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Salting Studies of 1- and 2-Naphthols and Their Thermodynamic Quantities of Transfer from Water to Salt Solutions at Different Temperatures

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The salting-in or salting-out effects of 1- and 2-naphthols have been explained on the basis of data obtained from free energies, enthalpies, and entropies of transfer from water to salt solution. These transfer thermodynamic quantities have been calculated from activity coefficients obtained from partition coefficients between water or salt solutions and cyclohexane and benzene at three temperatures, viz., 20, 30, and 40 °C.

Introduction

In an earlier communication (*1*) we reported some preliminary data on salting coefficients and transfer thermodynamic quantities of 1- and 2-naphthols pertaining to the partitioning between cyclohexane and aqueous salt solutions at 20 °C. This paper reports the results of detailed salting studies on these naphthols using benzene as well as cyclohexane as the organic solvent. The studies have been extended to 30 and 40 °C for cyclohexane and at 30 °C for benzene.

The distribution of an organic compound between two immiscible liquids in which it is soluble has been an important subject for experimentation and study for many years. The process of salting-out is studied by taking one of the phases as aqueous solution of the salt used as the salting agent. For organic compounds, it has been found that the process of salting-out is significantly affected by the nature of the salting-out agent, the extractant, and the substance distributed (*2*). The most extensive and useful partition coefficient data were obtained by simply shaking a solute with two immiscible solvents and then analyzing the solute concentration in one or both the phases.

Data on salt effect available in the literature are numerous and includes solid, liquid, and gaseous nonelectrolytes. We have earlier reported the salting effects of *p*-aminophenol in protic solvents by determining the saturation solubilities in the presence of salts (*3*). Salting studies of three substituted phenols, viz., *p*-chlorophenol, *p*-bromophenol, and *p*-nitrophenol have been discussed in detail in our previous communication (*4*).

In the present studies, free energies, enthalpies, and entropies of transfer were calculated from activity coefficients obtained from partition coefficients of 1- and 2-naphthols between water or salt solutions and cyclohexane at 20, 30, and 40 °C. Partitioning experiments were carried out for benzene at 30 °C.

Experimental Section

The naphthols of BDH AnalaR grade were vacuum-dried over anhydrous NaOH for removal of minute traces of water. All salts, viz., NaCl, Na_2SO_4, $NaClO_4$, and KSCN were of AnalaR grade and were used without further purification. Benzene and cyclohexane were distilled at temperatures much below their boiling points to remove traces of higher boiling impurities present. Stock solutions of the solute and salt were prepared by direct weighing and these were diluted accurately by using previously calibrated glassware to obtain different required concentrations.

The other experimental procedure is similar to that described earlier (*1*, *4*). The partitioning experiments were carried out at 20, 30, and 40 °C when cyclohexane was used and at 30 °C in case of benzene. 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 295 nm for 1-naphthol and at 330 nm for 2-naphthol for both aqueous and organic layers.

Results and Discussion

We may recall here that in two distribution experiments carried out (one with pure water and the other with salt solution) if the concentration of the nonelectrolyte (solute) in the organic phase (called the reference phase) is kept constant we have

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

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 solutions without salt, respectively; K_e is the partition coefficient of the solute between organic phase and water, C'_{org} is the solute concentration in the organic phase in the experiment with 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) can be calculated from eq 1.

The salting coefficient defined by the relationship

$$K_S = \lim_{C_S \to 0} [\mathrm{d} \log (f/f_0)/\mathrm{d}C_s] \qquad (2)$$

is obtained from the slope of the linear plots of log (f/f_0) vs. C_s as shown in Figures 1 and 2. The K_s values for the naphthols at different temperatures are listed in Table I. The Setschenow equation (*5*), $\log f/f_0 = K_s C_s$, was found to be precisely applicable to these systems. The standard free energy of transfer is related to the salting-out constant by the following equation

$$\Delta G_{tr} = RT \frac{\mathrm{d} \ln (f/f_0)}{\mathrm{d}C_s} = 2.303RTK_s \qquad (3)$$

