

## **Saturated Vapor pressure of HFA152a-ethanol and HFO1234ze(E)-ethanol binary mixtures**

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### **Summary**

Hydrofluoroalkane propellants HFA134a and HFA227ea are being phased down under the Kigali amendment due to their high global warming potential. Propellants HFA152a and HFO1234ze(E) have been proposed as potential alternatives for pressurised metered dose inhalers (pMDIs). Knowledge of the fundamental thermodynamic properties of these alternative propellants is essential to predict and optimise device performance. The vapor pressure of low-GWP propellant binary mixtures with ethanol for use in solution formulations are presently not available in the literature. In this paper, the saturated vapor pressures of HFA152a and HFO1234ze(E) have been measured using a constant-volume technique. For temperatures below 45°C the relative deviations of vapor pressures of HFA152a and HFO1234ze(E) are below 5% and 3.5% as compared with REFPROP10.0, respectively. We show the vapor pressure dependency on ethanol cosolvent concentration for HFA152a and HFO1234ze(E) at a concentration of 8% w/w.

### **Key Message**

The effect of ethanol concentration on saturated vapor pressures (SVP) of propellants HFA152a and HFO1234ze(E) was measured using a constant-volume technique. Experimental measurements are necessary to accurately model the SVP of propellant/cosolvent binary mixtures, particularly at high cosolvent concentrations.

### **Introduction**

Hydrofluoroalkane propellants such as HFA134a and HFA227ea used in pMDIs have a global warming potential (GWP) of 1300 and 3220 kgCO<sub>2</sub>-equivalent respectively [1]. Due to rising concerns over global warming, the transition to low-GWP propellants has become a high priority for industry and governments. Low-GWP propellants HFA152a (1,1-difluoroethane) and hydrofluoroolefin (HFO) 1234ze(E) (trans-1,3,3,3-tetrafluoroprop-1-ene) are potential alternatives for HFA134a and HFA227ea [1,2]. However, the transition to low-GWP propellants in pMDIs is not a straightforward procedure due to the differences in their thermodynamic and physicochemical properties.

Ethanol is a commonly used cosolvent in pMDIs. The addition of ethanol alters the thermophysical properties for instance, saturated vapor pressure, viscosity and surface tension of pMDI formulation [3]. This in turn influences the atomization process of the pMDI spray and properties of the droplets generated due to the differences in net surface charge [2,4]. The knowledge of thermophysical properties of pMDI formulations is essential to improve the overall performance of a pMDI product. The lack of an appropriate database with accurate properties for HFA152a/ethanol and HFO1234ze(E)/ethanol mixtures poses a challenge for pMDI device development and optimization. Therefore, in this paper vapor pressures of HFA152a/ethanol, and HFO1234ze(E)/ethanol binary mixtures were measured using a constant volume technique. The vapor pressure measurements were performed for a propellant-ethanol mixture at a cosolvent concentration of 8% w/w between 10°C to 50°C.

### **Experimental Procedure**

#### **Materials**

The chemical information and purity of the propellants used in this study are listed in Table 1. The propellants were used without further purification because of the high purity indicated by the supplier.

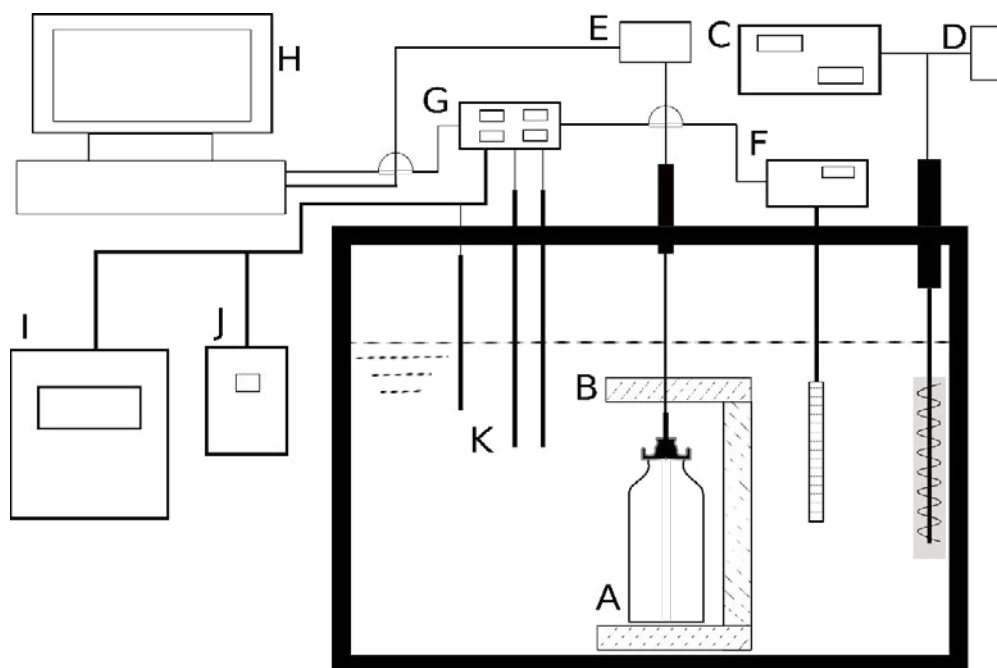
Compound	CAS Number	$T_c$ (°C)	$P_c$ (MPa)	Purity	GWP ( $CO_2 = 1$ )
HFA134a	811-97-2	101.06	4.059	99.5%	1300
HFA152a	75-37-6	113.26	4.516	99.5%	138
HFO1234ze(E)	29118-24-9	109.36	3.634	99.5%	<1

