

Ionic Liquids as new working fluids for use in absorption heat pumps or chillers :

Their thermodynamic properties

Ki-Sub Kim^a, Bae-Kun Shin, Huen Lee^{a*}, and Felix Ziegler^b

^a *Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea*

^b *Technische Universität Berlin, Institut für Energietechnik, Sekr. BH10
Ernst-Reuter-Platz 1, D-10587 Berlin*

E-mail : hlee@mail.kaist.ac.kr

* Corresponding author. Phone: 82-42-869-3917. Fax: 82-42-869-3910.
Email: hlee@mail.kaist.ac.kr

^b Phone: 49-30-314-22387; Fax: 49-30-314-22253; Email: felix.Ziegler@tu-berlin.de

Abstract

We report a novel application of ionic liquids: 1-Butyl-3-methyl imidazolium tetrafluoroborate ([BMIm][BF₄]) + 2,2,2-trifluoroethanol (TFE) and 1-butyl-3-methyl imidazolium bromide ([BMIm][Br]) + TFE mixtures as working fluids in absorption heat pumps or chillers. The long-term goal is to improve the efficiency of absorption heat pump processes with consecutive advantages in the aspect of energy saving.

Refractive indices, densities, and heat capacities of each pure ionic liquid were investigated in the temperature range of 298.2 to 323.2 K. Vapor pressures were measured by using the boiling point method in the concentration range of 40.0 to 90.0 mass-% of ionic liquid and were correlated with an Antoine-type equation. The average absolute deviations between experimental and calculated values were 0.6 % for the [BMIm][BF₄] + TFE and 0.4 % for the [BMIm][Br] + TFE system, respectively.

Introduction

Recently, considerable interest has been manifested in the use of room temperature ionic liquids owing to their unique electrochemical and physical properties [1,2]. They generally feature good stability in air and water, a wide liquid range, and relatively favorable viscosity and density characteristics. Moreover, either the length of side chain of cation or the specifically designed anion can be easily controlled for various uses [2]. These features facilitate applying ionic liquids to the working fluids used in the absorption heat pump. The technology of absorption heat pumps has received growing attention in the past years from the areas of air-conditioning and refrigeration, especially in connection with energy efficiency. Also, a heat driven cooling technology has been developed to reduce the demand of electric power. An absorption chiller transfers the heat from a low temperature to a high temperature with the help of thermodynamic input in the form of heat as opposed to mechanical work in the case of compression heat pumps [3]. In absorption technology a fluid with strong volatility is used as refrigerant, whereas a second fluid with much smaller volatility but strong affinity to the former is used as absorbent. The cooling cycle is energized by heat input to the solution of absorbent and refrigerant for regeneration of the absorbent. So, essentially all absorption cycle processes are based on absorption and separation between a refrigerant and an absorbent. The properties of the working fluids are key factors that affect the performance of absorption chillers. Various organic chemicals as alternatives to the conventional working fluids have been reported. These organic working fluids - mainly consisting of fluoroalcohol refrigerants and their partner organic absorbents - can surmount the difficulties of classical working fluids such as $\text{LiBr} + \text{H}_2\text{O}$ and $\text{H}_2\text{O} + \text{NH}_3$ system, but they have simultaneously given rise to new problems such as thermal instability, the volatility of the absorbent, and the low process efficiency [4,5].

In this research effort, the new challenge is to introduce ionic liquids as an absorbent to overcome the problems of the existing organic working fluids and to improve the overall process efficiency of absorption heat pump. After some preliminary considerations, 1-butyl-3-methyl imidazolium tetrafluoroborate ($[\text{BMIm}][\text{BF}_4]$) + 2,2,2-trifluoroethanol (TFE) and 1-butyl-3-methyl imidazolium bromide ($[\text{BMIm}][\text{Br}]$) + TFE mixtures were chosen as potential working fluids. The ionic liquids act as absorbents and TFE acts as refrigerant in both cases. TFE has good solubility in the suggested ionic liquids because of the permanent ion-dipole interaction. It is also worthwhile to note that two ionic compounds of $[\text{BMIm}][\text{Br}]$ and $[\text{BMIm}][\text{BF}_4]$ can be easily separated from TFE by a heat input (boiling)

because ionic liquids have a very low vapor pressure, but TFE is volatile.

