

# DOUBLE SYNERGISTIC EFFECTS AND EXTRACTION KINETICS OF A MICELLE MIXED EXTRACTANT SYSTEM<sup>①</sup>

## II EXTRACTION KINETICS

Yu, Jingfen

*Department of Chemical Engineering, Qinghua University, Beijing 100084, China*

### ABSTRACT

The controlling reaction for the micelle mixed extractant system  $D_2EHPA-MPA-Al^{3+}$  was proved to occur inside the micelle phase by the studies of extraction kinetics, extraction equilibria and interfacial chemistry. The extraction reaction mechanisms of the two components, i. e. the micelle mixed extractant system  $D_2EHPA-MPA-Al^{3+}$  and the single micelle extraction system  $MPA-Al^{3+}$ , in the micelle phase and liquid-liquid interfacial reaction regions, were suggested. The extraction reaction rate equations were obtained and the acceleration mechanism and characteristics for the micelle mixed extractant system were discussed.

**Key words:** extraction kinetics extraction equilibria controlling reaction extraction reaction mechanisms micelle mixed extractant system

## 1 INTRODUCTION

Part I of this paper reported the double synergistic effects of the micelle mixed extractant system  $D_2EHPA-MPA$  for the extraction of  $Al^{3+}$  ions, the thermodynamics of the synergistic extraction reactions, determined the synergistic complex compositions and studied the equilibrium mechanisms. Part II will report the results of the reaction kinetics study.

## 2 EXPERIMENTAL METHODS

The chemical reagents, extractants, apparatus, the analysis of  $Al^{3+}$ , the research method for extraction kinetics and data treatment process used in this paper are identical to those in refs. [1—3]. The experimental

conditions were chosen according to the study of interfacial chemistry of various extraction system.

## 3 RESULTS AND DISCUSSION

It was reported in ref. [1] that there exists non-micelle and micelle ranges in mixed extraction system  $D_2EHPA-MPA-Al^{3+}$ . These two ranges have different characteristics in interfacial chemistry, extraction kinetics, extraction equilibria and their mechanism. This part will mainly report the kinetics in the micelle range.

### 3.1 Reaction Rate Equation

The relationship between the reaction rate constant and the stirring speed (r/min)

① Supported by National Natural Science Foundation of China; manuscript received Aug. 29, 1992

in Fig. 1 shows that, at the initial stage, because the diffusion controlling factor is dominant, the first order apparent forward reaction rate constant ( $k_f$ ) increases with increasing stirring speed. When the stirring speed reaches 1 400 r/min, the chemical reaction rate changes very little with increasing stirring speed. Therefore, the following kinetic experiments are conducted under an stirring speed of 1 400 r/min.

With other conditions unchanged, the influences of  $[MPA]$ ,  $[D_2EHPA]$  and pH values on the extraction reaction rate of  $Al^{3+}$  ions are shown in Table 1.

Through linear regression treatment of the data in Table 1, six straight lines can be obtained, i. e.  $\ln k_f(k_r) \sim \ln [MPA]$ ,  $\ln k_f(k_r) \sim \ln [D_2EHPA]$ ,  $\ln k_f(k_r) \sim \ln [H^+]$ . The slopes of these six lines correspond to the indexes of the  $[MPA]$ ,  $[D_2EHPA]$  and  $[H^+]$  in the extraction reaction rate equation. Therefore, the extraction reaction rate for the micelle mixed extraction system  $D_2EHPA$ - $MPA$ - $Al^{3+}$  is as follows:

$$-\frac{dc}{dt} = k'_f [MPA]^{0.5} [D_2EHPA]^{0.15} \times [H^+]^{-1.0} - k'_r [MPA]^{-1.28} \times [D_2EHPA]^{-1.0} [H^+]^{1.7} \quad (1)$$

where  $k'_f$  and  $k'_r$  represent the forward and reverse reaction constants of the extraction system respectively.

