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Heat capacity and phase transitions of mixtures of neopentylglycol and pentaerythritol from 270 K to their melting points

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Abstract

The heat capacities and phase transition parameters for mixtures of neopentylglycol (NPG) and pentaerythritol (PE) in five mole ratios (NPG:PE = 20:80, 35:65, 50:50, 65:35 and 80:20) were measured from 270 K to their melting points by means of an automated adiabatic calorimeter. Three phase transitions, two solid–solid transitions and the third melting, were found for each mole ratio studied. The experimental results show that the transition parameters varied with the mole ratio of the mixtures.

INTRODUCTION

In order to research some solid–solid phase-change materials with transition parameters suitable for storage of solar energy and to provide more accurate thermal data for these materials, a series of adiabatic calorimetry measurements on polyalcohols and their mixtures is being carried out in this laboratory [1–4]. The heat capacities and transition parameters of neopentylglycol (NPG) and pentaerythritol (PE) have been reported [5,6]. The solid–solid transition enthalpy of NPG, used as a solid–solid phase-change material for the storage of solar energy or low-temperature heat energy, seems to be rather low, whereas the solid–solid transition temperature of PE seems to be rather high. Therefore, we intend to investigate mixtures of these two compounds in order to determine their suitability as energy storage material. This paper reports the heat capacities and transition parameters for the mixture in different mole ratios.

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EXPERIMENTAL

Samples for the experiments were prepared in the following manner. Neopentylglycol (No. 1 Reagent Manufactory, Shanghai) was sublimed twice. The purity of the calorimetric sample of the compound was found to be 99.37 mol.% from the analysis of its equilibrium melting curve [5]. Pentaerythritol (No. 1 Reagent Manufactory, Shanghai) was sublimed and recrystallized twice from distilled water. The purity of the calorimetric sample of the compound was found to be 99.96% by chemical analysis [6]. The two purified substances were mixed and ground into fine powder in the desired mole ratios. The mixture was heated to produce a clear liquid, and ground into a fine powder again after cooling to room temperature.

The heat capacity and phase transition parameters were measured by means of an automated adiabatic calorimeter [7]. The operation of the calorimeter was checked by means of the measurement of the heat capacity of α-Al_2O_3. The heat capacity of the empty container was measured again.

The experimental molar heat capacities for the mixtures in the five mole ratios are shown in Figs. 1–5 and are listed in Table 1.

From Figs. 1–5, three phase transition peaks can be seen for the mole ratio mixtures 20:80, 35:65, 50:50 and 65:35; two appear for the mole ratio 80:20. From macroscopic observation and an analysis of the experimental data, two of the three peaks indicate solid–solid transitions and the other indicates melting, in the cases of the former four mole ratios. For the mole ratio 80:20, one peak indicates a solid–solid transition and the other is considered to be an overlap of a solid–solid transition peak and a melting peak.

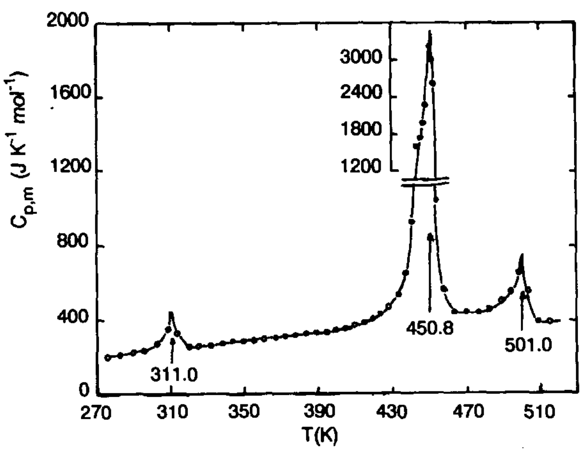

Fig. 1. Experimental molar heat capacity of mixture of NPG and PE in 20:80 mole ratio.

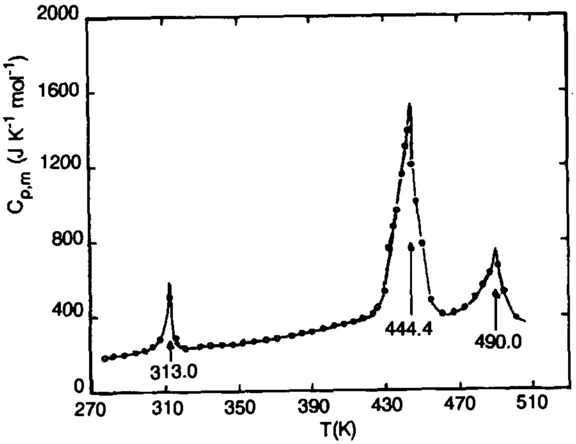

Fig. 2. Experimental molar heat capacity of mixture of NPG and PE in 35:65 mole ratio.

