VAPORIZATION BEHAVIOR OF TETRAOCTYLPHOSPHONIUM BIS(2-ETHYLHEXYL)PHOSPHATE IONIC LIQUID

JW McMurray, Y Zhou, HM Luo, and J Qu

ABSTRACT

The equilibrium vapor pressures, p_e , of the ionic liquid tetraoctylphosphonium bis(2-ethylhexyl)phosphate ($[P_{888}][DEHP]$) over the temperature range 409 – 495 K were determined for the first time using mass loss Knudsen effusion. The p_e versus temperature relationship compares well to 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_8mim][NTf_2]$) but is lower than that of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$) when measured using the same technique. The discrepancies between the p_e determined in this work for $[C_8mim][NTf_2]$ and $[C_2mim][NTf_2]$ with previous studies is discussed. The enthalpy and entropy of vaporization for all three fluids are estimated from the Clausius-Clapeyron relation.

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Introduction

An ionic liquid (IL) is a molten salt and the variation of cationic and anionic structures, along with their numerous combinations make ILs flexible in molecular design. Recent experimental determinations of equilibrium vapor pressure, p_e , below 500 K for ILs using mass loss Knudsen effusion and transpiration type measurements [1-3] show that low p_e are among ILs' unique physicochemical properties. This is key for potential applications including electrochemistry, chemical synthesis, catalysis, lubrication, etc. [4-6] and excellent descriptions on the current state of the field of bulky cations and anions can be found in [7-16]. Further, it has been pointed out by Bier and Dietrich [17] that ILs do not evaporate significantly even under ultrahigh vacuum (UHV). While this can be attributed to low p_e , it is also consequence of a low vaporization coefficient, α . Previous experimental p_e have assumed α values of unity [1, 2].

Specifically, phosphonium-phosphate ILs have recently been reported as effective oil-soluble anti-wear lubricant additives [18, 19]. However, their vapor liquid equilibrium (VLE) behavior has not been characterized. Here, we measure p_e with temperature using mass loss Knudsen effusion for tetraoctylphosphonium bis(2-ethylhexyl)phosphate ($[P_{888}][DEHP]$) along with two baseline ILs, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$) and 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_8mim][NTf_2]$). The results for $[C_8mim][NTf_2]$ and $[C_2mim][NTf_2]$ are compared to those from previous studies[2, 3] while p_e with temperature, T , relationship is reported here for the first time for $[P_{888}][DEHP]$ between 409 – 495 K. Further, α is calculated and estimates for the entropy and enthalpy of vaporization for all three ILs are given for the average T of the measurements.

Experimental

Sample preparation

All reagents and solvents were of the highest grade commercially available and were used without further purification. The ILs studied consist of the 1-*n*-alkyl-3-methylimidazolium cation $[C_nmim]$, where *n* is 2 or 8, the number of carbon atoms in the alkyl chain), paired with bis(trifluoromethanesulfonyl)amide, $[NTf_2^-]$. These ILs were prepared following methods detailed in the literature [20]. Tetraoctylphosphonium bis(2-ethylhexyl)phosphate ($[P_{888}][DEHP]$) was prepared according to our previous published paper[21]. The structures for each IL are presented in Fig. 1.

[Figure 1 here]

$[C_2mim][NTf_2]$ and $[C_8mim][NTf_2]$ were synthesized via modified procedure and metathesis reactions as described in [20, 22]. Equal mole ratio of 1-methylimidazole and bromoethane or 1-bromooctane were mixed at room temperature and stirred over a period of time and the reaction was monitored with NMR, the obtained $[C_2mim]Br$ or $[C_8mim]Br$ was then dissolved in D.I. H_2O and was added $LiNTf_2$ aqueous solution at 60

^oC, stirred for 2 hours. The lower organic phase was separated and the upper aqueous phase was extracted with dichloromethane three times. The combined organic phases were washed with D.I. H₂O four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^oC under vacuum for 4 h to yield [C₂mim][NTf₂] or [C₈mim][NTf₂] as a colorless liquid.

