

Properties of mixed-crystalline organic material prepared by zone levelling

IV. Melting properties and excess enthalpies of (*trans*-azobenzene + *trans*-stilbene)

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Homogeneous mixed crystals of (*trans*-azobenzene + *trans*-stilbene) were prepared. Molar heat capacities of the pure substances and the mixed crystals were determined at temperatures from 300 to 400 K. The melting temperatures and molar enthalpies of fusion were measured for *trans*-stilbene and *trans*-azobenzene. The melting temperatures are 341.06 K and 397.40 K; the molar enthalpies of fusion are $22.52 \text{ kJ} \cdot \text{mol}^{-1}$ and $27.69 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. From the measurements on the mixed crystals the excess molar enthalpy difference between the liquid and solid phases was obtained, and is about $-200x(1-x) \text{ J} \cdot \text{mol}^{-1}$. Finally the solidus and liquidus points were obtained from the heat-capacity curves of the levelled samples, the solidus curve was calculated, and was found to agree with the experimental solidus points (to within 1.5 K).

1. Introduction

This investigation is part of a project to study homogeneous mixed-crystalline organic material prepared by zone levelling. To form a continuous series of mixed crystals the pure substances must satisfy a number of conditions: the molecules must be similar in shape, they must be isostructural, and moreover the crystal structures must have almost the same packing coefficients.⁽¹⁾

Normally these mixed crystals are prepared by quenching a liquid mixture. This method often leads to inhomogeneities in the solid mixture. For organic crystals these inhomogeneities cannot be removed by annealing the solid mixture because of the low diffusion rate in the solid phase. Therefore in our laboratory an apparatus has been developed to prepare organic mixed crystals by the zone-levelling technique.⁽²⁾

In part I⁽³⁾ of this series we reported on the melting behaviour of zone-levelled samples of (*p*-dichlorobenzene + *p*-dibromobenzene). Our results showed that at a heating rate high enough to prevent molecule exchange between solid and liquid

phases the mixtures exhibit a melting behaviour which resembles that of a pure substance: if no exchange takes place the solid mixture can yield only a liquid mixture with identical composition. This implies that the solid mixtures start melting at that temperature for which the solid and liquid phases have equal chemical potentials. In part II⁽⁴⁾ we described the vapour-pressure measurements on the same mixture. Mixtures prepared by zone-levelling showed considerable lower vapour pressures than samples prepared by quenching. Recently we prepared mixed crystals of (*trans*-azobenzene + *trans*-stilbene). From this mixture it was possible not only to prepare homogeneous crystalline material but we also succeeded in preparing mixed single crystals, the crystal structures of which we solved by X-ray and neutron diffraction.⁽⁵⁾ In part III⁽⁶⁾ of this series we reported on the vapour-pressure measurements of (*trans*-azobenzene + *trans*-stilbene). In this part the main aim will be to determine the excess enthalpies of the solid and liquid mixtures and to study the melting behaviour of quenched and levelled samples. All the experiments were carried out using an adiabatic calorimeter.

2. Experimental

Trans-azobenzene was purified by vacuum sublimation. The purity of the sample was determined by adiabatic calorimetry and found to be (99.84 ± 0.04) moles per cent. *Trans*-stilbene, which was purified by counter-current crystallization, was supplied by the physical laboratory of T.N.O. Zeist, the Netherlands. The purity of the sample was determined by g.l.c.⁽⁷⁾ and by adiabatic calorimetry and was found to be (99.95 ± 0.05) moles per cent.

All measurements were carried out with a new automatic adiabatic calorimeter, which was calibrated with sapphire (N.B.S. Standard reference material). About 1000 Pa of Helium was admitted to the sample container to increase thermal conductivity. *Trans*-azobenzene, *trans*-stilbene, three levelled samples, and a mechanical mixture were measured. To obtain the difference between a levelled and a quenched sample one of the samples ($x = 0.503$) was quenched and measured again. The mole fractions of the samples and the experimental conditions are given in table 1.

