

Salting Coefficients and Transfer Thermodynamic Quantities of Some Phenolic Solutes from Water to Salt Solutions at Different Temperatures[†]

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Free energies, enthalpies, and entropies of transfer were calculated from activity coefficients obtained from partition coefficients of three substituted phenols, viz., *p*-chlorophenol (PCP), *p*-bromophenol (PBP), and *p*-nitrophenol (PNP), between water or salt solutions and benzene at three temperatures, viz., 20, 30, and 40 °C. The salting-out or salting-in effects were explained on the basis of these data.

Introduction

The prediction of the effects of structural modification on solution properties has been one of the primary objectives in the field of solution thermodynamics. The thermodynamic properties like activity coefficient, partition coefficient, and free energy of transfer of an organic solute between two phases/solutions are related to its solution behavior, hydrophobic interactions, extraction characteristics, or even structure-activity relationships. Such questions as the nature and strength of the driving force for altering the activity coefficient and for transfer and its sensitivity to substituents on the solute molecule as well as the nature of the additive and nonsolvent are our ultimate concern.

Salt increases the activity coefficient of an organic solute, *N*, in water and decreases that of water. Likewise addition of *N* decreases the solubility of a salt. This accompanies a salting-out process. In the reverse phenomenon of salting-in, electrostatic theories predict a higher dielectric constant in the aqueous solutions of organic solute than in pure water. In general, in a homologous series of molecules, the progressive addition of nonpolar hydrocarbon residues causes a progressive decrement in the dielectric constant of an aqueous solution per mole of solute. Quite often, it is not easy to interpret the activity coefficient data in terms of dielectric saturation or internal pressure in ternary aqueous ionic solutions. Another variant of solute-solvent interaction occurs when an organic solute with a permanent dipole moment is transferred from water to hydrocarbon phase.

A more illuminating and integrated approach is then through a chemical theory. One considers all possible interactions that may arise in such solutions. The observed thermodynamic parameters of transfer from water to salt solution or from water to an immiscible hydrocarbon phase can be regarded as the balance between several competitive equilibrium processes.

An exothermic enthalpy of interaction indicates a net structure breaker, while an endothermic value indicates a net structure maker. A knowledge of the sign and magnitude of the entropy change leads to further insight into the nature of

the molecular interaction involved in a given transfer process.

The salting-out may in part be explained by considering that the salts are preferentially solvated with water molecules. Thus, the availability of water for the nonelectrolyte is decreased. Hence, the free energy of the latter will rise; the largest change to be expected is that for the cation having the highest charge density. Apparently, the larger and more poorly hydrated ions have the opposite effect on the nonelectrolyte so that the free energy of the nonelectrolyte decreases and its solubility increases.

In the present studies, free energies, enthalpies, and entropies of transfer were calculated from activity coefficients obtained from partition coefficients of three substituted phenols, viz., *p*-chlorophenol, *p*-bromophenol, and *p*-nitrophenol, between water or salt solutions and benzene at three temperatures, viz., 20, 30, and 40 °C.

Experimental Section

p-Chlorophenol (PCP), *p*-bromophenol (PBP), and *p*-nitrophenol (PNP) of BDH AnalaR grade were vacuum dried over anhydrous NaOH for removal of minute traces of water. All salts, viz., NaCl, NaF, Na₂SO₄, NaClO₄, NaNO₃, KNO₃, KCl, KSCN, (NH₄)₂SO₄, were of AnalaR grade and were used without further purification. Benzene, taken as the organic solvent, was distilled at a temperature much below its boiling point to remove any traces of impurity present. Experiments were carried out by preparation of stock solutions by direct weighing of the solute and salts which were diluted accurately by previously calibrated glassware to obtain different required concentrations.

The other experimental procedure is similar to that described earlier (1, 2). All partitioning experiments were carried out at three temperatures, i.e., 20, 30, and 40 °C. The solute concentration was fixed (10⁻³ M) and the salt concentration varied from 0.2 to 2.0 M.

Absorbance measurements were carried out at 226 and 283 nm for the halogen-substituted phenols in the aqueous and organic layers, respectively, and at 395 nm for both layers in the case of PNP.

