Experimental Flash Points of Industrial Amines

John W. Mitchell, Menas S. Vratsanos, Brian F. Hanley,† and Vipul S. Parekh*

Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, Pennsylvania 18195-1501

Closed cup flash points have been measured at atmospheric pressure for 37 industrially important amines and amine solutions. The flash point measurements were made using either an ERDCO Engineering Corp. closed cup flash point tester or a Grabner Instruments automated closed cup flash point tester. The measured flash points have been compared against the standard literature sources for such material safety data, when available. The measured flash points show good agreement with reported values for 9 out of the 37 systems reported here. While literature data are found lacking for 19 amines, large discrepancies have been noted in reported values for the remaining 9 materials.

Introduction

The flash point is one of the most important physical properties used to determine the potential for fire and explosion hazards of industrial materials. The flash points are used by virtually all the environmental, health, and safety organizations in both government and industry to classify flammable liquids for safety and transportation regulations. An accurate knowledge of the flash point is important in developing appropriate preventive and control measures in industrial fire protection (Sax, 1979). The stringent regulations related to material safety have also made accurate measurements of flash points essential.

The flash point is the lowest temperature at which a liquid will give off sufficient flammable vapor near its surface such that it ignites when brought in contact with air and a spark or a flame (Sax, 1979). This occurs when the concentration of the flammable vapor in the headspace approaches the lower flammable limit (LFL) of the material. If the space is enclosed, the vapor will be a saturated mixture in air resulting in a more flammable mixture than when the space is open and the vapor is given free access to air. The former situation is created in closed cup flash point measurements, while the latter condition occurs in open cup flash point tests. The observed flash point temperature is generally several degrees lower in closed cup measurements due to higher vapor concentrations. While the open cup tests usually simulate the actual condition more closely, the closed cup values provide a conservative estimate of the flash point.

In our observation, flash points are often not reported in the literature for many of the industrially important materials. Even when the values are available, the reference source of the information is commonly not provided, leading to an uncertainty as to whether the value was measured experimentally or estimated via one of the several prediction methods (Prugh, 1970; Hu and Burns, 1970; Walsham, 1978). Frequently, one also comes across conflicting values of flash points in the literature. Owing to increasing importance of safety-related issues in the chemical industry, it is imperative the same attention is devoted to the experimental method used, measurement accuracy, and repeatability while reporting material safety data, as is the norm for physical property data used in the design and construction of chemical processes and plants. In this paper, we report measured flash points of 37 industrially important chemicals, including a series of anhydrous amines and aqueous amine solutions. These amines are typically used as feedstocks in a variety of applications, including as solvents, in water treatment, and as agricultural chemicals.

Experimental Section

Measurements. Amine flash point measurements were made on either an ERDCO Engineering Corp. closed cup flash point tester or a Grabner Instruments automated closed cup flash point tester. The ERDCO tester uses a method similar to that described in ASTM D 3828 (Standard Test Method for Flash Point by Small Scale Closed Tester) and relies on visual observation for the determination of the flash point. The Grabner CCA-FLA 8, shown schematically in Figure 1, is an eight position, automated, closed cup flash point tester whereby the flash point is detected by measuring the sudden pressure increase inside the closed chamber due to the flame. The configuration of the Grabner tester does not conform to the typical "Setaflash" (Fawcett and Wood, 1982) flash point tester. Also, the flash point definition used by the Grabner tester differs slightly from that used by ASTM; the flash points found with the Grabner instrument, however, are in good agreement with Setaflash closed cup results. For the experiments with the Grabner instrument the flash point measurements were performed with a temperature ramping rate of 3 °C/min, with a test for flash at 1 °C intervals.

Materials. All materials used in this study were obtained from commercial grade product from Air Products and Chemicals, Inc. Because of the very low flash points of some of these materials, liquid nitrogen was used to cool the ERDCO apparatus to approximately −73 °C. For these materials, samples were injected directly from a sample cylinder into the ERDCO tester sample cup. Prior to the measurement of any flash point data, the sample cup was quickly dried to remove any moisture. No estimates of repeatability and reproducibility are indicated in the ASTM method for materials with such low flash points. Given the extreme difficulty of the measurements and the possibility

* To whom correspondence should be addressed.
† Present address: Jaeger Products, Inc., 1611 Peachleaf, Houston, TX 77039.