Seen from Table 1 and equation (1), the forward and reverse rates respectively increase and decrease with increasing  $[MPA]$  and  $[D_2EHPA]$ . With decreasing pH values, the forward reaction rate decreases and the reverse reaction rate increases, so the total reaction rate decreases. This is consistent with the formation law of the micelle<sup>[1]</sup>, i. e. decreasing pH values and increasing  $[MPA]$  will help the formation of the MPA micelle, and then lead to increas-

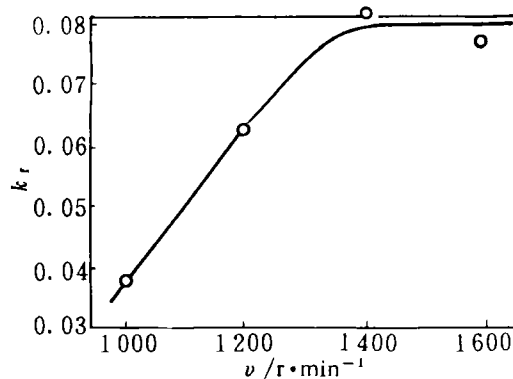


Fig. 1 Dependence of  $k_f$  on stirring speed  $v$  ( $r \cdot \min^{-1}$ )

$[MPA] = 0.15 \text{ mol/L}$ ;  $[Al^{3+}] = 0.17 \text{ g/L}$ ;  
 $[D_2EHPA] = 0.05 \text{ mol/L}$ ;  $pH = 0.77$

Table 1 Influences of  $[MPA]$ ,  $[D_2EHPA]$  and pH values on extraction reaction rate of  $Al^{3+}$  ions (micelle mixed extraction system)

pH	$[D_2EHPA]$ /mol·L <sup>-1</sup>	$[MPA]$ / mol·L <sup>-1</sup>	$k_f$ /min <sup>-1</sup>	$k_r$ /min <sup>-1</sup>
1.0	0.05	0.070	0.046	$3.51 \times 10^{-3}$
1.0	0.05	0.105	0.064	$1.41 \times 10^{-3}$
1.0	0.05	0.140	0.076	$1.03 \times 10^{-3}$
1.0	0.05	0.210	0.098	$4.89 \times 10^{-4}$
1.0	0.075	0.140	0.078	$6.4 \times 10^{-4}$
1.0	0.100	0.140	0.084	$5.1 \times 10^{-4}$
1.2	0.05	0.140	0.115	$5.1 \times 10^{-4}$
1.4	0.05	0.140	0.184	$2.1 \times 10^{-4}$

\* experimental conditions:  $[Al^{3+}] = 0.39 \text{ g/L}$ ,  $T = 25^\circ \text{C}$ .

$k_f$ ,  $k_r$  represent the first order apparent forward and reverse reaction constants respectively.

ing extraction reaction rate of  $Al^{3+}$  ions. Meanwhile, the  $^{31}\text{P}$  NMR spectra study demonstrates that the extraction of  $Al^{3+}$  using the mixed micelle system obeys the cation exchange extraction law. It is obvious that increasing pH values will lead to increasing reaction rate. The formation of synergistic complex is not only connected with

[MPA], but also with [D<sub>2</sub>EHPA]. The authors believe that the effect of D<sub>2</sub>EHPA on the reaction rate of Al<sup>3+</sup> extraction is mainly embodied through the interfacial aggregating effect of the MPA micelle, i.e. that the D<sub>2</sub>EHPA dissolves into the interiors of MPA micelle or enriches their interfaces, so that the concentration of the D<sub>2</sub>EHPA is higher than that in the bulk organic phase. Because of the controlling reaction occurring inside the micelle and the synergistic effect, the extraction reaction rate of the Al<sup>3+</sup> ions is accelerated. The above studies from an indirect side express that the controlling reaction of the Al<sup>3+</sup> extraction in the micelle mixed extraction system occurs inside the micelle phase. At the same time, the formation of the micelle and the micelle interfacial aggregating effect at their interfaces can also further expound the reaction rate equation of the studied extraction system.

### 3.2 Reaction Mechanism

Because opinions between the concerned researchers vary on why synergistic extractants can accelerate the extraction of metals<sup>[4]</sup>, it is very complex to study extraction process, especially the reaction mechanism of mixed extraction systems. The studied new type micelle mixed extraction system is even more complex. It is not only of thermodynamic synergistic effects, but can accelerate the extraction rate of metallic ions and has micelle component etc. From the studies of extraction interfacial chemistry, extraction kinetics, equilibrium characteristics and their mechanisms, we discuss the extraction reaction mechanisms as follows.