Results and Discussion

If for two experiments in the distribution of a nonelectrolyte between aqueous solutions and an immiscible nonaqueous reference phase, one involving pure water and the other a salt solution, the concentration of nonelectrolyte in the reference phase is constant, we can write

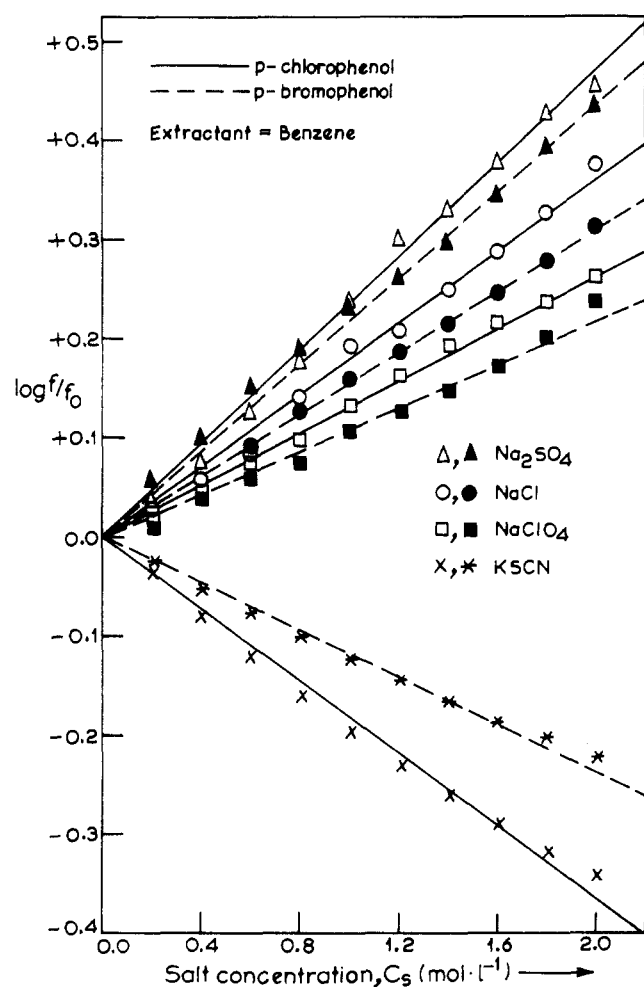
$$f/f_0 = C^0/C = (K_o C_{org})/(K_w C'_{org}) \quad (1)$$

where *f* and *f*₀ are molar activity coefficients of the nonelectrolyte, *C* and *C*⁰ are the molar concentration of the nonelectrolyte in salt solutions and salt-free solutions, respectively, *K*_o is the partition coefficient of the solute between the organic

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Table I. Salting Coefficient K_s for Different Solutes at 20, 30, and 40 °C

