Note

Application of inverse gas chromatography to solid propellants

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Inverse gas chromatography (IGC) has been widely used to study the physico-chemical properties and related thermodynamic parameters of polymers since it was first reported in 1966[1]. In this work, nitrocellulose (NC) or/and polyether (PE) gel, which are main components of solid propellants, and some small molecules including acetone, ethanol, diethyl ether and ethyl acetate were chosen as samples and their solubilities were characterized by IGC. This provides a method and measuring conditions for the study of system solubility. At the same time, it provides a basis for the formulation of recipes and the choice of processing conditions for the practical production of solid propellants.

NC is the main energetic ingredient of single-base, double-base and other complex gunpowders[2]. As its viscous fluid flow temperature (T_f) is higher than its decomposition temperature (T_d), it cannot be processed at increased temperatures. Therefore, with the help of small molecules, NC can be prepared as concentrated solutions so that it can be easily processed[3]. The solubility of NC–small molecules has a great influence on the physico-chemical properties, trajectory performance and processing behaviour of gunpowder and the quality of the final products. This has been studied previously[4-7], but the methods used were indirect, *i.e.*, the solubility of the system was studied by rheological analysis, which does not allow determination of the solubility of the NC system.

PE is a sticking agent in NEPE gunpowder and its solubility with other components of the system influences the properties of the gunpowder, such as mechanical properties, combustion performance and stability. The synthesis and study of the properties of PE have not previously been reported, and there are no conclusions on characterizing the solubility of PE.

THEORY

The Flory–Huggins interaction parameter for an infinitely dilute solution of a volatile component 1 in a polymer 2 is expressed by[8]

$$\chi_{12}^{\infty} = \ln\left(\frac{273.2RV_2}{P_1^0 V_g^0 V_1}\right) - 1 \tag{1}$$

where

$$V_g^0 = \frac{273.2}{W} \cdot \frac{t_R - t_M}{T_c} \cdot F_{corr} \cdot j$$

$$j = \frac{3}{2} \cdot \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}$$

$$F_{corr} = F_{obs} \cdot \left(\frac{P_0 - P_{0,flo}}{P_0}\right)$$

W (g) is the amount of stationary phase, t_R is the retention time of the sample on the stationary phase, t_M is the dead time, T_c is the column temperature (80°C in this work), F_{obs} is the volume flow-rate of the carrier gas when it is out of the column at atmospheric temperature (measured with a soap bubble flow meter and requiring a correction for saturation of the carrier gas with water vapour from the soap solution), P_0 is the outlet pressure, P_i is the inlet pressure, $P_{0,flo}$ is the saturated vapour pressure of water at the temperature of the flow meter, V_g (ml g^{-1}) is the elution volume corrected to 0°C per gram of stationary phase in the column and V_2 and V_1 are the specific volume of the polymer and sample, respectively.

The excess enthalpy of mixing is related to the temperature dependence of χ by[8]

$$\Delta H_M^\infty = \frac{\partial \chi/\partial(1/T)}{T} \tag{2}$$

The solubility parameter of the polymer (δ_2) can be calculated by eqn. 3 and substituted in eqn. 4:

$$\delta_2 = \frac{\Sigma F}{V} = \frac{\Sigma F}{M} \cdot d_2 \tag{3}$$

$$\Delta H_M = V\varphi_1\varphi_2(\delta_1 - \delta_2)^2 \, \bar{M}_n \tag{4}$$

where $V = V_1 + V_2$, $\varphi_1 = V_1/V$, $\varphi_2 = V_2/V$, ΣF is the sum of the attraction constant per mole in each repeat unit, M is the molecular weight of the repeat unit, δ_1 is the solubility of the sample and $\bar{M}_n$ is the number-average molecular weight of the polymer. If the φ_1, φ_2, δ_1 and $\bar{M}_n$ are known, we can obtain δ_2 from eqn. 4 approximately after measuring ΔH_M.

