec}/\text{volt}/\text{cm}$
			Direction		Direction		Avg.	
			Left	Right	Left	Right		
1	Tia Juana	a	4.43	4.23	4.34	4.32	4.33	4.53
		b	4.28	4.10	4.08	4.15	4.15	4.73
		c	4.30	4.22	4.44	4.32	4.32	4.54
8	Talco	a	4.94	4.99	4.87	4.95	4.94	3.98
		b	5.00	5.01	4.90	4.83	4.94	3.98
		c	4.70	4.93	5.13	4.94	4.93	3.98
10	Lagomar	a	4.09	4.07	4.31	4.51	4.25	4.62
		b	4.16	4.49	4.32	4.38	4.34	4.52
		c	4.33	4.33	4.26	4.33	4.31	4.55
16	Ill-Kan-Okla	a	5.46	5.10	4.71	4.73	5.00	3.92
		b	5.00	4.92	5.10	4.75	4.94	3.98
		c	5.03	4.86	5.53	5.45	5.22	3.77
20	Santa Maria	a	4.21	3.97	4.24	4.03	4.11	4.77
		b	4.32	4.10	4.33	4.01	4.19	4.67
		c	4.31	4.13	4.29	4.05	4.20	4.67
24	Baxterville, La.	a	4.65	4.71	4.77	4.77	4.73	4.15
		b	4.93	4.58	4.90	4.39	4.70	4.18
		c	4.72	4.50	4.72	4.50	4.61	4.26

^{a/} Expressed as seconds per 100 μ distance at an applied potential of 97 volts. Each entry is an average of 20 readings in a given direction.

The charge appears to be an inherent property of the asphaltenes, and is not due to such phenomenon as streaming potential, static effects, etc. This was proven experimentally by the facts that (a) no particle migration was observed unless a potential was applied, (b) the particles reversed direction upon reversal of the electric field, (c) the electrophoretic mobility of a given sample of asphaltenes in nitromethane did not decrease upon standing several weeks in the laboratory, and (d) asphaltenes exhibited positive velocity in a number of organic suspending liquids.

Further evidences that only real electrophoretic effects were observed in the asphaltene-nitromethane system were (a) the motion of the particles was uniform and rectilinear between electrodes, (b) the velocity was independent of the position in the observation area, (c) the velocity was proportional to the field strength, and (d) no evidence of particle chain formation indicating dielectric polarization was observed. According to Van der Minne and Hermanie [18], these are the criteria for real electrophoresis free from any other effects (e.g. electro-osmosis) which can cause particle mobility.

4.2 Sign of Asphaltene Charge

The results presented in Table 2 for the electrophoretic mobilities of asphaltenes from 24 asphalts, showed that all asphaltenes had positive velocity, i.e. were charged positively. While the charge intensity varied among asphaltenes from different asphalts, the sign of the charge did not.

These results are in agreement with the work of Swanson [4] who reported that asphaltenes show high adsorptivity on a glass surface which is negatively charged. The presence of a positive charge also supports the findings of Csanyi and Bassi [8] who, in their attempts to separate asphalt by electrical means, found that the asphaltenes from 13 out of the 15 asphalts studied deposited on the negative electrode.

The experimental work of Van der Minne and Hermanie [20] is strong evidence that the sign and magnitude of the charge is not due to the difference in magnitude of the dielectric constants of the two phases as indicated by Coehn's rule.

4.3 Source of Asphaltene Charge

The presence of an electrical charge on asphaltenes as determined by microelectrophoresis, provides essentially no information as to the source of the charge. Obviously, additional experimental work must be carried out to establish the charge source. It is postulated, however, that the charge may be due to any of three possibilities which are:

(a) A charged molecular complex formed by adsorption of aromatic maltenes by asphaltenes. The aromatic molecules act as an electron source for positively charged carbon atoms adjacent to electronegative nitrogen and oxygen atoms in the asphaltenes. This results in a deficiency of electrons in the adsorbed molecule and a net positive surface charge. (b) Interaction of the asphaltenes with the suspending liquid (nitromethane) in some way to produce a charge through ion formation, and (c) the presence of trace metals in the asphaltenes which may exhibit charge under the experimental conditions employed.