For synthesis of [P₈₈₈][DEHP] [19], tetraoctylphosphonium bromide ([P₈₈₈]Br, 40.58 g, 72.0 mmol) and Di(2-ethylhexyl)phosphoric acid (HDEHP, 23.2 g, 20.2 mmol) were mixed in 90 mL of deionized water (D.I. H₂O, 18.2 MΩ-cm) and 100 mL of hexanes. A solution of sodium hydroxide (NaOH, 2.88 g, 72.0 mmol) in 100 mL of D.I. H₂O was added drop wise at room temperature to this stirred suspension which became clear after the addition of NaOH was completed. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with D.I. H₂O four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator and the product was dried at 70 ^oC under vacuum for 4 h to yield [P₈₈₈][DEHP] as a viscous liquid (57.0 g, 70.8 mmol, yield: 93.8%). The water content of [P₈₈₈][DEHP] was 0.1%. The decomposition temperature is reported to be 573 – 623 K in air [21].

Experimental procedure

The mass loss Knudsen effusion experiments were conducted using thermogravimetric analysis (TGA) with an STA 449 F1 Jupiter apparatus from Netzsch Gerätebau GmbH, Selb, Bavaria, Germany. The unit has a SiC heating element to fix the temperature within an Al₂O₃ reaction chamber that can be evacuated down to 4.6×10⁻⁴ Pa. The samples were placed in a custom alumina crucible manufactured at Machined Ceramics shown in Fig. 2. This type of Knudsen cell is based on a design by Alfred Buchler, has a knife edge orifice [23, 24] with the lid and container of roughly equal mass, and is adapted for the STA 449 F1 Jupiter. The orifice and the sample chamber measure 0.64 mm and 7.95 mm respectively.

[Figure 2]

The mass loss was monitored and recorded *in situ* with the STA 449 F1 Jupiter microbalance, with a drift of less than ±10 µg. The temperature was evaluated with a thermocouple (TC), calibrated with an indium melting standard, in close proximity to the sample. All three ILs were first heated and held at ~450 K for 12 hours at 4.6×10⁻⁴ Pa to ensure removal of moisture and volatile impurities before actual vapor pressure data was collected. The measurement results were analyzed using Proteus, the STA 449 F1 Jupiter companion software; an example for [C₈mim][NTf₂] is given in Fig. 3.

[Figure 3]

Analysis approach

The measured vapor pressure (p_m) is related to the mass loss rate ($\dot{m}$) through Hertz-Knudsen-Langmuir (HKL) equation [23] rearranged into Eqn. 1:

$$p_m = \frac{\dot{m}\sqrt{2\pi RT/mw}}{A} + p \quad 1$$

where mw is the molecular weight, p is the partial pressure of the species in outside of the Knudsen cell, R is the ideal gas constant, T is the absolute temperature, and A is the cross-sectional area over which the effusing vapors escape.

The $\dot{m}$ value was used together with the mw , T , and $A=A_o$ to compute p_m from Eqn. 1.

It is not uncommon for some fluids to exhibit a vaporization coefficient, α , that departs substantially from unity [25]. While, in these cases, Langmuir experiments give measured vapor pressures (p_m) that are too low, by comparing these results to those obtained from the Knudsen effusion method α for both liquids and solids and, ergo p_e can be determined [25]. That approach was adopted here to calculate and characterize p_e for [C₂mim][NTf₂], [C₈mim][NTf₂], and [P₈₈₈₈][DEHP] with temperature and estimate the enthalpy of vaporization at 298 K using the Clausius-Clapeyron relation.

Assuming the Clausing factor (k) for the integral cell is unity while using the Whitman-Motzfeld adjustment [23], p_e is calculated with Eqn. 2:

$$p_e = p_m \times \left(1 + \frac{kA_b}{\alpha A_{cell}} - \frac{kA_b}{A_{cell}} \right) \quad 2$$

where A_{cell} is the cross-sectional area of the inner diameter of the cell. Equation 3 is used to estimate k where l and d are the orifice thickness and diameter respectively.

$$k = 0.0849 \left(\frac{2l}{d} \right)^2 - 0.4041 \left(\frac{2l}{d} \right) + 0.9898 \quad 3$$

The mw of the liquid was taken to be that effusing gas molecules assuming congruent vaporization.

