J Incl Phenom Macrocycl Chem (2012) 73:87–92
DOI 10.1007/s10847-011-0023-6

ORIGINAL ARTICLE

Study of complex formation between dicyclohexyl-18-crown-6 and UO_2^{2+} cation in some binary mixed non-aqueous solvents using conductometric method

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Received: 14 November 2010 / Accepted: 19 July 2011 / Published online: 18 August 2011

Abstract In the present work, the complexation process between UO_2^{2+} cation and the macrocyclic ligand, dicyclohexyl-18-crown-6 (DCH18C6) was studied in ethyl acetate/1,2-dichloroethane (EtOAc/DCE), acetonitrile/1,2-dichloroethane (AN/DCE), methanol/1,2-dichloroethane (MeOH/DCE) and ethanol/1,2-dichloroethane (EtOH/DCE) binary solutions at different temperatures using the conductometric method. The conductance data show that in most cases, the stoichiometry of the complex formed between DCH18C6 and UO_2^{2+} cation is 1:1 [M:L], but in some solvent systems also a 1:2 [M:L_2] complex is formed in solutions. The values of stability constant of $(DCH18C6 \cdot UO_2)^{2+}$ complex which were obtained from conductometric data, show that the stability of the complex is affected by the nature and also the composition of the solvent system and in all cases, a non-linear behavior is observed for the variation of (log K_f) of the $(DCH18C6 \cdot UO_2)^{2+}$ complex versus the composition of the binary mixed solvents. The values of thermodynamic quantities ΔH_c° and ΔS_c° for formation of $(DCH18C6 \cdot UO_2)^{2+}$ complex were obtained from temperature dependence of the stability constant using the van't Hoff plots. The experimental results show that depending on the nature and composition of the solvent systems, the complex is enthalpy stabilized or destabilized, but in most cases, it is stabilized from entropy view point and both thermodynamic parameters are affected by the nature and composition of the binary mixed solutions.

Keywords UO_2^{2+} cation · Dicyclohexyl-18-crown-6 · Acetonitrile · Ethyl acetate · Methanol · Ethanol · 1,2-Dichloroethane · Conductometry

Introduction

First group of macrocyclic compounds are crown ethers, which contain oxygen, sulfur and nitrogen as donor atoms. The first crown ether was synthesized in 1967 by Pedersen, who obtained dibenzo-18-crown-6, which has gained attention for its ability to form stable complexes with metal ions within its central cavity [1]. The stability and selectivity of crown ether complexes with metal cations are dependent on several molecular factors such as the cavity size of the ligand, the number and type of the ether donor atoms, the spatial distribution of ring binding sites, the charge density and polarizability of the cation and the cation diameter [2–5]. The solvent also plays a critical role in local structure optimization and complex stabilization [6]. Stability constants (K_f) of such macrocyclic complexes can vary over many order of magnitudes with the nature of the medium. Studies of crown ethers complexation in different solvents, show that the nature and composition of the solvent system, strongly influence the stoichiometry, selectivity, thermodynamic stability and exchange kinetics of metal ion–crown ether complexes [7, 8].

Although studies of crown ethers complexation with metal cations have been carried out in both aqueous and non-aqueous media, but most of the data have been published on equilibrium constants and thermodynamic functions of complex formation of these macrocyclic ligands

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with alkaline and alkaline earth metal cations and small organic molecules in pure organic solvents and also in some of their binary mixtures [9–13]. The small number of such data concerning the complex formation between the crown ethers with heavy metal cations, specially with rare earth elements in mixed non-aqueous solvents is the reason for undertaking the studies on the influence of solvent properties on the mechanism and thermodynamics of complexation reactions of these macrocyclic ligands with such metal cations.

Recent increase in nuclear power production, predominantly based on the uranium-based fuel, has led to the possibility of the release of ultra-trace amounts of uranium in natural aquifers. UO_2^{2+} is known to be nephrotoxic as a heavy metal ion and radiologically harmful as a radionuclide. Although radiological impact is determined by the total concentration of a particular uranium isotope, its chemical toxicity is dependent on the chemical form of its species that interacts with bio-molecules. The ability of uranium to form complex has been utilized for cleaning up uranium contamination in soil and in the nuclear industry where chelating agents are common constituents of fluids used to clean the reactor [14]. The interaction between uranyl cation and some of the macrocyclic ligands have been studied in few pure and binary mixed aqueous–nonaqueous and nonaqueous–nonaqueous solvents solutions [15–18].

