Triethylenediamine

Physical, Chemical, and Catalytic Properties

The synthesis, chemical and some physical properties, and catalytic characteristics of triethylenediamine are discussed in a companion article appearing in the October 1959 *Industrial and Engineering Chemistry* on page 1299 (*3*).

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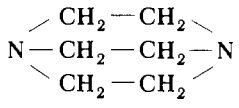
The amine, triethylenediamine, exhibits certain unusual properties which are due to its bicyclic or "cage" structure,



The most outstanding of these, such as high melting point and complexing ability, arise from the molecular symmetry and the lack of steric hinderance for both tertiary nitrogen atoms. Triethylenediamine, known also as 1,4-diazabicyclo-(2,2,2)-octane, has found a special commercial application as a catalyst in polyurethane foam manufacture. In this application, its ability to catalyze reactions between isocyanates and hydroxy compounds with great rapidity and yet with a desirable balance between rate of foaming and chain growth, is outstanding.

New data are presented on physical properties whose determination became possible with the recent availability of high purity triethylenediamine (Dabco, Houdry Process Corp.). Further information and data on the synthesis, chemical and physical properties, and particularly the catalytic characteristics of triethylenediamine are available in the companion article and in forthcoming publications dealing with polyurethane catalysis (*1, 2*).

PHYSICAL AND CHEMICAL PROPERTIES

The density of solid triethyenediamine is 1.14 grams per cc. at 28° C.; the melting point is 158° C., the boiling point, 174° C., and the flash point, >50° C. The phase diagram, Figure 1, illustrates the high melting point of the amine, its transition at 74° C., and the formation of two hydrates.

The vapor pressure of triethylenediamine and its solubility in various solvents are given in Table I, the Debye-Scherrer x-ray powder diffraction and mass spectrum data in Table II, and the infrared spectrum in Figure 2.

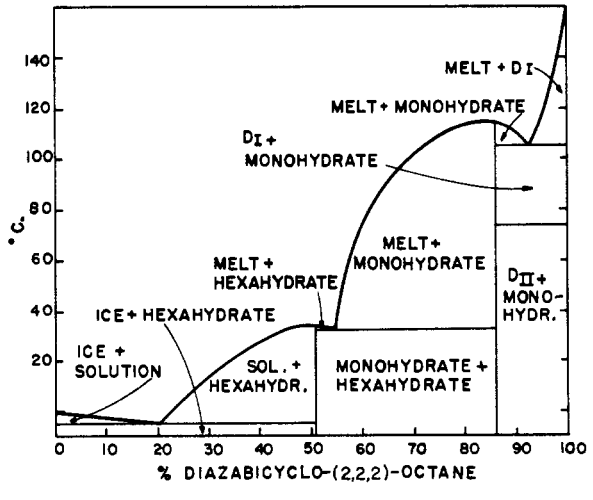


Figure 1. Phase diagram of diazabicyclo-(2,2,2)-octane–water system

D_I = High temperature form of diazabicyclo-(2,2,2)-octane
D_{II} = Low temperature form of diazabicyclo-(2,2,2)-octane
SOL = Solution

Table I. Vapor Pressure and Solubility of Triethylenediamine

Vapor Pressure		Solubility			
Temp., °C.	Mm. Hg	Temp., °C.	G./100 g. H_2O	Solvent	G./100 g. solvent at 25° C.
50	4				
60	7			Acetone	13
70	13	5	33	*n*-Pentane	4
80	22	25	61	Ether	5
90	36	45	127	Ethyl alcohol, 92%	77
100	58	65	144	Benzene	51

The chemical properties are those generally expected of a ditertiary amine, but, the steric availability of the two nitrogen atoms modifies its properties significantly. Chemical properties are discussed in a companion article with references (*3*). The melting points of single and double salts have been reported (*5–8*).

CATALYTIC PROPERTIES

The outstanding catalytic ability of triethylenediamino for the isocyanate-hydroxyl compound reaction is demonstrated by the properties of the polyurethane foams which are shown in Table III. These are characterized by low densities, relatively high tensile strength and low compression set. The high catalytic activity is as much as ten times greater than for other amine catalysts (*2,3*).

Table II. Mass Spectrum and X-Ray Diffraction Data for Triethylenediamine

Mass Spectrum [a]						X-Ray Diffraction [b]	
Mass-charge ratio, *m/e*	Relative intensities, 70 v.	Mass-charge ratio, *m/e*	Relative intensities, 70 v.	Mass-charge ratio, *m/e*	Relative intensities, 70 v.	*d/n*	I/I_0
24	0.12	53	0.93	81	0.92	5.3	0.90
25	0.91	54	9.52	82	3.30	4.7	1.00
26	11.31	55	61.59	83	5.20	2.93	0.70
27	28.24	56	30.57	84	9.66	2.72	0.60
28	34.13	57	48.76	85		2.6	0.20
29	21.51	58	18.98	86	0.11	2.38	0.65
30	10.26	59	0.83			2.16	0.30
31	0.38	60	0.03	94	0.03	2.02	0.30
				95	0.06	1.98	0.10
37	0.22	64	0.03	96	0.09	1.88(?)	0.02
38	0.72	65	0.03	97	2.10	1.86	0.10
39	3.32	66	0.09	98	0.15	1.79	0.30
40	4.31	67	0.68	99	0.03	1.69	0.05
41	22.40	68	1.98			1.61	0.02
42	100.00	69	4.79	107	0.03	1.58	0.05
43	4.59	70	11.79	108	0.03	1.24	0.02
44	4.53	71	0.83	109	0.03	1.205	0.02
45	0.39	72	0.26	110	0.15		
46	0.12			111	2.02		
		77	0.03	112 (p)	42.17		
50	0.14	78	0.13	113	3.10		
51	0.68	79	0.03	114	0.11		
52	1.96	80	0.19				

[a] Consolidated Mass Spectrometer Model 21-10, liquid sensitivity for *m/e* 42, div./1:1830, spectral ratio for *n*-butane *m/e* 58/43:0.1346, sensitivity for *n*-butane *m/e* 43, div./:74.3.
[b] Norelco x-ray unit and powder camera; radiation, 40 kv. cu.

