Electronic supplementary information for

"Thermodynamic screening of lignin dissolution in 1-butyl-3-methylimidazolium acetate–water mixtures"

Contents

1. Materials and methods

1.1 Materials

Enzymatically hydrolyzed lignin (EHL) was supplied by Shandong Longlive Bio-Technology Co., Ltd. (China). EHL isolation involves the removal of a substantial amount of the carbohydrate fraction by the cellulolytic enzyme hydrolysis of corncobs. This procedure was followed by extraction with a diluted sodium hydroxide solution and the subsequent hydrolysis with diluted sulfuric acid (2 wt%), which cleaves lignin–carbohydrate bonds. According to the test results by the National Food Quality Supervision and Inspection Center (NFQSIC; China), the residual carbohydrate content in EHL is 0.17%, and the phenolic hydroxyl group content is 8.0%. The weight-average molecular weight (M_w) for EHL is 297,420 g/mol, while the number-average molecular weight (M_n) is 7930 g/mol. Alkali lignin and organsoolv lignin were purchased from Sigma Aldrich Co. The M_w of alkali lignin is about 10000 g/mol, while that of organosolv lignin is 52200 g/mol.

Ionic liquid (IL) 1-butyl-3-methylimidazolium acetate ([C$_4$mim]OAc) (>98% purity) was supplied by the Lanzhou Institute of Chemical Physics (China). [C$_4$mim]OAc and deionized (DI) water were mixed to form solvents with different IL weight percentages (60–100 wt%).

1.2 Experimental procedure

The heat of dissolution was measured with a precise solution in a dissolution vessel by TAM Air (TA Instruments). All the experiments were performed at 50 °C, and 1.5 g of the corresponding solvent (pure IL or IL–water mixture) was used to dissolve

the EHL (25 mg). The EHL was placed in a glass ampoule. A precise amount of solvent (pure IL or IL–water mixture) was drawn into the injector, which was placed above the glass ampoule. Both the solvent and the glass ampoule were kept inside the calorimeter for approximately 15 h of thermal equilibration. The solvent was injected into the glass ampoule, and the EHL was dissolved through mechanical agitation. The relaxation of heat was measured until the heat flow reached steady levels around the baseline.

To confirm the heat effects of injecting the solvent into the glass ampoule, heat relaxation without lignin (blank experiment) was also conducted under the same experimental conditions.

The heat flow profiles of the dissolution and blank experiments were integrated by the TAM Air software. The enthalpy of dissolution was counted by deducting the blank values. Each test was performed at least thrice to measure the error limit.
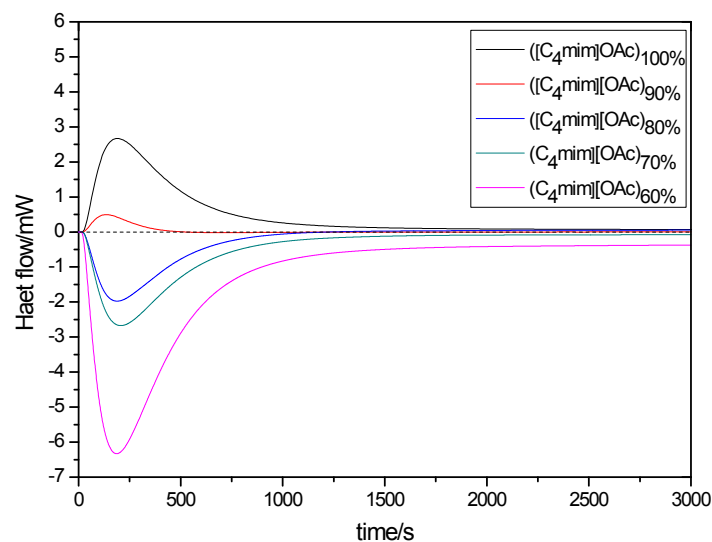
2. Characteristic time of the dissolution process

Table S1 Characteristic time of EHL dissolution in different [C$_4$mim]OAc–water mixtures at 50 °C.

	[C$_4$mim]OAc content (wt%)				
	100	90	80	70	60
t_c (s) [a]	212	192	188	144	121

[a] t_c is the characteristic time of solvent diffusion.