In order to design an absorption heat pump and to decide whether the ionic liquid + TFE systems are suitable as a novel working pair the basic thermodynamic data must be first determined and carefully checked. In this investigation, refractive indices, densities, vapor pressures and heat capacities of the working fluids were measured as a function of temperature and concentration.

Experimental Section

Materials. The 2,2,2-trifluoroethanol (99 + %), 1-methylimidazole (99%), 1-chlorobutane (99.5%), 1-bromobutane (99%), 1,1,1-trichloroethane (99.5%), ethylacetate, and sodium tetrafluoroborate (98%) were supplied by Aldrich. Dichloromethane and acetonitrile were supplied by KAUTO and MERCK, respectively. All materials were used without any further purification.

Synthesis of ionic liquids

[BMIm][BF₄] and [BMIm][Br] were prepared according to literature procedures [6-8].
Representative synthesis : [BMIm][BF₄] A 1000 mL three-neck round-bottom flask fitted with a water condenser and a gas inlet and provided with a Teflon coated magnetic bar was charged under N₂ with 1-methylimidazole (246.3 g, 3 mol). Butyl chloride (390 mL) was added into the reaction vessel with continuous magnetic stirring in batches of 20mL. The reaction mixture was heated under nitrogen N₂ at 80 °C for 72 h with stirring until two phases formed. The top phase, containing unreacted starting material, was decanted and ethyl acetate (300 ml) was added with through mixing. The ethyl acetate was decanted followed by the addition of fresh ethyl acetate and this step was repeated twice. After the third decanting of ethyl acetate, any remaining ethyl acetate was removed by heating the bottom phase to 60 °C and stirring while on a vacuum line. The product is slightly yellow and may be crystalline at room temperature, depending on the amount of water present in that phase. The product was recrystallized from dry acetonitrile and dried under vacuum at 70°C for 12 h to yield pure crystalline [BMIm][Cl]. To a solution of [BMIm][Cl] (93 g, 0.531mol) in acetone (500 cm³) at room temperature was added sodium tetrafluoroborate (58.3g, 0.531 mol). After 24 h stirring, the resulting NaCl precipitate was then filtered through a plug of celite and the volatiles were removed by rotary evaporation to leave a yellowish, clear liquid. The liquid was dissolved in dichloromethane and the organic phase was then washed twice more with water to ensure complete removal of the chloride salt.

The organic layer was then dried over anhydrous MgSO_4 filtered, and finally dried for more than 10 h under high vacuum at 70-80 °C. The chemical shift for ^1H NMR spectrum(ppm, D_2O) appear as follows : δ 8.71[s, 1H, H(2)], 7.49[s, 1H, H(4)], 7.44[s, 1H, H(5)], 4.21[t, 2H, NCH_2], 3.91[s, 3H, NCH_3], 1.87[m, 2H, NCH_2CH_2], 1.35[m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$] and 0.94[t, 3H, CH_3]. The ^{13}C NMR spectrum(ppm, D_2O) contains peaks : 137.12[C(2)], 123.49[C(4)], 123.12[C(5)], 50.54 [NCH_2], 36.36[NCH_3], 32.45[NCH_2CH_2], 20.06[$\text{NCH}_2\text{CH}_2\text{CH}_2$] and 13.90[CH_3].

[BMIm][Br] The ^1H NMR spectrum (ppm, D_2O) contains peaks : δ 8.91[s, 1H, H(2)], 7.64[s, 1H, H(4)], 7.59[s, 1H, H(5)], 4.32[t, 2H, NCH_2], 4.02 [s, 3H, NCH_3], 1.95 [m, 2H, NCH_2CH_2], 1.42 [m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$], 1.00 [t, 3H, CH_3]. The ^{13}C NMR spectrum(ppm, D_2O) contains peaks : δ 138.31[C(2)], 124.35[C(4)], 123.18[C(5)], 49.65[NCH_2], 36.53[NCH_3], 32.80[NCH_2CH_2], 19.81[$\text{NCH}_2\text{CH}_2\text{CH}_2$], and 13.69[CH_3]

Apparatus and Procedure.

