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HEAT CAPACITY AND PHASE TRANSITIONS OF MIXTURES OF PENTAERYTHRITOL AND TRIMETHYLOLPROPANE OVER THE SUPERAMBIENT TEMPERATURE RANGE

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ABSTRACT

The heat capacities and enthalpies of phase transition for mixtures of pentaerythritol and trimethylolpropane in different mole ratios were measured over the superambient temperature range by means of an automated adiabatic calorimeter. Two phase transitions, one a solid–solid transition and the other melting, were found for each mole ratio studied. The solid–solid transition of the mixture is considered to be due to the melting of trimethylolpropane among the lattice sites of pentaerythritol. The melting enthalpy of the mixture is mainly attributed to the breaking of the pentaerythritol lattice.

INTRODUCTION

The solid–solid transition temperature of pentaerythritol (PE), used as a solid–solid phase change material for storage of solar energy or low-temperature heat energy, seems to be rather high. The use of dopants is a effective method for reducing the solid–solid transition temperature of the compound. Chandra et al. [1] reported that the most effective dopant was trimethylolpropane (TMP), which lowered the transition temperature of PE from 461 to 321.4 K with a resultant enthalpy of 16.97 kJ mol^{-1} for the 50 : 50 mole-ratio system. To verify this interesting result and to study the temperature dependence of the transition enthalpies on the mole ratio for the PE–TMP system, we measured the heat capacities and phase transition parameters for this system at different mole ratios by means of an automated adiabatic calorimeter.

EXPERIMENTAL

Samples for the experiments were prepared in the following manner. Pentaerythritol reagent (No. 1 Reagent Manufactory, Shanghai) was sublimed and recrystallised twice from distilled water. Its purity was found to

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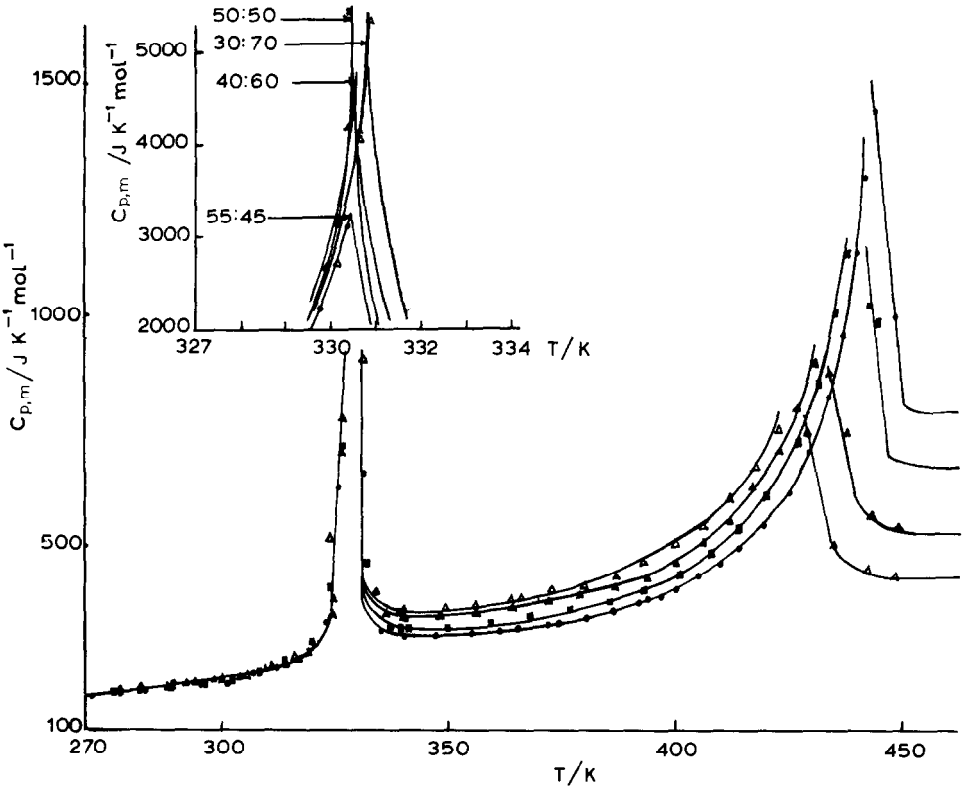

Fig. 1. Experimental molar heat capacities for the pentaerythritol–trimethylolpropane system in different mole ratios: ●,55 : 45; ■, 50 : 50; ▲, 40 : 60; △, 30 : 70.

be 99.96% by chemical analysis. Trimethylolpropane reagent (No. 1 Reagent Manufactory, Shanghai) was recrystallised from dry ether. The purity was found to be 99.12 mol% from the analysis of its equilibrium melting curve [2]. 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 [3]. The operation of the calorimeter was checked by means of the measurement of the heat capacity of α-Al_2O_3. A calorimetric cell, made of silver, contained 27.5980, 25.9031, 27.5974 and 29.6849 g, of the mixtures in the mole ratios 55 : 45, 50 : 50, 40 : 60 and 30 : 70, respectively.