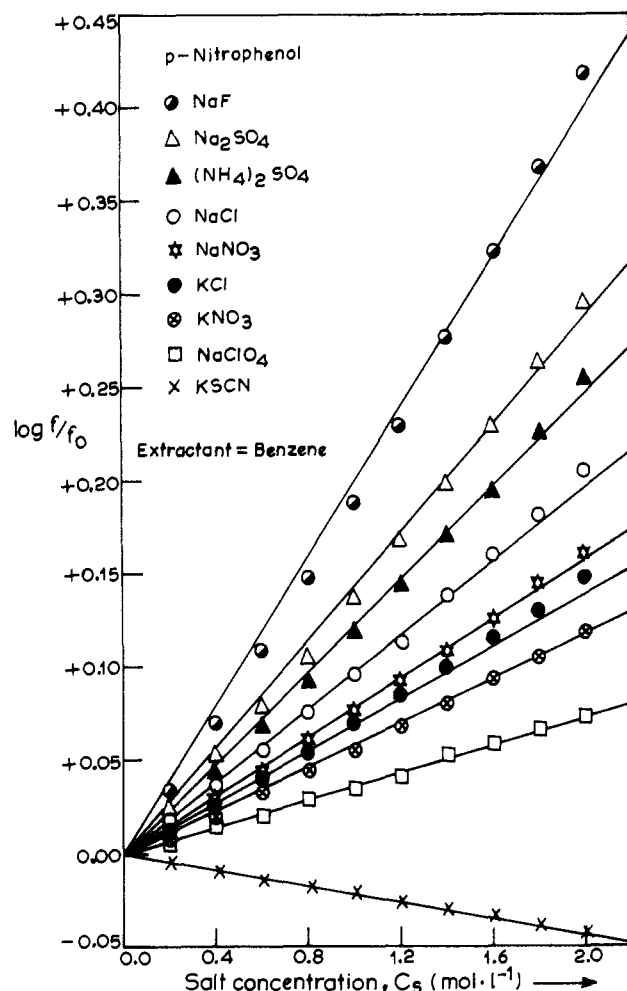
salt	<i>p</i> -chlorophenol			<i>p</i> -bromophenol			<i>p</i> -nitrophenol		
	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C	20 °C	30 °C	40 °C
Na ₂ SO ₄	0.237 ± 0.001	0.214 ± 0.003	0.185 ± 0.001	0.220 ± 0.005	0.180 ± 0.004	0.173 ± 0.002	0.143 ± 0.004	0.129 ± 0.006	0.119 ± 0.008
NaCl	0.180 ± 0.002	0.171 ± 0.002	0.130 ± 0.003	0.155 ± 0.010	0.122 ± 0.006	0.105 ± 0.001	0.100 ± 0.002	0.086 ± 0.004	0.078 ± 0.003
NaClO ₄	0.134 ± 0.001	0.111 ± 0.002	0.075 ± 0.002	0.110 ± 0.002	0.088 ± 0.002	0.067 ± 0.003	0.037 ± 0.002	0.026 ± 0.001	0.019 ± 0.003
KSCN	-0.175 ± 0.002	-0.171 ± 0.001	-0.150 ± 0.001	-0.116 ± 0.001	-0.100 ± 0.003	-0.048 ± 0.006	-0.020 ± 0.001	-0.014 ± 0.000	-0.009 ± 0.000
NaF							0.198 ± 0.008	0.179 ± 0.010	0.170 ± 0.005
NaNO ₃							0.078 ± 0.002	0.069 ± 0.003	0.059 ± 0.002
KCl							0.069 ± 0.002		
KNO ₃							0.058 ± 0.003		
(NH ₄) ₂ SO ₄							0.125 ± 0.005		

Figure 1. Least-squares plot of $\log f/f_0$ vs. salt concentration at 20 °C (*p*-chlorophenol and *p*-bromophenol).

phase and the salt solution of concentration C_s , K_w is the partition coefficient of the solute between the organic phase and water, C'_{org} is the solute concentration in the organic phase in the experiment with the salt solution, and C_{org} is the solute concentration in the organic phase in the experiment with pure water. The values of $\log f/f_0$ have been calculated from eq 1.

The salting coefficient, K_s , was obtained from the relationship

$$K_s = \lim_{C_s \rightarrow 0} d \log f/f_0 / dC_s \quad (2)$$

Figure 2. Least-squares plot of $\log f/f_0$ vs. salt concentration at 20 °C (*p*-nitrophenol).

The plot of $\log f/f_0$ against C_s gave straight lines as shown in Figure 1 for PCP and PBP and Figure 2 for PNP at 20 °C only. The values of K_s were calculated from the slopes. These are listed in Table I. The Setschenow equation (3), $\log f/f_0 = K_s C_s$, was precisely applicable to these systems.

The standard free energy of transfer of a mole of nonelectrolyte from pure water to a salt solution C_s is calculated from the equation

$$\Delta G_{tr} = RT(d \ln f/f_0 / dC_s) = 2.303RTK_s \quad (3)$$

Table II. Thermodynamic Quantities of Transfer of the Nonelectrolytes from Water to Salt Solutions at 20, 30, and 40 °C^a