A least squares analysis using Eqn. 4 was performed on the data resulting from the measurements in order to derive a relation for p_m for Knudsen (p_K) and Langmuir free evaporation (p_L) techniques respectively.

$$\ln p_m = A - \frac{B}{T} \quad 4$$

The slopes fit to the Knudsen ($-B_K$) and the Langmuir ($-B_L$) data for each IL sometimes varied. For convenience, however, α was calculated with Eqn. 5 using B_K for both the $\ln p_L$ and $\ln p_K$ dependency on $1/T$; i.e. the A values for $\ln p_L$ were recalculated by fixing $B=B_K$. The rationale for this is the overall Whiteman-Motzfled adjustment is less sensitive to changes in α than is $1/\alpha$ and therefore $\ln p_K$ should naturally exhibit more linearity versus reciprocal temperature. Further, there were more measurements made using the Knudsen technique translating into more confidence in the linear regression.

$$p_e = p_K \times \left(1 + \frac{kA_b}{\alpha A_{cell}} - \frac{kA_b}{A_{cell}} \right) = p_L / \alpha \quad 5$$

Results

The experimental procedure and analysis approach described above was first validated using the commercial lubricant Fomblin Y HVAC 18/8; Fig. 4 shows a good fit between the manufacturer (Solvay S.A., Brussels, Belgium) and the data determined in this work. The $\ln p_e$ versus reciprocal temperature relationship is plotted in Figs. 5 – 8 and in tabular form in Table 1.

[Figure 4]

[Table 1]

The coefficients A and B along with the enthalpy and entropy of vaporization computed using Eqns. 6 and 7 are given in Table 2.

$$\Delta H_{vap} = BR \quad 6$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} + R \ln(p(T)/101325 \text{ Pa}) \quad 7$$

[Table 2]

The uncertainty, u , was calculated with Eqn. 8 assuming independent random propagation of the errors in T and $\dot{m}$.

$$u = \sqrt{\left(\frac{\partial p_e}{\partial \dot{m}} u(\dot{m})\right)^2 + \left(\frac{\partial p_e}{\partial T} u(T)\right)^2} \quad 8$$

The small $u(T)$ proved to have little effect on Eqn. 8.

[Figure 5]

The Knudsen number (Kn) is equal to λ/d_o where λ is given by Eqn. 9.

$$\lambda = \frac{1}{\sqrt{2\pi(N_A p_{tot}/RT)D^2}} \quad 9$$

where N_A is Avogadro's number, p_{tot} is the total pressure and D is the atomic or molecular diameter. Here, D was conservatively estimated to be 1 nm.

[Figure 6]

As a rule, Knudsen measurements give accurate results when Kn is 8 or greater [23]. For Kn between 0.4 and 8, an additional 2.5% was added to the magnitude of $u(p_K)$ [26]. Finally, the uncertainties reported in Table 1 for the natural logarithm of p_e are computed using Eqn. 10.

$$u(\ln p_e) = \sqrt{\left(\frac{u(p_e)}{p_e}\right)^2} \quad 10$$

Discussion

Zaitsau et al. [2] observed mass loss from vaporization of volatile impurities from [C₂mim][NTf₂] and [C₈mim][NTf₂] reporting several days for complete removal at 323 – 443 K. Therefore [C₂mim][NTf₂] and [C₈mim][NTf₂] samples were heated and held at ~450 K for 3 days primarily to accurately determine the minimum required time needed to accomplish this conditioning or purification step. The removal of impurities was determined to be complete after cessation of a continually decreasing change in $\dot{m}$, i.e. $\dot{m}$ coincident with p_e for either pure [C₂mim][NTf₂] or [C₈mim][NTf₂]. The results of this experiment show different VLE behavior for the [C₂mim][NTf₂] and [C₈mim][NTf₂] samples in this work compared to those in [2, 3].

