

PARTITION INVESTIGATIONS OF SALICYLIC ACID BETWEEN AQUEOUS AND DIFFERENT ORGANIC PHASES AT VARIOUS TEMPERATURES

Part. I

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Distribution of salicylic acid in 'A', 'B', 'C' and 'D' systems has been investigated at seven temperatures ranging from 20 to 50°. The distribution coefficients (K_1 's) of undissociated monomeric salicylic acid between aqueous and nonaqueous phases and equilibrium constants (K_{12} 's) for dissociation of salicylic acid dimers to monomers in organic layers have been evaluated at each of the seven temperatures.

Thermodynamic data (ΔH° , ΔG° , and ΔS°) for distribution of the acid in each solvent pair and dissociation of the dimerized salicylic acid in each organic solvent at each temperature have been calculated. The values of distribution and dissociation constants have been found to increase with rise in temperature in all cases except in "A" system, where they show decrease with increase in temperature. These constants are found to increase with increase in dielectric constants of the solvent as well.

Key words: A = Water-carbon disulphide; B = Water-carbon tetrachloride; C = Water-benzene and D = Water-chloroform systems.

INTRODUCTION

Numerous investigations of the dimerization of benzoic acid and substituted benzoic acids have been reported [1-11]. The partition method has been widely used for determination of dimerization constants and thermodynamic data of organic acids [12-16] in solvents which are slightly miscible with water. Recently, Treiner and Chattopadhyay [17] have studied partition coefficient of aromatic and aliphatic molecules with various polar moieties i.e. aliphatic amines, esters, alcohols, ketones and polar aromatic molecules with nitrile, ketone and aldehyde groups, except organic carboxylic acids, in octanol-water solvent system using several phase-transfer catalysts.

The literature [12-15] survey has shown inconsistency in the reported values of distribution and dissociation equilibrium constants and consequently those of thermodynamic functions for these processes for salicylic acid in water-organic solvent systems.

EXPERIMENTAL

Reagents and apparatus. E. Merck's analar chemicals were used after further purification [24]. De-ionized water was used for washing of glass wares and making of solutions. Class A glass apparatus by "WITEG" - Diffico, West Germany was used.

Procedure.

Aqueous solutions in the concentration range of 1.449 - 8.696 m mol dm⁻³ were prepared. 25ml of each

solution of its respective concentration were mixed with 25 ml of each organic solvent in well stoppered bottles. The solutions after thorough mixing were transferred to separating funnels and thermostated at precontrolled temperatures for three hours with occasional shaking. The two solvent layers were separated and concentration of the acid in each solvent was determined by titrating against carbonate free 0.01M NaOH solution using phenolphthalein as an indicator.

RESULTS AND DISCUSSION

The present work was undertaken with a view to investigate systematically the substituent and its positional effects on the transportation and thermodynamic functions of substituted benzoic acids between water and organic solvents like benzene, chloroform, carbon tetrachloride and carbon disulphide, at seven different temperatures ranging from 20.0 to 50.0 ± 0.1°. Salicylic acid is selected first in this series of investigation. The experimental data are treated using Moelwyn-Hughes [12] expression.

$$\frac{C_o}{C_w(1-\alpha)} = K_1 \frac{2K_1^2}{K_{12}} C_w(1-\alpha) \dots \dots \dots (1)$$

where C_o is the observed total molar concentration of the acid in organic layer, C_w , the total acid molarity in the aqueous phase and α , the degree of ionization of the acid in water. K_1 is the Nernst distribution constant governing the transfer of unionized monomeric molecules from the

aqueous layer to the organic solvent, and K_{12} is the dissociation equilibrium constant of dimer to monomer in the organic solvent. The value of α used in equation (1) is obtained from known values of dissociation constant [18], K_a , given by the expression.

$$K_a = \frac{C_w \alpha^2}{(1-\alpha)} \dots \dots \dots (2)$$

The present data were subjected to a simple linear least squares procedure for plotting $C_o/C_w (1-\alpha)$ versus $C_w(1-\alpha)$ which yielded straight lines (Fig. 1). The values of K_1 's and K_{12} 's were obtained from the intercepts and slopes of the straight lines respectively, (Tables 1 and 2). Similarly plots of $\log K_1$ and $\log K_{12}$ versus $1/T$ gave straight lines, (Figs. 2 and 3). From the slopes of these lines, the corresponding values of ΔH^0 's were calculated.

