Summary of physico-chemical, environmental fate, and acute hazard data for mono-ureas of TDI and MDI

III Scientific Office

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Various substituted polyureas are formed during reaction of TDI and MDI under heterogeneous mixing with water. The mono-ureas represent the first intermediate products in the stepwise formation of polyurea which is the ultimate end-product of such hydrolysis reactions. The isocyanato-terminated ureas are transient species. To the extent soluble, the terminal isocyanate (NCO) groups hydrolyze in water (see e.g., Gahlmann[1] et al., 1993). Like isocyanates and their corresponding amines, the terminal NCO and amino (NH_2) groups of the ureas will react to form oligo- and poly-ureas as the final hydrolysis product (see e.g., Yakabe[2] et al., 1999; Ahn[3] et al., 2013). Ahn et al. could detect up to 11 coupled urea units after 1 hour reaction time.

As the mono-ureas exhibit the lowest-possible molecular weights and octanol-water partition coefficients (log P_{ow}) and conversely the highest water solubility for these transformation products of TDI and MDI hydrolysis, they are expected to represent the "worst-case" with regards to bio-availability and potential hazard in the environment. Since environmental exposure properties and aquatic hazard potential of substances are often well-correlated to log P_{ow} and molecular weight, it is useful to understand the relationship of urea molecular weight (i.e., # of urea linkages) to log P_{ow} of these substituted ureas of TDI and MDI. Examples of these structure-property relationships for the amine- and isocyanate-terminated urea species of TDI and MDI are shown in Table 1. Selected physical-chemical, environmental fate, and

[1] Gahlmann, R., Herbold, B., Ruckes, A., and Seel, K. (1993). *Zbl Arbeitsmed* 43: 34-38.
[2] Yakabe, Y., Henderson, K.M., Thompson, W.C., Pemberton, D., Tury, B., and Bailey R.E. (1999). *Environ Sci Technol* 33: 2579-2583.
[3] Ahn, Y.H., Kim, J.S., and Kim, S.H. (2013). *Anal Sci* 29: 703-708.

acute hazard properties have been determined for representative amine- and isocyanate-terminated mono-ureas of TDI (Figures 1a-b, 2) and MDI (Figures 3a-b, 4) are summarized in Table 2.

Table 1. Relationship of molecular weight and octanol-water partition coefficient (log P_{ow}) for representative amine- and isocyanate-terminated oligo-ureas of TDI and MDI

Number of urea links	TDI-based ureas				MDI-based ureas			
	Isocyanato-terminated		Amino-terminated		Isocyanato-terminated		Amino-terminated	
	MW [g/mol]	log P_{ow}[4]	MW [g/mol]	log P_{ow}	MW [g/mol]	log P_{ow}	MW [g/mol]	log P_{ow}
0	174	3.7	122	0.2	250	5.2	198	2.2
1	322	5.3	270	1.1	475	8.2	423	5.2
2	470	6.2	418	2.1	699	11.2	647	8.2
3	619	7.2	567	3.1	923	14.2	871	11.2
4	767	8.2	715	4.0	1147	17.2	1095	14.2
5	915	9.2	863	5.0	1372	20.2	1320	17.2

For TDI-derived urea substances, conversion of the two isocyanate groups to amino groups reduces log P_{ow} by approximately 4 log units. Every added urea link increases log P_{ow} by 1 log unit, and MW by 148 g/mole. For MDI-derived urea substances, conversion of the two isocyanate groups to amino groups reduces log P_{ow} by approximately 3 log units. Every added urea link increases log P_{ow} by 3 log units, and MW by 224 g/mole.

[4] Log P_{ow} values calculated with EPI Suite KOWWIN v1.68.