TABLE 1. The mole fractions x , the sample masses m , time t_1 for heater on, time t_2 for heater off, and experimental conditions used during the measurements on $\{(1-x)\text{trans-C}_6\text{H}_5\text{N}:\text{NC}_6\text{H}_5 + (x)\text{trans-C}_6\text{H}_5\text{CH}:\text{CHC}_6\text{H}_5\}$

x	m/g	t_1/s	t_2/s	sample	x	m/g	t_1/s	t_2/s	sample
0 (1) ^a	7.1	1000	1500	—	0.715	1.6	500	1000	levelled
0 (2) ^a	4.9	1500	2000	—	0.503	2.4	500	1000	quenched
0.226	2.3	500	1000	levelled	0.506	4.3	500	1000	mechanical mixture
0.503	2.4	500	1000	levelled	1	5.6	1500	2000	—

^a For *trans*-azobenzene ($x = 0$) (1) refers to the first sample used and (2) refers to the second sample used.

3. Results and discussion

MOLAR HEAT CAPACITIES AND ENTHALPIES OF FUSION

The molar heat capacities of sapphire are given in table 2. From table 3 it can be inferred that at round temperatures the deviation between the values published by the N.B.S.⁽⁸⁾ and those measured by us are all within 0.15 per cent. Between 300 and 400 K we obtained a molar enthalpy difference of $8848 \text{ J} \cdot \text{mol}^{-1}$, the value of the N.B.S. being $8844 \text{ J} \cdot \text{mol}^{-1}$.

The molar heat capacities of the pure substances and those of the mixtures are given in table 4. For *trans*-azobenzene an unexpected effect was observed. After the first series of measurements the sample was quenched and measured again. The molar heat capacities of the solid phase obtained during the second run differed from those of the first run. Therefore a second sample of *trans*-azobenzene was put into the calorimeter vessel and three alternating measuring and quenching cycles were carried out. Again a difference was found between the first and second run: the heat capacities of the solid phase obtained during the first run were again lower than those of the second run. Because this trend was not continued in the third run (see figure 1) we concluded that the change in the molar heat capacities of the solid phase could not be caused by decomposition of *trans*-azobenzene during the measurements but must be due to a change in the solid phase, although this could not be confirmed by powder diffraction. In our calculations (see below) we used the

TABLE 2. Molar heat capacities of sapphire

$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$
304.57	80.21	338.53	86.88	364.02	91.12	388.89	94.66
308.40	81.03	342.21	87.57	367.61	91.66	392.40	95.12
312.22	81.82	345.88	88.13	371.18	92.18	395.90	95.57
316.03	82.60	349.53	88.76	374.75	92.70	399.40	95.99
319.83	82.34	353.17	89.58	378.30	93.21	402.88	96.59
327.38	84.81	356.80	89.96	381.84	93.70	406.36	96.96
331.11	85.51	360.42	90.52	385.37	94.19	409.83	97.30
334.83	86.20						

TABLE 3. Molar heat capacities of sapphire at round temperatures

$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$		$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	
	our results	N.B.S. ⁽⁸⁾		our results	N.B.S. ⁽⁸⁾
310	81.42	81.52	360	90.45	90.45
320	83.40	83.49	370	92.00	91.97
330	85.31	85.37	380	93.44	93.41
340	87.20	87.16	390	94.81	94.78
350	88.85	88.84	400	96.10	96.08

TABLE 4. Experimental heat capacities of $\{(1-x)\text{trans-C}_6\text{H}_5\text{N}:\text{NC}_6\text{H}_5 + (x)\text{trans-C}_6\text{H}_5\text{CH}:\text{CHC}_6\text{H}_5\}$

