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A SMALL STATIC TOTAL PRESSURE VAPOUR-LIQUID EQUILIBRIUM CELL A CASE STUDY WITH METHANOL_METHYLFORMATE

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Abstract
A small static total pressure apparatus was developed. Vapour-Liquid Equilibrium was measured for the methanol+methylformate system in the temperature range from 303 K to 353 K. Additionally two isothermal measurements were made with a larger volume apparatus at 342 K and 359 K to validate the small VLE cell measurements. The developed VLE model could describe the literature data. Azeotropic behavior was detected.

Keywords: vapour-liquid equilibrium, methanol, methylformate, measurement

1. Introduction

The miniaturization of phase equilibrium measurement devices reduces chemical consumption and enables rapid temperature changes, which are appealing characteristics. The drawback is the increased demand on the accuracy of the pumps which are used to inject the components. Also the general size of the equipment components currently available can reduce the feasibility for miniaturization of phase equilibrium measurement apparatus. Nevertheless a substantial increase in the amount of data produced can be achieved by reducing the size of the equipment.

2. Objectives and approach

The objective of the work was to construct a small phase equilibrium measurement cell composed of affordable components readily available from vendors. The vapour pressures of methanol, methylformate and propane were measured to demonstrate the capability of rapid vapour pressure measurements with the equipment.

Static total pressure data of the methanol+methylformate system was measured in the temperature range from 303 K to 353 K. The measurements were compared with earlier work [1-4] and also with measurements carried out using a static total pressure type apparatus with a cell volume of approximately 113 cm^3 at 342 K and 359 K[5]. Finally all the results measured with the apparatuses in this work were treated with the Barker method[5, 6] to obtain a VLE model for the whole measured temperature range.

3. Equipment

The pressure was measured with a Druck PDCR 4021 transducer (0-2000 kPa full scale) connected to a Druck DPI-280 pressure display. The calibration of the pressure measurement was carried out with a Beamex MC2 pressure calibrator. The only exception was for the vapour pressure measurements of propane, for which the PDCR 4020 transducer was destroyed by moisture before calibration was performed. The pressure measurement error was estimated to be 2.5 kPa for the systems measured except for propane for which the error is larger; approximately 5 kPa. Change of pressure transducer and pressure range is fast since the stainless steel cell exterior resembles a nut (Figure 1b). The sealing between the equilibrium cell and pressure transducer was achieved with an aluminium seal. A schematic depicting the equipment set-up is presented in Figure 1a.

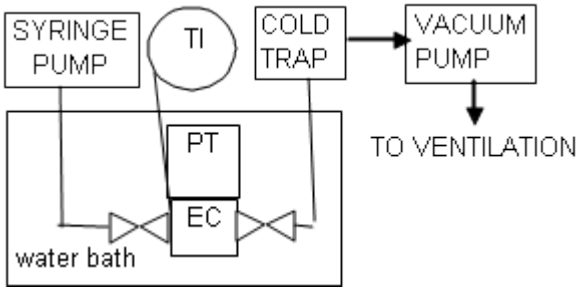

Figure 1a. Small static total pressure apparatus. EC equilibrium cell, PT pressure transducer, TI temperature indicator connected to a temperature meter.

Figure 1b. Small VLE-cell.

The temperature measurement consisted of a Pt-100 probe connected to an AMETEK-100 temperature meter (uncertainty ±0.04 K, the resolution of the meter was 0.01 K). The probe was located in contact with the equilibrium cell. The pressure transducer was isolated from water by attaching a fiber reinforced hose with a sealing paste on the exterior of the transducer. The pressure transducer was temperature compensated up to 80°C, which limited the possible temperature range. The valves and the equilibrium cell were directly in contact with the temperature controlled water.

The degassed components were injected to the equilibrium cell with an Isco 260 syringe pump. The uncertainty of the volume of the injected compounds was 0.02 cm^3. The equilibrium cell was immersed in a Lauda Ecoline 200 thermostat.

