Partition Equilibria of 2-Methyl 5-Ethyl Pyridine in the Systems of Benzene-Water and Chloroform-Water

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It is well known that 2-methyl 5-ethyl pyridine (M. E. P.) is prepared through the condensation of paraldehyde with aqueous ammonia[1], where benzene and chloroform are used to extract M. E. P. from the reaction product[2,3].

This paper presents a brief discussion on the partition equilibria of M. E. P. in the above-mentioned systems.

Experimental

A thermostat adjusted to ±0.1°C, and conical flasks of 300 cc. with tight stoppers were used. M. E. P. was prepared by catalytic condensation of paraldehyde with aqueous ammonia[1]. The crude M. E. P. was rectified for several times; b. p. 74°C/20 mmHg, n_D^{20}, 1.4966.

Benzene and chloroform were rectified, and their boiling points were 80~81°C and 61~62°C respectively. Several solutions, being varied in concentration of M. E. P. (less than 3.0 mol./l.) in benzene and chloroform (50 cc.) were prepared in the flasks. Distilled water (150 cc.) was added to each of them, and they were settled for a certain time after being subjected to vigorous shaking every 5~6 min.

Each group of five samples was brought side by side in the thermostat for 2 hr. at 10, 20, 30, 40 and 50°C, and used for analysis.

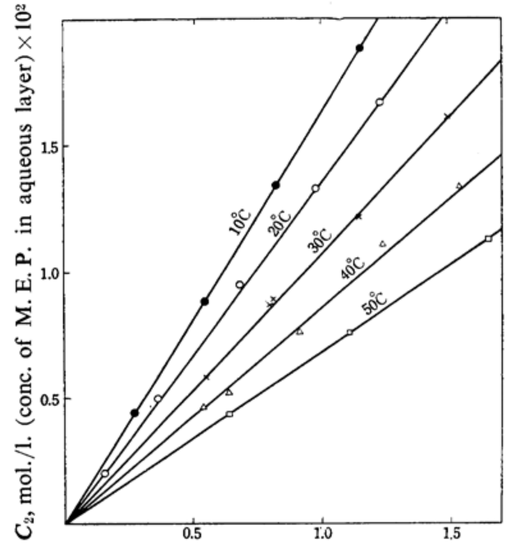
The concentration of M. E. P. was easily determined by titration with N/2 HCl, where methyl orange was used as an indicator.

Volumes of samples employed for analysis were 5 cc. for benzene and chloroform layer and 100 cc. for the aqueous layer, where the former was titrated in the mixed solvent (100 cc.) of isopropyl benzene and ethylene glycol.

Results and Discussion

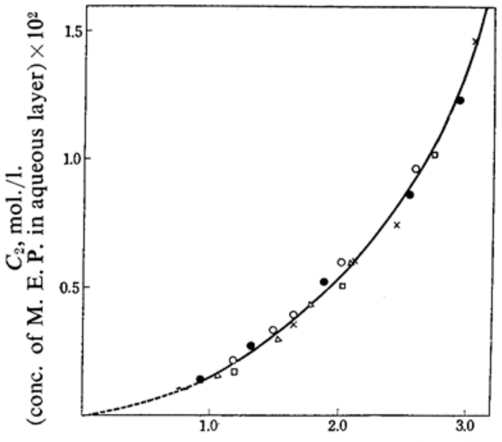
In Fig. 1 (2), C_1 and C_2 are the concentrations of M. E. P. in benzene (chloroform) and aqueous layers and both of them were calculated from volumes of consumed N/2 HCl (cc.), while titrating volumes were corrected by blank tests.

In the system of benzene-water, the constancy of $K(C_2/C_1)$ with the change of C_1 or C_2 at each temperature is confirmed, and the linear relation between $\log K$ and $1/T$ (T: absolute temperature, °K) shown in Fig. 3 suggests that it satisfies the following thermodynamic formula.



C_1, mol./l. (conc. of M. E. P. in benzene layer)

Fig. 1. Equilibrium concentrations of M. E. P. in benzene and water.



C_1, mol./l. (conc. of M. E. P. in chloroform layer)

Fig. 2. Equilibrium concentrations of M. E. P. in chloroform and water.

—●— 10°C
—○— 20 〃
—×— 30 〃
—△— 40°C
—□— 50 〃

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[1] U. S. Pat., 2,615,022 (1952).
[2] U. S. Pat., 2,703,804 (1955).
[3] U. S. Pat., 2,769,007 (1956).

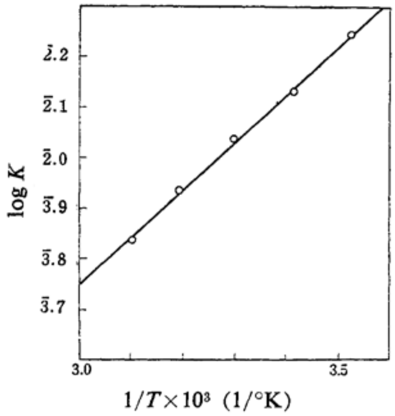

Fig. 3. Equilibrium constant K (benzene-water).

$$\ln K_2/K_1 = -\boldsymbol{Q}/\boldsymbol{R}(1/T_1-1/T_2)$$

where $\boldsymbol{R}$ is gas constant, and Q the heat of transference of 1 mol. M. E. P. from benzene to water under equilibrium state.

Thus Q was determined to be 4.3 kcal./mol. Therefore the equilibrium constant K of M. E. P. between benzene and water satisfies the following formula

$$K=7.7_6\times10^{-6}\,e^{2.19\times10^3/T}$$

In the system of chloroform-water, the parabolic relation between C_1 and C_2 was found (Fig. 2) and the constancy of K ($\sqrt{C_2}/C_1$) at each temperature was confirmed, as shown in Fig. 4.

This means that the molecular weight of M. E. P. in chloroform is half of that in water or benzene, so the molecules of M. E. P. in latter solvents seem to associate with each other. Furthermore, the values of K in each temperature are uniformly equal to 3.7×10^{-2}, and their changes with temperatures (10∼50°C) are negligibly small.

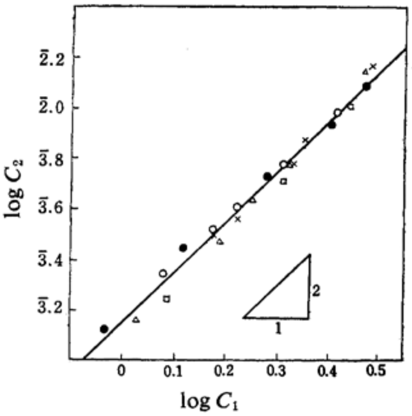

Fig. 4. Linear relation of $\sqrt{C_2}$ to C$_1$ (chloroform-water).

—●— 10°C
—○— 20 〃
—×— 30 〃
—△— 40°C
—□— 50 〃

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