EXPERIMENTAL

Instruments
        A Model SP-2305 gas chromatograph (Beijing Analytical Instrument Factory, China) with a thermal conductivity detector and a U-shaped stainless-steel column (0.5 × 4 mm I.D.) was employed with hydrogen as the carrier gas. A standard Calvet microcalorimeter (Setaram, France) was used.

TABLE I

CHARACTERISTIC PARAMETERS OF NC SAMPLES

No. of NC	Nitrogen content (%)	Degree of nitration, v	Density, d_2^{25} $(g\ cm^{-3})$	Solubility parameter, δ_2 $(cal^{1/2}\ cm^{-3/2})$
1	13.47	2.75	1.66	9.12
2	12.11	2.29	1.64	9.60
3	11.90	2.25	1.64	10.02

Samples

NC samples 1–3 were provided by Xinan Chemical Factory (China) and their characteristics are listed in Table I. PE was provided by the Institute of Chemistry, Academic Sinica (Beijing, China) and its properties are as follows: $\bar{M}_n$ = 1620, OH value = 0.6046 mequiv./g (mequiv. = milligram equivalents), degree of polymerization DP = 1.62, density = 1.0267 g cm^{-3}. The small molecules used were dimethyl sulphoxide (DMSO), diethyl ether, ethanol, ethyl acetate and acetone. The support was white support 101 produced by the Shanghai Reagent Factory (Shanghai, China), containing SiO_2 (89.9%), Al_2O_3 (3.6%), Fe_2O_3 (1.65%),TiO_2 (0.30%) and CaO + MgO (2.45%).

Processing

The required amount of sample, according to the loading, was dissolved in acetone to form a solution, then a suitable amount of support was slowly added with stirring. After evaporation of the solvent, the NC or PE sample was loaded on the column as the stationary phase. Finally, the column was conditioned at 60°C for 6–8 h.

RESULTS AND DISCUSSION

Measurement of reliability of the instruments

There are many factors that influence the heat of mixing, *e.g.*, error of weighing PE (0.05%), instrumental error of the Calvet microcalorimeter (0.2%), error of measuring column loading (0.5%), error of measuring carrier gas flow-rate (1–2%), calculation error (0.5%) and the error involved in IGC itself (1%). The errors in the data from two different methods were within the range of the experimental error, as indicated in Table II. Hence the instruments used were suitable for studying the solubility of the components in solid propellants.

TABLE II

HEATS OF MIXING OF PE–ETHANOL SYSTEM

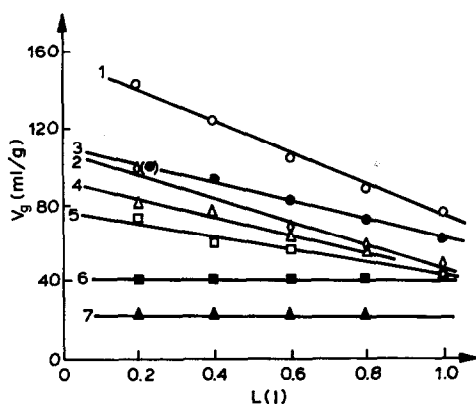| Parameter	Calvet method	IGC method
Heat of mixing, ΔH_M (kJ mol^{-1})	22.75	20.89
Relative standard deviation (%)	<5	<5

Fig. 1. V_g–L graphs for samples on NC 3 column. 1 = Ethyl acetate, F_{corr} = 13.7 ml min^{-1}, W = 6.4%; 2 = ethyl acetate, F_{corr} = 7.2 ml min^{-1}, W = 7.2%; 3 = ethyl acetate, F_{corr} = 13.7 ml min^{-1}, W = 8.2%; 4 = ethanol, F_{corr} = 20.3 ml min^{-1}, W = 6.4%; 5 = ethanol, F_{corr} = 26.8 ml min^{-1}, W = 7.2%; 6 = diethyl ether, F_{corr} = 39.9 ml min^{-1}, W = 2.7%; 7 = diethyl ether, F_{corr} = 33.4 ml min^{-1}, W = 6.4%.

