The Chemistry
of
Asphalt Emulsions

Jack N. Dybaiski
Manager, Asphalt Technology

Akzo Chemicals Inc.
McCook, Illinois

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INTRODUCTION

Asphalt emulsions, used in road construction and maintenance, may be defined as an homogeneous mixture of minute asphalt droplets suspended in a continuous water phase. These types of emulsions are usually termed oil-in-water (o/w) emulsions. Their preparation involves the use of a high speed, high shear mechanical device, such as a colloid mill. The colloid mill breaks down molten asphalt into minute droplets in the presence of water and a chemical, surface-active emulsifier. The emulsifier imparts its properties to the dispersed asphalt arid is most influential in maintaining stable asphalt droplet suspension.

The three chemical components of emulsified asphalt, that is, asphalt, water and emulsifier, joined together by the chemical influence of a colloid mill, are the necessary ingredients in the chemistry and related production of paving asphalt emulsions.

CHEMICAL COMPONENTS

1. **Asphalt** - Paving asphalts are colloidal dispersions of high molecular weight aromatic hydrocarbons called asphaltenes dispersed in a continuous phase of lower molecular weight oily-resinous (paraffins and aromatic resins) material called maltenes.

   The asphaltenes tend to be insoluble in the oily constituent(s). They exist in asphalts as fine to coarse dispersions due to their peptization by the more aromatic resin constituent(s). The resins are considered to be part of the oily medium or in solution in it, but due to an aromaticity higher than the oily medium itself, they are adsorbed more readily by the asphaltenes than the remaining oils.

This adsorbed material is the peptizing agent or co11oidal stabilizer. (1)

The one physico-chemical property of paving asphalts that most influences the preparation of stable emulsions is the degree to which the asphaltene fraction is peptized by the maltene fraction into stable, colloidally and uniformly dispersed micelles.

Unfortunately, no single predictive procedure yet exists for determining the quality of an asphalt as an emulsion base. Some of the references given in Transportation Research Board publications[2] relating to those compositional factors which contribute to the formation of true sol asphalts having the best time durability characteristics almost invariably constitute the best emulsion-base asphalts. The most effective way, found thus far, of determining the quality of an asphalt as an emulsion base is to prepare a series of emulsions (4-6) with a single surfactant system at varying concentrations basis weight of emulsion. Using known photomicroscopy techniques (at least 100x microscope with suitable camera attachment), comparative projectable transparencies can be obtained which, when laid over a micron grid, will show particle size and distribution of the emulsified asphalt particles. Similar data can be obtained more easily but with more costly electronic equipment such as the Coulter Counter or the Micromeretics Sedigraph.

The emulsifier concentration that provides the smallest and most uniform particle size is selected as optimum for the asphalt in question. Repeating the procedure with asphalts from varying crude oil sources and processing units will allow the investigator to differentiate poor emulsion base asphalts from those that are acceptable.

A typically acceptable emulsion-base asphalt using an optimum concentration of emulsifier provides an average particle size and distribution of 28% at <l micron, 57% at 1-5 microns and 15% at 5-10 microns as determined by photomicroscopy and the two electronic systems mentioned previously.

Research has been recently completed on the synthesis of two proprietary chemicals which possess the ability to augment the peptisation of the asphaltene constituent in many asphalt cements now found to be deficient as emulsion-base asphalts. It is possible to uprade a deficient asphalt to an acceptable emulsion-base material with the addition of such chemicals to molten asphalt and a one to two day ageing period with agitation to facilitate de-aggregating and re-distribution of the asphaltenes.

2. **Water** - While water might be considered the least important of the asphalt emulsion components, water can possess chemical ionic constituents that can either be beneficial or detrimental to the formation of a stable asphalt emulsion.

The presence of calcium and magnesium ions (Ca++ and benefit the formation of a stable cationic asphalt emulsion. Calcium chloride is often added to cationic formulations to enhance storage stability. Calcium and magnesium ions could be detrimental to the formation of anionic emulsion formulations because of the formation or water insoluble calcium and magnesium salts due to reaction with the water soluble Sodium or Potassium organic acid salts normally used as anionic emulsifiers.

The presence of carbonate and bicarbonate ions (CO_3= and $Hco_{3\sim}$) could be detrimental to the formation of a stable cationic emulsion, particularly the rapid setting type of cationic emulsion. The more water insoluble salt will tend to form due to reaction with the water-soluble amine hydrochlorides normally used as a cationic emulsifier. By contrast the presence of carbonate arid bicarbonate ions could be beneficial to the formation of an anionic emulsion because of their buffering effect.

