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# THERMODYNAMICS OF FORMATION OF LANTHANIDE COMPLEXES WITH 1,2-DIAMINOCYCLOPENTANE-*N,N,N',N'*-TETRAACETIC ACID

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ABSTRACT

Coordination enthalpies and entropies of tripositive lanthanide ions with ligand *trans*-1,2-diaminocyclopentane-*NNN'N'*-tetraacetic acid (CPDTA) have been determined using a non-isothermal reaction calorimeter. From the experimental $\Delta H_c^0$ values and literature free-energy data the coordination entropies, $\Delta S_c^0$, were calculated. Besides the expected irregular dependence of either $\Delta H_c^0$ or $\Delta S_c^0$ on $r_+^{-1}$, very significant correlations of $\Delta S_c^0$ with $\bar{S}_{Ln}^0$ as well as with $\Delta H_c^0$ have been observed.

INTRODUCTION

The thermodynamics of formation of lanthanide aminopolycarboxylates have been the subject of many investigations. Various irregularities, *e.g.* "gadolinium break"[1] and the frequently observed lack of correlation between the thermodynamic and structural parameters have been reported. Some attempts to rationalize the solution chemistry of these elements have had a definite, though partial success[2-4]. In this paper the thermochemical data are reported for the formation of lanthanide complexes with 1,2-diaminocyclopentane-*NNN'N'*-tetraacetic acid (CPDTA), a ligand whose complexes with alkaline-earth and transition metal ions have been the subject of our previous studies[5].

EXPERIMENTAL

The heats of formation of lanthanide – CPDTA chelates were determined by the "substitution method" according to Mackey *et al.*[6] with only minor simplifications.

## *Reagents*

All the chemicals used were of analytical reagent grade. The water was deionised and then distilled in an all-glass (Pyrex) still.

For calorimetric determinations *ca.* 0.2M lanthanide nitrate solutions were prepared by dissolving respective „Specpure" sesquioxides (Johnson & Mathey) in nitric acid and then neutralising to a pH of 5.0±0.2 with $CO_2$-free sodium hydroxide (this was prepared according to Pregl[7]). Lanthanide stock solutions were standardised compleximetrically[8]. Stock solution of the magnesium–CPDTA complex (3.5 mM) was prepared by dissolving $H_4CPDTA$ in carbonate-free NaOH, adding a slight excess of carefully standardised[8] $MgCl_2$ solution and the pH of the solution was then brought to 6.3. All the above-mentioned solutions were 0.1M in $NaNO_3$ so that a nearly constant ionic strength was maintained (the concentrations of all investigated species did not exceed 3.5mM). The solution of $Na_4CPDTA$ was prepared in a similar way, but without the addition of $MgCl_2$ solution. The final pH was 12.5±0.1.

*Calorimeter*

The calorimeter used in this work was based on a non-isothermal apparatus described by one of the present authors[9]. The whole calorimeter, consisting of three main parts: a Dewar reaction vessel, a lid and a support, was submerged into a water bath thermostatted to 20.00±0.01°. All metal parts were made of chromium-plated copper. The lid could be fitted to the Dewar by means of two brass rods provided with screws and a clamp. The tubes accomodating the thermistor, heater, cooler, piston burette and the stirrer were welded to the metal part of the lid. The inner part of the lid was made of Styropor to ensure an adequate thermic insulation. A synchronous motor (75 V, *ca.* 300 r.p.m.) was connected to the stirrer by a flexible shaft.

The piston burette consisted of a glass tube with a small-bore (0.1 mm diameter) Teflon ending and a Textolite piston that was also provided with a Teflon ending. The piston is operated with a micrometer screw. The burette was designed so that the whole volume of reagent to be dispensed in a calorimetric run was in thermal contact with the calorimeter contents, the thermal equilibration time being about 15–20 min.

The cooler consisted of a gold-plated brass tube and an inner inlet tube reaching almost to the bottom of the main tube; it was fed with tap water and was held outside the calorimeter during the experiment.

*Thermometric and electrical calibration circuits*

The temperature sensor was a 2,000-Ω thermistor (Standard Telephones Co., F 23) connected in one arm of a d.c. Wheatstone bridge and its output was measured with a current recorder. The bridge was fed from a 4.5 V dry battery the current drain being 3 mA. This circuit was essentially the same as that described previously[9]. To enable the instrument to be used with recorders of lower sensitivity the bridge output could be optionally amplified by an operational amplifier (Analog Devices, Model 106 A).