It can be seen in Fig. 3 that $\dot{m}$ for [C₈mim][NTf₂] remains a constant over a period of ~94 hours at 450.9 K and 4.6×10^{-4} Pa suggesting moisture and other volatiles have already been removed during the initial temperature ramp under vacuum. For [C₂mim][NTf₂], the behavior is the same, exhibiting $\dot{m}$ corresponding to the vapor pressures shown in Fig. 7, for all temperatures from the initial conditioning step up until all the liquid had

been evaporated. After each run, the residual [C₂mim][NTf₂] and [C₈mim][NTf₂] were visually inspected. Both exhibited a tawny hue with brown colored precipitates.

[Figure 7]

As can be seen in Figs. 6 and 7, p_e for [C₂mim][NTf₂] and [C₈mim][NTf₂] determined from this work are higher than those from both [2] and [3]. For this particular case, a possible explanation is the synthesis route and therefore the types of impurities, not the level, more profoundly affect the vapor pressure. Both [C₂mim][NTf₂] and [C₈mim][NTf₂] can be made using either a Cl or Br containing precursor. It is unclear how these two ILs were made for the vapor pressure investigations reported by Zaitsau et al. [2] and Emel'yanenko et al. [3], but both studies were conducted using samples that shared a common pedigree. While a color change and the appearance of precipitates for [C₂mim][NTf₂] and [C₈mim][NTf₂] was not reported in [2, 3] for the residual liquid, Zaitsau et al. [2] did note slight discoloration of the condensate.

[Figure 8]

In contrast to [C₂mim][NTf₂] and [C₈mim][NTf₂], the conditioning step made a significant impact on correctly characterizing the p_e as a volatile component, most likely H₂O, was quickly removed early on during the isothermal vacuum treatment at ~450 K and 4.6×10⁻⁴ Pa. For the [P₈₈₈][DEHP], little to no observable color change was associated with the IL after the measurements. This IL showed the least reproducibility when comparing the mass loss at similar isotherms during heating to those during cooling steps. While this behavior is generally always present, it led to deviations of up to two orders of magnitude. Further, the trend is reversed in [C₈mim][NTf₂] showing decreased mass loss on cooling compared to isotherms during heating suggesting a real phenomenon as opposed to an experimental artifact. The cause of this behavior is unknown and will be the subject of a future investigation.

Both sets of samples for [C₂mim][NTf₂] and [C₈mim][NTf₂] from this work and those studied in [2, 3] were very pure; therefore, the feedstock material likely plays a role in the VLE of these ILs. This means [C₂mim][NTf₂] and [C₈mim][NTf₂] between batches could exhibit different vapor pressure behavior. It is unclear if the situation is the same for [P₈₈₈][DEHP] but merits further investigation. When employing ILs for applications critically dependent upon VLE, care should be exercised as the behavior may vary substantially depending not only on the purity of the final product but the precursor used in its synthesis.

Conclusions

Evaporation behavior is necessary to consider when selecting a lubricant and/or additive for a given application. A material with a lower p_e will, in general, experience less operative loss from volatilization, which should, barring other factors, translate into longer lifetimes. Another property influencing evaporation behavior is α which becomes increasingly significant with larger fluid surface areas and gas chamber volumes. These

factors, p_e and α , are especially important when lubricants are used in environments with elevated temperatures and/or vacuum conditions, such as space applications for example.

The p_e versus T relationship for [P₈₈₈][DEHP] compares well to [C₈mim][NTf₂] but is lower than [C₂mim][NTf₂] synthesized for this study. The α values are comparable for [P₈₈₈][DEHP] and [C₂mim][NTf₂] but that of [C₈mim][NTf₂] was determined to be an order of magnitude higher. This suggests that while [C₈mim][NTf₂] does have a low p_e , its α could make the IL unsuitable for vacuum applications where large evaporation surfaces might be present. The discrepancies between the p_e for [C₂mim][NTf₂] and [C₈mim][NTf₂] likely result from differences in synthesis precursors and therefore the types of impurities present.

Acknowledgements

The author would like to thank Dr. Nathan S. Jacobson of NASA Glenn Research Center and Dr. Barbara J. Frame of Oak Ridge National Laboratory for invaluable guidance as well as the helpful comments and reviews by Dr. Christian Contescu and Mr. Brian Jolly of Oak Ridge National Laboratory. The work was supported by the US Department of Energy, Office of Nuclear Energy Fuel Cycle Research and Development Program.

