



ELECTROCHEMICAL STUDIES ON BINARY COMPLEXES IN DIFFERENT DIELECTRIC ENVIRONMENT

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ABSTRACT

The interaction of uranyl (IV) ion with benzoic acid have been investigated pHmetrically in different dielectric environment of 10%, 20%, 30%, 40% and 50%, dioxane- water mixtures. Bjerrum's potentiometric titration as adopted by Calvin and Wilson have been used to determine proton –ligand and metal-ligand stability constant using Irving-Rossoti's expression. The variation in values of \bar{n} , \bar{n}_A , $\log K_1$ and $\log K_2$ at different percentage compositions of dioxane-water shows favourable effect on complexation equilibria.

Key words: Potentiometry, Uranyl, Benzoic acid, Dielectric constant, Dioxane.

INTRODUCTION

Complex formation between uranyl (IV) ion and aliphatic, aromatic or dicarboxylic acid have been extensively studied.¹⁻⁶ It is very interesting to note the combined effects of dicarboxylic acids on complexation equilibria in the higher order complexes.⁷⁻¹¹ In view of wide pharmaceutical and analytical applications of benzoic acid, it seems interesting to study the effect of dielectric constant on complexation tendency of benzoic acid.

EXPERIMENTAL

All the chemicals used for experiment such as dioxane, potassium chloride, sodium hydroxide, perchloric acid, sodium perchlorate, uranyl nitrate, benzoic acid etc. were of analytical grade. The potentiometric pH titrations were carried out on an Equip-tronics EQ 611 pH meter. The electrode was calibrated with standard buffer solutions prepared

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according to NBS specification. The NaOH solution used for titrations was standardized by titrating it with standard HCl (E. Merck GR) by standard procedure. The measurements were carried out at $35 \pm 1^\circ\text{C}$. The experimental procedure involved potentiometric titrations of carbonate free solutions of the mixture (i) Free HClO_4 ($1.00 \times 10^{-2}\text{M}$), (ii) Free HClO_4 ($1.00 \times 10^{-2}\text{M}$) + ligand ($20 \times 10^{-4}\text{M}$), (iii) Free HClO_4 ($1.00 \times 10^{-2}\text{M}$) + ligand ($20 \times 10^{-4}\text{M}$) + metal ion solution ($4 \times 10^{-4}\text{M}$) against a standard solution of sodium hydroxide (0.25M) The ionic strength of all solutions was maintained constant by adding appropriate quantity of 1M sodium perchlorate solution. Titrations of above three sets were carried out in different percentage of dioxane–water mixtures (10%, 20%, 30%, 40% and 50%) at $35 \pm 1^\circ\text{C}$. The titrations were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through an assembly containing electrodes in order to drive out CO_2 . Representative curves of volume of NaOH vs pH, \bar{n} vs pH for only three compositions 10%, 30% and 50% have been given.

Table 1: Potentiometric data of the proton-ligand constant (\bar{n}_A) and metal-ligand stability constant (\bar{n}) at various pH values using different percentages of dioxane-water mixture

pH	10%		20%		30%		40%		50%	
	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}
4.0	0.722	2.267	0.695	1.090	0.822	0.615				
4.2	0.696	2.530	0.670	1.508	0.822	0.769				
4.4	0.697	2.710	0.695	1.762	0.797	0.952	0.974	0.391		
4.6	0.646	3.308	0.645	1.762	0.797	1.110	0.974	0.521	0.948	0.401
4.8	0.621	3.442	0.594	2.123	0.797	1.427	0.974	0.521	0.948	0.539
5.0	0.621	3.643	0.569	2.217	0.772	1.473	0.974	0.521	0.923	0.554
5.2	0.596	4.006	0.543	2.552	0.746	1.523	0.898	0.706	0.897	0.997
5.4	0.571	4.181	0.518	2.920	0.721	1.629	0.873	0.872	0.871	1.173
5.6	0.571	4.179	0.493	3.068	0.721	1.751	0.796	0.954	0.846	1.208
5.8	0.546	4.140	0.468	3.503	0.721	1.926	0.746	1.019	0.820	1.245
6.0	0.521	4.338	0.442	3.701	0.696	1.995	0.746	1.528	0.795	1.446

