

Coacervation in Aqueous Cationic Soap Solutions

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Abstract

The properties of several coacervating long-chain quaternary ammonium salts were studied by means of light-scattering, viscosity, and diffusion measurements. The aqueous quaternary ammonium-electrolyte solutions, Hyamine 1622-NaCl, Hyamine 1622-NaNO₃ and EHDDAB-NaNO₃ systems, which form coacervates, show the following distinctive characteristics as compared to the non-coacervating Hyamine 1622-NaAc system:

a) The micellar solute species in a coacervate system is one of relatively low charge density.

b) The addition of electrolyte to a coacervate system produces a tremendous growth of the micellar species prior to two phase formation, in many cases larger than a one hundred fold increase as compared to the salt free solution.

c) The phenomenon of two phase formation in these cationic soap systems shows a pronounced specificity to the anion of the added electrolyte. This specificity may be qualitatively correlated to the ionization properties of the micellar species in the presence of added electrolyte.

d) A relatively narrow electrolyte transition range (ETR) may be described for coacervating systems, intermediate between zero electrolyte concentration and the critical electrolyte concentration necessary for two phase formation, in which a radical reorganization of the soap micelle occurs. Light-scattering, viscosity and diffusion data for a typical coacervating system, Hyamine 1622-NaCl-H₂O, indicate that for electrolyte concentrations below the electrolyte transition range, the soap micelle is isotropic. For electrolyte concentration in excess of the electrolyte transition range, the data are consistent with a cylindrical rod-shaped micellar solute particle.

Introduction

A NUMBER of dilute aqueous solutions of proteins (1), polyelectrolytes (2), and association colloids (3,4) behave as coacervates. The essential feature of coacervation phenomena is the separation of a homogeneous macromolecular or macroion solution into two solution phases under a variety of conditions, depending upon the nature of the macromolecular species. A unique property of aqueous two solution phase coacervate systems is the fact that the solvent component of the two phases is the same chemical species, i.e., H₂O. This is a major distinguishing characteristic of coacervates as compared to two phase systems involving immiscible solvents or unmixing in a homogeneous two component system upon the addition of a third component, such as occurs in alcohol-H₂O-K₂CO₃ systems. A colloidal solute particle migrating across the interface of a two phase coacervate system finds itself in essentially the same environment on either side of the interface. As a direct consequence of this special property of coacervate systems, these systems show a very weak

interfacial tension which cannot be precisely measured by conventional means.

From the point of view of composition, the difference between the two phases is a difference in concentration of the solute species. Structurally, the two phases differ in that the colloidal solute of the one phase (the equilibrium phase) is randomly oriented and the colloidal solute of the second phase (the coacervate phase) shows a great deal of order (5). In all cases where coacervation has been observed, the solute species are geometrically anisotropic particles. The driving force for coacervation phenomena is solute-particle interactions rather than solute-solvent interactions. These interactions involve both coulombic and long range vanderWall interactions of large aggregates in solution. Theories related to the solution properties of anisotropic colloidal solutes have been applied to coacervate systems (6,7,8,9) with some success in providing a qualitative rationale for the properties of these systems.

Coacervation is observed in some dilute soap solutions. This investigation is concerned with coacervation in several long chain quaternary ammonium salt solutions in which two solution phases are formed by the addition of simple electrolyte such as NaCl, NaNO₃, and Na₂SO₄ to a homogeneous cationic soap solution. This phenomenon is classified as a form of simple coacervation involving a single micellar polyion species.

It has previously been reported (10) that a) coacervation in cationic soap systems shows a pronounced specificity to the anion and a lesser sensitivity to the cation of the added electrolyte; b) the onset of two solution phase formation is characterized by an intense turbidity, a large increase in viscosity, and a decrease in the self-diffusion coefficient of the micellar solute; and c) a precondition for coacervation in soap systems is the transformation of the growing soap micelle from a geometrically isotropic particle to an anisotropic particle under the influence of electrolyte added to the system. Where this transformation does not occur (11), coacervation is not observed in soap systems with the addition of an electrolyte to the solution.