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Table 1. Natural logarithm of the equilibrium vapor pressures with temperature for the fluids studied in this work.

Material	Method	$10^3 K/T$	$\ln p/\text{Pa}$	$u(\ln p/\text{Pa})$
[P ₈₈₈][DEHP]	Knudsen	2.33	-4.04	1.2E-01
[P ₈₈₈][DEHP]	Knudsen	2.44	-5.71	6.3E-01
[P ₈₈₈][DEHP]	Knudsen	2.28	-3.44	6.7E-02
[P ₈₈₈][DEHP]	Knudsen	2.22	-3.02	4.4E-02
[P ₈₈₈][DEHP]	Knudsen	2.17	-2.33	2.3E-02
[P ₈₈₈][DEHP]	Knudsen	2.12	-1.72	1.2E-02
[P ₈₈₈][DEHP]	Knudsen	2.07	-2.03	9.3E-03
[P ₈₈₈][DEHP]	Knudsen	2.12	-2.92	8.2E-03
[P ₈₈₈][DEHP]	Knudsen	2.17	-3.69	1.7E-02
[P ₈₈₈][DEHP]	Knudsen	2.22	-4.35	4.1E-02
[P ₈₈₈][DEHP]	Knudsen	2.28	-5.11	8.8E-02
[P ₈₈₈][DEHP]	Langmuir	2.34	-4.68	2.78E-02
[P ₈₈₈][DEHP]	Langmuir	2.29	-4.10	1.57E-02
[P ₈₈₈][DEHP]	Langmuir	2.23	-3.53	9.05E-03
[P ₈₈₈][DEHP]	Langmuir	2.07	-1.93	1.89E-03
[C ₂ mim][NTf ₂]	Knudsen	2.38	-1.55	1.25E-02
[C ₂ mim][NTf ₂]	Knudsen	2.20	0.14	2.74E-02
[C ₂ mim][NTf ₂]	Knudsen	2.16	0.27	2.71E-02
[C ₂ mim][NTf ₂]	Knudsen	2.11	0.44	2.68E-02
[C ₂ mim][NTf ₂]	Knudsen	2.07	0.70	2.64E-02
[C ₂ mim][NTf ₂]	Knudsen	2.11	0.36	2.70E-02
[C ₂ mim][NTf ₂]	Knudsen	2.79	-5.91	2.09E-01
[C ₂ mim][NTf ₂]	Langmuir	2.79	-5.91	2.09E-01
[C ₂ mim][NTf ₂]	Langmuir	2.59	-4.92	8.03E-02
[C ₂ mim][NTf ₂]	Langmuir	2.24	-0.33	8.75E-04
[C ₂ mim][NTf ₂]	Langmuir	2.35	-1.76	3.60E-03
[C ₂ mim][NTf ₂]	Langmuir	2.29	-0.99	1.67E-03
[C ₂ mim][NTf ₂]	Langmuir	2.10	1.21	1.95E-04
[C ₈ mim][NTf ₂]	Knudsen	2.22	-3.74	8.28E-02
[C ₈ mim][NTf ₂]	Knudsen	2.16	-2.83	3.39E-02
[C ₈ mim][NTf ₂]	Knudsen	2.11	-2.26	1.93E-02
[C ₈ mim][NTf ₂]	Knudsen	2.07	-1.65	1.05E-02
[C ₈ mim][NTf ₂]	Knudsen	2.03	-0.74	4.29E-03
[C ₈ mim][NTf ₂]	Knudsen	2.07	-1.34	7.79E-03
[C ₈ mim][NTf ₂]	Knudsen	2.12	-1.77	1.18E-02
[C ₈ mim][NTf ₂]	Knudsen	2.16	-1.94	1.38E-02
[C ₈ mim][NTf ₂]	Knudsen	2.07	-1.34	7.79E-03
[C ₈ mim][NTf ₂]	Knudsen	2.12	-1.77	1.18E-02
[C ₈ mim][NTf ₂]	Knudsen	2.16	-1.94	1.38E-02
[C ₈ mim][NTf ₂]	Knudsen	2.22	-2.71	2.94E-02
[C ₈ mim][NTf ₂]	Langmuir	2.39	-5.18	9.26E-03
[C ₈ mim][NTf ₂]	Langmuir	2.33	-4.34	4.02E-03
[C ₈ mim][NTf ₂]	Langmuir	2.28	-3.54	1.83E-03
[C ₈ mim][NTf ₂]	Langmuir	2.22	-2.99	1.07E-03
[C ₈ mim][NTf ₂]	Langmuir	2.08	-1.74	3.18E-04
Fomblin Y HVAC 18/8	Knudsen	2.99	-7.39	1.96E+00
Fomblin Y HVAC 18/8	Knudsen	2.64	-2.82	2.15E-02
Fomblin Y HVAC 18/8	Knudsen	2.51	-1.14	4.13E-03