(1) Vapor pressure. The vapor pressures were measured by the boiling point method. The apparatus for vapor pressure measurement primarily consisted of an equilibrium vessel with an internal volume of 100 cm^3 , a constant temperature bath, a condenser, a U-tube mercury manometer capable of reading to 0.05 mm, a K-type thermocouple with the accuracy of ± 0.1 K of reading and two stirrers. A sample solution of a desired absorbent concentration was prepared. The sample solution with an approximate volume of 50 cm^3 was placed in the vessel and evacuated to a proper degree of pressure. The sample solution was then heated and stirred well with a magnetic stirrer to prevent superheating. After thermal equilibrium reached, the temperature of the sample solution and the pressure of the apparatus were measured. The condenser was worked with sufficiently cooled ethanol ($\approx -10^\circ\text{C}$) to minimize the amount of condensed vapor because this TFE-rich vapor can vary the initial concentration of the sample solution. The initial concentration that was calculated in preparing each sample solution was scarcely varied by the increase of less than 0.1 mass % absorbent. The apparatus, procedure, and verification were already carried out in our previous investigation [5].

(2) Heat capacity. A differential scanning calorimeter (TA Instruments DSC Q100) was used for the measurements. The calorimeter was calibrated by measuring the heat capacities of a standard sample synthetic sapphire at different temperatures. A test experiment was done with a lithium bromide + 1,3-propanediol + water mixture and resulting relative error

was within 1.5% [9]. A sample of 5mg was placed in a stainless steel sample container, which was then placed in the calorimeter. Another empty container of the same size was put in the calorimeter as a reference.

(3) Refractive indices All measurements were made with an Abbe refractometer [10]. The instrument was calibrated by measuring the refractive index of deionized water. The sample holder was rinsed with acetone, dried with a paper towel. The uncertainty of measurement was ± 0.01

(4) Density A pycnometer was used to measure the densities of each ionic liquid [4]. The experimental apparatus consisted of a pycnometer, a thermometer, and a water bath to control the temperatures of the solutions. The density measurements were performed with the accuracy of $\pm 0.001 \text{ g} \cdot \text{cm}^{-3}$

Results and Discussions

(1) Refractive index, Density, and Heat capacity. Refractive indices, densities, and heat capacities of the pure ionic liquids [BMIm][Br] and [BMIm][BF₄] were measured in the temperature range from 298.2 to 323.2 K. The experimental results are presented in Table 1 and Figure 1. As expected, the density values decrease, but the heat capacities increase with increasing temperature. The temperature effect on refractive index appears to be almost negligible.

(2) Vapor pressure The vapor pressures of the TFE + ionic liquid systems were measured by using a boiling point method in the concentration range from 40 to 90 mass percent of the ionic liquids. The vapor pressure data are the most important to analyze an absorption heat pump cycle. The experimental results are listed in Tables 2 and 3. These values were correlated with an Antoine-type equation which expresses the vapor pressure as a function of temperature and concentration:

$$\log P = \sum_{i=0}^3 [A_i + 1000 B_i / (T - 43.15)] X^i \quad (1)$$

where P is the vapor pressure in kPa, A_i and B_i the regression parameters, T absolute temperature in K, and X the mass percent of ionic liquid. The parameters A_i and B_i were determined by a least-square method, and the results are shown in Table 4. The average absolute deviations between the experimental and calculated values was found to be 0.6 and 0.4 % for [BMIm][BF₄] + TFE and [BMIm][Br] + TFE mixtures, respectively. These experimental and calculated results are plotted in Figures 2 and 3. The figures show that the

$\log P$ vs. $1000 / (T-43.15)$ (see equation 1) relation at a given concentration appears to be linear over the pressure and temperature ranges considered.