4.4 Relationship Between Asphaltene Charge and Various Properties of the Original Asphalt

The presence of an electrical charge on asphaltenes means that potential electrostatic^{6/} bonding forces exist in asphalt. The electrostatic bonds may be both intramolecular and intermolecular. In the latter case, electrostatic bonds could be formed between two asphaltene molecules or an asphaltene and a maltene molecule. Furthermore, if the electrostatic bonding forces between maltenes and asphaltenes were of sufficient order of magnitude, a direct relationship should exist between the electrophoretic mobility rate of the asphaltenes and those properties of the original asphalt, such as natural weathering durability, which are due to asphaltene-maltene association as proposed by Kleinschmidt and Snoke [21] and Greenfield [22, 23].

Table 3 was compiled in order to make a comparison of the electrophoretic mobility values of asphaltenes and various properties of the original asphalt; namely, accelerated weathering durability, carbonyl index, critical solubility parameter, and asphaltene content. Asphalt No. 20 has the highest asphaltene - electrophoretic mobility of the six asphalts. It also has the highest carbonyl index, the lowest filtration time and the largest solubility parameter value. The asphaltene content is above the 40% limit established for more durable asphalts [24], and the accelerated weathering durability is in the low-intermediate range. Conversely, asphalt No. 16 which has the lowest asphaltene - electrophoretic mobility

^{6/} The term electrostatic is used here to indicate some form of polar bonding forces. Conversely, all of the bonding forces in asphalt are not of the covalent type.

also has the lowest carbonyl index, the highest filtration time, the smallest solubility parameter value, and the longest accelerated weathering durability. The asphaltene content is in the range of the more durable asphalts. For the remaining four asphalts whose properties are intermediate between those of asphalts 20 and 16, no pattern can be found relating asphaltene - electrophoretic mobility to these properties. Since there appears to be no correlation between asphaltene - electrophoretic mobility and other properties of the asphalt, it is concluded that electrostatic bonding forces play a minor role in asphaltene-maltene association or asphalt durability. This is in agreement with the work of Heithaus [25] who found that asphaltene peptizability, as determined by flocculation ratio, played a minor role in asphalt weathering life.

4.5 Reproducibility of Results

The data in Table 4 were used to determine the reproducibility of results for the electrophoretic mobility measurements of asphaltenes in nitromethane. A statistical analysis of these data, with one instrument, one observer, and a constant voltage, for six asphalts with three samples each, showed that the computed standard deviation for the mobility values is $0.077 \mu/\text{sec}/\text{volt}/\text{cm}$, based on 10 degrees of freedom. Equivalently, the standard error of the average value of three samples is $\frac{0.077}{\sqrt{3}} = 0.045$. Correspondingly, the 95% confidence limits for the average of three samples are:

$$\text{Average of three samples} \pm 2.228 \times 0.045 =$$

$$\text{average of three samples} \pm 0.10 \mu/\text{sec}/\text{volt}/\text{cm}.$$

This compares favorably with the results of Gittens and James [19] who report that the confidence limit for a single mean at $p = 0.05$, is $\pm 3\%$.

5. SUMMARY

The electrophoretic mobilities of asphaltenes from 24 asphalts were measured by the microelectrophoresis method in a nonaqueous system using nitromethane as the suspending liquid. The experimental results showed that real electrophoretic effects were being observed, and that in the asphaltene-nitromethane system electrophoresis can be measured normally and in the same way as in the aqueous system. All asphaltenes were found to carry a positive electrical charge. The presence of an electrical charge on asphaltenes supports the colloid theory of asphalts.

The relationship between asphaltene electrophoretic mobility and various properties of the original asphalt is not clear. It is concluded that while electrostatic bonding forces may be present, these are not predominant in asphaltene-maltene association or asphalt weathering durability.

The reproducibility of the experimental method was found to be $\pm 0.1 \mu/\text{sec}/\text{volt}/\text{cm}$ at the 95% confidence level.

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