T K	$C_{p,m}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T K	$C_{p,m}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T K	$C_{p,m}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T K	$C_{p,m}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
<i>trans-azobenzene</i>							
299.14	228.94	335.67	262.21	350.76	47028	364.67	312.79
301.33	230.32	337.72	279.71	340.78	44898	367.55	314.25
303.15	232.06	339.33	666.49	340.81	51552	370.51	315.71
305.69	233.44	340.07	4293.1	340.83	64862	373.46	317.22
307.87	235.24	340.26	9246	341.72	362.52	376.40	318.70
310.04	237.25	340.36	14437	343.57	302.53	379.34	320.25
312.21	239.10	340.43	20276	345.50	303.42	382.27	321.56
314.37	240.81	340.48	26317	347.44	304.51	385.19	323.25
316.53	242.51	340.52	31402	349.37	304.96	388.11	324.50
318.69	244.28	340.55	36432	351.29	305.97	391.02	325.82
320.84	246.03	340.58	42939	353.21	306.96	393.93	327.04
323.00	247.80	340.61	42249	355.13	307.95	396.83	328.77
325.14	248.05	340.64	44917	357.04	308.95	399.72	330.36
327.27	251.54	340.66	51222	358.96	309.95	402.62	331.63
329.38	253.09	340.68	49614	360.86	310.94	405.50	333.04
331.49	255.26	340.71	48717	362.77	311.81	408.39	334.40
333.59	257.30	340.73	47705				
<i>trans-stilbene</i>							
317.36	248.96	354.93	280.67	390.55	311.58	397.40	102693
320.86	252.01	358.25	283.42	393.71	318.50	397.40	162171
324.36	254.71	361.54	286.44	396.30	696.42	397.40	800866
327.84	255.65	364.82	289.08	397.34	56253	398.76	430.85
331.30	260.64	368.09	291.81	397.37	227504	401.61	353.56
334.72	263.55	371.34	294.40	397.38	370028	404.60	354.70
338.13	266.39	374.57	296.91	397.38	501281	407.59	356.19
341.53	269.36	377.79	300.13	397.39	503197	410.57	357.67
344.90	272.35	381.00	302.61	397.39	667368		
348.26	275.08	384.19	305.79	397.39	696906		
351.61	277.88	387.38	307.77				
mixed crystal (levelled) $x = 0.226$							
295.96	226.50	331.51	254.38	352.19	2738.1	374.44	321.39
297.52	226.46	333.03	255.66	352.71	2416.3	375.87	321.94
299.07	228.19	334.54	257.30	353.26	2383.4	377.30	322.44
300.63	229.60	336.05	258.62	353.82	2305.8	378.73	322.87
302.18	231.08	337.56	259.93	354.40	2090.4	380.16	323.43
303.74	231.96	339.07	262.40	355.03	1923.3	381.58	324.32
305.29	233.53	340.58	263.37	355.69	1687.9	383.01	325.23
306.85	234.89	342.08	264.58	356.42	1457.0	385.85	327.18
308.40	236.70	343.58	268.38	357.21	1307.8	387.27	327.94
309.96	237.30	345.08	278.47	358.04	1225.8	388.70	328.58
311.51	238.74	346.54	310.10	358.94	945.34	390.12	328.98
313.06	239.99	347.90	498.57	360.13	340.96	391.54	329.62
314.62	240.78	348.89	1614.22	361.55	317.45	392.97	330.74
316.17	242.37	349.45	3453.6	362.99	318.32	394.39	331.44
320.82	245.73	349.82	4750.1	364.42	318.55	397.24	333.39
322.35	247.04	350.13	5478.7	365.86	317.42	398.66	333.48
323.48	248.32	350.41	5677.3	367.29	317.87	400.08	333.75
325.41	249.84	350.70	5423.6	368.72	318.61	401.50	334.80
326.94	250.82	351.00	4804.7	370.16	319.00	402.91	335.47
328.47	251.73	351.34	4138.5	371.59	319.06	404.33	336.32
329.99	253.71	351.73	3457.81	373.02	319.68		