The solubility of a refrigerant in an absorbent is one of the major factors for deciding the suitability of a working fluid. It mainly depends on the interaction between the refrigerant and the absorbent. Thus, the vapor pressure measurement can be a method to evaluate the affinity between a refrigerant and an absorbent, and consequently their applicability to sorption machines. This means that the vapor pressure lines will be steeper, the required temperature for regeneration will be smaller, but the Coefficient of Performance (COP) will be lower also.

Conclusion

Novel working fluids for an absorption heat pump have been proposed by investigating the environmentally friendly ionic liquids and fluoroalcohol. The pairs [BMIm][Br] + TFE and [BMIm][BF₄] + TFE have been considered as potential working pairs for the first time. The refractive indices, densities, heat capacities and vapor pressures were measured over a wide concentration and temperature range. The vapor pressure data were correlated with an Antoine-type equation, and reasonable agreements were obtained between calculated and experimental values. The [BMIm][Br] + TFE system was found to be more favorable than the [BMIm][BF₄] + TFE from the results of vapor pressure. However, for the detailed investigation of the suggested working fluids, more properties such as viscosity, surface tension, and thermal conductivity are required.

Acknowledgement

This work was supported by Grant 20006-307-04-2 from the Cooperative Research Program of Korean KOSEF and German DFG and also partially by the Brain Korea 21 Project.

References

- [1] Welton T., Chem. Rev. 99 (1999) 2071.5. Welton T., Chem. Rev. 1999, 99, 2071.
- [2] Marsh K.N., Korean J. Chem. Eng. 19(3) (2002) 357
- [3] F. Ziegler, Recent developments and future prospects of sorption heat pump systems. International Journal of Thermal Science, 38 (1999) 191-2088. Scurto A.M., Aki SNVK, Brennecke J.F., J. AM. Chem. Soc. 2002, 124(35), 10276.
- [4] Kim K.S. and Lee H., J. Chem. Eng. Data. 47 (2002) 216.
- [5] Lee J.W., Kim K.S., and Lee H., J. Chem. Eng. Data. 48 (2003) 314-316
- [6] Bonhote P., Dias A.P., Papageorgiou N., Kalyanasundaram K., and Gratzel M., Inorg. Chem. 35 (1996) 1168.
- [7] Suarez P.A.Z., Dullius J.E.L., Einloft S., Souza R.F.D., and Dupont J., Polyhedron 15(7) (1996) 1217.
- [8] Dyson P.J., Grossel M.C., Srinivasan N., Vine T., Welton T., Williams D.J., White A.J.P., and Zigras T., DALTON (1997) 3465.
- [9] Kim J.S., Park Y., Yu S.I., and Lee H., J. Chem. Eng. Data 1997, 42, 371
- [10] Kim J.S., Park Y., and Lee H., J. Chem. Eng. Data 41 (1996)

Figure Captions

Figure 1. Heat capacities of the [BMIm][Br] and [BMIm][BF₄] : (●) [BMIm][BF₄] + TFE; (○) [BMIm][Br] + TFE

Figure 2. Vapor pressures of the [BMIm][Br] + TFE system : (○) 0%; (●) 40%; (▲) 50%; (◇) 60%; (■) 80%; (▽) 90%, mass % of [BMIm][Br]; (—) calculated, (···) literature⁹

Figure 3. Vapor pressures of the [BMIm][BF₄] + TFE system : (▽) 0%; (●) 40%; (◇) 60%;

(■) 80%; (△) 90%, mass % of [BMIm][BF₄]; (—) calculated, (···) literature⁹

Table 1. Measured Refractive indices and densities of each [BMIm][Br] and [BMIm][BF₄]