3. Blank experiments

Fig. S1 Heat flow profiles of blank experiments of IL–water mixtures with different [C$_4$mim]OAc contents.

In the case of the blank experiments, the solvent (1.5 g of pure [C$_4$mim]OAc or the [C$_4$mim]OAc–water mixture) was injected into an empty glass ampoule. As shown in Fig. S1, the exothermic peak during the blank experiment with pure [C$_4$mim]OAc is attributed to the friction during the injection. In the case of the blank experiments with [C$_4$mim]OAc–water ([C$_4$mim]OAc content ≤80 wt%), endothermic peaks were observed, and the peaks were attributed to the a small quantity of water evaporation at 50 °C.

4. Heat flow profiles of the dissolution of water and the lignin model monomer in [C$_4$mim]OAc
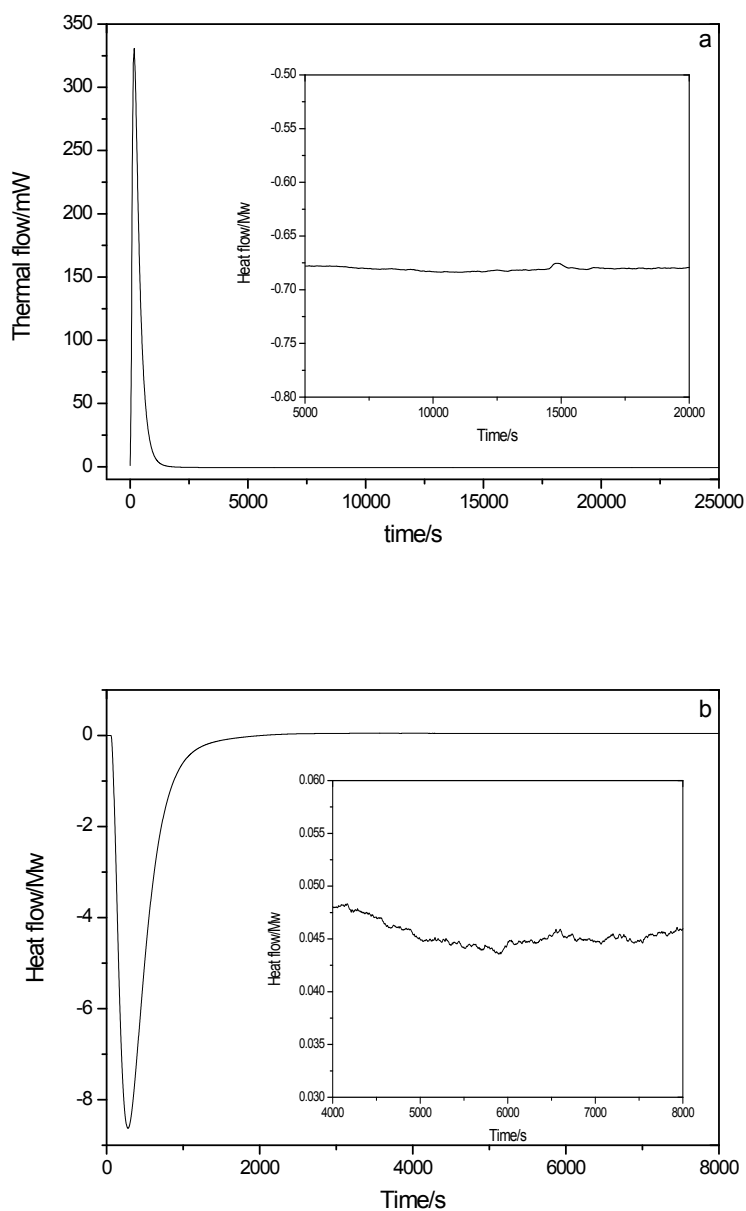
Fig. S2 Heat flow profiles of mixing 1.5 g of [C$_4$mim]OAc with 0.6 g of water at 50 °C (a) and dissolving 50 mg of the lignin model monomer (2,6- dimethoxyphenol) in 1.5 g [C$_4$mim]OAc (b).