#### 3.2.1 The Reaction Sites of the Extraction Rate Controlling Step

The authors have proved<sup>[5]</sup> that the reaction rate of the Al<sup>3+</sup> extraction in the stud-

ied mixed system is controlled by diffusion in combination with chemical reaction. There probably exists three types of regions act as the sites of chemical reactions—the interiors of the organic phase, or the micelle phase, the interfaces and the interiors of the aqueous phase. Based on the following analyses, the authors believe that the rate controlling reaction of Al<sup>3+</sup> extraction in the studied mixed system occurs in essential inside the micelle phase.

(1) The dissolvability of the D<sub>2</sub>EHPA and MPA in aqueous phases are very small, but the MPA can dissolve well in nonpolar solvents, forms reversal micelle, and forms oil-affinitive synergistic complex in combination with the D<sub>2</sub>EHPA-Al<sup>3+</sup>. Although the [H<sup>+</sup>] in the aqueous phase influences the extraction rate of Al<sup>3+</sup> ions (Table 1), it does not mean that the extraction reaction occurs in the aqueous phase. The influence of [H<sup>+</sup>] is based on the aggregating effect of Al<sup>3+</sup> at the nucleus of MPA micelle and that extraction of the studied extraction system obeys the cation exchange extraction law. This excludes the possibility that the extraction occurs in the aqueous phase.

(2) In order to further prove that the extraction reaction occurs in essential inside the micelle and that there also exists liquid-liquid interfacial reaction, the authors make the following analyses on the basis of the relationship between interfacial chemistry and extraction kinetics.

First, in the range of [MPA] > CMC (critical micelle concentration), the relationships between  $C$ ,  $mC_m$  and  $C_t$  are shown in Fig. 2, where  $C$  is the concentration of the MPA monomers, mol/L;  $C_m$  is the concentration of the MPA micelle, mol/L;  $C_t$  is the total concentration of the MPA, mol/L;  $m$  is the polymeric number of MPA micelle.

From Fig. 2, it is clear that  $mC_m$  increas-

es linearly with increasing  $C_t$ , while  $C$  increases very little. This is because that the MPA forms reversal micelle in non-polar solvent, the increasing  $C_t$  mainly leads to increasing concentration of the micelle, then consequently make the non-micelle and micelle mixed extraction systems greatly different in interfacial absorption behaviors of the MPA. For the non-micelle extraction system, the interfacial tension  $\gamma$  and interfacial pressure  $\pi$  sharply decreases or increases

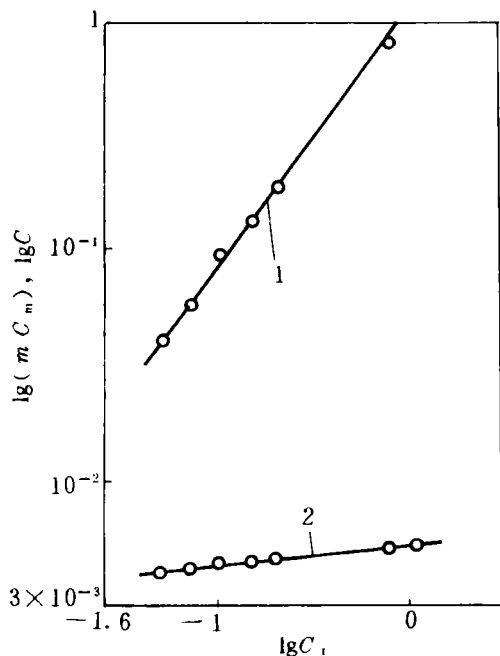


Fig. 2 Relationships between  $C$  or  $mC_m$  and  $C_t$   
 $[D_2EHPA] = 0.05 \text{ mol/L}$ ;  $pH = 0.76$ ;  
 $[Al] = 0.17 \text{ g/L}$ ; solvent: 12-docadane;  
 $T = 25^\circ\text{C}$   
 1— $mC_m$ ; 2— $C_t$

with increasing  $C_t$ . However, for the micelle extraction system, they gradually decrease or increase. Under the above conditions, if the controlling step is liquid-liquid interfacial reaction, then the extraction rate of  $Al^{3+}$  ions correspondingly increases very little. But in fact, the extraction reaction rate of the  $Al^{3+}$  ions increases faster in the

