Short Communication

Characterization of Bitumens by Means of Potentiometric Titrations

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Petroleum bitumens are considered to be colloids in which polar asphaltenes are dispersed in a continuous phase of lower molecular mass.[1] The asphaltene micelles are surrounded by polar aromatics which serve as protective colloids. The polarity of bitumens, which is due to the acidic and basic functional groups of the asphaltenes and the peptizing molecules, is an important factor that affects their physical and chemical properties. These acids and bases are usually weak and can be determined, among other methods, by means of non-aqueous potentiometric titrations.[2-5]

Fig. 1. Titration curves of a Laguna bitumen.

The ASTM-IP standard titration procedure[2] used in determining the acidity and basicity of oil products, including bitumens, is fairly simple. The solvent is a mixture of toluene, isopropyl alcohol and water (500:495:5 v/v). The sample is titrated to a certain potential or using indicators with KOH or HCl dissolved in isopropyl alcohol. Very weak acids or bases cannot be detected,[3] but in its application range the method gives even more information than the original standard describes.

In this study, samples of different bitumens were thus titrated using a conventional pH meter (Orion Research SA250) equipped with a glass calomel combination electrode (with 3 M aqueous KCl as salt bridge). It was standardized with two aqueous buffer solutions. As a typical example, the titration curve of a Laguna bitumen (Venezuela) is shown in Fig. 1. The representation is the same as used for amino acids:[6] the upper right branch of the curve represents the titration of acids, the lower left branch corresponds to bases. The contribution of the solvent was subtracted. The observed pH meter readings are given instead of potentials. These readings do not directly express the acidity of the solution, as in this mixed solvent there is a liquid junction potential of unknown magnitude at the reference electrode. The results can, however, be interpreted by titrating certain model compounds in the same way. As shown in Fig. 2, there is a satisfactory linear correlation (slope 0.98) between the half-neutralization potentials in this solvent (expressed in pH meter readings) and the pK_a values reported for carboxylic acids and phenols in water.[7] On average, the acids are titrated at 4.2 pH units higher than in aqueous solutions. For the amine bases, the slope of the correlation line is 0.90 (with pyridine excluded). Bases with pK_b values of 7 and 11 are thus titrated, respectively, at 1.9 and 1.5 pH units lower than in water. The resulting pK scales have been marked in Fig. 1.
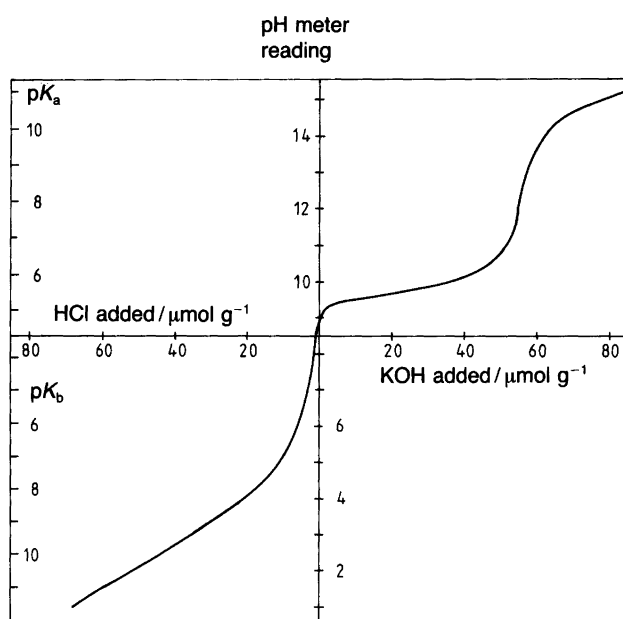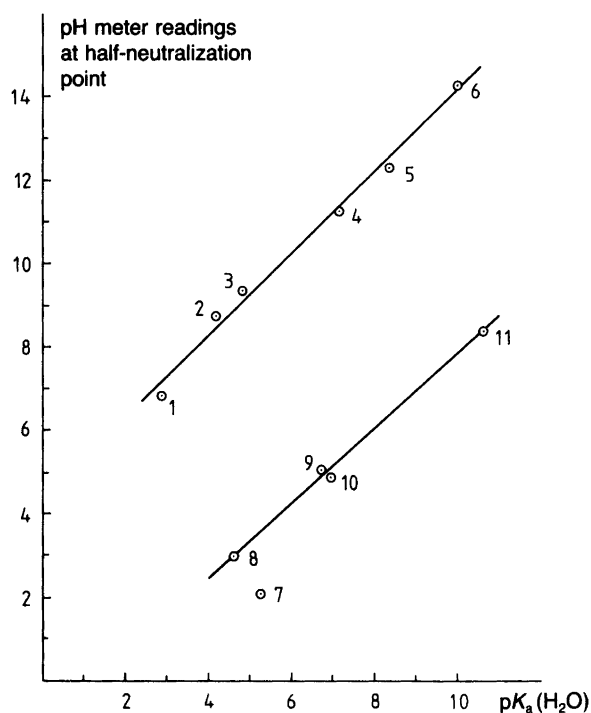
Fig. 2. Relationship between the found half-neutralization points and pK_a values for some model protolytes. The compounds are: (1) chloroacetic acid, (2) benzoic acid, (3) n-pentanoic acid, (4) 4-nitrophenol, (5) 3-nitrophenol, (6) phenol, (7) pyridine, (8) aniline, (9) 2-aminopyridine, (10) imidazole and (11) n-butylamine.

