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THERMODYNAMICS OF FORMATION OF TRIIODIDE COMPLEXES AND SOLVATION OF REAGENTS IN ALKANOLIC SOLUTIONS OF ELECTROLYTES

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Abstract

The aim of this investigation was to study the influence of electrolytes on a reaction of triiodide complex formation. Investigation of the salt effect as concerns the thermodynamics of I_3^- formation in methanol, ethanol and *n*-propanol solutions revealed regularities of the influence of the electrolyte on triiodide complex formation connected with a multifactorial effect of the ionic medium. The quasichemical model presented was used to calculate parameters reflecting the overall salt effect.

Keywords: activity coefficients, complex formation, salt effect, solvation, specific interactions, stability constant triiodide

Introduction

This work is a continuation of systematic investigations of polyhalides in non-aqueous solutions [1], systems which are widely applied in photoelectrochemical converters and current sources. This work reports results of an investigation of the salt effect as concerns the thermodynamics of triiodide formation in solutions of electrolytes in methanol, ethanol or propanol.

The aim of the investigation was to establish the influence of electrolytes in non-aqueous media, taking the insufficiently studied anion – molecular reactions as example.

Methanol, ethanol and propanol were chosen as solvents to reveal the influence of the physico-chemical properties of the medium on the salt effect.

The reaction chosen as model was triiodide formation:

$$I_2 + I^- = I_3^- \qquad (1)$$

Experimental

The solvents used were distilled twice. All electrolytes used were recrystallized twice from aqueous solution. Iodine was sublimed twice.

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The stability constants of I_3^- in lithium, sodium and calcium nitrate and perchlorate solutions were determined by a potentiometric method based on a reverse chain E measurement:

$Pt/I_2, I^-, I_3^-, MNO_3\ (ClO_4^-)$, solvent / KCl (0.1 M aqueous methanol), Ag/AgCl

The measurements were performed in a thermostated cell (T=298.15 K). The E values were measured to within 0.0001 V. E was determined via the correlation of the oxidized and reduced iodine forms according to the Nernst equation:

$$E = E^{o} + \frac{RT}{zF}\ln\frac{a_{ox}}{a_{red}} \tag{2}$$

The essence of the method used was to determine the potentials $E_{1,2}^{o}$ of the reactions I_3^-/I^- and I_3^-/I_2.

If the stability constant of I_3^- is high, in the case of a twofold excess of one of the components at constant ionic strength and diffusion-phase potential, correlations (3) and (4) should hold [2]:

$$E = E_1^{o} + 0.029\log[I_3^-] - 0.088\log[I^-] \tag{3}$$

$$E = E_2^{o} + 0.059\log[I_3] + 0.088\log[I_2] \tag{4}$$

In this case, via Eqs (3) and (4), the stability constant can be calculated as follows [3]:

$$\log K = \frac{E_2^{o} - E_1^{o}}{0.088} \tag{5}$$

To verify the reproducibility of E in each experiment, two series of titrations were carried out. The reproducibility of E in the series was within ±0.0001 V. This makes the error in the calculated E_1^{o} value within ±0.0002 V.

The measurements were carried out with a reference electrode filled with 0.1 mol dm^{-3} KCl aqueous solution and one filled with methanol solution, the results being different. However, the log$K$ values calculated with Eq. (5) were the same. This testifies to diffusion-phase potential elimination.

The log$K$ values are listed in Table 1 at various ionic strengths of the background electrolytes, while Table 2 lists the data in the absence of a background electrolyte.

The solubility of iodine in the electrolyte solutions was determined by the titration of solutions prepared by an isothermal saturation method against sodium thiosulfate solution of exact concentration. The accuracy of the titrant volume determination was within ±0.01 cm^{-3}. This makes the accuary of the solubility measurement within ±0.001 mol dm^{-3}.

Table 1 Dependence of log$K$ values of triiodide complexes upon ionic strength of background electrolyte ($NaClO_4$) in alkanol solutions

			Methanol			
I_{NaClO_4}	0.5	0.8	1.0	1.5	2.0	3.0
$\log K(I_3^-)$	4.20	4.19	4.18	4.19	4.16	4.14
			Ethanol			
I_{NaClO_4}	0.1	0.5	0.8	1.0	1.5	
$\log K(I_3^-)$	4.61	4.58	4.54	4.51	4.50	
			Propanol			
I_{NaClO_4}	0.05	0.10	0.15	0.20		
$\log K(I_3^-)$	4.66	4.63	4.60	4.57		

Table 2 Constants (log$K$) of triiodide complex formation in alkanols without background electrolyte

Solvents	log$K$
Methanol	4.14
Ethanol	4.65
Propanol	4.66

The reagent activity transfer coefficients are listed in Table 3 as a function of the background electrolyte ionic strength. The extrapolated equation coefficients are given in Table 4.