Table 2. Summary of key physical-chemical, environmental fate, and acute hazard properties of amine- and isocyanate-terminated mono-ureas of TDI and MDI

Property	Method	Notes	NCO-terminated mono-urea of TDI	NH_2-terminated mono-urea of TDI	NCO-terminated mono-urea of 4,4'-MDI	NH_2-terminated mono-urea of 4,4'-MDI
CASRN			Not available	Not available	93805-48-2	172944-17-1
Physicochemical properties (data summarized from III Reports 11700[5] and 11741[6])						
Relative Density at 20 °C	DIN EN ISO/IEC 17025		1.333 (2,4-TDI) 1.341 (80:20 TDI)	1.266 (2,4-TDI)	1.336	1.354
Vapor pressure at 25 °C [Pa]	Estimation EPI Suite MPBWIN v1.43		7.0×10^{-7}	1.1×10^{-7}	2.6×10^{-11}	5.0×10^{-12}
Melting point [°C]	OECD 102 (DTA/DSC)		193	196	203	200
Water solubility at 20 °C [mg/L]	OECD 105		0.020	56	<0.002	39 (pH 2) <0.004 (pH≥7)

[5] Loddenkemper, T., Pirkl, H.-G., Tajvidi, K., Allmendinger, H., Moldenhauer, J., and Tury, B. (2017). Oligo-ureas of TDI: synthesis, characterization, and determination of selected physico-chemical properties. III Report 11700.
[6] Neuhahn, A., Neuland, M., and Sadler, T. (2020). Mono-ureas of MDA and MDI: determination of physico-chemical properties, biodegradability, and acute aquatic toxicity. III Report 11741.

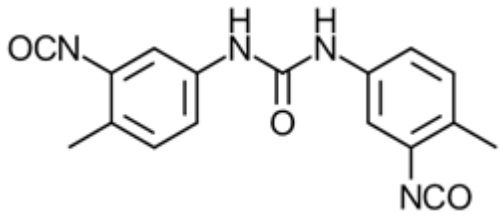
Property	Method	Notes	NCO-terminated mono-urea of TDI	NH_2-terminated mono-urea of TDI	NCO-terminated mono-urea of 4,4'-MDI	NH_2-terminated mono-urea of 4,4'-MDI
Acid dissociation constant (pK_a) terminal amino group	Estimation EPI Suite KOWWIN v1.68	Cannot be measured – insoluble in water	Not applicable	4.6 +/- 0.1	Not applicable	5.1 +/- 0.3
Acid dissociation constant (pK_a) urea group	Estimation EPI Suite KOWWIN v1.68	Cannot be measured – insoluble in water	0.7 (NH_2^+ →NH) 13.7 (NH → N^-)	Not determined	Not determined	14.2 (NH → N-)
Octanol-water partition coefficient (log Pow) at 25 °C	OECD 117 (TDI) EPI Suite KOWWIN v1.68 (MDI)	Measurement unsuccessful for MDI-urea	3.7-4.7 (depending on isomer)	1.3-1.4 (depending on isomer)	- 8.2	- 5.2
Acute toxicity information (data summarized from III Reports 11729[7] and 11741)						
Ready Biodegradability	OECD 301F	Not readily biodegradable				
72 h Algae Growth Inhibition [mg/L][8]	OECD 201	E_rL_{50} E_rC_{50} NOELR NOEC	>100 - >100 -	>100 - >100 -	>100 - >100 -	>100 - >100 -

[7] Loddenkemper, T., Allmendinger, H., Neuhahn, A., and Neuland, M. (2019). TDA mono urea: preparation and determination of physico-chemical properties, biodegradability, and acute aquatic toxicity. III Report 11729.
[8] Effects on algae are derived from inhibition of growth rate (i.e., ErC50, ErL50, NOELRr, NOECr).