4. Experimental procedure

4.1 Vapour pressure measurement

The chemicals (Methanol puriss. p.a 99.8 %, Sigma Aldrich, methylformate 99 %, Sigma-Aldrich, propane, Linde Aga Oy, 99.999 %) used in the measurements were dried with molecular sieve. The cell was completely filled with the compound. The compound was degassed in the cell by opening the valve to the vacuum line periodically. This was continued until a stable vapour pressure reading was obtained. A part of the line connecting the cell to the syringe pump and the line to the vacuum system was made of a small diameter capillary. It was possible to use the degassing procedure presented in this work even for propane because the inner diameter of the capillary tubing was small enough to reduce the flow rate from the cell sufficiently. The time needed for producing one vapour pressure point ranged from 5 to 8 minutes when the cell assembly was immersed in the water bath. When the cell was kept in an oven (in air) then the equilibration time was substantially longer due to lower heat transfer rate in comparison to using a water bath.

4.2 VLE measurements

A predetermined amount of degassed compound 1 was injected to the cell by opening and closing the cell valve. Then the syringe pump was evacuated and the second compound was fed to the pump. After the equilibration of the temperature a predetermined amount of compound 2 was injected to the cell. Since the syringe pump had a coarse injection resolution for an equilibrium cell of this size (1.78 cm^3), the volumes of the injected compounds were optimized so that a large amount of substance with respect to cell volume was injected.

The cell was mixed with a magnetic stirrer lifted out of the water bath after the addition. It took approximately from 20 to 25 minutes until a steady pressure reading was obtained at room temperature. The mixing was continued a further 10 minutes to ensure good mixing of the cell content. After mixing the cell was placed in the temperature controlled water bath. The water bath temperature was maintained at one experimental temperature for 20 minutes and the pressure and temperature were recorded. The experimental temperatures were scanned through.

From three to seven mixture points were measured in one measurement cycle with the small cell. After a measurement cycle the cell was evacuated and a new set of mixtures were loaded in a

different composition range. Two isothermal static total pressure data sets were measured with an automated set-up similar as presented in.[9]

5. Results

5.1 Pure component vapour pressure

Vapour pressures for propane, methylformate and methanol measured with the equipment are presented in figure 2a. The vapour pressure measurements were well in-line with literature values [7, 8] and from 6 to 8 vapour pressure points were obtained in an hour. The vapour pressure measured deviated by substantially larger values for propane than the other compounds measured as presented in Figure 2b. The reason as explained earlier was that the transducer used was destroyed prior to calibration at several temperatures. Usually during VLE measurements, according to our experiences the transducer temperature is practically constant in an isothermal run. In the measurements with the small scale apparatus transducer temperature changed with the experimental temperature and pressure calibrations had to be made at several temperature even though the pressure transducer was temperature compensated.

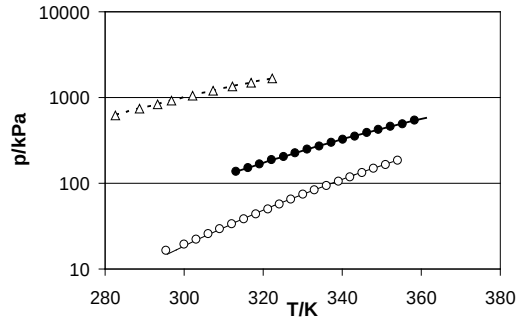

Figure 2a. Measured vapour pressure and vapour pressures calculated from correlations. △, propane; ●, methyl formate; ○, methanol, ----, propane[7]; ━ methylformate[8]; — methanol[7].

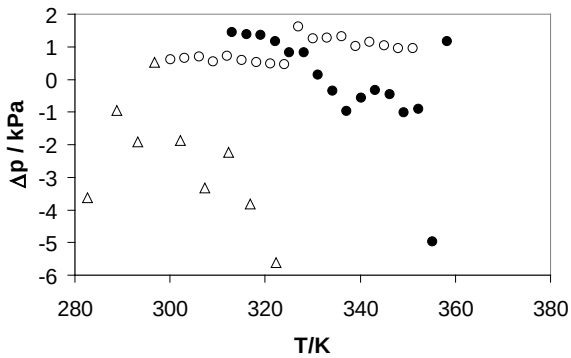

Figure 2b. Deviation of measured vapour pressure and vapour pressure calculated from correlations. △, propane; ●, methyl formate; ○, methanol.