The purpose of this study is a detailed examination of the micellar structure in typical coacervating aqueous cationic soap systems with particular emphasis on the properties of the system at the onset of two phase formation. The experimental techniques employed in this study are those which are sensitive to the size and shape of the colloidal solute species.

Experimental

Materials. The following cationic soaps were used in this investigation

1. Hyamine 1622, di-isobutylphenoxyethoxyethyl-dimethylbenzylammonium chloride monohydrate.
2. HDTAB, hexadecyltrimethylammonium bromide
3. EHDDAB, ethylhexadecyldimethylammonium bromide
4. Cetol, hexadecyldimethylbenzylammonium chloride.

Hyamine 1622 was obtained from Rohm and Haas and contained 1.5% water as the only appreciable impurity. The EHDDAB and HDTAB were obtained

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from Eastman Organic Chemicals, and the Cetol from Fine Organics, Inc. All of the inorganic electrolytes used in this investigation were of C.P. grade.

Apparatus. Light-Scattering. Light scattering measurements were performed in a Brice-Phoenix photometer, using incident unpolarized monochromatic light of wave length 4360Å. The measurements were carried out in a cylindrical cell, with solution which had been filtered through mpore filters of 0.45 pore size. Refractive index increments (dn/dc) were determined with a Zeiss dipping refractometer. For soap concentrations above the critical micelle concentration, the refractive index increment is independent of the electrolyte concentration.

Viscosity. The viscosity measurements were performed in a modified Ubbelohde viscometer as described by Immergut and Schurz (12). The following equation was used to obtain the constants needed to calculate the kinetic energy corrections:

$$\eta = A\epsilon + B\epsilon/t \quad [1]$$

where η is the absolute viscosity, ϵ is the density of the solvent at the temperature of the experiment, t is the time of flow through each bulb and A and B are constants which were determined by measuring the viscosities of a standard liquid at two different temperatures. Hence, the absolute viscosity in each bulb was first calculated according to equation 1, and from these values the relative, specific, reduced, and intrinsic viscosities were determined in the usual manner. The average rate of shear (β) was calculated from the equation:

$$\beta = 8V/(3\pi r^3 t) \quad [2]$$

where r is the radius of the capillary, V is the volume of the bulb and t is the time of flow through the bulb under consideration. The reduced viscosities were extrapolated to zero shear gradient.

Diffusion. The diffusion measurements were carried out by the open-end capillary technique devised by Anderson and Saddington (13). The diffusion cells had an ID of about 1 mm and a height of about 5 cm. The diffusing micellar species was labeled by means of the water-insoluble dye, azobenzene (14). The concentration measurements before and after diffusion were determined spectrophotometrically. Diffusion times ranged from 3 to 8 days.

The solution of Fick's law for boundary conditions of these experiments is given by the equation:

$$D = 0.93321 L^2/t \log_{10} 0.81055 C_o/C_{av} \quad [3]$$

where D is the self-diffusion coefficient in cm^2/sec , L is the length of the diffusion cell, t is the time in seconds and C_o and C_{av} are the concentrations of the diffusing species in the cell before and after diffusion respectively.

Results and Discussion

Light Scattering—Viscosity—Diffusion. The light scattering properties of solutions consisting of cation soap-electrolyte- H_2O were studied at fixed soap concentration and constant temperature as a function of electrolyte concentration. Three of the cationic soaps studied, Hyamine 1622, Cetol, EHDDAB, showed the same general properties with several coacervating electrolytes. Figure 1 is a graph of the light scattering dissymmetries of a 3% Hyamine 1622- NaCl - H_2O system at 30C. In the absence of electrolyte and at low electrolyte concentrations, the dissymmetries are close to unity. The dissymmetry minimum at 0.09M NaCl is typical of polyelectrolytes and is associated with

TABLE I
Micellar Molecular Weights and Micellar Lengths of Coacervating Quaternary Ammonium Salts

Quat. amm. salt	Electrolyte	Micellar mol wt	L^2 (Å) micellar length
Hyamine 1622.....	0.20M NaCl	3.57×10^5	590
Hyamine 1622.....	0.30M NaCl	7.25×10^5	1120
HDDAB.....	0.233M KBr	1.86×10^6	1312
Cetol.....	1.10M NaCl	2000
EHDDAB.....	1.5M NaCl	3.5×10^6	2616

