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Studying Deliquescent Relative Humidity Lowering in Mixtures of Five Fertilizer Ingredients Using Mixture Experiments and a Special Cubic Equation

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Abstract

The lowering phenomenon of deliquescent relative humidity (DRH) in the binary to the quinary systems was studied. Gravimetric moisture sorption isotherm experiments were employed to obtain data for estimating DRH. A special cubic model was constructed for the purpose of predicting DRH. The predictive equation described the significant factors which were all the ingredients, all the binary interactions, and one of their ternary interactions. It gave accurate predictions with an average relative deviation of 1.8% compared to the values between 2.3% and 32.4% produced by equations reported elsewhere. DRH lowering occurred in all possible combinations of the ingredients, and the magnitudes of DRH lowering were exceptionally high when urea and one or more deliquescent ingredients were present together. Despite its insoluble nature, kaolin-based filler also caused DRH lowering. However, its presences in the quaternary and quinary systems alleviated the DRH lowering that was caused by other ingredients.

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1. Introduction

Interactions between moisture and solid ingredients are phenomena that significantly affect physical and chemical stabilities of hygroscopic materials such as fertilizers. Moisture can interact through various mechanisms such as adsorption, absorption, capillary condensation, and deliquescence.[1] Among these mechanisms, deliquescence appears to be the most problematic one. It occurs when the relative humidity (RH) of a deliquescent material is equal to or greater than its deliquescence relative humidity (DRH),[2] whereas Gibbs free energy of liquid solution is lower than those of separated solid and liquid phases.[3] The vapor pressure of the liquid solution, as being lower than that of water, also allows moisture in surrounding environment to condense, and thus the remaining deliquescent solid would further dissolved.[1] The moisture sorption and the material dissolution can continue until the system has no material to dissolve.[4] When the environment becomes less humid, the material adjusts its RH to match the decreasing environmental RH through desorption. Below its DRH, the liquid solution can become saturated and recrystallized.[5,6] Chains of sorption, dissolution, desorption, and recrystallization that have cycled through an extended period of time would eventually result in severe caking of granular materials by either forming an extensive network of strong crystal bridges among granules,[7,8] or turning a bulk of free flowing granules into a continuous mass.[6,9,10]

The deliquescence is also influenced by ingredients presented. The DRH of a mixture is usually lower than those of its ingredients when they are kept separately.[11-13] Compound fertilizers, which generally composed of several

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deliquescent ingredients, are among the products that are susceptible to DRH lowering. In fact, one of the earliest reports on the DRH lowering was devised by comparing the DRHs of straight fertilizers including calcium nitrate, ammonium nitrate, potassium chloride, ammonium sulphate, and potassium nitrate, against the DRHs of their binary mixtures.[14] A lower DRH means a lower bottom level of RH in which a significant amount of moisture can be absorbed, and it gives a granular material problems such as reduced physical and chemical stabilities and increased caking tendency.[1,13]

Severe caking is often prevented or at least delayed by coating the surface of granules with an anti-caking agent. However, its effectiveness can be somewhat limited when it is used with materials like compound fertilizers. This is because their deliquescent ingredients have been mixed before the anti-caking agent is applied[15]. The study conducted by Tyc *et al.*[16] reported that DRH lowering resulted in a significant reduction in the effectiveness of anti-caking agents when they were applied to a calcium nitrate/ammonium nitrate compound fertilizer. Lipasek *et al*.[17] observed that DRH lowering in some cases far outweighed the capability of anti-caking agents to increase the DRH levels of the coated materials. Moreover, several studies suggested that the magnitude of DRH lowering depended on the components and the composition of mixtures. A work conducted by Kwok *et al*.[18] reported that DRH lowering was more pronounced in fructose/citric acid mixtures than in sodium chloride/sucrose mixtures. Allan *et al*.[19] noted that the DRH lowering in the mixtures of ingredients with a common ion were not as strong as those in the mixtures that did not share a common ion. The work on various binary mixtures reported by Langlet *et al*.[20] showed that the magnitude of DRH lowering depended on the chemical composition, and DRH reached the lowest level at specific composition.

The works mentioned above implied that understanding the significance of ingredient interactions that causes the DRH lowering are important. However, it could be challenging, since without a robust design the number of experiments required to distinguish the influences of ingredients would be beyond the point of practicability when many ingredients are present. This obstacle might be an important reason that the majority of the studies on the DRH lowering only involved binary and ternary mixtures.[4,11-13,18-24]

The present study was aimed to establish a predictive equation and information that could accurately describe the deliquescent behavior in the mixtures of diammonium phosphate (DAP), muriate of potash (MOP), urea (U), ammonium sulphate (AS), and kaolin-based filler (KF), which are common ingredients for compound fertilizers. To the best of the authors' knowledge, information currently available in literature for these ingredients explain only up to certain ternary combinations, and mathematic equations proposed in literature seem to have problems with the accuracy of predicting DRH when the contributions of ingredient interactions are strong.

The DRH results necessary for constructing and evaluating mathematic equations were obtained through a series of moisture sorption isotherm (MSI) experiments. A robust criterion and a computer software were employed to specify the experimental points, or compositions so that the effects of the ingredients and their interactions were as thoroughly described as possible, while the number of experiments were maintained at the minimum. Statistical tools were used to give unbiased evaluations of the data and to determine the best fit equations. All the modelling and evaluating algorithms were pre-programmed with the required parameters and automatically executed. The processes were reiterated as many times as necessarily to devise the optimal results, which could not be easily executed manually. These approaches allowed the required outcome to be obtained within the resource and time constraints.

Some assumptions and the compromise between the expected outcomes and the practicable number of experiments still had to be made, and that, to certain extents, became the limitations of the work. Firstly, the predictive equation would certainly cover only the mixtures of the five ingredients. Secondly, all the ingredients were assumed to be single entities, and so the effects of impurities within were only accounted arbitrarily. The accuracy of prediction could therefore be affected when the types or the fractions of impurities are different from those found in the ingredients present here. Deviations could also come from certain differences in the sample preparation method, as they may alter physical or chemical aspects of samples in different ways. Lastly, certain types of interactions were assumed to be negligible, and that could become a cause of predictive errors in cases that they had strong effects. However, based on information in literature and preliminary studies, the last assumption was not expected to cause any problem or would become a problem outside the mixing ratios of interest here.

The results that this study made available would give a clear insight into the complexity that the ingredients behave toward the DRH lowering. It is important for research on the behavior and mechanisms of caking, and the development of novel and customizable anti-caking agents. The methodology can be applied for studying other mixing systems, and the results obtained in this manner can be directly used to identify

control parameters, *e.g.*, critical controlling windows, mixing tolerances, as-produced RH levels, and to select an optimal choice of anti-caking agents for research, manufacturing, and quality control purposes.

2. Materials & methods

2.1 Materials

The fertilizer ingredients used in the study were kindly given by Thai Central Chemical Company PLC, one of the major fertilizer manufacturers in Thailand. The ingredients were industrial grades and were among the common raw materials used by the company for producing compound fertilizers. They were DAP, a source of nitrogen and phosphorus; MOP, a source of potassium; U and AS, sources of nitrogen; KF, an agent for binding and completing a formula. Each ingredient came from a single source. The origins and impurity contents were classified by the donor. To normalize the effects of compositional fluctuation, each ingredient was randomly sampled at five locations in the stockpile. The collected samples of the same ingredient were mixed and stored at room temperature in sealed bags.

2.2 Design of mixture experiments

Many mixture experiments reported in literature had been done by following either the simplex centroid[25,26] or the simplex lattice[27,28] design methodology proposed by Scheffé[29,30] to reduce the number of experiments. However, they were criticized for underestimating the effects of ternary mixing since most experimental points only represented ingredients and binary mixtures.[31] Other common design methods for mixture experiments included D-optimal[32,33] and I-optimal[34,35] criteria. The D-optimal criterion appeared to be more common and suggested a smaller number of experiments, but it was considered to be only suitable for constructing an estimating-based equation and for identifying significant interactions.[36-38] The I-optimal criterion, on the other hand, was recommended for situations in which accurate predictions were expected.[36] It also satisfied the criteria required for identifying significant interactions.[39,40]

As dictated by the aim of study, I-optimal was selected as the experimental design criterion. The necessary calculations were executed by using algorithms in Design Expert software. The essential input information included: (i) the initial variables, or the factors, which in this case were the ingredients, with their weight fractions varied between 0 and 1.00 and the total content was maintained at a fraction of 1.00; (ii) the DRH as the outcome, or the response; (iii) the type of model to be employed in fitting the experimental data (see Section 2.3 for more detail on the model selection).