5.2 Binary VLE data

The data reduction was carried out with the Barker method [5] as implemented in [6]. A four parameter Wilson model was used as the activity coefficient model [9]. The error estimation was made as presented in [10]. The VLE –measurement error is larger when a small scale cell was utilized, which was caused by the larger relative error due to smaller injection volumes and also in this case the somewhat larger error compared to the automated apparatus due to the pressure transducer accuracy. Therefore in the future it is desirable to utilize syringe pumps in the volume range from 2 cm^3 to 5 cm^3 and pressure transducers more suitable for the range to be measured in terms of full scale.

Physical properties used in the regression and the vapour pressure correlation parameters used are presented in Table 1. The regressed VLE measured with the small static total pressure apparatus and the automated total pressure apparatus for methylformate + methanol system is presented Figure 3a. The VLE-measurements and the Wilson model agree well with the literature values as presented in Figure 3b. Literature data was not utilized for the regression of the Wilson model.

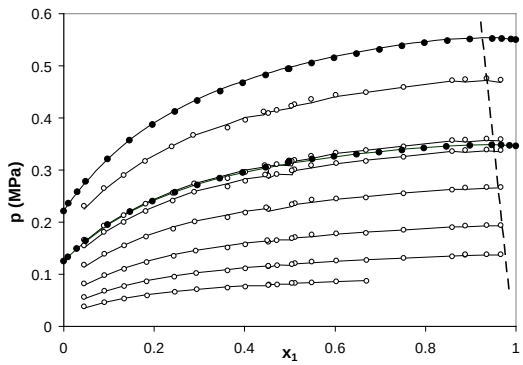

Figure 3a. Measured methylformate + methanol. ●, Static apparatus 342 and 359K; ○, Small static apparatus 303-353K; —, Wilson model; -----, Azeotrope.

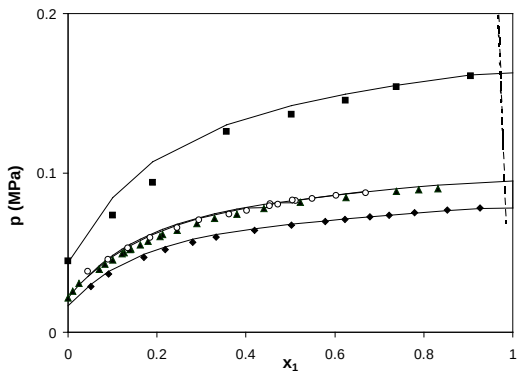

Figure 3b. Qualitative comparison of the regressed model with VLE from literature. ○, Small static apparatus 303K; ▲, 302K[1]; ◆, 298K[2]; ■ 318K[3]; —, Wilson model.

Table 1. Physical properties and vapour pressure correlation parameters used in the data regression for methyl formate(1) + methanol(2). Critical temperature T_c, Critical pressure P_c, Molar volume used in the Wilson data regression v_i. Temperature dependant Wilson parameters and pressure residuals obtained from the regression of all measured data.

	(1)	(2)	Wilson model	
T_c/K [7]	487.2	512.5	λ_{12}/ K^{-1}	731.41
P_c/MPa [7]	6.00	8.06	λ_{21}/ K^{-1}	456.764
ω [7]	0.2555	0.5658	λ_{12}	-1.04567
v_i/cm^3/mol [7]	62.10	40.26	λ_{21}	-1.13993
A	7.5550	68.902	Δp/kPa	0.6
B	2590.5	-6904.5	$\lvert\Delta p\rvert$ /kPa	1.8
C	-41.538	-8.8622		
D		7.4664E-06		
E		2[7]		

