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Applications of thermodynamics and calorimetry to the petroleum industry [a]

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Abstract

The applications of thermodynamics and calorimetry in the petroleum industry are very extensive. This paper focuses on applications to oil recovery, and particularly to enhanced oil recovery. All work reported here has been done or is in progress in this laboratory. Results obtained are presented and discussed.

INTRODUCTION

China, like many other countries, has a big problem with energy resources, especially petroleum resources. Even through China produces 130 million tons of petroleum per year, this is far from sufficient for a population of 1.1 billion. Also, the present rate of production of conventional petroleum has been declining steadily in the older oilfields, and will continue to decline. China still has, however, considerable amounts of recoverable non-conventional petroleum, such as heavy oils and bitumens. Because the viscosity of these resources is too high to be suitable for conventional production, there are plenty of difficult problems to be solved in obtaining the desired liquid fuels. China has therefore to accept the fact that the petroleum available is finite and has to develop enhanced oil recovery. For this reason we are working on research projects which are directed towards oil recovery. Some of the projects undertaken in our laboratory, and also in collaboration with L.G. Hepler's laboratory at the University of Alberta, Canada, will be reviewed briefly.

HEATS OF COMBUSTION AND SPECIFIC HEAT CAPACITIES

The heats of combustion of oils, bitumens, heavy oils, pitches, asphaltenes and cokes are required for heat balance calculations in industrial processes

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and for evaluating the quality of fuels. Because of the lack of these data in the literature, heats of combustion of many samples from China, Canada and the United States have been measured using static and rotating bomb calorimeters [1,2]. The following idealized combustion reaction was used to calculate the heat of combustion ΔU°

$$\mathrm{C}_a\mathrm{H}_b\mathrm{O}_c\mathrm{N}_e(\mathrm{l\ or\ s}) + (a + d + b/4 - c/2)\mathrm{O}_2(\mathrm{g})$$
$$= a\mathrm{CO}_2(\mathrm{g}) + (b/2)\mathrm{H}_2\mathrm{O}(\mathrm{l}) + d\mathrm{SO}_2(\mathrm{g}) + (e/2)\mathrm{N}_2(\mathrm{g})$$

in which the reactants and the products are in their thermodynamic standard states at 298.15 K.

On the basis of elemental analysis of the sample, the results of measurements of heats of combustion can be summarized with useful accuracy by an empirical equation of the form

$$\Delta U^\circ = A(\mathrm{wt.\%\ C}) + B(\mathrm{wt.\%\ H}) + C(\mathrm{wt/\%\ S}) + D(\mathrm{wt.\%\ O} + \mathrm{wt.\%\ N})$$

in which ΔU° represents the heat of combustion in kJ g^{-1}, and A, B, C and D are constants.

Specific heats of various substances heated or cooled in all thermal processes are needed for industrial design and calculations. Many specific heats of heavy oils, bitumens, minerals, rocks and clays have been measured. In order to suit the recovery requirements of heavy oils and bitumens in China, we have made measurements of the specific heats of heavy oils, bitumens and minerals taken from the Xinjiang and Liaohe oilfields with a differential scanning calorimeter over the temperature range 300–650 K. Some empirical equations were established from such measurements and expressed in terms of an equation of the form [3]

$$C_p = a + bT + cT^2$$

in which C_p represents the specific heat (J K^{-1} g^{-1}), T is the temperature on the Kelvin scale, and a, b and c are constants.

THERMODYNAMICS OF MINERAL–WATER/SOLUTION INTERACTIONS

Thermodynamics of interaction of aqueous solutions with various minerals are important in many phases of oil recovery. We have been working on the adsorption of surfactants onto minerals by means of adsorption microcalorimetry. Many experiments on adsorption of anionic surfactants, such as sodium decyl sulfate, sodium dodecyl sulfate and sodium tetradecyl sulfate, onto silica gel or minerals were carried out at concentrations below and above their critical micelle concentration (c.m.c.). The adsorption curves for surfactant concentrations above the c.m.c. are quite different from those for surfactant concentration below the cmc, whereas the desorption curves vary little. It might be understood that when the surfactant concentration is

TABLE 1

Heats of immersion of water on silica gel

Sample	No. experiments	ΔH_i (J g^{-1})
Treated water	9	-94.4 ± 1.3
Untreated water	12	-105.4 ± 1.9

above the c.m.c., two other processes are involved in the adsorption reaction besides adsorption: adsorption demicellization and dilution demicellization. The heat data of adsorption and desorption are considered with regard to these three processes. For the alkyl sulfate homologues, the inflection points of the enthalpy isotherms corresponded to their respective c.m.c. The silica gel has an enlarged surface but with weak adsorption. The homologues were adsorbed by a similar mechanism, such that the adsorption involved only a transfer of monomers from the bulk to the interface without appreciable adsorbate–adsorbate interaction [4].

The properties of water and solvents immersing the minerals are very important for enhanced oil recovery. We have carried out many measurements of heats of immersion using an LKB-2107 batch adsorption microcalorimeter. More recently, magnetic technology has been widely used for oil recovery in China and other countries. For practical purposes, our laboratory is involved with the research project on magnetic field effects directed towards oil recovery. We have been studying calorimetrically the effect of a magnetic field on the interaction between water/solution and minerals. Table 1 gives the experimental results of heats of immersion of magnetically treated and untreated water on silica gel. From the results in Table 1, it can be seen that the heats of immersion of magnetically treated water on silica gel are decreased by about 10% in comparison with those of magnetically untreated water [5,6].