To satisfy the I-optimal criterion, the software used the input data to find the set of experimental points that gave the lowest average of variances.[41] The process began with randomly selecting experimental points within the experimental region and calculating the corresponding "optimality" values. The experimental points with low optimality values were replaced, and the optimality values of the new points were calculated. This process was repeated until the optimal set was found. The software suggested that 40 experimental points and a total of 45 experiments (or runs) were required, in which 25 points were dedicated to modeling, 15 extra points for estimating the lack of fit, and 5 additional runs for replicating certain designed points. The experimental order was randomly arranged to normalize the influences of factors that could not be controlled in the experiments. The orders and the weight fractions of ingredients for all experiments are listed in Table 1.

2.3 Model selection

Scheffé[30] proposed four models for describing experimental responses produced by mixtures. In Scheffé's linear model, the response was solely dependent on the fractions of ingredients. His quadratic model had additional terms representing binary interactions. His cubic and special cubic models considered both binary and ternary interactions. The special cubic model was a simplified version of the cubic model, as it did not include the terms describing interactions that changed in forms of sinusoidal waves. Other literature, *e.g.*, Gorman and Hinman[42] and Lambrakis,[43] proposed higher-order models to account for more complex and higher-level interactions. However, their applications were rare. Examples were the studies done by Sahraee *et al*.[44] and Aydar *et al*.[45]

Certain assumptions and compromises had to be made in selecting a model as an input for the experimental design software, since limited information was known at this stage. With the I-optimal criterion and five ingredients, complex models like the quartic and the special quartic models would require 70 and 45 experimental points, respectively, just for constructing an equation, whereas the cubic and the special cubic models required only 35 and 25 experimental points for the same purpose. A certain level of predictive accuracy was sacrificed by ignoring quaternary and quinary interactions so that the number of experiments could be within 50 runs in total and finished within 6 months. There was also a possibility that the mixing system would exhibit no significant effect of the ternary interactions. However, designing experiments to cover them from the beginning would be a wise strategy.[46] Should all ternary interactions later be found insignificant, the data would be more than sufficient to construct an equation based

Table 1. Experimental order and weight fractions of ingredients.

Order	Ingredient weight fractions					Order	Ingredient weight fractions				
	DAP	MOP	U	AS	KF		DAP	MOP	U	AS	KF
1	0.50	0.00	0.00	0.50	0.00	24	0.55	0.00	0.13	0.11	0.21
2	0.00	0.00	0.50	0.00	0.50	25	0.32	0.32	0.32	0.04	0.00
3	0.00	0.33	0.33	0.34	0.00	26	0.50	0.00	0.50	0.00	0.00
4	0.00	0.00	1.00	0.00	0.00	27	0.33	0.32	0.03	0.00	0.32
5	0.75	0.00	0.00	0.25	0.00	28	0.00	0.50	0.00	0.00	0.50
6	0.32	0.04	0.34	0.00	0.30	29	0.00	0.00	0.00	0.50	0.50
7	0.00	0.32	0.32	0.04	0.32	30	1.00	0.00	0.00	0.00	0.00
8	0.03	0.00	0.32	0.33	0.32	31	0.00	0.75	0.00	0.25	0.00
9	0.20	0.00	0.00	0.17	0.63	32	0.00	0.75	0.00	0.00	0.25
10	0.00	0.50	0.50	0.00	0.00	33	0.00	0.00	0.50	0.50	0.00
11	0.03	0.00	0.32	0.33	0.32	34	0.50	0.50	0.00	0.00	0.00
12	0.00	0.50	0.00	0.50	0.00	35	0.33	0.03	0.32	0.32	0.00
13	0.03	0.32	0.00	0.33	0.32	36	0.00	0.00	0.00	0.75	0.25
14	0.00	0.23	0.05	0.00	0.72	37	0.33	0.03	0.32	0.32	0.00
15	0.00	0.00	0.25	0.75	0.00	38	0.65	0.28	0.07	0.00	0.00
16	0.00	1.00	0.00	0.00	0.00	39	0.00	0.00	0.75	0.25	0.00
17	0.33	0.32	0.03	0.00	0.32	40	0.10	0.50	0.15	0.15	0.10
18	0.03	0.32	0.00	0.33	0.32	41	0.00	0.00	0.00	0.00	1.00
19	0.00	0.00	0.00	1.00	0.00	42	0.50	0.00	0.00	0.00	0.50
20	0.33	0.31	0.00	0.33	0.03	43	0.24	0.00	0.69	0.00	0.07
21	0.00	0.25	0.00	0.75	0.00	44	0.75	0.00	0.25	0.00	0.00
22	0.33	0.00	0.03	0.32	0.32	45	0.33	0.31	0.00	0.33	0.03
23	0.00	0.18	0.61	0.00	0.21						

on the quadratic model.

The choices were therefore left with Scheffé's cubic and special cubic models. The special cubic model was chosen based on an assumption drawn from what had been observed in binary mixtures, and that the response surfaces describing the DRH of deliquescent mixtures would rather be smooth than have a sinusoidal element.[1,11,19] The model can be generally described as:[29]

$$\mathrm{DRH} = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q-1} \sum_{j}^{q} \beta_{ij} x_i x_j + \sum_{i<j}^{q-2} \sum_{j<k}^{q-1} \sum_{k}^{q} \beta_{ijk} x_i x_j x_k \quad (1)$$

where the main effects of ingredients in a mixture were represented by the magnitudes β_i and the ingredient fractions x_i in the terms $\beta_i x_i$. The terms $\beta_{ij} x_i x_j$ were used for describing binary interactions, and the terms $\beta_{ijk} x_i x_j x_k$ for ternary interactions. The values of β_i, β_{ij} and β_{ijk} would be estimated by fitting experimental results. The final equation based on this model would account the main effects of the five ingredients, and their significant binary and ternary interactions.

2.4 Sample preparation

All preparation steps were conducted in a climate-controlled room with its RH kept below 40%, which was the starting RH of all the experiments, to prevent the samples from prematurely gaining moisture before starting the experiments. The ingredients were separately ground in a mortar and then sieved by an ASTM E11 #35 test sieve to obtain granules with no larger than 0.5 mm diameters. The ground materials were dried in a Binder ED-56 drying oven set at 75°C for six hours to ensure that their RH levels were below 40%. For the samples that needed more than one ingredient, the dried ingredients were mixed to the required compositions in a flask and were manually shaken for 2 minutes. Individual samples, either ingredient or mixture samples, were weight to 5 ± 0.05 g on a Mettler Toledo AX205 analytical balance having an accuracy of 10^{-5} g. Each sample was evenly spread on a 60 mm diameter petri dish, and immediately put into a constant climate chamber to conduct an MSI experiment.

2.5 MSI experiments and DRH estimation

MSI – a graphical description of the relationship between RH and equilibrium moisture content (EMC) of a sample at a constant temperature[47] – was essential for determining DRH. The MSI results for all samples were established by using the static gravimetric method which measured weight changes after samples had absorbed moisture and reached equilibriums at specific RH points.[48,49] The MSI experiments were

conducted at a constant temperature of 25 °C and with a starting RH of 40%. The environmental conditions were created by a Memmert HPP 110 constant climate chamber having the ranges of working temperatures between 5 °C and 70 °C and RHs between 10% and 90%, with controlling accuracies of 0.1 °C and 0.5%, respectively.

The samples were weighed to the fourth decimal of grams every 24 hours on the Mettler Toledo AX205 analytical balance. They were considered reaching EMCs when the weight differences between two consecutive measurements were less than 0.0050 g, which was 0.1% of the initial weight.[48,49] The RH level was then increased by 2%, and the same procedure was repeated. Each experiment continued until three or four measuring points of abrupt increases in EMC were observed so that the deliquescent point could be identified.[20] DRH was the value of RH read at the intersection of two trendlines extrapolated from data on either side, as graphically illustrated in Fig. 1.

