

# Temperature effect on vertical detachment energy of bulk hydrated electron by dielectric continuum theory

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Received: 20 January 2015 / Accepted: 23 March 2015 / Published online: 1 April 2015  
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**Abstract** In this work, vertical detachment energy (VDE), continuum slope (CS) and solvent reorganization energy (SRE) of solvated electrons in bulk liquids were calculated by the formulas derived from electron cavity model within the framework of dielectric continuum (DC) theory. The predicted VDE was in good agreement with the reported experimental data, which indicated that DC theory was a good approach to describe the energy level of solvated electrons in vertical detachment. Moreover, the effects of temperature on VDE, CS and SRE of bulk hydrated electron were discussed from 25 to 500 °C at an extreme pressure of 25 MPa. As temperature increases, VDE and CS were found to shift to lower energies (spectral red-shift), while SRE exhibited a maximum under supercritical condition and decreased significantly to about 0.53 eV at 500 °C. Those significant energy changes near 375 °C may be caused by extraordinary water properties at the critical point.

**Keywords** Hydrated electron · Vertical detachment energy · Solvent reorganization energy · Temperature effect · Dielectric continuum theory

## 1 Introduction

Solvated electron motivates considerable interest because of its essentiality in electron transfers [1–12] and in a series of aqueous reactions [13–17]. As a particularly important example of electron solvation, this amazing substance can not only be trapped by molecules to form negative clusters, or traced near the liquid surface [6, 7], but

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also can solvates in bulk solvents [18, 19]. A number of theoretical studies have been performed to address the basic question of how an excess electron solvates in fluids. However, some structural and dynamic properties are still controversy. In fact, due to the different aqueous environment and solvent polarization, the solvated electrons in different liquids generally exhibited different solvated configurations, energy levels and electronic properties. Representative examples such as water, benzene [20], toluene [20], methanol [4, 21], ethanol [21], tetrahydrofuran [22], acetonitrile [23–26] and liquid ammonia [27], have extensively been tabulated for a long time.

In recent several decades, various spectroscopic studies of excess electron in liquids have been performed, the most widely used techniques are absorption spectroscopy and photoelectron spectroscopy. Undoubtedly, the first observation of a transient broad absorption peaking at 720 nm in pure liquid water at room temperature was a meaningful landmark for spectral analysis about hydrated electron [28]. By this pulse radiation method, subsequent femtosecond studies [1–3] provided the radiationless relaxation and the nature of solvation of excess electrons. Moreover, most literature reported absorption spectrum about hydrated electron at different thermodynamic conditions [29]. For example, Jou and Freeman [30] investigated the absorption spectrum parameters of hydrated electron at different temperatures; Katsumura group reported macroscopic properties in sub- and super-critical conditions [28–35]. Those researches showed that the maximum absorption always shifts to lower energy as temperature increases. Otherwise, another significant accomplishment is the direct experimental measurements for the vertical detachment energy (VDE) of hydrated electron by Abel et al [36], Suzuki et al [37], Neumark et al [38], Lübcke et al [39] respectively. The experimental observations with values of about 3.30–3.60 eV are close to the extrapolations from finite clusters to bulk water [40–44]. Meanwhile, Suzuki group [45] also reported the values of VDE in the solvents of methanol and ethanol to be about 3.10 eV which are higher than experimental extrapolations (about 2.6 eV) [21]. In addition to the experiments at ambient condition, photoelectron spectrum was also used to characterize the VDE for hydrated electron at ultralow temperatures [46], and corresponding molecule dynamic simulations were carried out in cold water clusters [47]. However, due to the complicated experimental techniques, there is no related work so far for the VDE of solvated electron in bulk solvents at high temperatures. In the present work, we investigate this temperature effect on photoelectron macroscopic features of solvated electron in bulk solvents by dielectric continuum (DC) theory.

