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ASPHALT–AGGREGATE BONDING ENERGY MEASUREMENTS BY MICROCALORIMETRIC METHODS

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ABSTRACT

Bonding energy measurements were found for several asphalts and aggregates using a microcalorimeter designed for the study. Bonding energies are related to highway performance. A temperature–bonding energy study indicates that rate of bonding is controlled by adsorption rather than diffusion to the aggregate surface or interphase region.

INTRODUCTION

The bonding between asphalts and aggregates in paving mixtures is one of the most important bonds to our mobile society. It is also one of the least understood bonds, partly due to the complexity of the asphalt and partly due to the variety of surfaces of aggregates with which the asphalt comes into contact.

Empirically, asphalt–aggregate bonding has been studied by such methods as scraping and peeling [1,2] contact angle [3], water stripping [4,5], and infrared analysis [6,7]. Asphalt–aggregate bonding has also been studied by measuring the interaction using microcalorimeters [8,9]. Recent modifications to the method of interacting asphalts and aggregates improved the accuracy of bonding energy measurements.

In this paper, the addressed areas include the relation between bonding and water stripping, bonding and tenderness of mixes, and effect of temperature on the bonding energy of oxidized asphalts.

Water stripping occurs when water displaces the asphalt from the aggregate surface. Resistance to water stripping is necessary for desirable highway performance because almost all paved highways come into contact with moisture. Even without rain, sleet, or snow, condensation due to thermal changes can cause moisture to condense inside pavement mixtures. Also ground moisture can seep into asphalt and cause severe stripping.

Bonding energy measurements [9] suggest that a multilayer adsorption process occurs when asphalt in the molten state is contacted with an aggregate surface. This multilayer is referred to as an interphase region with both solid and liquid characteristics. Bonding energy measurements allow for comparisons of relative thicknesses of the interphase region. Greater thicknesses of the interphase region should lead to greater water resistance and improved highway performance.

In an attempt to compare the bonding energy measurements with highway performance, our data are compared with a current highway study by Lottman [10]. He examined both freshly prepared laboratory specimens and pavement cores for moisture resistance. Data obtained include tensile strengths of briquette specimens dry, wet, and freeze–thaw cycled. Part of the data are reported later in this paper. We examined the Lottman asphalt–aggregate systems by measuring bonding energies. The correlation between the two methods are discussed.

The second area addressed was the tender mix problem. A tender mix is manifested in several ways: (a) it is difficult to compact or tends to flow; (b) it sets slowly, requiring delayed traffic usage; (c) it ruts prematurely. A group of eight asphalts, some of which had produced tender pavement mixtures was examined with the microcalorimeter. Designation of an asphalt as tender implies that the asphalt produced a tender mix and it is assumed that the asphalt was the principal source of the problem.

The final area examined was the effect of temperature on bonding energy between an oxidized asphalt and a selected standard aggregate. Rate of bonding varies in a very complex way with temperature and some of the complexities are discussed with the data. Using the data from the study of the effect of temperature on bonding energies, two possible rate-controlling steps were examined—diffusion to the interface and adsorption at the interface.

EXPERIMENTAL PROCEDURE AND APPARATUS

The microcalorimeter specifically constructed to measure the bonding energy has been discussed previously [8]. However, three methods of bringing the aggregate into contact with the asphalt were used in this work with only one being discussed in the above reference. In that previous study and in the present study of the tender-mix asphalt, the aggregate is contained in an aggregate holder as shown in Fig. 1, the teflon-topped cell. A trap door holding the weighed aggregate is tripped from the outside of the oven, allowing the aggregate to fall into the asphalt.