**Table 1. Properties of the propellants used in this study [5], [1]**

### Methods

The schematic of the experimental procedure used in this work is shown in Fig.1. The equilibrium cell (pMDI canister with modified continuous flow valve (BK 357, Bepak, UK)) was filled with the respective weight fraction of ethanol to 8%w/w and pressure filled with each propellant. The measurement bath was filled with silicone-oil (CAS-No: 63148-62-9) and the temperature of the bath was changed in increments of 5°C. Using a canister holder, the equilibrium cell was depressed and placed inside the silicone-oil bath and allowed to equilibrate. The equilibrium cell vapor pressures were measured for temperatures between 10°C to 50°C. The pressure was measured using a pressure transducer (Omega, Model: PX409) which has an accuracy of  $\pm 0.08\%$ . The pressure transducer was connected to the equilibrium cell through a stainless-steel tube to the canister holder. Temperatures above 20°C were obtained using a PID-controlled heater. The equilibrium cell temperature was monitored using a 100  $\Omega$  standard platinum resistance thermometer as shown in Fig.1. For temperatures below 20°C the apparatus was placed in a low temperature freezer and the PID controlled heater was used to achieve the required bath temperature.

Equilibrium cells of pure propellant (without ethanol cosolvent) were used as a control and measured vapour pressures compared with the NIST REFPROP database [5] to correct for small systematic errors in the temperature measurement.



**Figure 1 - Saturated vapor pressure experimental apparatus** A: Equilibrium cell, B: Canister holder, C: Heater, D: Heater transformer, E: Pressure transducer, F: Standard platinum resistance thermometer, G: Data collection port, H: Monitor, I: Freezer, J: Sub-Heater, K: Thermocouples (K-type)

## Result and Discussion

Saturated vapor pressures for pure propellants (HFA152a and HFO1234ze(E)) were measured at temperatures ranging between 10°C to 50°C as shown in Figure 2(a). The measured vapor pressures of pure propellants were compared with the NIST REFPROP 10.0 database [5]. The relative deviations of the measured vapor pressures and NIST REFPROP values were within 5% and 3.5% respectively for HFA152a and HFO1234ze(E), at temperatures below 45°C Fig.2(b). The vapor pressure values confirm that this methodology is appropriate for measurement of binary mixture vapor pressures. The measured temperature and pressure had a maximum uncertainty of 0.49°C and 0.017 MPa respectively.

Measured saturated vapor pressures of binary mixtures of HFA152a/cosolvent and HFA1234ze(E)/cosolvent are given in Figure 3 for temperatures between 10°C and 50°C at an ethanol cosolvent concentration of 8% w/w. As given in [4], the addition of ethanol results in the reduction of vapor pressures in binary mixture and the measured vapor pressures agrees with the HFA134a trends.

