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Solubility Studies of Ion-pairs in Organic Solvents

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Synopsis. The solubilities of several types of ion-pairs were measured in many organic solvents at 25 °C. A good correlation holds between the logarithmic solubilities and the solubility parameters of solvents over the whole range of polarity.

In the previous paper,[1] the extraction behavior of ion-pairs of the $Ru(phen)_3A_2$ type was studied from the viewpoint of the ionic equilibrium involved in the extraction system. However, no clear discussion was given of the distribution ratio in connection with the physical parameter of the extraction solvent. The distribution ratio is generally determined as the ratio of the solubilities of the solute in the two phases. Therefore, the solubility measurement of the ion-pairs in the organic solvents seems to be useful in order to elucidate the solvent characters, which mainly govern the distribution ratio.

In this paper, the solubilities of several types of ion-pairs, such as $Ru(phen)_3A_2$ and MA will be measured; M refers to the alkali metal ions, and A, to the chloride ion, the perchlorate ion, and the tetraphenylborate ion. The results obtained will be discussed with respect to the two characteristic parameters of solvents, *i.e.*, the solubility parameter and the dielectric constant.

Experimental

Reagents. The organic solvents used here were purified several times by using a 1 m distillation column packed with helical steel wire, as was recommended in the literature.[2] The $Ru(phen)_3A_2$ salts were prepared as follows: 200 mg of $RuCl_3 \cdot H_2O$, 526 mg of *o*-phenanthroline, and 218 mg of hydroxylammonium sulfate were dissolved in 50 ml of an ethanol–water (1 : 1) solution and the pH of the solution was adjusted to 6 with a saturated $Ba(OH)_2$ solution. After refluxing for two days at 100 °C, the $BaSO_4$ was filtered out and the excess *o*-phenanthroline was removed by washing the solution several times with chloroform and then with *n*-hexane. After the resulting solution had been dried *in vacuo*, the residue was dissolved with a minimum volume of acetonitrile and any undissolved precipitates present were filtered out. $Ru(phen)_3Cl_2$ could be crystallized by adding chloroform to the filtrate. $Ru(phen)_3(ClO_4)_2$ was obtained by adding a large excess of sodium perchlorate to a slightly acidic solution of $Ru(phen)_3Cl_2$. $Ru(phen)_3(B(C_6H_5)_4)_2$ (abbreviated as $Ru(phen)_3(BPh_4)_2$) was prepared by adding a slight excess of sodium tetraphenylborate to an aqueous solution of $Ru(phen)_3Cl_2$. The addition of sodium tetraphenylborate should be restricted to a minimum; otherwise, contamination with the excessive tetraphenylborate ions takes place. All the precipitates were dried for two days *in vacuo*. (Calcd for $Ru(phen)_3Cl_2$: C: N: Cl, 6.10: 1.19: 1.0; Found: 6.09: 1.17: 1.0, Calcd for $Ru(phen)_3(BPh_4)_2$: H, 5.03; C, 78.81; N, 6.56%; Found: H, 4.81; C, 78.78; N, 6.60%.) The $KBPh_4$ and $CsBPh_4$ were prepared by adding small excesses of KCl and CsCl respectively to an aqueous sodium tetraphenylborate solution. After the precipitates had been washed several times with water, they were dried for two days *in vacuo*. The other reagents were purchased with reagent-grade purities.

Solubility. The solubility measurements were carried out as follows. After the $Ru(phen)_3A_2$ and $MBPh_4$ had been added to approximately 10-ml portions of pure solvents in test tubes equipped with ground stoppers, the equilibration was performed in a thermostat at 25 °C by shaking the solution

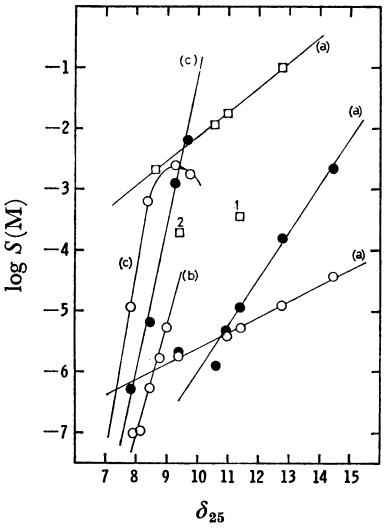

Fig. 1. The relations between the solubilities of $Ru(phen)_3A_2$ and the solubility parameters of solvents.
(a): alcohols, (b): esters, (c): ketones.
(○): $Ru(phen)_3(BPh_4)_2$, (●): $Ru(phen)_3(ClO_4)_2$, (□): $Ru(phen)_3Cl_2$ (1): 2-propanol, (2): 2-butanol

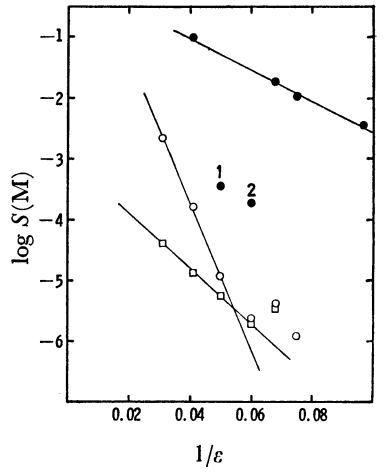

Fig. 2. The relations between the solubilities of $Ru(phen)_3A_2$ and $1/\varepsilon$ of alcohols.
(□): $Ru(phen)_3(BPh_4)_2$, (○): $Ru(phen)_3(ClO_4)_2$, (●): $Ru(phen)_3Cl_2$
(1): 2-propanol, (2): 2-butanol