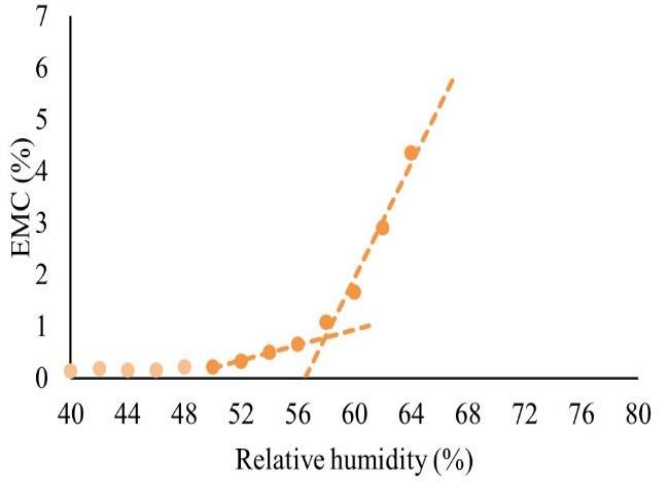

Fig. 1 Determination of DRH by using the intersection of two extrapolated trend lines.

2.6 Statistical analysis and equation construction

The values of DRH estimated from the MSI experiments were first examined to ensure that the influences of uncontrolled factors had been well randomized. It was done by plotting the order of experiments against the values of estimated DRH. The results were considered suitable for further uses if the points were randomly distributed without exhibiting a specific pattern or tendency. Otherwise, actions such as data transformation or an alternative experimental design that considered the cause of blocking would be required.[50]

The data were used for constructing equations based on Scheffé's special cubic model. The best fit β parameters were first identified for the "full-form" equation by using the least-square method.[46] The values of DRH predicted by the best fit equation were then subjected to analysis of variance (ANOVA)[51] for identifying the effects that were significant to DRH. The null hypothesis (H_0) was rejected and the alternative hypothesis (H_1: there was a difference in the values of DRH contributed by a change in the composition or an interaction) was accepted when the corresponding *P*-value was less than 0.05. The insignificant effects were removed from the equation, and the best fit β parameters were again identified by the least-square method for the terms that remained in the "reduced-form" equation.

The fitness of equations in either full or reduced form, was determined by the adjusted coefficient of determination (*Adj-*R^2) and the predicted coefficient of determination (*Pred-*R^2). *Adj-*R^2 measured the proportion of variation in the DRH results that could be explained by the variables, as it could measure the reduction in the estimated error variances when a variable term was removed.[52] The value of *Adj-*R^2 was expected to increase if an unimportant term had been removed, which helped identify equations that provided good fits without overfitting.[53] *Pred-*R^2 was used as an indicator for the capability of an equation in making accurate predictions for new observation points.[51] All the calculations and analyses were conducted in the Design Expert software. The best fit equation that exhibited the highest values of *Adj-*R^2 and *Pred-*R^2 would be selected. The values of DRH estimated from the experimental results were then plotted against those predicted by the selected equation. Their differences, or residuals, were also plotted against the normal probabilities of their occurrences and the predicted values of DRH. These plots were used to confirm the suitability of the equation for the DRH lowering study.

3. Results and discussion

3.1 MSI and DRH of ingredients and mixtures

The gravimetric MSI plots of ingredient samples (Fig. 2) including DAP, MOP, U, and AS exhibited typical behaviors of Type III MSI.[54] Initially, the values of EMC increased slightly and had a linear relationship with the values of RH, indicating no significant change caused by interactions between the ingredients and water.[55] The values of EMC increased a little more sharply when approaching the deliquescent point. After the deliquescent point had been passed, the MSI plot exhibited notably sharp increases in the values of EMC. The DRH values estimated from the plots were 72%, 76%, 70%, and 72% for DAP, MOP, U, and AS, respectively. It is also worth noting that U absorbed more moisture than the others after passing the deliquescent points; its moisture level was approximately 0.26%, 0.19% and 0.51% more than those of DAP, MOP and AS, respectively, for the

same interval of RH change. The MSI plot of KF showed no deliquescent point, and the values of EMC increased in a straight line without any abrupt change throughout the range of RH tested. However, the plot showed that KF contained almost twice as much moisture as the others did before becoming deliquescent.

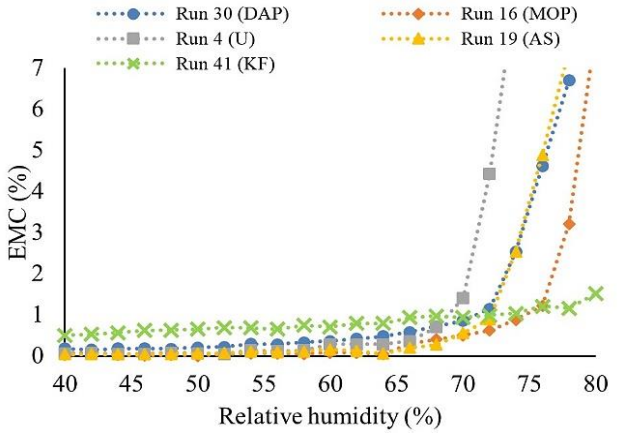

Fig. 2 MSI of ingredients.

The mixture samples exhibited the same MSI behavior as DAP, MOP, U, and AS. Examples are shown in Fig. 3, and the MSI results of all the experimental runs are provided in the supplementary information (Figs. S1-45). The values of DRH estimated from the experimental results are summarized in Table 2. DRH lowering was observed in all the mixture samples. Their DRH levels were generally lower than those of their deliquescent ingredients. The highest value of DRH amongst the mixtures was 68%, found in Runs 5, 32, and 36. The lowest DRH, which was 48%, was found in Runs 3, 10, 25, and 33. It is also worth pointing that all the KF-containing binary mixture samples (Runs 2, 28, 29, 32, 36, and 42) had lower values of DRH than their other ingredients. This was clear evidence of its effect on DRH lowering. Further discussion on the DRH lowering can be found in Sections 3.3-3.6.

3.2 Predictive models and statistical analysis

The plot of the experimental orders against the values of DRH estimated from the experimental results in Fig. 4 suggested that the influences of uncontrolled factors were randomly distributed, as the values of DRH were randomly scattered without any specific tendency or pattern. Thus, the data were considered suitable for further uses.

The DRH results were used to construct full-form equations based on Scheffé's special cubic model. After several repeating calculations, the best fit equation was obtained as described in Eq. (2):

Table 2. DRH of experimental samples.

Run	DRH	Run	DRH	Run	DRH	Run	DRH	Run	DRH
1	66 %	10	48 %	19	72 %	28	62 %	37	50 %
2	64 %	11	52 %	20	62 %	29	66 %	38	58 %
3	48 %	12	64 %	21	64 %	30	72 %	39	50 %
4	70 %	13	58 %	22	58 %	31	66 %	40	52 %
5	68 %	14	64 %	23	54 %	32	68 %	41	-[a]
6	54 %	15	54 %	24	54 %	33	48 %	42	62 %
7	50 %	16	76 %	25	48 %	34	64 %	43	54 %
8	54 %	17	54 %	26	52 %	35	50 %	44	56 %
9	66 %	18	60 %	27	54 %	36	68 %	45	64 %

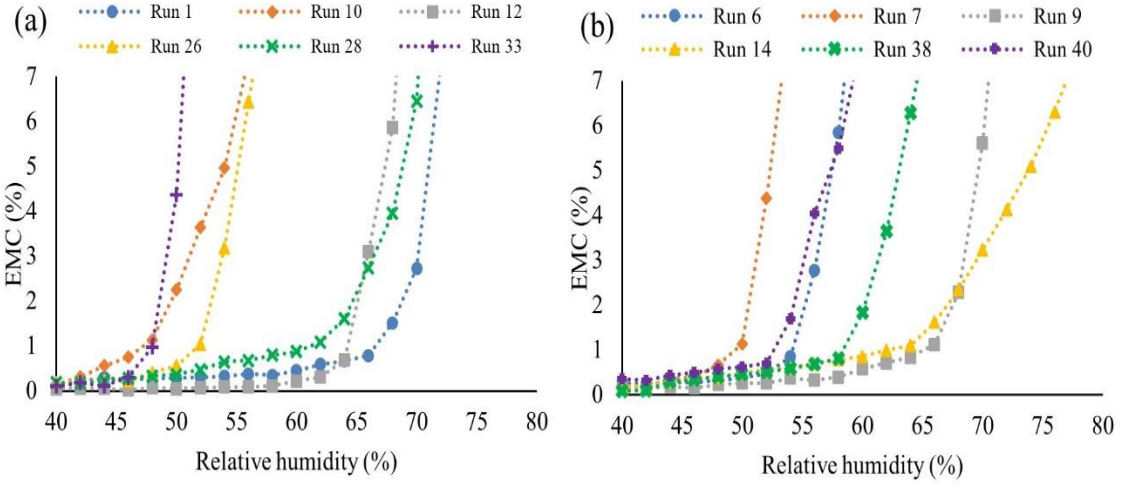

Fig. 3 Examples of MSI: (a) binary; (b) ternary and higher-order mixture samples.