The question of how excess electron exists in solvents will be simplified and clarified if one considers the electron cavity model [48] which postulates that by occupying a sphere cavity the excess electron is trapped in the potential well formed by the polarization of dielectric medium. The electron cavity model can be applied to intercept the macroscopic field of the solvent acting on the excess electron in different liquids [49]. Besides, this model can provide many important insights into the solvent effects on the electron solvation in polar liquids. Within the frame of DC theory and considering the solvent reorganization, it can easily deduce the linear extrapolation from finite cluster size to liquid bulk [44], which refers to the VDE, solvent reorganization energy (SRE) and continuum slope (CS) [41].

The scope of the present work is to investigate the vertical detachment of solvated electrons in liquids by DC model. In an effort to gain more insight into the excess

electrons in solvents, two different expressions of the VDE have been employed in this paper. The first one is derived from constrained equilibrium theory [50–54], the second approach is derived with irreversible work approach [55–58] by nonequilibrium theory. The paper is organized as follows: the formula of VDE, CS and SRE by DC theory at different conditions are given in theory section; The VDEs of excess electrons are calculated in different fluids at ordinary conditions and temperature dependences of VDE, SRE and CS in bulk water at 25 MPa are also discussed. We close with conclusions at the end of article.

## 2 Theory

### 2.1 VDE, CS and SRE by DC theory

The vertical detachment of solvated electron in bulk solvents corresponds to the removal for an excess electron from bulk liquid into the vacuum without a change in solvent configuration. The energy needed in this process is called as VDE. Supposing the excess electron located at the centre of a spherical cavity in finite clusters or bulk solvents, the relation of VDE, SRE and CS of solvated electron in vertical detachment are given by DC theory [50] as

$$\text{VDE}(n) = \text{VDE}(\infty) - CSn^{-1/3} \tag{1}$$

with

$$\text{VDE}(\infty) = \frac{1}{2} \left[ 1 - \frac{1}{\epsilon_s} + \frac{(\epsilon_s - \epsilon_{op})^2}{\epsilon_s \epsilon_{op}^2 (\epsilon_s - 1)} \right] \frac{1}{R} \tag{2}$$

$$CS = \frac{1}{2} \left[ 1 - \frac{1}{\epsilon_s} + \frac{(\epsilon_s - \epsilon_{op})^2}{\epsilon_s \epsilon_{op}^2 (\epsilon_s - 1)} \right] \frac{1}{a_0} \tag{3}$$

and

$$\text{SRE}(\infty) = \frac{1}{2} \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \frac{\epsilon_s - \epsilon_{op}}{\epsilon_{op} (\epsilon_s - 1)} \frac{1}{R} \tag{4}$$

where  $\text{VDE}(n)$  is VDE of solvated electron in solvent molecules with cluster size  $n$  and  $\text{VDE}(\infty)$  is in bulk solvent. CS is the slope of the relation between VDE and  $n^{-1/3}$ .  $\epsilon_s$  and  $\epsilon_{op}$  are the static and optical dielectric constant of medium respectively.  $a_0$  is the radius of single solvent molecule.  $R$  is the electron cavity radius and  $\text{SRE}(\infty)$  is SRE in bulk solvent.

Similarly, the irreversible work approach gives the expressions [55,56,59–61] of VDE, CS and SRE as follows:

$$\text{VDE}'(\infty) = (1 + 1/\epsilon_{op} - 2/\epsilon_s)/2R \tag{5}$$

$$CS' = (1 + 1/\epsilon_{op} - 2/\epsilon_s)/2a_0 \tag{6}$$

$$\text{SRE}'(\infty) = (1/\epsilon_{op} - 1/\epsilon_s)/2R \tag{7}$$

Obviously, the two theories would predict different values of VDE, CS and SRE. However, the ratio between  $VDE(\infty)$  and CS is a constant, i.e.,

$$VDE(\infty)/CS = a_0/R \quad (8)$$

This equation shows that the ratio between VDE in bulk solvent and slope CS solely depends on the ratio of the size of a single solvent molecule and the cavity radius of hydrated electron.