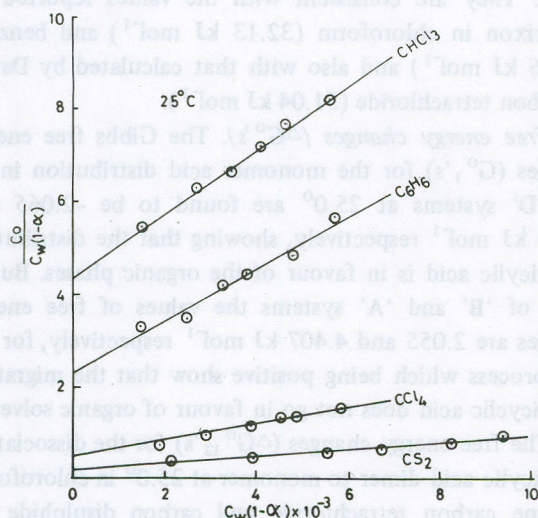


Fig. 1. Graph between $C_o/C_w(1-\alpha)$ Vs. $C_w(1-\alpha) \times 10^{-3}$ for salicylic acid.

Table 1. Distribution constants (K_1 's) for salicylic acid between water and organic solvents at seven different temperatures.

| Solvent systems | Abbreviation | Temperature °C | | | | | | |
|----------------------------|--------------|----------------|-------|-------|-------|-------|-------|-------|
| | | 20.0 | 25.0 | 30.0 | 35.0 | 40.0 | 45.0 | 50.0 |
| Water-chloroform | D | 4.325 | 4.385 | 4.470 | 4.520 | 4.580 | 4.700 | 4.750 |
| Water-benzene | C | 2.090 | 2.300 | 2.490 | 2.607 | 2.734 | 2.833 | 2.956 |
| Water-carbon tetrachloride | B | 0.418 | 0.436 | 0.445 | 0.447 | 0.508 | 0.541 | 0.557 |
| Water-carbon disulphide | A | 0.213 | 0.169 | 0.108 | 0.065 | - | - | - |

Table 2. Dissociation constants ($10^{-4} \times K_{12}$'s $\text{mol}^{-1} \text{dm}^{-3}$) for salicylic acid dimer in organic solvents at seven various temperatures.

| Solvent | Temperature °C | | | | | | |
|----------------------|----------------|-------|-------|-------|-------|--------|--------|
| | 20.0 | 25.0 | 30.0 | 35.0 | 40.0 | 45.0 | 50.0 |
| Chloroform | 447.0 | 577.0 | 643.0 | 938.0 | 979.0 | 1240.0 | 1510.0 |
| Benzene | 115.0 | 190.0 | 234.0 | 275.0 | 310.0 | 345.0 | 390.0 |
| Carbon tetrachloride | 18.40 | 21.0 | 29.0 | 38.0 | 48.0 | 80.0 | 130.0 |
| Carbon disulphide | 17.13 | 7.78 | 2.28 | 0.72 | - | - | - |

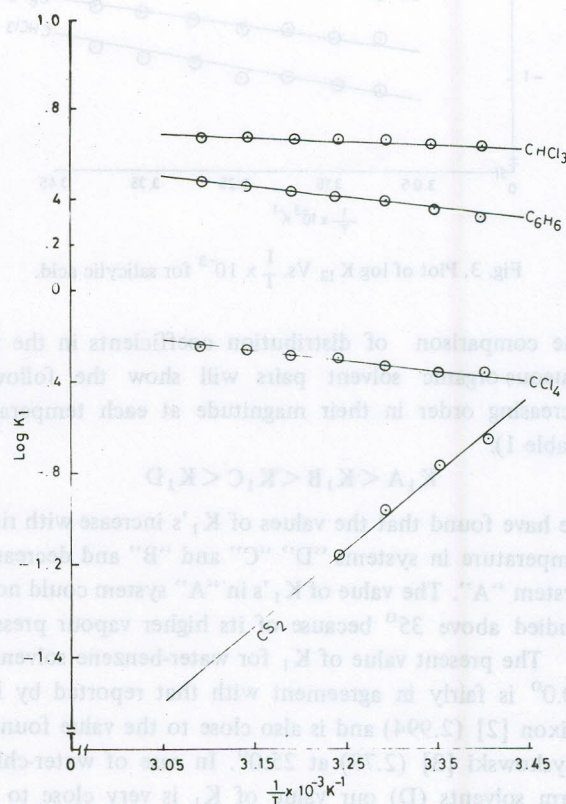


Fig. 2. Plot of $\log K_1$ Vs. $\frac{1}{T} \times 10^{-3}$ for salicylic acid.

culated in accordance with Vant Hoff equation. The values of ΔG^0 's and ΔS^0 's were calculated by using usual thermodynamic relations at 25.0° .