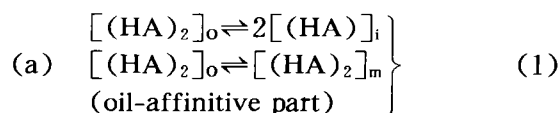
micelle range, especially in the transition region from non-micelle extraction system (Table 2) to micelle extraction system (Table 1), the reaction rate of the  $Al^{3+}$  increases significantly. Therefore, the increasing extraction reaction rate of the  $Al^{3+}$  ions can be attributed to the existence of the micelle and has very little relation to the interfacial absorption behaviors. In addition, the reason for the existence of  $D_2EHPA$  can accelerate the extraction of  $Al^{3+}$  is the synergistic effects and the interfacial aggregating effect of MPA micelle.

Based on the above analyses, it can be concluded that the reaction rate of the  $Al^{3+}$  extraction is closely related to the compositions of the organic phase and the interfacial aggregating effect of the MPA, and that it is almost not influenced by the liquid-liquid interfacial adsorption behaviors. Therefore, the controlling reaction occurs in essential inside the micelle, not at the liquid-liquid interfaces. Certainly, the liquid-liquid interfacial reaction still exists but it is not the reaction rate controlling step.

### 3.2.2 The Mechanisms

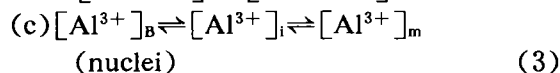
According to our studies of the interfacial chemistry, equilibrium mechanisms and extraction kinetics<sup>[1,6,7]</sup> and the experimental results in this paper, the authors believe there exist simultaneously two components—the micelle mixed extractant component  $D_2EHPA$ -MPA and the single MPA component, which react with the  $Al^{3+}$  ions inside the micelle region or liquid-liquid interfacial reaction region.

The basic steps of the two components in extracting the  $Al^{3+}$  ions in the above two regions are as follows:

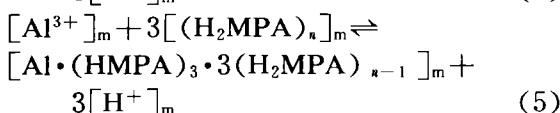
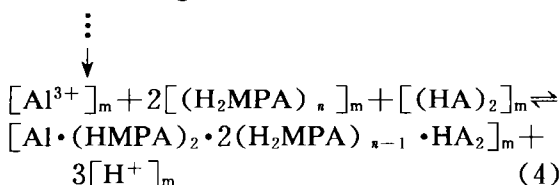


**Table 2** Dependence of  $k_t$  on  $[MPA]$  in non-micelle mixed extraction system\*

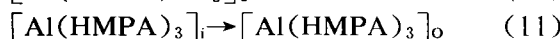
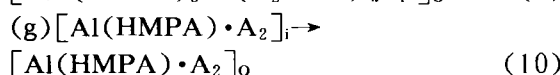
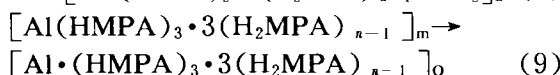
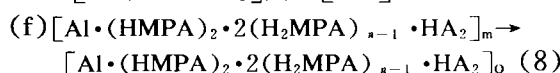
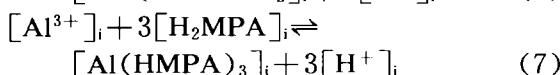
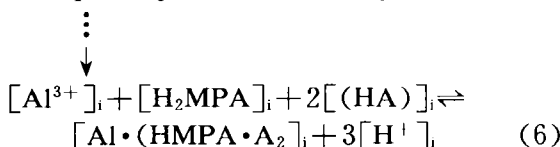
$[MPA]$ /mol·L <sup>-1</sup>	0.01	0.02	0.03	0.04	0.07
$k_t$ /min <sup>-1</sup>	0.004	0.008	0.010	0.0127	0.0190