Refractive indices			Densities / g · cm ⁻³		
T / K	[BMIm][Br]	[BMIm][BF ₄]	T / K	[BMIm][Br]	[BMIm][BF ₄]
298.3	1.54	1.42	298.4	1.299	1.202
303.2	1.54	1.42	303.4	1.296	1.198
308.0	1.54	1.42	308.0	1.292	1.195
313.2	1.54	1.42	313.0	1.290	1.191
318.0	1.54	1.42	318.0	1.287	1.188
323.0	1.54	1.42	323.0	1.284	1.185

Table 2. Measured vapor pressures of the [BMIm][Br] (X) + TFE mixtures

T / K	P / kPa	T / K	P / kPa	T / K	P / kPa
X = 0 %		X = 40 %		X = 50 %	
293.2	7.2	308.4	4.9	329.6	7.4
297.9	9.5	338.0	19.7	353.8	21.0
312.2	20.9	353.0	36.6	369.2	38.1
323.0	36.0	364.0	55.8	382.6	61.4
328.5	46.6	374.0	79.6	393.4	85.1
343.2	88.3	380.8	100.1	398.8	99.9
X = 60 %		X = 80 %		X = 90 %	
358.2	14.1	397.6	15.3	409.4	11.1
377.6	30.6	416.0	28.1	425.6	19.2
401.2	63.7	430.0	43.4	448.4	36.8
411.8	87.0	442.0	64.1	456.4	47.0
416.6	101.0	456.2	88.3	465.0	56.8
		459.6	99.9	469.4	67.1

Table 3. Measured vapor pressures of the [BMIm][BF₄] (X) + TFE mixtures

T / K	P / kPa						
X = 40 %		X = 60 %		X = 80 %		X = 90 %	
315.2	10.5	321.6	6.8	353.8	7.1	430.4	27.4
325.2	17.7	341.0	15.3	376.0	15.3	442.4	36.0
334.0	26.1	350.6	22.5	387.8	23.1	451.6	44.2
340.8	34.1	361.4	35.5	396.8	30.8	461.2	54.4
346.8	43.7	367.2	41.8	407.2	40.0	465.2	63.7
351.8	53.2	373.0	50.6	414.4	49.7	469.4	73.8
357.2	64.2	379.0	60.6	418.4	59.0		
362.6	77.8	384.4	70.5	425.8	69.4		
370.2	100.5	388.4	82.1	432.8	85.6		
		395.4	100.3	439.0	99.8		

Table 4. Parameters for the Correlation of Eq. (1)

i	A	B	AAD %
		[BMIm][BF ₄] + TFE	
0	0.843 E+01	-0.124 E+01	0.58
1	-0.568 E-01	-0.240 E-01	
2	0.481 E-03	0.543 E-03	
3	-0.150 E-05	-0.388 E-05	
		[BMIm][Br] + TFE	
0	0.564 E+01	-0.866 E+00	0.43
1	0.740 E-01	-0.367 E-01	
2	-0.147 E-02	0.589 E-03	
3	0.848 E-05	-0.362 E-05	