Distribution coefficients (K_1 's). The values of distribution coefficients for salicylic acid between different pairs of solvent systems are found to increase linearly, in each case, with rise in temperature from 20.0 to $50.0 \pm 0.1^\circ$ (Table 1 and Fig. 1). This indicates that the monomer acid migrates to the organic layer from the aqueous layer. It is well known that intermolecularly hydrogen bonded salicylic acid is more established in nonaqueous media through dispersive interactions than in aqueous medium through hydrogen bonding and polar interactions, hence concentration of the acid increases in organic solvents.

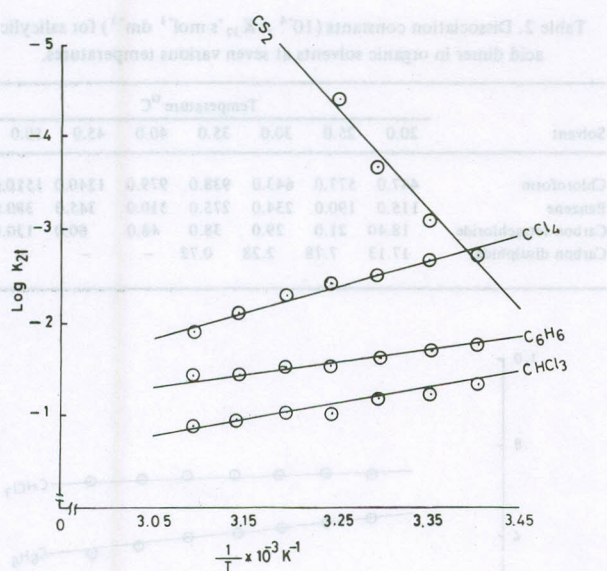


Fig. 3. Plot of $\log K_{12}$ Vs. $\frac{1}{T} \times 10^3$ for salicylic acid.

The comparison of distribution coefficients in the four aqueous-organic solvent pairs will show the following increasing order in their magnitude at each temperature (Table 1).

$$K_{1A} < K_{1B} < K_{1C} < K_{1D}$$

We have found that the values of K_1 's increase with rise in temperature in systems "D" "C" and "B" and decrease in System "A". The value of K_1 's in "A" system could not be studied above 35° because of its higher vapour pressure.

The present value of K_1 for water-benzene solvents at 40.0° is fairly in agreement with that reported by Hendrixon [2] (2.994) and is also close to the value found by Szyskowski [3] (2.79) at 25.0° . In case of water-chloroform solvents (D) our value of K_1 is very close to that reported by Davies [6] (4.50) at 35.0° but is different from that given by Hendrixon (2.50) at 40.0° . In "D" the value reported by Smith and White [4] (3.13) differs significantly from the present value at 25° but our value is in good agreement with that reported by Davies (0.498) at 40.0° .

Dissociation constants (K_{12} 's). The dissociation constants K_{12} 's of the salicylic acid for the process, dimer \rightleftharpoons monomer, as given in Table 2 indicate that they also increase linearly with rise in temperature in CHCl_3 , C_6H_6 and CCl_4 solvents except in CS_2 , where a gradual decrease is observed. The following increasing order in the values of K_{12} 's is observed at each temperature:

$$K_{12}(\text{CCl}_4) < K_{12}(\text{C}_6\text{H}_6) < K_{12}(\text{CHCl}_3)$$

In chloroform the present values (Table 2) agree well with those reported by Davies (938.0×10^{-4}) at 35.0° and

Hendrixon (950.0×10^{-4}) at 40.0° , but again are markedly different from that evaluated by Smith and White (132.0×10^{-4}) at 25.0° . In the case of carbon tetrachloride our value is in good agreement with that estimated by Davies (47.7×10^{-4}) at 40.0° .