\*  $[D_2EHPA] = 0.15 \text{ mol/L}$ ;  $pH = 1$ ;  $T = 25^\circ \text{C}$ 

(d) micelle region



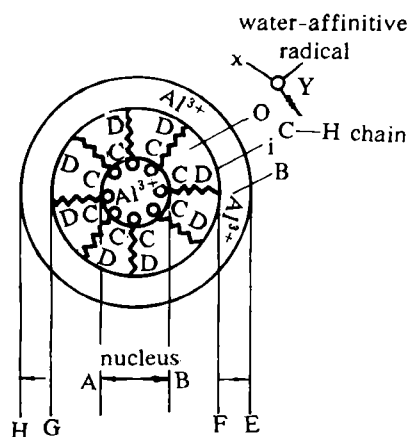
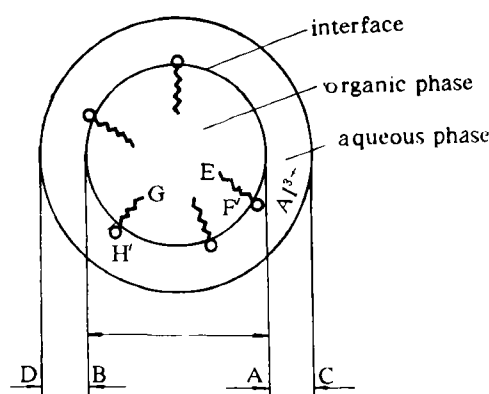
(e) liquid-liquid interfacial region



In equations (1)~(13), m, i, B, O represent micelle phase, interfacial phase, aqueous phase and organic phase respectively;  $n$  is the polymeric number of the micelle.

In order to further expound the reactions occurring in the two regions, the schematic diagrams of the MPA micelle and

MPA monomers are respectively shown in Figs. 3 and 4.

**Fig. 3** Schematic diagram of an MPA reversal micelle**Fig. 4** Schematic diagram of MPA and  $D_2EHPA$  monomers in liquid-liquid interfacial reaction region

In Fig. 3 the polar ends of MPA reverse micelle (water-affinitive ends) gather at the inner part of the micelle, and form a water-affinitive center, i. e. the micelle nucleus (represented by AB). The nonpolar ends of the MPA (oil-affinitive ends, represented by CD)—CH tail, stretch into the nonpolar diluent, i. e. normal dodecane, and form liquid-liquid interface (represented by i) with aqueous phase (represented by E).

and GH). In Fig. 4, AB represents organic phase zone (expressed by O), AC and BD represent aqueous phase zone (expressed by B), i represents the interface of the organic phase and the aqueous phase, E' F' and G' H' represent MPA and D<sub>2</sub>EHPA monomers respectively.

Equations (1)~(13) are illustrated as follows:

(a) Equation (1) indicates that the bulk phase—dimer HA (D<sub>2</sub>EHPA) diffuses toward the micelle and dissolves into the oil-affinitive part of the MPA micelle, and that part of the dimer HA in the bulk phase decomposes into monomers and adheres to the interfaces.

(b) Equation (2) indicates that the MPA polymers are in equilibrium with the MPA monomers at the interfaces.

(c) Equation (3) indicates the increasing dissolving of Al<sup>3+</sup> in the micelle region; Al<sup>3+</sup> ions in the aqueous phase diffuse toward the interfaces; part of them at the interfaces further diffuse toward the micelle phase and dissolve into the nucleus of MPA micelle and their surfaces.

(d) Equations (4) and (5) indicate respectively the synergistic and complexing reactions between the Al<sup>3+</sup> ions and the MPA-D<sub>2</sub>EHPA mixed extraction systems or the single MPA extraction system. The synergistic extraction complex diffuses toward the bulk organic phase (equations (8) and (9)).

(e) Equations (6) and (7) respectively indicates the liquid-liquid interfacial complexing reactions between the Al<sup>3+</sup> ions and the MPA-D<sub>2</sub>EHPA mixed extractant or the single MPA extractant. The formed synergistic complex diffuses toward the bulk organic phase (see equations (10) and (11)).

(f) The H<sup>+</sup> ions discharged from the micelle in the micelle region and the liquid-liquid interfacial reaction region diffuse to-

ward the bulk aqueous phase (see equations (12) and (13)).

It should be noted that for the above basic reactions, the micelle mixed extractant D<sub>2</sub>EHPA-MPA is the primary extractant and the single MPA extractant is the auxiliary; the micelle reaction region is the primary reaction region and the liquid-liquid interfacial reaction region is the auxiliary. In addition, the influence of the single D<sub>2</sub>EHPA extractant on the extraction of the Al<sup>3+</sup> ions can be neglected because of its lower reaction rate and extraction power.