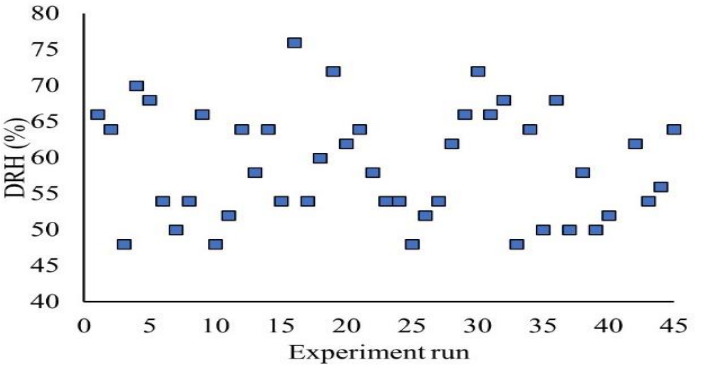

Fig. 4 Plot of run order versus estimated DRH.

$$\mathrm{DRH} = 72.29x_{\mathrm{DAP}} + 76.63x_{\mathrm{MOP}} + 70.27x_{\mathrm{U}} + 72.18x_{\mathrm{AS}} + 79.70x_{\mathrm{KF}} - 48.56x_{\mathrm{DAP}}x_{\mathrm{MOP}} - 80.67x_{\mathrm{DAP}}x_{\mathrm{U}} - 23.91x_{\mathrm{DAP}}x_{\mathrm{AS}} - 54.56x_{\mathrm{DAP}}x_{\mathrm{KF}} - 100.89x_{\mathrm{MOP}}x_{\mathrm{U}} - 44.25x_{\mathrm{MOP}}x_{\mathrm{AS}} - 61.98x_{\mathrm{MOP}}x_{\mathrm{KF}} - 93.16x_{\mathrm{U}}x_{\mathrm{AS}} - 43.03x_{\mathrm{U}}x_{\mathrm{KF}} - 35.68x_{\mathrm{AS}}x_{\mathrm{KF}} - 7.78x_{\mathrm{DAP}}x_{\mathrm{MOP}}x_{\mathrm{U}} + 95.82x_{\mathrm{DAP}}x_{\mathrm{MOP}}x_{\mathrm{AS}} - 83.02x_{\mathrm{DAP}}x_{\mathrm{MOP}}x_{\mathrm{KF}} + 5.51x_{\mathrm{DAP}}x_{\mathrm{U}}x_{\mathrm{AS}} - 10.67x_{\mathrm{DAP}}x_{\mathrm{U}}x_{\mathrm{KF}} - 58.58x_{\mathrm{DAP}}x_{\mathrm{AS}}x_{\mathrm{KF}} + 26.09x_{\mathrm{MOP}}x_{\mathrm{U}}x_{\mathrm{AS}} - 54.57x_{\mathrm{MOP}}x_{\mathrm{U}}x_{\mathrm{KF}} - 13.80x_{\mathrm{MOP}}x_{\mathrm{AS}}x_{\mathrm{KF}} - 40.26x_{\mathrm{U}}x_{\mathrm{AS}}x_{\mathrm{KF}} \quad (2)$$

where x_{DAP}, x_{MOP}, x_{U}, x_{AS}, and x_{KF} were the fractions of the specified ingredients. All the relevant β parameters expressed in Eq. (1) were replaced by specific values suggested by the software. The values of *Adj*-R^2 and *Pred*-R^2 for the equation were 0.968 and 0.861, respectively, which indicated fair fit of the predictions to the values of DRH estimated from the experiments with relatively small errors.

The DRH predictions made by the equation and those estimated were subjected to ANOVA so that the equation and its terms for describing the main effects, the binary interactions, and the ternary interactions could be tested for their significance. The essential calculations are summarized in Table 3. The equation gave the overall *P*-value less than 0.05 signifying that the values of β parameters used for fitting

Table 3. Essential ANOVA calculations for the best-fitted, full-form equation.

Source		Sum of squares	df[a]	Mean square	*F*-value	*P*-value
Overall model		2953.47	24	123.06	56.81	< 0.0001
Linear mixture		743.25	4	185.81	85.77	< 0.0001
	DAP-MOP	121.05	1	121.05	55.88	< 0.0001
	DAP-U	359.32	1	359.32	165.87	< 0.0001
	DAP-AS	30.32	1	30.32	14.00	0.0013
	DAP-KF	132.82	1	132.82	61.31	< 0.0001
Binary	MOP-U	450.59	1	450.59	208.00	< 0.0001
interactions	MOP-AS	116.26	1	116.26	53.67	< 0.0001
	MOP-KF	208.11	1	208.11	96.07	< 0.0001
	U-AS	468.56	1	468.56	216.29	< 0.0001
	U-KF	81.08	1	81.08	37.43	< 0.0001
	AS-KF	67.30	1	67.30	31.07	< 0.0001
	DAP-MOP-U	0.0489	1	0.0489	0.0226	0.8820
	DAP-MOP-AS	12.19	1	12.19	5.63	0.0278
	DAP-MOP-KF	8.93	1	8.93	4.12	0.0558
	DAP-U-AS	0.0398	1	0.0398	0.0184	0.8935
Ternary	DAP-U-KF	0.1045	1	0.1045	0.0483	0.8284
interactions	DAP-AS-KF	3.22	1	3.22	1.49	0.2367
	MOP-U-AS	0.5798	1	0.5798	0.2677	0.6106
	MOP-U-KF	2.74	1	2.74	1.27	0.2740
	MOP-AS-KF	0.2611	1	0.2611	0.1206	0.7321
	U-AS-KF	2.08	1	2.08	0.9622	0.3384
		43.33	20	2.17		
Residuals	Lack of fit	37.33	15	2.49	2.07	0.2158
	Pure errors	6.00	5	1.20		

[a] Degree of freedom

the data were truly devised from the influential factors and not from the experimental errors. Based on the mean square of residuals, the predictive errors were considerably small compared to the contributions of the main effects and the interactions. The proportion of residuals contributed by the lack of fit was insignificant, as indicated by a *P*-value greater than 0.05, meaning that the equation had adequate parameters to describe the contributing factors. All the main effects and binary interactions were significant in predicting DRH. For the ternary interactions, only the interaction among DAP, MOP and AS was found significant. Detailed explanations on the interpretation of ANOVA results can be found in literature.[46,56]

The software was again used to find the best-fitted equation with the insignificant terms removed. This best-fitted equation can be described as follows:

$$\mathrm{DRH} = 72.63x_{\mathrm{DAP}} + 77.10x_{\mathrm{MOP}} + 70.42x_{\mathrm{U}} + 72.46x_{\mathrm{AS}} + 80.29x_{\mathrm{KF}} - 53.51x_{\mathrm{DAP}}x_{\mathrm{MOP}} - 80.89x_{\mathrm{DAP}}x_{\mathrm{U}} - 25.75x_{\mathrm{DAP}}x_{\mathrm{AS}} - 62.65x_{\mathrm{DAP}}x_{\mathrm{KF}} - 103.04x_{\mathrm{MOP}}x_{\mathrm{U}} - 45.43x_{\mathrm{MOP}}x_{\mathrm{AS}} - 68.06x_{\mathrm{MOP}}x_{\mathrm{KF}} - 93.89x_{\mathrm{U}}x_{\mathrm{AS}} - 48.56x_{\mathrm{U}}x_{\mathrm{KF}} - 40.16x_{\mathrm{AS}}x_{\mathrm{KF}} + 99.93x_{\mathrm{DAP}}x_{\mathrm{MOP}}x_{\mathrm{AS}} \quad (3)$$

This equation was improved in fitness, with the *Pred-*R^2 value increased from 0.861 to 0.949. The value of *Adj-*R^2 also increased, albeit slightly, from 0.968 to 0.970. The plots of DRH estimated by the experiments versus DRH predicted by the reduced-form equation clustered around the best-fitted line (Fig. 5a). This indicated a good predictive accuracy of the equation. The plots of residuals versus normal probability (Fig. 5b) showed that the residuals of predictions followed a normal distribution. The plots of the predicted DRHs against residuals (Fig. 5c) exhibited random scattering within the boundaries, meaning that the predictions followed a constant variation assumption and had no data outlier. Lastly, the ANOVA results confirmed that the overall performance of the full-form equation was retained in the reduced-form equation (Table 3 compared to the same terms in Table 4).