salt	20 °C			30 °C		40 °C	
	ΔG	ΔH	ΔS	ΔG	ΔS	ΔG	ΔS
				<i>p</i> -Chlorophenol			
Na ₂ SO ₄	317.77	-942.13	-4.30	296.72	-4.09	264.98	-3.86
NaCl	241.34	-1094.20	-4.56	237.10	-4.39	186.20	-4.09
NaClO ₄	179.67	-970.70	-3.93	153.91	-3.71	107.42	-3.44
KSCN	-234.64	508.50	2.54	-237.10	2.46	-214.85	2.31
				<i>p</i> -Bromophenol			
Na ₂ SO ₄	294.97	-980.58	-4.35	249.58	-4.06	247.79	-3.93
NaCl	207.82	-1016.90	-4.18	169.16	-3.91	150.39	-3.73
NaClO ₄	147.49	-994.80	-3.90	122.02	-3.69	95.96	-3.49
KSCN	-155.53	1525.30	5.74	-138.65	5.49	-68.75	5.09
				<i>p</i> -Nitrophenol			
NaF	265.48	-610.13	-2.99	248.19	-2.83	243.49	-2.73
Na ₂ SO ₄	191.73	-485.34	-2.31	178.86	-2.19	170.44	-2.10
(NH ₄) ₂ SO ₄	167.59						
NaCl	134.08	-490.28	-2.13	119.24	-2.01	111.72	-1.92
NaNO ₃	104.58	-440.00	-1.86	95.67	-1.77	84.51	-1.68
KCl	92.58						
KNO ₃	77.76						
NaClO ₄	34.86	-397.92	-1.48	36.05	-1.43	27.21	-1.36
KSCN	-26.82	233.47	0.89	-19.41	0.84	-12.89	0.79

^a ΔG_{tr} and ΔH_{tr} in cal mol⁻¹; ΔS_{tr} in cal mol⁻¹ deg⁻¹.

The enthalpy of transfer is calculated by applying the van't Hoff isochore to K_s values at different temperatures. The $\log f/f_0$ values vs. the inverse of the temperature are plotted and their slopes give the ΔH_{tr} values. The entropy of transfer values are obtained from the relation

$$-\Delta S_{tr} = RT(\ln f/f_0/dT) + R \ln f/f_0 \quad (4)$$

Results show that K_s values for PCP are consistently higher than those of PBP at all temperatures; PNP comes next in order. The K_s values decrease with an increase in temperature. The salting order is $SO_4^{2-} > Cl^- > ClO_4^- > SCN^-$ for PCP and PBP, and this is in accordance with our previous studies with naphthols (1) and *p*-aminophenol (2). The salting order for PNP is found to be $NaF > Na_2SO_4 > (NH_4)_2SO_4 > NaCl > NaNO_3 > KCl > KNO_3 > NaClO_4 > KSCN$. With KSCN negative K_s values (salting-in) are observed while studies with other salts show positive values (salting-out). The low salting-out effects of ClO_4^- and SCN^- ions are due to the disruptive action of these ions on the structure of water. For the cations, the order of decreasing salting-out is $Na^+ > NH_4^+ > K^+$.

The systematic increase in salting-out constant of polar solute can be explained by the decrease in solubility of the solute or an increase in hydrophobicity; the less soluble is a compound in water, the more readily it is salted-out by a given electrolyte.

Table II records the three thermodynamic parameters of transfer for all solutes. The values show that the free energies for the phenols at all temperatures are positive for all salts except KSCN, which shows negative values. At a particular temperature for a particular salt, the order of ΔG_{tr} is $PCP > PBP > PNP$. With the increase in temperature the ΔG_{tr} values decrease. The temperature effect is more pronounced between 20 and 30 °C, about 10%, and almost one-half in the next higher interval.

The positive ΔG_{tr} values obtained in the case of most of the salts can be explained by the fact that, during salting-out, salts are preferentially solvated with water molecules, thus decreasing the availability of water for the nonelectrolyte. Hence, the ΔG_{tr} values for the latter will rise. In the case of KSCN in studies with all solutes and $NaClO_4$ in studies with PAP, negative ΔG_{tr} values are obtained. This is due to the "structure-making" property of these salts; and hence the free energy of the nonelectrolyte decreases, thus increasing its solubility in these salt solutions.

The highest ΔG_{tr} value is obtained with the F^- ion. The small F^- ion is thought to immobilize the water structure due to its higher localized charge density and hence make relatively less water available for dissolving the nonelectrolyte than the larger nitrate or perchlorate ions. In accordance with this view ΔG is found to decrease with increasing ion size.

The table shows that ΔG_{tr} values for K salts are lower than those for Na salts. This order from electrolyte to electrolyte has been found to hold approximately for other nonelectrolytes also. The ion size has also to play a specific role in the free energy of transfer values.