In the present paper, we report the results which are obtained from conductometric study of the complexation reaction of UO_2^{2+} cation and the macrocyclic ligand, dicyclohexyl-18-crown-6 (DCH18C6) (Scheme 1) in ethylacetate/1,2-dichloroethane (EtOAc/DCE), acetonitrile/1,2-dichloroethane (AN/DCE), and methanol/1,2-dichloroethane (MeOH/DCE) and ethanol/1,2-dichloroethane (EtOH/DCE) binary solutions at different temperatures.

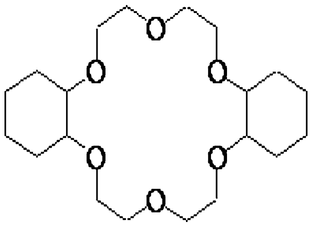
Experimental

Reagents and solvents

Dicyclohexyl-18-crown-6 (Fluka) and $UO_2(NO_3)_2 \cdot 6H_2O$ (Riedel company) were used without further purification. The solvents: ethyl acetate (Riedel) and ethanol, acetonitrile, methanol and 1,2-dichloroethane all from Merck company were used with the highest purity.

Method and apparatus

The experimental procedure for study of the complexation process is as follows: a solution of metal salt (1.0×10^{-4} M) was placed in a titration cell, thermostated at a given temperature, and the conductance of the solution was measured. Then a step-by-step increase of the crown ether solution prepared in the same solvent (2.0×10^{-3} M) was carried out by a rapid transfer to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature. The conductance measurements were performed using a digital AMEL conductivity apparatus, model 60, in a water bath thermostated at a constant temperature which maintained within ±0.03 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The cell constant was 0.73 cm^{-1}.



Scheme 1 Structure of dicyclohexyl-18-crown-6 (DCH18C6)

Theory

According to the mole ratio plots, in most cases metal–ligand complexes have a 1:1 stoichiometry, so the 1:1 binding of the metal ions with the ligands, can be expressed by the following equilibrium:

$$M^{n+} + L \leftrightarrow ML^{n+} \tag{1}$$

The corresponding equilibrium constant, K_f, is given by:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{ML^{n+}}}{f_{M^{n+}} f_L} \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, [L] and f, represent the equilibrium molar concentrations of the complex, free cation, free ligand and the activity coefficient of the species indicated, respectively [19]. Under the highly dilute experimental conditions which we used in this study, the activity coefficient of the uncharged ligand, f_L, can be reasonably assumed as unity [20]. The use of Debye–Huckel limiting law leads to the conclusion that, $f_{M^{n+}} \sim f_{ML^{n+}}$, therefore, the activity coefficients in Eq. 2 could be canceled.

The mass balance equation of ML^{n+} type complex (Eqs. 3 and 4 used in computer program GENPLOT) should be solved in order to obtain Eq. 5 for the free ligand concentration [L].

$$C_{M^{n+}} = [M^{n+}] + [ML^{n+}] \tag{3}$$

$$C_L = [L] + [ML^{n+}] \tag{4}$$

Substitution of Eqs. 3 and 4 into Eq. 2 and rearrangement yields:

$$K_f[L]^2 + (1 + K_f(C_{M^{n+}} - C_L))[L] - C_L = 0 \tag{5}$$

The complex formation constant in terms of the molar conductance can be expressed as:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_{M^{n+}} - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{6}$$

where

$$[L] = C_L - \frac{C_{M^{n+}}(\Lambda_{M^{n+}} - \Lambda_{obs})}{(\Lambda_{M^{n+}} - \Lambda_{ML^{n+}})} \tag{7}$$

Here, $\Lambda_{ML}{}^{n+}$ is the molar conductance of the metal nitrate before addition of the ligand, Λ_{obs} is the molar conductance of the solution during titration and $\Lambda_{ML}{}^{n+}$ is the molar conductance of the complexed ion. C_L is the analytical concentration of the ligand added and $C_M{}^{n+}$ is the analytical concentration of the metal nitrate.

