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Supporting Information

Investigation of the Solid-liquid Ternary Phase Diagrams of 2HNIW·HMX Cocrystal

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Experimental section

Solubility Measurements

An excess of HNIW and HMX was separately added to the solvents. A thermostatic water bath (Chang'an University, China) was used to control the vessel temperature with an uncertainty of ± 0.01 ℃. The solutions were agitated for 72 h to ensure that solid-liquid equilibrium was established. A volume of the upper portion of the solution was sampled onto a weighed glass vial (m_1). The glass vial was weighed again to record the mass of solution (m_2), and the solvent was dried for more than 12 h under vacuum at 60 ℃. After drying, the glass vial was reweighed to determine the mass of residue solid (m_3). All of the masses in the experiment were weighted with an accuracy of 0.1 mg. Each solubility experiment was repeated three times to obtain the average values of experimental data.

The solubilities of HNIW and HMX in the selected solvents can be calculated by the following equation:

$$Solubility = \frac{(m_3 - m_1)/M_1}{(m_3 - m_1)/M_1 + (m_2 - m_3)/M_2} \quad \text{(S1)}$$

where (m_3 - m_1) represents the mass of the solute, (m_2 – m_3) represents the mass of the solvent, M_1 and M_2 represent the molecular weight of the solute and the solvent, respectively.

The purpose of selecting solvents is to cover conditions for congruent and incongruent dissolution system. A symmetric and congruent system would be obtained when the two pure components have similar solubility, and an asymmetric and incongruent system is expected for larger solubility difference. Based on this, preliminary solubility experiments were carried out. The solubilities of HNIW and HMX in acetonitrile, ethyl acetate, butanone, *N,N*-dimethylformamide and dimethylacetamide were investigated at 25 °C by using a gravimetric method, respectively. Table S1 lists the experimental solubility data of HNIW and HMX in the selected solvents. As shown in Table S1, the solubility ratio of the two pure components in acetonitrile was the largest, and that in dimethylacetamide was lowest. According to the result of the experimental solubility data, acetonitrile and dimethylacetamide should

be selected as likely examples for congruent and incongruent dissolution system, respectively. However, in the actual experimental process, the solvent is difficult to completely volatilize when dimethylacetamide is used as the solvent to prepare 2HNIW·HMX cocrystal. In this case, combined with the experimental solubility data, acetonitrile and ethyl acetate were selected as the dissolution system to discuss the effect of different solvents and temperature on the phase behavior of 2HNIW·HMX.

Table S1 Experimental solubility values of HNIW and HMX in different solvents at 25 ℃

Solvent	Solubility (mol solute/solvent)		Solubility ratio (TNT/HNIW)
	HNIW	HMX	
Acetonitrile	0.0598	0.0030	19.93
Ethyl acetate	0.1080	0.0101	10.69
Butanone	0.1250	0.0114	10.96
N,N-dimethylformamide	0.1378	0.0093	14.82
Dimethylacetamide	0.4888	0.0602	8.12

The calibration lines

The calibration lines, i.e., the relationship between peak area and concentrations of the solute in the solvent, are required for determining the solubility by HPLC. Standard solutions with different concentration of HNIW and HMX were prepared to determine the peak areas. According to the measured peak areas and the corresponding concentrations, the calibration curves were obtained (Figs. S1 and S2). The calibration lines showed excellent linearity ($R^2 > 0.9990$).