Table 4. Essential ANOVA calculations for the best-fitted, reduced-form equation.

Source		Sum of squares	df[a]	Mean square	*F*-value	*P*-value
Overall model		2943.33	16	183.96	96.33	< 0.0001
Residuals		53.47	28	1.91		
	Lack of fit	47.47	23	2.06	1.72	0.2861
	Pure errors	6.00	5	1.20		

[a] Degree of freedom

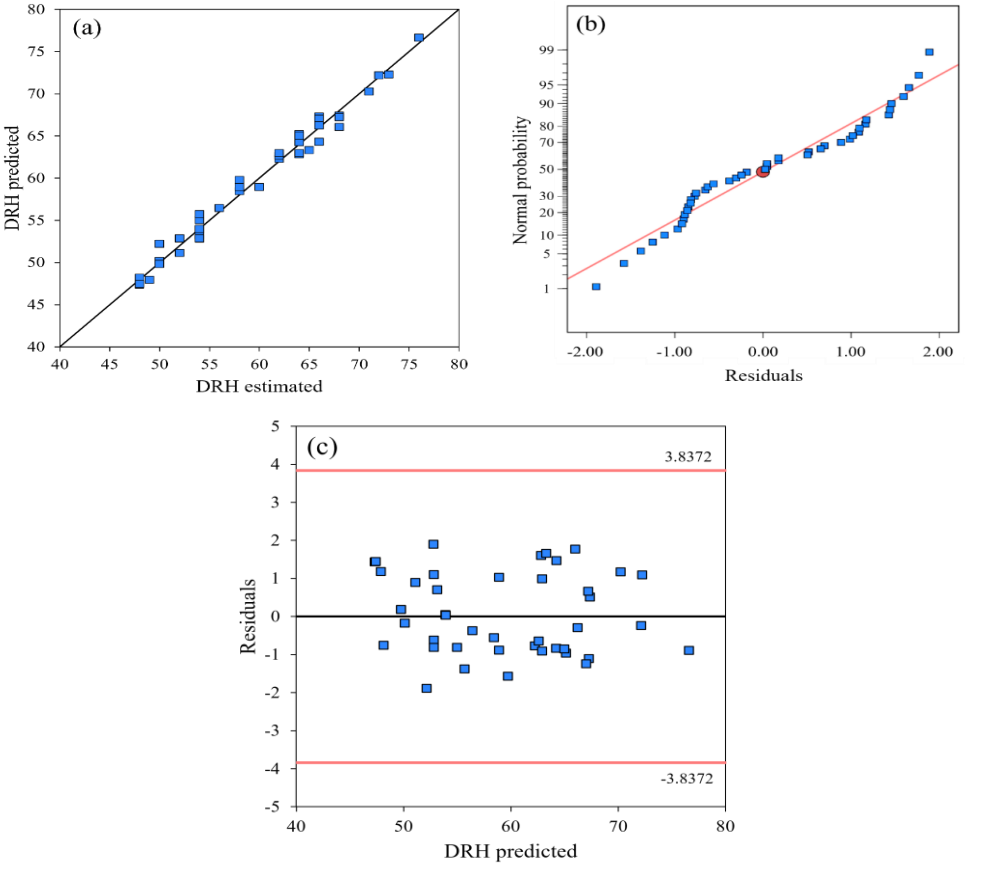

Fig. 5 Graphical plots indicating certain performances of the best-fitted, reduced-form equation: (a) estimated DRH versus predicted DRH; (b) residuals versus normal probability; (c) predicted DRH versus residuals.

The reduced-form equation gave the average of the relative deviations (ARD) between the predicted DRHs and the estimated DRHs as 1.8%, as calculated by using the equation proposed by Veith *et al*.[57] This value signified that the approach used in the study could give relatively more accurate predictions when compared with those made by using other approaches. For example, the predictions based on Ross' equation, as reported by previous works[16,17,58,59] gave ARDs between 4.8% and 8.7%. The predictions made by other approaches[17,57] yielded ARDs between 2.3% and 32.4%. With the confirmations by all the analyses and comparisons, the reduced-form equation was therefore used as the tool for studying the DRH lowering of the mixtures to be discussed in the following sections.

3.3 DRH lowering in binary mixtures

The compositions, DRHs, and DRH lowering magnitudes at the eutonic points[12] of all the systems were predicted by using the reduced-form equation and with the aid of Microsoft Excel Solver. The results are summarized in Table 5.

Trace plots were also constructed by using the equation and the Design Expert software to describe the relationships between the ingredient fractions and the predicted values of DRH. The trace plots describing the relationships in the binary mixtures are shown in Fig. 6 – the fractions of the second ingredients in these plots are changed in accordance with the changes in the fractions of the first ingredients to maintain a total fraction of 1. Each plot generally appeared as a curved line having the lowest value of DRH at a specific fraction other than 0 or 1. The plots were divided into two groups: one with deep lowering and the other with subtle lowering. Those with deep lowering had U presented together with another deliquescent ingredient, *i.e.*, DAP, MOP or AS. The values

Table 5. Eutonic composition, EDRH and DRH drop for all the mixing systems.

Mixing system	Eutonic composition					EDRH	DRH drop from ingredients' DRH (%)				
	DAP	MOP	U	AS	KF	(%)	DAP	MOP	U	AS	KF
DAP-MOP	0.54	0.46				61	11	15			
DAP-U	0.49		0.51			51	21		19		
DAP-AS	0.50			0.50		66	6			6	
DAP-KF	0.56				0.44	61	11				-
MOP-U		0.47	0.53			48		28	22		
MOP-AS		0.45		0.55		63		13		9	
MOP-KF		0.52			0.48	62		14			-
U-AS			0.51	0.49		48			22	24	
U-KF			0.60		0.40	63			7		-
AS-KF				0.60	0.40	66				6	-
DAP-MOP-U	0.22	0.33	0.45			46	26	30	24		
DAP-MOP-AS	0.54	0.46		0.00		61	11	15		11	
DAP-MOP-KF	0.36	0.32			0.32	56	16	20			-
DAP-U-AS	0.13		0.48	0.39		48	24		22	24	
DAP-U-KF	0.45		0.46		0.09	51	21		19		-
DAP-AS-KF	0.47			0.14	0.38	60	12			12	-
MOP-U-AS		0.27	0.46	0.27		45		31	25	27	
MOP-U-KF		0.47	0.53		0.00	48		28	22		-
MOP-AS-KF		0.39		0.29	0.32	59		17		13	-
U-AS-KF			0.51	0.49	0.00	48			22	24	-
DAP-MOP-U-AS	0.00	0.27	0.46	0.27		45	27	31	25	27	
DAP-MOP-U-KF	0.22	0.33	0.45		0.00	46	26	30	24		-
DAP-MOP-AS-KF	0.36	0.32		0.00	0.32	56	16	20		16	-
DAP-U-AS-KF	0.13		0.48	0.39	0.00	48	24		22	24	-
MOP-U-AS-KF		0.27	0.46	0.27	0.00	45		31	25	27	-
DAP-MOP-U-AS-KF	0.00	0.27	0.46	0.27	0.00	45	27	31	25	27	-

of eutonic DRH (EDRH) were between 48% and 51%. The eutonic compositions were close to 1:1, but the fractions of U were always higher than the second ingredients. The highest magnitude of DRH lowering was found when U was mixed with MOP. It was 28% and 22% lower than the DRH values of MOP and U, respectively. When U coexisted with DAP or AS, the magnitudes of DRH lowering were 21% and 24% below the DRH values of DAP and AS, and 19% and 22% below the DRH value of U.