Factors influencing V_g

Sample size, L. Fig. 1 illustrates V_g–L graphs for different sample probes on an NC 3 column. These graphs are linear and the slopes (k) decrease in the order ethyl acetate, ethanol, diethyl ether. The order of symmetry of the peak shapes is diethyl ether, ethanol, ethyl acetate. The solubility order of NC 3–small molecule systems is[9]
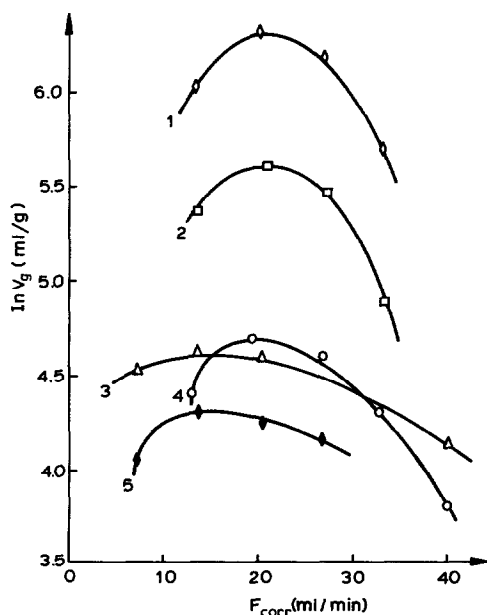

Fig. 2. Ln V_g–F_{corr} graphs for samples on NC 3 column. Column temperature, 80°C. 1 = Ethyl acetate, W = 2.7%; 2 = ethanol, W = 2.7%; 3 = ethyl acetate, W = 8.2%; 4 = diethyl ether, W = 2.7%; 5 = ethanol, W = 8.2%.

NC–ethyl acetate, NC–ethanol, NC–diethyl ether. From these results, it can be concluded that the better the solubility of the system, the stronger is the dependence of V_g on L and the more asymmetric is the peak shape. V_g can be obtained correctly when L is extrapolated to zero.

Carrier gas flow-rate, F_{corr}. Ln V_g–F_{corr} graphs for different samples on the NC 3 column are shown in Fig. 2. If F_{corr} is within a certain range ($20 \pm 5 \, ml \, min^{-1}$), V_g is independent of F_{corr}. This provides a basis for the choice of a suitable F_{corr} in NC systems with different percentages of nitrogen.

Column loading, W. Fig. 3 illustrates ln V_g–W graphs for different samples on different NC columns. It can be concluded that, for different NC columns, there exist critical values (W_c) that are related to the percentage of nitrogen in the NC. The higher is the percentage of nitrogen, the smaller is W_c. When W is lower than W_c, both an interaction between sample and the active group of the stationary phase surface and an interaction between the sample and the bulk polymer exist simultaneously, and are independent of each other. In contrast, when W is higher than W_c, surface action can be omitted and only the contribution of bulk action need be considered. V_g is independent of W. Therefore, the retention behaviour of a sample on an NC column is in accordance with the parallel retention model[10].

Study of solubility of NC–small molecule systems

Thermodynamics of NC–small molecule solution systems. Table III lists the characteristic parameters of NC–small molecule systems. It can be seen that the greater the $\Delta\delta$ of the system, the smaller is V_g of the sample on NC column, the greater are ΔH_M and χ_{12} and the worse is the solubility of the systems. These parameters are of identical use in judging the solubility of the system.