The stability constant of $(DCH18C6{\cdot}UO_2)^{2+}$ complex at each temperature was obtained from computer fitting of Eqs. 6 and 7 to the molar conductance–mole ratio data using a non-linear least squares program, GENPLOT [21].

Results

The changes of molar conductivity (Λ_m) versus the ligand to the cation molar ratio, ($[DCH18C6]/[UO_2{}^{2+}]$), for complexation of DCH18C6 with $UO_2{}^{2+}$ cation were measured in pure MeOH, EtOH, AN, EtOAc and also in DCE-AN, DCE-MeOH, DCE-EtOAc and DCE–EtOH binary systems at different temperatures. Two typical series of molar conductance values as a function of $[L]_t/[M]_t$ in EtOAc/DCE (mol%DCE = 25), and in AN/DCE (mol%DCE = 25), binary solutions are shown in Figs. 1 and 2, respectively. The values of stability constant (log K_f) for $(DCH18C6{\cdot}UO_2)^{2+}$ complex in various solvent systems are listed in Table 1. Assuming that the activity coefficients of the cation and the complex have the same value, K_f is a thermodynamic equilibrium constant on the molar concentration scale, related to the Gibbs standard free energy of complexation reaction, (ΔG_c°). The van't Hoff plots of ln K_f versus 1/T for all of the investigated systems were constructed. A typical example of these plots is shown in Fig. 3. The changes in standard enthalpy (ΔH_c°) for complexation reactions were obtained from the slope of the van't Hoff plots assuming that (ΔC_P) is equal to zero over the entire temperature range investigated. The changes in standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c,298.15}^\circ = \Delta H_c^\circ - 298.15\Delta S_c^\circ$. The results are summarized in Table 2. The changes of log K_f of $(DCH18C6{\cdot}UO_2)^{2+}$ complex versus the mole fraction of EtOH in DCE–EtOH binary system at different temperatures are shown in Fig. 4.

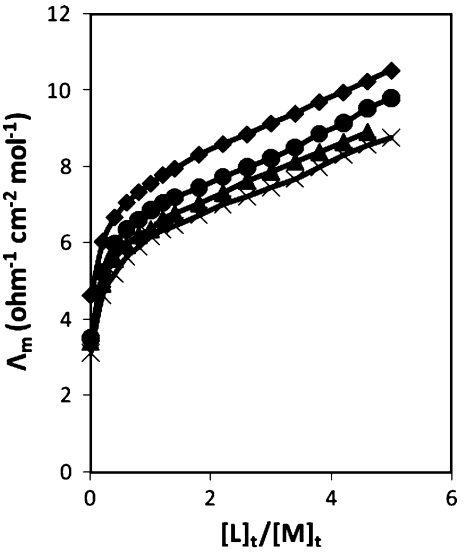


Fig. 1 Molar conductance–mole ratio plots for $(DCH18C6{\cdot}UO_2)^{2+}$ complex in [EtOAc/DCE (mol%DCE = 25)] binary system at different temperatures: *filled diamond* 15 °C, *filled circle* 25 °C, *filled triangle* 35 °C, *cross* 45 °C

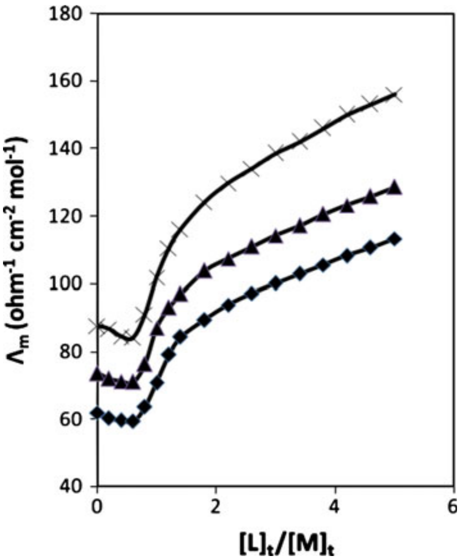


Fig. 2 Molar conductance–mole ratio plots for $(DCH18C6{\cdot}UO_2)^{2+}$ complex in [AN/DCE (mol%DCE = 25)] binary system at different temperatures: *filled diamond* 15 °C, *filled triangle* 35 °C, *cross* 45 °C)