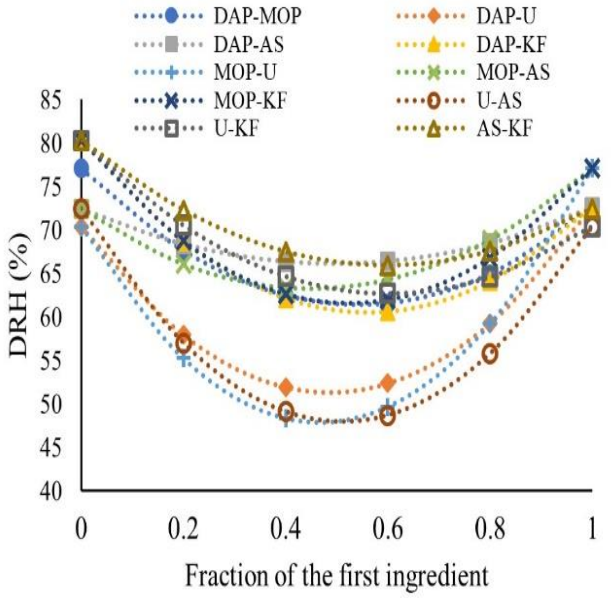

Fig. 6 Relationships between ingredient fractions and DRHs in all the binary mixtures.

The other binary systems had subtle DRH lowering. The values of EDRH were between 61% and 66%, 6% and 15% lower than the DRH values of the corresponding deliquescent ingredients. The DAP-AS and AS-KF systems had the least drop of DRH at the eutonic points, which was only 6% below the DRH values of their deliquescent ingredients. Their eutonic compositions were also close to 1:1. The effect of KF also became apparent, as all KF-containing systems exhibited the curved trace plots, and the EDRH values were lower than the DRH values of their deliquescent ingredients.

3.4 DRH lowering in ternary mixtures

Significant lowering of DRH also appeared in the ternary mixtures when U was presented. The values of EDRH were in the range between 22% and 31% below the DRH values of the deliquescent ingredients, and the lowest EDRH went slightly lower, from 48% in the binary ones to 45%. Both the highest drop in the value of DRH and the lowest EDRH were found in the MOP-U-AS system. The systems that did not contain U had the DRH drops only between 11% and 20%; even the DAP-MOP-AS system, in which all the ingredients were deliquescent, had the drops of no more than 15% from the DRH values of the ingredients. The contour plots (see Figs. S46-55 in the supplementary information), which illustrated the relationships between the compositions and the values of DRH, were also divided into two groups, *i.e.*, ones with red and dark orange zones indicating the values of DRH near or below 50% (see examples in Figs. 7a and 7c) and the others without it (Figs. 7b and 7d). Again, the contour plots that belonged to the first group always had U present, while the others did not. When the relationships were viewed in three dimensions, they would appear as response surfaces that curved down according to the magnitudes of DRH lowering toward the eutonic points, as shown in Fig. 7e.

The EDRH values of the ternary systems were between 45% and 61%, which were slightly lower than 48% - 68% EDRH range of the binary systems. Further study on the effects of individual ingredients was conducted by using the trace plots describing the relationships between the ingredients of interest and DRH. Some results are shown in Fig. 8; all the trace plots of the ternary and the higher-order systems can be found in the supplementary information Figs. S56-71. It should be noted for these trace plots that the fractions of the other ingredients in the systems were equally changed in accordance with the changes in the fractions of the ingredients of interest to maintain a total fraction of 1.

Five out of the ten ternary systems, including DAP-MOP-U, DAP-MOP-KF, DAP-AS-KF, MOP-U-AS and MOP-AS-KF, had the values of EDRH lower than those in the binary systems that were composed of their ingredients. In other words, the ternary combinations aggravated the DRH lowering. Each of their trace plots was characterized by a curved line having the lowest value of DRH at a specific fraction other than 0 (see an example in Fig. 8a). The DAP-MOP-AS, MOP-U-KF, and U-AS-KF systems, on the other hand, had the eutonic points when AS, KF and KF, respectively, were absent. The mixtures represented by the trace plots of these systems had the magnitude of DRH lowering decreased with increasing fractions of the extra ingredients (an example in Fig. 8b), *i.e.*, their presence alleviated the DRH lowering made by the other two ingredients. The presence of DAP and KF in the DAP-U-AS and DAP-U-KF systems appeared to have neither positive nor negative effects on the EDRH results that were already contributed by mixing U with AS and DAP, respectively. However, in the mixtures represented by the trace plots (see Fig. 8c for an example), the extra ingredients gave this null effect up to about a fraction of 0.20, but their presence at higher fractions helped lessen the DRH lowering produced by the other ingredients. It is also worth noting that U had to be

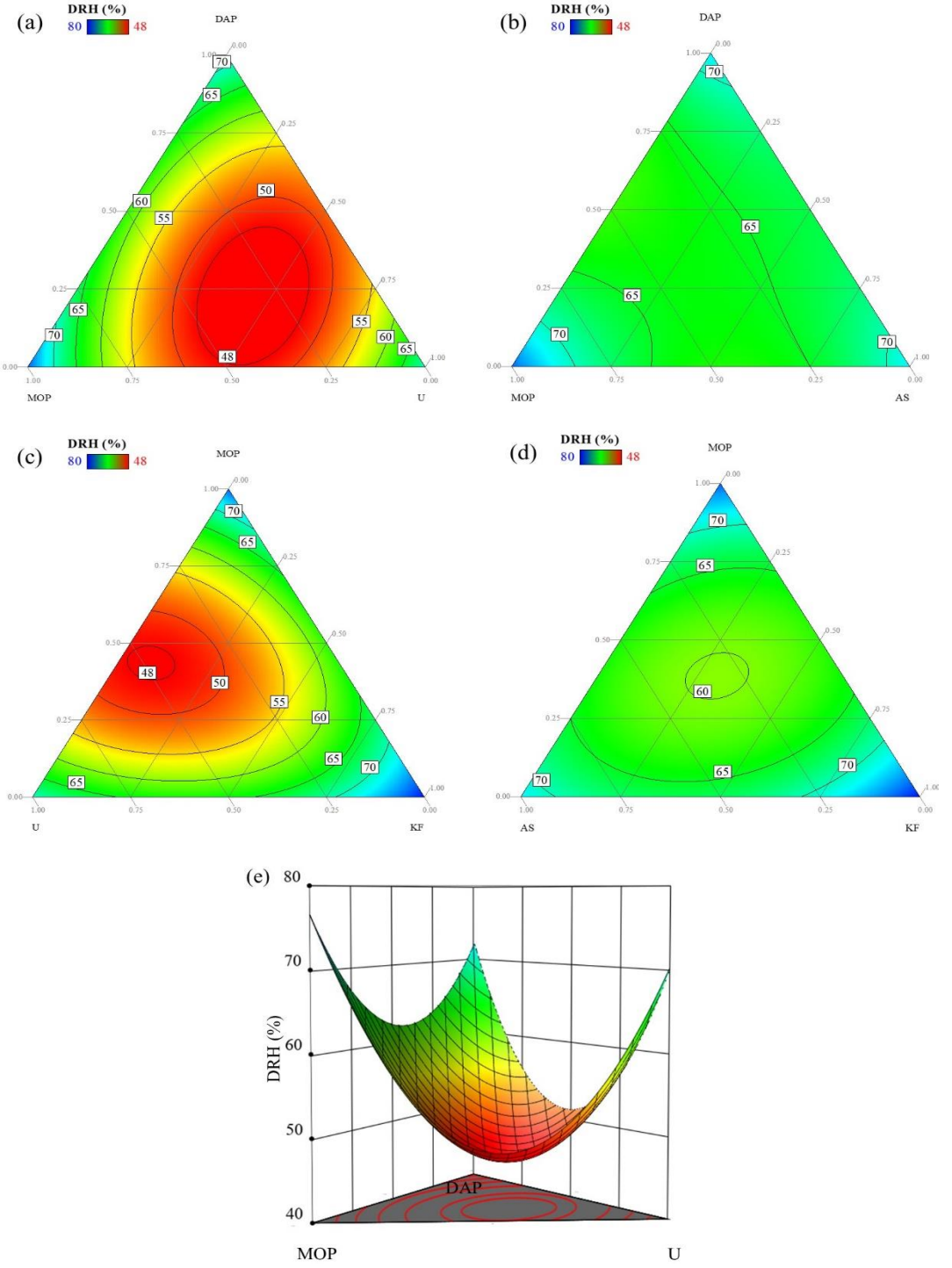

Fig. 7 Contour plots of DRH in ternary systems: (a) DAP-MOP-U; (b) DAP-MOP-AS; (c) MOP-U-KF; (d) MOP-AS-KF and (e) response surface of the DAP-MOP-U system.

presented in a fraction around 0.50 to give the lowest possible DRH.