Solubility dynamics of NC–small molecule systems. When dissolved in good solvents, NC first swells. As it swells continuously, the orientational domain of the NC chain disappears gradually, and NC can be dissolved to give a homogeneous system. The phenomena in Fig. 4 can be explained easily according to the model mentioned above: if the sample is not a good solvent for NC it can only be absorbed by solid NC
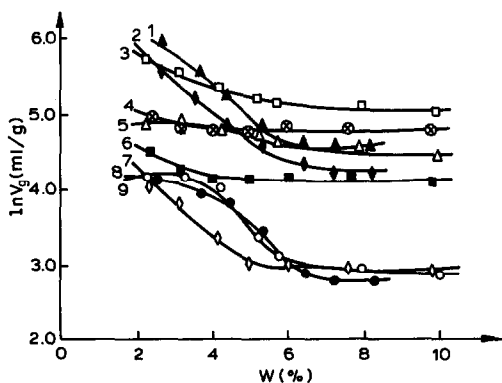

Fig. 3. Ln V_g–W graphs for samples on NC columns. Column temperature, 80°C; F_{corr} = 20.3 ml min^{-1}. 1 = Ethyl acetate (NC 3); 2 = ethanol (NC 3); 3 = ethyl acetate (NC 2); 4 = ethyl acetate (NC 1); 5 = ethanol (NC 2); 6 = ethanol (NC 1); 7 = diethyl ether (NC 1); 8 = diethyl ether (NC 3); 9 = diethyl ether (NC 2).

TABLE III

CHARACTERISTIC PARAMETERS OF NC–SMALL MOLECULE SYSTEMS

No. of NC	Sample	$\Delta\delta$ $(cal^{1/2}\ cm^{-3/2})$	V_g $(ml\ g^{-1})$	χ_{12}	ΔH_M $(kJ\ mol^{-1})$
1	Diethyl ether	1.72	18.39	−0.31	2.51
	Ethanol	3.58	66.07	0.44	3.20
	Ethyl acetate	0.02	117.16	−0.68	−6.13
2	Diethyl ether	2.20	17.40	−0.23	3.17
	Ethanol	3.10	67.57	0.44	2.37
	Ethyl acetate	0.50	104.41	−0.55	−4.78
3	Diethyl ether	2.62	16.46	−0.18	3.50
	Ethanol	2.68	71.26	−0.38	1.54
	Ethyl acetate	0.92	95.44	−0.46	−0.63

and does not destroy the ordered sequence portion of NC. As the carrier gas flows continuously, it is desorbed from NC and flows out of column to form a chromatographic peak. On the other hand, if the sample is a good solvent for NC, some of it can be absorbed by NC, then desorbed from NC, and flows out of the column to form the first peak (this mechanism is similar to that with poor solvents). The rest of the sample penetrates the bulk of NC, dissolves slowly in NC, and flows out of the column with the carrier gas to form the second peak. The severe tailing of the second peak indicates that the dissolution process is very slow. Fig. 5 shows that the solution involves two steps, the first being endothermic and the second exothermic.

Study of solubility of PE–small molecule systems

Solubility thermodynamics of PE–small molecule systems. ΔH_M of PE was measured with a Calvet microcalorimeter and calculated from theory. The results are listed in Table IV.
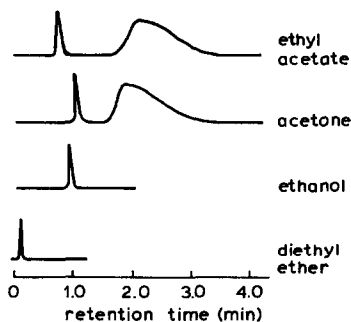

Fig. 4. Schematic chromatograms of samples on NC 3 column. Column temperatures, 80°C; F_{corr} = 20.3 ml min^{-1}; W = 5.3%.
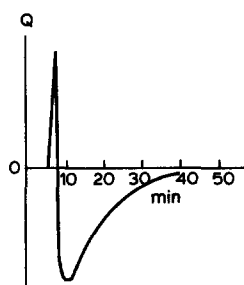
Fig. 5. Heat of solution of NC 3–acetone system determined with a Calvet microcalorimeter.