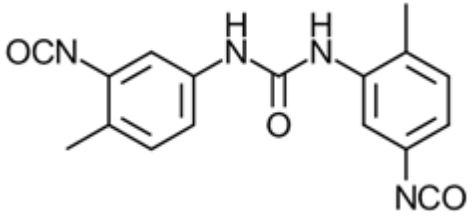
Property	Method	Notes	NCO-terminated mono-urea of TDI	NH_2-terminated mono-urea of TDI	NCO-terminated mono-urea of 4,4'-MDI	NH_2-terminated mono-urea of 4,4'-MDI
48 h Daphnia magna Immobilization [mg/L]	OECD 202	EL_{50} EC_{50}	>100 -	- >100	>100 -	- >100
96 h Danio rerio Lethality [mg/L]	OECD 203	LL_{50} EC_{50}	>100 -	- >100	>100 -	- >100
Acute oral toxicity in rat [mg/kg_{bw}][9]		LD_{50}	Not determined	>15,000	Not determined	>15,000

[9] Steinhoff, D. (1973). Acute oral toxicities of (note: NCO-free) polyureas prepared from 80/20 TDI and 4,4'-MDI (peanut oil medium, rat). III Report 10658.

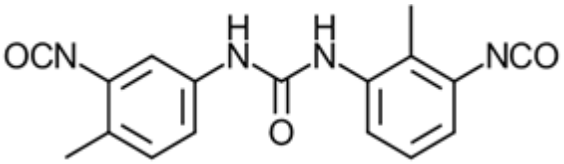
Figure 1a. Isocyanato-terminated mono-ureas of TDI (examples of possible isomers):



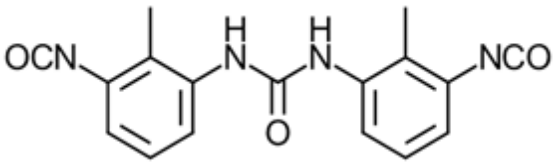
4,4’-urea of 2,4-TDI



4,2’-urea of 2,4-TDI

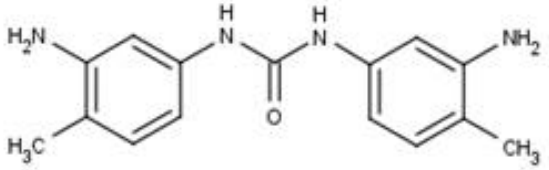


4,2’-urea of 2,4- and 2,6-TDI



2,2’-urea of 2,6-TDI

Figure 1b. Amino-terminated mono-urea of TDI (example of possible isomers):



4,4’-urea of 2,4-TDI

Figure 2. Photograph of polyureas obtained from stirring of 50 g/L TDI (80:20 2,4-:2,6) in distilled water for 14 d:

Figure 3a. Isocyanato-terminated mono-urea of 4,4’-MDI (isomer for which data were determined):

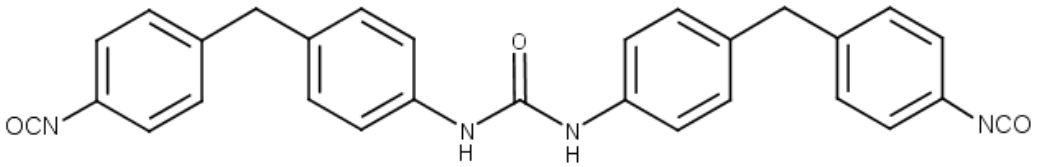


Figure 3b. Amino-terminated mono-urea of 4,4’-MDI (isomer for which data were determined):

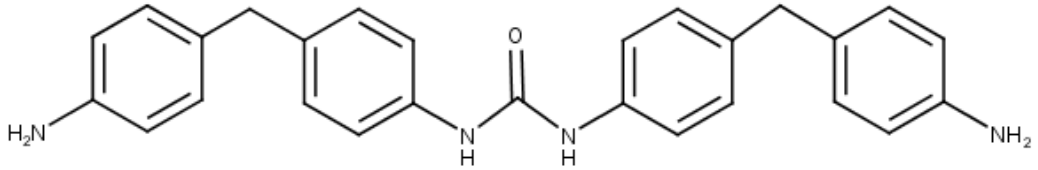


Figure 4. Photograph of polyureas obtained from stirring of 50 g/L pMDI in distilled water for 14 d: