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The effect of salt concentration on the distribution of phenol between aqueous sodium chloride and carbon tetrachloride

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Summary

The effect of salt concentration on the distribution of phenol between aqueous sodium chloride solution and carbon tetrachloride has been measured over the temperature range 10–30 °C. The distribution increased with increase in salt concentration as described by a modified Setschenow equation. The change of distribution was enthalpy-controlled and a good correlation between ΔH and the concentration of free water (water activity) was obtained.

Introduction

The distribution behaviour of organic solutes between aqueous solution and various organic solvents has been studied by many authors (for a detailed review see Leo et al., 1971; Davis et al., 1974). Partition coefficient values or constituent group contributions are used widely in analytical chemistry and structure activity correlations (Martin, 1978). However, despite the fact that pharmaceutical and biological processes can occur at different concentrations of salt, little attention has been paid to the variation of distribution behaviour with ionic strength. Indeed many authors have used water or buffer solutions of uncontrolled ionic strength to determine

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distribution data. In a previous paper we described the thermodynamics of distribution of para-substituted phenols between organic solvents and sodium chloride solution (Kojima and Davis, 1984). In the present work we report on the effect of sodium chloride concentration on the distribution constant of phenol at different temperatures. Carbon tetrachloride was chosen as a model organic solvent.

Materials and Methods

The shake flask method was used as described previously (Kojima and Davis, 1984). A Beckman model 25 spectrophotometer was used for the determination of phenol concentrations. Water was distilled from an all-glass still. Phenol (99.99%) from British Drug Houses was used after recrystallization. Carbon tetrachloride from Hopkins and Williams was washed successively with sodium hydroxide solution, distilled water, concentrated sulphuric acid and finally 5 times with distilled water. NaCl (Analar, British Drug Houses) was used without additional purification. The procedure for the determination of distribution constants at different temperatures was as described by Kojima and Davis (1984). A shaking time of 24 h was used throughout; the flasks were well closed to keep atmospheric absorption of carbon dioxide to a minimum during the equilibration period. The volumes of the aqueous and organic phases were both 20 ml and the absorbance of phenol in aqueous solution was measured at 270 nm against distilled water as blank.

Results and Discussion

The distribution constants of phenol between CCl_4 and aqueous NaCl solution increased with increase in NaCl concentration for all temperatures studied (Table 1). This behaviour can be described by an equation analogous to the well-known Setschenow's formulae (Coetzee and Rotchie, 1976; Korenman, 1978):

$$\log \frac{K_d}{K_d^0} = kC \tag{1}$$

where K_d^0 is the distribution constant of the solute between the organic solvent and pure water, K_d the distribution constant between the same organic solvent and the aqueous salt solution, C the concentration of the salt and k is a constant. The plot of $\log K_d$ against NaCl concentration gave a straight line with correlation coefficient of 1.000 at 25 °C as shown in Fig. 1 and Eqn 2.

$$\log K_d = 0.168\,[\mathrm{NaCl}] - 0.3342 \tag{2}$$

Excellent linear plots were also obtained at the other temperatures (Table 1). Similar relationships have been observed for some phenols between aqueous NaCl solution and benzene, CCl_4 and octane (Korenman and Bortnikova, 1979) and for some

TABLE 1

DISTRIBUTION CONSTANTS OF PHENOL AT DIFFERENT NaCl CONCENTRATIONS AND DIFFERENT TEMPERATURES

[NaCl] (mol·dm^{-3})	Distribution constant			
	9.8 °C	15.0 °C	25.0 °C	30.0 °C
0.050	0.341	0.379	0.470	0.519
0.100	0.347	0.391	0.479	0.533
0.150	0.355	0.398	0.489	0.540
0.200	0.361	0.406	0.498	0.551
0.500	0.409	0.460	0.565	0.619
1.000	0.505	0.568	0.689	0.751
1.500	0.615	0.688	0.833	0.907
2.000	0.750	0.838	1.009	1.098
3.000	1.121	1.221	1.477	1.595
4.000	1.695	1.792	2.164	2.312
Regression equations				
at 9.8 °C:	$\log K_d = 0.1761[NaCl] - 0.4763$	($r = 1.000$) *		
at 15 °C:	$\log K_d = 0.1705[NaCl] - 0.4234$	($r = 1.000$)		
at 25 °C:	$\log K_d = 0.1681[NaCl] - 0.3342$	($r = 1.000$)		
at 30 °C:	$\log K_d = 0.1644[NaCl] - 0.2908$	($r = 1.000$)		

* Correlation coefficient.

carboxylic acids between aqueous $NaClO_4$ solution and CCl_4 (Sekina et al., 1969). The phenomenon described by Eqn. 1 can be explained by a salting out effect of NaCl on the solubility of phenol in aqueous solution.

The enthalpy and entropy changes of phenol transfer were obtained from the linear plot of $\ln K_d^x$ against $1/T$, where $\ln K_d^x$ is the distribution constant expressed in mole fraction concentration units (Fig. 2). The values obtained are summarized in Table 2. ΔH decreases with increase in NaCl concentration but ΔS is constant. That is, when only the NaCl concentration is varied, the free energy change for the transfer of phenol from an aqueous environment to organic phase is enthalpy-controlled. ΔH is a term that describes the solute–solvent interactions.