In the study of the temperature effect on bonding of oxidized asphalts, the aggregate was pushed into the asphalt with a rod as shown in Fig. 1, left-hand side. (Oxidized asphalts in the molten state tend to form a scum on the surface, making the above method difficult to use.) The aggregate is contained in the cylindrical holder with a teflon trap door on the bottom

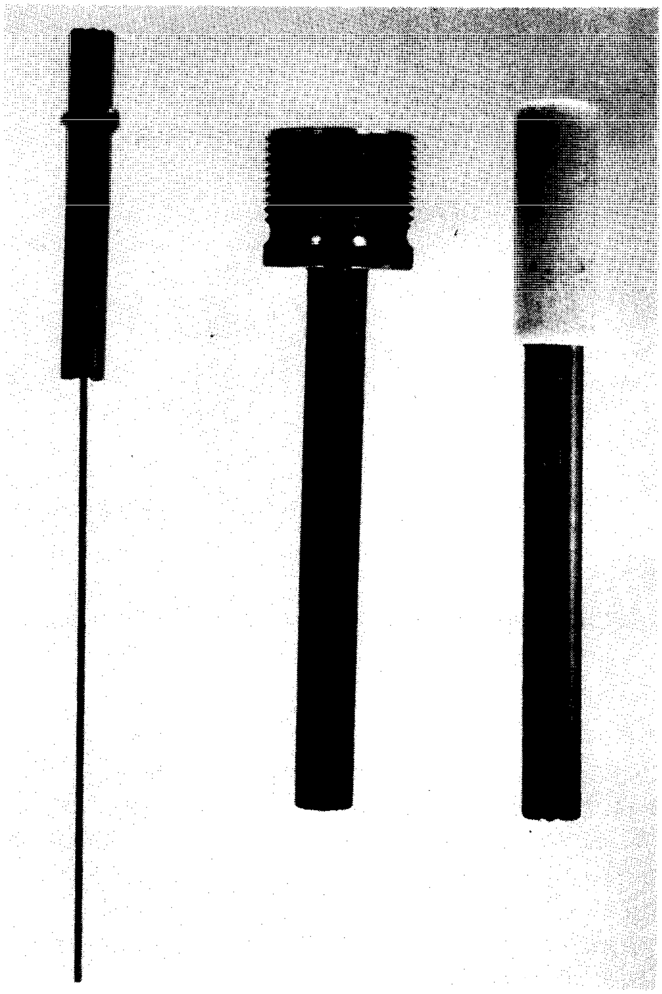

Fig. 1. Three microcalorimeter cells used to obtain data. The cell to the left holds aggregate only, the center cell contains asphalt only, while the cell to the right contained aggregate in the teflon compartment, and asphalt in the lower metal compartment.

which is pushed out by means of a rod extending to the outside of the oven. The testing of the asphalts and aggregates in the Lottman Phase II employed a second improvement. Aggregate is contained in a cyclinder as mentioned above, but submerged in the asphalt. By pushing a teflon trap door on the bottom of the cylinder, asphalt under slight hydrostatic pressure flows into the cell and up through the aggregate. The small energy required to push the teflon door is negligible, thus, the complete curve can be used for analysis. The center threaded container in Fig. 1 served to hold the asphalt. Because of the negligible blank, future work will employ this method.

The energy released during the asphalt–aggregate interaction is measured by a 1200-thermopile microcalorimeter [8]. The resulting signal is fed into a Keithley 149 millimicrovoltmeter and recorded. Electrical calibration of the

TABLE 1

Aggregates and surface areas for $-35+48$ mesh

Aggregate	Type	Surface area ($m^2 g^{-1}$) $-35+48$ mesh
Arizona	Santa Cruz river gravel	3.00
Colorado	Morrison crushed stone Platte River	1.95
FHWA Region 10	Washington–Oregon region Pole Creek stockpile	1.92
Georgia	Granite gneiss	0.10
Idaho	Salmon River gravel	2.30
Montana	Bench gravel	0.47
Virginia	Granite	2.61

microcalorimeter allows for the displacement on the recorder to be expressed in rate of energy flow.

Materials

The asphalts and aggregates used in this study were of the same source as those used by Lottman [10] and were supplied by various states involved with the Lottman study. They represent materials from both problem and nonproblem pavements. Limited information is available on the asphalts; however, aggregate information is given in Table 1. The asphalts used in the tender mix study were supplied by the Federal Highway Administration (FHWA) and are described elsewhere [11].