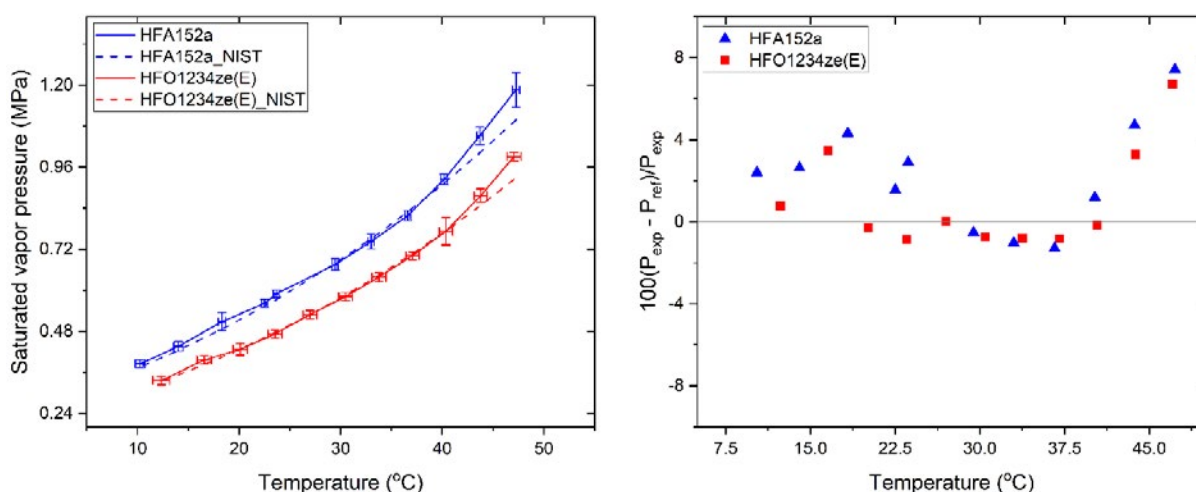


Figure 2 – (a) Comparison of pure propellant vapor pressures with REFPROP database [5] (b) Relative deviation of measured and reference vapor pressure for pure propellants

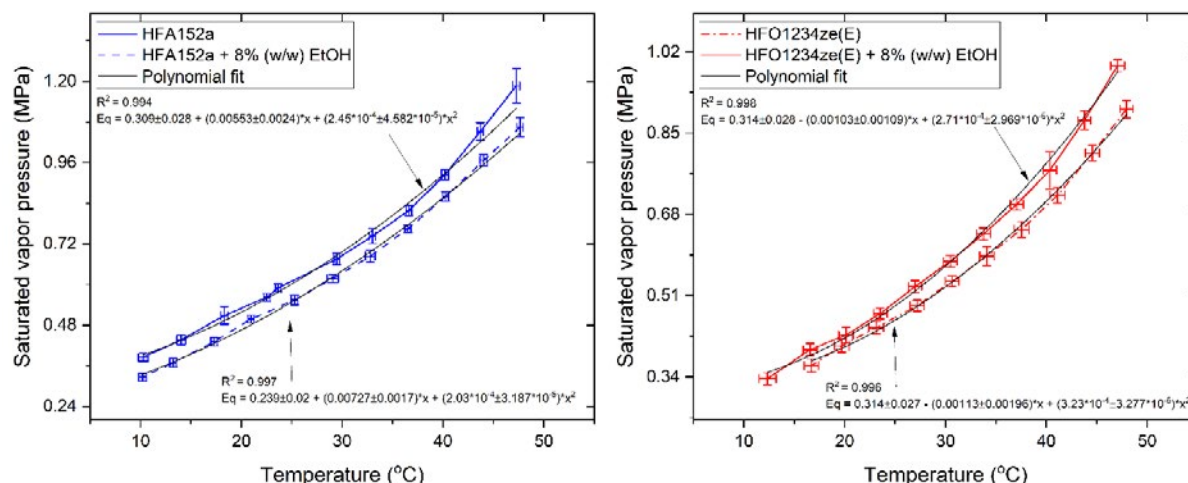


Figure 3 – Saturated vapor pressures of pure propellants (a) HFA152a and (b) HFO1234ze(E) and their binary mixtures with ethanol cosolvent concentration of 8% w/w

## Conclusions

The saturated vapor pressure of binary mixtures of HFA152a and HFO1234ze(E) with an ethanol cosolvent concentration of 8% w/w was experimentally measured using a constant volume method at temperatures ranging between 10°C to 50°C. The measured pure propellant saturated vapor pressures agree well with the NIST REFPROP database [5] with an uncertainty of 0.49°C and 0.017 MPa for temperature and pressure respectively. The addition of ethanol cosolvent results in suppression of propellant vapor pressures in line with previous trends observed for HFA134a-ethanol binary mixtures [4].

## **Acknowledgements**

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## **References**

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