The electrical calibration was performed in the usual way, *i.e.* by means of a heater fed from a stabilised (to ±0.1%) power supply. The heater consisted of 0.15 mm (diameter) constantan wire (net resistance 10.319±0.016 Ω) wound on a piece of stainless steel isolated with mica. The heater was coated with Teflon and sealed — at its upper end — to a Pyrex glass tube having a plastic cap. The potential and current carrying leads were made of copper wires (0.1 and 0.2 mm in diameter, respectively). The heater resistance was measured by means of a precision Wheatstone bridge and its constancy controlled once a week in the same way. The potential drop on the heater (*ca.* 2 V) was measured with a vacuum tube voltmeter (Radiometer Titrator TTT 1c in connection with Scale Expander pHA 630) to $\pm 0.0002$ V, and the heating time with a stop watch (mechanically coupled with the heater switch). The readout accuracy of the stop watch was $\pm 0.02$ sec. The combined instrumental error of estimating the electrical energy input was below 0.2%.

*Units and calculations*

All the electrical instruments were calibrated in absolute units, so that the calorie is also defined as 4.1840 abs. J. The corrected temperature rise in calorimetric runs was determined by the well-known Dickinson's method. pH calibrations were performed according to the NBS scale[10]. For the details of other calculations see Refs. 5 and 6.

*Testing of the calorimeter*

The correctness of the calorimeter functioning was tested in the following way: (*a*) In seven separate runs varying electrical energy inputs were applied and the corrected rise of the output current, which was shown to be an almost perfectly linear function of the electrical energy input, was measured. The regression data are as follows: slope (scale div./cal) = 11.513; std. error of the slope = 0.057 (0.5%); intercept insignificant at $P < 0.001$ probability level. (*b*) Seven independent runs with nearly the same energy input gave the value for effective heat capacity (calorimetric constant) $C = 85.65 \pm 0.16$ mcal/scale div., the relative standard error of the mean being 0.2%. (*c*) The heat of neutralisation of NaOH with $HNO_3$ was measured at 20°C and an ionic strength of 3.5 mM. Under these conditions, a value of $-13.905 \pm 0.011$ kcal/mole was obtained which — recalculated to infinite dilution using the extended Debye–Hückel formula — gave $-13.869 \pm 0.031$ kcal/mole. This value is by *ca.* 1.5% higher than the results quoted by Papee *et al.*[11] ($-13.75 \pm 0.02$) and Pitzer[12] ($-13.612 \pm 0.012$ kcal/mole). It should be mentioned that the values originally quoted by Papee *et al.* and Pitzer were determined at 25°C but were recalculated here using Pitzer's formula[12]. As far as the present authors are aware, there are no recent data available for 20°C.

From the results quoted it was concluded that the calorimeter is capable of a rather satisfactory precision, but possesses a slight systematic error probably caused by the heat leakage through the heater leads. However, this systematic error is not very great in comparison with the reproducibility of thermochemical data where far larger differences are often encountered.

*Calorimetric determination of coordination heats*

The displacement method described by Mackey *et al.*[6] was applied for determining the heats of formation of lanthanide $(CPDTA)^-$ $[Ln(CPDTA)^-]$ species.

The calorimeter was charged with 70.0 ml of a 3.5 mM Mg(CPDTA) solution in 0.1 M $NaNO_3$ the pH of which had been previously adjusted to $6.3 \pm 0.1$ with carbonate-free NaOH. The burette was filled with *ca.* 0.2 M $Ln(NO_3)_3$ solution and inserted into the calorimeter. This was followed by flushing, for at least 20 min, with purified nitrogen gas. The calorimeter was then submerged into the thermostatted bath and left for some ½ h to achieve the thermal steady state which was checked by observing the shape of the time–temperature curve. By taking a temperature in the $20.00 \pm 0.01$ °C range as the zero-point, the temperature calibration was performed and the initial rating period was started. In a suitable moment, the addition of the reagent was accomplished. The dispensing of the reagent from burette lasted *ca.* ½ min. After achieving a new thermal steady state, the final rating was run. Both the initial and final rating periods had a duration of 5 min. The calibration runs were made in an analogous way but, instead of adding the reagent, the electrical heating took place. During the heater operation (duration also *ca.* ½ min) the voltage drop across the heater was measured 3–4 times. These calibration runs were always performed after the main experiment.