The experimental molar heat capacities for the PE–TMP system are shown in Fig. 1. The deviation between the experimental points in non-phase transition regions and their smoothed values is within $\pm 0.3\%$.

The experimental molar heat capacities for the PE–TMP system are also listed in Table 1.

Direct enthalpy measurements were made on the PE–TMP system and the parameters of the phase transitions thus obtained are given in Table 2, in which T_1 and T_2 are the starting and finishing temperatures of the experiments, respectively, in the direct enthalpy measurements. The 'normal heat capacities' in the transition regions were obtained by extrapolation of the experimental heat capacities in the non-transition regions.

DISCUSSION

Figure 1 shows two transitions for the PE–TMP system at each mole ratio studied: the one at the lower temperature is the solid–solid transition and the higher temperature one is melting, depending on macroscopic observations. The temperature and enthalpy dependences of the solid–solid transition on the mole ratio of the PE–TMP system are shown in Fig. 2. To discuss the nature of the solid–solid transitions, the melting temperature and enthalpy of TMP are also shown in Fig. 2 as the starting point of the two curves in the figure. As seen from Fig. 2, the temperatures and enthalpies of the solid–solid transitions are lower than the melting temperature and

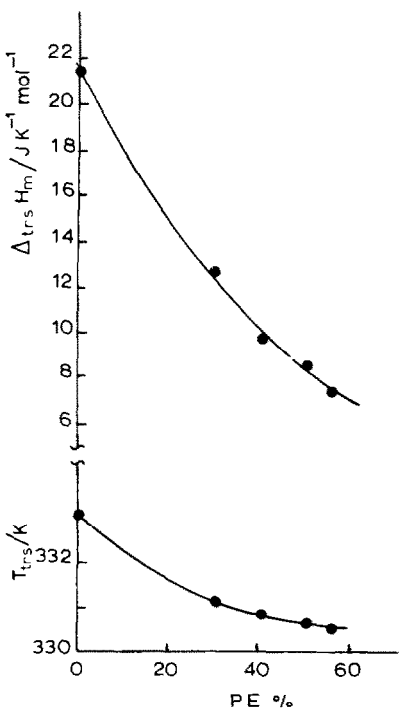

Fig. 2. The temperature and enthalpy dependences of the solid–solid transition on the mole ratio for the pentaerythritol–trimethylolpropane system.

TABLE 1

Experimental molar heat capacities of pentaerythritol–trimethylolpropane 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})
PE (55 mol%)–TMP (45 mol%)		PE (50 mol%)–TMP (50 mol%)		PE (40 mol%)–TMP (60 mol%)		PE (30 mol%)–TMP (70 mol%)	
271.73	180.39	277.19	193.06	292.91	203.69	277.53	192.40
278.17	187.84	283.26	196.19	299.08	210.04	283.57	199.18
284.32	193.52	290.73	202.87	304.71	217.91	289.69	200.59
290.26	202.33	297.00	209.60	310.07	226.86	295.02	208.76
296.39	203.03	303.25	217.74	315.34	245.24	295.44	213.80
302.28	209.83	309.29	229.18	317.77	259.28	300.98	210.30
307.88	221.99	314.87	261.43	320.44	265.58	306.58	222.65
313.27	238.95	320.06	304.44	320.08	261.48	311.91	241.58
318.71	256.00	324.55	417.74	324.62	354.62	316.89	269.09
323.34	342.35	327.85	727.35	324.78	388.30	324.47	517.84
326.65	630.99	329.54	1852.3	327.64	782.48	327.33	702.49
328.84	1172.7	330.33	3478.5	329.20	1709.0	329.25	1699.0
329.93	2307.0	330.64	5545.7	330.02	2744.4	330.26	2794.9
330.52	3594.7	332.46	463.20	330.51	4285.0	330.78	4154.3
331.83	662.16	336.87	313.41	330.79	4247.0	331.11	5450.75
335.17	299.22	341.59	322.34	331.62	1038.8	332.44	907.08
340.67	298.44	340.47	309.39	334.18	401.99	335.69	337.18
347.29	311.13	349.87	324.69	337.90	368.16	340.04	345.30
355.05	315.20	359.57	338.57	340.01	347.43	340.26	355.52