Table V illustrates that the greater is $\Delta\delta$ between PE and a small molecule, the greater is ΔH_M and the worse is the solubility of the system. This demonstrates further that the results from the IGC method and the Calvet microcalorimeter method are identical. For some explosive solvents which are often used during the practical production, if ΔH_M cannot easily be measured by other methods, good solvents can be selected according to $\Delta\delta$ of the PE–solvent system. Therefore, the results provide an important basis for the choice of suitable solvents.

Solubility dynamics of PE–small molecule systems. In view of the dynamic factors, PE reacts faster with polar protonated solvents (*e.g.*, ethanol) than with polar non-protonated solvents (*e.g.*, DMSO). However, the solubility of PE–solvent systems is dependent not only on dynamic factors but also on their thermodynamic properties

TABLE IV

ESTIMATED δ_2 OF PE

System	Weight (PE), W_2 (g)	Volume (PE), V_2 (cm³)	V (cm³)	φ_2 (V_2/V)	ΔH_M (kJ mol⁻¹)	$\delta_2{}^\star$ (cal¹ᐟ² cm⁻³ᐟ²)
PE–ethanol	0.2270	0.2209	2.7209	0.08	22.57	8.6
PE–ethanol	0.2040	0.1985	2.6985	0.07	23.00	8.3
PE–DMSO	0.1270	0.1236	2.6236	0.05	16.61	8.9
PE–DMSO	0.2302	0.2250	2.7250	0.08	16.76	9.8

$\star$ Calculated δ_2 of PE = 9.0.

TABLE V

CHARACTERISTIC PARAMETERS OF PE–SMALL MOLECULE SYSTEMS

Sample	δ_1 (cal¹ᐟ² cm⁻³ᐟ²)	$\Delta\delta$ (cal¹ᐟ² cm⁻³ᐟ²)	ΔH_M (kJ mol⁻¹)
Ethanol	12.7	2.9–4.4	20.87
Diethyl ether	7.4	0.9–2.4	13.77
Acetone	9.9	0.1–1.6	10.85
Ethyl acetate	9.1	0.7–0.8	7.24

and on other factors that affect the solubility. The explosive solvents used in production are generally nitro compounds, which are non-protonated solvents, and which react with PE very slowly. This factor should be considered when selecting processing conditions.

CONCLUSION

Characteristic parameters, including V_g, χ_{12} and ΔH_M, of different NCs with various small molecules were systematically measured and used to establish the solubility of different systems. This provides the characteristic parameters for concentrated solutions of NC with different percentages of nitrogen.

Various factors that affect V_g were investigated. The results indicate that the better the solubility of NC–small molecule systems, the more sensitive is V_g to L and F_{corr}; when L is extrapolated to zero, V_g can be obtained correctly. When F_{corr} is within a certain range (20 $\pm$ 5 ml min^{-1}), V_g remains constant. As a result, measuring conditions can be determined for the study of different systems.

There exist different critical values, W_c, for different NC columns. W_c is related directly to the percentage of nitrogen in the NC; the higher is the percentage of nitrogen, the smaller is W_c. Experiments demonstrated the retention mechanism of samples on NC columns.

The basic model of the dissolution of NC in good solvents was demonstrated by IGC and Calvet microcalorimeter experiments. This provides theoretical and experimental bases for the study of the solubility dynamics of concentrated NC systems.

The solubility parameter, δ_2, of PE was calculated from theory and measured with a Calvet microcalorimeter, and was used to judge the solubility of PE–small molecule systems. The results are in accordance with the results of IGC experiments. This provides data for judging the solubility between PE and explosive solvents and for selecting suitable energetic solvents.

The solubility dynamics of the system composed of PE and two typical solvents (protonated solvent, ethanol; polar non-protonated solvent, DMSO) were studied, and it was shown that the interaction between PE and the protonated solvent is faster than that between PE and the non-protonated solvent. This indicated that the interaction of the PE–energetic system is very slow. These results provide a basis for selecting suitable processing conditions.

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