The heat of formation of $Mg(CPDTA)^-$ chelate was determined in a similar way as previously described by Simeon *et al.*[5], the only difference being the high working pH (12.5) that enabled the protonation of CPDTA anion to be neglected.

## RESULTS

The heats of metathetic reactions of the type

$$Mg(CPDTA)^{2-}\cdot\text{solvent} + Ln^{3+}\cdot\text{solvent} \rightleftharpoons Ln(CPDTA)^{-}\cdot\text{solvent} + Mg^{2+}\cdot\text{solvent} - \Delta H_1 \quad (1)$$

are quoted in Table I, together with all relevant primary experimental data. The reproducibility of these values, as seen from the primary data and the ranges of $\Delta H_1$ values quoted in the last column, was very satisfactory (since only two or three replicate determinations for each system were made it was not attempted to calculate either the standard errors or confidence limits for $\Delta H_1$; the range was considered as a more reliable dispersion parameter[13]).

As mentioned above, it was necessary to determine the heat of formation of $Mg(CPDTA)^-$ species in 0.1 M $NaNO_3$:

$$Mg^{2+}\cdot\text{solvent} + (CPDTA)^{4-}\cdot\text{solvent} \rightleftharpoons Mg(CPDTA)^{2-}\cdot\text{solvent} - \Delta H_2 \quad (2)$$

in order to be able to calculate the heats of formation of lanthanide–CPDTA complexes from $Ln^{3+}$ and ligand anion. The value for $Mg(CPDTA)^{2-}$ reported previously[5] was determined in a different ionic medium (1 M KCl) so it could not be used *a priori*. Two measurements were made and the overall heat effects of $-0.689$ and $-0.693$ cal were observed for the formation of 0.1569 mmole of magnesium complex. After allowing for heats of dilution ($-0.089$ and $-0.083$ cal, respectively) and of neutralisation (43 and 114 cal/mole, respectively) the enthalpy of magnesium complex formation $\Delta H_2 = 4.340 \pm 0.010$ kcal/mole was obtained . This is in excellent agreement with 4.37 kcal/mole found by Simeon *et al.*[5] using a somewhat different apparatus and 1 M KCl solvent.

TABLE I

HEATS OF FORMATION[a] OF $Ln(CPDTA)^-$ FROM $Ln^{3+}$ AND $Mg(CPDTA)^{2-}$ AT 20°C IN 0.1M $NaNO_3$

| $Ln^{3+}$ | *Mmoles* $Ln(NO_3)_3$ | *q (cal)* | $q_{dil.}$ *(cal)* | $q_{corr.}$ *(cal)* | $-\Delta H_m$ *(kcal/mole)* |
|---|---|---|---|---|---|
| $La^{3+}$ | 0.2456 | 1.283 | −0.195 | 1.478 | |
| | | 1.275 | −0.201 | 1.476 | |
| | | 1.274 | −0.202 | 1.476 | 6.014±0.003 |
| $Ce^{3+}$ | 0.2870 | 1.855 | 0.139 | 1.716 | |
| | | 1.828 | 0.122 | 1.706 | 5.963±0.019 |
| $Pr^{3+}$ | 0.2641 | 1.394 | −0.401 | 1.795 | |
| | | 1.419 | −0.383 | 1.800 | 6.807±0.010 |
| $Nd^{3+}$ | 0.2713 | 1.485 | −0.427 | 1.912 | |
| | | 1.505 | −0.409 | 1.914 | 7.052±0.003 |
| $Sm^{3+}$ | 0.2713 | 1.551 | −0.351 | 1.902 | |
| | | 1.576 | −0.318 | 1.895 | |
| | | 1.545 | −0.352 | 1.897 | 7.000±0.011 |
| $Eu^{3+}$ | 0.2727 | 1.062 | −0.627 | 1.689 | |
| | | 1.087 | −0.599 | 1.685 | 6.185±0.007 |
| $Gd^{3+}$ | 0.2056 | 0.845 | −0.298 | 1.144 | |
| | | 0.864 | −0.281 | 1.146 | 5.565±0.003 |
| $Tb^{3+}$ | 0.1242 | −14.292 | −14.867 | 0.574 | |
| | | −14.282 | | 0.584 | 4.678±0.025 |
| $Dy^{3+}$ | 0.2656 | 0.151 | −0.749 | 0.899 | |
| | | 0.120 | −0.776 | 0.895 | 3.381±0.010 |
| $Ho^{3+}$ | 0.3041 | 0.526 | −0.310 | 0.836 | |
| | | 0.523 | | 0.833 | 2.743±0.005 |
| $Er^{3+}$ | 0.2941 | 0.276 | −0.638 | 0.913 | |
| | | 0.249 | −0.667 | 0.915 | |
| | | 0.266 | −0.666 | 0.932 | 3.127±0.042 |
| $Tm^{3+}$ | 0.2913 | 0.907 | −0.426 | 1.333 | |
| | | 0.917 | | 1.343 | 4.593±0.017 |
| $Yb^{3+}$ | 0.2913 | 1.099 | −0.701 | 1.801 | |
| | | 1.104 | −0.701 | 1.806 | 6.191±0.009 |
| $Lu^{3+}$ | 0.2556 | −0.081 | −1.120 | 1.039 | |
| | | −0.111 | −1.124 | 1.013 | |
| | | −0.077 | −1.103 | 1.026 | 4.016±0.051 |