The asphalts in the Lottman study and in the tender mix study were used as received. All aggregates were ground to $-35+48$ mesh, washed, and dried. For the tender mix and temperature study, a standard quartz aggregate, Ottawa sand, and a dolomitic limestone, Riverton limestone, were selected as representing silicate and limestone aggregates.

The oxidized asphalt was prepared by passing air through stirred molten asphalt at 150°C for 24 h. The increase in oxidation was monitored by observing the carbonyl infrared absorption peak band at 1700 cm^{-1}. Viscosity changes were monitored using a Sabolt viscometer at 150°C.

RESULTS AND DISCUSSION

General discussion

Asphalt has been proposed as highly associated [9] (*n*-mers) and dissociates to produce molecules available for bonding. These individual molecules

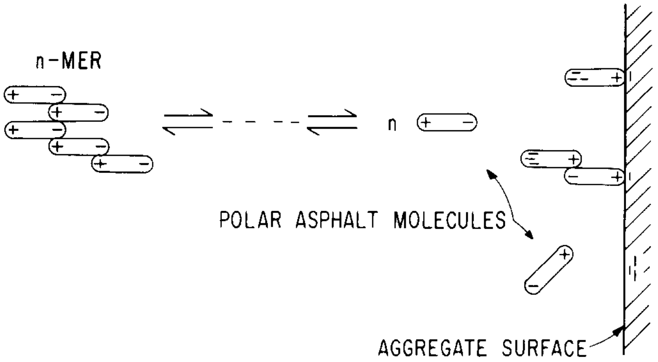

Fig. 2. Diagram depicting hypothetically asphalt molecular dissociation and adsorption of asphalt molecules on the aggregate surface.

with large dipoles are attracted to a site on the aggregate surface where there are sites with large electric fields [8,9]. Figure 2 depicts the proposed bonding mechanism. The attached molecule becomes further polarized with the end opposite to the attached end becoming a new site for a second molecular attachment. By a propagated polarization mechanism the asphalt builds up an interphase region around the aggregate. This interphase region should provide a protective or water resistant layer.

In Fig. 3 is seen a typical bonding-energy curve. Almost all asphalt–aggregate bonding-energy curves show an initial peak, maximizing within a half-hour, followed by a gradually decreasing energy curve tail. Often the curve tail is parallel to the base line for several hours. The extended energy release after asphalt–aggregate contact is unique. Most solid–liquid systems

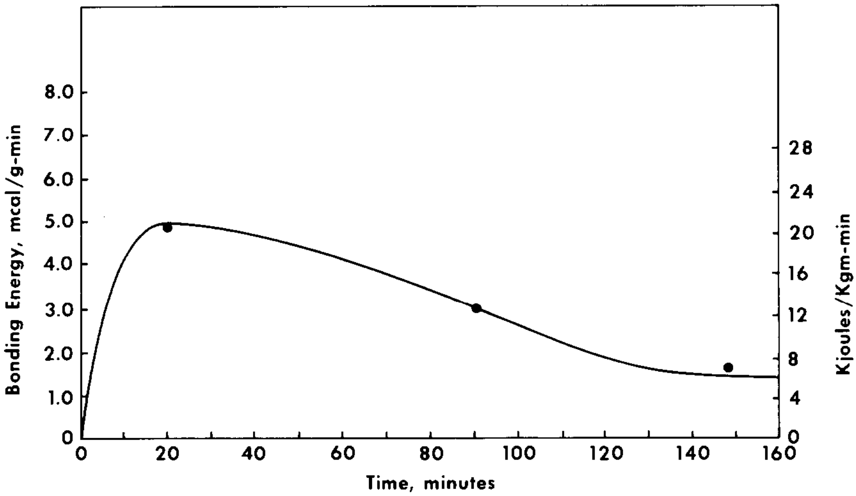

Fig. 3. Typical bonding energy curve for a good interacting system.

release energy for only a short time allowing a finite heat-of-wetting or heat-of-immersion value to be calculated.