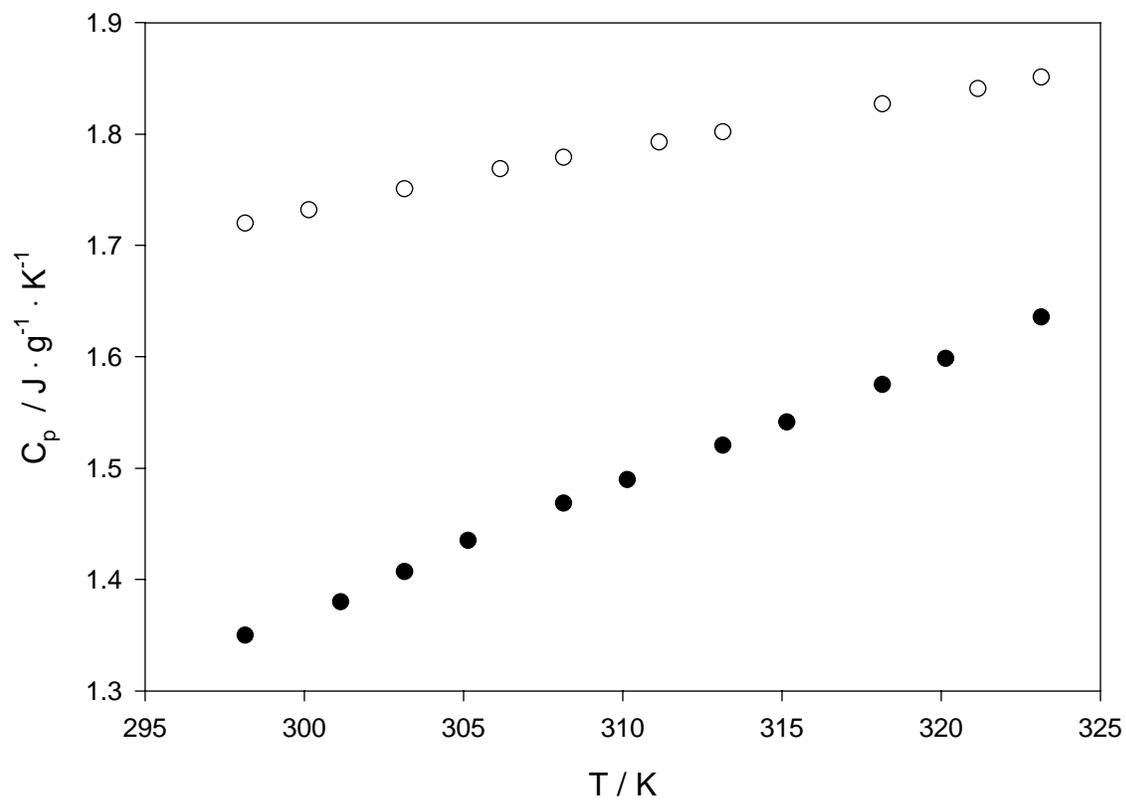


Figure 1.