3.5 DRH lowering in higher-order mixtures

As real compound fertilizers often consist of four or more ingredients, the DRH lowering in the quaternary and the quinary systems would be more relevant to practicality. Table 5 showed that the eutonic points occurred when these systems consisted of three ingredients, *i.e.*, when they turned into ternary systems, and the eutonic compositions and the values of EDRH were also the same as in these systems. These so-called "null ingredients" included: KF when U was present; AS when U was absent; DAP when all the deliquescent ingredients were present. Moreover, the mixtures that were represented by the quaternary and the quinary trace plots in Fig. 9 and Figs. S66-71 in the supplementary information had

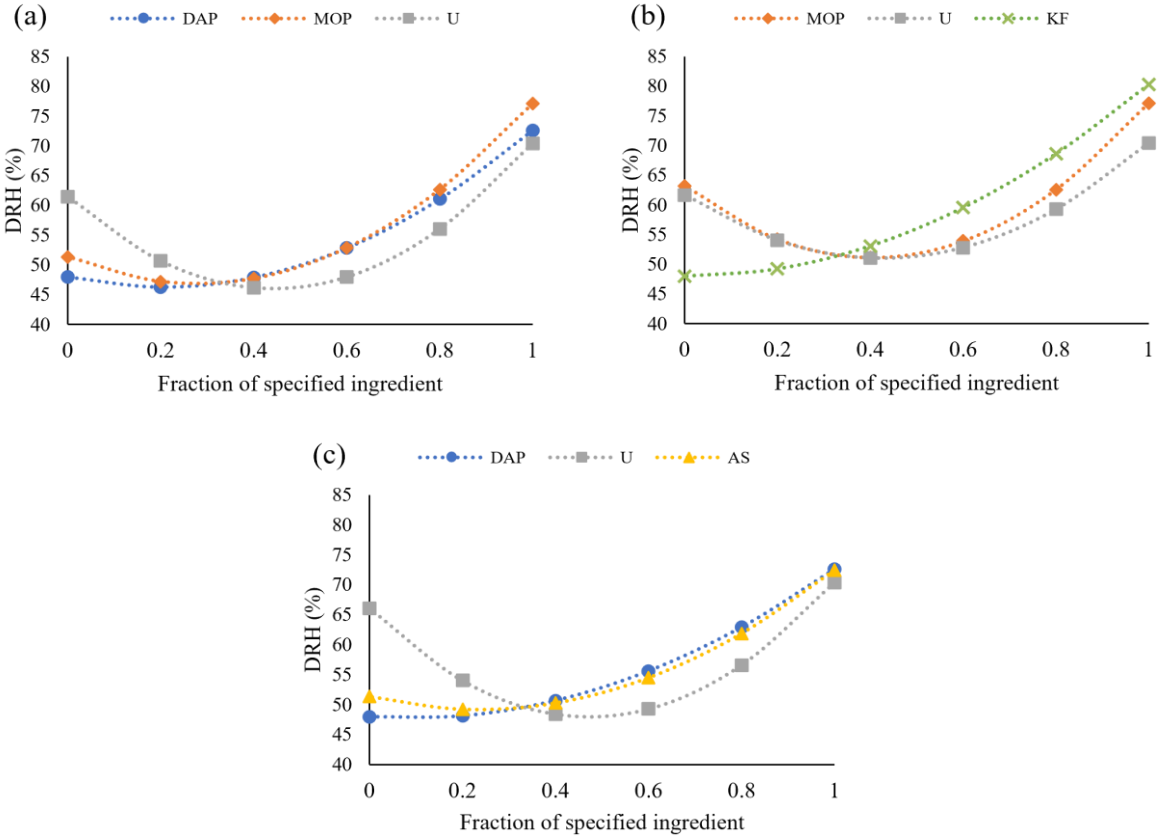

Fig. 8 Trace plots of ingredient fraction and DRH relationships in ternary systems: (a) DAP-MOP-U; (b) MOP-U-KF; (c) DAP-U-AS.

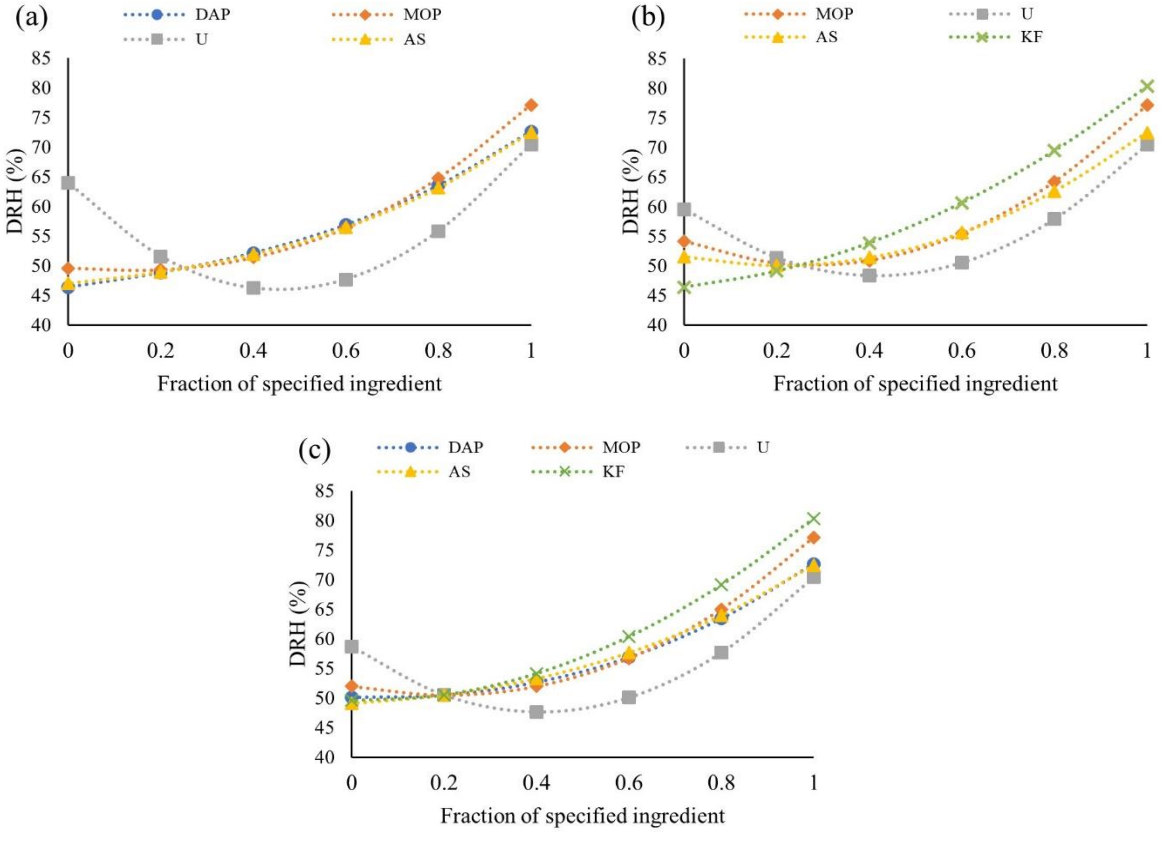

Fig. 9 Trace plots of ingredient fraction and DRH relationships in higher-order systems: (a) DAP-MOP-U-AS; (b) MOP-U-AS-KF; (c) DAP-MOP-U-AS-KF.

the magnitude of DRH lowering reduced when these extra or null ingredients were present.

U was still the primary ingredient responsible for the DRH lowering. The effect of U found here also supported its contribution to fertilizer hygroscopicity and caking formation which had been reported in literature.[60,61] However, large fractions, between 0.45 and 0.48, of U were required to reach the eutonic points. In the mixtures represented by the trace plots, a large DRH drop close to the values of EDRH could still exist at fractions of U around ± 0.10 of the eutonic compositions. However, these fractions were considerably high and were not necessarily required in actual fertilizers. Nonetheless, the magnitude of DRH lowering significantly decreased when the fraction of U was kept low or became zero. KF appeared to be the most effective ingredient in alleviating DRH lowering in the higher-order systems, although it was one of the DRH lowering ingredients. However, its presence in a large fraction is also not possible in reality because it gives no benefit to plants.