Discussion

As is seen from Fig. 1, addition of (DCH18C6) to a solution of uranyl cation in EtOAc/DCE (mol%DCE = 25) binary mixture at different temperatures shows a gradual increase in molar conductivity with an increase in the ligand concentration. This behaviour indicates that the $(DCH18C6{\cdot}UO_2)^{2+}$ complex is more mobile than free solvated $UO_2{}^{2+}$ cation. Similar behaviour was observed in

Table 1 Log K_f values of $(DCH18C6{\cdot}UO_2)^{+2}$ complex in various solvent systems

Medium (mol%DCE)	Log K_f ± (SD)			
	15 °C	25 °C	35 °C	45 °C
DCE-AN[a]				
75	3.87 ± 0.10	3.59 ± 0.10	3.60 ± 0.10	3.54 ± 0.10
50	–	–	–	–
25	–	–	–	–
0	4.60 ± 0.10	4.43 ± 0.10	4.44 ± 0.20	4.42 ± 0.20
DCE-MeOH[a]				
75	3.02 ± 0.05	3.02 ± 0.04	3.16 ± 0.05	3.24 ± 0.03
50	3.26 ± 0.03	3.28 ± 0.04	3.24 ± 0.09	3.24 ± 0.10
25	3.30 ± 0.05	3.11 ± 0.06	3.24 ± 0.05	2.78 ± 0.03
0	2.98 ± 0.08	2.24 ± 0.05	3.32 ± 0.04	3.17 ± 0.06
DCE-EtOH[a]				
75	2.72 ± 0.20	2.82 ± 0.09	2.93 ± 0.20	3.24 ± 0.1
50	2.79 ± 0.09	2.70 ± 0.10	2.72 ± 0.10	2.79 ± 0.10
25	3.15 ± 0.10	3.22 ± 0.10	3.28 ± 0.10	3.25 ± 0.10
0	2.69 ± 0.08	2.59 ± 0.17	2.71 ± 0.14	2.87 ± 0.09
DCE-EtOAc[a]				
75	3.70 ± 0.05	3.60 ± 0.05	3.54 ± 0.06	3.54 ± 0.05
50	3.73 ± 0.10	3.62 ± 0.10	3.63 ± 0.10	3.68 ± 0.10
25	3.85 ± 0.10	3.92 ± 0.20	3.91 ± 0.20	3.95 ± 0.20
0	3.81 ± 0.09	3.96 ± 0.10	3.63 ± 0.07	3.98 ± 0.08

SD standard deviation

–, The data cannot be fitted in equation

[a] The composition of solvent systems is expressed in mol % of each solvent

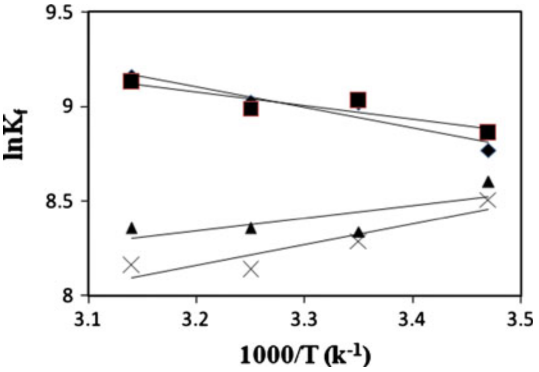


Fig. 3 Van't Hoff for $(DCH18C6{\cdot}UO_2)^{2+}$ complex in EtOAc/DCE binary system (*filled diamond* mol% EtOAc = 100, *filled square* mol% EtOAc = 75, *filled triangle* mol% EtOAc = 50, *cross* mol% EtOAc = 25)

some of the other solvent systems. The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes at the point where the ligand to cation mole ratio is about one, which is an evidence for formation of a 1:1 [M:L] complex in solution. It is obvious from this figure that as the temperature increases, the curvature of the molar conductivity plots of $(DCH18C6{\cdot}UO_2)^{2+}$ complex decreases, which is an evidence for formation of a weaker complex at high temperatures. Therefore, the complexation process between DB18C6 and uranyl cation is exothermic in this binary solution.

