Solution thermodynamics of rare-earth metal ions – physicochemical study–

To cite this article: Sh K Amerkhanova *et al* 2009 *IOP Conf. Ser.: Mater. Sci. Eng.* **1** 012016

Solution thermodynamics of rare-earth metal ions – physicochemical study–

Sh K Amerkhanova, R M Shlyapov and A S Uali

Buketov Karaganda state university, University str., 28, Karaganda, 100028, Kazakhstan

E-mail: amerkhanova_sh@mail.ru

Abstract. The results of the studying of interactions in multicomponent systems “polyvinyl alcohol (PVA) - rare-earth element ion - nitrate of sodium - water” are represented. It is established that for rubidium (I) ions temperature and ionic strength is render destroying action, and for yttrium (III) ions the influence of these factors has return character which is connected with features of an electronic structure of metal ion. It is revealed that a dominating role of non-electrostatic formation composed, hence, the formation of donor-acceptor connection of "metal - ligand” occurs through atom of oxygen.

1. Introduction

The interest which has increased for last years to polymeric complexes of the rare-earth elements used in various areas of a science and engineering causes studying physical and chemical parameters of formation processes of the given complexes, and these compounds possess the valuable physical and chemical functions, in particular investigated systems find application in quality catalytic additives [1]. In article [2] action non-metallocen metalloorganic derivative of rare-earth metals in catalysis of transformations of nonsaturated substrata is considered. At research dialkyl complexes of yttrium, stabilized monoanion tetradentate N-donor ligands (L), in polymerization of ethene [3], deciding influence of ligand nature on catalytic activity of the cation complexes formed in systems $LY(CH_2SiMe_3)_2$-$[PhNMe_2H][B(C_6F_5)_4]$ are established.

Last ten-year appeared very fruitful by way of search the new ligand systems alternative and capable to stabilize high reactive metalloorganic derivatives of rare-earth metals. But, dates on complex compounds of rare-earth elements with high molecular ligands are not found. In this connection, research of physical and chemical bases of complex formation processes of polyvinyl alcohol (PVA) with rare-earth elements is actually.

2. Experimental Procedure

pH-metric measurements carry out on pH-metr pH-410 with help of glass electrode of mark ESK-10601/7. Molecular weigth of polyvinyl alcohol was determined by cryoscopy method [4] and equal to 9188 g/mole. Conductometric and viscosimetric researches carry out in accord [5]. Calculation of base parameters of binding of metal ions carries out with use of complex function according to [6]. As salts of rare-earth elements were take Rb_2CO_3 and $Y(NO_3)_3$, as background electrolyte serve sodium nitrate. Used reagents have qualification «ch.p.», «p.f.a.» and «s.p».

3. Results and Discussions

For optimization of experiment the mathematical planning method [6] was used. Also the mathematical models have been received, allowing carrying out an estimation of sizes of balance constants of complex formation processes in view of influence of each factor (the equations 1 and 2 for systems Y^{3+}- PVA and Rb^{3+} - PVA accordingly).

$$\lg\beta = \frac{(-1\cdot10^{-4}T^3+1.63\cdot10^{-2}\cdot T^2-7.00\cdot10^{-1}\cdot T+18.69)}{1}\times$$
$$\times\frac{(-21.07\cdot I^4+31.24\cdot I^3-5.56\cdot I^2-5.15\cdot I+10.85)}{1}\times$$
$$\times\frac{(1861.80\cdot C_{PVA}^4-2110.40\cdot C_{PVA}^3+811.48\cdot C_{PVA}^2-124.30\cdot C_{PVA}+16.43)}{10.04^2} \quad (1)$$

$$\lg\beta = \frac{(-2\cdot10^{-5}\cdot T^3+3.8\cdot10^{-3}\cdot T^2-2.26\cdot10^{-1}\cdot T+11.78)}{1}\times$$
$$\times\frac{(6.29\cdot I^3-8.07\cdot I^2+1.36\cdot I+8.05)}{1}\times$$
$$\times\frac{(5.46\cdot C_{PVA}^3-1.24\cdot C_{PVA}^2-2.26\cdot10^{-1}\cdot C_{PVA}+8.61)}{10.17} \quad (2)$$

For an estimation of adequacy of values of the response functions received experimentally and the settlement way, factors of plural correlation [6], (table 1) are calculated.