Fig. 3. The buffer capacity distribution for a Laguna bitumen derived from Fig. 1.

According to the Henderson–Hasselbalch equation,[8] weak acids and bases are mainly titrated around their pK_a values. Thus the derivative of the titration curve, or buffer capacity, can be used to characterize the protolytes of a sample. The buffer capacity distribution derived from the example titration curve is presented in Fig. 3. The acidity of this Laguna bitumen seems to be mainly due to carboxyl groups, while a smaller part comes from phenolic functionalities. Outside the upper limit there are weak acids which cannot be determined by this method. No prominent basic species can be distinguished, but the sample behaves like a continuous mixture of fairly weak bases. The method is not suitable for the analysis of very weak bases.
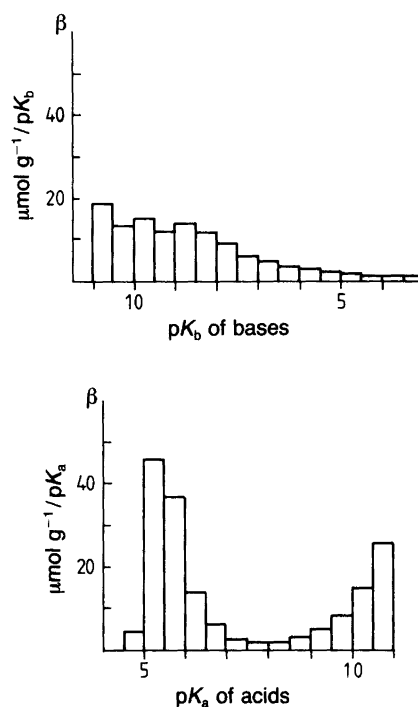
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Ternary Phases in the System Au–Cu–Sn

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This short communication gives a brief account of three, hitherto unknown, genuine ternary phases in the Au–Cu–Sn system. A comprehensive report on the Au–Cu–Sn phase diagram (including aspects such as temperature and composition dependences of intermediate phases, tie-lines etc.) as well as reaction kinetic features for some of the phases concerned will be published in due course. The study of the Au–Cu–Sn system is part of a program on ternary tin systems aimed at various goals; these include the fundamental nature of crystal growth in tin flux melts, and more applied aspects such as the reaction between soft solder and metals. In addition, tin phases often provide challenging characterization problems for metallography, X-ray diffraction etc.