The dependence of log$K(I_3^-)$ upon the background electrolyte concentration in ethanol is plotted in Fig. 1.

Results and discussion

According to some contemporary approaches, the change in the non-electrolyte stability constant when an electrolyte of definite concentration is added is connected with the combination of part of the solvent by solvate formation.

From a theoretical aspect, the constant of the anion-molecular complexes in aqueous solution are not very sensitive to salt effects because the activity coefficients of the ions are not strongly dependent upon the ionic strength [4].

In practice, the triiodide stability constants in aqueous solution are independent of the ionic strength and the nature of the background electrolyte. In non-aqueous media, they are connected with both the nature of the solvent and the nature of the electrolyte.

Table 3 Standard thermodynamic characteristics of I_3^- formation reaction, obtained by extrapolation of dependence log*K*=log*K*+*bI* to zero ionic strength

Electrolyte	log*K*	*b*
Methanol		
$NaClO_4$	4.21±0.01	–0.023±0.004
$Ca(NO_3)_2$	4.12±0.02	0.001±0.001
$LiNO_3$	4.18±0.01	–0.007±0.007
$LiClO_4$	4.14±0.01	–0.039±0.007
Ethanol		
$NaClO_4$	4.60±0.02	–0.058±0.017
$Ca(NO_3)_2$	4.49±0.01	–0.141±0.007
$LiNO_3$	4.58±0.02	–0.249±0.013
$LiClO_4$	4.60±0.01	–0.114±0.004
Propanol		
$NaClO_4$	4.69±0.01	–0.600±0.001
$Ca(NO_3)_2$	4.72±0.01	–0.280±0.007
$LiNO_3$	4.59±0.01	–0.191±0.007

At the same time, the tendency of iodide and triiodide anions to associate with the cations of the background electrolytes and the tendency of iodine to undergo donor–acceptor interactions with organic solvents make this system a highly sensitive indicator of the specific solute–solute–solvent interactions.

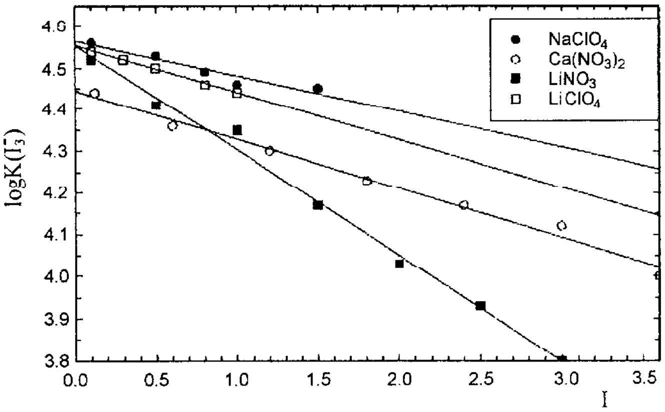

Fig. 1 Dependence of log*K*(I_3^-) upon the background electrolyte concentration in ethanol

Table 4 Dependence of activity transfer coefficients of reagents on ionic strength of background electrolyte ($NaClO_4$) in alkanol solutions

			Methanol			
I_{NaClO_4}	0.5	0.8	1.0	1.5	2.0	3.0
$\Delta_{tr}\log\gamma_{I_2}$	0.120	0.186	0.236	0.365	0.485	0.731
$-\Delta_{tr}\log(\gamma_{I_3^-}/\gamma_{I^-})$	0.13	0.21	0.27	0.39	0.54	0.80
			Ethanol			
I_{NaClO_4}	0.1	0.5	0.8	1.0	1.5	
$\Delta_{tr}\log\gamma_{I_2}$	0.007	0.093	0.146	0.184	0.312	
$-\Delta_{tr}\log(\gamma_{I_3^-}/\gamma_{I^-})$	0.01	0.12	0.22	0.28	0.42	
			Propanol			
I_{NaClO_4}	0.05	0.10	0.15	0.20		
$\Delta_{tr}\log\gamma_{I_2}$	0.003	0.006	0.009	0.012		
$-\Delta_{tr}\log(\gamma_{I_3^-}/\gamma_{I^-})$	0.04	0.08	0.11	0.15		