A different behaviour was observed for complexation of UO_2^{2+} cation with DCH18C6 in AN/DCE (mol%DCE = 25) binary system. As is clear from Fig. 2, a V-shaped curve was obtained for the molar conductance–mole ratio plots at different temperatures in this binary solvent solution. Addition of (DCH18C6) to UO_2^{2+} cation in this binary solution at different temperatures, causes the molar conductivity to initially decreases until the mole ratio reaches to about [1:1], and then increases. Such behaviour may be explained according to following equilibria:

$$(UO_2^{2+}, 2NO_3^-) + DCH18C6 \rightarrow (DCH18C6 \cdot UO_2^{2+}, 2NO_3^-) \qquad \text{(I)}$$

$$(DCH18C6 \cdot UO_2^{2+}, 2NO_3^-) + DCH18C6 \rightarrow [(DCH18C6)_2 UO_2^{2+}] + 2NO_3^- \qquad \text{(II)}$$

Similar behaviour was also observed for complexation of UO_2^{2+} cation with the ligand in another AN/DCE (mol%DCE = 50) binary system. It seems that addition of the ligand to uranyl cation solution, results in formation of a relatively stable [1:1] complex which is present as an ion-pair (I), then addition of the second ligand to the ion-pair complex, causes formation of a stable [1:2] complex with a sandwich structure $[(DCH18C6)_2UO_2^{2+}]$, which decreases the space for diffusion and interaction of NO_3^- anion with UO_2^{2+} cation, which results in dissociation of the ion pair (II), and hence, the conductivity increases. As is evident from these results, the stoichiometry and the mechanism of

Table 2 Thermodynamic parameters for $(DCH18C6{\cdot}UO_2)^{+2}$ complex in various solvents systems

Medium (mol%DCE)	$\Delta G_c^\circ \pm SD$ (KJ mol^{-1})	$\Delta H_c^\circ \pm SD$ (KJ mol^{-1})	$\Delta S_c^\circ \pm SD$ (J mol^{-1} K^{-1})
DCE-AN[a]			
75	−23.67 ± 2.56	−16.36 ± 3.82	–
0	−25.28 ± 1.09	−9.66 ± 4.63	53.65 ± 15.31
DCE-MeOH[a]			
75	−17.25 ± 0.09	20.11 ± 3.07	125.42 ± 9.96
50	−18.72 ± 0.06	−3.92 ± 1.48	49.55 ± 4.80
25	−17.77 ± 0.11	−28.83 ± 8.60	–
0	−18.50 ± 0.07	30.24 ± 7.36	–
DCE-EtOH[a]			
75	−16.11 ± 0.01	40.69 ± 11.22	–
50	−15.54 ± 0.02	–	–
25	−18.39 ± 0.15	5.18 ± 2.27	78.63 ± 7.54
0	−14.77 ± 1.77	25.76 ± 1.35	135.80 ± 4.38
DCE-EtOAc[a]			
75	−20.55 ± 0.03	−9.13 ± 2.93	–
50	−20.68 ± 0.06	–	–
25	−22.39 ± 0.06	6.48 ± 2.01	94.52 ± 6.63
0	−22.61 ± 0.02	9.82 ± 3.05	107.01 ± 7.76