361.46	322.65	368.27	353.39	348.02	350.22	348.85	361.32
365.49	328.44	377.19	364.66	356.26	359.26	356.47	366.50
371.82	333.92	385.53	377.77	364.05	366.89	363.93	385.11
373.85	338.39	393.49	404.02	371.75	383.76	366.08	392.28
380.08	348.82	400.89	437.84	379.62	393.14	373.19	411.30
386.05	363.86	407.72	478.70	386.96	398.33	380.30	419.97
391.89	375.52	414.04	529.75	393.80	430.20	387.09	436.81
394.33	384.44	419.98	601.67	400.14	469.03	393.56	465.82
397.49	385.05	426.87	725.42	406.08	502.03	399.64	501.18
399.80	405.76	431.55	851.98	411.78	555.27	405.96	546.48
404.97	434.72	435.61	1011.4	417.20	632.17	412.46	601.52
409.91	456.29	439.18	1137.3	422.91	711.97	418.34	673.13
414.55	493.92	442.70	1025.0	427.17	803.35	423.63	755.97
419.58	542.19	446.46	1000.0	431.00	899.62	428.76	748.52
424.84	614.52			434.64	884.12	434.87	503.77
429.48	710.08			438.60	746.54	442.28	445.30
433.58	827.40			443.43	567.88	448.03	443.17
437.16	959.42			448.98	543.59		
440.27	1138.1						
442.97	1301.6						
445.39	1452.9						
447.12	2935.4						
449.32	1002.8						

TABLE 2

Transition parameters of the pentaerythritol–trimethylolpropane system

T_{trs} (K)	T_1 (K)	T_2 (K)	$\Delta_{trs}H_m$ (kJ mol^{-1})	$\Delta_{trs}S_m$ (J K^{-1} mol^{-1})
PE (55 mol%)–TMP (45 mol%)				
Solid–solid				
330.52	315.06	334.63	7.39	
	315.92	339.32	7.56	
		mean value:	7.48	22.63
Melting				
447	397.28	448.25	12.01	26.86
PE (50 mol%)–TMP (50 mol%)				
Solid–solid				
330.64	321.78	335.13	8.97	
	317.76	334.20	8.22	
		mean value:	8.60	26.01
Melting				
439	412.28	450.97	6.49	14.79
PE (40 mol%)–TMP (60 mol%)				
Solid–solid				
330.79	319.85	336.08	10.07	
	317.60	339.82	9.37	
		mean value:	9.72	29.38
Melting				
431	383.35	446.12	5.77	13.38
PE (30 mol%)–TMP (70 mol%)				
Solid–solid				
331.11	321.38	333.17	12.70	
	320.62	336.16	12.83	
	319.18	338.08	12.57	
		mean value:	12.70	38.35
Melting				
423	390.49	439.02	5.10	12.06

enthalpy of TMP respectively, and decrease with the mole increment of PE in the PE–TMP system.

Using the data in Table 2, the ratios of the solid–solid transition enthalpy to the melting enthalpy of the TMP component for the PE–TMP systems at each mole ratio are calculated to be about 0.8. Also the entropies of the solid–solid transition of the system decreases rapidly with increasing PE content. This implies that the positional disorder of TMP molecules in the PE–TMP system, as it is molten, is limited by the molecules of PE at their lattice sites, and that complete disorder is not attained at the melting point of pure TMP. Furthermore, depending on macroscopic observations, the mechanical strength of the PE–TMP system at temperatures above the

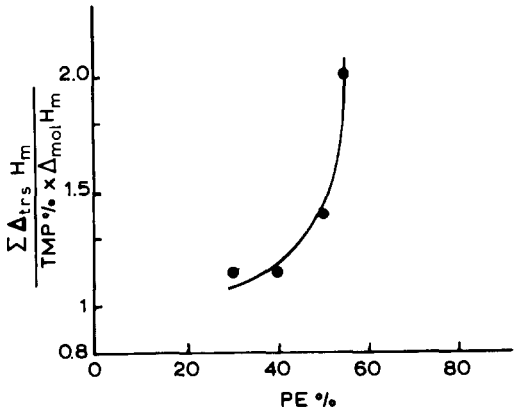

Fig. 3. The ratio of total transition enthalpy to the melting enthalpy of TMP component for the pentaerythritol–trimethylolpropane system.

solid–solid transitions decreases with increasing PE content. Therefore the solid–solid transition of the PE–TMP system can be considered to be due to the melting of TMP among the PE lattice.

The ratios of the total enthalpy, including the solid–solid and melting transition enthalpies, to the melting enthalpy of the TMP component for each mole ratio in the PE–TMP system are shown in Fig. 3. As seen from Fig. 3, these ratios are larger than 1, and increase with the mole content of PE. This shows that the melting enthalpy of the system is mainly attributed to the breaking of the PE lattice.

Due to its asymmetric molecular structure and high melting entropy (64.3 $J\ K^{-1}\ mol^{-1}$) [2], TMP could not be a plastic crystal, while PE is a typical plastic crystal. Apparently, mixing the two substances cannot produce a continuous range of solid solution. Moreover, the experimental solid–solid transition enthalpy obtained in this work for the PE–TMP system for the 50 : 50 mole ratio is much lower than the value obtained by Chandra et al. [1]. Therefore, we doubt whether the PE–TMP system could be a useful solid–solid phase change material for storage of solar energy or low-temperature heat energy.

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