The initial peak height probably reflects the initial layer of asphalt molecules becoming attached to the aggregate surface. Further buildup of asphalt molecules by propagated polarization probably accounts for the curve tail or extended energy release. A strong initial bond at the interface plus a buildup of molecules in the interphase region should be a necessary condition for a good asphalt–aggregate bond. It may not be a sufficient condition to simply have a strong bond because other parameters can influence durability such as void content, environment, etc. Without an initially strong asphalt–aggregate interaction, however, a poor pavement mix would probably result.

Molecular dipole alignment of the type discussed above would indicate that asphalt molecules have characteristics similar to liquid crystals; that is, it is perhaps reasonable to postulate that large polar asphalt molecules can be aligned by the electric fields due to the aggregate surface in a manner similar to liquid crystal alignment in electric fields. Although individual molecules in asphalt have not been identified because of their variety, high molecular weight and complexity, considerable information exists on the dominant chemical functionality present that may play a role in aggregate-induced molecular structuring. Polar functionality normally present or formed on oxidation includes pyridinic and pyrrolic nitrogen, 2-quinoline types, phenolics, ketones, anhydrides, carboxylic acids and sulfoxides [6,12]. These functionalities may act in concert with highly condensed and polarizable aromatic ring systems to form the structural arrays. Both the mobility of the pi electrons in the large aromatic ring systems and the planar structure of the rings should favor the formation of structural complexes. Thixotopy or molecular structuring is a property of most asphalts and has been related to the presence of the so-called asphaltene fraction [13] which characteristically contains the large condensed aromatic-ring systems and the highest concentration of polar, heteroatomic functionality. Chemical studies of the asphalt–aggregate interactions have shown that aggregate surfaces have a high affinity for the polar, heteroatom functionality in asphalt [11] further supporting their involvement in the aggregate-induced structuring phenomenon. Relationships between moisture damage in field pavements and the types of chemical functionality strongly adsorbed by aggregate surfaces have been observed [6].

Study of the Lottman systems

A laboratory test method for predicting moisture damage in asphaltic pavements was developed by Lottman [10]. The test method consists of exposing compacted asphalt–aggregate mixes to accelerated conditioning and comparing the tensile strengths of the conditioned specimens with those

TABLE 2

Comparison of briquette tensile strength to bonding (tensile strengths were measured by Lottman [10]. Bonding energies are reported for the energy released in the 2-h time interval; temp. = 130°C, 266°F)

State or region	Tensile strength			Bonding energy	
	Dry (psi)	Cond. (psi)	Ratio	(mcal g^{-1})	(kJ kg^{-1} $\times 10^3$)
FHWA Region 10	135	85	0.6	313	1308
Virginia	56	20	0.4	158	660
Arizona	222	47	0.2	110	460
Montana	74	44	0.6	83	346
Idaho	83	68	0.8	129	539
Colorado	41	9	0.2	57	238
Georgia	87	0	0	9	37

of the corresponding dry unconditioned specimens. Results are reported as a ratio of the strength of the conditioned to unconditioned specimens.

A summary of Lottman's results appears in Table 2 along with more recent bonding energy measurements. Although tensile strengths, wet or dry, do not correlate one to one, there is reasonable agreement between retained tensile strength after conditioning of compacted laboratory specimens and bonding energy measurements in corresponding asphalt–aggregate systems.

Good bonding, as reflected in the bonding energy curves should result in both a better dry strength and a better freeze–thaw cycled specimen. Region 10, Virginia, and Idaho asphalt–aggregate systems gave the highest bonding energies with Georgia the lowest, indicating the most moisture resistant and moisture sensitive mixtures, respectively. This agrees in general with the Lottman data.

Tender-mix study

A group of eight asphalts supplied by the Federal Highway Administration was studied using the microcalorimeter. Bonding energies were measured at 130°C using Ottawa sand as a standard aggregate. The group contained some asphalts that were reported to produce tender mixes. Tenderness refers to problems arising in the first few days after a pavement mix is laid down. Mixes that are difficult to spread or are slow to set, i.e., rut easily, are tagged as tender asphalts.

