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TEMPERATURE EFFECT ON THE PARTITION AND DIMERIZATION CONSTANT OF BENZOIC ACID

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ABSTRACT

Making use of the regular solution theory with binary coefficients, the partition of benzoic acid between aqueous benzene phases was investigated. ΔH, ΔS and ΔG thermodynamic functions associated with the hydration-corrected partition and dimerization were calculated. It was found that the partition was spontaneous at high temperatures and of the hydrates of benzoic acid, the monohydrate monomer was dominant at high temperatures.

INTRODUCTION

The partition method has been widely used for the determination of dimerization constants of carboxylic acids in solvents only slightly miscible with water [1–4]. The reported values of the dimerization constant determined by IR spectroscopy and the partition method have indicated that there have been considerable discrepancies among them [3]. The disagreement has been interpreted in terms of hydration and association equilibria by Christian and co-workers [5–8]. According to Tanaka and co-workers [9–11], monomer monohyrate, dimer, monomer dihydrate and dimer monohydrate of benzoic acid might have formed in the benzene phase saturated with water. Barcza et al. [12], however, have reported that the hydration-corrected dimerization constants of benzoic acid given by partition agreed fairly well with that from the IR method.

Owing to the fact that measuring the hydration change of the acid monomer and dimer in the organic phase with temperature is difficult, the partition and dimerization equilibria in the systems under consideration have not been investigated in terms of the temperature effect. In this study, an attempt to examine this subject has been made, making use of the regular solution theory [13].

EXPERIMENTAL

All substances used in this study were purchased from Merck.

Benzoic acid was purified by recrystallization twice from water, m.p.

122.0°C. Benzene was washed successively with dilute sodium hydroxide, water, and concentrated sulfuric acid and, finally, five times with distilled water. The chief impurities in ordinary water, viz. ammonia and carbon dioxide, were removed by treatment with alkaline permanganate, followed by distillation.

Benzene containing benzoic acid (15 cm^3) and 0.1 M $(Na,H)ClO_4$ (15 cm^3) aqueous solutions were equilibrated in a 50-cm^3 tube immersed in a Haake FS thermostat. The benzoic acid concentration in the two equilibrated phases was established by volumetric titration with 0.1 M NaOH solution free from carbonate. The liquid densities were measured by a 10-ml picnometer.

RESULTS AND DISCUSSION

Let benzoic acid be denoted by HA and its monomeric and dimeric forms by HA and $(HA)_2$, respectively. For the partition of the acid between water and benzene, we have then the following equilibria to consider

$$HA_w \overset{K'_{D,HA}}{\rightleftharpoons} HA'_o \tag{1}$$

$$HA'_o + HA'_o \overset{K'_2}{\rightleftharpoons} (HA)'_{2,o} \tag{2}$$

It follows that the ratio of the total concentration of benzoic acid in the benzene and water layers is

$$\frac{[HA]_o}{[HA]_w} = D = K'_{D,HA} + 2K'^2_{D,HA}K'_2[HA]_w \tag{3}$$

Let it be supposed that the hydrated species of the acid in the organic phase are denoted as $HA \cdot (H_2O)_m$ and $(HA)_2 \cdot (H_2O)_n$. Then, the following association equilibria can be written

$$2HA_o \overset{K_2}{\rightleftharpoons} (HA)_{2,o} \tag{4}$$

$$HA_o + mH_2O_o \overset{B_{1,m}}{\rightleftharpoons} HA \cdot (H_2O)_{m,o} \tag{5}$$

$$(HA)_{2,o} + nH_2O_o \overset{B_{2,n}}{\rightleftharpoons} (HA)_2 \cdot (H_2O)_{n,o} \tag{6}$$

From the equilibria given above, the non-hydration-corrected dimerization constant, K'_2, is related to the hydration-corrected dimerization constant, K_2, as follows

$$K_2 = K'_2(1 + \Sigma B_{1,m}[H_2O]^m_o)^2(1 + \Sigma B_{2,n}[H_2O]^n_o)^{-1} \tag{7}$$