Submitting Eq. 8 into Eq. 1, the relation of  $VDE(n)$  and  $VDE(\infty)$  can be expressed as

$$VDE(n) = VDE(\infty) \left(1 - \frac{R}{a}\right) \quad (9)$$

Here  $a = a_0 n^{1/3}$  is the radius of solvent molecules with cluster size  $n$ . The minimal cluster size  $n$  which can bind an excess electron can be predicted as  $(R/a_0)^{1/3}$  if setting  $VDE(n) = 0$ .

## 2.2 Solvent parameters at different conditions

In fact, solvated electrons are widely investigated by many theoretical models [62] such as molecular field model, semi-continuum and DC model. The most popular and simple model is the DC model [63]. The solvent is represented by the static dielectric constant ( $\epsilon_s$ ) and optical dielectric constant ( $\epsilon_{op}$ ). As a consequence, it is convenient to estimate the solvent properties at different thermodynamic conditions, by regarding the static and optical dielectric constants as functions of temperature and pressure. Taking water as an example, static dielectric constant of solvent can be regarded as a function of temperature ( $t$ ) and pressure ( $p$ ) [64]. Similarly, the optical dielectric constant can be obtained from the square of the refractive index ( $n_0$ ) [65] which is determined by the temperature ( $t$ ) and density ( $\rho$ ) of solvent [66], i.e.,

$$\epsilon_s = f(t, p) \quad (10)$$

$$n_0 = f(t, \rho(t)) \quad (11)$$

$$\epsilon_{op} = n_0^2 \quad (12)$$

Besides dielectric constants, cavity radius ( $R$ ) of the hydrated electron is one of most important parameters in electron cavity model. The estimation of  $R$  at ambient condition can be easily achieved by fitting corresponding thermodynamic parameters [67, 68] or using theoretical simulations [29, 69]. Additionally,  $R$  can be approximately estimated by the calculation of moments of the absorption spectrum [70]. According to the experimental absorption lineshapes of bulk hydrated electron at various temperatures and pressures [71], Coe et al. [72] performed moment analysis with the data from Tuttle-Golden [71] and Jou-Freeman [73], and the cavity radius  $R$  with the temperature dependence was summarized as

$$R_{TG} = 1.9995 + 8.65 \times 10^{-4}T + 1.9413 \times 10^{-6}T^2 \quad (13)$$

Another crucial parameter is the radius of single solvent molecule which can be estimated from the density of the solvent or the molar volume of solvent molecule. It can be obtained as

$$a_0(t, p) = (3M/4\pi N_A \rho(t, p))^{1/3} \quad (14)$$

Here,  $M$  is molar mass and  $N_A$  is Avogadro's number.

According to the equations mentioned above, we can calculate the vertical detachment energies of bulk solvated electrons at different thermodynamic conditions.

### 3 Results and discussion

#### 3.1 VDE( $\infty$ ), CS and SRE( $\infty$ ) in different solvents at ambient condition

As a simple electron solvation, excess electron can readily solvate in various solvents. Table 1 summarizes the solvent parameters at room temperature and constant pressure and lists the predicted values for VDE( $\infty$ ), CS and SRE( $\infty$ ) in eight ordinary fluids by the DC theory. Based on the solvent parameters, the predictions of VDE( $\infty$ ) for solvated electrons (in water, acetone, methanol, ethanol, tetrahydrofuran, toluene and benzene) by using Eq. 2 are quite close to the experimental extrapolations determined by the VDEs of the clusters. This indicates that this simple and empirical model has good reliability for high polar solvents and weakly polar solvents. However, in the solvent of liquid ammonia, DC theory overestimates the value of VDE( $\infty$ ) which gives a high solvation ability. The disagreement between the calculated and experimental values for VDE results is from the inaccuracy of electron cavity radius. Experimental value for VDE( $\infty$ ) (1.25 eV) requires a value of  $\sim 7\text{--}8 \text{ \AA}$  for electron cavity radius which is significantly larger than the value of  $3.1 \text{ \AA}$  for liquid ammonia estimated from the electron volume [79]. Despite the simplicity of this model, DC theory to a certain extent can give reasonable evaluations for VDE( $\infty$ ) of solvated electrons in most solvents.