The presence of particulate matter in water could be detrimental to the formation of a cationic emulsion due to rapid adsorption of cationic surfactants by the usually negatively charged particulate matter. This electrochemical adsorption tends to reduce the amount of cationic surfactant originally in solution which can affect initial emulsification and performance properties of the finished emulsion.

3. **Emulsifier** - Certain substances, even when present in very low concentrations, possess the unique property of altering the surface energy of their solvents to an extreme degree. Almost always, a lowering rather than an increase of the surface energy is affected.

Substances or solutes possessing such properties are known as surface-active agents or surfactants and their unique effect is known as surface activity.

By broad definition then, surface-active chemicals are soluble substances whose presence in solution markedly changes the properties of the solvent and the surfaces they contact. They are categorized according to the manner in which they dissociate or ionize in water and are characterized, structurally, by possessing a molecular balance of a long lipophilic, hydrocarbon "tail" and a polar, hydrophilic "head".

Surface-active agents owe their physiochemical behavior to their property of being adsorbed at the interface between liquids and gases or liquid and solid phases. They tend to concentrate in an oriented manner, at the interface, in such a way that, almost entirely, they turn a majority of their hydrophilic groups toward the more polar phase and a majority of their lipophilic groups away from the more polar phase and perhaps even into a non-polar medium. The surface active molectile or ion, in a sense, acts as sort of a bridge between two phases and makes any transition between them less abrupt.

Basically, there are three types of chemical surface-active agents which.are classified according to their dissociation characteristics in water. These are:

1. Anionic Surfactants - Where the electrovalent and polar hydrocarbon group is part of the negatively charged ion, when the compound ionizes:

<u>ANIONIC</u>

$$CH_3(CH_2)_{16}COO^- Na+$$

2. Nonionic Surfactants - Where the hycrophilic group is covalent and polar and which dissolves without ionization:

<u>NONIONIC</u>

$$CH_3(CH_2)_{16}COO(CH_2CH_2O)_xH$$

3. Cationic Surfactants - Where the electrovalent arid polar hydrocarbon group is part of the positively charged ion when the compound ionizes:

<u>CATIONIC</u>

$$CH_3(CH_2)_{17}NH3^+ Cl^-$$

Alternately called surface-active chemical or surfactant, the emulsifier is the single most important component in any paving asphalt, oil-in-water, emulsion formulation. To be an effective emulsifier for asphalt, a surfactant must be water soluble arid must possess a proper balance between the hydrophilic arid lipophilic properties inherently found in each true surfactant-type chemical. The emulsifier, when used in combination with an acceptable asphalt, good quality water arid adequate mechanical input, is the major factor which influences initial emulsification, emulsion stability arid ultimate field performance.

ZETA POTENTIAL

Zeta potential is a relatively new concept for use in asphalt emulsions, yet the concept of zeta potential has been a tool of science since 1879. That is when Hermann Ludwig von Helmholtz systematized zeta potential and laid the foundation for understanding stability in colloid systems.

Zeta potential is determined by the motion of the colloidal particles in an electrical field, and this electrophoretic mobility can be measured with an instrument called the Zeta Meter.

There is a difference in the electrical potential between the .surface of a dispersed colloidal particle and the bulk aqueous solution. This net electrical potential difference is called the zeta potential.

The existence of zeta potential is brought about by the adsorption of ions onto a colloidal particle surface which in this case is asphalt. The asphalt particles assume the overall character of the adsorbing ions A double layer of ions and counter-ions exists in solution surrounding each particle of dispersed asphalt. The extent of attraction and quantity of counter-ions depends on the concentration, pH and ionic intensity of the emulsifier used.

This double layer is what ultimately affects the ability of the charged asphalt particles arid also the stability of the emulsion system. The greater the double layer the greater the zeta potential and thus the faster the charged particle will move in an electric field. In most cases, a large zeta potential indicates large repulsive forces between the individual particles in an emulsion and good stability. The zeta potential imparted to the asphalt droplet by the presence of the emulsifier is thus one of the important factors that assist in keeping the asphalt particles uniformly dispersed.

The pH of the solution effects the ability of the colloidal particles to adsorb ions which directly affects the double layer arid therefore the zeta potential.

The concentration of the emulsifier also has a direct affect upon the double layer. As the concentration of the emulsifier is increased the double layer is compressed and the zeta potential is decreased.