Table 1. Correlation coefficients of the equations for systems M^{n+}– PVA - sodium nitrate – water

M^{n+}	Rb^+		Y^{3+}	
Function	R	t_R	R	t_R
$lg\beta=f(T)$	0.92	21.49	0.99	595.50
$lg\beta=f(C_{HMC})$	0.99	595.50	0.98	145.48
$lg\beta=f(I)$	0.98	115.48	0.99	595.50

From table 1 it is visible, that the specified dependences of stability constants of complexes on each of the resulted factors adequately describe proceeding processes as the calculated correlation coefficients of and dimension of the importance of functions have high enough values. Synthesis optimal parameters of complexes of REE ions with polyvinyl alcohol in aqueous solutions were determined: for Y^{3+} - T=328 K, C_{PVA}= 0.1 %, I = 0.25; for Rb^+ - T=328 K, C_{PVA} = 0.3 %, I = 0.75 and T=298 K, C_{PVA} = 0.1 %, I = 0.10.

Apparently from table 1, dimensions of correlation coefficients have high values; hence, the received equations can be used at interpretation and forecasting of a degree of linkage metal ions by high-molecular ligand. Paying attention to high parameters of the importance of functions, we shall note, that the mathematical models are significant which confirm an opportunity of their application in synthesis of polymer-metal complexes (PMC). Further stability constants of rubidium complexes (fig. 1) have been determined.

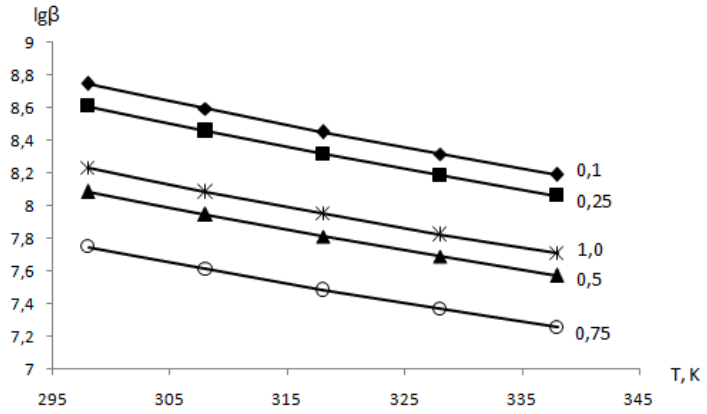

Figure 1. Temperature dependence of stability constants of complexes Rb^+ ions with PVA at influence ionic strength

It is shown, that the mechanism of this process will consist in the following: at rise in temperature there is a destruction of hydrogen connections between molecules of water, there is a hydration amplification of metal ion, and as corollary is reduction of stability constants. At increase of ionic strength up to 0.75 decreases in stability of polymer-metal complexes (PMC) it is caused by competing influence of a nitrate - ion [7]. However, the increase in stability constants in an interval of ionic strength from 0.75 up to 1.0 is connected with dehydrated action of background electrolyte be relative hydrated rubidium ions. Therefore thermodynamic parameters (table 2) have been calculated.

The data about enthalpy allow to judge, course of processes of association between metal ion and macromolecules, it is accompanied by additional expenses of energy. On the other hand The rubidium ion is softer acid in comparison with an yttrium ion according to positions of HSAB (hard and soft acids and bases) Pyrson theory which mainly reacts with the soft base - PVA. It is shown, that at interaction with ligand is observed insignificant decrease of entropy for the account complex formation. Whereas this interaction results in removal of H_2O molecules from hydrated environments of rubidium – entropy values reveal this.