## 5. C^{13}-NMR spectra and chemical shift changes of the main signals

All NMR spectra were obtained with a BrukerAvance III 400 spectrometer. Data processing was performed with the MestReNova 6.0 software. Analyses were performed with 500 μL of the appropriate ionic liquid in a 5 mm NMR outer tube with DMSO-d_6 (99.8% D) in an internal tube. The spectra were rerun, and any changes in the chemical shift were noted by calibrating both spectra to the same chemical shift for DMSO.

The signals corresponding to the carbon at the 2-position and the carbon of the carbonyl group in the cation are shown in Fig. S3 (the full spectra are presented in Fig. S4). After EHL was dissolved in [C$_4$mim]OAc, the signals corresponding to the carbon at the 2- (Fig. 2a), 4-, and 5-positions (Fig. 5Sa) were shifted up-field compared with the signals of [C$_4$mim]OAc. The signals corresponding to the carbon of carbonyl were shifted down-field. The changes could be derived from hydrogen bonds between the anion and the hydroxyl of the lignin. These band shifts were maintained even at 48 h after lignin dissolution, thus suggesting that the microscopic environment of [C$_4$mim]OAc always changed in this period. A long time was required to achieve the thermodynamic stable state of the [C$_4$mim]OAc–lignin binary system.

As shown in Figs. S3c and S3d, a similar phenomenon was observed when the EHL was dissolved in ([C$_4$mim]OAc)$_{90\%}$ compared with pure [C$_4$mim]OAc. However, the signals for the carbon of carbonyl were up-field shifted when the EHL was dissolved for 48 h rather than for 3 h. These shifts were the opposite of the shifts with pure [C$_4$mim]OAc. The opposite trends were probably caused by the competition between

