THE HEAT OF IMMERSION OF SILICA GEL IN VARIOUS PETROLEUM SUBSTANCES

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In a study of the retention of crude oils by sands, it becomes of interest to know what particular kinds of petroleum substances are most likely to resist removal by the ordinary production methods. As a starting point for laboratory investigations, the oil sands may be considered as agglomerates of fine grains under pressure, a picture which is probably not oversimplified. Such a porous structure has, of course, capillary properties and undoubtedly will give rise to selective adsorption phenomena. It is the purpose of this paper to consider a means of arriving at some quantitative conclusions regarding such adsorption processes. For the sake of further simplicity the following considerations will be limited to silica–oil systems.

In order to determine the capillary characteristics of the various petroleum constituents, their selective adsorption might conceivably be directly measured. However, the experimental difficulties are considerable, and a simpler method was sought. The one decided upon was the measurement of the "heat of wetting," better called the heat of immersion, that is, the heat evolved when silica is brought into contact with an excess of a petroleum substance. It was thought that this heat effect might give an insight into the relative adsorption tendencies of such substances. While such values cannot be directly applied to adsorption equations such as that of Gibbs, the complexity of systems such as crude oils and their sands precludes at present such thermodynamic treatment, and more than a prediction of the relative adsorption tendencies can hardly be expected.

The literature contains comparatively few data on the heats of immersion of solids in hydrocarbons. Parks[1] has given results on the heats of immersion of silica and silica gel in water and has estimated the heat evolved per unit area, but considering the experimental procedure the values are probably far from accurate. Gaudechon[2] has made some determinations on the heats of immersion of a silica "dite amorphe" in various liquids, including pentane and hexane. No information is given as to the methods of the experiment, so that these data are also of uncertain value. Recently Grimm, Raudenbusch and Wolff[3] have measured

[1] Parks, *Phil. Mag.*, [6] **4**, 240 (1902).

[2] Gaudechon, *Compt. rend.*, **157**, 209 (1913).

[3] Grimm, Raudenbusch and Wolff, *Z. angew. Chem.*, **41**, 105 (1928).

the heats of immersion of silica gel in a number of substances in connection with their investigation of the fractionation of binary mixtures with the aid of silica gel. Bartell and Ying Fu[4] have made similar measurements using both a "dehydrated" and a hydrated silica gel. Harkins and Dahlstrom[5] have measured the heats of immersion of pigments in a number of liquids and have confirmed the observations of Grimm, Raudenbusch and Wolff that great care in removing polar substances from the organic liquids is necessary in order to obtain reliable results. The necessity for such precautions seems to have escaped the earlier workers. The results of these investigations will be discussed later. It is pertinent to note, however, that the various heat effects obtained by different authors show poor agreement even in the relative values.

Bartell and Miller[6] have developed a method for obtaining "adhesion tensions" of silica with various liquids which appears promising but evidently requires further extension to establish the thermodynamic relationships involved.

I. Preliminary Investigations

During the preliminary work it was thought desirable to determine the heat of immersion of finely ground quartz, which would allow an estimate of surface area to be made. However, the heat effects, though positive, were discouragingly small, even when large amounts of the powder were mixed with just sufficient oil for thorough wetting. For a silica which passed a 200-mesh sieve and had been dried in a current of dry air at 1000° for several hours, these heat effects were of the order of 0.05 calorie·per gram, corresponding to less than 10^{-4} calories per square centimeter. This is about one-tenth the effect obtained by Parks[1] for the heat of immersion of silica in water. Koehler and Mathews[7] found no net heat effect at all when they immersed finely divided lead sulfate in a saturated lead sulfate solution, even with areas as large as 32,000 sq. cm./g. It was obvious then that in order to measure a heat effect with powdered silica, the ordinary calorimetric methods would need to be considerably modified.

The use of powdered silica being thus found inadvisable, silica gel was used instead. The most recent views as to the nature of this material are that it is essentially an aggregate of capillary pores, offering a large surface per unit weight.[8] As a first step, then, it was decided to study the heat of immersion of silica gel in various petroleum substances.

II. Apparatus and Materials

1. Calorimeter.—The method of calorimetry was similar to that used by Patrick and Grimm.[9] The calorimeter consisted of a 100-cc. vacuum-walled flask over which was fitted a hard rubber cover. In this cover were mounted a Beckmann thermometer, a nichrome wire heater, and a copper stirrup which served at once as a stirrer and as a holder for the glass bulbs in which the silica gel had been sealed. The glass bulbs were broken by means of a rod to the end of which was fastened a four-pointed "tooth."