Comparing to the experimental extrapolations by clusters, DC theory obtains excellent CS predictions in high polar water and weakly polar toluene and benzene, but significant larger slopes in other solvents by using Eq. 3 or 6. The bias estimation may be caused by the intrinsic nature of DC model which ignores the number and orientation of solvent molecules around the excess electron. Coincidentally, CS predicted by Eq. 6 are about 1.2 times than those by Eq. 3. Similarly, for SRE( $\infty$ ) in eight solvents, due to the factor of  $(\epsilon_s - \epsilon_{op})(\epsilon_s - 1)^{-1} \epsilon_{op}^{-1}$ , the calculated SRE( $\infty$ ) from Eq. 4 are about half as much as those from Eq. 7. Obviously, the prediction of SRE( $\infty$ ) is determined for the most part by the difference of  $\epsilon_s$  and  $\epsilon_{op}$ . Comparing to the available experimental values, DC theory yields underestimations of SRE( $\infty$ ) for excess electron in bulk fluids. Especially the predicted bulk SREs are nearly zero in the solvents of toluene and benzene, which seriously underestimate the values (about 0.25–0.35 eV [20]) obtained by photoelectron spectra. This manifests little solvent reorganization induced by an electron detachment from the solvents with  $\epsilon_s \approx \epsilon_{op}$ .

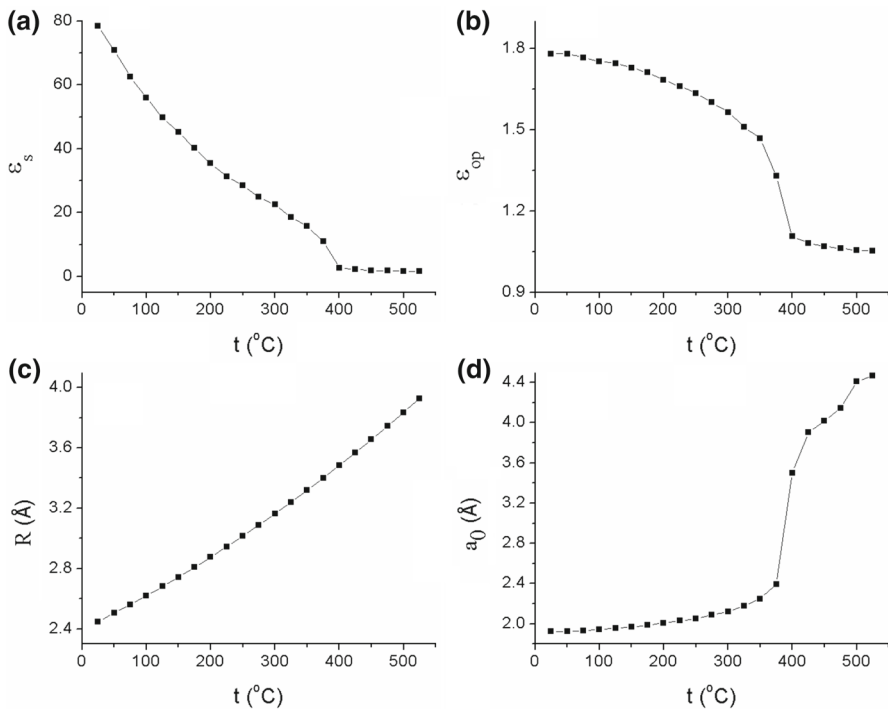
**Table 1** Solvent parameters and calculated VDE( $\infty$ ), CS and SRE( $\infty$ ) of solvated electrons at 25 °C (unit: eV)