*As determined from dissymmetry measurements assuming rod-shaped particles.

coulombic inter-particle interactions. For NaCl concentrations in excess of 0.17M, a sharp linear rise in dissymmetry occurs. This abrupt change in dissymmetry in a narrow range of electrolyte concentration is typical of the coacervating soap systems investigated. At 0.30M NaCl , the data are consistent with an anisotropic colloidal particle of approximately 1120Å in length. The vertical dotted line represents the critical NaCl concentration necessary for two phase formation. The curve to the right of the critical electrolyte concentration (C.E.C.) represents the dissymmetries of the coacervate phase. The sharp drop in dissymmetry with further additions of electrolyte, in excess of the C.E.C., indicates a high degree of order in this phase resulting in considerable destructive interference of the scattered radiation. The drop in dissymmetry is consistent with theory which dictates that the coacervate phase is a highly ordered phase.

For the Cetol- NaCl - H_2O system, the onset of two phase formation shows a dissymmetry of 1.8 which may be interpreted as arising from a micellar particle with a length of $\sim 2000\text{Å}$. For the EHDDAB- NaNO_3 - H_2O system under the same conditions, a particle length of 2616Å is indicated. These measure-

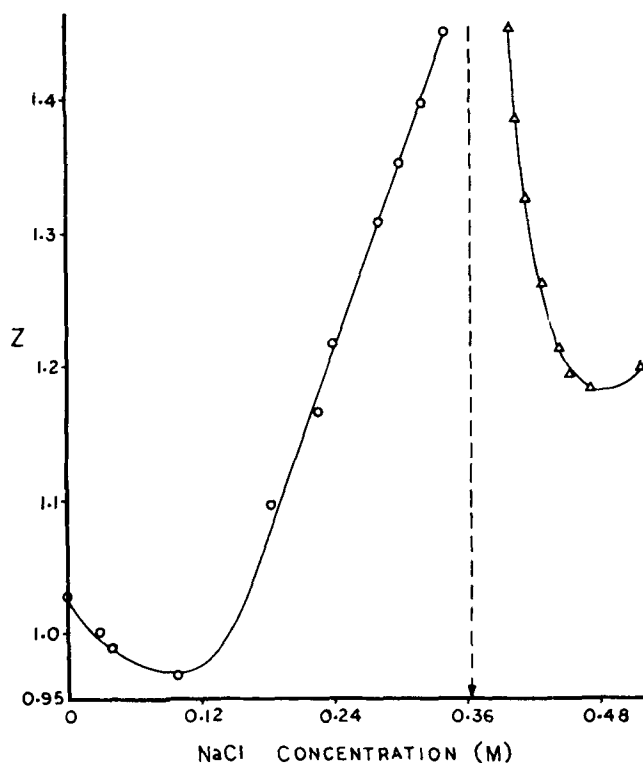


FIG. 1. Dissymmetry of hyamine 1622 at constant temperature ($T = 30\text{C}$) vs. NaCl concentration.

○—○ Homogenous systems
 △—△ Soap-rich layer of 2-phase systems
 - - - Critical electrolyte concn.
 Hyamine 1622 concn. = 3%.
 $\lambda = 4360\text{Å}$