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

$$-\Delta S_{tr} = RT(\mathrm{d} \ln f/f_0/\mathrm{d}T) + R \ln f/f_0 \qquad (4)$$

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

	1-naphthol				2-naphthol			
salt	20 °C	30 °C		40 °C	20 °C	30 °C		40 °C
NaCl	0.197 ± 0.001	0.166 ± 0.010	0.102 ± 0.001[a]	0.163 ± 0.001	0.144 ± 0.006	0.142 ± 0.001	0.093 ± 0.009[a]	0.130 ± 0.001
Na_2SO_4	0.472 ± 0.017	0.462 ± 0.015	0.375 ± 0.008	0.440 ± 0.003	0.393 ± 0.001	0.385 ± 0.017	0.371 ± 0.006	0.377 ± 0.000
$NaClO_4$	0.081 ± 0.002	0.073 ± 0.007	0.055 ± 0.006	0.071 ± 0.002	0.080 ± 0.003	0.060 ± 0.001	0.054 ± 0.002	0.054 ± 0.008
KSCN	−0.032 ± 0.001	−0.026 ± 0.002	−0.063 ± 0.001	−0.018 ± 0.001	−0.046 ± 0.003	−0.038 ± 0.000	−0.110 ± 0.009	−0.036 ± 0.002

[a] Benzene used as extractant, cyclohexane for all other cases.

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

	20 °C			30 °C			40 °C	
salt	ΔG	ΔH	ΔS	ΔG		ΔS	ΔG	ΔS
				1-Naphthol				
NaCl	264.13	−295.23	−1.91	230.17	141.43[b]	−2.05	233.47	−1.87
Na_2SO_4	632.85	−352.00	−3.36	640.58	519.95	−3.44	630.22	−2.96
$NaClO_4$	108.60	−183.04	−1.00	101.22	76.26	−0.99	101.69	−0.91
KSCN	−45.83	1062.30	3.78	−36.05	−87.35	3.64	−25.78	3.48
				2-Naphthol				
NaCl	193.07	−645.34	−2.86	196.89	128.95[b]	−3.07	186.20	−2.83
Na_2SO_4	526.93	−699.11	−4.18	533.82	514.41	−4.18	539.98	−3.79
$NaClO_4$	85.81	−208.00	−1.00	83.19	74.87	−1.01	77.34	−0.91
KSCN	−65.89	1398.20	5.00	−52.69	−152.52	4.82	−51.56	4.63

[a] ΔG and ΔH in cal mol^{-1}; ΔS in cal mol^{-1} deg^{-1}. [b] For benzene as extractant. All others for cyclohexane.

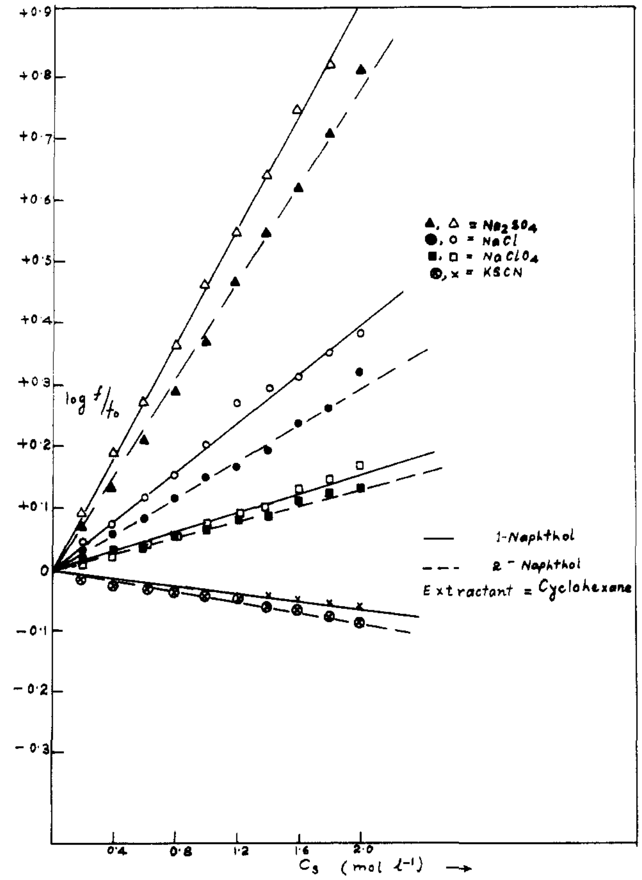

Figure 1. Least-squares plot of log f/f_0 vs. salt concentration at 20 °C.

