diagrams developed from the experimental data for each mixture.

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Glossary

A	Helmholtz free energy
B	second virial coefficient
C	third virial coefficient
C_v	specific heat capacity at constant volume
G	Gibbs free energy
H	enthalpy
P	pressure
R	universal gas constant
S	entropy
T	absolute temperature
U	internal energy
Z	compressibility factor
Greek Letters	
ρ	density
Superscripts	
*	perfect gas value
Subscripts	
ref	reference-state value

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Phase Diagrams of Binary Solid Azole Systems

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Phase diagrams of the binary solid azoles pyrazole, imidazole, triazole, and tetrazole were measured. It was found that all binary mixtures formed simple eutectic systems except the imidazole–tetrazole system, which was found to form a 1:1 solid addition compound. Enthalpies of fusion for the pure solids were measured and used to calculate ideal phase diagrams. With the exception of tetrazole-rich mixtures, the simple eutectic systems approached ideality.

Introduction

Mixtures of imidazole ($C_3H_4N_2$), pyrazole ($C_3H_4N_2$), triazole ($C_2H_3N_3$), and tetrazole (CH_2N_4) have been shown to possess remarkable conducting properties at relatively low temperatures (*1*). Various binary and ternary mixtures of these azoles were shown to have specific conductivities in the range of 10^{-2}–10^{-3} Ω^{-1} cm^{-1} at 298 K. These mixtures also showed good solvent properties, dissolving many organic solvents and water. We measured the binary phase diagrams of these four solid azoles along with the enthalpies of fusion of the pure solids. All binary pairs except imidazole–tetrazole were found to form simple eutectic systems with several mixtures showing near-ideal behavior.

Experimental Section

Materials. Imidazole (99%), pyrazole (98%), 1,2,4-triazole (98%), and 1*H*-tetrazole (99%) from Aldrich Chemical Co. were twice sublimed, giving melting points of 363.7, 343.2, 393.5, and 430.7 K, respectively. All compounds completely melted within a range of 1 K.

Melting Points. Phase transitions were determined by a sealed-tube method (*2*). Ampules were made from 7-mm glass tubing. The tube was purged with nitrogen, a small Teflon-coated stirring bar was inserted, and appropriate amounts of pure compounds were weighed into the tube. The tube was again purged with nitrogen, and a thermocouple well made of 4-mm glass tubing was inserted and the tube sealed closed. Temperatures were measured using a copper–constantan thermocouple attached to appropriate computer interfacing and the data read directly into a microcomputer. The thermocouples were calibrated against an NBS Certified thermometer while in the measuring cell. The transition points were measured in an oil bath whose temperature was carefully controlled to ±0.1 °C; a bright backlight was used to observe the pres-

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Table I. (Solid + Liquid) Phase Equilibria[a]