In our study, the interaction between asphalt and aggregate occurred when quartz aggregate was dropped into the asphalt. Bonding energy results are given in Table 3, along with the percent asphaltene [11] content in asphalt. Both curve tail heights and the area under the curve for a 2-h (arbitrarily selected) duration are reported. Asphalts that would produce a tender mix are probably low interactors or produce a bonding energy tail

TABLE 3

Asphaltene content and bonding energy measurements for eight asphalts (both curve tail height at 3 h and total bonding energy for a 2-h interval after the first 20 min are reported)

Asphalt	Property	Asphaltene content (%)	Bonding energy curve tail height		Bonding energy 2-h interval	
			(mcal g^{-1} min^{-1})	(kJ kg^{-1} $min^{-1} \times 10^3$)	(mcal g^{-1})	(kJ kg^{-1} $\times 10^3$)
B-5684	Non-tender	11.8	2.80	11.7	443	1851
B-5644	Non-tender	16.9	2.02	8.4	198	827
B-5669	Non-tender	15.8	1.23	5.1	280	1170
B-5685	Non-tender	8.6	1.10	4.6	228	953
B-5645	Tender	20.7	0.60	2.5	150	627
B-5646	Tender	11.3	0.43	26.0	165	689
B-5621	Tender	15.3	0.12	0.5	63	263
B-5679	Tender	13.8	0.00	0.0	90	376

curve height at 2 h which is less than 0.6 mcal g-min^{-1} or, using an alternate measurement, produce a curve with the total area under a 2-h section of the curve with less than 150 mcal g^{-1}.

The polar asphaltene molecules are prime candidates for promoting bonding. Consequently, it might be assumed that bonding energies are proportional to asphaltene content. However, the results in Table 3 indicate that bonding is not proportional to asphaltene content. What is more important than total asphaltene content is dispersed asphaltene content. The remaining components of asphalt (maltenes, resins, and oils) play an important role in asphalt behavior and probably act as dispersants. Therefore, the intermolecular interaction and interactions between asphalt molecules and aggregate surfaces are influenced by the mixture of asphalts molecules rather than the fraction [13].

Tender mixes are perhaps a manifestation of more than just bonding, but one might argue that a good bond initially is a necessary condition to prevent a tender mix. If a sufficiently strong bond is formed between an asphalt and aggregate in the mixing operation, the asphalt and aggregate would behave as a homogeneous material rather than the two materials moving independently of one another as they would in a poorly-bonded mix. This agrees very well with the data for bonding between a selected quartz-type aggregate (Ottawa sand) and the tender and non-tender mix asphalts.

Influence of temperature on the bonding of oxidized asphalt

An asphalt labeled "Hawkins" (Hawkins indicates field source) was oxidized as described in the experimental section. Bonding energies were determined for Riverton limestone and the oxidized asphalt at four different temperatures. The curves are shown in Fig. 4.

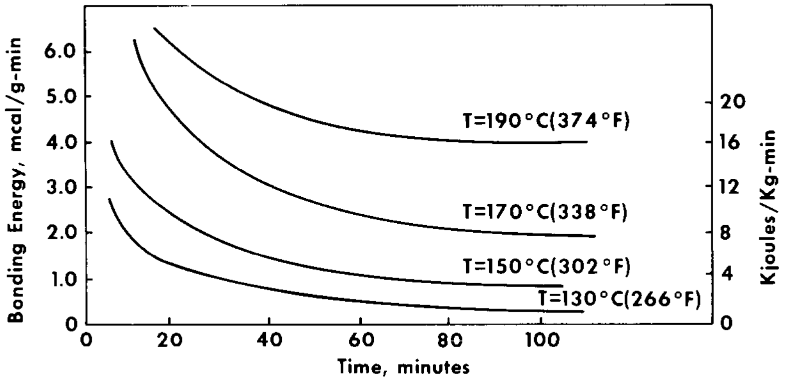

Fig. 4. Bonding energy curves for the interaction between an oxidized asphalt and dolomitic limestone at four temperatures. Initial peak heights are not shown due to scale limitations.