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Fomblin Y HVAC 18/8	Knudsen	2.40	0.50	8.18E-04
Fomblin Y HVAC 18/8	Knudsen	2.28	1.77	2.36E-04
Fomblin Y HVAC 18/8	Knudsen	2.40	-0.34	1.89E-03
Fomblin Y HVAC 18/8	Knudsen	2.51	-2.22	1.21E-02
Fomblin Y HVAC 18/8	Langmuir	2.83	-7.22	3.28E-01
Fomblin Y HVAC 18/8	Langmuir	2.68	-3.98	1.33E-02
Fomblin Y HVAC 18/8	Langmuir	2.54	-1.91	1.71E-03
Fomblin Y HVAC 18/8	Langmuir	2.42	-0.57	4.60E-04
Fomblin Y HVAC 18/8	Langmuir	2.31	0.41	1.76E-04

Table 2. Thermodynamic parameters for vapor liquid equilibrium of the ILs investigated in this study as well as the Fomblin Y HVAC 18/8 used as a standard.

Material	$\langle T \rangle / K$	A	$B \times 10^{-3} / K$	$\Delta H_{\text{vap}}^{\langle T \rangle} / \text{kJ} \cdot \text{mole}^{-1}$	$\Delta S_{\text{vap}}^{\langle T \rangle} / \text{J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$	$\alpha^{\langle T \rangle}$
[P ₈₈₈][DEHP]	455.7	19.7±1.6	10.4±1.6	86.52±13.3	67.78±28.4	0.047
[C ₂ mim][NTf ₂]	438.3	21.9±10.6	10.1±1.3	83.68±10.8	86.52±10.7	0.022
[C ₈ mim][NTf ₂]	459.5	21.6±1.96	11.1±0.9	92.43±7.5	83.48±16.4	0.231
Fomblin standard	388.9	32.60±2.2	13.61±0.9	113.18±7.5	175.19±18.17	0.013

Figure 1. Structure of the ILs investigated in this work.

Figure 2. Diagram of the Knudsen cell used for the effusion measurements.

Figure 3. Recorded mass (solid) and temperature (dashed) curves for a typical Knudsen measurement, in this case for $[\text{C}_8\text{mim}][\text{NTf}_2]$. The inset corresponds to the shaded area and shows the mass loss per hour at each isotherm.

Figure 4. .

Figure 5. Vapor pressure versus temperature plot (line) for Fomblin Y HVAC 18/8. Error bars are given in (a) for the three data points exhibiting the largest estimated uncertainty for reference. The residuals associated with each measurement are given in (b).

Figure 6. Least squares fit of the natural logarithm of the vapor pressure versus reciprocal temperature for [C₈mim][NTf₂] using the combined Knudsen effusion and Langmuir free evaporation methods **(a)** and the residuals associated with each measurement **(b)**.

Figure 7. Least squares fit of the natural logarithm of the vapor pressure versus reciprocal temperature for [C₂mim][NTf₂] using the combined Knudsen effusion and Langmuir free evaporation methods **(a)** and the residuals associated with each measurement **(b)**.

Figure 8. Least squares fit of the natural logarithm of the vapor pressure versus reciprocal temperature for $[P_{888}][\text{DEHP}]$ using the combined Knudsen effusion and Langmuir free evaporation methods **(a)** and the residuals associated with each measurement **(b)**.

Side view base

Side view lid

Top view lid