TABLE 4—continued

T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$
mixed crystal (levelled) $x = 0.503$							
300.37	231.16	333.74	259.15	361.35	2354.7	373.74	1580.9
301.89	233.05	335.23	260.44	361.82	3196.6	374.43	1627.0
303.41	233.82	336.72	261.78	362.24	3212.2	375.11	1646.9
304.94	235.07	338.21	262.98	362.68	2838.6	375.81	1439.0
306.46	236.77	339.70	264.20	363.18	2326.2	376.80	490.02
307.98	237.78	341.18	265.78	363.74	1978.2	378.13	329.24
309.51	239.30	342.67	267.05	364.36	1851.7	379.53	329.73
311.03	240.11	344.15	268.05	365.00	1722.7	380.93	330.10
312.55	241.55	345.63	269.43	365.66	1684.2	382.33	330.98
314.08	242.63	347.10	270.64	366.32	1719.2	383.73	331.87
315.60	244.22	348.58	271.92	366.98	1686.5	385.13	332.61
317.12	245.55	350.05	273.16	367.65	1668.5	386.53	333.14
318.65	246.77	351.52	274.56	368.32	1666.2	387.93	333.87
320.17	248.73	352.99	276.38	368.99	1670.3	389.32	334.57
321.69	249.43	354.46	278.58	369.66	1669.5	390.72	335.09
324.74	252.25	355.92	283.51	370.33	1681.4	392.11	335.99
326.24	252.93	357.37	305.10	371.00	1680.1	393.50	336.46
327.75	254.23	358.73	430.22	371.67	1654.1	394.90	337.88
329.25	255.56	359.87	851.98	372.35	1629.4	396.29	338.41
330.75	257.85	360.72	1489.57	373.04	1569.8	397.68	343.09
332.24	258.03						
mixed crystal (levelled) $x = 0.715$							
297.96	233.42	337.05	263.72	369.28	371.88	384.89	2676.5
299.93	232.37	338.97	265.50	370.98	553.39	385.70	2238.8
301.89	234.12	340.89	267.39	372.47	913.35	386.99	428.80
303.85	235.34	342.81	268.93	373.65	1671.0	388.76	338.80
305.82	237.41	344.73	270.56	374.53	1773.3	390.57	340.11
307.78	238.75	346.64	272.12	375.28	2738.4	392.39	340.80
309.74	240.02	348.55	273.73	376.11	1998.5	394.20	342.08
311.70	242.53	350.45	275.53	377.08	1619.1	396.01	347.37
313.67	243.97	352.36	277.22	378.11	1652.8	397.83	343.32
315.63	245.77	354.26	279.05	379.10	1823.8	399.65	344.09
317.60	247.53	356.16	280.68	380.04	1994.7	401.46	345.58
319.57	249.32	358.05	282.70	380.93	2151.4	403.27	349.60
325.44	253.69	359.95	284.90	381.79	2329.8	405.08	346.92
327.38	255.40	361.83	287.10	382.60	2528.0	406.89	347.19
329.32	256.99	363.72	290.63	383.37	2666.9	408.70	348.31
331.26	258.61	365.59	297.37	384.13	2684.6	410.51	349.19
333.19	260.47	367.46	314.75				
mixed crystal (quenched) $x = 0.503$							
301.81	232.64	320.04	247.89	336.59	263.86	350.40	465.01
304.85	235.19	321.37	249.03	338.08	268.05	351.65	493.09
306.37	236.38	323.09	250.36	339.55	279.76	352.87	528.65
309.41	239.40	326.13	252.96	340.99	311.77	354.06	579.48
310.93	240.46	327.63	253.82	342.40	347.29	355.20	640.07
312.45	241.65	329.13	255.10	343.77	362.18	356.29	711.78
313.96	242.94	330.63	256.54	345.13	373.29	357.33	796.11
315.48	244.08	332.13	258.01	346.48	385.39	358.32	895.24
317.00	245.53	333.62	259.60	347.82	402.91	359.25	988.41
318.52	246.58	335.11	262.58	349.12	432.57	360.13	1127.3