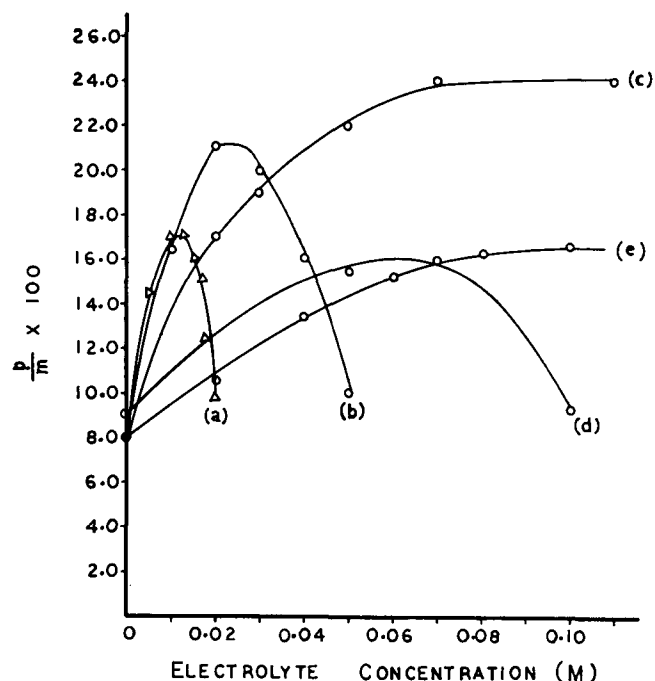


FIG. 2. Variation of micellar charge density (p/m) with addition of simple monovalent electrolyte.

- | | |
|---|---|
| (a) Hyamine 1622- NaNO_3 ,
T = 30C. | (c) Hyamine 1622- NaAc ,
T = 30C. |
| (b) Hyamine 1622- NaCl ,
T = 30C. | (d) EHDDAB- NaNO_3 ,
T = 36C. |
| | (e) HDTAB-KBr, T = 30C. |

Micellar charges (p) and aggregation numbers (m) are derived from light scattering data (1).

ments show that coacervation in cationic soap systems occurs over a wide range of micellar particle length. Table I summarizes the particle length data for solutions at the onset of two phase formation. This wide range of micellar particle length would indicate that although micellar geometric anisotropy is an apparent necessary condition for coacervation, micellar particle length is not the sole critical factor involved in coacervation phenomena in soap systems.

Two additional properties of coacervating cationic soap systems were derived from light scattering experiments. By the slope-intercept method previously described (10), micellar charge was determined for a number of systems for low electrolyte concentrations. Figure 2 represents three coacervating systems (curves a,b,d,) and two non-coacervating systems (curves c,e). The coacervating systems are (a) Hyamine 1622- $\text{NaNO}_3\text{-H}_2\text{O}$; (b) Hyamine 1622- $\text{NaCl-H}_2\text{O}$; (d) EHDDAB- $\text{NaNO}_3\text{-H}_2\text{O}$. The non-coacervating systems are, (c) Hyamine 1622- $\text{NaAc-H}_2\text{O}$ and (e) HDTAB-KBr- H_2O .

A common feature of the charged properties of coacervating soap systems, as a function of added electrolyte, is the appearance of an ionization maximum followed by a suppression of micellar ionization to a value of <10%. A 10% ionization represents an array of charged sites on the micelle periphery in which each charged site is separated from a neighboring charged site, on the average, by three uncharged polar head sites to which counter ions are bound. Curve (c) represents a more common soap micellar charge pattern (11). This curve represents the Hyamine 1622- $\text{NaAc-H}_2\text{O}$ system in which the micellar ionization rises to a limiting value of 25-27% and does not pass through a maximum value. Here, charged sites occur at alternate polar head positions on the micelle periphery. Curve (e) represents

the HDDAB- $\text{NaBr-H}_2\text{O}$ system where the ionization rises to a limiting value of 15%. The HDDAB- $\text{NaBr-H}_2\text{O}$ system is an intermediate case, in which neighboring micellar charged sites are separated by two uncharged polar head sites. The latter two systems are non-coacervating systems although structurally they are very different from each other. The micelles of the Hyamine 1622- $\text{NaAc-H}_2\text{O}$ system grow to a limiting micellar molecular weight of 54,000 and the light scattering data for this system are consistent with a spherical micellar model. For the HDDAB- $\text{NaBr-H}_2\text{O}$ system, Debye (15) has reported a cylindrical rod-shaped micelle of 1312A in length in 0.233M NaBr solutions. The HDDAB system shows the same micellar structure as the coacervating systems investigated. However, the system differs from coacervating systems in its charge properties. The micelles of the HDDAB- $\text{NaBr-H}_2\text{O}$ show a higher degree of ionization than a comparable coacervating system, the Hyamine 1622- $\text{NaCl-H}_2\text{O}$ system. A critical suppression of micellar ionization is not observed in the HDDAB- $\text{NaBr-H}_2\text{O}$ system with the addition of NaBr . The properties of the HDDAB- $\text{NaBr-H}_2\text{O}$ system would indicate that in addition to micellar geometric anisotropy, a low charge density of the micelle is a necessary condition for coacervation in cationic soap systems.