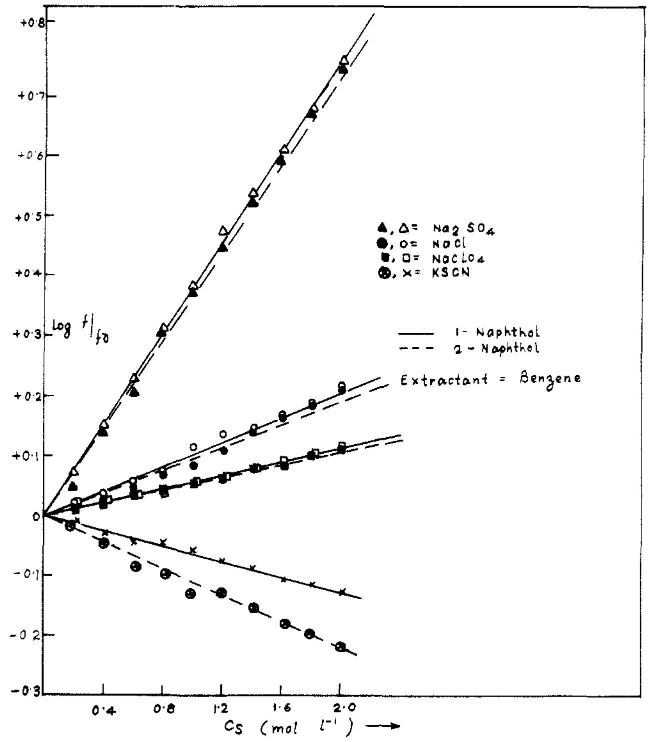

Figure 2. Least-squares plot of log f/f_0 vs. salt concentration at 30 °C.

The three thermodynamic parameters of transfer for all solutes are reported in Table II.

Perusal of Table I shows that K_s values for 1-naphthol are consistently higher than those of 2-naphthol at all temperatures and that the K_s values decrease with an increase in temperature. The salting order observed is $SO_4^{2-} > Cl^- > ClO_4^- > SCN^-$ which tallies with the salting order for a number of solutes of widely varying chemical nature (1, 3, 4, 6). 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^- are due to the structure-making property of these ions. This is also in agreement with the relative influence of these ions on water structure (7). Among the structure makers, KSCN has a greater structure-making tendency (compared to $NaClO_4$) and hence shows salting-in. The ionic charge also seems to play an important role in salting-out. Thus, among the structure breakers SO_4^{2-} has a greater charge than Cl^{1-} and shows more pronounced salting-out effect.

The salting-out process is significantly affected by the nature of the extractant used. The solvents studied by us include cyclohexane and benzene. In the present case of naphthols, though the distribution coefficient increases significantly with benzene as extractant, compared to that with cyclohexane, the

Table III. Thermodynamic Quantities of Transfer from Organic to Water Phase at 30 °C

solute	organic solvent	ΔG_{tr}, cal mol^{-1}	ΔH_{tr}, cal mol^{-1}	ΔS_{tr}, cal mol^{-1} deg^{-1}
1-naphthol	cyclohexane	−4808.00	2942.00	−27.10
2-naphthol	cyclohexane	−5268.00	2590.00	−24.43
1-naphthol	benzene	−47751.00		
2-naphthol	benzene	−47740.00		

K_s values are consistently lower.

