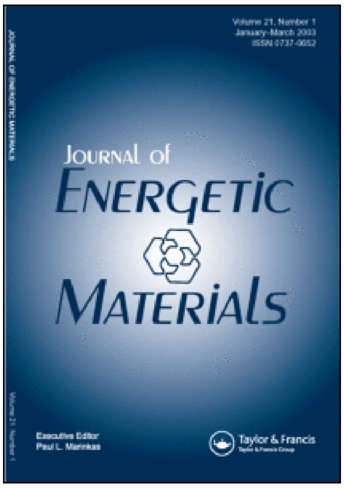

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ANALYSIS ON COMPUTATION OF KAMLET PARAMETER Φ FOR CHNO EXPLOSIVE MIXTURES

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ABSTRACT

Kamlet parameter ϕ has been used to predict many explosive performances within applicable errors. There are three computation methods of ϕ for an explosive mixture in references: Kamlet's original definition of ϕ (as ϕ_{I}), by using weighted-average N, M and Q values of pure components (as ϕ_{II}) and by adding the weighted ϕ values of pure components (as ϕ_{III}). In this paper, analysis shows that the three ϕ values can predict detonation velocity and detonation pressure within applicable accuracies over a broader range of chemical types for CHNO explosive mixtures. Note that ϕ_{III} gives the best prediction results and has the simplest computation.

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INTRODUCTION

In a series of interesting papers, Kamlet and coworkers[1-11] and other workers[12-14] have presented empirical correlations to predict the explosive performances of a condensed explosive in terms of ϕ and ρ (the loading density) of the explosive. Table 1 lists these simple prediction equations of explosive performances in terms of ϕ and ρ. Kamlet parameter ϕ is defined by:

$$\phi = NM^{1/2}Q^{1/2} \qquad \text{Eq.1}$$

where N is the number of moles of gaseous products of detonation per gram of explosive, M is the average molecular weight of the gaseous products and Q is the " heat of detonation " in calories per gram of explosive. For an explosive having the general formula $C_aH_bN_cO_d$, ϕ may be determined from the H_2O-CO_2 arbitrary assumption of detonation product compositions (Table 2).

Because explosives are usually used as mixtures, it is necessary to discuss the computation of Kamlet ϕ for explosive mixtures or formulations. The explosive mixtures contain one or more explosive compounds and one or more ingredients such as binders, plasticizers, sensitizers or desensitizers, oxidizers, metals, and a coloring agent. In this paper we will limit our discussion to explosive mixtures containing only C, H, N, and O atoms because Kamlet correlations (see Table 1) can give good predictions of explosive performances for pure $C_aH_bN_cO_d$ explosive compounds. There are three computation methods of ϕ for an explosive mixture in references. The first method is Kamlet's original definition of ϕ (defined as ϕ_{I} in this paper); the second is using weighted-average N, M and Q values of pure components (defined as ϕ_{II}); the third is adding the weighted ϕ values of pure components (defined as ϕ_{III}):

$$\phi_{III} = \sum x_i \phi_i \qquad \text{Eq.2}$$

where x_i and ϕ_i are the weight percent and Kamlet ϕ of the i-th component of the explosive mixture.

In this paper we will give a comparison of ϕ_{I}, ϕ_{II} and ϕ_{III} and then will evaluate the effectiveness of the various ϕ in predicting explosive performances.

RESULTS AND DISCUSSION

For purposes of illustration about various computation methods of ϕ, 21 explosive mixtures with composition of $C_aH_bN_cO_d$ are arbitrarily chosen to serve as the examples and presented in Table 3. These explosive mixtures are considered to cover a broader range of explosive types. The corresponding ϕ_{I}, ϕ_{II} and ϕ_{III} values are also assembled in Table 3.