10.1021/je980144h CCC: $18.00
Published on Web 01/14/1999

Table 1. Flash Point Measurements for Industrial Amines

material	CAS reg no.	flash point, °C: this work closed cup	Lenga (1985) closed cup	Lewis (1996) closed cup	Lewis (1996) open cup	NFPA[a] (1994) closed cup	NFPA[a] (1994) open cup	Hanley (1998) predicted
monomethylamine, anhydrous	74-89-5	−62	0	0				−57.84
monomethylamine, 25 wt % aqueous solution		−4						
monomethylamine, 40 wt % aqueous solution		−11						
monomethylamine, 50 wt % aqueous solution		−23						
dimethylamine, anhydrous	124-40-3	−57						−54.8
dimethylamine, 1 wt % aqueous solution		65.6						
dimethylamine, 2 wt % aqueous solution		52.8						
dimethylamine, 5 wt % aqueous solution		39.4						
dimethylamine, 10 wt % aqueous solution		25.6						
dimethylamine, 40 wt % aqueous solution		−18	15					
dimethylamine, 50 wt % aqueous solution		−27						
dimethylamine, 60 wt % aqueous solution		−34						
dimethylamine, 65 wt % aqueous solution		−42						
trimethylamine, anhydrous	75-50-3	−71			−6.7			−69.13
trimethylamine, 25 wt % aqueous solution		3.3	3					
trimethylamine, 40 wt % aqueous solution		−17						
di-*n*-propylamine	142-84-7	7.5	3		17		17	
tri-*n*-propylamine	102-69-2	33.5	36		41		41	
mono-*n*-butylamine	109-73-9	<−10	−1	−12	−12	−12		
di-*n*-butylamine	111-92-2	42.5	41		52	47		
tri-*n*-butylamine	102-82-9	72.5	63		86		86	
ethyl-n butylamine	13360-63-9	8.1	18				18	
diisobutylamine	110-96-3	24.2	29	21		29		
aminobutryaldehyde dimethyl acetal	19060-15-2	69.2						
cyclohexylamine, anhydrous	108-91-8	26.5	32	21		31		
cyclohexylamine, 60 wt % aqueous solution		50.5						
1,8-diazabicyclo[5.4.0]undec-7-ene	6674-22-2	115.5	>112					
dicyclohexylamine	101-83-7	99.5	96		>99		>99	
N,*N*-diethylcyclohexylamine	91-65-6	59.5	57					
(dimethylamino)propylamine	109-55-7	30.5	15		38		38	
N-ethylcyclohexylamine	5459-93-8	45.1			30		30	
N-ethyl-1,2-dimethylpropylamine	2738-06-9	10.2						
2-methylcyclohexylamine	7003-32-9	35.2	21					
methoxyisopropylamine	37143-54-7	7.2						
bis(paraamino)cyclohexylmethane	1761-71-3	153.5						
tetramethyliminobis(propylamine)	6711-48-4	82.5						
N,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine	110-95-2	30.5	31					

of nonisothermal conditions, the accuracy of flash points is estimated to be approximately ±3 °C.

Results and Discussion

Flash points of the 37 materials measured in this work are listed in Table 1. The values reported in the standard sources of safety data (Lewis, 1996; Lenga, 1985; National Fire Protection Association, 1994) are also listed, along with theoretical predictions based on flammability and vapor pressure data (Hanley, 1998), whenever available. Good agreement with reported values has been obtained for 9 amines. These include an aqueous solution of 25 wt % trimethylamine, tri-*n*-propylamine, mono-*n*-butylamine, di-*n*-butylamine, diisobutylamine, 1,8-diazabicyclo[5.4.0]-undec-7-ene, dicyclohexylamine, *N*,*N*-diethylcyclohexyl-amine, and *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine. However, it must be noted for mono-*n*-butylamine and diisobutylamine, while our values are in fairly close agreement with those tabulated in Lewis (1996), the flash points in Lenga (1985) are considerably higher. The lack of reference information of flash point data in both of these literature sources makes it difficult to gauge the quality of reported values.

A large discrepancy between the experimental values of this work and the reported literature numbers can be noticed for 9 systems. It is especially significant to observe the discrepancy in the reported flash point of anhydrous monomethylamine. Even though identical values have been reported in Lewis (1996) and Lenga (1985) for monomethylamine flash point, their value of 0 °C appears unusually high in relation to the monomethylamine boiling point of −6.3 °C. Repeated measurements in our work yielded the lower value of −62 °C, which we now believe is the most reliable number for monomethylamine flash point. The value reported in a theoretical prediction (Hanley, 1998) is also in good agreement with the measurement from the present study.

The measured flash points of ethyl-*n*-butylamine and an aqueous solution of 40 wt % dimethylamine are also seen to be lower than tabulated values. The flash points of di-*n*-propylamine, tri-*n*-butylamine, (dimethylamino)propylamine, and 2-methylcyclohexylamine in this work are higher than the reported numbers in Lenga (1985). For anhydrous cyclohexylamine, however, the measured flash point is bracketed by the literature values in Lewis (1996) and Lenga (1985).