Equation (1) was used for the methylformate vapour pressure calculation. The parameters for this equation are presented in Table 1, the parameter values were obtained from literature sources[8].

$$\ln(p/Mpa)=A-(B/((T/K)+C)) \quad (1)$$

Equation (2) was used for the methanol vapour pressure calculation. Also these parameter values were obtained from literature sources[7].

$$\ln(p/Mpa)=A+(B/(T/K))+C\ln(T/K)+D(T/K)^E \quad (2)$$

5.3 Infinite dilution activity coefficients

Infinite dilution activity coefficients were obtained by regression of the data from literature using the vapour pressure correlations presented in Table 1. The infinite dilution activity coefficients of [4] agree quite well with the values obtained from this work as presented in Figure 4. The amount of data points is somewhat low for an extremely accurate extrapolation of the literature data to the infinite dilution range. Maximum pressure azeotropic behavior was observed for the system studied. Published data in the literature do not cover the composition range where the azeotrope is located. Azeotropic behavior was observed by the regression of [4], even though the data points measured do not cover the azeotropic range. Also none of the other literature sources found [1-3] cover the azeotropic range.

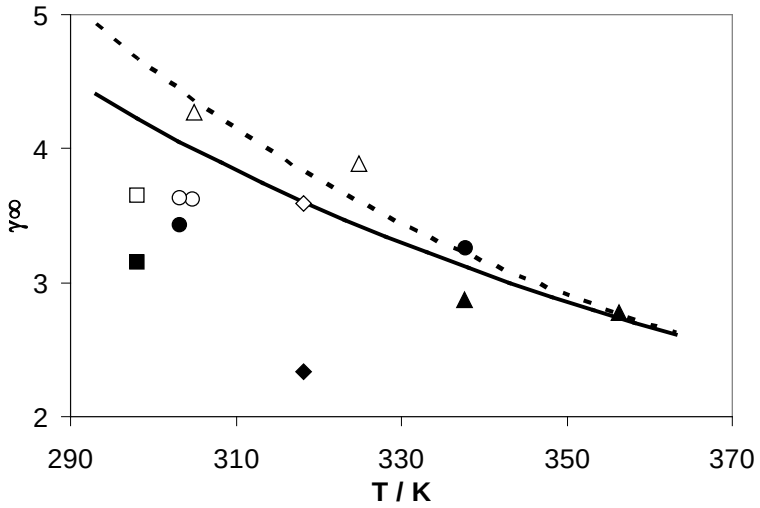

Figure 4. Infinite dilution activity coefficients of methanol in methylformate and methylformate in methanol. ●, methyl formate[1]; ■ methylformate[2]; ◆, methylformate[3]; ▲, methylformate[4]; ○, methanol[1]; □, methanol[2]; ◇, methanol[3]; △, methanol[4].

6. Conclusions

A new small scale static total pressure apparatus was built. The volume of the equilibrium cell was 1.78 cm^3. The automated scanning of a wide temperature range with small temperature increments and the data acquisition will be easy to implement. A syringe pump was used for injecting the compounds with a somewhat low accuracy in comparison to earlier designs. One of the challenging tasks is to find a suitable syringe pump that has pressure control and a more accurate resolution.

Firstly the equipment was tested by measuring vapour pressures of methanol, methyl formate and propane. The measurements were in accordance with correlations found from literature sources.

Secondly over 200 new equilibrium points were measured in the temperature range from 303K to 359K for the methylformate + methanol system. For one vapour liquid equilibrium point approximately 20 minutes was needed. A comparison was made with the measurements available from literature sources. Some, not all of data from literature agreed well with the data from this work. Azeotropic behavior was found for the methyl formate+methanol system.

The miniaturization of phase equilibrium measurement devices may go even one step further than presented in this work. The volumes can possibly be reduced from milliliter scale to a magnitude of microliters. For microliter sized equipment designs piston pumps for accurate component injections and valves with small dead volume are crucial. Small scale phase equilibrium equipment can lead to a productivity increase in the amount of measurements and temperatures covered.

Acknowledgements

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