[a]Calorimeter contents: 70.0 ml of 3.5 mM $Mg(CPDTA)^{2-}$ (pH=6.3) in 0.1 M $NaNO_3$; volume of $Ln^{3+}$ solution added: 1.428±0.001 ml.

Both $\Delta H_1$ and $\Delta H_2$ values were considered to approximate reasonably well the respective standard values because the reactant and product concentrations were comparatively low (<3.5 mM) both in an absolute sense and in relation to the concentration of the supporting electrolyte which was in a nearly 30-fold excess. The standard state is here defined as a hypothetical ideal molar solution in 0.1 M $NaNO_3$ solvent.

The thermodynamic functions $\Delta G_c^0$, $\Delta H_c^0$ and $\Delta S_c^0$ for the reaction

$$Ln^{3+}\cdot\text{solvent} + (CPDTA)^{4-}\cdot\text{solvent} \Rightarrow Ln(CPDTA)^{-}\cdot\text{solvent} - \Delta H_c^0 \quad (3)$$

where

$$\Delta H_c^0 = \Delta H_1 + \Delta H_2 \quad (3a)$$

are quoted in Table II. Coordination free enthalpies, $\Delta G_c^0$, were calculated from the stability constants of lanthanide–CPDTA complexes determined by Weber and Voloder[14] using a competitive polarographic method similar to that used by Schwarzenbach and his coworkers[1,15]. These values are also reproduced in Table II. From known values for $\Delta G_c^0$ and $\Delta H_c^0$ the coordination entropies, $\Delta S_c^0$, were calculated using Gibbs–Helmholtz equation. Since the precision of both coordination enthalpies and free enthalpies is about ±20 cal/mole, the non-systematic part of the error in $\Delta S_c^0$ is about ±0.2 e.u./mole.

TABLE II

THERMODYNAMIC DATA FOR THE FORMATION OF $Ln(CPDTA)^{-}$ CHELATES FROM $Ln^{3+}$ AND $(CPDTA)^{4-}$ AT 20°C IN 0.1 M $NaNO_3$

| $Ln^{3+}$ | $^a\log K_{LnY}$ | $-\Delta G^0$ (kcal/mole) | $\Delta H^0$ (kcal/mole) | $\Delta S^0$ (e.u./mole) |
|---|---|---|---|---|
| $La^{3+}$ | 17.01 | 22.817 | −1.684 | 72.1 |
| $Ce^{3+}$ | 17.28 | 23.180 | −1.633 | 73.5 |
| $Pr^{3+}$ | 17.47 | 23.434 | −2.477 | 71.5 |
| $Nd^{3+}$ | 17.72 | 23.770 | −2.722 | 71.8 |
| $Sm^{3+}$ | 18.11 | 24.293 | −2.670 | 73.8 |
| $Eu^{3+}$ | 18.21 | 24.427 | −1.855 | 77.0 |
| $Gd^{3+}$ | 18.24 | 24.467 | −1.235 | 79.3 |
| $Tb^{3+}$ | 18.64 | 25.004 | −0.348 | 84.1 |
| $Dy^{3+}$ | 18.94 | 25.406 | +0.949 | 89.9 |
| $Ho^{3+}$ | 19.24 | 25.809 | +1.587 | 93.5 |
| $Er^{3+}$ | 19.49 | 26.144 | +1.203 | 93.3 |
| $Tm^{3+}$ | 19.71 | 26.439 | −0.263 | 89.3 |
| $Yb^{3+}$ | 19.95 | 26.761 | −1.861 | 84.9 |
| $Lu^{3+}$ | 20.20 | 27.096 | +0.214 | 93.2 |