Micellar molecular weights were calculated for the Hyamine 1622- $\text{NaCl-H}_2\text{O}$ system using the general expression (Fig. 2, curve a):

$$H P_{90}(C-C_0)/(\tau-\tau_0) = 1/M + 2BC \quad [4]$$

where the terms of this equation have their usual meaning. For NaCl concentrations in excess of 0.05M the second term on the right hand side of this equation goes to zero. For 0.05M NaCl and at higher NaCl concentrations the intermicellar coulombic interactions are sufficiently screened so that the medium behaves as a theta solvent. Theta solvent properties are displayed at relatively low electrolyte concentrations in coacervating Cetol-electrolyte- H_2O and EHDDAB-electrolyte- H_2O systems which is further evidence that in coacervating systems the micelles are species of low charge density.

The data for the micelle molecular weights of the Hyamine 1622- $\text{NaCl-H}_2\text{O}$ system have been combined with viscosity and diffusion data in Figure 3 to illustrate another important property of coacervating cationic soap systems. In a narrow range of electrolyte concentration, between 0.17M NaCl and 0.19M NaCl , there occurs a transformation of micelle from a geometrically isotropic particle to a distinctly anisotropic particle.

Curve (a) of Figure 3 shows the changes in micelle molecular weight with the addition of NaCl to a 3% Hyamine 1622 solution maintained at a constant temperature of 30C. At low NaCl concentrations, a relatively slow increase in micellar molecular weight occurs. Between 0.17-0.19M NaCl , a sharp rise in micellar molecular weight occurs. For NaCl concentrations in excess of 0.19M, the micellar mol wt increases at a rate greater than the initial rate (for low NaCl concentrations) but lower than the rate of increase in the interval 0.17-0.19M NaCl .

Curve (b) of Figure 3 represents the intrinsic viscosity at zero shear gradient of the Hyamine 1622- $\text{NaCl-H}_2\text{O}$ system as a function of NaCl concentration at 30C. In the NaCl concentration range of 0.17-0.19M a discontinuity in the viscosity properties of the system is observed. In addition, for NaCl concentration below this transition range, the intrinsic