TABLE 4--continued

T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$
mixed crystal (quenched) $x = 0.503$ —continued							
360.96	1207.0	368.22	1598.8	374.80	1588.7	387.63	335.17
361.76	1285.6	368.90	1613.8	375.55	1214.3	390.41	336.51
362.54	1363.0	369.58	1628.2	376.56	526.59	391.80	337.06
363.28	1429.9	370.26	1654.6	377.86	328.51	393.19	337.62
364.01	1478.9	370.92	1704.6	379.26	329.52	394.58	338.17
364.73	1519.7	371.58	1738.4	380.66	330.67	395.97	339.26
365.44	1541.5	372.23	1780.1	382.06	331.83	397.36	339.94
366.14	1561.0	372.86	1818.2	383.45	332.66	398.74	340.65
366.83	1573.8	373.49	1824.4	384.85	333.48	400.13	341.43
367.53	1585.6	374.13	1759.7	386.24	334.18		
mechanical mixture $x = 0.506$							
314.76	244.22	343.61	527.26	367.35	1052.7	381.60	369.40
316.05	244.82	344.59	437.97	367.97	1100.9	382.73	339.64
317.36	246.16	345.67	346.13	368.56	1122.1	383.88	331.94
318.66	247.31	346.84	294.42	369.16	1125.5	385.04	332.57
319.96	248.46	348.06	285.60	369.75	1132.3	386.19	333.42
321.26	251.21	349.36	198.98	370.34	1154.6	387.35	333.79
326.42	253.29	350.64	314.81	370.92	1176.0	388.50	334.14
327.70	254.45	351.78	372.89	371.49	1187.4	389.66	334.80
328.98	255.67	352.86	410.54	372.06	1190.2	390.81	335.36
330.25	256.45	353.89	441.68	372.63	1193.0	391.96	335.92
331.52	257.52	354.90	467.07	373.21	1171.4	393.11	336.48
332.79	258.58	355.88	496.26	373.79	1149.8	394.26	337.11
334.05	260.19	356.83	529.24	374.38	1090.1	395.41	337.89
335.31	261.77	357.75	561.07	375.00	1024.5	396.56	338.37
336.57	263.48	358.64	606.66	375.64	1013.3	397.71	338.85
337.83	267.26	359.49	656.35	376.28	990.9	398.85	339.79
339.05	304.11	360.30	734.65	376.92	1011.0	400.00	339.86
339.98	954.26	361.08	738.41	377.57	984.5	401.14	342.89
340.47	2613.5	361.85	758.81	376.81	5586.9	402.29	340.77
340.78	2603.7	362.60	797.53	377.24	875.05	403.43	341.66
341.02	4635.9	363.34	834.78	377.97	762.37	404.57	341.74
341.09	9636.4	364.05	872.65	378.66	1065.65	405.72	343.07
341.42	1295.7	364.74	904.88	379.48	437.86	406.86	343.54
342.04	889.10	365.42	941.89	380.52	414.34	408.00	344.08
342.76	768.72	366.08	977.02			409.14	347.57
		366.72	1011.8				

results obtained during the first run on the first sample. These results are in good agreement with those obtained during the first run on the second sample, as can be inferred from table 7: the $\Delta_{320K}^{400K} H_m$ values, *i.e.* the enthalpy changes between 320 and 400 K, of these two runs are consistent. The smoothed molar heat capacities at round temperatures are given in table 5. From this table it can be concluded that: the excess heat capacities of $\{(1-x)trans-C_6H_5N:NC_6H_5 + (x)trans-C_6H_5CH:CHC_6H_5\}$ are zero within the experimental error which means that they can be expressed as

$$C_{p,m}(T, x) = (1-x)C_{p,m}(T, 0) + xC_{p,m}(T, 1). \quad (1)$$

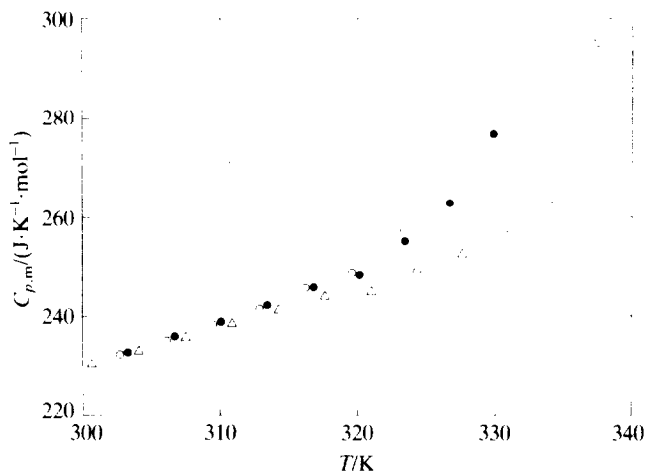


FIGURE 1. Molar heat-capacity curves of the solid phases of *trans*-azobenzene in three succeeding runs. Δ , First run; \circ , second run; \bullet , third run.