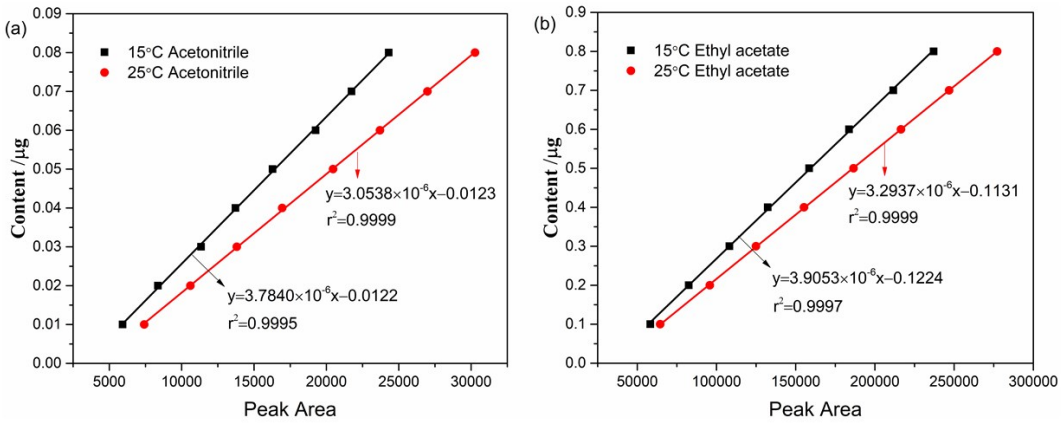

Fig. S1 The calibration curves of HMX in acetonitrile (a) and ethyl acetate (b).

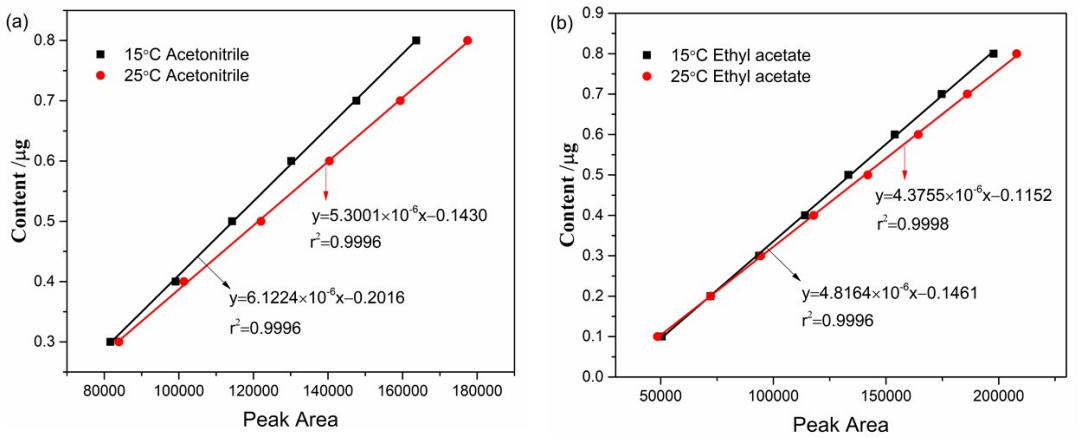

Fig. S2 The calibration curves of HNIW in acetonitrile (a) and ethyl acetate (b).

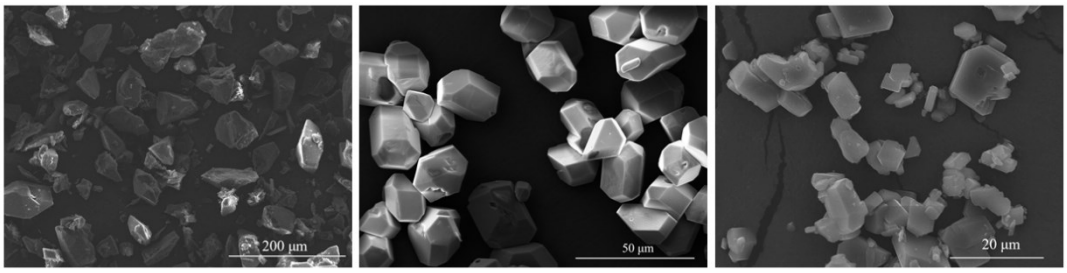

Fig. S3 SEM images of HNIW (a), HMX (b), and 2HNIW·HMX cocrystal (c).