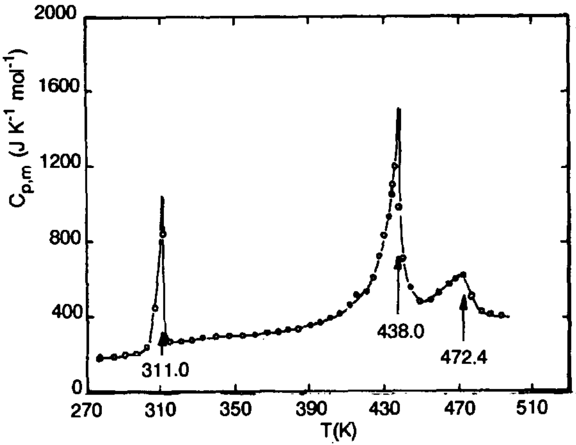

Fig. 3. Experimental molar heat capacity of mixture of NPG and PE in 50:50 mole ratio.

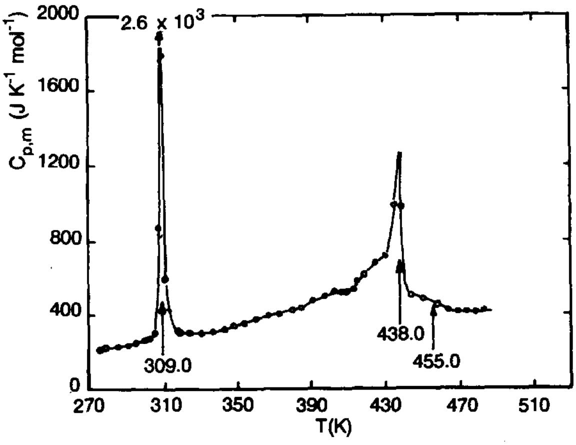

Fig. 4. Experimental molar heat capacity of mixture of NPG and PE in 65:35 mole ratio.

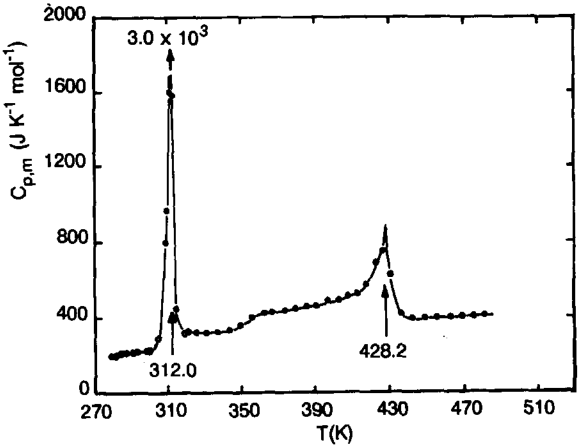

Fig. 5. Experimental molar heat capacity of mixture of NPG and PE in 80:20 mole ratio.

The enthalpies of the mixtures in the five mole ratios were obtained by numerical integration of the heat capacity points checked against large-scale plots; the transition parameters thus obtained are given in Table 2. The "normal heat capacities" in the transition regions were obtained by extrapolation of the experimental heat capacities in the non-transition regions. Because the continuous solid–solid transition overlaps with the melting, the total enthalpies of the two transitions were measured in the wider temperature ranges for the mixtures in mole ratios 65:35 and 80:20. The transition parameters of pure NPG and PE are also given in Table 2 for purposes of comparison.

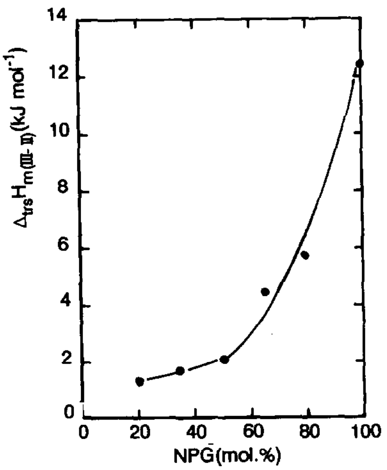

Fig. 6. The enthalpy dependences of the solid III → II transition on the mole ratio of the NPG–PE mixtures.