Table 2. Thermodynamic parameters of complex formation processes in system Rb^+ – PVA - sodium nitrate – water, C (PVC)=0.3%

I	298 K	308 K	318 K	328 K	338 K
$\Delta_r H_T^o$, kJ/mole					
0.1	26.84	26.84	26.83	26.83	26.83
0.5	24.81	24.81	24.81	24.81	24.81
1	25.25	25.25	25.25	25.25	25.25
$-\Delta_r G_T^o$, kJ/mole					
0.1	49.91	50.68	51.46	52.23	53.01
0.5	46.14	46.86	47.57	48.29	49.01
1	46.96	47.69	48.42	49.15	49.87
$\Delta_r S_T^o$, J/(mole·K)					
0.1	77.43	77.43	77.43	77.43	77.43
0.5	71.59	71.59	71.59	71.59	71.59
1	72.86	72.86	72.86	72.86	72.86

Decrease endothermic effect with increase of ionic strength up to 0.75 is connected to processes of a competition between nitrate ions and polyligand. Decrease of entropy in an interval from 0.1 up to 0.75 is caused by processes of shielding of PVA circuit [7]. Further complex formation processes yttrium (III) ion with PVA in aqueous solution of nitrate-ions (fig. 2) have been studied.

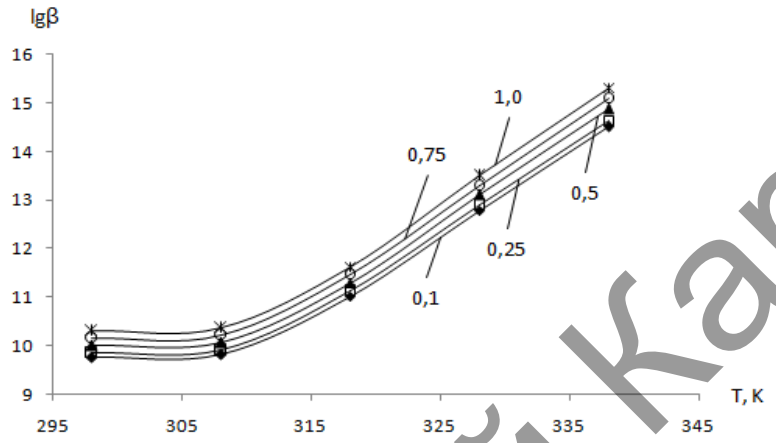

Figure 2. Stability constants of complex compounds, formating in system Y^{3+} – PVA - sodium nitrate – water, C (PVC)=0.2%

The increase in stability constants with temperature indicate dehydrated influence of last due to that the probability of co-ordination of yttrium ions with PVA grows. Similar influence is rendered with ionic strength of a solution which consists in change of structure of the water connected to of metal and ligand ions. Hence, there is a necessity of calculation of thermodynamic functions of the investigated processes (table 3).

Table 3. Thermodynamic parameters of complex formation processes in system Y^{3+} – PVA - sodium nitrate – water , C (PVC)=0.2%

I	298 K	308 K	318 K	328 K	318 K
$\Delta_r H_T^\circ$, kJ/mole					
0.1	-67.54	87.10	241.74	396.39	551.03
0.5	-69.21	247.71	406.17	406.17	564.63
1	-71.29	255.16	418.39	418.39	581.62
$-\Delta_r G_T^\circ$, kJ/mole					
0.1	55.73	57.90	67.12	80.31	93.92
0.5	57.11	59.33	68.78	82.29	96.24
1	58.82	61.11	70.85	84.77	99.13
$\Delta_r S_T^\circ$, J/(mole·K)					
0.1	-39.64	470.78	971.28	1453.35	1908.13
0.5	-40.62	996.87	1493.54	1489.21	1955.21
1	-41.84	1026.87	1538.49	1534.03	2014.06

At low temperatures interaction between metal ion and ligand at which more compact complexes [8] are formed is determining. Increase of temperature on 10°C results in the sharp changes caused by removal of water molecules, as from hydrated environments of metal ion and a grid of polymer, and stabilization of a complex yttrium due to formation of hydrogen connections

with ligands. The given effects amplify with rise in temperature that speaks about prevalence the entropy contribution to stability of system. Dependence enthalpy and entropy from ionic strength has linear character. At low temperature action of background electrolyte is limited to processes of replacement of water in external hydrated environment of metal ion [9]. Whereas at 308 K the boomerang effect owing to more flared-out condition of macromolecular circuits takes place, nitrate-ion coordinates water molecules segregated owing to thermal interaction. Thus presence of nitrate of sodium serves as the stabilizing factor.