A continuous increase in bonding energies is noted as the temperature increases. There are probably two reasons for this increase. One is that the viscosity is lowered as the temperature increases. Thus, molecules can migrate more rapidly to the bonding sites. A second reason is that an increase in temperature leads to a more dissociated asphalt [9]. Species that bond are probably individual molecules rather than agglomerates. Single asphalt molecules are probably very polar, and these polar molecules find sites of electric fields that further increase the polarity of the molecule after bonding. Therefore, even though increases in temperature usually favor debonding, the decrease in viscosity coupled with the increase in dissociation overcome the bonding hindrances due to the increase in temperature.

TWO POSSIBLE RATE-CONTROLLING STEPS IN BONDING

Diffusion-controlled bonding

The proposed bonding mechanism of an asphalt molecule to an aggregate surface consists of three steps:

(1) dissociation of associated asphalt agglomerates;

(2) diffusion to the aggregate interfacial region;

(3) adsorption.

Dissociation is rapid as seen in attempting to measure the phenomenon with a microcalorimeter. The dissociation is so rapid that attempts to measure it by placing associated asphalt at room temperature in the microcalorimeter at 130–190°C have failed because of the time it requires for the microcalorimeter to reach thermal equilibrium. When studies of micelle dissociation are undertaken, equipment that can measure in the picosecond range, or faster, is employed. Thus, diffusion to the aggregate interfacial region and subsequent adsorption are probably the rate-controlling steps assuming that asphalt associated species are similar to micelles.

Diffusion formulas or formulas for the coefficient of diffusion come in a variety of forms, but usually the diffusion coefficient, D, is expressed as directly proportional to the temperature, T, and inversely proportional to the viscosity, η. For example, in the Stokes equation [14] for spherical molecules of radius r, the diffusion equation is

$$D = \frac{RT}{N_0 6 \pi r \eta} \tag{1}$$

where R = gas constant, N_0 = Avogadro's number. The rate $\mathrm{d}N/\mathrm{d}t$, at which molecules cross a plane of area O, parallel to the adsorption surface is [15]

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -DO\frac{\mathrm{d}n}{\mathrm{d}x} \tag{2}$$

where $\mathrm{d}n/\mathrm{d}x$ = concentration gradient. Substituting for D in eqn. (1) and representing the collected constants by C, we can write for a unit area

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{-CT}{\eta r}\frac{\mathrm{d}n}{\mathrm{d}x} \tag{3}$$

Or the rate at which molecules of a given radius arrive at the adsorbing surface or interphase region is directly proportional to the absolute temperature and concentration gradient, and inversely proportional to the viscosity and size of a spherical molecule when electrical effects are equal.

Temperature influences both the viscosity and gradient and thus is manifested in three terms on the right-hand side of the equation. Many formulas have been written expressing viscosity as a function of the temperature [16], the most popular being an exponential form

$$\eta = A\mathrm{e}^{E/RT} \tag{4}$$

where A = proportionally constant, E = viscosity activation energy, R = gas constant, 1.98 cal deg^{-1} mol^{-1}.

By substituting η into eqn. (3), we may now write

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{-CT\mathrm{e}^{-E/RT}}{Ar}\frac{\mathrm{d}n}{\mathrm{d}x} \tag{5}$$

or in logarithmic form,

$$\ln\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{-E}{RT} + \ln\frac{-CT}{Ar}\frac{\mathrm{d}n}{\mathrm{d}x} \tag{6}$$

If the above equation is written collecting the temperature terms we have,

$$\ln\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{-E}{RT} + \ln T + \ln\frac{-C}{Ar}\frac{\mathrm{d}n}{\mathrm{d}x}$$

where $\mathrm{d}N/\mathrm{d}t$ is proportional to the energy flow rate or the curve tail height whose value is taken from the curves in Fig. 4. If we combine this proportionality constant with the last logarithm term and call all of this ln K, it is found from solving simultaneous equations that ln K is about -5. Using this K value and solving the equations for E for a given $\mathrm{d}N/\mathrm{d}t$ and corresponding T, we obtain an average energy of activation value of 18 ± 4 kcal mol^{-1}. This value is near the value 14 kcal mol^{-1} for intermolecular interaction activation energies [17] but far below the activation energy 54 kcal mol^{-1} for viscosities [18]. The conclusion is that adsorption is probably controlled by rate of adsorption or some mechanism not viscosity controlled.

