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PYRIDINIUM IONIC LIQUIDS AS PHASE CHANGE MATERIALS FOR ENERGY STORAGE

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Phase change materials (PCM) are a promising solution for renewable energy storage as they can store and release thermal energy via a reversible phase transition. PCMs with melting point in the intermediate temperature range, durable and inexpensive are the main target of this research field.[1,2] This work describes a family of pyridinium ionic liquids and their thermophysical properties targeting the benefit of protic ionic liquids reported as benchmark in the PCM field.[3] Various pyridine structural isomers were used to explore the correlation between the enthalpy of fusion and melting point with molecular features. The results show that small structural variations in the cation can drastically change the thermophysical properties of the material. Within this work the melting temperatures varied between 357 ± 1 K and 499 ± 1 K, and enthalpies of fusion covered a wide spectrum from 38 to 190 J g^{-1} ± 5 % (see Table 1 and 2). The most promising results in terms of PCM application, and one of the best among all protic ionic liquids reported thus far, were obtained for 2-hydroxypyridinium methanesulfonate [2-OHpyH][CH_3SO_3] (T_m = 433 K and ΔH_f = 190 J g^{-1}, see Figure 1 and 2).

Table 1. Specific thermal properties of organic salts based on the pyridinium cation.

Material	T_g ± 1 K	T_{ss} ± 1 K	T_m ± 1 K	ΔH_f J g^{-1} ± 5%	T_c ± 1 K	ΔH_c J g^{-1} ± 5%	ΔT ± 1 K
[pyH][CH_3SO_3]		264	453	21^{ss}, 77^{f}	437	104	16
[pyH][CF_3SO_3]		312, 363, 403	499	24^{ss}, 38^{f}	458	37	41
[pyH][$C_6H_5SO_3$]			408	123^{f}	328	100	80
[4-^{t}BupyH][CH_3SO_3]			345	73^{f}	304	68	41
[2-MepyH][CH_3SO_3]	197		357	51^{f}	272	57	d
[3-MepyH][CH_3SO_3]			372	136^{f}	304	118	68
[4-MepyH][CH_3SO_3]			369	83^{f}	329	91	40
[2-OHpyH][CH_3SO_3]			433	190^{f}	420	193	13
[2-NH_2pyH][CH_3SO_3]	233		398	111^{f}	272[a]	84	c
[2-NH_2,3-OHpyH][CH_3SO_3]	255		403	63^{f}	322[b]	58	c

[a] – large supercooling, crystallization during heating cycle, different behavior between cycles.
[b] – large supercooling, crystallization during heating cycle.
[c] – unusual crystallization behavior (large supercooling – crystallization on heating cycle or two crystallization events).
ss - Σ of all enthalpies obtained for solid-solid phase transitions (ΔH_{ss}).
f – enthalpy of fusion (ΔH_f).
ΔT – degree of supercooling, difference between T_m and T_c
DSC conditions: sample size 3-8 mg, nitrogen flow 20 ml h^{-1}, heating rate10 °C min^{-1}. Transition temperatures were considered as the peak maximum and ΔH was calculated as the area of the melting peak.