In an ionic solution five main types of interactions can be identified: solute-solute, solute-ion, solute-water, water-water, and ion-water. On the contrary, in pure water, only three kinds of interactions, viz., solute-water, solute-solute, and water-water, are possible. A larger hydrophobicity of the solute molecules causes a stronger solute aggregation. Evidently, neither the aggregation nor the solvation of the solute can be favored over the influence of ions on water structure. The nitrophenol, so to say, is more "at home" in electrolyte solutions, because they can form multiple ion associates in the dielectrically saturated water in addition to the dipolar and/or multipole interactions.

The ΔH_{tr} values are negative in all cases except for the thiocyanates in studies with the nonelectrolytes. An exothermic ΔH_{tr} value indicates a net structure breaker and an endothermic value indicates a net structure maker. In the case of PCP and PBP, these values for different salts do not show any regular trend though their values do not differ considerably. In the case of PNP, studies with NaF show highest exothermic values, that with Na_2SO_4 and NaCl being next in order and almost equal in magnitude, followed by $NaNO_3$ and $NaClO_4$ and finally KSCN showing an endothermic value. That heat is required when nonelectrolyte is to be accommodated in a solution of a structure-promoting salt implies that no strong solute-water or solute-salt interactions occur in the presence of these ions.

The ΔS_{tr} values in the case of all solutes in studies with all salts except KSCN are found to be negative and small. Studies with KSCN show positive values. Thus, we find that, when nonelectrolytes are transferred from water to salt solutions, the forces on the neighboring solvent molecules are modified, decreasing the net entropy. Since the ΔS_{tr} values seem to be small, it is reasonable to assume that the nonelectrolytes have relatively little influence on the solvent molecules in the pres-

Table III. Thermodynamic Quantities of Transfer of Nonelectrolytes from Organic to Water Phase with a Few Literature Values

solute	organic solvent	ΔG_{tr} , cal mol ⁻¹	ΔH_{tr} , cal mol ⁻¹	ΔS_{tr} , cal mol ⁻¹ deg ⁻¹	temp, K	ref
<i>p</i> -bromophenol	benzene	-19276.00	-3224.00	-52.98	303	PW ^a
<i>p</i> -chlorophenol	benzene	-15486.00	-4335.00	-36.80	303	PW ^a
<i>p</i> -nitrophenol	benzene	-1761.00	-1152.00	-2.01	303	PW ^a
methane	benzene	2600.00	-2800.00	-18.00	298	5
<i>n</i> -butane	pure liquid	6060.00	-800.00	-23.00	293	6
1-butanol	pure liquid	2400.00	-2250.00	-15.60	298	6
<i>n</i> -butyric acid	toluene	-1220.00	-3520.00	-77.00	298	7
phenol	<i>n</i> -hexane		-4680.00		298	} b
	MeOH		2090.00		298	
<i>p</i> -chlorophenol	CCl ₄		-2360.00		298	
<i>p</i> -nitrophenol	<i>n</i> -hexane		3130.00		298	
	CCl ₄		1450.00		298	
	MeOH		3330.00		298	
2-naphthol	CCl ₄		-5930.00		298	

^a Present work. ^b Recalculated value of ΔH_{tr} (8).

ence of significant ionic fields. The small magnitude also indicates that entropy is only a secondary driving force for the particular transfer process.

Table III shows the thermodynamic quantities of transfer from the organic to the water phase. Here we obtain free energies of transfer of nonelectrolyte, which are negative in contrast to a positive ΔG for transfer from water to salt solution. The order of negative ΔG_{tr} for the various solutes in benzene is PBP > PCP > PNP. The negative ΔS_{tr} values imply a high degree of ordering when nonelectrolytes are transferred from organic solvents to water. The phenols being polar can bring about a high degree of ordering with the water molecules arranging themselves around them, and forming hydrogen bonds at the same time and thus stabilizing the water molecules.