SD Standard deviation

–, With high uncertainty

[a] The composition of solvent systems is expressed in mol % of each solvent

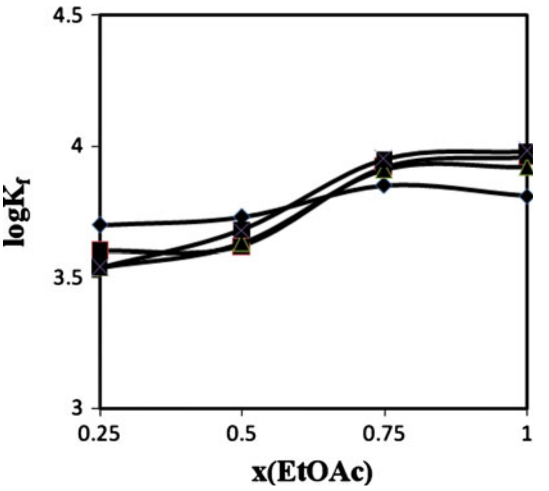


Fig. 4 Change of the stability constant (log K_f) of $(DCH18C6{\cdot}UO_2)^{2+}$ complex with the composition of the EtOAc/DCE binary mixture at different temperature: *filled diamond* 15 °C, *filled square* 25 °C, *filled triangle* 35 °C, *cross* 45 °C)

the complexation processes between the metal cations and macrocyclic ligands may change with the composition of the binary mixed solvent solutions.

The values of the stability constant (log K_f) for $(DCH18C6{\cdot}UO_2)^{2+}$ complex in pure and in mixed solvents are listed in Table 1. As is obvious from this Table, the stability constant of $(DCH18C6{\cdot}UO_2)^{2+}$ complex in various pure solvents at 25 °C decreases in order: AN > EtOAc > MeOH > EtOH, and in the case of binary solvents at 25 °C is: DCE-AN ≅ DCE-EtOAc > DCE-MeOH > DCE-EtOH.

The standard thermodynamic parameters (ΔH_c°) and (ΔS_c°) for complex formation between the macrocyclic ligand and uranyl cation are given in Table 2. The experimental results in this Table, show that depending on the nature and composition of the solvent systems, the $(DCH18C6{\cdot}UO_2)^{2+}$ complex is enthalpy stabilized or destabilized, but in most cases it is stabilized from entropy view point and both thermodynamic parameters are affected by the nature and composition of the binary mixed solvents. Since the values of standard entropy (ΔS_c°) and standard enthalpy (ΔH_c°) for formation of $(DCH18C6{\cdot}UO_2)^{2+}$ complex in solution, vary with different parameters such as changes in the flexibility of the macrocyclic ligand during the complexation process, and also with the extent of cation–solvent, ligand–solvent and complex–solvent interactions and even with the solvent–solvent interactions, therefore, as is evident in Table 2, these thermodynamic quantities change non-monotonically with the nature and composition of the used solvent systems. As is obvious from Fig. 4, the change in the stability constant (log K_f) of $(DCH18C6{\cdot}UO_2)^{2+}$ complex versus

Table 3 Log K_f values for complexes of UO_2^{2+} cation with DB18C6, 18C6 and DCH18C6 at 25 °C in AN

AN	DB18C6	18C6	DCH18C6
UO_2^{2+}	3.26[a]	4.03[b]	4.43[c]

[a] Ref. [15], [b] Ref. [22], [c] this work

the composition of EtOAc/DCE binary solvent solution at various temperatures is not linear. Somewhat similar behaviour was observed in other binary solutions. This behaviour may be due to solvent–solvent interactions and also to the preferential solvation of the cation and the macrocyclic ligand in the mixed solvent systems.

The results obtained from studying of complexation reactions of 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) and dicyclohexyl 18-crown-6 (DCH18C6) with uranyl cation in acetonitrile solutions at 25 °C are given in Table 3. As is obvious from these data, the benzo groups in DB18C6, decrease the binding strength of this ligand to uranyl cation. This is attributable to the fact that DB18C6 has two aromatic ether oxygen atoms whose basicity is lower than those of the aliphatic ether oxygen atoms. Since the sp^2 hybridized oxygen atoms are less basic than the sp^3 hybridized oxygen atoms in the parent and the sp^2-hybridized electron pairs are perpendicular to the aromatic ring [23], therefore, the two aromatic ether oxygen atoms have lower basicity than those of the aliphatic ether oxygen atoms. Thus the $(DB18C6 \cdot UO_2)^{2+}$ complex is less stable than $(18C6 \cdot UO_2)^{2+}$ in pure acetonitrile solutions.

Acknowledgment The authors gratefully acknowledge the support of this research by Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran.

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