When compared with single extraction systems MPA-Al<sup>3+</sup> and D<sub>2</sub>EHPA-Al<sup>3+</sup>[7], and the non-micelle mixed extraction systems<sup>[2]</sup>, the micelle mixed extractant system D<sub>2</sub>EHPA-MPA can accelerate the extraction of Al<sup>3+</sup>. The reasons and characteristics are:

(a) The micelle mixed extractant system has double synergistic effects, and the existence of the reversal MPA micelle further enriches the characteristics of the synergistic effects.

(b) The double synergistic effects appear both in the micelle and liquid-liquid interfacial reaction regions, and there are two components—D<sub>2</sub>EHPA-MPA and single MPA take part in extraction reactions.

(c) When the non-micelle mixed extraction system transits to the micelle one, the controlling step for the Al<sup>3+</sup> extraction transits from chemical reaction to chemical reaction in combination with diffusion<sup>[4,5]</sup>; the sites of the controlling reaction transits from liquid-liquid interfaces to interiors of the micelle; the compositions of the synergistic complex formed change.

Among the factors accelerating the Al<sup>3+</sup> extraction, the effect and characteristics of the MPA should be emphasized. The

(To page 49)

temperature of the molten electrolyte is 760 ~ 795 °C, the density is 2.50 ~ 2.60 g/cm<sup>3</sup>, the electrical conductivity is 1.6 ~ 1.9 Ω<sup>-1</sup>·cm<sup>-1</sup>. The electrical conductivity increases by 60 ~ 90 percent than that of the traditional electrolyte.

#### 4 SUMMAR<sup>y</sup>

(1) In this paper, the research range of the NaF-AlF<sub>3</sub>-BaCl<sub>2</sub>-NaCl system was widened. In past studies, bath ratio was up to 2.5, adding amount of NaCl was up to 8%. In this paper, the bath ratio was raised to 6.7, NaCl adding amount was raised to 15%.

(2) Liquidus temperature, temperature-varied electrical conductivity and density of this electrolytic system were studied. Conclusions reached in varying temperature conditions were very different from that un-

der constant temperature condition, which can closely represent practical condition.

(3) The relationships between each physico-chemical property and each factor of the electrolyte system NaF-AlF<sub>3</sub>-BaCl<sub>2</sub>-NaCl were summarized and described. Considering the requests of industry production for electrolyte, three groups of energy-saving electrolyte composition whose electrical conductivity was increased by 30 ~ 90 percent than that of the electrolyte adopted traditionally in industry and other properties which also meet with request were proposed in the basis of researches.

(4) One of the three groups of electrolyte composition proposed above has come into use in Guizhou Aluminium Plant. The energy consumption was reduced by 1200 kWh/t·Al, the output of refined aluminium was increased by 8 percent.

(From page 25)

MPA acts both as reacting medium and reacting extractant, then leads to the change of the reaction mechanisms. The accelerating characteristics of the MPA micelle are different from those of the micelle catalysis which only acts as reacting medium and accelerates the reactions, but does not changes its mechanism.

#### 4 CONCLUSIONS

(1) It was proved that the controlling reaction of the micelle mixed extractant system D<sub>2</sub>EHPA-MPA for the Al<sup>3+</sup> extraction occurs inside the micelle phase.

(2) The reaction rate equations were established for Al<sup>3+</sup> extraction of the studied extractant system.

(3) The two components, in the micelle region of the studied system, and their

reaction mechanisms, in the micelle and liquid-liquid interfacial reaction regions, were proposed.

(4) The accelerating mechanisms and their characteristics of the studied micelle mixed system were proposed and analysed.

#### REFERENCES

- 1 Yu, Jingfen *et al.* Acta Metallurgica Sinica 1990, 26(6): B385.
- 2 Fletl, D S. JINC, 1973, 35: 2471.
- 3 Chiarigia *et al.* JINC, 1976, 38: 1367.
- 4 Yu, Jingfen *et al.* Nonferrous Metals, 1990, (2): 67.
- 5 Yu, Jingfen; Ji, Chen. Chemical Journal of Chinese Universities, 1992, 13(2): 224.
- 6 Yu, Jingfen *et al.* ICHM' 88. Beijing; International Academic Publisher, 1988, 567.
- 7 Yu, Jingfen. Uranium Mining and Metallurgy of Uranium, 1993, (2): 21.