The readings obtained from the Zeta-Meter are converted to the zeta potential by monographs based on the Helmholtz-Smoluchowski formula, assuming spherical colloid particles.[3~]

The Helmholtz-Smoluchowski formula for determining Zeta Potential is as follows:

(1) $ZP = EM.\ 4\pi Vt/Dt$ or (2) $EM = ZP.\ Dt/4\pi Vt$

ZP Zeta Potential of the particle in electrostatic volts (esu)

EM = Electrophoretic Mobility of the particle in em/sec. per esu volt/cm.

Vt = Viscosity of the suspending liquid in <u>poises</u> at any given temperature

Dt = Dielectric constant of the suspending liquid at any given temperature (at infinite wavelength, in vacuum or air) .*

4π = A constant (12.57)

It is evident from equation (1), that at constant temperature, ZP varies directly with the EM.

Simplifying the EM unit, we have: (3) EM F/H
Where F = velocity of the particle in cm/sec.

H = esu voltage drop per centimeter length of the suspending liquid. (For the Zeta-Meter electrophoresis cell, this represents voltage drop per cm of cell-tube length between ports. For conventional cells, this drop must be computed, after determining the conductivity of the liquid in a standard conductivity cell.)

The Zeta Potential of equation (1) can therefore be expressed as:

(4) $ZP = (F/H).4\pi Vt/Dt$

Since the above voltage is expressed in "esu" units, it is desirable to convert this to "practical"volts. (One practical" volt 1/300 esu volt.)

Equation (4) therefore becomes:

(5) $ZP/300 = 4\pi\ Vt/Dt\ .\ F/(H/300)$ (6) $ZP/300 = 4\pi Vt/Dt\ .\ 300F/H$

(7) $ZP = 4\pi Vt/Dt\ .\ 90000F/H$ (8) since from equation (1) $EM=F/H$
then: $AP=4\pi Vt/Dt\ .\ 90000EM$

The Zeta Potential for anionic and cationic surfactants normally used as emulsifiers for asphalt range from -80 millivolts (mv) to -30 millivolts (mv) for the anionic types and +128 mv to +18 mv for the cationic types. Each chemical possesses a distinct characteristic Zeta which is imparted quantitatively to the asphalt during emulsification.

Since almost all naturally occurring mineral aggregates used in road construction possess a negative surface charge a partially predictive relationship exists between the Zeta Potential of aggregates, their surface area and the Zeta Potential of cationic surfactants. Since anionic surfactants possess a negative charge, the same as most aggregates, and nonionic surfactants possess no charge they both deposit asphalt onto an aggregate surface primarily through evaporation and absorption of the continuous water-phase of the emulsion. When sufficient water has been depleted from the emulsion layer an unstable condition is reached where the asphalt cannot remain in suspension and it pads out and coalesces on the surface of the aggregate.

Cationically emulsified asphalt, by contrast, begins to deposit on the surface of an aggregate at the moment of contact. The influence of the negative surface charge of the aggregate and its surface area causes the cationically emulsified asphalt to be adsorbed by the aggregate by cathodic effect. This affinity of an aggregate for cations is stronger than its affinity for water, hence, water is displaced, Asphalt films deposited in this manner, whether continuous or discontinuous, are very difficult to remove by the action of subsequent water. In effect the cationic surfactant provides an anti-stripping action similar to that obtained with oil-soluble anti-stripping agents in asphalt cement and cutbacks.

The relationship of cationic emulsion Zeta Potential to aggregate Zeta Potential and aggregate surface area in an emulsion-aggregate mixture, can be stated in an over simplified manner as follows:

1. As cationic Zeta decreases, aggregate Zeta can increase and vice versa.

2. As cationic Zeta decreases, aggregate surface area can increase and vice versa. (See Chart I.)

Other aggregate factors that influence the chemistry of cationic asphalt emulsions are:

1. Aggregate surface charge (Zeta) increases as aggregate surface area increases.

2. Freshly cleaved (crushed) aggregate surfaces require a period of ageing to reach their original surface charge equilibrium.

During the past several years, a misconception of the surface charge of calcareous aggregates has existed. It has been incorrectly assumed that since siliceous aggregates are acidic and possess an electronegative surface charge that calcareous aggregates being alkaline must possess an electro-positive surface charge.