[4] Bartell and Ying Fu, "Colloid Symposium Annual," 1929, Vol. VII, p. 135.

[5] Harkins and Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930).

[6] Bartell and Miller, *ibid.*, **20**, 738 (1928).

[7] Koehler and Mathews, THIS JOURNAL, **46**, 1158 (1924).

[8] Patrick, "Colloid Symposium Annual," 1929, Vol. VII, p. 129.

[9] Patrick and Grimm, THIS JOURNAL, **43**, 2144 (1921).

The bulbs could thus be broken beneath the surface of the liquid, which was considered essential since it was found that exposure of the gel to the vapors for an appreciable length of time changed the heat effect considerably. The heater had a resistance of 1.64 ohms, and was connected to a number of dry cells in parallel. The vacuum flask required a charge of only 35 cc. of oil and it was found that intermittent manual stirring was sufficient to keep the temperature equalized. Repeated calibration using a measured heat input through the nichrome coil showed that the reproducibility of the calorimetric technique was well within 0.1 cal. and thus within the experimental error as shown below.

Since the metallic parts of the apparatus would be attacked by the mercaptan sample, the copper cradle and breaker rod were replaced by glass and the nichrome heating coil immersed in a thin-walled glass tube filled with oil when that substance was used.

2. **Silica Gel.**—This was a commercial silica gel powder which was purified by repeated washings with hydrochloric acid and finally with distilled water until free from chlorides. It was then air dried and sifted through a 40-mesh screen. The extremely fine particles had, of course, been removed by the decantation process so that only the grainy material was left. This was then placed in a furnace and dried for three to four hours in a current of air (dried by phosphorus pentoxide) at a temperature of 250–300°. About 500 g. of the material was prepared in this way, 50 g. at a time; then all of it was placed in a large bottle, thoroughly mixed by shaking, and then distributed to ten 100-cc. flasks which were tightly stoppered and placed in a cabinet containing silica gel as a desiccator. This cabinet was so arranged that the gel could be transferred from the flasks to the glass bulbs without exposure to the laboratory atmosphere. In this way it is believed that the charges used in the experiments were very nearly identical in composition.

An analysis of the gel showed a water content of 4.5% and impurities 0.075%. The latter are not considered of significance for the purposes of these experiments.

3. **Hydrocarbons.**—The samples of benzene, n-hexane, n-decane, cyclohexane and n-butyl mercaptan were all c. p. products from the Eastman Kodak Laboratories. All but the last were redistilled and the fractions used had a boiling range of about half a degree.

III. Experimental Procedure and Results

In making the heat of immersion determinations, about 0.7 g. of the silica gel was transferred to the previously weighed glass bulbs in the atmosphere of the desiccated cabinet, then the neck of the bulb was sealed off and the final weight obtained. The bulb was then placed in the cradle, the cover of the calorimeter put into place, the thermometer inserted and the whole placed in an air-bath, the temperature of which was automatically regulated to within 0.1° at about 29.5°. Since the temperature coefficient of the heat of immersion is probably nearly equal to zero[10] the values obtained will be valid for a considerable range above and below this temperature.

After the apparatus had been in the air-bath for one hour, the calorimeter temperature was about 2 degrees below that of the bath. Temperature readings were now recorded, and after about thirty minutes the glass bulb was broken. The temperature rise was usually about 0.5°, and the readings were continued until temperature equilibrium had again been established. Then the heater was turned on and a quantity of heat approximately equal to that developed by the silica gel was introduced. By plotting the temperature–time curves, the actual temperature rise could be determined and from this could be calculated the heat capacity of the apparatus and the heat of immersion of the gel in the liquid. Previous calibration had shown that a simple graphical method could be employed which would give the true temperature differences.

[10] *Cf.* Brown and Mathews, "Colloid Chemistry," 1926, p. 457, Alexander ed.

Such an empirical method was necessary since the usual heat loss formulas are hardly applicable to a vacuum flask type of calorimeter. This method of determining the heat capacity of each charge eliminated any uncertainties which would be introduced by the use of calculated heat capacities. It should be mentioned that the dry cells were short-circuited for about a minute through a resistance equal to that of the calorimeter heater before the latter was turned on, so that no fluctuation of the current would occur due to polarization. A typical set of data is tabulated below:

Sample: n-decane; silica gel, 0.8384 g.

Heat capacity

Amps.	0.835	Final temp.	2.604
Sec.	25.4	Initial temp.	2.311
Calories	6.96	Temp. rise	0.293°

Heat Capacity = 6.96/0.293 = 23.8 cal./°C.