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lignin and water. The water interacted with the anion when a certain amount of water was added. When lignin was dissolved in the [C$_4$mim]OAc–water mixtures, the lignin gradually supplanted the interaction between the anion and a portion of water. The hydrogen bonds between the anion and lignin were weaker than those between the anion and water. Thus, the signal had an up-field shift, and a more obvious phenomenon was found in the ([C$_4$mim]OAc)$_{70\%}$ solvent (when EHL was dissolved, the signal corresponding to the carbon of carbonyl group was shifted up-field). Otherwise, almost no shift was observed in the signals corresponding to the carbon at the 2-position and the carbon of the carbonyl group in the ([C$_4$mim]OAc)$_{90\%}$ and ([C$_4$mim]OAc)$_{70\%}$ solvents at 48 h after EHL dissolution. The same phenomenon was noted for other positions (Table S4). Moreover, the signal corresponding to the carbon at the 2-position did not shift at 3 h after the EHL dissolution. Therefore, the addition of water promotes the stable state of the mixtures to some extent.
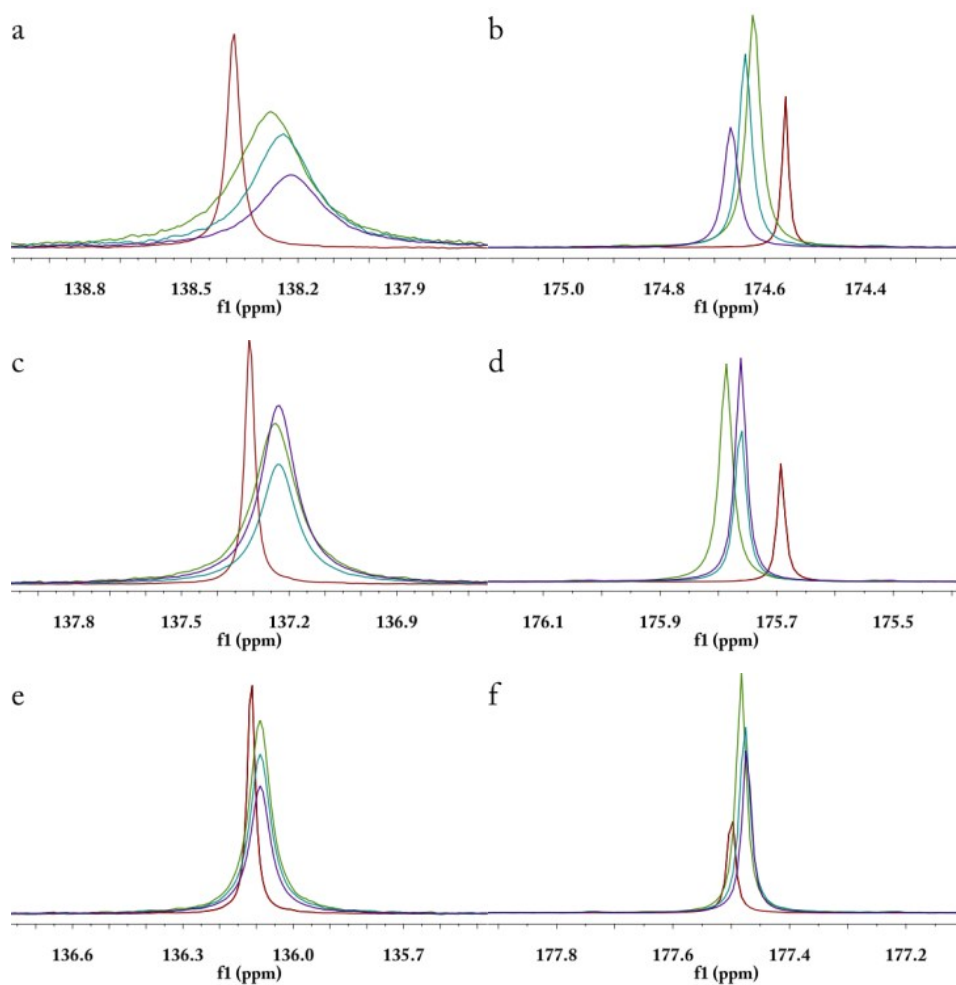
Fig. S3. ^{13}C-NMR spectra of the signals corresponding to the carbon at the 2-position (a, c, e) and the carbon of the carbonyl group (b, d, f) of [C$_4$mim]OAc in the [C$_4$mim]OAc–water mixture without EHL (red) and with 6.6 wt% of EHL dissolved for 3 h (cyan), 48 h (green), or 5 d (purple). ([C$_4$mim]OAc)$_{100\%}$ (a, b), ([C$_4$mim]OAc)$_{90\%}$ (c, d), and ([C$_4$mim]OAc)$_{70\%}$ (e, f) were used as the corresponding solvents.