The purities as well as the melting temperatures of the pure substances were calculated from the reciprocal ($1/F$) of the melted fraction as a function of T . Using this method no marked change in purity was found between the first and second run on the *trans*-azobenzene samples. This again indicates that the observed change in heat capacity is not caused by the decomposition of *trans*-azobenzene. The enthalpies of fusion and the melting temperatures are collected in table 6. Some difficulties were encountered in calculating the enthalpies of fusion of the mixed crystals and the excess molar enthalpy difference $\Delta_{320\text{ K}}^{400\text{ K}} H_m^E(x)$ between liquid at 400 K and solid phase at 320 K. Due to the relatively large temperature range of melting of the mixed crystals the subtraction of the base values from the heat capacities gives rise to some inaccuracies. Although these errors are relatively small

TABLE 5. Smoothed molar heat capacities at round temperatures of the pure substances and the mixed crystals of $\{(1-x)\textit{trans}\text{-C}_6\text{H}_5\text{N}:\text{NC}_6\text{H}_5 + (x)\textit{trans}\text{-C}_6\text{H}_5\text{CH}:\text{CCH}_6\text{H}_5\}$

T/K	x	$C_{p,m}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$					
		0	0.226 levelled	0.503 levelled	0.503 quenched	0.506 mechanical	0.715 levelled
300		229.33	229.10	230.22			232.42
310		237.22	237.34	239.62	239.85		240.29
320		245.31	245.08	248.62	247.83	248.58	249.71
330		253.64	253.71	256.69	255.93	256.25	257.55
340		3810.69	263.16	264.53	288.11	1098.57	266.52
350		305.12	5231.16	273.12	455.89	197.96	275.07
360		310.51	366.44	926.75	1109.65	713.37	284.96
370		315.54	318.98	1671.71	1641.67	1140.72	427.08
380		320.81	323.35	300.49	321.55		1987.45
390		325.67	328.95	334.82	337.58	334.96	337.13
400		330.41	333.72		341.36	339.80	344.77
410							348.99
							354.64

TABLE 6. The triple-point temperatures and molar enthalpies of fusion of the pure substances

<i>l</i>	<i>trans</i> -azobenzene		<i>trans</i> -stilbene	
	this work	reference 9	this work	reference 9
$\Delta_{\text{fus}}^l H_m / (\text{kJ} \cdot \text{mol}^{-1})$	22.53 ± 0.03	22.53 ± 0.02	27.69 ± 0.02	27.4
$T_{\text{fus}} / \text{K}$	341.06	341.03	397.40	398 ± 0.5

in comparison with the molar enthalpy of fusion (less than 1 per cent), they determine to a large extent the accuracy of the excess molar enthalpy differences, which are expected to be very small. Therefore we decided to determine the molar enthalpy difference $\Delta_{320\text{ K}}^{400\text{ K}} H_m$ between 320 and 400 K for each sample. The enthalpy of fusion for all samples is incorporated in this temperature range. To obtain $\Delta_{320\text{ K}}^{400\text{ K}} H_m$, molar enthalpies of the solid and liquid phases were fitted to a second-order equation from which the values at 320 and 400 K were calculated. As can be inferred from the scheme shown in figure 2 the excess molar enthalpy difference $\Delta_{320\text{ K}}^{400\text{ K}} H_m^E(x)$ can be calculated from the measurements of the levelled (quenched) samples:

$$\Delta_{320\text{ K}}^{400\text{ K}} H_m^E(x) = \Delta_{320\text{ K}}^{400\text{ K}} H_m(x) - (1-x)\Delta_{320\text{ K}}^{400\text{ K}} H_m(0) - x\Delta_{320\text{ K}}^{400\text{ K}} H_m(1), \quad (2)$$

in which $\Delta_{320\text{ K}}^{400\text{ K}} H_m(x)$ stands for the molar enthalpy difference of the levelled (quenched) mixture and $\Delta_{320\text{ K}}^{400\text{ K}} H_m(0)$ and $\Delta_{320\text{ K}}^{400\text{ K}} H_m(1)$ stand for the molar enthalpy difference of *trans*-azobenzene and *trans*-stilbene respectively. Because the excess molar heat capacities are within the experimental error these are not incorporated in the calculations. The excess molar enthalpy of the liquid phase can be calculated from measurements done on a mechanical mixture:

$$H_m^{E,L}(400\text{ K}, x) = \Delta_{320\text{ K}}^{400\text{ K}} H_{m,\text{mech}}(x) - (1-x)\Delta_{320\text{ K}}^{400\text{ K}} H_m(0) - x\Delta_{320\text{ K}}^{400\text{ K}} H_m(1), \quad (3)$$