x	$T_{m(1)}$	$T_{m(2)}$	x	$T_{m(1)}$	$T_{m(2)}$
		(x)Pyrazole + (1 − x)Imidazole			
0.000	363.7		0.519	300.1	298.7
0.107	352.9		0.550	303.5	298.8
0.197	345.3		0.601	309.3	298.0
0.312	332.9		0.673	317.2	297.7
0.391	322.2	297.2	0.748	325.1	298.3
0.448	313.2	298.1	0.864	332.9	
0.484	307.7	298.5	1.000	343.2	
0.500	298.7	298.7			
		(x)Imidazole + (1 − x)Triazole			
0.000	393.5		0.569	329.2	327.4
0.104	386.0		0.585	327.5	327.5
0.212	376.4		0.604	331.2	329.7
0.238	373.3		0.696	337.2	329.8
0.325	365.0		0.804	345.8	
0.401	355.7	329.4	0.899	356.0	
0.448	348.7	329.7	1.000	363.7	
0.530	337.7	327.0			
		(x)Pyrazole + (1 − x)Triazole			
0.000	393.5		0.693	320.6	319.8
0.118	385.5		0.702	320.9	319.9
0.203	376.8		0.732	323.4	320.0
0.285	370.9		0.753	324.6	319.7
0.402	359.7		0.778	327.4	319.9
0.416	358.8		0.805	330.4	
0.501	346.1	319.9	0.828	331.9	
0.599	334.6	319.7	0.891	336.4	
0.653	324.6	319.7	1.000	343.2	
0.683	319.9	319.9			
		(x)Pyrazole + (1 − x)Tetrazole			
0.000	430.7		0.671	333.6	319.2
0.112	418.0		0.694	326.5	319.5
0.180	410.5		0.708	321.2	319.3
0.277	401.2		0.717	319.3	319.3
0.329	393.4		0.752	323.2	319.4
0.402	384.0		0.796	326.9	319.1
0.457	376.0		0.852	331.1	
0.501	370.5		0.902	335.1	
0.547	362.1	319.1	0.950	339.3	
0.607	349.5	319.4	1.000	343.2	
0.645	341.2	319.2			
		(x)Triazole + (1 − x)Tetrazole			
0.000	430.7		0.554	345.8	345.7
0.093	419.5		0.593	350.1	345.8
0.108	415.4		0.636	357.0	345.5
0.199	402.8		0.661	360.0	345.9
0.292	392.3		0.696	364.6	345.6
0.348	384.6		0.756	369.7	
0.412	373.7	345.6	0.827	378.2	
0.475	361.0	346.0	0.929	387.8	
0.534	352.2	345.8	1.000	393.5	
		(x)Imidazole + (1 − x)Tetrazole			
0.000	430.7		0.550	341.2	
0.102	409.0		0.595	337.0	
0.216	378.6		0.649	327.0	305.1
0.294	352.4		0.703	317.5	305.5
0.351	332.5	328.6	0.757	307.8	305.2
0.374	330.1	328.7	0.795	323.7	305.6
0.388	333.0	328.4	0.830	328.7	305.0
0.452	342.2		0.905	346.1	
0.500	344.7		1.000	363.2	
0.531	342.7				

[a] $T_{m(1)}$ denotes the first solid phase formation temperature, and $T_{m(2)}$ denotes the eutectic freezing point (if observed).

ence or absence of solid crystals. The sealed tubes were found to give transition points that were reproducible to ±0.2 °C over 4 weeks. (*Note*: Several of the high mole fraction tetrazole samples exploded when melted for the third time.) For some compositions eutectic halts were observed by graphing the computer output. The triazole–imidazole and triazole–pyrazole mixtures were observed to be hygroscopic and were prepared in a drybox. The other mixtures did not show this property; samples prepared in and out of the drybox showed no difference in phase transition points.

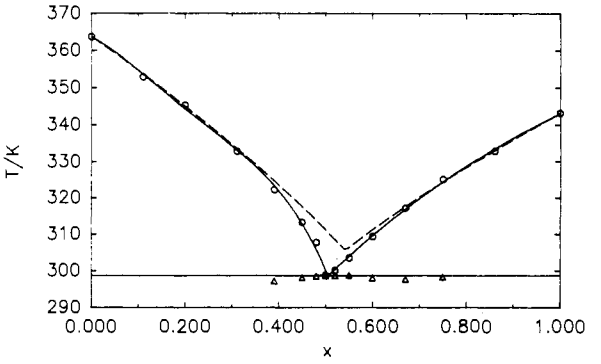

Figure 1. (Solid + liquid) phase diagram for (x)pyrazole + (1 − x)-imidazole. —, experimentally observed temperatures; ---, temperatures calculated by using eq 1; O, first solid phase formation temperature; Δ, eutectic freezing point (if observed).

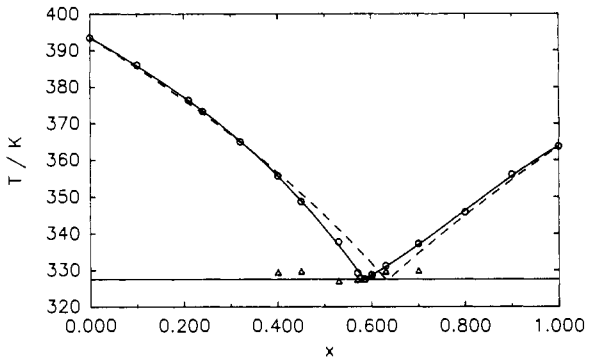

Figure 2. (Solid + liquid) phase diagram for (x)imidaozle + (1 − x)triazole. —, experimentally observed temperatures; ---, temperatures calculated by using eq 1; O, first solid phase formation temperature; Δ, eutectic freezing point (if observed).