Cont...

pH	10%		20%		30%		40%		50%	
	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}	\bar{n}_A	\bar{n}
6.2	0.521	4.336	0.417	3.923	0.670	2.259	0.695	1.639	0.769	1.493
6.4	0.521	4.335	0.392	4.495	0.670	2.258	0.695	1.821	0.769	1.659
6.6	0.496	4.299	0.367	4.804	0.645	2.542	0.669	2.078	0.769	1.659
6.8	0.471	4.260	0.341	5.156	0.620	2.644	0.644	2.159	0.744	1.887
7.0	0.445	7.310	0.316	5.964	0.595	2.967	0.619	2.246	0.718	2.131
7.2	0.395	8.237	0.316	5.961	0.569	3.098	0.593	2.342	0.693	2.761
7.4	0.395	8.233	0.316	6.358	0.544	3.473	0.568	2.445	0.667	3.057
7.6	0.370	8.787	0.291	6.909	0.519	3.640	0.543	2.790	0.642	3.376
7.8	0.345	9.058	0.291	7.336	0.493	4.081	0.518	3.169	0.642	3.772
8.0	0.320	9.761	0.266	8.032	0.468	4.301	0.518	3.412	0.616	3.926
8.2	0.320	9.755	0.240	9.395	0.443	4.827	0.492	3.585	0.591	4.094
8.4	0.320	9.750	0.215	10.496	0.418	5.119	0.493	3.840	0.565	4.503
8.6	0.295	10.147	0.190	12.549	0.418	5.119	0.467	4.045	0.540	4.714
8.8	0.295	10.141	0.190	13.196	0.392	5.765	0.467	4.313	0.514	5.192
9.0	0.270	10.611	0.190	13.856	0.342	6.610	0.382	4.844	0.489	5.720

Table 2

%	pH (at 0.5)	pH (at 1.5)	log K ₁	log K ₂
10	2.3	3.4	0.361728	0.531479
20	3.3	4.2	0.518514	0.623249
30	3.9	5.1	0.653213	0.70757
40	4.5	5.9	0.653213	0.770852
50	4.7	6.2	0.672098	0.792392