THERMODYNAMIC PROPERTIES OF SURFACTANT SOLUTIONS

Various aqueous surfactants have proved to be useful in enhanced oil recoveries both from conventional oils and from heavy oils and bitumens, and also in breaking variously produced emulsions and treating tailings. For surfactant solutions, the c.m.c. is an important property. With due regard to conditions at different oilfields, the thermodynamics of the formation of micelles were investigated using microcalorimeters, a titration calorimeter and a solution calorimeter.

We have investigated the variation of c.m.c. with temperature by measuring surface tension at different temperatures and varying concentrations. From the results obtained, some thermodynamic quantities of micelle formation have been calculated. We have also measured calorimetrically the heats of dilution of aqueous surfactants at concentrations above and below the c.m.c. Calorimetric results lead to the enthalpies of micelle formation, which agree well with the calculated values [7].

Steam flooding is now one of the principal methods for recovering heavy oils and bitumens, but for some reason its efficiency is still not high. In order to improve the recovery efficiency, various chemicals are frequently used as additives in steam flooding. Choosing a suitable surfactant for thermal recovery is more difficult than for conventional ambient temperature recovery because the substance is to be used at elevated temperatures and pressures. For the choice and evaluation of such surfactants, calorimetry is very important in studies of the thermal and phase behavior as well as interactions between the surfactant and components of the oil reservoir. Precise calorimetric measurements and data analyses can provide thermodynamic information on relationships between the properties and structure of surfactants.

As mentioned above, the study concerned with the effect of magnetic fields is a very interesting but difficult problem. We have also made many measurements related to the effect of magnetic fields on physicochemical properties of surfactants. The results showed that when the surfactant solutions were treated magnetically under certain conditions, some unusual changes in their physicochemical properties could be observed [8,9]. These unusual changes have proved to be useful in many types of oil recovery, such as injecting water, breaking emulsions, treating tailings, restraining clay swelling, and improving permeability.

THERMODYNAMICS OF GASES IN LIQUIDS/HEAVY OILS AND BITUMENS

Solubilities of gases in liquids are important in both practical applications and pure science. Although investigations on the solubilities of gases in liquids have been undertaken for one and a half centuries, researchers are still maintaining their interest in these fields. Our interest is concentrated on both basic scientific research and practical applications directed towards recoveries of heavy oils and bitumens. It is therefore our purpose to build an apparatus for solubility measurements on gas–liquid systems which can be operated easily and readily at high temperatures and high pressures with reasonable precision.

For thermal recovery, data for the gas solubility, viscosity and density of gas-saturated heavy oils and bitumens are required for a mathematical model, for simulating the in situ process of their extraction, and also for recovery from mined oils sands by solvent extraction. Because the chemical compositions and physical and chemical properties of these materials, particularly their highly viscous nature, are very complex and vary considerably from one reservoir to another, it is not easy to measure these equilibrium properties directly by conventional methods. Moreover, these kinds of experiment are time consuming, tedious and costly, and therefore precise data on these properties are seldom available in the literature. Consequently, empirical correlations based on such data would not and cannot give satisfactory predictions. Our involvement in the thermal recovery of heavy oils and bitumens has made us realize the importance of such data in China and in the world at large. Therefore a three-function apparatus for accurately, readily and easily measuring solubilities of gases in liquids (also in heavy oils and bitumens), viscosities and densities of gas-saturated heavy oils and bitumens at temperatures up to 590 K and pressures up to 12 MPa has been designed and constructed in our laboratory [10]. The precisions achieved for the solubility, viscosity and density measurements of heavy oils and bitumens are ±1% (±0.2% for common liquids), ±5% and ±0.5% respectively. The time to reach equilibrium is about 4–6 h for common liquids and 10 h for heavy oils and bitumens.

Using this apparatus, more than one thousand experiments on the solubilities of gases in pure solvents, mixed solvents, heavy oils and bitumens and on the viscosities and densities of gas-saturated heavy oils/bitumens have been carried out. For most purposes, it is more useful and convenient to have empirical equations. For pure and mixed solvents, the relationship between solubilities and pressures can be expressed by an equation of the form

$$\ln X_2 = A + BP_2 + CP_2^2 + D \ln P_2$$

in which X_2 represents the solubility as a mole fraction, P_2 represents the partial pressure (MPa) of the solution and A, B, C and D are constants.

Changes in the Henry's Law constant H with temperature are fitted by the least-squares method to the following equation:

$$\ln H = a + b(1/T) + c(1/T)^2 + d \ln(1/T)$$

in which a, b, c and d are constants, indicating that they are associated with the absolute temperatures, represented by T.

From the results obtained, some thermodynamic quantities have been calculated and discussed [11,12].

As to practical application of the experimental results, they are employed in three ways: firstly, they are used directly for mathematical model and design calculations of recovery processes; secondly, they are used to set up theoretical models to predict and estimate other new properties; thirdly, according to the different conditions of oil reservoirs, they can be used to improve and develop recovery methods to raise the recovery efficiency.

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