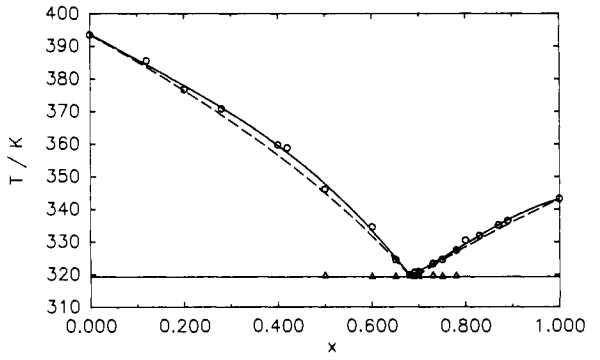

Figure 3. (Solid + liquid) phase diagram for (x)pyrazole + (1 − x)-triazole. —, experimentally observed temperatures; ---, temperatures calculated by using eq 1; O, first solid phase formation temperature; Δ, eutectic freezing point (if observed).

Enthalpies of Fusion. Enthalpies of fusion of approximately 10-mg samples were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter using an indium standard. Because of the possible reaction of the compounds with the aluminum pans, all samples were measured immediately after their preparation and then discarded. The data were read directly into a microcomputer used to determine peak areas. Enthalpies of fusion of the pure compounds measured at their melting points were as follows: imidazole, 12.5 kJ·mol^{-1}, pyrazole, 14.2 kJ·mol^{-1}, triazole, 16.1 kJ·mol^{-1}, and tetrazole, 18.4 kJ·mol^{-1}. All heats were reproducible to ±0.1 kJ·mol^{-1} over a minimum of 20 samples. All measurements showed melting points within 1 K of the previously reported values.

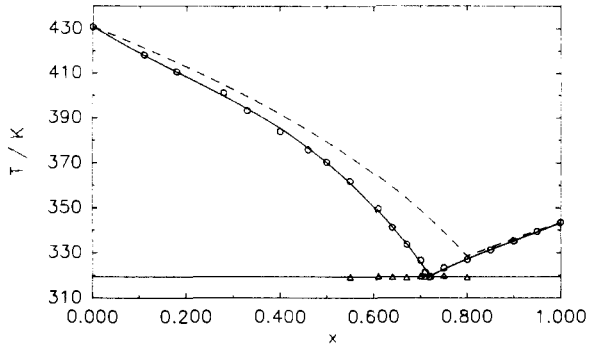

Figure 4. (Solid + liquid) phase diagram for (x)pyrazole + (1 − x)-tetrazole. —, experimentally observed temperatures; ---, temperatures calculated by using eq 1; O, first solid phase formation temperature; Δ, eutectic freezing point (if observed).

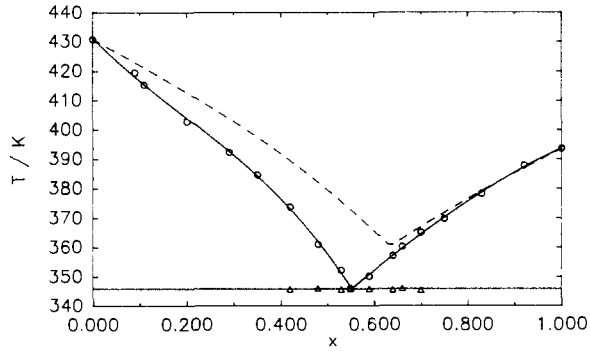

Figure 5. (Solid + liquid) phase diagram for (x)triazole + (1 − x)-tetrazole. —, experimentally observed temperatures; ---, temperatures calculated by using eq 1; O, first solid phase formation temperature; Δ, eutectic freezing point (if observed).