McGlashan and Bule in their 1961 paper "^{t}Determination of Electrokinetic Potential and Surface Charge of Highway Aggregates" stated: "The negative surface charge of calcite (calcite = calcium carbonate ($CAC0_3$) the basic constituent of limestone) is brought about by the preferential abstraction of calcium ions (Ca++) from the lattice; bicarbonate (HCO_3^-) and hydroxyl (OH-) ions affect the zeta potential through adsorption at the inner Helmholtz plane; and hydrated calcium ions accumulate near the surface to form the diffuse layer and maintain electroneutrality."

In 1967, w. Cullen Sherwood in his "Determination of the Surface Charges of Certain Highway Aggregates By Streaming Potential Methods" stated: "All aggregates under study were found to have negative surface charge.' (These included granite, limestone, dolomite, marble, sandstone, silica, basalt and quartz.) There is basic agreement with both of these earlier works since our investigations have repeatedly verified that calcareous aggregates have a negative surface charge.

The zeta potential determination of 87 naturally occurring aggregates obtained worldwide from North and South America, Asia, Europe and Africa has recently been completed. or these 87 aggregates, 31+ were limestone and dolomite and the remaining 53 were varying siliceous types. In every instance a negative surface charge, ranging in zeta potential intensity from 11.91+ my to -88.1+6 uw, was obtained.

To enhance the study, chemically pure calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgcO_3$) were subject to zeta potential determination. The chemically pure calcium carbonate had a negative surface charge with an average zeta potential of -9.31 mv at a 9.4 pH in distilled water. Magnesiun carbonate had a positive surface charge with a zeta potential of +12.44 mv at a 12.5 pH in distilled water.

This reversal of charge is probably due to the greater insolubility of the magnesium carbonate with less tendency for the magnesium ion to leave the lattice structure. The zeta determination does, in fact, indicate that the difference between the heat of hydration and the lattice energy is greater for the carbonate ion than the magnesium ion. This, as opposed to calcium carbonate, would leave a slightly greater number of magnesiun ions on the surface accounting for the weakly positive charge.

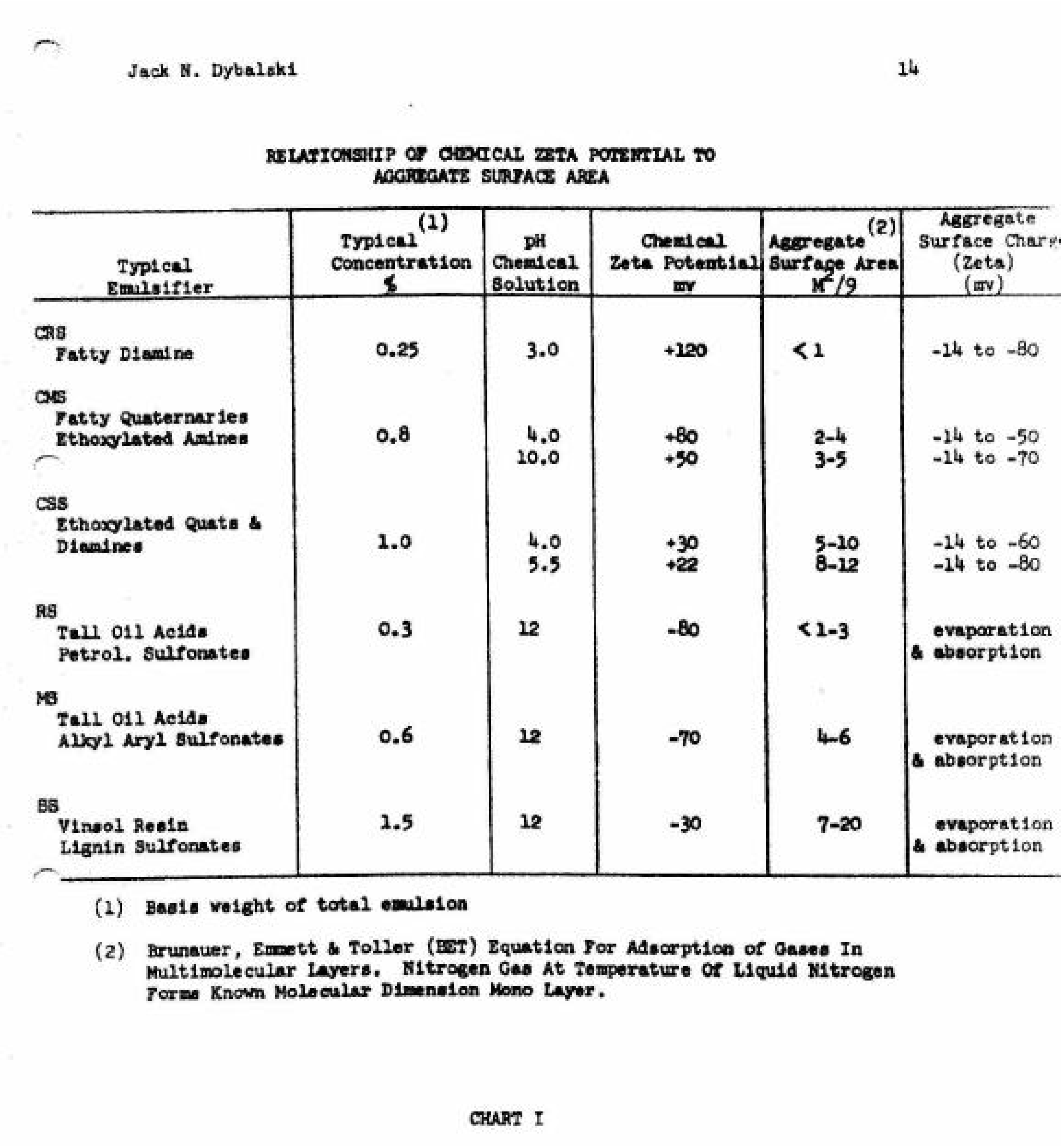
The surface charge of calcareous aggregate then is related to the concentration of calcium carbonate ($CaCO_3$) which is usually dominant in naturally occurring calcareous aggregates.