Heat of immersion

Final temp.	2.192
Initial temp.	1.916
Temp. rise	0.276°

Heat of immersion = (0.276)(23.8)/0.838 = 7.84 cal./g.

Preliminary determinations confirmed the observations of Grimm, Raudenbusch and Wolff[3] and of Harkins and Dahlstrom[5] that minute quantities of foreign substances, especially water, in the organic liquids greatly affected the heats evolved. This is illustrated by the following table, in which the heats of immersion of the undried substances are compared with the final values of the dried substances.

EFFECT OF DRYING ON THE HEAT OF IMMERSION

Substance	Heat of immersion (cal./g.)		
	Undried		Dry
Water		25.4	
Benzene	17.4		13.1
Hexane	16.6		7.9

Thus it became necessary to find means of effectively drying the liquids. Benzene was thoroughly dried by sodium shavings and redistilled in an atmosphere of air dried with phosphorus pentoxide. It was then transferred without contact with the laboratory atmosphere to the calorimeter, which had previously also been dried by passage through it of dry air for several hours. The heat of immersion thus obtained was 13.0 and 13.2 cal./g. for two consecutive runs.

Another method was then tried in which the benzene without previous drying was placed in the calorimeter, then 4 g. of silica gel added and the mixture allowed to stand for about two hours to attain equilibrium. The heat of immersion was now determined as before, and the values 13.1 and 13.0 cal./g. obtained. These results show that careful drying by sodium or silica gel gave the same values, which is in accord with the experience of Grimm and co-workers mentioned above. Since drying by means of a preliminary charge of silica gel was more convenient, and since it would remove other incidental impurities besides water, this method was used in the remainder of the determinations.

The accuracy of the method is thus dependent on two main factors, providing the calorimetric technique is adequate. One is the reproducibility of the samples of the solid used. Most of the previous workers have activated each sample separately, which introduces the possibility of a variation that was avoided in this work by activating be-

forehand all the gel required. The other is the effectiveness of the drying procedure. It was found that as successively larger quantities of the dehydrating charge (of silica gel) were used, the heat effects reached a limiting minimum value. Thus when 1 g. of the gel was used as the dehydrant, the heat effect was lower than with an undried sample but not yet at the lowest value. When more than 2 g. was used, the final limiting value was obtained, and these were reproducible within 0.2–0.3 cal./g. The heat effect due to the breaking of the glass bulbs was determined and found to be somewhat less than 0.1 cal. but could not, of course, be corrected for.

Thus it can be seen that the calorimetric procedure is of secondary importance compared to the necessity of ridding the liquid of the last traces of impurities. It is believed that the preliminary wetting with silica gel accomplished this conveniently and quite thoroughly.

The final values thus obtained are given in the first column of Table I. Comparison of these values with those of other authors is not directly possible because the magnitudes of the heats of immersion appear to be functions both of the water content of the gel and of its method of preparation. This would lead to the conclusion that heat of immersion data on silica gel are valueless except for the specific gel under consideration. However, it is now evident that one of the principal reasons for the decided disparity in such values is the remarkable effect which even traces of water in the liquid used have upon the heat of immersion. Of the values on silica gel published to date, only those of Grimm, Raudenbusch and Wolff[3] seem to have been obtained with due precautions against contamination by moisture.

TABLE I

HEAT OF IMMERSION OF SILICA GEL IN VARIOUS SUBSTANCES

(Calories per Gram of Gel)

| Substance | Observed values | | | | | | Values relative to water and benzene | | | "q" for water interface ergs |
	This paper	Grimm wide pores	R. & W. narrow pores	Patrick et al.	Bartell and Ying Fu "dry"	hydr.	This paper	Grimm wide pores	R. & W. narrow pores	
Cyclohexane	6.5	3.6	6.2				5.0	5.5	5.5	
n-Hexane	7.9	3.6	6.5				6.0	5.5	5.7	58.6
n-Decane	7.8						6.0			
Carbon tetrachloride		4.7	7.3	8.4	10.0			7.2	6.5	43.3
Chloroform		6.2	10.9		14.5			9.5	9.6	
Toluene		6.4	11.3					9.8	10.0	
Benzene	13.1	6.5	11.3	11.1	12.7	21.5	(10.0)	(10.0)	(10.0)	65.0
Water	25.4	14.6	20.9	19.2	15.9	24.3	(20.0)	(20.0)	(20.0)	117.0
Ethyl alcohol		12.8	23.7	22.6	16.6	26.9		17.5	22.7	
Methyl alcohol		13.4	22.9					18.4	21.9	
n-Butyl mercaptan	25.9						20.4			