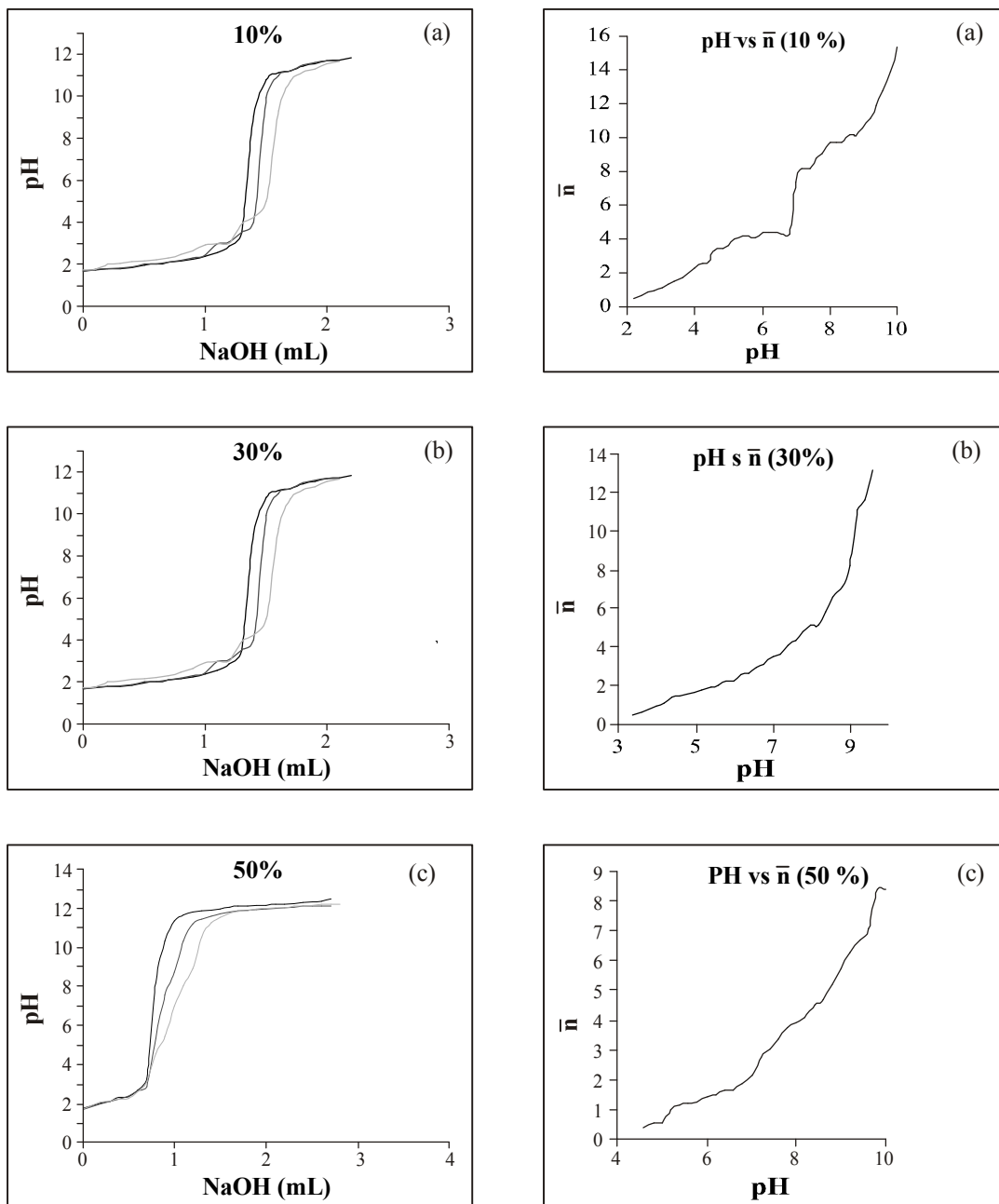


Fig. 1: Variation of pH vs volume of NaOH and \bar{n} vs pH at different compositions of dioxane-water mixture (a) 10% (b) 30% and (c) 50%

RESULTS AND DISCUSSION

The values of \bar{n} , \bar{n}_A , $\log K_1$ and $\log K_2$ at different concentrations of dioxane-water mixture are given in Tables 1 and 2. Values of \bar{n} were calculated by using Irving-Rossoti's equation¹². The values of \bar{n} presented are used to access the effect of percentage composition of dioxane-water mixture on stability constants. The formation curves are constructed between \bar{n}_A and pH. pH meter readings were converted into true values by making correction given by Van Ultert and Hass method¹¹. The pK values of ligands in different dioxane-water compositions were determined from half integral method as well as point wise calculation methods. The pH at $\bar{n} = 0.5$ corresponds to pK value of ligand in different dioxane-water composition. It is observed that as the percentage of dioxane in water was increased, the values of \bar{n} and \bar{n}_A also increases, which shows that increasing concentration of dioxane increases the deprotonation of ligand to form $-\text{COO}^-$ group. At the same time, increase in the value of \bar{n} indicates the more favourableness of increasing volume of dioxane in water mixture¹³. The earlier deprotonation of ligand has been observed with increasing composition of dioxane in water. It is observed that 1 : 1 complex is fairly stable up to pH 7.0 (approximately) where as 1 : 2 complex exists in lower pH range and is stable up to 5 to 6 pH. The lower stability of 1 : 2 complex is due to dimerisation of benzoic acid in the acidic range, where complexation is not favoured over dimerisation. This is also evident from values of $\log K_1$ and $\log K_2$ given in Table 2. With increasing dielectric constant of the medium, benzoic acid tends to be dimerised rather than participating in complex formation¹⁴. This shows that at higher pH range, benzoic acid exists as dimer and it is a probable reason for lower stability of 1 : 2 complex.

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