Adsorption-controlled bonding

The long tail on the bonding energy curves implies that a zero-order mechanism is governing the rate of adsorption. Glasstone et al. [14] discuss the zero-order reaction with respect to adsorption. A zero-order adsorption equation could be expected when the surface is almost completely covered by adsorbed molecules, a condition that probably develops quickly when asphalt comes into contact with the aggregate surface.

The zero-order equation is

$$\frac{\mathrm{d}N}{\mathrm{d}t} = k \tag{7}$$

or the rate of adsorption of molecules, $\mathrm{d}N/\mathrm{d}t$, remains constant during the adsorption process. Although we cannot calculate $\mathrm{d}N/\mathrm{d}t$, it should be

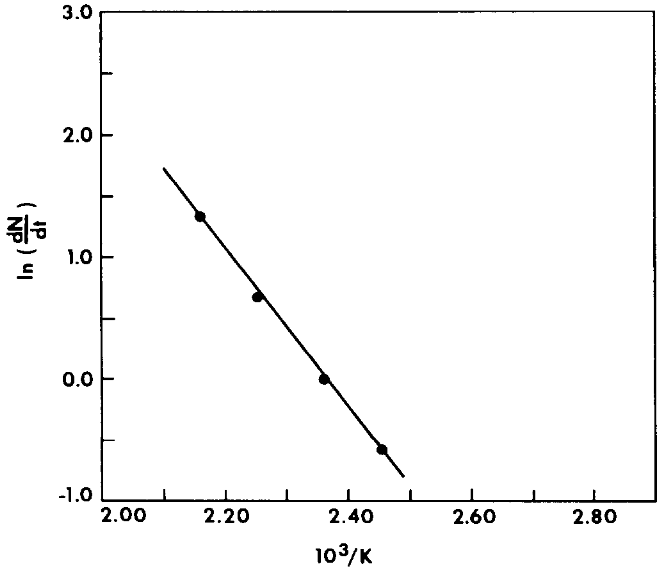

Fig. 5. Plot of ln (rate of adsorption) vs. reciprocal of absolute temperature. An assumption is made that rate of adsorption is directly proportional to the rate at which energy is released as detected by the microcalorimeter.

directly proportional to the rate of energy being released or proportional to the bonding-curve tail height. Thus, the logarithm of the rate $\mathrm{d}N/\mathrm{d}t$ equals the logarithm of the rate of energy plus a proportionality term. In other words, the logarithm of the energy is proportional to the logarithm of k for zero-order phenomenon.

Recalling the Arrhenius equation

$$k = A\mathrm{e}^{E/RT} \tag{8}$$

we note that a plot of ln k vs. $1/T$ allows the calculation of the energy of activation. Or a plot of ln(energy flow rate) vs. $1/T$ also would produce a straight line from which the activation energy of adsorption can be calculated. It is, therefore, not surprising that the activation energy, 14 kcal mol^{-1}, calculated from the curve in Fig. 5 agrees with the activation energy of association. An agreement implies that the two phenomena are similar.

We would expect the multilayer region to be similar in structure to an associated material in as much as both systems represent a highly structured system or bonding of asphalt to an aggregate surface is controlled by adsorption at the interface rather than diffusion to the interface.

CONCLUSIONS

Microcalorimetric measurements on asphalt–aggregate systems indicate that there is probably an optimum mix or bonding temperature that dissociates the asphalts, lowers the viscosity, and is not too high to cause desorption of asphalt from the aggregate.

The formation of a structured layer of asphalt molecules on an aggregate surface should be a protective layer against water stripping and increase the strength of the asphalt–aggregate bond, thus reducing problems associated with tender mixes.

ACKOWLEDGEMENTS

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