Table I gives the important values of the heats of immersion of silica gel in various liquids. The values of Parks and of Gaudechon[2] are not given because of their uncertainty. The first three columns of the table show the values obtained by the above authors and those of this paper. One of their gels was designated as "wide-pored," the other as "narrow-pored," the difference evidently being determined by the apparent density of the gels. As can be seen from the table, there is no

agreement in the absolute values among any of the gels used. However, there does seem to be possible a general classification in each group, on the one hand of the non-polar liquids like hexane and benzene, and on the other of water and other polar liquids. The former show low heat effects, the latter high ones. This suggests a correlation with dielectric constants, molecular volumes, etc., but none of these appear to be fruitful in indicating the direct cause of the difference in the heat effects.

Upon analyzing the data, it was found that the non-polar, water-insoluble liquids could be compared by using, say, benzene as a standard and computing the relative values for the others. Thus the heat effect for benzene and a hypothetical gel may be chosen as 10 cal./g., and if the actual gels are considered to differ merely in specific surface, the heat effects for the other substances may be converted to relative values for the hypothetical gel. The results are shown in the table, and bring the values for the three different gels into fairly good agreement. This is believed to be the first instance in which differently prepared samples of silica gel have been found to give comparable values, and the reason is to be found undoubtedly in the precautions used to insure removal of the last traces of water and similar impurities.

In a similar way, water may be assigned a value of 20 cal./g. and the water-like substances compared on this basis. The author did not study the alcohols, so that no comparison of the values for this class of substances can be made.

IV. Discussion

The cause of the heat effect attending the immersion of a solid in a liquid is usually considered to be the replacement of the solid surface by a solid–liquid interface. Since the interfacial energy cannot be measured, only the difference between the two total energies is determined by the heat effect. On the hypothesis that the thermodynamics of plane surfaces can be applied to such substances as silica gel, Bartell and Ying Fu[4] have attempted to calculate the free energies of immersion from the heat effects. This involves an assumption of the independence of temperature of k in the equation $\sigma_1 - \sigma_{12} = k\sigma_2$ where σ_1 and σ_2 are the surface tensions of the solid and the liquid, and σ_{12} is their interfacial tension. This cannot be tested for solid–liquid interfaces, but for interfaces such as water–organic liquid, k is found to vary with the temperature, so that it is hardly safe to assume it to be constant for the former.

An analogy which suggests itself and which was made use of by Harkins and Dahlstrom[5] is the comparison of the heat of immersion of silica gel with a hypothetical heat of immersion of water in the same liquids. Thus if it is considered that drops of water of 1 sq. cm. surface area are immersed in an organic liquid having an interfacial tension of σ_i against water, the total heat evolved would be the difference between the total

energy of the water surface before immersion and the total energy of the interface after immersion. This can be expressed as

$$\text{Heat evolved} = q = E_{\text{water}} - E_{\text{interface}}$$

But the total energy of the interface is given by

$$E_{\text{interface}} = \sigma_i - T \frac{d\sigma_i}{dT}$$

and the total surface energy of water at 25° is 117.0 ergs/sq. cm., so that

$$q = 117.0 - \sigma_i + T \frac{d\sigma_i}{dT}$$

These values have been calculated for those liquids for which the temperature coefficients of the interfacial tensions are available and are given in the column headed "q." While there is a similarity in the relative values, it is not sufficiently quantitative to warrant the conclusion that the two surfaces are alike in their behavior toward organic liquids. The Harkins and Dahlstrom data show similar trends.

For the present, then, the energies of immersion must be relied upon to give the best indication of the capillary characteristics of porous and finely divided substances toward the various liquids.

V. Conclusions

1. The heats of immersion of silica gel in various substances have been determined.

2. A method of correlation of heats of immersion of silica gel has been suggested, and the results of this paper have been found to agree with those of previous workers representing three differently prepared samples of silica gel.

3. The results indicate that the hydrocarbons investigated may be divided into three general groups. The paraffin and naphthene hydrocarbons, giving low heats of immersion; the aromatics, giving intermediate values; and the alcohols and sulfur compounds, showing high capillary activity not greatly different from that of water itself.

4. It is suggested that since at present the free energy changes attending the immersion of porous and finely divided solids cannot be determined, the heats of immersion furnish the best indication of the capillary characteristics of such solids.

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