solvent	$\epsilon_s$	$\epsilon_{op}$	$a_0$ (Å) <sup>a</sup>	$R$ (Å) <sup>b</sup>	Constrained			Irreversible			Exp <sup>c</sup>		
					VDE	CS	SRE	VDE	CS	SRE	VDE	CS	SRE
water	78.39	1.776	1.628	2.98	3.13	5.73	0.74	3.72	6.81	1.33	3.30–3.60	5.73	1.60
acetonitrile	36.64	1.806	2.340	3.40	2.66	3.87	0.60	3.17	4.61	0.69	2.61	2.14	
methanol	32.63	1.758	2.133	2.50	3.65	4.28	0.86	4.34	5.09	1.55	3.36–3.38	2.41	
ethanol	24.55	1.847	2.411	2.40	3.65	3.65	0.78	4.37	4.36	1.01	3.28–3.38		
ammonia	22.70	1.756	1.685	3.25	2.76	5.32	0.64	3.28	6.33	1.16	1.25	2.40	
THF	7.58	1.971	2.684	2.50	2.96	2.76	0.46	3.58	3.34	1.09	3.10	1.74	0.25–0.35
toluene	2.38	2.23	2.939	4.558	0.92	1.43	0.003	0.96	1.49	0.04	0.90	1.40	0.30–0.34
benzene	2.247	2.244	2.769	4.545	0.88	1.44	0	0.88	1.45	0	0.84	1.38	0.25–0.35

<sup>a</sup> Estimated from the molar volume of solvent

<sup>b</sup> Solvated electron cavity. H<sub>2</sub>O from ref [67], CH<sub>3</sub>CN from ref [74], CH<sub>3</sub>OH from ref [21]; C<sub>2</sub>H<sub>5</sub>OH from ref [75], liquid NH<sub>3</sub> from ref [27], THF from ref [49, 76], C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> are estimated by Eq. 8

<sup>c</sup> Experimental VDE( $\infty$ ), CS and SRE( $\infty$ ). H<sub>2</sub>O from ref [36,41, 77], CH<sub>3</sub>CN from ref [78], CH<sub>3</sub>OH from ref [4,21]; C<sub>2</sub>H<sub>5</sub>OH from ref [78], liquid NH<sub>3</sub> from ref [63], THF from ref [22], C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> from ref [20]