3.6 Key elements, future researches and applications

The awareness of DRH lowering as a result of mixing may not be very useful with respect to finding an optimal composition since the fertilizers' formulae, like in other mixing products, are primarily determined by the nutrition or the properties required for specific applications. However, understanding the DRH lowering and being capable of predicting it accurately is still beneficial in many aspects. As examples, the DRH and moisture data provided by MSI can help in predicting possible severity and forms of caking that would occur, *i.e.*, whether a fertilizer would form crystal bridges for a certain period before having a mass flow to become a large continuous mass, or it would more likely take a shorter route to become a large continuous mass. The DRH data can be used to assist in selecting a suitable and cost-effective measure against severe caking such as alternative choices of ingredients for a higher DRH level, and a lower initial or as-produced moisture level to delay the onset of caking.

The DRH data can also be used to assist in establishing an optimal tolerance of compositional variation. Locations in a fertilizer bulk where the compositional fluctuations are too large often exhibit significantly low DRH levels, especially, when an unusually high concentration of a problematic ingredient is present. On the other hand, an unnecessarily tight tolerance of compositional control will give rise to the production cost and difficulties. Using a predictive equation is a quick way to attain the DRH data for the entire compositional range of interest. With a suitable tolerance, the fertilizer will be more consistent in properties and more difficult to cake. The same approach is also applied in tackling problems associated with non-uniformity in applying an anti-caking agent.

The methodology employed in this study can be adopted to make the process of obtaining the DRH data and constructing a predictive equation became less cumbersome and give more meaningful results. However, ones should be aware of differences in the conditions that may impact their findings. Careful attention to detail is crucial. Some experiences are shared here as examples. Firstly, it was observed that DRH was sensitive to several factors in the manufacturing process, *e.g.*, granulator's rotational speed, temperatures, time, and moisture contents. Thus, the samples used for obtaining MSI must be carefully prepared by a method which is truly mimics the process that the results will represent. Secondly, impurities and compositional fluctuations in ingredients were also found to affect DRH, so raw materials must also be representative. Another point worth mentioning is that static sorption methods are usually employed for studying products in storage and drying conditions, although using one of these methods to establish a comprehensive series of MSI is often a resource and time challenge. Whenever applicable, they may be replaced with a dynamic sorption method, such as dynamic vapor sorption (DVS) and dynamic dewpoint isotherm (DDI), which is much quicker. However, these methods required an investment in equipment specifically designed for the purpose. The methodology is also potential to be applied across various scientific domains. Whether exploring the composition of pharmaceutical formulations, food products, or chemical blends, the underlying principles remain applicable. MSI can always be replaced with other tools to serve alternative purposes. Interactions amongst ingredients are always an essential key to the predictive accuracies of equations. The number of experimental points will inevitably increase when a higher level of interactions is taken into account. On the other hand, taking these interactions into account unnecessarily will certainly be a waste. The dilemma is that the choice of models, and the levels of interactions to be included, must be decided at the beginning of experimental design before their significances are proven. Making this decision is not necessarily easy: it may need preliminary studies to find supporting evidence, since relevant information is not always available in literature.

Trace plots are used here to illustrate complex behaviors of ingredients toward the DRH lowering. Ones may argue that the DRH lowering in real fertilizers can seldomly be described by a trace plot as the fractions of ingredients are unlikely to change or fluctuate in a specific pattern. However, the trace plot remains as a valuable tool in studying the DRH lowering.

This is because they allow the effects of ingredients to be readily displayed. In systems higher than ternary, they also complement tools like the response surface and the contour plots which can only visualize the effects by having the fractions of one or more ingredients remain constants. Nevertheless, the magnitude of DRH lowering for a particular formula can always be predicted directly by using the governing equation.

As represented in Eq. (3), DRH was affected by not only the fractions of ingredients but also various possible chemical and physical interactions that were arbitrarily represented by mathematical terms. The contributions of the interactions then became even more significant as the number of ingredients was increased, and this in turn has very much effect on the accuracy of prediction. All the binary interactions had adverse effects on DRH, *i.e.*, they increased the magnitude of lowering, while the only ternary interaction gave the opposite effect. The terms representing the interactions between U and other deliquescent ingredients were also reflected its significant lowering effect by their relatively high values of β_{ij}.

In terms of mechanism, Mauer and Taylor[1], and Mauer[4] proposed that the DRH lowering, in general, occurred as a result of the simultaneous dissolution of ingredients in water. Although, it could be the primary mechanism responsible for the DRH lowering, the differences in the lowering magnitudes and the eutotic compositions perhaps indicated the contributions given by other mechanisms, and chemical and physical differences or similarities amongst the ingredients.[18,19,62] An explanation for U was hypothesized from the work of Hammami *et al*.[63] That, the structure formed when U bonded with water could act as a "breaker" of DAP, MOP, and AS internal ionic bonds, facilitating their dissolution in water. The need for U in fractions greater than the others to reach the EDRH point perhaps indicated that it needed to be in good contact with the others to effectively lower DRH. On the other hand, the bond-breaking process could not happen to KF because of its non-soluble nature. Thus, the magnitudes of DRH lowering became less when KF replaced parts of deliquescent ingredients, as the effect of extra water in KF could not outperform the effect of bond breaking. Since the present study only involved mathematic modelling in describing the DRH lowering and only limited information could be drawn from literature for explanation, the above hypotheses had to be left unproven. Nonetheless, the results at least confirmed that the DRH lowering in the mixtures of these five ingredients is complex. Several mechanisms can play parts in the process through several possible physical and chemical interactions and could either counteract or complement one another. An individual ingredient can also behave differently depending on the presence of other ingredients and their proportion.

DRH lowering, whether strong or weak, makes a fertilizer more prone to a permanent change in its effectiveness for the intended purpose. The effect could be, for examples, changing the rate of nutrition release and the appearance, although much more severe effects can be resulted in products such as food and medicines. The change can occur through several associated phenomena; *e.g.*, dissolution, deliquescence, chemical reaction, and salt formation[7,10,13] depending on the moisture level and the ingredient combination. Physical alterations of fertilizers through phenomena such as shape deformation, crystal bridge formation, and mass flow will cause caking.[64-66] A mild level of caking would be easily broken. Stronger cake could not be broken easily and that would render a fertilizer useless for automatic dispersion, which now become a norm in most parts of the world. The most severe caking would make the fertilizer useless by any forms of dispersion and give an unpleasant impression to end users.

More work needs to be done. The work should be extended into other ingredients essential to compound fertilizers, as well as other deliquescent materials, particularly, those used in food and pharmaceutical industries, to gain a comprehensive understanding of their influences. In addition, experiments that are designed to give more detail about the DRH lowering for the composition around the formulae of interest are also worth exploring.

A long-term stability study should be employed to assess the mechanisms and the enduring impacts of DRH lowering on physical and chemical properties; it involves maintaining samples under a controlled environment for a specific storage duration, followed by thorough monitoring and characterizing at intervals. This would further enhance the understanding in the diverse contributions of ingredients and the long-term behaviors of a deliquescent system. The extended information can be utilized to establish correlations and to provide insights into the underlying factors that lead to the varying DRH lowering effects in different mixtures of ingredients.

4. Conclusion

A special cubic equation was successfully constructed. The I-optimal design criterion was very useful in reducing the number of experiments. With the nature of the criterion and the adoption of Scheffé's special cubic model, the equation gave good accuracy in predicting the values of DRH. The performances of the equation were confirmed by various statistical tools, and the value of ARD was better than those of the predictions made by other approaches reported elsewhere.

Both DRH values estimated from the experimental data and predicted by the equation indicated that the DRH lowering occurred at all possible combinations and ingredient fractions, albeit with different magnitudes. All the ingredients had complex roles in the DRH lowering and exercised their roles through interactions with one another. Urea was the most significant ingredient for the DRH lowering, especially in the presence of other deliquescent ingredients. In certain ingredient combinations, the presence of ingredients, such as DAP, AS or KS, helped alleviate DRH lowering.

The study provides comprehensive information on the deliquescent behavior and the DRH lowering in the mixtures of five common fertilizer ingredients. The information can be useful in manufacturing, quality control, and research. Understanding the influences of individual components on deliquescence can lead to the development of more caking resistant fertilizers and more effective, customizable, or target-specific anti-caking agents. The methodology employed here holds promise for the identification of affecting components in mixtures. It can be applied to not only other fertilizers but also other moisture-sensitive systems, such as foods and medicines, to identify their optimal formulations and ensure their stability. The practical value of this methodology is emphasized by minimizing the number of experiments necessarily required to adequately describe mixtures, and the time required to obtain an optimal solution. It accelerates the investigating process and renders mixture experiments more accessible and executable by industrial practitioners.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Applicable.

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