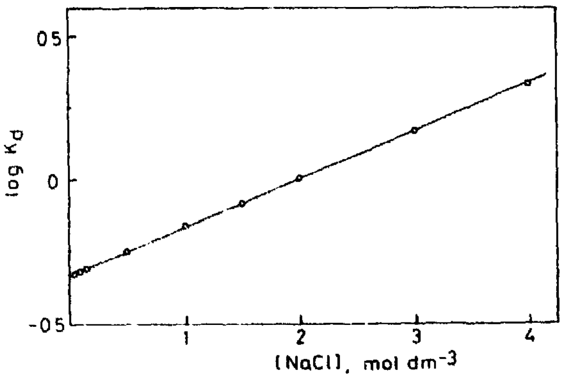

Fig. 1. Relation between distribution constant ($\log K_d$) and sodium chloride concentration.

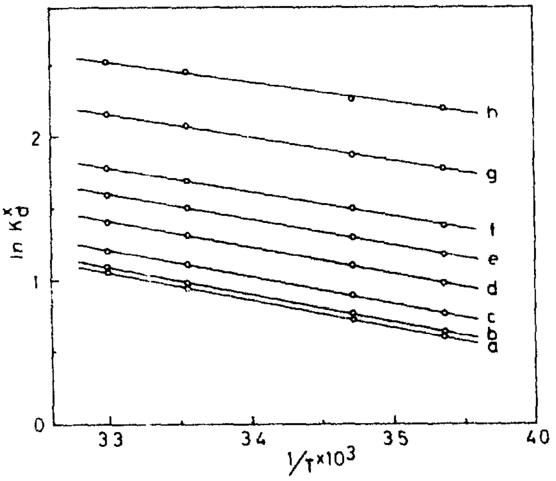

Fig. 2. Plots of ln K_d^x vs 1/T for phenol at different ionic strengths. The letters a–h refer to the NaCl concentrations in Table 2.

The concentration of free water not bound to NaCl in aqueous solution can be calculated from:

$$[H_2O]_{free} = 55.51 - 7.9\,[NaCl] \tag{3}$$

where 7.9 is the hydration number of NaCl (Robinson and Stokes, 1959). The free water concentration can be equated with the water activity in different NaCl solutions and a plot of ΔH against free water concentration gives a straight line as

TABLE 2

THERMODYNAMIC CONSTANTS FOR THE DISTRIBUTION OF PHENOL BETWEEN AQUEOUS SODIUM CHLORIDE SOLUTIONS AND CARBON TETRACHLORIDE AT 25°C

[NaCl] ($mol \cdot dm^{-3}$)	$-\Delta G$	ΔH	ΔS	r[a]	[Free water][b]	Line Fig. 2
0.050	2.301	15.6	59.9	1.000	55.11	-
0.100	2.347	15.6	60.2	1.000	54.76	a
0.150	2.386	15.4	59.9	1.000	54.32	-
0.200	2.445	15.6	60.4	1.000	53.97	b
0.500	2.755	15.3	60.6	1.000	51.60	c
1.000	3.249	14.7	60.3	1.000	47.65	d
1.500	3.717	14.3	60.6	1.000	43.70	e
2.000	4.193	14.1	61.3	1.000	39.75	f
3.000	5.139	13.6	62.8	0.999	31.85	g
4.000	6.085	12.5	62.5	0.996	23.95	h

ΔG and ΔH are given in $kJ \cdot mol^{-1}$.
ΔS is given in $J \cdot mol^{-1} \cdot K^{-1}$.
[a] Correlation coefficient for a linear plot of ln K_d^x versus 1/T.
[b] From Eqn. 3.

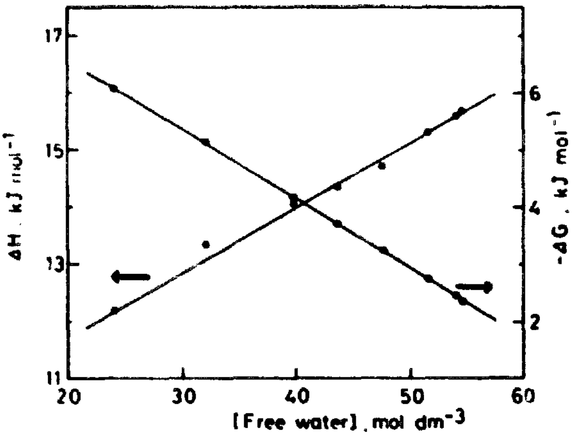

Fig. 3. Relation between free energy ΔG and enthalpy (ΔH) of transfer and free water concentration.

shown in Fig. 3.

$$\Delta H = 0.966\,[H_2O]_{free} + 10.27 \quad (r = 0.990)$$

A plot of ΔG against free water concentration also gives a good linear relationship:

$$\Delta G = 0.121\,[H_2O]_{free} + 9.00 \quad (r = 1.00)$$

Thus the enthalpy (and free energy) of distribution of phenol between aqueous NaCl solutions and carbon tetrachloride is determined directly by the activity of water in the system. The progressive increase in the distribution constant with salt concentration represents a salting out phenomenon.

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