Table 1 also lists the flash points of aqueous solutions of dimethylamine at 8 different concentrations in addition to the flash point of anhydrous dimethylamine. Figure 2 displays these flash points as a function of dimethylamine concentration. The drop in flash point at increasingly higher dimethylamine concentrations is similar to that predicted by theory (Hanley, 1998). These data are helpful in understanding the flash points of binary systems containing an inert component, which in this case is water. In this case, the flash point depends not only on the vapor pressure of the flammable component but also on its activity in the solution. At high concentrations of dimethyl-

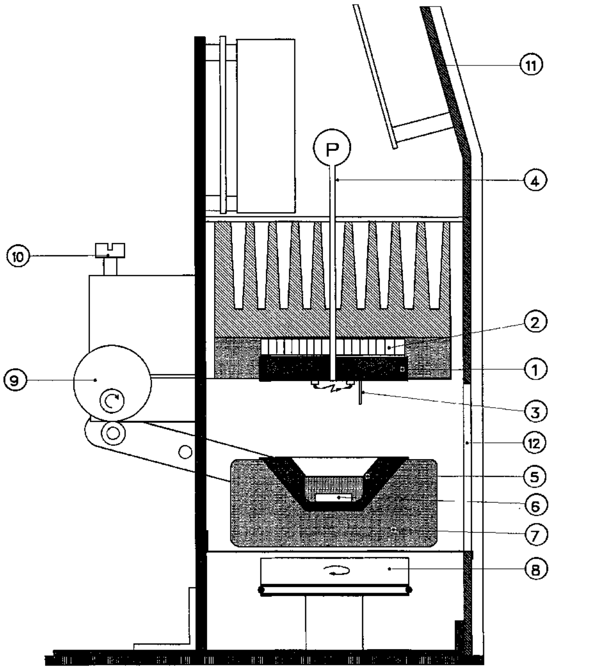

Figure 1. Schematic of Grabner Instruments CCA-FLA 8 automated closed cup flash point tester.

amine, the mixture flash point approaches the flash point of pure dimethylamine as its activity coefficient approaches unity. At lower concentrations, the flash point temperature increases with the increasing activity of dimethylamine and it increases sharply in the limit of infinite dilution of dimethylamine in water. It is important to observe this large change in the flash point temperature for a small change in the concentration of the dilute flammable component in Figure 2. This is of special significance to the chemical industry since safety considerations for exit streams and waste streams from manufacturing processes often contain small concentrations of flammable compounds in inert solvents such as water.

It is important to note no values are reported in standard literature sources for as many as 19 out of the 37 materials studied here. This work strives to fill this gap in the literature information of flash points for industrially important amines. Similar gaps can be noticed in the

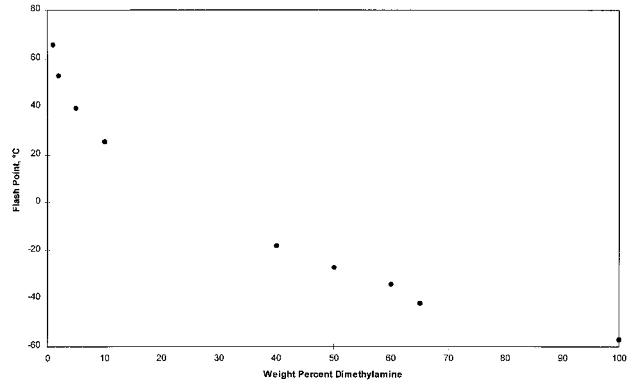

Figure 2. Experimental flash points of aqueous dimethylamine solutions as a function of dimethylamine concentration.

literature for flash points of other industrial chemicals as well as other material safety data such as flammability limits and autoignition temperatures of many important chemicals. It is expected more studies will be reported in the literature to provide accurate and reliable safety data for the chemical industry.

Acknowledgment

We gratefully acknowledge the experimental contributions of Dr. Bruce D. Lawrey, Andrew A. Leffel, and Leonard J. Dzierzanowski. We thank Petrolab Co. for permission to use the flash point tester schematic.

Literature Cited

Fawcett, H. H.; Wood, W. S. *Safety and Accident Prevention in Chemical Operations*, 2nd ed.; Wiley-Interscience: New York, 1982; p 342.

Hanley, B. F. A Model for the Calculation and the Verification of Closed Cup Flash Points for Multicomponent Mixtures. *Process Saf. Prog.* **1998**, *17*, 86−97.

Hu, J.; Burns, A. M. New Method Predicts Cloud, Pour, Flash Points of Distillate Blends. *Hydrocarbon Process.* **1970**, *49*, 213−216.

Lenga, R. E. *The Sigma Aldrich Library of Chemical Safety Data*, Edition I; Sigma-Aldrich Corp.: Milwaukee, 1985.

Lewis, R. J., Sr. *Sax's Dangerous Properties of Industrial Materials*, 9th ed.; Van Nostrand Reinhold: New York, 1996.

National Fire Protection Association. NFPA 325 Guide to Fire Hazards Properties and Flammable Liquids, Gases, and Volatile Solids. *Fire Protection Guide to Hazardous Materials*; National Fire Protection Association: 1994.

Prugh, R. W. Estimation of Flash Point Temperature. *J. Chem. Educ.* **1970**, *50*, A85−A89.

Sax, I. N. *Dangerous Properties of Industrial Materials*, 5th ed.; Van Nostrand Reinhold: New York, 1979.

Walsham, J. G. *Prediction of Flash Points for Solvent Mixtures*. Advances in Chemistry Series 124; American Chemical Society: Washington, D.C., 1978.

Received for review June 26, 1998. Accepted November 23, 1998.

JE980144H