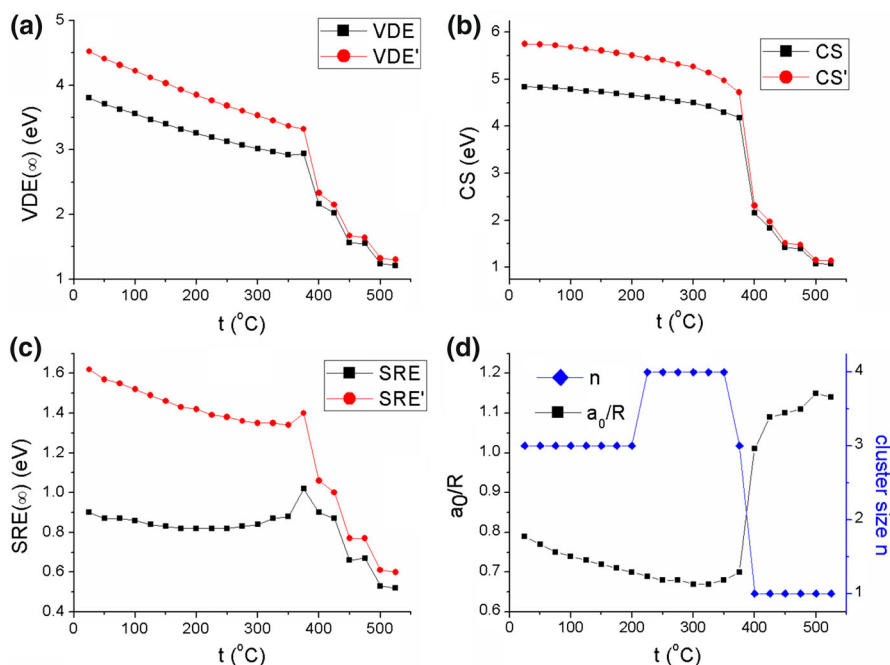


**Fig. 1** Water properties at different temperatures under 25MPa. **a** Ref [64], **b** Ref [66], **c** Ref [71–73], **d** Prediction by Eq. 14, the density data from Ref [64]

### 3.2 VDE, CS and SRE of hydrated electron at different temperatures

Encouraged by good agreement between DC theory and experiment observation, we wanted to study electron detachment from bulk water at extreme conditions. Figure 1 lists the solvent parameters at different temperatures. Experimentally, Cline et al measured  $\epsilon_s$  of water at different temperatures and 25 MPa [64];  $\epsilon_{op}$  can be obtained by refractive index of water measured by Harvey et al [66];  $a_0$  can be estimated from water density at different temperatures and 25 MPa [64]. Similarly,  $R$  had been estimated by Freeman et al by Monte Carlo simulations [71–73]. Based on those properties at different thermodynamic conditions, VDE( $\infty$ ), CS and SRE( $\infty$ ) of hydrated electron can be easily predicted by DC theory. The temperature effects on bulk VDE, CS and SRE of hydrated electron at 25 MPa are listed in Fig. 2.

As temperature increases, the VDE( $\infty$ ) decreases gradually (see Fig. 2a), which indicates that corresponding maximum peak of photoelectron spectrum appears red-shift. This energy decrease also indicates that the excess electron escapes more easily from the polarized potential well formed by electron and solvent molecules. This is explained by applying Einstein's relation  $VDE = h\nu - E_k$ , in which  $h\nu$  represents the energy of radiated light inducing photoelectric ionization in measurement of photoemission spectroscopy and  $E_k$  is the kinetic energy of emitted electron which can predict by  $3RT/2$  [80]. At high temperatures, the omitted electron would have superior



**Fig. 2**  $VDE(\infty)$ , CS,  $SRE(\infty)$  and  $VDE(\infty)/CS$  of hydrated electron at different temperatures under 25 MPa. VDE, CS and SRE were results from constrained equilibrium theory,  $VDE'$ ,  $CS'$  and  $SRE'$  were from traditional nonequilibrium theory

$E_k$  value and becomes more active in the vertical detachment. Considering a constant of  $h\nu$ , VDE naturally decreases as temperature increases. As shown in Fig 2a, from 25 to 375 °C, VDE for hydrated electron shifts linearly from 3.76 to 3.0 eV, the value of  $d(VDE)/dT$  is about  $-0.005$  eV/°C which is quite close to the experimental value of  $-0.0024$  eV/°C [4, 30]. Distinctly, with temperature increasing from 375 to 500 °C, the VDE decreases dramatically from 3.0 to 1.23 eV. It seems that 375 °C is a critical temperature and a boundary for VDE variation degree. VDE is weak sensitive to temperature under 375 °C, but is significantly influenced by temperature above this critical temperature. Actually, the condition at 375 °C and 25 MPa is a critical point [32], and the water properties differ greatly near this supercritical condition. Obviously, the dielectric constant of water changes sharply from 10.94 to 2.57 in range of 375–400 °C, corresponding to VDE decreasing dramatically from 3.0 to 2.15 eV. It should be pointed out that there are no available experimental VDE values at high temperatures, however, the spectral red-shift for VDE with the temperature increasing (or density decreasing) is in good agreement with the photoabsorption spectrum of solvated electron [31–33].