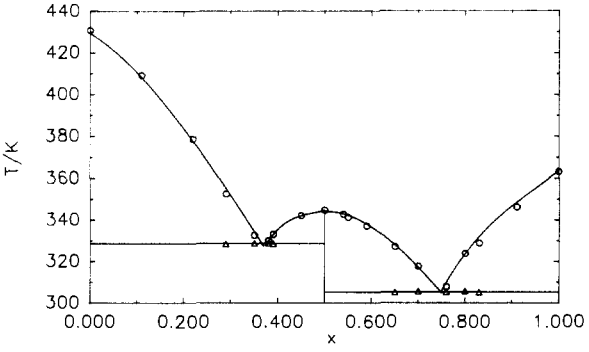

Figure 6. (Solid + liquid) phase diagram for (x)imidazole + (1 − x)tetrazole. —, experimentally observed temperatures; O, first solid phase formation temperature; Δ, eutectic freezing point (if observed).

Results and Discussion

Melting points of the binary mixtures are given in Table I, and phase diagrams are shown in Figures 1–6. All phase diagrams except tetrazole–imidazole show simple eutectic mixtures. For an ideal system, melting points are expected to obey the equation

$$\ln x = \Delta H_A^{fus}(T_m - T_A)/RT_mT_A \qquad (1)$$

where x is the mole fraction of component A in the mixture

Table II

binary pair	observed		calculated	
	mole fracn	temp	mole fracn	temp
pyrazole–imidazole	0.500	298.7	0.542	305.6
triazole–imidazole	0.585	327.5	0.632	327.1
triazole–pyrazole	0.680	319.9	0.684	318.9
tetrazole–pyrazole	0.720	319.9	0.798	328.3
tetrazole–triazole	0.550	345.8	0.634	360.2

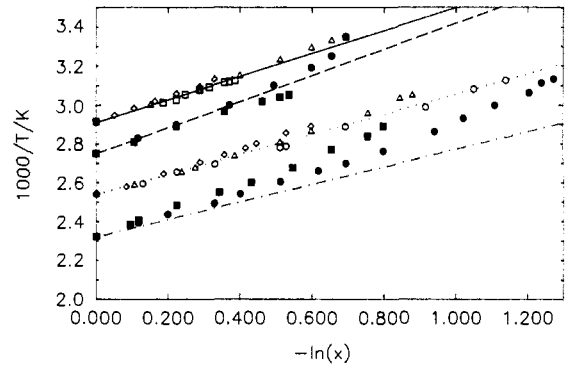

Figure 7. −ln x vs $1/T$ for all eutectic systems. —, pyrazole data; ---, imidazole data, ···, triazole data; –·–, represents tetrazole data; Δ, imidazole solute; O or ●, pyrazole solute; □ or ■, triazole solute; ◇, tetrazole solute.

melting at T_m, T_A is the melting point of pure A, and ΔH_A^{fus} is the enthalpy of fusion of the pure compound at the melting point of pure A, assuming that the enthalpies of fusion are independent of temperature (*3*). Table II shows the ideal and observed mole fractions and melting points for the minimum melting mixtures reported.

An alternative way of showing the ideality of the behavior of the systems is with a plot of $1/T_m$ vs −ln x for $1 > x > x_{eut}$. If the systems were ideal, these graphs would converge to the ideal slope, $R/\Delta H^{fus}$, in the limit as x approaches 1. Figure 7 shows these data for the above five phase diagrams that show a simple eutectic along with the line showing ideal behavior. The fact that the data does deviate from the ideality may be an indication that a small amount of solid-phase solubility occurs.

It is noted that the systems rich in tetrazole deviate the most from ideal behavior. NMR of the tetrazole–pyrazole and tetrazole–triazole systems in D_2O showed only peaks present in the pure components, indicating no compound formation. In the case of tetrazole–imidazole however, the 0.5 mole fraction sample showed a very different spectrum from the pure components, giving further evidence of the presence of a 1:1 solid addition compound.

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