For approval of the specified effects temperature-dependent and temperature-independent parameters of processes of linkage of metals ion, according to the approach based on Herny representations [10] (table IV) have been calculated.

Table 4. Change of $-\Delta_r G_e^o$, $-\Delta_r G_{ne}^o$, $-\Delta_r H_{ne}^o$ controbutions in Gibbs energy в complex formatiom processes at 298 K

I	Rb^+ - PVA		Y^{3+} - PVA	
	$-\Delta_r G_e^0$ kJ/mole	$-\Delta_r G_{ne}^o = -\Delta_r H_{ne}^o$, kJ/mole	$-\Delta_r G_e^o$ kJ/mole	$-\Delta_r G_{ne}^o = -\Delta_r H_{ne}^o$, kJ/mole
0.1	18.80	41.07	-3.44	89.03
0.25	18.53	40.55	-3.52	89.62
0.5	17.51	38.59	-3.66	90.62
0.75	16.85	37.31	-3.79	91.61
1	17.79	39.12	-3.93	92.60

Influence of electrostatic characteristics of Rb^+ ions is shown in case of formation of complexes with PVA. The temperature-dependent contribution of standard Gibbs energy increases at formation of these complexes. The power of processes in the greater degree is determined by non-electrostatic contribution, i.e. covalent character of linkage with atom of oxygen grows. And, growth of concentration of background electrolyte weakens both contributions that are connected to decrease of a positive charge value of metal ion. Comparison of changes of standard Gibbs energy at formation of yttrium complexes (III) shows, that the temperature-independent contribution has the maximal positive values whereas the electrostatic contribution has high negative values that speaks about a prevailing role of donor-acceptor interactions in formed compounds with oxygen atom. Increase $-\Delta_r G_{ne}^o$, $-\Delta_r H_{ne}^o$ and reduction $-\Delta_r G_e^o$, with ionic strength indicates, introduction of additional pair electrons of nitrate-ion on free d-orbital an yttrium (III) ion, which stabilizes cation and reduces a positive charge on metal ion.

4. Conclusion

- The mathematical models describing process of interaction of rare-earth elements ions with PVA have been received;
- The estimation of applicability of the equations is carried out. Stability constants of complexes are determined;
- The contribution of electrostatic and non-electrostatic interactions of Gibbs energy of systems is established;
- The received results can be used by development highly effective catalytic systems on the basis of rubidium which are applied in thin organic synthesis.

References

[1] Pomogailo A V, Kestelman N 2005 *Metallopolymer nanocomposites* (Springer, Heidelberg) p 563

[2] Trifonov A.A. 2007 *Russian Journal "Uspekhi chimii",* **11-76** 1122

[3] Bambirra S, Van Leusen D, Meetsma A, Hessen B, Teuben, J H, 2001 *Chem. Commun.*, 637

[4] *Practical work on physics and chemistry of polymers*, 1990 ed. V F Kurenkov. Chemistry, Moscow, p 300

[5] Karetnikov G S, Kozyreva N A, Kydryashov I V, 1986 *Practical work on physical chemistry*, (High school, Moscow) p 495

[6] Malyshev V P, 1981 *The random-determined planning of experiment*, (Science, Almaty) p 16

[7] Bekturov E A, 2007 *Polymer electrolytes, hydro gels, complexes and catalytic agents*, (Almaty) p 242

[8] Ospanov Kh K, 2004 *Physical and chemical foundations for selective dissolution of minerals* (Flint River, London) p 175

[9] Bakeev M I, 2007 *Theory of hydration and properties of electrolyte solutions*, (Publ. house of KarSU, Karaganda) p 221

[10] Vasil'ev V P, Volkov A V, Gorboletova G G, Kochergina A A, 2001 *Russian Journal of Physical Chemistry* **4-75** 590