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Factors That Affect the Potential of the Saturated Corrosive Sublimate (in Ethylenediamine) Electrode

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The system, $Hg/HgCl_2$ (satd.), LiCl (satd.) in ethylenediamine, after being aged for 24 hours, has a potential reproducible to within ±0.5 mv. and a temperature coefficient of −1.3 mv. per ° C. at room temperature. Introduction of water causes the potential to shift positive, but the effect is less than 3 mv. for not more than 2.5% of water. At 25° C., the apparent potential of the saturated corrosive sublimate electrode (SCSE) with respect to a pH-meter-type (aqueous) saturated calomel electrode is −450 mv. Aging for 2 weeks causes the SCSE to become ~11 mv. negative to a 24-hour SCSE. The difference persists at this value for several days.

STUDIES in a nonaqueous solvent are sometimes made with the aid of a reference electrode that is essentially a saturated calomel electrode made in the chosen solvent. Although solvents such as methanol (*4*) or acetic acid (*2*) can be used, a calomel electrode prepared with ethylenediamine (EDA) is unsatisfactory because of the reaction between calomel and EDA. In their studies on equilibria in EDA solutions, Bruckenstein and Mukherjee (*3*) introduced the saturated corrosive sublimate electrode (SCSE). This consists of a mercury pool in contact with an EDA solution that is saturated with respect to both mercury (II) chloride and lithium chloride. These workers found that duplicate electrodes agreed in potential to within several tenths of a millivolt. The present work is concerned mainly with the effects of age, temperature, and added water on the potential of the system.

EXPERIMENTAL

Chemicals. EDA, lithium chloride, and mercury(II) chloride, dried as was done previously (*5*), contained, respectively, 0.058, 0.10, and 0.04 gram of water per 100 grams of sample.

Apparatus. Each ~80-ml. borosilicate glass half-cell vessel *A* had near the bottom a short side arm pointing upwards at ~45° and terminating in a 10/30 female cone. Twin mercury-pool J-tube electrodes were sealed to the underside of the 29/42 stopper in the mouth of the vessel. Contact to each 5-mm. diameter pool was made by a platinum wire sealed through a septum in the J-tube and brought out through the stopper. The vessels, used only for solutions without added water, were joined by a Λ-shaped junction tube, the ends of which carried 7-mm. diameter fine-porosity glass frits on the ends of 10/30 male cones. Vessel *B*, with two side arms and an additional capped opening near the stopper, was used to carry the saturated (aqueous) calomel electrode or, with J-tube electrodes inserted, for solutions containing added water. When in use, vessel *B* was connected through junction tubes to two type-*A* vessels. Cell assemblies were mounted in a grounded copper box that was almost completely immersed in a thermostat bath. In temperature-difference studies, boxes containing the individual half-cells were placed in adjacent baths. Temperatures were controlled to better than ±0.01° C.

E.m.f. measurements were made through shielded leads to a calibrated Leeds and Northrup Model 7664 pH meter. When necessary, the meter sensitivity was increased to 70 mv. full scale deflection by insertion of Accessory Resistor No. 115077. The (aqueous) saturated calomel electrode was Leeds and Northrup Type 1199–31.

Procedure. All operations other than in closed vessels were brief and carried out in dry nitrogen. About 40 ml. of EDA was distilled into each half-cell vessel that contained lithium chloride and mercury(II) chloride in amounts ~10% greater than required to saturate the final solution. When necessary, water was measured in from a microburet. The vessels were then closed and gently agitated at the desired temperature for ~24 hours. The electrodes were inserted, the side arms uncapped, and the junction tube was attached. This tube was filled with EDA saturated at 25.0° C. with both lithium chloride and mercury(II) chloride. A cell used from 24 to 30 hours after insertion of the electrodes is termed a "fresh half-cell."