When the present program was planned and started, only two rather peripheral studies[1,2] on the Au–Cu–Sn system were available. Shortly before the present report was concluded a third paper[3] came to hand which deals with low-temperature diffusion of Sn into Au–Cu alloys. The composition of two new ternary phases was reported: $Au_{25}Cu_{55}Sn_{20}$ and $Au_{33.3}Cu_{33.3}Sn_{33.3}$. These compositions belong to the phase regions B and C, respectively, in the present paper.

Samples were made by melting (heated at 1100–1200 °C for ca. 1 min under vigorous shaking) appropriate amounts of 99.95 % Au (K. A. Rasmussen), 99.9 % Cu (J. T. Baker) and 99.98 % Sn (E. Merck) in sealed, evacuated silica-glass tubes. This initial heat treatment was concluded by quenching the samples from the molten state into ice water. Most of the samples were afterwards annealed at 360 °C and in some cases also at various other temperatures. The homogeneity, composition and structural state of the samples at room temperature were examined by powder X-ray (Guinier) diffraction, metallography, scanning electron microscopy (SEM), density measurements and differential thermal analysis (DTA). For details of the experiments and documentation of results reference is made to the forthcoming comprehensive report[4] on our findings.

The isothermal section of the Au–Cu–Sn phase diagram

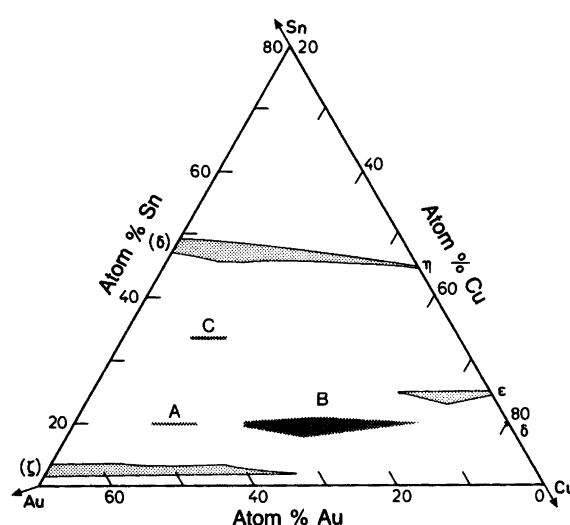* To whom correspondence should be addressed.

Fig. 1. Isothermal portion of the Au–Cu–Sn phase diagram at 360 °C. A, B and C refer to genuine ternary phases. Notations for binary phases (of which most extend into the ternary region) correspond to those for the binary systems.

at 360 °C shown in Fig. 1 includes the three genuine ternary phases of the system. For want of a suitable rational notation we have adopted the notation A, B and C. As also seen from the illustration most of the binary phases of the Au–Sn and Cu–Sn systems extend into the ternary region.

Phase A comprises 20 atom % Sn, but has an appreciable range of homogeneity with respect to Au and Cu. At 360 °C this phase is stable between the $Au_{43}Cu_{37}Sn_{20}$ and $Au_{49}Cu_{31}Sn_{20}$ (viz. 43–49 atom % Au). However, phase limits are very susceptible to temperature, the homogeneity range extending to $Au_{15}Cu_{65}Sn_{20}$ at 550 °C. Phase A is quenchable, and powder X-ray diffraction diagrams obtained from quenched samples at room temperature are indexed (cf. the data for $Au_{200}Cu_{600}Sn_{200}$ in Table 1) on a b.c.c. unit cell. The unit cell dimension varies linearly with the atom % Au from a = 912.1(5) pm for $Au_{15}Cu_{65}Sn_{20}$ to a = 948.4(6) pm for $Au_{48}Cu_{32}Sn_{20}$. The pycnometric density of 11.20 g cm^{-3} for $Au_{200}Cu_{600}Sn_{200}$ (quenched from 550 °C) shows that the unit cell comprises 52 (51.6 according to the density) atoms. It will later be documented that the crystal