TABLE 1

Experimental molar heat capacities of NPG–PE mixtures in different mole ratios

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
20:80 mole ratio		35:65 mole ratio		50:50 mole ratio		65:35 mole ratio		80:20 mole ratio	
276.07	201.85	277.17	182.62	277.69	175.28	275.40	207.82	278.61	192.96
282.61	213.45	281.93	194.72	284.53	182.14	277.95	218.73	281.98	196.47
289.90	224.09	287.93	194.85	290.75	195.19	285.03	222.55	284.81	204.23
295.61	233.69	293.70	207.97	297.03	196.47	290.81	234.93	287.42	209.13
302.69	278.30	299.20	221.31	302.69	229.19	295.81	245.31	291.42	213.74
308.56	351.12	303.31	241.65	306.85	445.09	299.20	258.50	293.64	216.32
313.84	324.12	307.13	277.64	311.06	839.47	302.45	275.86	298.13	223.22
319.97	258.15	312.24	500.76	314.96	262.98	305.53	298.96	300.26	226.63
325.31	260.58	315.81	282.32	320.70	263.01	307.82	867.08	305.30	283.28
331.66	265.94	320.59	231.86	326.42	271.65	308.93	2593.7	308.89	795.19
337.72	276.62	328.97	241.90	332.94	282.78	309.68	1691.9	310.22	960.51
343.76	282.69	334.97	244.98	339.87	286.41	311.08	594.19	311.52	1588.7
349.70	286.32	340.85	250.51	346.70	293.95	317.53	311.80	312.46	1578.8
355.52	291.36	346.65	252.15	354.07	297.34	318.40	309.00	314.72	443.41
361.16	297.52	352.23	262.32	360.81	303.33	324.02	306.52	318.84	307.79
366.85	305.88	358.38	271.77	367.30	311.36	330.05	304.68	320.50	319.92
371.95	312.81	365.25	278.61	373.65	315.53	336.20	309.96	324.83	319.94
377.66	319.51	371.81	292.03	378.29	328.31	342.51	316.94	330.76	317.14
383.27	321.92	378.43	297.51	384.55	336.52	348.08	339.50	336.58	315.56
388.80	330.28	384.63	308.06	390.44	354.64	354.38	349.09	342.40	315.40
394.31	330.34	390.63	317.47	396.22	367.45	360.74	371.09	343.22	328.37
399.66	342.05	396.42	333.97	401.59	394.08	366.92	390.96	349.38	355.79
404.76	358.66	402.06	344.35	406.58	418.80	373.17	401.58	355.66	389.30
409.74	370.97	407.65	356.54	411.22	459.55	379.79	422.93	362.07	418.41
414.58	385.77	413.03	366.88	415.42	513.28	384.90	434.66	366.81	421.21
419.22	405.10	418.21	393.42	420.65	532.95	391.31	468.97	373.18	432.26
423.64	431.28	422.99	416.24	424.23	602.96	397.41	495.52	379.31	441.58
428.41	472.25	425.67	443.97	427.36	722.52	403.50	521.08	385.36	451.50
433.36	536.68	429.95	521.01	430.14	826.93	406.30	511.80	391.26	456.88
437.67	648.67	431.94	756.93	432.51	934.33	409.72	521.08	396.83	485.35
441.15	920.88	434.69	873.35	434.65	1049.3	412.91	532.72	402.28	489.91
443.49	1587.1	437.30	956.84	435.27	1101.1	415.83	570.47	407.96	515.38
445.25	1707.8	439.71	1142.0	436.46	1198.6	419.07	606.86	412.87	521.22
446.69	1966.2	441.86	1297.9	438.55	979.95	424.69	674.43	417.73	566.18
447.99	2259.1	443.71	1385.2	440.71	708.63	429.95	716.24	422.19	682.61
449.24	2496.4	445.71	1198.9	444.39	555.81	434.36	981.53	426.21	747.09
450.23	3220.4	447.71	1006.8	449.30	486.40	438.14	975.11	430.49	625.07
451.23	2994.0	450.56	783.72	454.78	489.26	443.31	494.91	436.05	417.26
452.17	2626.3	455.11	479.13	459.62	535.81	450.41	485.28	442.53	390.92
454.05	1039.8	461.54	406.18	464.19	571.56	457.25	455.75	449.12	392.25
457.93	566.25	467.43	417.55	468.50	602.25	463.69	418.67	455.65	395.44
463.45	445.96	473.00	444.42	472.65	623.47	468.72	416.54	462.13	399.23
470.09	441.76	478.19	494.29	476.95	510.42	473.37	414.76	468.40	398.92
476.21	440.90	482.91	562.52	482.04	423.92	478.12	415.35	474.58	401.90
482.44	463.32	487.16	619.80	487.53	409.97	482.65	419.46	480.70	405.73