Table 1. Solubilities of $Ru(phen)_3A_2$ in organic solvents
M represents Ru(II)(phen)$_3$ here

Solvent	δ_{25}	ε	$M(B(C_6H_5)_4)_2$	$M(ClO_4)_2$	MCl_2
Methanol	14.5	32.7	3.84×10^{-5}	2.16×10^{-3}	
Ethanol	12.9	24.6	1.30×10^{-5}	1.60×10^{-4}	1.00×10^{-1}
2-Propanol	11.5	19.9	5.41×10^{-6}	1.20×10^{-5}	3.62×10^{-4}
Isoamyl alcohol	11.0(10.8)[a]	14.7	3.78×10^{-6}	4.11×10^{-6}	1.83×10^{-2}
2-Butanol	9.4(11.1)[a]	16.6	2.05×10^{-6}	2.32×10^{-6}	1.88×10^{-4}
1-Hexanol	10.7	13.3		1.19×10^{-6}	1.04×10^{-2}
1-Octanol	8.7(10.2)[a]				1.96×10^{-3}
Benzyl alcohol	12.1	13.1	2.68×10^{-4}	3.43×10^{-3}	
Acetone	9.8	20.7	2.02×10^{-3}	6.81×10^{-3}	1.60×10^{-4}
Methyl ethyl ketone	9.3	18.5	2.45×10^{-3}	1.39×10^{-3}	2.89×10^{-4}
Methyl isobutyl ketone	8.4	13.1	6.92×10^{-4}	5.59×10^{-6}	$<10^{-7}$
Diisobutyl ketone	7.8		1.19×10^{-5}	5.40×10^{-7}	$<10^{-7}$
Tetrahydrofuran	9.3	7.6	6.03×10^{-4}		
Isopropyl ether	7.0		4.32×10^{-7}		
Methyl acetate		6.7		1.21×10^{-5}	$<10^{-7}$
Ethyl acetate	9.1	6.0	5.41×10^{-6}	$<10^{-7}$	$<10^{-7}$
n-Propyl acetate	8.8	6.0	1.62×10^{-6}	$<10^{-7}$	$<10^{-7}$
n-Butyl acetate	8.5	5.0	5.94×10^{-7}	$<10^{-7}$	$<10^{-7}$
Isobutyl acetate	8.3	5.3	1.08×10^{-7}	$<10^{-7}$	$<10^{-7}$
Isoamyl acetate	8.1		$\sim10^{-7}$	$<10^{-7}$	$<10^{-7}$
Chloroform	9.2	4.8	1.29×10^{-4}		9.7×10^{-5}
1,2-Dichloroethane	9.9	10.4	4.18×10^{-4}		
Monochlorobenzene	9.5	5.6	7.03×10^{-6}		$<10^{-7}$
o-Dichlorobenzene		9.9			$<10^{-7}$
1-Nitropropane	10.5	23.2	4.22×10^{-3}		7.29×10^{-4}
Bis(2-chloroethyl) ether		21.2	1.26×10^{-2}		2.90×10^{-3}

a) The value calculated according to the Hildebrand rule using ΔH_{25} in the literature.[2]

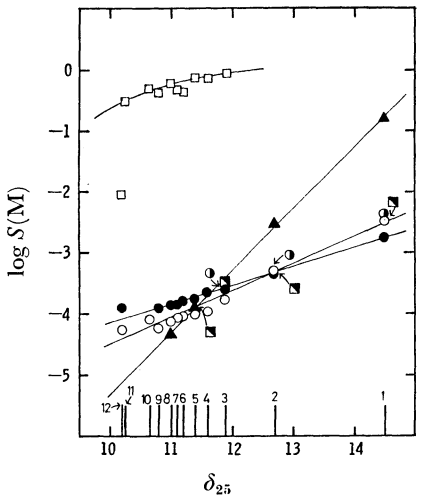

Fig. 3. The relations between the solubilities of some other salts and the solubility parameters of alcohols.
(□): $NaBPh_4$, (○): $KBPh_4$, (●): $CsBPh_4$, (◑): $CsClO_4$, (—): $RbClO_4$, (▲): CsCl.
(1): methanol, (2): ethanol, (3): 1-propanol, (4): 2-propanol, (5): 1-butanol, (6): isobutyl alcohol, (7): 2-butanol, (8): 1-pentanol, (9): isoamy lalcohol, (10): 1-hexanol, (11): 1-octanol, (12): *tert*-amyl alcohol

for 7—8 days. The absorbance of the equilibrated solution was measured at 448 nm for $Ru(phen)_3A_2$ and at 274 nm for $MBPh_4$, from the molar absorptivities, 18500[1] and 1950 respectively. The solubilities of the other salts were measured gravimetrically.

Results

The observed solubilities of $Ru(phen)_3A_2$ in various solvents are listed in Table 1, together with the characteristic parameters of the solvents. The logarithmic solubilities ($\log S$) are shown as a function of the solubility parameters (δ) of the solvents (Fig. 1) and of the reciprocal of the dielectric constants ($1/\varepsilon$) of the solvents (Fig. 2). In Fig. 3, the solubilities of the other salts are plotted against δ values of the solvents.

As a result, a good correlation can be obtained between $\log S$ and δ in the solvents of the same sort, although the slopes of the plots are different from one sort of solvent to another. No clear relation, however, could be drawn between the dielectric constants and the solubilities in the low-polarity range.

References

1) T. Takamatsu, This Bulletin, **47**, 118 (1974).
2) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry, 2, Organic Solvents," Wiley-Interscience., New York (1970).