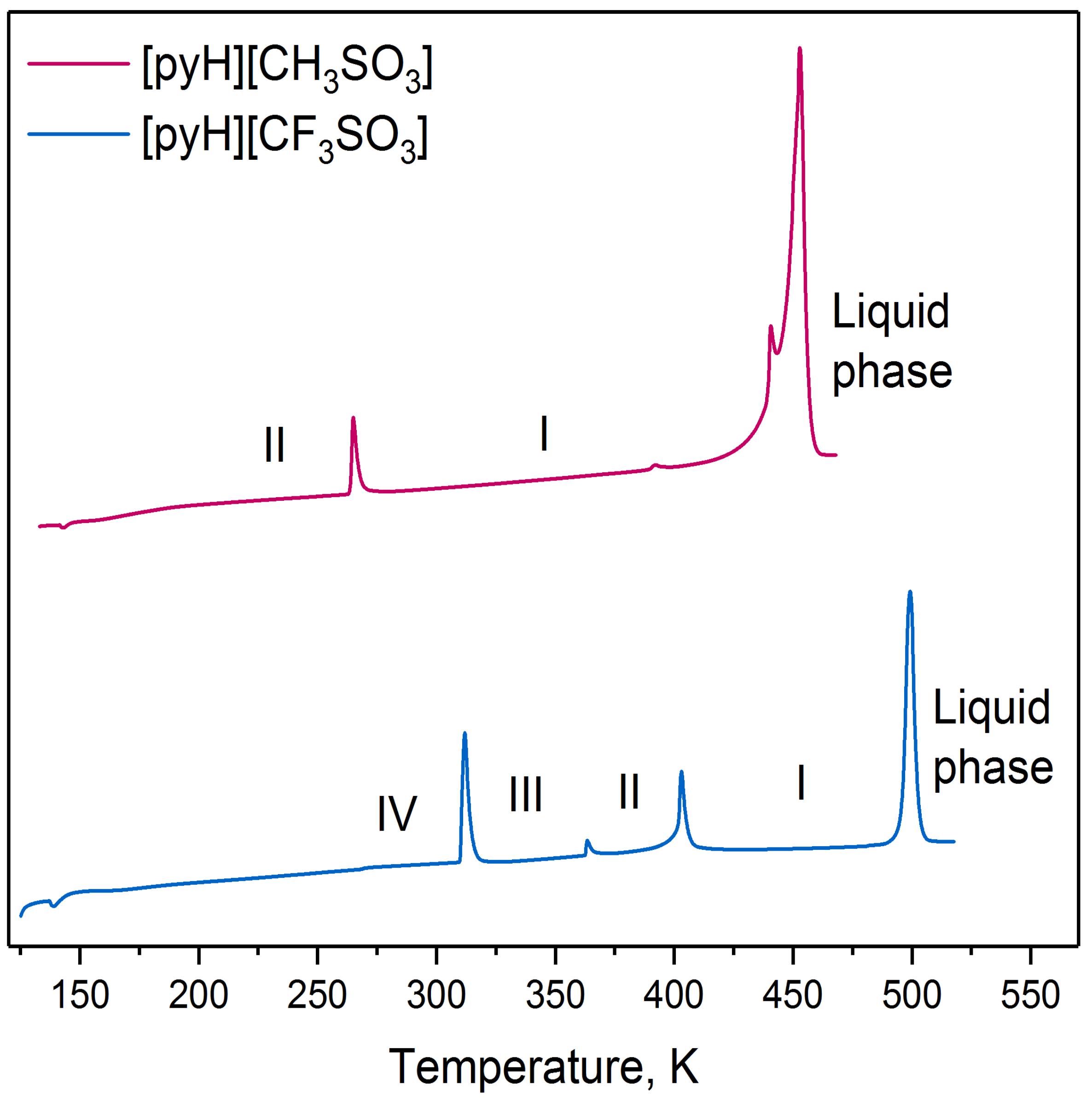

Figure 1. DSC traces of [pyH][CH_3SO_3] and [pyH][CF_3SO_3] on a second heating cycle showing solid-solid phase transitions.

Table 2. Thermodynamic properties of organic salts based on the pyridinium cation.

Material	ΔH_{ss} kJ mol^{-1} ± 5%	ΔH_f kJ mol^{-1} ± 5%	ΔS_f J mol^{-1} K^{-1} ± 5%	ΔS_{tot} J mol^{-1} K^{-1} ± 5%	N	T_d, K
[pyH][CH_3SO_3]	4	13	30	38	36	445
[pyH][CF_3SO_3]	6	9	17	28	8	553
[pyH][$C_6H_5SO_3$]	-	29	72	-	5474	418
[4-^{t}BupyH][CH_3SO_3]	-	17	49	-	361	418
[2-MepyH][CH_3SO_3]	-	10	27	-	26	418
[3-MepyH][CH_3SO_3]	-	26	69	-	4126	418
[4-MepyH][CH_3SO_3]	-	16	43	-	168	418
[2-OHpyH][CH_3SO_3]	-	36	84	-	24248	498
[2-NH_2pyH][CH_3SO_3]	-	21	53	-	592	498
[2-NH_2,3-OHpyH][CH_3SO_3]	-	13	32	-	48	503

T_d – decomposition temperature, taken as the onset of decomposition
N – degree of disorder, as a ratio of the maximum number of configurations per molecule in the disordered phase, compared to the completely ordered phase (Dd = exp(ΔS_f/R)).