TABLE 1 (continued)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
20:80 mole ratio		35:65 mole ratio		50:50 mole ratio		65:35 mole ratio		80:20 mole ratio	
488.37	505.01	490.95	666.10	493.32	405.71				
493.92	549.51	494.66	528.47						
498.54	645.24	500.75	380.07						
503.51	556.90								
509.40	388.35								
515.70	391.90								

DISCUSSION

It is noteworthy that the heat capacities from 350 K to the temperature of the solid–solid transition for mixtures of mole ratios 65:35 and 80:20 are clearly higher than those for the mixtures of mole ratios 20:80, 35:65 and 50:50. This higher heat capacity is considered to represent a combined effect of the melting of excess NPG in the mixtures and the solid III → II transition. We think that the mixtures in mole ratios 65:35 and 80:20 have considerable fluidity from 350 K to the temperature of the solid II → I transition, although they are not liquid.

From Table 2 it can be seen that the solid III → II transitions for the NPG–PE mixtures occur in the temperature range from 309.0 to 312.0 K, which is slightly lower than 314.8 K, the temperature of the solid–solid transition of pure NPG. From Fig. 6 it can be seen that the enthalpies of the solid III → II transition for the mixtures decrease with increasing content of PE in the mixtures. This information seems to suggest that NPG–PE mixture is not a valuable solid–solid phase-change material for the storage of thermal energy in the temperature range 300–400 K.

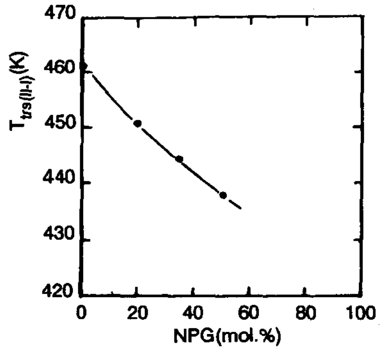

Fig. 7. The temperature dependences of the solid II → I transition on the mole ratio of the NPG–PE mixtures.

TABLE 2

Transition parameters of NPG, PE and their mixtures in different mole ratios

NPG mol.%	$T_{trs(III \to II)}$ (K)	$\Delta_{trs}H_{m(III \to II)}$ (kJ mol^{-1})	$T_{trs(II \to I)}$ (K)	$\Delta_{trs}H_{m(II \to I)}$ (kJ mol^{-1})	$T_{(II \to melt)}$ (K)	$\Delta_{trs}H_{(II \to melt)}$ (kJ mol^{-1})	T_{melt} (K)	$\Delta_{melt}H_m$ (kJ mol^{-1})
0			461.6 [a]	41.37 [a]			531 [b]	5.0 [b]
20	311.0	1.29	450.8	27.18			501.0	3.14
35	313.0	1.71	444.4	14.14			490.0	3.53
50	311.0	2.06	438.0	8.77			472.4	2.48
65	309.0	4.42			350–464	8.61		
80	312.0	5.72			350–442	7.24		
100	314.8 [c]	12.41 [c]					403.3 [c]	4.44 [c]

[a] From ref. 6.
[b] From ref. 8.
[c] From ref. 5.

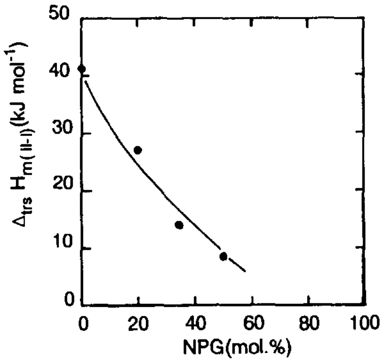

Fig. 8. The enthalpy dependences of the solid II → I transition on the mole ratio of the NPG–PE mixtures.

The temperature and enthalpy dependences of the solid II → I transition on the mole ratio of the NPG–PE mixtures are shown in Figs. 7 and 8, respectively. They indicate that both the temperature and the enthalpy of the solid II → I transition decrease with decreasing content of PE in the mixture. Therefore, we consider that NPG–PE mixtures have some potential use in the storage of thermal energy in the temperature range 438–461 K, depending on the practical need for the temperature and enthalpy of the solid–solid transition.

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