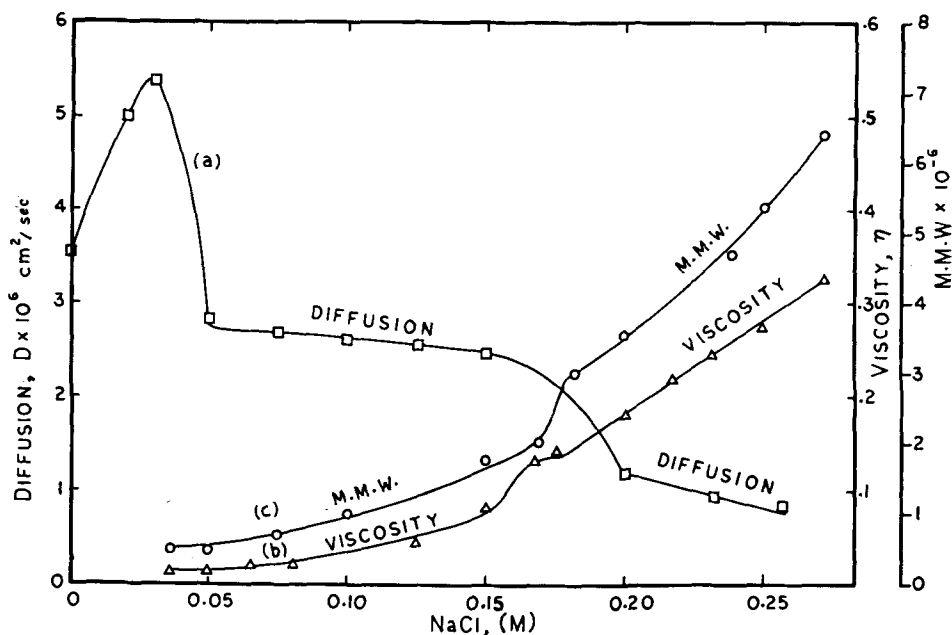


FIG. 3. Hyamine 1622-NaCl-H₂O systems. (a) Micelle mol wt vs. NaCl concn. (b) Intrinsic viscosity vs. NaCl concn. (c) Self-diffusion coefficient vs. NaCl concn. 3% Hyamine solution at 30C.

viscosity shows no shear dependence. For NaCl concentrations in excess of 0.19M, the intrinsic viscosity is shear dependent, indicative of an anisotropic micellar species in this range of NaCl concentration.

Curve (c) of Figure 3 is a plot of the self-diffusion constant for the Hyamine 1622-NaCl-H₂O system as a function of NaCl concentration. The diffusion constant maximum at 0.02M NaCl is coincident with the ionization maximum previously described. The slow linear decrease between 0.06M and 0.15M is consistent with a growing isotropic particle in this NaCl concentration interval. A sharp drop in the self-diffusion constant occurs in the NaCl concentration range of 0.16-0.18M, essentially the same electrolyte concentration region in which discontinuities are observed in the micelle molecular weights derived from light scattering data, and in intrinsic viscosity.

All of the cationic soap systems investigated, in which coacervation was observed, showed a typical narrow electrolyte transition range (ETR) in which a pronounced reorganization of the soap micelle is observed. Combining light scattering with viscosity data for NaCl concentrations greater than the ETR, the following linear relationships hold:

$$\eta = KM^{3/2} \quad [5]$$

$$\eta = K' L^{3/2}/M \quad [6]$$

where M is the micellar molecular weight, L is the length of the anisotropic micelle derived from dissymmetry measurements and K and K' are constants. These relationships are consistent with a soap micellar model which is a relatively rigid, cylindrical, rod-shaped particle.

TABLE II
Electrolyte Specificity

Soap-electrolyte-H ₂ O Systems	Electrolyte concentrations (M)			Critical electrolyte concn (CEC)
	Ionization maximum	Theta solvent	Electrolyte transition range (ETR)	
Hyamine 1622-NaNO ₃ -H ₂ O	0.015M	0.025M	0.018-.02M	0.067M
Hyamine 1622-NaBr ₃ -H ₂ O	0.015	0.025	0.018-.02	0.066
Hyamine 1622-NaCl-H ₂ O	0.03	0.05	0.17-0.19	0.36
Cetol-NaCl H ₂ O	0.05	0.08	0.35	1.20
EHDDAB-NaNO ₃ -H ₂ O	0.07	0.10	2.0 -2.4	5.0

Table II shows the correlation of the properties of the homogeneous phase of coacervating cationic soap systems, and indicates the electrolyte specificity of these systems in terms of the electrolyte concentration at which characteristic changes in these systems occur. The key property of these systems is micellar ionization suppression. The lower the electrolyte concentration at which the micellar ionization is critically depressed, the lower are the electrolyte concentrations at which theta solvent properties, the ETR and the CEC, are observed. An examination of several coacervating and non-coacervating systems indicates that the charge properties of these micellar systems is an essential determining property related to the central phenomenon, coacervation, and the electrolyte specificity observed in coacervating soap systems.

Conclusions

The following micellar model is consistent with the data developed in this investigation. In an electrolyte-free solution and at low electrolyte concentrations, the micelle is a Hartley spherical micelle. For the systems in which the micellar ionization is critically suppressed there occurs a micellar reorganization from an essentially isotropic micellar species to a rod-shaped, cylindrical micellar model. This micellar reorganization takes place in a narrow electrolyte transition range (ETR) which for the Hyamine 1622-NaCl-H₂O system spans 0.02 mole from 0.17 to 0.19M NaCl.