Enthalpy changes (ΔH°_1 's). The present value of enthalpy changes (ΔH°_1 's) for the distribution of monomer salicylic acid in 'D', 'C', 'B' and 'A' systems are 2.51, 8.77, 7.997 and $-64.10 \text{ kJ mol}^{-1}$ respectively. The value obtained in 'D' is quite in agreement with that reported by Hendrixon (2.15 kJ mol^{-1}) and also with the value estimated by Davies (8.37 kJ mol^{-1}) for 'B' system.

The values of enthalpy changes (ΔH°_{12} 's) for the dissociation of salicylic acid dimer to monomer in chloroform, benzene, carbon tetrachloride and carbon disulphide are 31.60, 2.98, 51.36 and $-189.25 \text{ kJ mol}^{-1}$ respectively. They are consistent with the values reported by Hendrixon in chloroform ($32.13 \text{ kJ mol}^{-1}$) and benzene ($23.56 \text{ kJ mol}^{-1}$) and also with that calculated by Davies in carbon tetrachloride ($51.04 \text{ kJ mol}^{-1}$).

Free energy changes (ΔG°_1 's). The Gibbs free energy changes (G°_1 's) for the monomer acid distribution in 'C' and 'D' systems at 25.0° are found to be -2.065 and $3.663 \text{ kJ mol}^{-1}$ respectively, showing that the distribution of salicylic acid is in favour of the organic phases. But in cases of 'B' and 'A' systems the values of free energy changes are 2.055 and $4.407 \text{ kJ mol}^{-1}$ respectively, for the said process which being positive show that the migration of salicylic acid does not go in favour of organic solvents.

The free energy changes (ΔG°_{12} 's) for the dissociation of salicylic acid dimer to monomer at 25.0° in chloroform, benzene carbon tetrachloride and carbon disulphide are 7.07, 9.82, 15.28 and $17.74 \text{ kJ mol}^{-1}$ respectively, reflecting that dissociation of dimeric acid is not favoured in the organic phases.

Entropy changes (ΔS°_1 's). The entropy changes (ΔS°_1 's) for the distribution of salicylic acid in 'C' 'D' and 'B' systems at 25.0° are found to be 22.49, 20.70 and $19.92 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively. In case of 'A' system entropy change for the distribution is found to be $-223.8 \text{ J mol}^{-1} \text{ K}^{-1}$.

The present values of ΔS°_1 's for salicylic acid in 'D' system are fairly close to that reported by Hendrixon ($24.30 \text{ J mol}^{-1} \text{ K}^{-1}$) and also to that calculated by Davies ($21.76 \text{ J mol}^{-1} \text{ K}^{-1}$).

The entropy changes (ΔS°_{12} 's) for the dissociation of dimer salicylic acid in benzene, chloroform and carbon tetrachloride at 25.0° are 47.49, 82.23 and $117.66 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively, but in carbon disulphide is $-694.2 \text{ J mol}^{-1} \text{ K}^{-1}$. Our value of ΔS°_{12} in chloroform is in good

agreement with that calculated by Hendrixon ($86.19 \text{ J mol}^{-1} \text{ K}^{-1}$) at 40.0° and also agrees well with that reported by Davies ($117.15 \text{ J mol}^{-1} \text{ K}^{-1}$) at 40.0° for carbon tetrachloride.

The values of entropy changes for both distribution of acid between water and organic phases and dissociation of the acid in organic solvents are found to be quite small in comparison with the corresponding enthalpy changes for these two processes, showing that they are not influenced significantly by the entropy changes but are enthalpy controlled. Duyne [19] *et al.* have proposed the presence of acid dimer, monomer monohydrate, monomer dihydrate and dimer monohydrate species in their investigations of benzoic acids distribution between water and benzene. The hydration of carboxylic acids in benzene has also been reported by Fujii and Tanaka [20-22] in their studies of the partition of aliphatic carboxylic acids between benzene and aqueous solution of 0.1 mol dm^{-3} (H, Na) and ClO_4 at 25.0° . It needs experimental verification if similar hydrates are also formed in the present case, which might influence the distribution of the acid and dependent thermodynamic quantities.

Solvent effect. The values of distribution and dissociation constants are found to increase with increase in dielectric constants [23]. It is assumed that in polar aprotic solvents, the solubility of dimer goes on increasing with increase in polarity of solvents due to greater solvation of the dimer. But in case of CS_2 solubility of dimer decreases although its polarity lies in between benzene and chloroform. This decrease might be due to low solvation of dimer formed in system "A" and high vapour pressure at the working temperatures.

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