The process of triiodide complex formation in solutions with an MA electrolyte background may be represented by the sum of the following equations:

$$I^- + I_2 \overset{K}{\rightleftarrows} I_3^- \qquad (6)$$

$$M^+ + I^- \overset{K_1}{\rightleftarrows} MI \qquad (7)$$

$$M^+ + I_3^- \overset{K_2}{\rightleftarrows} MI_3 \qquad (8)$$

$$A^- + I_2 \overset{K_3}{\rightleftarrows} I_2A^- \qquad (9)$$

At fixed ionic strength, the analytical concentrations of the reagents are given by the following equations:

$$C_I = [I^-] + [MI] \qquad (10)$$

$$C_{I_3^-} = [I_3^-] + [MI_3] \qquad (11)$$

$$C_{I_2} = [I_2] + [I_2A^-] \qquad (12)$$

Accordingly, the concentration stability constant may be expressed as

$$K_c = \frac{C_{I_3^-}}{C_{I^-}C_{I_2}} = \frac{\left([I_3^-]+[MI_3]\right)}{\left([I^-]+[MI]\right)\left([I_2]+[I_2A^-]\right)} \tag{13}$$

If Eqs (6)–(12) are taken into account, K_c can be rewritten as

$$K_c = K\frac{(1+K_2[M^+])}{(1+K_1[M^+])(1+K_3[A^-])} \tag{14}$$

Equation (14) expresses a multifactorial effect of the medium even for such a relatively simple reaction as triiodide complex formation.

The dependence of K upon the ionic strength, I, is determined by the interactions which can be described within the Debye-Hückel theory. The iodide and triiodide ions differ in size by a factor of about 4-fold. For this system, the use of an average mean value of the closest approach parameter a is impossible.

$$\log K = \log K - \frac{AZ^2_{I_3^-}\sqrt{I}}{1+Ba_{I_3^-}\sqrt{I}} + b_{I_3}I - \frac{AZ^2_{I^-}\sqrt{I}}{1+Ba_{I^-}\sqrt{I}} - b_{I^-}I - b_{I_2}I \tag{15}$$

The parameters $b_{I_3^-}$, b_{I^-} and b_{I_2} are characterized mainly by the effect of association of part of the solvent with the background ions. These parameters depend very little upon the solid type. As a result, $b_{I_3^-}$ and b_{I^-} compensate each other and the overall effect of the salt on the value of b is determined by the contribution b_{I_2}.

The values of coefficients b_{I_2} and the complex formation constants of the reaction $I_2+A^-=I_2A^-$ are calculated from the data for iodine solubility in the corresponding electrolyte systems:

$$\log\frac{S}{S^o} = b_{I_2}C_{MA} - \log(1+K_3A^-) \tag{16}$$

Solvation number characteristics obtained from the solubility data on the basis of the Izmaylov method [5] are listed in Table 5.

Table 5 Components of effects of ionic media of triiodide stability constants in alkanols on background electrolyte ($NaClO_4$) at T=298.15 K (molar scale)

Solvent	n_s±1 $NaClO_4$	b_{I_2}	$\alpha(I_3^-/I^-)$ exp.	$\alpha(I_3^-/I^-)$ calc.	K_1	K_2	K_3	$\log K_{I_3^-}$
Methanol	8	0.301	0.286	0.210	5.05	5.01	0.152	4.21
Ethanol	6	0.394	0.298	0.310	78.5	74.2	0.601	4.60
Propanol	3	0.179	0.775	0.720	4.01	0.64	0.101	4.69

The electrostatic potential contribution ($\alpha_{\mathrm{calc.}}$)

$$\alpha_{\mathrm{calc.}}(I)=\frac{AZ_{I^-}^2\sqrt{I}}{1+Ba_{I^-}\sqrt{I}}-\frac{AZ_{I_3^-}^2\sqrt{I}}{1+Ba_{I_3^-}\sqrt{I}}$$

connected with the difference in the geometric parameters of the ions $a_{I_3^-}$ and a_{I^-} in Eq. (15) depend almost linearly on the ionic strength, especially at high I. It can be calculated from the assumption that the closest approach parameters $a_{I_3^-}$ and a_{I^-} are correlated as 2:1. The slope ($\alpha_{\mathrm{calc.}}$) depends very little upon a_{I^-}, in the range from 1 Å to 6 Å for the solvent. The calculation results for a_{I^-}=4.9 Å are given in Table 5.

The α, K_1 and K_2 values could be calculated by the consistent approximation method on the basis of the equation reflecting the salt effect for the triiodide complex stability constants, from which the contribution (16) connected with iodine solvation and its interaction with the background ions is removed.

$$\log\frac{\gamma_{I_3^-}}{\gamma_{I^-}}=\alpha C_{\mathrm{MA}}+\log\frac{1+K_2[\mathrm{M}^+]}{1+K_1[\mathrm{M}^+]} \qquad (17)$$

These calculation parameter results are listed in Table 5.

An analysis of the salt effect components reveals the presence of compensation of the solvate (b_{I_2}) and the electrostatic (α) contributions, independently of the solvent type. Consequently, on association of the reagents with the background ions absent, the I_3^- stability constants will not be changed with change of the ionic strength.

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