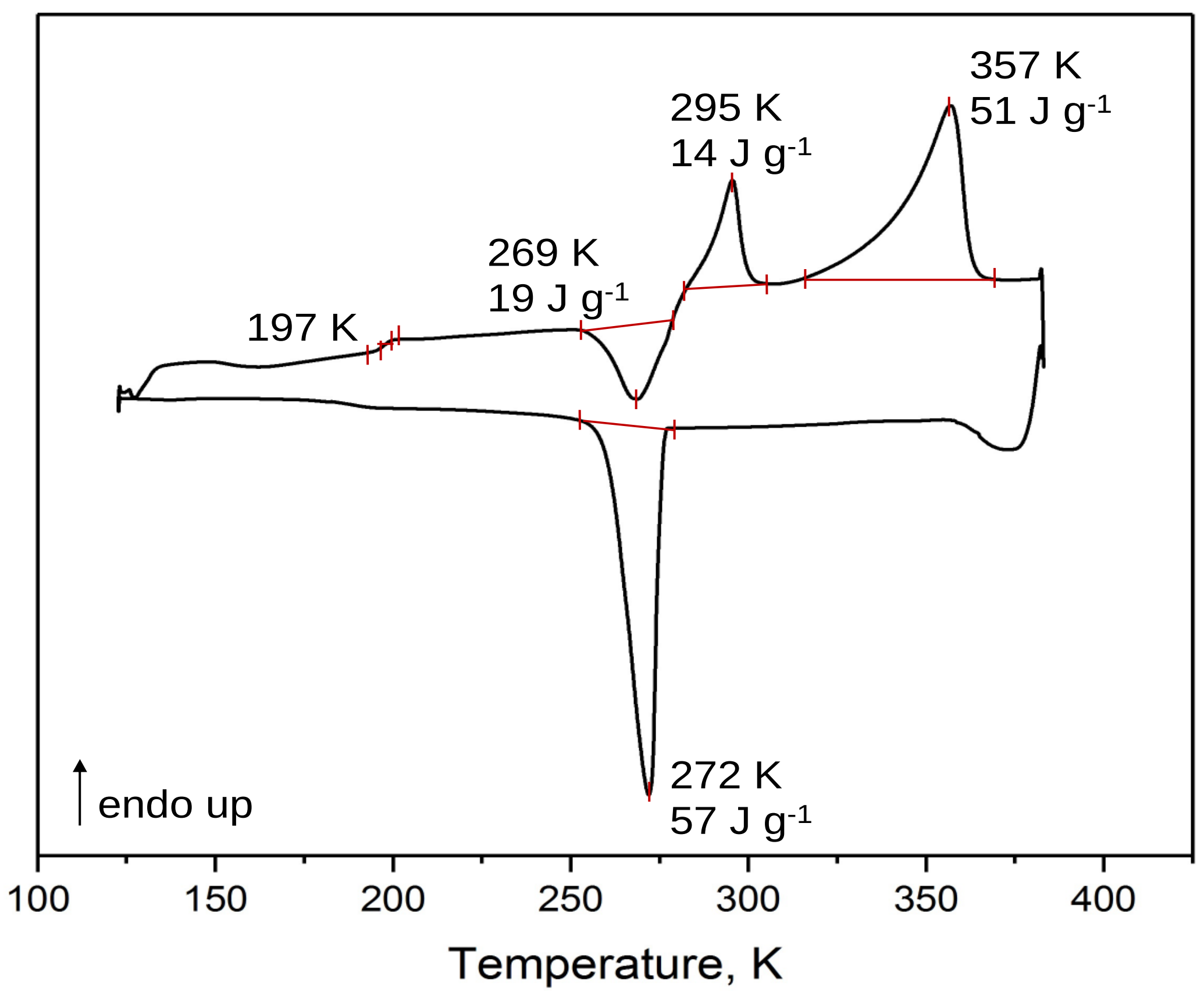

Figure 2. DSC trace of [2-MepyH][CH_3SO_3]. Data recorded during second cycle.

REFERENCES

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