$^a$O. A. Weber and K. Voloder, unpublished results, *cf.* Vl. Simeon, *Arh. Hig. Rada Toksikol.*, 19 (1968) 106.

## DISCUSSION

The most important features of the solution chemistry of lanthanide ions have been outlined concisely by Grenthe[4] and, more recently, by Beech[16]. It seems that there is no doubt about the very important role played by variable cation hydration throughout the lanthanide series: as a consequence of this, both the coordination enthalpies and the entropies vary in an irregular fashion with cation radius. This is also the case with the results obtained in this work. By combining the coordination enthalpies with the dissolution heats of a series of isomorphous lanthanide salts, Staveley and his coworkers[2] were able to eliminate the irregularities connected with variable hydration. Their method is applicable only to those systems where coordinatively saturated complexes are involved as reaction products, as confirmed later by Carson *et al.*[17]. As expected, CPDTA behaves in this respect quite similarly as EDTA since both are sexidentate ligands and therefore are not capable of occupying all the coordinating positions of $Ln^{3+}$ ions. Also, we were not able to find any correlation of either enthalpies or entropies of coordination with the ionization potentials of the metals studied in this work; the lack of such a correlation was also observed with our data on alkaline-earth aminopolycarboxylates.

Bertha and Choppin[3] have calculated the partial molar entropies of lanthanide ions, $\bar{S}^0_M$, which should be related with coordination entropies (in our notation $\Delta S^0_c$) in the following way:

$$\Delta S^0_c = \bar{S}^0_{ML} + w\bar{S}^0_{H_2O} - \bar{S}^0_L - \bar{S}^0_M \tag{4}$$

where $w$ stands for the number of water molecules displaced on coordination, and $\bar{S}^0_{ML}$, $\bar{S}^0_{H_2O}$ and $\bar{S}^0_L$ are partial molar entropies of the respective 1:1 complex, water and ligand, respectively. For CPDTA complexes of the series of lanthanide ions, $\bar{S}^0_L$ remains constant throughout and the term $w\bar{S}^0_{H_2O}$ probably does not change dramatically. The first term of Eqn. (4) may change throughout the series to a certain extent because of the variable degree of hydration. The scatter diagram for the correlation of $\Delta S^0_c$ with $\bar{S}^0_M$ is shown in Fig. 1 from which it can be seen that a definite correlation does exist. The calculations yielded a correlation coefficient $r = -0.822$

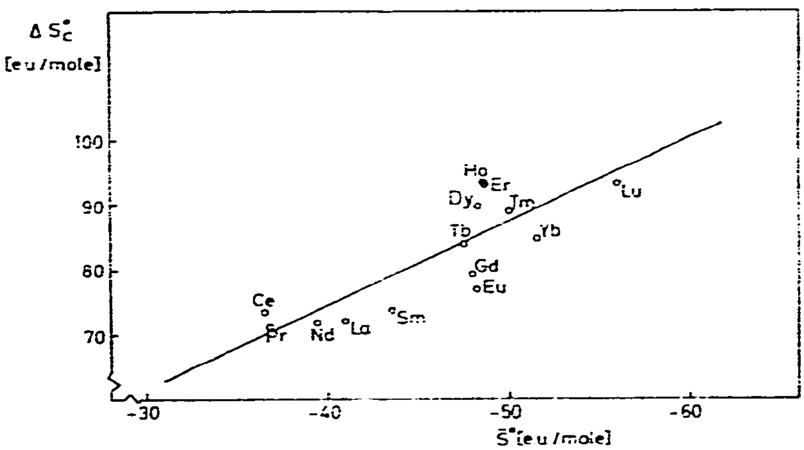


Fig. 1. Correlation of formation entropy of lanthanide CPDTA complexes with the standard partial molar entropies of the cations.

which is significant at a probability level $P<0.001$. The respective regression equation is given as

$$\Delta S_c^0 = (1.26 \pm 0.25)\,\bar{S}_M^0 + 22.4 \pm 11.6 \tag{5}$$

The slope does not differ significantly from unity while the intercept is scarcely significant ($0.05<P<0.1$).