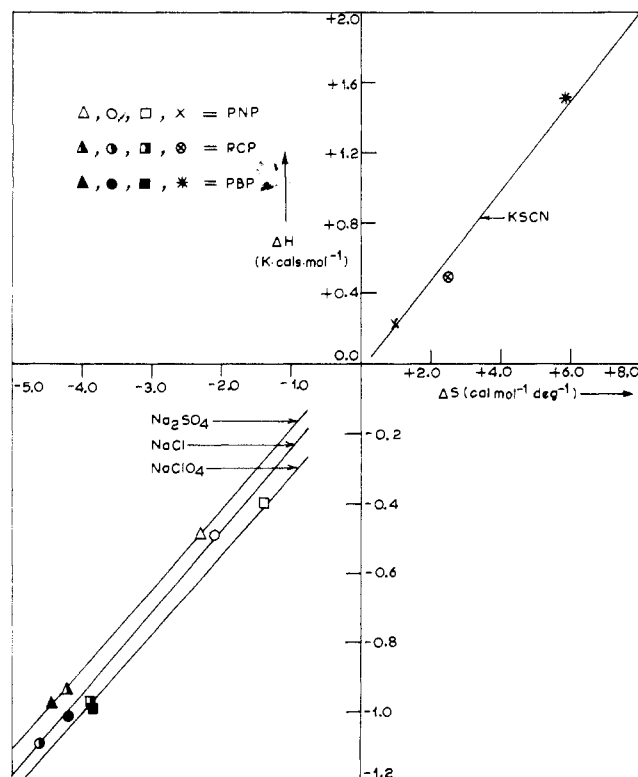
In Table III some literature values for the transfer of various nonelectrolytes from organic to water phases have been included for the sake of comparison. Methane shows a favorable enthalpy change with the evolution of heat when it is transferred from benzene to water. Solubility studies of hydrocarbons in water show that, although the ΔH of solution are negative, these compounds are insoluble in water. It is the large energy of reordering the hydrocarbon solute and the water molecules that keeps them in separate phases. The table shows data for the transfer of *n*-butane and 1-butanol from the respective pure liquids to water and also the data for the transfer of *n*-butyric acid from toluene to water. Thus, by replacing a methyl group with a carboxyl group in water, about 3 kcal mol⁻¹ is evolved, and the entropy change is also much more favorable in the case of the carboxyl group. This enthalpy differences arises from more energetic H bonding between COOH groups and water molecules than between water molecules, and the entropy difference reflects less structuring of H₂O molecules around a COOH group than around a CH₃ group.

The enthalpy of transfer of phenol from *n*-hexane and methanol to water shows favorable enthalpy changes in the former case. Obviously the phenol-*n*-hexane interactions are very small compared to the phenol-water interactions owing to the more energetic H bonding in the latter situation. In methanol, phenol is known to act as a proton donor toward the solvent molecules. So energy would be required to break these bonds and transfer the solute to the aqueous phase.

PNP shows unfavorable enthalpy changes when it is transferred from *n*-hexane, CCl₄, or methanol to water. Our results show that ΔH_{tr} from benzene to water is positive and is about 1 kcal mol⁻¹. This can be explained by the higher degree of association of PNP in *n*-hexane than in benzene. In CCl₄, the degree of association is the least, and a PNP-methanol donor-acceptor complex is quite stable. PCP and 2-naphthol in CCl₄ show negative enthalpy changes. These values again

Table IV. Literature Values of Transfer Thermodynamic Quantities of Nonelectrolyte from Water to Aqueous Electrolyte Solutions at 298 K

solute	electrolyte	ΔG_{tr} , cal mol ⁻¹	ΔH_{tr} , cal mol ⁻¹	ΔS_{tr} , cal mol ⁻¹ deg ⁻¹	ref
argon	NaCl	188.7	0.20	248.3	9
	KCl	170.9	0.77	400.4	9
ethyl acetate	NaCl	227.0	204.00	-0.1	10
	KCl	195.0	50.00	-0.5	10
nitromethane	NaCl	76.0	83.00	0.0	11
	KCl	12.0	-145.00	-0.5	11
butanol	NaCl	255.7	275.20	408.6	12
	Na ₂ SO ₄	697.8	956.00	881.9	12

Figure 3. Plots of ΔH_{tr} vs. ΔS_{tr} .

show that in aqueous solution H bonding of these solutes with water is the dominating factors with a favorable enthalpy change.

Table IV shows literature values of thermodynamic quantities of transfer of various solutes from water to salt solutions. The

ΔG_{tr} values are highest in the case of Na_2SO_4 followed by NaCl and KCl and they are all positive. Those for sodium salts are higher than those for potassium salts. In the case of argon all transfer quantities are found to be positive. Argon, being an inert molecule, forms a water clathrate structure with ease; hence, it has a larger positive ΔS_{tr} . Butanol and ethyl acetate and the polar solutes show the same trend as the phenols studied in the present case.