The computation of ϕ_{I} is based on the assumption of complete equilibration, i.e., all components are assumed to react completely with each other on detonation to form the same set of products that one would expect from a homogeneous explosiveof the same elemental composition. Some ΔH^{o}_{f} values of explosive mixtures are taken from Ref.15 and Ref.16, the others are estimated by the present authors in the following way:

$$\Delta H^{o}_{f} = \sum (100x_i/MW_i)\, \Delta H^{o}_{fi} \qquad \text{Eq.3}$$

where x_i , MW_i and ΔH^o_{fi} are the weight percent, molecular weight and heat of formation of the i-th component of the explosive mixture (MW of an explosive mixture is considered to be 100). ΔH^o_{fi} values are taken from Table 5-1 of Ref.15. Some N, M and Q or ϕ_i values of pure components are taken from Ref.1 and Ref.3, the others are calculated by the present authors according to Eq.1 and Table 2. It should be noted that the expected small contribution from an ingredient (when $57800b + \Delta H^o_f < 0$) is ignored in the computations of ϕ_{II} and ϕ_{III}.

The data in Table 3 show that: (1) ϕ_{III} corresponds closely to ϕ_{II} and the difference between ϕ_{III} and ϕ_{II} is very small in most cases, but ϕ_{III} differs increasingly from ϕ_{II} as the detonation product species from all components are not common (i.e., the components are in different column of Table 2); (2) ϕ_I also corresponds closely to ϕ_{II} or ϕ_{III} if the components are in the same column of Table 2. It should be noted that ϕ_I values based on ΔH^o_f of Ref.16 are larger than those based on ΔH^o_f taken from Ref.15 or estimated from Eq.3. The original proposer, Kamlet, did not discuss the computation of ϕ for explosive mixtures, but used ϕ_{II} for most of explosive mixtures in his papers.

Now we can consider the effectiveness of various ϕ values in predicting the explosive performances for explosive mixtures. The detonation velocity (D) and detonation pressure (P) are two basic performance properties of an explosive and are usually taken as the subject of evaluation. In present paper we will also select detonation velocity and detonation pressure as examples although we can easily extend our evaluation to other explosive performances (see Table 1).

In Table 4, we have listed the calculated D and P values from ϕ_{I}, ϕ_{II} and ϕ_{III} together with the experimental D and P values. The experimental D and P values are from Ref.3-4 and Ref.15-17. The explosives in Table 4 have the same numbers in Table 3.

The experimental and calculated values are treated by linear equation of $y = ax + b$, where y is for the experimental data, x is for the corresponding calculated value, and r is the correlation coefficient. The results of these treatments are given in Table 5 (29 data sets). In each column of Table 5, two values are given, the upper is for detonation velocity data; the lower is for detonation pressure data. As indicated in Table 5, good agreements are obtained between the experimental and calculated D and P values from the three ϕ values (accuracies generally attributed to experimental measurements are a few percent for D and ± 10 % for P[16]), and the calculated D and P by ϕ_{III} correspond closestly to experimental values.

CONCLUSION

Kamlet parameter ϕ may be used to predict many explosive performances within applicable errors. The heat of formation (ΔH^{o}_{f}) of an explosive mixture for the computation of ϕ is not readily available in references, and when it is, often the accuracy of it is low. There are three computation methods of ϕ for an explosive mixture in references: the first is Kamlet's original definition of ϕ (as ϕ_I); the second is using weighted-average N, M and Q values of pure components (as ϕ_{II}); the third is adding the weighted ϕ values of pure components (as ϕ_{III}).

In this paper, comparison are presented for the three ϕ values of 21 explosive mixtures over a broader range of chemical types. The effectiveness of the three ϕ values in predicting explosive performances is also evaluated (detonation velocity and detonation pressure are taken as examples of evaluation). Good agreements are obtained between the experimental and calculated D and P values (29 data sets), and ϕ_{III} may give the best prediction results. The computation of ϕ_{III} is very simple. It may be available for engineering calculations of explosive mixtures.