Another regularity which can be observed with present data is a highly significant correlation between the coordination enthalpies and corresponding entropies. The respective scatter diagram is shown in Fig. 2

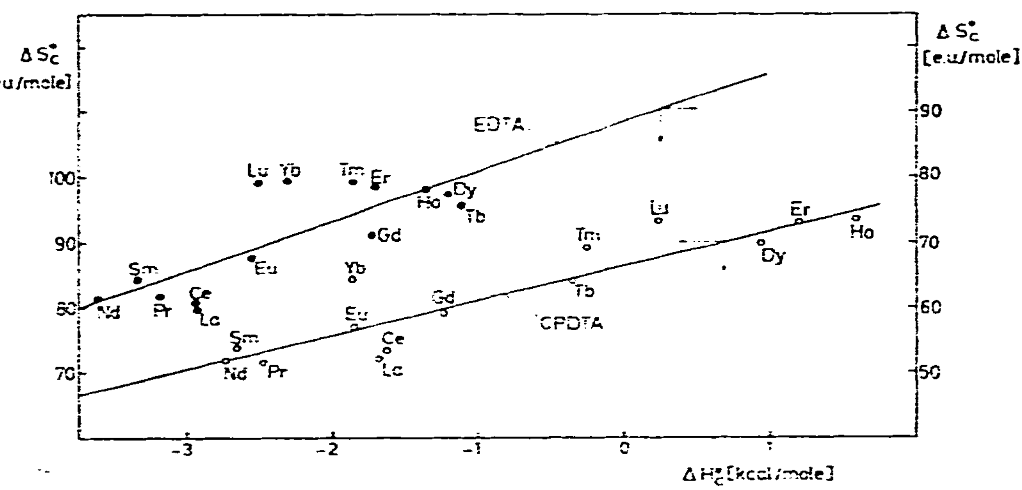


Fig. 2. Coordination entropy *vs.* enthalpy relationship for the formation of EDTA and CPDTA lanthanide complexes. Data for EDTA are taken from Ref. 6.

where the corresponding data of Mackey *et al.*[6] for EDTA are also plotted. The correlation coefficients for CPDTA and EDTA are 0.908 and 0.786, respectively, indicating a highly significant correlation ($P<0.001$ in both cases). The corresponding regression equations are as follows:

$$\Delta S_c^0 = (7.6 \pm 1.7)\,\Delta H_1^0 + 89 \pm 4 \tag{6}$$

for EDTA, and

$$\Delta S_c^0 = (5.4 \pm 0.7)\,\Delta H_1^0 + 87 \pm 1 \tag{7}$$

for CPDTA. The slopes in Eqns. (6) and (7) are significantly different while the intercepts are apparently equal. Similar correlation has been observed previously[5] for the entropies and enthalpies of coordination of alkaline-earth cations with four *C,C'*-substituted EDTA derivatives; a slope of $2.29 \pm 0.99$ and an intercept $42 \pm 17$ were calculated. Person[18] has discussed the theoretical aspects of the correlations of this kind for organic donor–acceptor complexes. Unfortunately, his conclusions cannot at present time be extended to metal aminopolycarboxylate complexes because the necessary spectroscopic data are still not available.

By comparing the common (average) value for the intercept in the case of the lanthanide aminopolycarboxylates ($88 \pm 4$) with the corresponding value for the alkaline-earth chelates ($42 \pm 17$) it can be observed that their ratio ($88/42 = 2.10$) is almost equal to the ratio of the squares of the respective cationic charges ($3^2/2^2 = 2.25$). Although this finding may possibly be fortuitous it is to be pointed out that it is based on a reasonably large number of observations (34). It appears, therefore, to be justified to search for its theoretical explanation and further experimental support.

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