Continuum slope shows a similar trend with VDE. As shown in Fig. 2b, with the temperature increasing from 25 to 375 °C, the predicted CS shifts to lower energy, and decreases to be about 0.65 eV from 4.83 to 4.18 eV. Similarly, the calculated CS from Eq. 6 predicts a decrease from 5.75 eV at 25 °C to 4.72 eV at 375 °C, and the



difference is about 1.03 eV. In the range from 375 to 400 °C, the value of CS changes sharply from 4.18 to 2.14 eV due to the significantly decrease of dielectric polarity. At 500 °C, the CS is about 1.06 eV. This monotone decreasing indicates that the elevation of temperature narrows the energy gap between  $VDE(n + 1)$  and  $VDE(n)$ . That is to say, the value of  $VDE(n + 1) - VDE(n)$  at high temperature is smaller than the one at low temperature. With the cluster size increasing from  $n$  to  $n + 1$ , the added water molecule improves the difficulty of vertical detachment for excess electron because of the interaction between excess electron and water molecule. It seems that the increasing of temperature diminishes this interaction between excess electron and added water molecule.

The trend of  $SRE(\infty)$  exhibits some differences compared with  $VDE(\infty)$  and CS. The DC theory predicts that bulk SRE is gradually reduced from 0.90 eV at 25 °C to 0.82 eV at about 250 °C, and then increases to 1.02 eV under supercritical condition. However, a shallow minimum for  $SRE(\infty)$  seems to exist at about 250 °C in the range of 25–350 °C. The smooth trend demonstrates that the  $SRE(\infty)$  is weakly sensitive to the temperature from the ambient to sub-supercritical condition. Besides, a prominent maximum appears at 375 °C. Furthermore, with the temperature further increasing,  $SRE(\infty)$  decreases significantly to about 0.53 eV at 500 °C.

The minimal size of water cluster which can accommodate an excess electron at different temperatures can be predicted by the value of  $(R/a_0)^{1/3}$ . From Fig. 2d, we can observe that the minimal water cluster size at 25 MPa is step-shaped in the range of 25–500 °C. From 25 to 350 °C, the critical size is about 3 and jumps to 4 at 250 °C, which indicates that hydrogen-bonding can reform between the minimal negative clusters and another water molecule as the temperature increases. As the density of bulk water continues decreasing, the critical size jumps off from 4 at 350 °C to 3 at 375 °C, at last to 1 at 400 °C. This significant variation is an indication of the breaking of hydrogen-bonding in the negative clusters because of the loss of water molecules. Besides, at 375 °C which is close to the critical point, DC theory gives the dominant existence of hydrated electron is trimer, which is in good agreement with the results from first principle study [81]. Furthermore, it is interesting that DC theory predicts that the water monomer can bind an excess electron above supercritical condition (above 400 °C and 25 MPa), which is a complete contrast to the ambient condition [28].

## 4 Conclusions

In this work, the VDE, CS and SRE of different solvated electrons are investigated theoretically by DC theory in eight liquids: water, acetonitrile, benzene, toluene, methanol, ethanol, liquid ammonia and tetrahydrofuran. The results show that DC theory can give good predictions for bulk VDE in most solvents. Moreover,  $VDE(\infty)$ , CS and  $SRE(\infty)$  of hydrated electron are also investigated with the temperature range from 25 to 500 °C at 25 MPa. The results show that VDE shifts significantly to lower energies as temperature increases, which indicates that the maximum peak of photoelectron spectrum exhibits spectral red-shift. CS are also found to shift to lower energies as temperature increases, while  $SRE(\infty)$  exhibits the maximum value at critical point

and decreases significantly to 0.53 eV at 500 °C. Those significant energy changes near 375 °C may be caused by the extraordinary water properties at supercritical condition.

**Acknowledgments** This work is supported by a Project of Shandong Province Higher Educational Science and Technology Program (J12LD07).

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