a

b

c
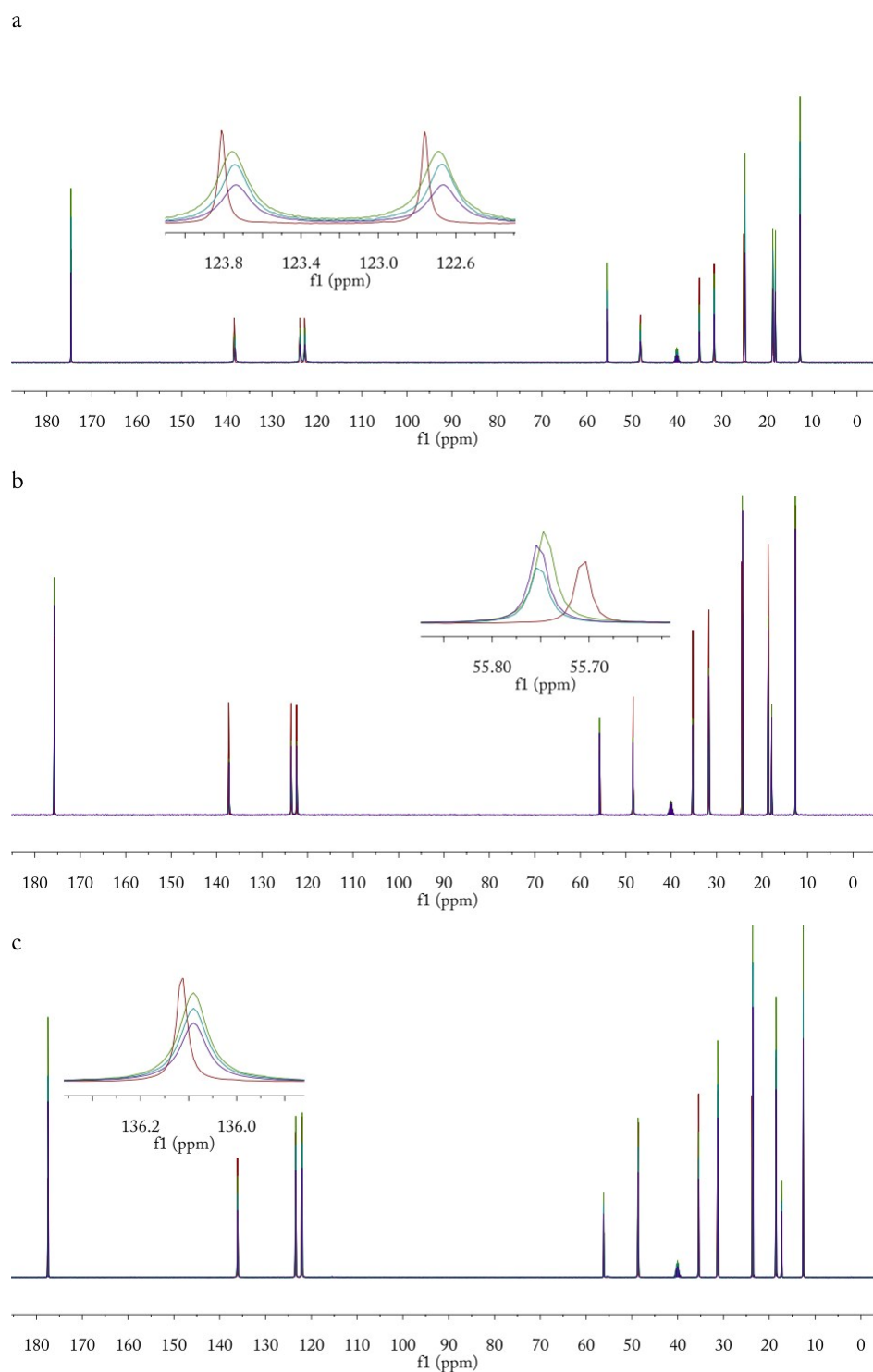
Fig. S4. Full ^{13}C-NMR spectra of the [C$_4$mim]OAc signals in the [C$_4$mim]OAc–water mixtures without EHL (red) and with 6.6 wt% of EHL dissolved for 3 h (cyan), 48 h (green), or 5 d (purple).

Table S2 Chemical shift change (ppm) of signals during EHL dissolution in ([C$_4$mim]OAc)$_{100\%}$.

| Time of EHL dissolution	Change in chemical shift (ppm)					
	NC$\underline{H}$N	NC$\underline{H}$CHN	NC$\underline{H}_3$	NC$\underline{H}$CHCHCH$_3$	CH$_3$C$\underline{}$OO	C$\underline{H}_3$COO
3 h	-0.119	-0.067	0.029	0.007	0.048	-0.041
48 h	-0.154	-0.081	0.039	0.011	0.065	-0.042
5 d	-0.162	-0.090	0.046	0.013	0.090	-0.042

Table S3 Chemical shift change (ppm) of signals during EHL dissolution in ([C$_4$mim]OAc)$_{90\%}$.

Time of EHL dissolution	Change in chemical shift (ppm)					
	NC$\underline{H}$N	NC$\underline{H}$CHN	NC$\underline{H}_3$	NC$\underline{H}$CHCHCH$_3$	CH$_3$C$\underline{}$OO	C$\underline{H}_3$COO
3 h	-0.071	-0.004	0.049	0.055	0.094	-0.014
48 h	-0.081	-0.013	0.047	0.049	0.069	-0.033
5 d	-0.080	-0.012	0.048	0.050	0.069	-0.033

Table S4 Chemical shift change (ppm) of signals during EHL dissolution in ([C$_4$mim][OAc])$_{70\%}$.