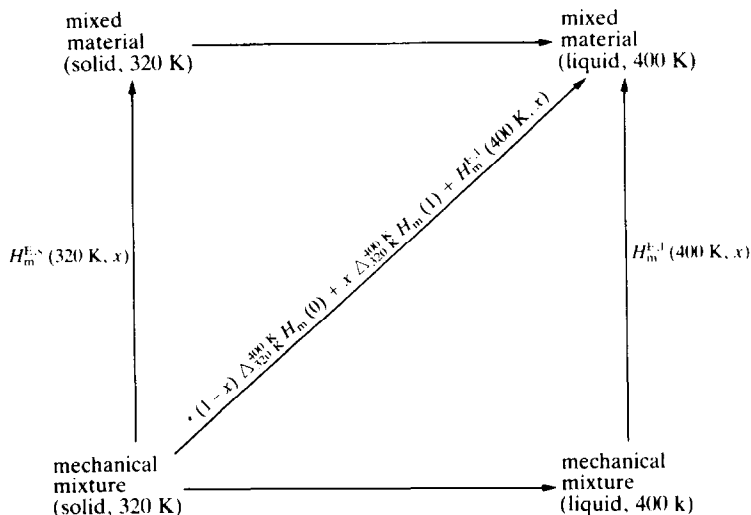


FIGURE 2. Flow diagram, which shows the relations between the enthalpies used.

in which $\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m, mech}}(x)$ denotes the molar enthalpy difference between the liquid mixture at 400 K and the mechanical solid mixture at 320 K. Finally, $H_{\text{m}}^{\text{E}, \text{l}}(400\text{ K}, x)$ and $\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}^{\text{E}}(x)$ can be used to calculate the excess molar enthalpy of the solid phase:

$$H_{\text{m}}^{\text{E}, \text{s}}(320\text{ K}, x) = H_{\text{m}}^{\text{E}, \text{l}}(400\text{ K}, x) - \Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}^{\text{E}}(x). \quad (4)$$

The results of the calculations are given in table 7 from which it is clear that $\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}^{\text{E}}(x)$ obtained for the levelled samples has very small negative values and

TABLE 7. The molar enthalpy difference $\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}(x)$ between 320 and 400 K, the excess molar enthalpy difference $\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}^{\text{E}}(x)$, and the excess molar enthalpy $H_{\text{m}}^{\text{E}, \text{l}}(400\text{ K}, x)$ of the liquid phase

x	$\frac{\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}(x)}{\text{J} \cdot \text{mol}^{-1}}$	$\frac{\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}^{\text{E}}(x)}{\text{J} \cdot \text{mol}^{-1}}$	$\frac{H_{\text{m}}^{\text{E}, \text{l}}(400\text{ K}, x)}{\text{J} \cdot \text{mol}^{-1}}$	
0	46477 (1, run 1) ^a			—
0	46432 (1, run 2)			—
0	46474 (2, run 1)			—
0	46377 (2, run 2)			—
0.227	47336	—65		levelled
0.501	48502	—51		levelled
0.501	48474	—37		quenched
0.506	48604		56	mechanical mixture
0.715	49234	—167		levelled
1	50569			—

^a (1, run 1) refers to the first run of the first sample used.

that no marked difference has been found between the levelled mixture and the quenched mixture. When expressed in parabolic form the excess molar enthalpy difference is given approximately by

$$\Delta_{320\text{ K}}^{400\text{ K}} H_{\text{m}}^{\text{E}}(x) \approx x(1-x)\{-200 \pm 300\} \text{ J} \cdot \text{mol}^{-1}.$$

The results of the measurements on the mechanical mixture indicate that the excess molar enthalpies of both the liquid and solid phase have small positive values.

MELTING BEHAVIOUR

The melting behaviour of the quenched and levelled mixtures is shown in figure 3. The levelled mixture melts over a smaller temperature range than the quenched mixture. This difference in melting behaviour between the levelled and quenched mixtures must be linked with inhomogeneities in the solid mixtures. This can be explained as follows. In cooling experiments the first solid appears at the liquidus temperature. On further solidification the composition of newly formed solid material changes and due to the low diffusion rate these composition changes will be maintained in the solid phase. Therefore the final amount of liquid mixture does not disappear at the solidus curve but a lowering of the solidus temperature occurs.