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TABLE 1

SIMPLE PREDICTIONS OF EXPLOSIVE PERFORMANCES IN TERMS OF KAMLET PARAMETER ϕ

Explosive Performance	Symbol	Unit	Prediction Equation	Ref.
Detonation Pressure	P	GPa	$P = 1.558\ \phi\ \rho^{2}$	3
Detonation Velocity	D	km/s	$D = 1.01\ \phi^{1/2}(1+1.30\ \rho)$	4
Calcule Ballistique	$CB^{1/2}$	km/s	$CB^{1/2} = \{1.2\ \rho/(1+1.30\ \rho)\}\ \phi^{1/2}$	12
Gurney Velocity	$(2E)^{1/2}$	Km/s	$(2E)^{1/2} = 0.53(1.44\ \phi\ \rho)^{1/2} + 0.60$	13
	$(2E)^{1/2}$	Km/s	$(2E)^{1/2} = 0.887\ \phi^{1/2}\ \rho^{0.4}$	9
Cylinder Velocity	V	km/s	$V = 0.368\ \phi^{0.54}\ \rho^{0.84}$	7
	V_{20}	km/s	$(V_{20})^{2} = 0.200\ \phi\ \rho^{1.50}\{1.104-0.265MF(H_2O)\}$	11
Cylinder Energy	$E_{cyl}(6mm)$	MJ/Kg	$E_{cyl}(6mm) = 0.0659\ \phi\ \rho^{1.8}$	10
	$E_{cyl}(19mm)$	MJ/Kg	$E_{cyl}(19mm) = 0.0927\ \phi\ \rho^{1.6}$	10
Relative Detonation Impulse				
	I_{rel}		$I_{rel} = 15.06\ \phi^{0.726}\ \rho^{1.182}$	10
Adiabatic Exponent	γ		$\gamma = 184(N^{2}M/\phi)\ \rho + 1.168$*	14

* The original equation has been written according to $\phi = NM^{1/2}Q^{1/2}$

□

TABLE 2

THE COMPUTATION OF N, M AND Q FOR $C_aH_bN_cO_d$[a]

	$d \geqq 2a+(b/2)$	$2a+(b/2) > d \geqq b/2$	$b/2 > d$
N	$\frac{b+2c+2d}{48a+4b+56c+64d}$	$\frac{b+2c+2d}{48a+4b+56c+64d}$	$\frac{b+c}{24a+2b+28c+32d}$
M	$\frac{48a+4b+56c+64d}{b+2c+2d}$	$\frac{56c+88d-8b}{b+2c+2d}$	$\frac{2b+28c+32d}{b+c}$
Q	$\frac{28900b+94000a+\Delta H_f^\circ}{12a+b+14c+16d}$	$\frac{5400b+47000d+\Delta H_f^\circ}{12a+b+14c+16d}$	$\frac{57800d+\Delta H_f^\circ}{12a+b+14c+16d}$

[a] ΔH_f° is the standard heat of formation of the unreacted explosive in cal/mol.

TABLE 3

COMPARISON RESULTS OF ϕ_{I}, ϕ_{II} AND ϕ_{III}

No.	Explosive	ϕ_{I}	ϕ_{II}	ϕ_{III}
1.	RDX/TNT-50/50	5.803[c]	5.806	5.811
2.	RDX/TNT-60/40	6.032[d]	5.992	6.006
3.	RDX/TNT-64/36	6.237[e]	6.063	6.083
4.	RDX/TNT-65/35	6.089[c]	6.086	6.103
5.	RDX/TNT-75/25	6.290[d]	6.292	6.298
6.	RDX/TNT-77/23	6.503[e]	6.319	6.336
7.	RDX/TNT-78/22	6.343[c]	6.331	6.356
8.	HMX/TNT-76.3/23.7	6.480[e]	6.310	6.314
9.	HMX/Estane-90/10	6.205[d]	6.318	6.194
10.	LX-14	6.516[d]	6.545	6.483
11.	PBX-9404	6.597[d]	6.321	6.518
12.	PETN/TNT-35/65	5.516[c]	5.492	5.526
13.	PETN/TNT-40/60	5.609[c]	5.586	5.625
14.	PETN/TNT-45/55	5.706[c]	5.680	5.723
15.	PETN/TNT-50/50	5.789[d]	5.796	5.822
16.	EDC-11	6.087[e]	5.924	6.057
17.	EDC-24	6.638[e]	6.112	6.433
18.	MB/NM-14.5/85.5[a]	5.857[e]	4.792	5.606
19.	NM/TNM-1/0.071[b]	7.333[e]	6.193	6.084
20.	NM/TNM-1/0.25[b]	7.770[e]	5.610	5.421
21.	NM/TNM-1/0.50[b]	6.810[e]	5.173	4.986

[a] MB = Toluene. [b] Mixture proportions by mole.

[c] ΔH_f^{o} is estimated. [d] ΔH_f^{o} is taken from Ref. 15.

[e] ΔH_f^{o} is taken from Ref. 16.