Figure 3 shows a plot of ΔH_{tr} vs. ΔS_{tr} for the phenolics from water to salt solutions (Na_2SO_4 , NaCl , NaClO_4 , KSCN). Lumry (4) has discussed such plots for reactions involving small molecules and proteins and has attributed a linear behavior to properties of water as a solvent, especially water structure.

The plots are approximately parallel straight lines with slopes in the range 200–230 K. The "isoequilibrium" temperature thus tallies with those (285–340 K) for several ionization and H-bonding reactions in water. Such linear compensations of $\Delta H - \Delta S$ in the absence of any other known strong reaction involving the solute is strong evidence that hydrophobic interaction is the driving force for the transfer phenomenon. In the transfer from organic liquids to water, however, no such correlation is expected nor is it obtained, indicating water structure does not have any special significance here.

Acknowledgment

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Registry No. NaF , 7681-49-4; Na_2SO_4 , 7757-82-6; $(\text{NH}_4)_2\text{SO}_4$, 7783-20-2; NaCl , 7647-14-5; NaNO_3 , 7631-99-4; KCl , 7447-40-7; KNO_3 , 7757-79-1; NaClO_4 , 7601-89-0; KSCN , 333-20-0; *p*-chlorophenol, 106-48-9; *p*-bromophenol, 106-41-2; *p*-nitrophenol, 100-02-7; benzene, 71-43-2.

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Electrophoretic Studies of Cobalt(II)–, Zinc(II)–, Beryllium(II)–, Uranyl(II)–, Chromium(III)–, and Thorium(IV)–Oxalate–Nitrilotriacetate Complexes in Solution

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A new method involving the use of paper electrophoresis (PE) is described for the study of equilibria in mixed-ligand complex systems in solution. This technique is based on the movement of a spot of a metal ion under a potential field, with the complexants added in the background electrolyte (0.1 M sodium perchlorate), at pH 10.0. The concentration of one of the complexants, L, is kept constant, while that of the second, L^1 , is varied. A graph of $-\log [L]$ against mobility is used to obtain information on the formation of the mixed-ligand complex and to calculate the stability constant. With this technique, the values of the overall stability constants of the complex metal–oxalate–nitrilotriacetate have been found to be $10^{7.49}$, $10^{6.58}$, $10^{7.42}$, $10^{8.98}$, $10^{9.89}$, and $10^{9.74}$ for Co^{II} , Zn^{II} , Be^{II} , U^{IV} , Cr^{III} , and Th^{IV} complexes, respectively, at $\mu = 0.1$ and temperature = 40 °C.

Introduction

Paper electrophoresis (PE) has been applied to the study of metal complexes in solution, and attempts have been made to determine the stability constant of the complex species (1–3). In recent work (4) of this laboratory, a new method was developed for the study of the stepwise formation of complexes formed between various metal ions and tartaric acid. Although the use of PE for the study of metal complex systems with a single ligand seems to be well established, there is not systematic study of the formation of mixed-ligand complexes using this technique. However, Czakis-Sulkowska (6) made some

observations on the formation of mixed-halide complexes of mercury(II) using the PE technique, but the studies were only qualitative and did not throw light either on the nature of the species or on their stabilities.

Theoretical Section

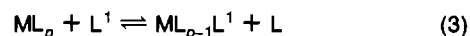
A metal ion M is assumed to complex with ligand anions L to give complex ions as follows, the charges of the ions being ignored:



The gross stability constant is given by the expression

$$\beta_{ML_p} = [ML_p] / ([M][L]^p) \quad (2)$$

Addition of another ligand, L^1 , to the system may lead to its partial substitution in the complex species, forming a mixed complex unit.



The equilibrium constant for the above equilibrium is given by

$$K_{ML_{p-1}L^1} = [ML_{p-1}L^1][L] / ([ML_p][L^1]) \quad (4)$$

Substituting the value of $[ML_p]$ by $\beta_{ML_p}[M][L]^p$ from eq 2 into eq 4, one obtains the gross stability constant of the mixed-ligand complex.

$$\beta_{ML_p} K_{ML_{p-1}L^1} = [ML_{p-1}L^1] / ([M][L]^{p-1}[L^1]) = \beta_{ML_{p-1}L^1} \quad (5)$$