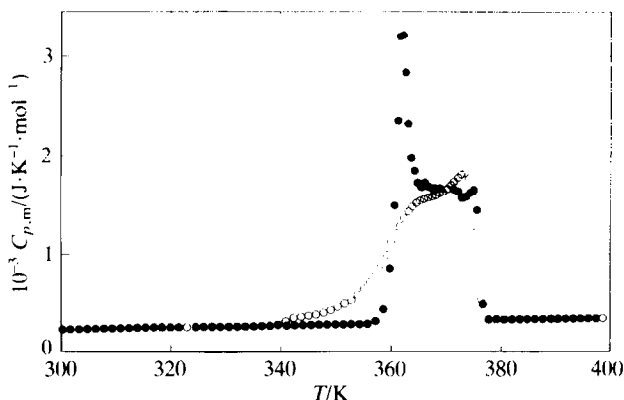


FIGURE 3. Heat-capacity curve of a levelled and a quenched mixture both with a mole fraction $x = 0.503$. ●, Levelled mixture; ○, quenched mixture.

On heating, the reverse process takes place: the solid mixture starts melting below the solidus temperature which corresponds to the mean composition of this mixture.

From the heat-capacity curves against temperature of the levelled mixtures one can determine the temperature at which the melting starts and the temperature at which the final amount of solid disappears (liquidus point). To check if the onset of melting does correspond to a solidus point we adopted the following course. The solidus curve can be obtained from the experimental liquidus points by an iterative procedure (referred to as LIQFIT),⁽¹⁰⁾ which makes use of intermediate phase-diagram calculations. Moreover the excess molar Gibbs energy difference between solid and liquid mixture can be calculated. From these calculations it appeared (see figure 4) that the experimental solidus points agree very well with the calculated

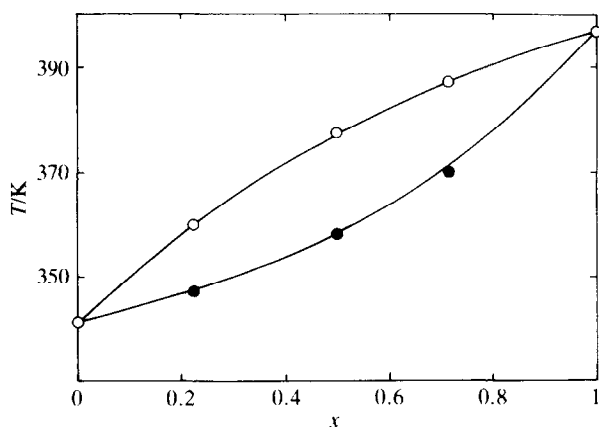


FIGURE 4. Phase diagram of the solid-liquid equilibrium of (*trans*-azobenzene + *trans*-stilbene). ○, Experimental liquidus points; ●, experimental solidus points; —, calculated solidus and liquidus curves.

solidus curve. The corresponding excess molar Gibbs energy difference is given by

$$\Delta_s^l G_m^E(x) = x(1-x)\{-530 - 360(1-2x)\} \text{ J} \cdot \text{mol}^{-1}.$$

This function is in agreement with those functions found from calculations⁽⁶⁾ using the experimental liquidus results from Vetter *et al.*⁽¹¹⁾ and from Kofler and Brandstätter.⁽¹²⁾

The melting behaviour of the levelled mixture heated in an adiabatic calorimeter is different from the melting behaviour of levelled samples measured with a d.s.c. (heating rate $0.01 \text{ K} \cdot \text{s}^{-1}$). The d.s.c. melting behaviour corresponds to that of the pure components, the difference being caused by a difference in heating rate. In the experiments carried out in this investigation the heating period (input period) is followed by a stabilization period. The total melting process takes about 24 h. This causes a near equilibrium state in the calorimeter vessel and an exchange of molecules between solid and liquid phases occurs at the solid-to-liquid interface. This process allows the solid mixture to melt on the solidus curve.

(*Trans*-azobenzene + *trans*-stilbene) does form nearly ideal mixed crystals over the whole mole-fraction range. The measurements show that the zone-levelling technique does form homogeneous mixed crystals and that those crystals do show a different melting behaviour from solid mixtures prepared by quenching.

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