According to eqn. (3), the intercepts corresponding to zero aqueous

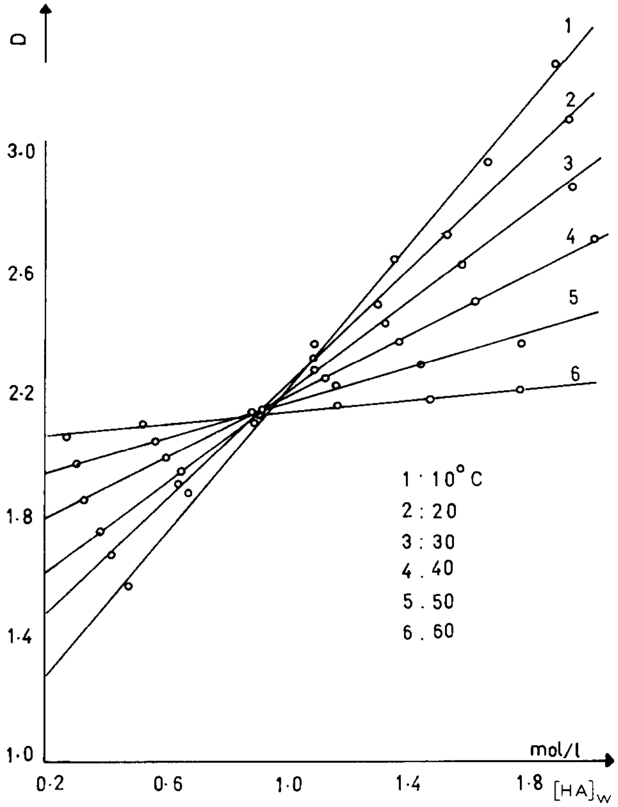

Fig. 1. Partition constants of benzoic acid as a function of $[HA]_w$ at constant temperatures.

solution concentration in Fig. 1 drawn between D and $[HA]_w$ at various temperatures yield $K'_{D,HA}$ constants shown in Table 1.

Recalling that $C_7H_6O_2$, $C_7H_6O_2 \cdot H_2O$, $(C_7H_6O_2)_2$, $C_7H_6O_2 \cdot (H_2O)_2$ and $(C_7H_6O_2)_2 \cdot H_2O$ species, and two possible structures of dimeric carboxylic acids such as open dimer and cyclic dimer, are assumed to be present in the aqueous phase, one expects interactions among these species. Also, based on the fact that, as is seen from Fig. 1, the partition of benzoic acid has changed with temperature and tended to a constant value in the vicinity of $[HA]_w = 0.9$ mol l^{-1}, a mechanism of partition governed by thermodynamic functions should be considered.

Instead of using the rigid geometric mean assumption involved in the

TABLE 1

Non-hydration-corrected partition constants

t (°C)	10	20	30	40	50	60
$K'_{D,HA}$	1.046	1.320	1.472	1.699	1.892	2.060

TABLE 2

Molar volumes and solubility parameters

t (°C)	V_w ($cm^3\ mol^{-1}$)	V_o ($cm^3\ mol^{-1}$)	d_w ($J^{1/2}\ cm^{-3/2}$)	d_o ($J^{1/2}\ cm^{-3/2}$)
10	18.025	87.719	48.32	19.19
20	18.052	88.731	48.03	18.87
30	18.098	89.847	47.71	18.54
40	18.161	90.992	47.32	18.23
50	18.237	92.081	46.90	17.92
60	18.327	93.283	46.50	17.61

usual regular solution theory [13], Fujii et al. [11] included an empricial binary coefficient, $l_{HA,s}$. Hence, one obtains the following equation for the activity coefficient of a solute HA, a_{HA}

$$RT \ln a_{HA} = RT\{\ln[HA]_s - \ln 1000V_{HA}^{-1} + Q_s(1 - V_{HA}V_s^{-1})\} + V_{HA}Q_s^2\left[(d_s - d_{HA})^2 + 2l_{HA,s}d_{HA}d_s\right] \tag{8}$$

where V_s, d_s and Q_s denote the molar volume, solubility parameter and volume fraction of solvent, respectively. V_{HA} and d_{HA}, however, refer to the molar volume and solubility parameter of the solute HA, respectively.

When the solute is partitioned between the aqueous and organic phase, i.e., $a_{HA,w} = a_{HA,o}$, and when the concentration of solute is sufficiently low in both phases, i.e., $Q_w = 1$ and $Q_o = 1$, the following expression for the partition constant of HA, $K_{D,HA}$, is obtained

$$\log K_{D,HA} = V_{HA}\left[(d_w - d_{HA})^2 - (d_o - d_{HA})^2 + 2l_{HA,w}d_{HA}d_w - 2l_{HA,o}d_{HA}d_o + RT(V_o^{-1} - V_w^{-1})\right]/2.303RT \tag{9}$$

The molar volumes calculated from densities and the solubility parameters evaluated from the heats of vaporization [14,15] are collected in Table 2.