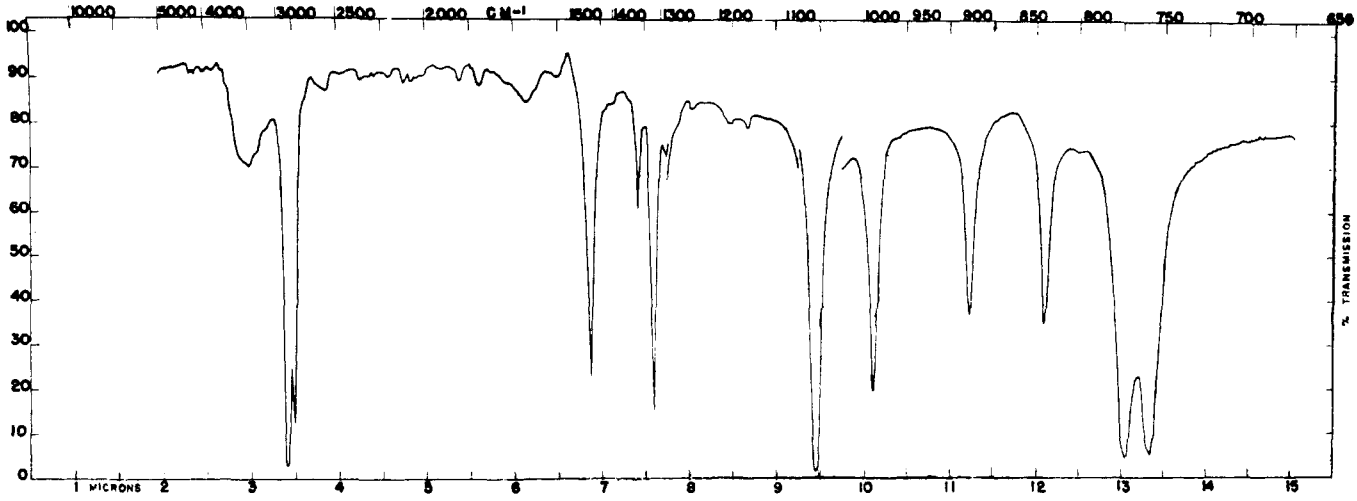


Figure 2. Infrared spectrum of diazabicyclo-(2,2,2)-octane

Perkin Elmer Spectrometer Model 21.
Concentration 1.01 g./100 ml.
1.0 mm. NaCl Prism
2–7.75μ and 9.25–9.75μ: solvent CCl_4
7.75–9.25μ and 9.75–15.00μ: solvent CS_2

Table III. Formulation and Properties of Polyurethane Foams Using Triethylenediamine Catalyst

Formulation	Hand Mix					Machine Mix		
PPG [a]	100	83.3	66.7	50	33.3	71	71	
LHT-67 [b]		16.7	33.3	50	66.7			
LG-56 [b]						29	29	100
TDI [c]	37	→				37	37	37
H_2O	2.5	→				2.76	2.98	2.9
X-520 [d]	0.58	→				1.0	0.49	0.5
DABCO [e]	0.58	→				0.58	0.58	0.5
Foam properties							*	**
Density, lb./cu. ft.	2.65	2.40	2.5	2.48	2.20	2.46	2.11	2.22
Tensile strength, p.s.i.	12.9	14.6	13.1	13.2	11.7	17.1	16.2	18.6
Tear resistance, lb./inch	4.5	3.88	3.4	2.58	2.40	3.92	3.34	1.82
Compression load, p.s.i. at 25% deflection	0.48	0.41	0.37	0.36	0.43	0.35	0.30	0.36
Compression set, % of original height, 50% deflection 22 hr. at 70° C.	8.9	7	6.9	8.1	0.7	11.8	8.9	7.7

Tests after curing at 250° F.—3 hr. except *1 and **2 hours.

[a] Polypropylene glycol 2000, Union Carbide Chemical Co., Wyandotte Chemical Co., Dow Chemical Co.
[b] Niax Triol, Union Carbide Chemical Co.
[c] Toluene diisocyanate (80-25).
[d] Silicone, Union Carbide Corp.
[e] Triethylenediamine, Houdry Process Corp.

TOXICITY AND PHARMACOLOGICAL EFFECTS

According to tests carried out by the Upjohn Co., the 50% lethal dose of triethylenediamine is 200 mg. per kg. for mice (accurate to minus 50% to plus 100% of reported figure) while the anabolic-androgenic, antivirial, diuretic, and analgetic-narcotic activity of triethylenediamino proved to be negative in all cases.

Mann and Baker (7) tested triethylenediamine on roundworm of mice, cats, and litomosoides of cotton rats but found it to be inactive, or of transient effect. According to Friess (4) triethylenediamine is completely inactive as inhibitor of acetylcholinesterase.

In handling triethylenediamine, ingestion or inhalation of the dust, or its contact with eyes or skin should be avoided.

ACKNOWLEDGMENT

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