Time of EHL dissolution	Change in chemical shift (ppm)					
	NC̲HN	NC̲HCHN	NC̲H$_3$	NC̲HCHCHCH$_3$	CH$_3$C̲OO	C̲H$_3$COO
3 h	-0.024	-0.007	0.014	0.049	-0.016	0.020
48 h	-0.024	-0.007	0.016	0.052	-0.023	0.021
5 d	-0.024	-0.007	0.017	0.053	-0.025	0.020

6. Heat flow profiles of the dissolution of alkali lignin and organosolv lignin in ([C$_4$mim]OAc)$_{80\%}$
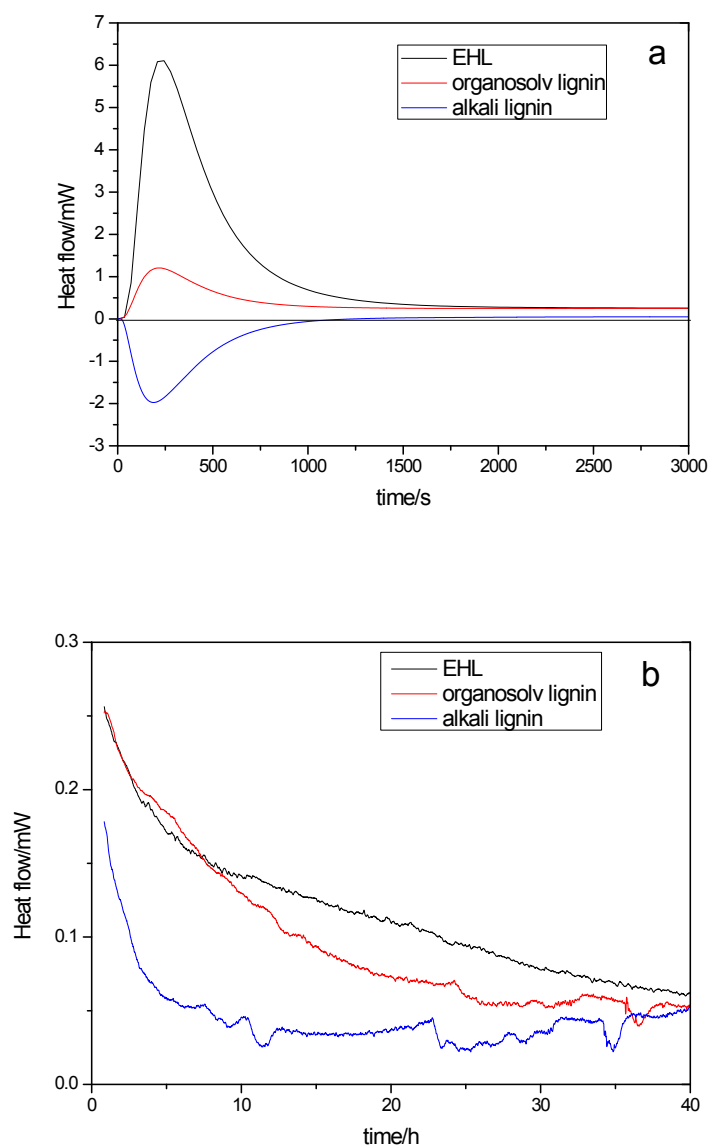
Fig. S5 Heat flow profiles of the dissolution of alkali lignin and organosolv lignin in ([C$_4$mim]OAc)$_{80\%}$ at 50 °C. Heat relaxation in the first stage (a) and in the second stage (b) during lignin dissolution.

7. Enthalpy changes during the dissolution of alkali lignin and organosolv lignin in ([C$_4$mim]OAc)$_{80\%}$ at 50 °C

Table S5 Enthalpy changes during the dissolution of alkali lignin and organosolv lignin in ([C$_4$mim]OAc)$_{80\%}$ at 50 °C

	Enthalpy change[a] (J/g)			t_c (s)[b]
	ΔH_1	ΔH_2	ΔH	
organosolv lignin	-16 ± 2	-285 ± 21	-301 ± 23	153
alkali lignin	- 5± 0.8	-83 ±7	-88 ±6	122

[a]ΔH_1 represents the enthalpy change of the first stage of lignin dissolution (mixing of the lginin in [C$_4$mim]OAc–water mixtures within 50 min). ΔH_2 represents the enthalpy change of the second stage of lignin dissolution (at 50 min after mixing lignin in [C$_4$mim]OAc–water mixtures). ΔH represents the enthalpy of lignin dissolution, $\Delta H = \Delta H_1 + \Delta H_2$

[b] t_c is the characteristic time of solvent diffusion.