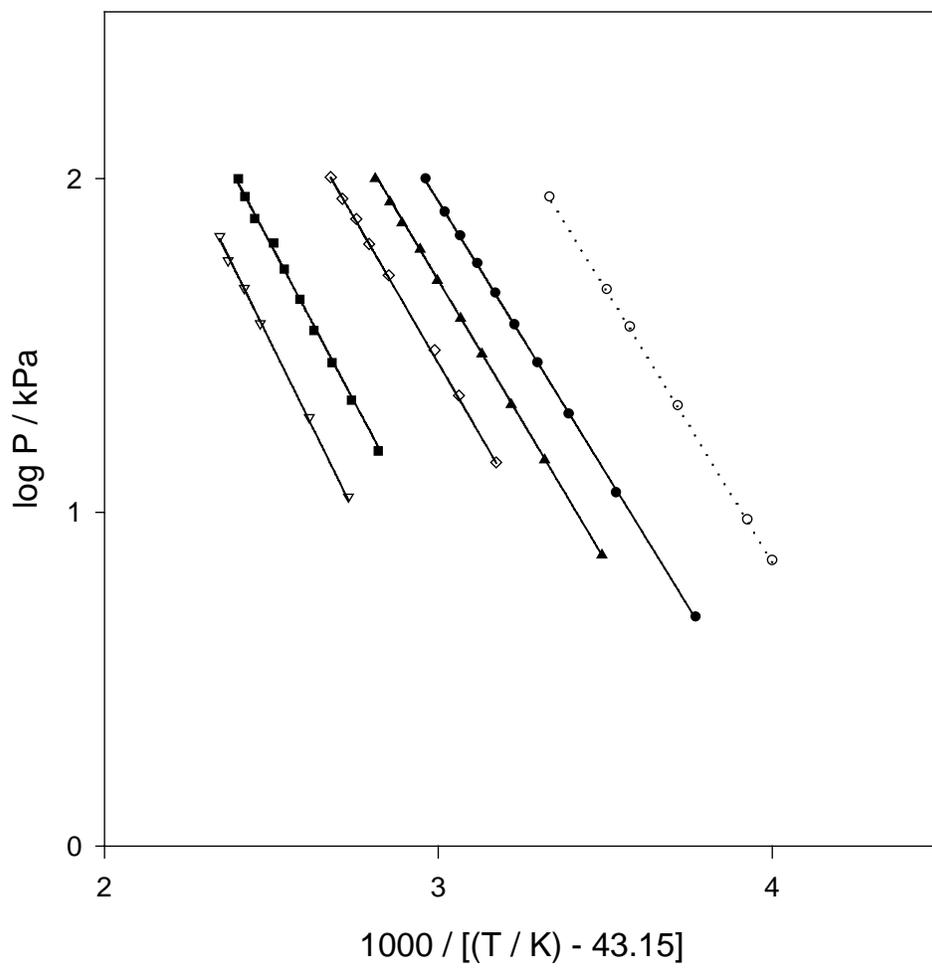


Figure 2.

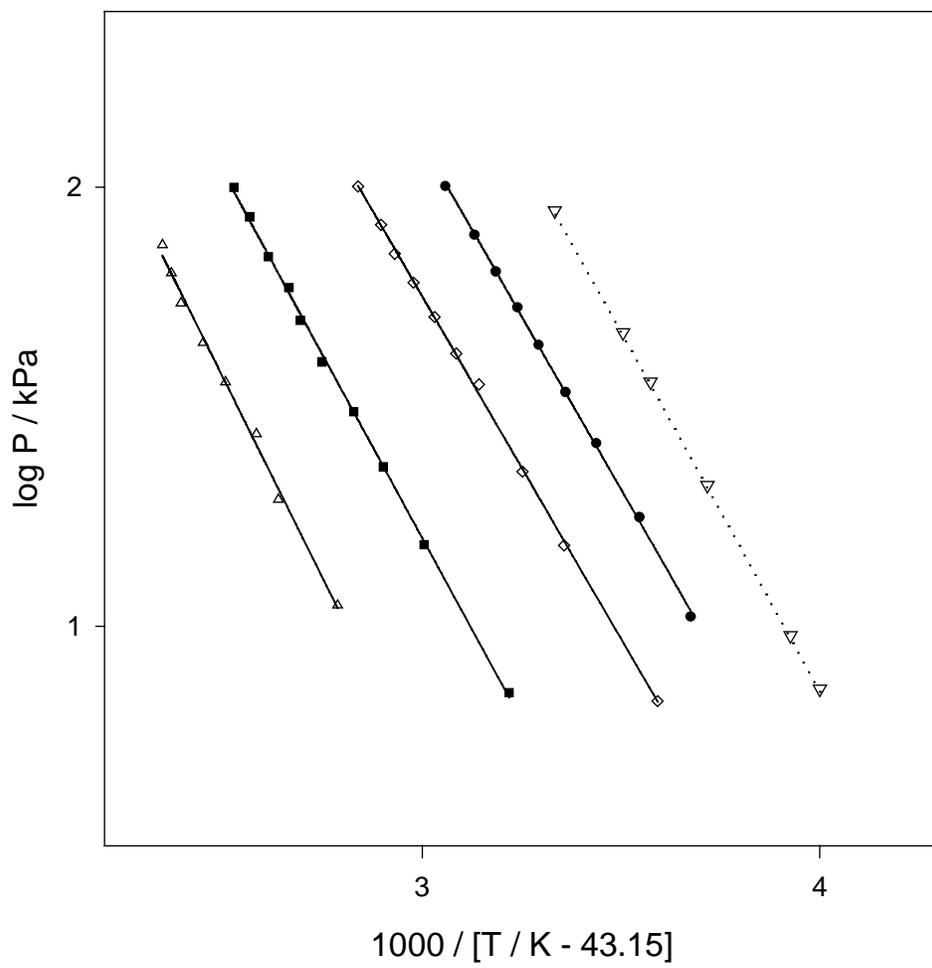


Figure 3.