Results. Fresh half-cells prepared from distilled (0.058 gram water per 100 grams of distillate) EDA agreed with one another and with a half-cell of pool diameter ~20 mm. to within 0.5 mv. At 25.0° C., a fresh half-cell was 6.5 ± 0.5 mv. negative to a similar half-cell at 20.0° C. This potential difference remained essentially constant for 1 to 2 days, then slowly increased. After 4 to 5 days, a white film appeared on the mercury in the warmer half-cell. Renewal of all mercury surfaces without changing the solutions or the temperatures caused the potential difference to revert to 6.5 ± 0.5 mv. At 25.0° C., a half-cell aged for 2 weeks was

Table I. Effect of Water on the Potential of the SCSE at 25.0° C.

Added water, grams/100 grams solvent[a]	0.258	0.387	0.644	1.16	1.81	2.58	3.35	4.25	5.16
Potential, mv.[b]	+1.1	+1.6	+1.7	+2.1	+2.3	+2.8	+3.1	+3.3	+3.6

[a] Distilled ethylenediamine. [b] ±0.5 mv. With respect to a similar half-cell with no added water.

~ 11 mv. negative to a fresh half-cell at the same temperature, and remained thus until observations were terminated about 1 week later. This effect has been confirmed by Bruckenstein (*1*), who noted that the spurious potential difference decreased on prolonged aging. Bruckenstein found that the difference was only 5.5 mv. after 27 days, and that a half-cell aged for 51 days at room temperature agreed with a fresh half-cell to within 0.5 mv.

The potentials of two fresh half-cells at 25.0° C., 450 ± 2 mv. negative with respect to the saturated (aqueous) calomel electrode at the same temperature, remained essentially constant for ~ 5 hours and then slowly fell numerically. Readings were −440, −425, −415, and −395 mv. (all ± 2 mv.) after 1, 2, 3, and 5 days, respectively, but remained close to −395 mv. during the next few days. The cell contents were not disturbed, apart from renewing the mercury surfaces in the EDA half-cells before readings were taken. These experiments were made only to obtain an approximate relationship between the potential of the SCSE and that of a common aqueous reference electrode. The pronounced drift may be due to inconstancy of the junction potential between the EDA and water systems.

Addition of water to a fresh half-cell caused its potential to become positive to that of an unadulterated half-cell. The results in Table I, taken 24 hours after each addition of water, were obtained in a single run. The surfaces of all six mercury pools were renewed before a reading was taken.

The potential of a fresh half-cell remained essentially constant during the passage of 6 liters of carbon dioxide over the surface of the solution.

DISCUSSION

Although the saturated corrosive sublimate electrode system of Bruckenstein and Mukherjee (*3*) has satisfactory short-term reproducibility, the potential should be checked at intervals if operations are extended. The temperature coefficient, −1.3 mv. per ° C. at room temperature, is about double that of the saturated (aqueous) calomel electrode. The potential of the SCSE shifts in the positive direction as water is introduced, but the shift is less than 3 mv. for not more than 2.5% of water.

ACKNOWLEDGMENT

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Identification of Some Cyclic Sulfides in a Wasson, Texas, Crude Oil Distillate Boiling from 111° to 150° C.

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Knowledge of the sulfide sulfur content of petroleum is both of theoretical interest and of practical value to the petroleum industry. This paper discusses a procedure for the isolation and identification of cyclic sulfides in petroleum and reports the identification of 17 cyclic sulfides in a 111° to 150° C. boiling-range distillate. This procedure should have general application in the characterization of petroleum distillates.

THE IDENTIFICATION of sulfur compounds in petroleum has special significance for petroleum scientists. Information about these sulfur-containing constituents is valuable, both as an addition to fundamental knowledge and as an aid in processing applications.

Historically, cyclic sulfides first were found in petroleum by Mabery (*6*) in 1900. In 1925, Thierry (*8*) corroborated the presence of cyclic sulfides in a Persian crude oil, and since then other investigators (*1, 2, 7*) also have found them in various crude oils. Previous studies by the author and coworkers report the identification of 22 chain sulfides (*9*) and 35 thiols (*3*) in a 111° to 150° C. boiling-range distillate of Wasson, Tex., crude oil. This paper presents a systematic procedure for the isolation and identification