The three thermodynamic parameters of transfer for the naphthols are recorded in Table II. The values show that the free energies of transfer for the naphthols at all temperatures are positive for all salts except KSCN which shows negative values. Also ΔG_{tr} values at a particular temperature and for a particular salt are higher in 1-naphthol than in 2-naphthol. With the increase in temperature the ΔG_{tr} values decrease, the effect being pronounced between 20 and 30 °C.

During salting-out, salts are solvated with water molecules thus decreasing the availability of water for the nonelectrolyte. As a result the free energy for the latter rises thereby showing positive ΔG_{tr} values. The reverse phenomenon occurs in the case of KSCN, i.e., increasing the solubility of the nonelectrolyte in KSCN solutions thereby resulting in salting-in.

The ΔH_{tr} values are negative in all cases except in the case of KSCN. An exothermic ΔH_{tr} value indicates a net structure breaker and an endothermic value indicates a net structure maker. The exothermic ΔH_{tr} values are highest in the case of studies with Na_2SO_4 followed by NaCl, $NaClO_4$, and endothermic in case of KSCN. When the naphthols enter salt solution, where the salt is KSCN, heat is required to accommodate the naphthol molecules, thereby showing the structure-making tendency of KSCN, solute–water or solute–salt interaction being negligibly small.

The ΔS_{tr} values are found to be small and negative in case of studies with all salts except KSCN where positive values are obtained. Thus we can say when the naphthols are transferred from water to salt solutions, the forces on the neighboring water molecules are modified, decreasing the net entropy. As the ΔS_{tr} values are small it is logical to state that in the presence of ionic fields, the naphthols have relatively little influence on the solvent molecules. The small values of entropy also indicate that for a particular transfer process, entropy is only a secondary driving force. Table III shows the thermodynamic quantities of transfer from the organic to the water phase. Here we obtain free energies of transfer which are negative in contrast to those obtained in case of transfer from water to salt solutions. The free energy of nonelectrolyte in organic solvents are expected to be higher than in water solutions. Interestingly, these values for the naphthols with benzene in the organic phase are much lower than when benzene is replaced by cyclohexane. A plausible explanation of this behavior undoubtedly lies in the fact that in benzene solutions, strong π–π interactions operate which is absent in cyclohexane (*8*). This may be a major factor contributing to the observed difference in ΔG_{tr} in the two cases reported in Table III.

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Registry No. NaCl, 7647-14-5; Na_2SO_4, 7757-82-6; $NaClO_4$, 7601-89-0; KSCN, 333-20-0; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3; cyclohexane, 110-82-7; benzene, 71-43-2.

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Diffusion, Viscosity, and Refractivity Data on the System Dimethylformamide–Water at 20 and 40 °C

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The diffusion coefficients of the system dimethylformamide–water at 20 and 40 °C were measured in all the ranges of concentration by the Gouy technique. In the same ranges viscosities and densities were also measured. From these data the activation energies for diffusion and viscosity have been calculated. From diffusion data molar refractivities were obtained. It was confirmed that dimethylformamide and water have a strong interaction. We suggest that this interaction does not have the character of complex formation but rather that of an extended, clusterlike structure where the H bonds play a relevant role.

Introduction

In a previous article (*1*) the diffusive properties of *N*,*N*-dimethylformamide (DMF) at 5 °C were examined. In the present article we report diffusion data collected at 20 and 40 °C.

The interest of these data comes from the use of DMF as a solvent for the polymeric material used in membrane casting with the technique of "phase inversion" (*2*, *3*).

Notwithstanding the mechanism of membrane formation is not readily explicable, the solvent/nonsolvent interdiffusion process is certainly important (*4*–*6*). Water is generally the nonsolvent used with DMF. There is a lack of accurate diffusion data (*7*) for the DMF–H_2O system. For this reason we have collected the diffusion data through all the composition range and in a wide temperature interval.

Density, refractivity, and viscosity data have also been collected at the same temperatures.

Experimental Section

Material. Dimethylformamide, reagent grade (C. Erba, Milan and Baker Chemicals, Holland), was used without further pu-

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