SUMMARY

The chemistry of asphalt emulsions, their chemical components arid their individual functions of those components have been delineated.

A suitable emulsion-base asphalt has been described as a sol type possessing a naturally or synthetically peptized asphaltene constituent which provides colloidally and uniformly dispersed asphaltenes micelles. The water used in emulsification has been described as possibly containing either beneficial or detrimental soluble ions in the form of calcium and magnesium or carbonate and bicarbonate. The singularly important role of the surfactant type chemicals used to emulsify asphalt have been defined. The physio-chemical properties of anionic, nonionic and cationic surfactants have been described as well as the influence of Zeta Potential and its relationship to the Zeta Potential and surface area of aggregates.

Asphalt emulsions are useful and effective materials for road building when used properly. However, the user should be aware that the mechanism of use is different from hot mixes and cutbacks. The molten asphalt in hot mix and the solvent in cutbacks provides the lubrication necessary for the mixing process ~ both are physico-mechanical in their action. By contrast, emulsions are physico-chemical in action. They require that water be added to the aggregate prior to the addition of the emulsion to provide the necessary carrier for uniform distribution of the emulsified asphalt particles in cold mixes. Users cannot expect to properly use emulsions without an understanding of these basic differences and a willingness to alter some of their older road building practices.



RELATIONSHIP OF CHEMICAL ZETA POTENTIAL TO AGGREGATE SURFACE AREA

Typical Emulsifier	Typical Concentration (1) %	pH Chemical Solution	Chemical Zeta Potential mv	Aggregate Surface Area (2) M^2/g	Aggregate Surface Charg (Zeta) (mv)
CRS Fatty Diamine	0.25	3.0	+120	<1	-14 to -80
CMS Fatty Quaternaries Ethoxylated Amines	0.8	4.0 10.0	+80 +50	2-4 3-5	-14 to -50 -14 to -70
CSS Ethoxylated Quats & Diamines	1.0	4.0 5.5	+30 +22	5-10 8-12	-14 to -60 -14 to -80
RS Tall Oil Acids Petrol. Sulfonates	0.3	12	-80	<1-3	evaporation & absorption
MS Tall Oil Acids Alkyl Aryl Sulfonates	0.6	12	-70	4-6	evaporation & absorption
SS Vinsol Resin Lignin Sulfonates	1.5	12	-30	7-20	evaporation & absorption

(1) Basis weight of total emulsion

(2) Brunauer, Emmett & Toller (BET) Equation For Adsorption of Gases In Multimolecular Layers. Nitrogen Gas At Temperature Of Liquid Nitrogen Forms Known Molecular Dimension Mono Layer.

CHART I

References

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3. Zeta-Meter Manual, 2nd Edition, Zeta Meter, Inc.1720 First Avenue, Nev York, N.Y. 10028