The binary coefficients are determined by means of the following equation derived from eqn. (9)

$$\log[HA]_s = 3 - \log V_{HA} - 0.4343Q_w(1 - V_{HA}V_w^{-1}) - 0.4343V_{HA}Q_w^2 \times \left[(d_w - d_{HA})^2 + 2l_{HA,w}d_{HA}d_w\right]/RT \tag{10}$$

Calculating the slope of the plots in Fig. 2 and intersecting the slope to zero [H_2O], we obtained the following equation from which the binary coefficients in Table 3 were evaluated, taking $V_{HA} = 102$ cm^3 mol^{-1} and $d_{HA} = 24.27$ J$^{1/2}$ cm$^{-3/2}$ [10].

$$0.052V_{HA}(d_o - d_{HA})^2 + 2l_{HA,o}d_{HA}d_o = 568 \tag{11}$$

$$0.052V_{HA}(d_w - d_{HA})^2 + 2l_{HA,w}d_{HA}d_w = 0 \tag{12}$$

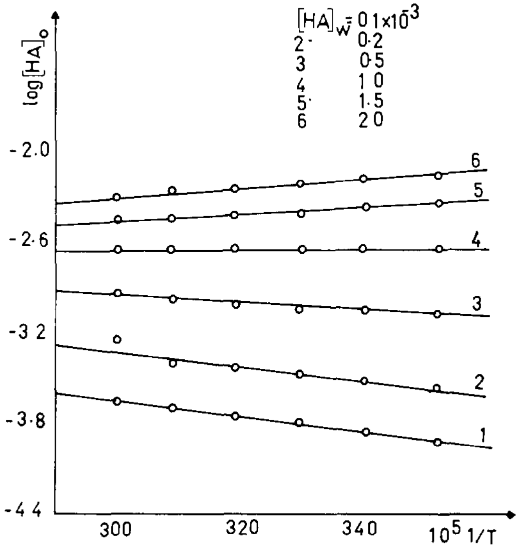

Fig. 2. Change of $\log[\mathrm{HA}]_o$ with $1/T$ at varying $[\mathrm{HA}]_w$ values.

TABLE 3

Binary coefficients

t (°C)	$l_{\mathrm{HA,o}}$	$l_{\mathrm{HA,w}}$
10	0.08726	−0.24630
20	0.08508	−0.24158
30	0.08253	−0.23709
40	0.07979	−0.23100
50	0.07676	−0.22495
60	0.07338	−0.21895

With the determined values in Tables 2 and 3 at hand, the values of $\log K_{D,\mathrm{HA}}$ in Table 4 were evaluated from eqn. (9).

Owing to the fact that the present values of $K_{D,\mathrm{HA}}$ at 25°C and those

TABLE 4

Hydration-corrected partition constants

t (°C)	$\log K_{D,\mathrm{HA}}$	$K_{D,\mathrm{HA}}$
10	−0.06750	0.855
20	0.00112	1.002
30	0.06508	1.164
40	0.12555	1.333
50	0.18201	1.520
60	0.23470	1.717

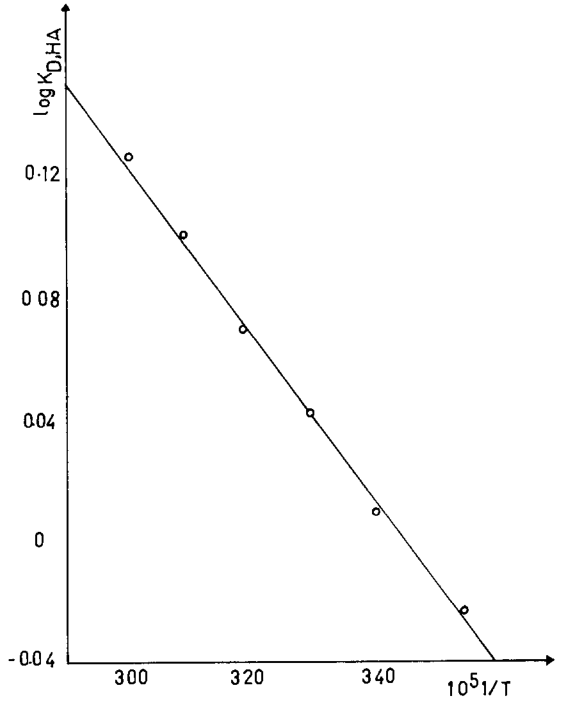

Fig. 3. Change of log $K_{D,\mathrm{HA}}$ with $1/T$.

which have been given by Fujii et al. [10], in which $[H_2O]_o$ has been measured coulometrically are consistent with each other, it should be noted that the regular solution theory with binary coefficients is adequately employed, even though the action of temperature is involved.