TABLE 4

EXPERIMENTAL AND CALCULATED DETONATION PROPERTIES

		D(km/s)				P(GPa)			
	ρ		calculated				calculated		
No.	(g/cm^3)	exp.	ϕ_{I}	ϕ_{II}	ϕ_{III}	exp.	ϕ_{I}	ϕ_{II}	ϕ_{III}
1.	1.627	7.660	7.579	7.581	7.584	23.11	23.93	23.94	23.97
2a.	1.715	7.89[a]	8.027	8.000	8.010	28.7	27.80	27.46	27.52
2b.	1.68	7.95	7.898	7.870	7.881	28.3	26.52	26.34	26.39
3a.	1.713	8.018	8.139	8.025	8.038	29.22	28.51	27.72	27.81
3b.	1.713	8.030	8.139	8.025	8.038	29.4	28.51	27.72	27.81
3c.	1.717	7.99	8.153	8.036	8.051	29.5	28.65	27.84	27.94
4.	1.715	8.060	8.049	8.044	8.058	29.2	27.90	27.89	27.97
5.	1.648	7.952	7.960	7.960	7.965	27.59	26.62	26.62	26.65
6a.	1.743	8.252	8.412	8.292	8.303	31.25	30.78	29.91	29.99
6b.	1.752	8.250[b]	8.448	8.332	8.339	31.6	31.10	30.22	30.30
7.	1.755	8.306	8.347	8.344	8.356	31.7	30.44	30.38	30.50
8a.	1.809	8.452	8.617	8.504	8.506	33.8	33.04	32.17	32.19
8b.	1.809	8.476	8.617	8.504	8.506	34.3	33.04	32.17	32.19
9a.	1.767	8.500	8.295	8.370	8.288	29.8	30.18	30.73	30.13
9b.	1.783	8.37[c]	8.338	8.413	8.330	32.8	30.73	31.29	30.68

[a] ρ = 1.72 g/cm^3. [b] ρ = 1.754 g/cm^3. [c] ρ = 1.78 g/cm^3.

TABLE 4 (CONTINUED)

		D(km/s)				P(GPa)			
	ρ		calculated				calculated		
No.	(g/cm^3)	exp.	ϕ_{I}	ϕ_{II}	ϕ_{III}	exp.	ϕ_{I}	ϕ_{II}	ϕ_{III}
10.	1.833	8.83[d]	8.728	8.749	8.706	37.0	34.11	34.26	33.94
11a.	1.844	8.802	8.813	8.627	8.760	36.8	34.95	33.49	34.53
11b.	1.84	8.80	8.799	8.613	8.747	37.5	34.80	33.34	34.38
11c.	0.969	5.905	5.862	5.738	5.827	9.20	9.65	9.25	9.54
12.	1.668	7.358	7.516	7.499	7.523	23.85	23.91	23.81	23.95
13.	1.673	7.303	7.594	7.579	7.605	23.83	24.46	24.36	24.53
14.	1.677	7.420	7.672	7.655	7.684	23.96	25.00	24.89	25.07
15.	1.682	7.662	7.744	7.748	7.766	24.55	25.52	25.55	25.66
16.	1.782	8.213	8.264	8.153	8.244	31.5	30.12	29.31	29.97
17.	1.776	8.713	8.610	8.262	8.476	34.2	32.62	30.04	31.61
18.	1.088	5.840	5.902	5.338	5.774	10.0	10.80	8.84	10.34
19.	1.197	6.570	6.991	6.425	6.368	13.8	16.37	13.82	13.58
20.	1.310	6.880	7.610	6.466	6.356	15.6	20.77	15.00	14.50
21.	1.397	6.780	7.422	6.469	6.351	16.8	20.71	15.73	15.06

[d] ρ = 1.835 g/cm^3.

TABLE 5

ANALYSIS OF PREDICTION RESULTS

	a	b	r	±Δ*	±Δ%**
ϕ_{I}	1.066	-0.635	0.968	0.158	2.13
	1.183	-4.73	0.984	1.41	6.14
ϕ_{II}	0.907	0.778	0.978	0.137	1.88
	1.093	-1.23	0.985	1.49	5.18
ϕ_{III}	0.923	0.628	0.980	0.121	1.63
	1.094	-1.43	0.991	1.38	4.87

* The average difference.

** The average absolute deviation.