This transformation may be attributed to the screening of the coulombic interaction of the relatively widely separated, adjacent charge sites on the micelle, with the addition of a sufficient amount of external electrolyte. For electrolyte concentrations in excess of the ETR, the electrical field associated with micellar charge does not constitute a severe restriction on the micellar shape or growth. In this electrolyte concentration range, the micelles tend to pack as aggregates of soap molecules consisting of uncharged polar heads attached to long hydrocarbon chains. Here, micellar growth and shape are governed by vanderWaal dispersion forces, thermal forces, and solvation effects.

Coacervation in cationic soap solutions is a function of micellar charge and micellar size, expressed in terms of micellar length or axial ratios. Within limits, not as yet clearly defined, the lower the micellar charge density, the shorter is the critical length of the micelles necessary for coacervation in cationic soap systems.

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The Extraction and Constitution of Peat Wax. Chromatographic Fractionation of Wax

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Abstract

The extraction and properties of crude peat wax were investigated. The composition of this wax obtained with various solvents was assessed in terms of the components: resin, asphalt, and wax. It was concluded that extraction processes using benzene were likely to be of greatest value. Crude peat wax was further fractionated by chromatography to yield nine major fractions. These were distinguished by chromatographic behavior, fluorescence and spectral characteristics, and analytical composition. Preliminary work toward identification of individual components showed the presence of compounds of various types including hydrocarbons (e.g. perylene and many compounds containing one or more carboxyl, ester, carbonyl, or hydroxyl groups).

EXTRACTION of peat with organic solvents yields a dark colored wax of 5 to 15% yield, the amount depending on the source of the peat, its pretreatment, and on the solvent used. Chemical interest in this wax arises from the information it might yield as a possible precursor of coal, and as material of potential industrial value with applications similar to montan wax.

The term "crude peat wax" designates the residue after evaporation of the organic solvent. Earlier work has been reported (1,2,3,4). Most workers have regarded crude peat wax as consisting of three main fractions: resin, wax, and asphalt (5), though several methods have been adopted to separate the three sub-fractions. The resin is composed of polar compounds usually extractable with cold alcohol. The wax fraction is soluble in light petroleum, while the asphalt fraction is insoluble in this solvent. The relative proportions of these fractions obtained from any given wax specimen depend on the solvent used for the original extraction. This aspect will be considered further but the usual range is: resin 9-40%, wax 45-90%, and asphalt 1-18%.

Separation of individual constituents of peat wax has been reported by the authors (4). Since then

Wiedenhoff (6) has surveyed four plant waxes, using separations on alumina columns, followed by X-ray analysis of the fractions. Some hydrocarbons and alcohol components were detected. Cole and Brown (7) have examined ouricuri wax on alumina columns and consider that there is *a priori* evidence that the constituents of natural plant waxes are not simply mixtures of esters. In the case of sugar cane wax Lambertson and Redcliffe (8) have suggested that long-chain aldehydes in polymeric form are a major constituent. Although hydrocarbons and free alcohols and acids were also present there was no conclusive evidence for the presence of esters.

Published work indicates that most workers have preferred to use saponification and other severe reactions as a preliminary fractionation step. These methods are likely to degrade or destroy the natural constituents, and complicate any subsequent assembly of the results. In the present work the chromatographic fractionation of peat wax has been carried out directly. Nine major fractions were obtained and the further separation of these is under study. Results on extraction yields, and general chemical and physical properties of the wax are also presented.

Experimental

Materials. For this work peat was obtained from a bog situated east of Londonderry and referred to as "Altnahullion" in the Northern Ireland Peat Bog Survey (9). The material received was irregularly shaped pieces the size of bricks. Moisture content by the Dean and Stark method was 25 to 30%. Before extraction the peat was broken down in a jaw crusher and reduced in a hammer mill. A fraction passing a 3.2 mm but retained on a 2 mm sieve was used.

Wax. A crude wax extracted with benzene was used for the entire investigation. This was selected after preliminary separations had demonstrated that each of the three main components: resin, wax, and asphalt were present in benzene extracts. A further consideration was that benzene extraction appeared most feasible for commercial scale production.

Reference Compounds. As a guide in the selection of suitable adsorbent and solvent systems for chro-