Figure 3 plots log $K_{D,\mathrm{HA}}$ against $1/T$ to compute the thermodynamic functions of the system by means of the following equation

$$\log K_{D,\mathrm{HA}} = \Delta S^0/R - \Delta H^0/RT \tag{13}$$

For benzoic acid, we obtained $\Delta H^0 = 2259$ J mol^{-1}, $\Delta S^0 = 36.4$ J mol^{-1} K^{-1} and $\Delta G^0 = -4588$ J mol^{-1}. These results lead to the conclusion that the partition of benzoic acid between aqueous and organic phases is spontaneous at high temperatures.

By utilising the values of $K_{D,\mathrm{HA}}$ in Table 4 and the data in Fig. 1, the hydration-corrected dimerization constant, K_2, was obtained from eqn. (3). The results are plotted against $1/T$ in Fig. 4 from which the heats of dimerization in Table 5 were calculated through the Arrhenius equation.

Based on the conclusion that the hydration-corrected dimerization constant of benzoic acid decreases with rising temperature and $[H_2O]_o$ concentration, it can be assumed that of the hydrated species proposed by Fujii

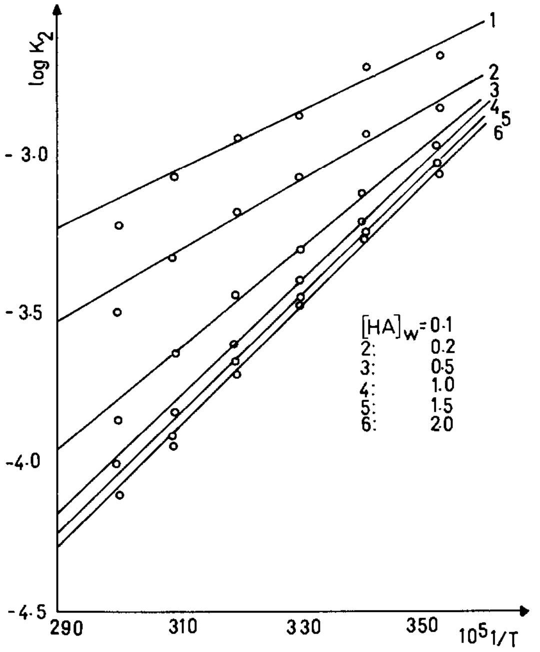

Fig. 4. Dimerization constants of benzoic acid as a function of $1/T$ at varying $[\mathrm{HA}]_w$ values.

TABLE 5

Heat of dimerization

$10^3[\mathrm{HA}]_w$	0.1	0.2	0.5	1.0	1.5	2.0
ΔH(kJ mol^{-1})	74.4	90.0	129.2	148.7	151.9	154.2

et al. [9,10], the dominating species at high temperatures is the monomer monohydrate.

In order to link the hydration-corrected partition constant, $K_{D,\mathrm{HA}}$, to the non-hydration-corrected partition constant, $K'_{D,\mathrm{HA}}$, we derived, from eqns. (1) and (5), the following equation in which B_{11} refers to the hydration constant associated with acid monomer hydration.

$$K_{D,\mathrm{HA}} = K'_{D,\mathrm{HA}}\left(1 + B_{11}[\mathrm{H_2O}]_o\right)^{-1} \qquad (14)$$

Using the previously given values of $[\mathrm{H_2O}]_o$ one obtains the constant B_{11} from eqn. (14) [16,17]. Figure 5 shows the plot of log B_{11} against $1/T$ from which the heat of acid monomer hydration was found to be 5.74 kJ mol^{-1}.

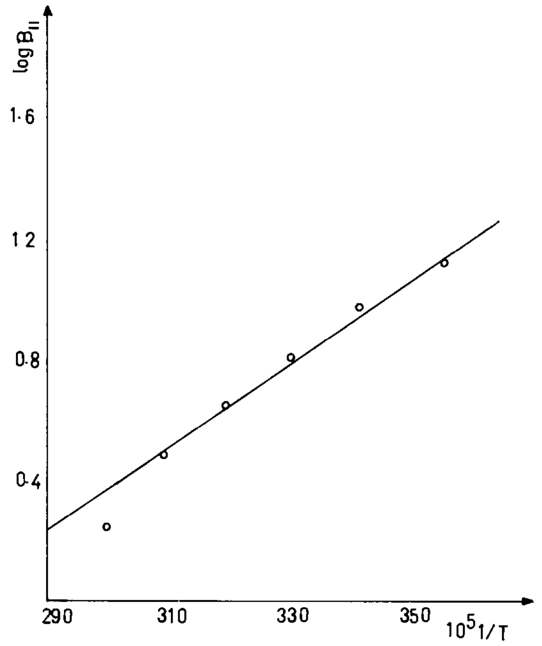

Fig. 5. Monomer hydration constants of benzoic acid as a function of $1/T$.

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