

ESTIMATING VLE OF BINARY LIQUID SOLUTIONS BY ARC AND GC

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Abstract

A method for estimating the vapor-liquid equilibria of binary liquid solutions using an Accelerating Rate Calorimeter (ARC) is described. ARC provided data in the ranges: (0–14) kPa and (300–450) K. The experimental PTx data were reduced to partial pressures and vapor phase compositions using Barker's method. The well-known system, benzene/cyclopentane, was selected to evaluate the ARC method. GC-headspace analysis confirmed the vapor phase compositions. Both GC and ARC data on the vapor phase agree with literature data to within ± 0.0085 mol fraction units. Experimental pressure data agree with literature data to within ± 2 kPa. Model pressure data agree with literature data to within ± 1.5 kPa. Also described is the high-pressure VLE of the phosgene-chlorobenzene binary at 448 K.

Keywords: ARC, phosgene, vapor pressure, VLE

Introduction

The estimation of VLE data is important in solving many process design problems, including separations, and there exists a vast field of literature on the subject [1]. Such data are also used for emergency pressure-relief design [2] and an excellent example that illustrates the use of ARC data in the high-pressure regime has recently been published [3]. There are many approaches to obtaining VLE data. One way is to sample the equilibrium vapor (after making a vapor pressure measurement) and determine the concentrations of each component by refractive index, or density or some other appropriate physical property measurement [4]. Direct chemical analysis of the equilibrium vapor can be achieved by the GC-headspace technique [5]. Mathematical analysis of the equilibrium pressure data is an alternative that requires no sampling or chemical analysis. This approach involves reducing isothermal pressure-mole fraction data (PTx) to isothermal y - x data via a mathematical model of the VLE [6–8].

In this article, we take the PTx approach and use GC-headspace analysis to confirm the model predictions. To obtain the required pressure data we find the ARC useful. ARC has the advantages of being applicable over large pressure and tem-

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perature ranges. Designed for the purpose of obtaining data on energetic and potentially hazardous materials [9–11], the ARC is uniquely-suited for VLE studies on such. The calorimeter is temperature-programmed and can be used to acquire data for any given charge composition at several temperatures, overnight.

Experimental

Materials

Benzene (GC standard > 99.9%) and cyclopentane (GC standard > 99.5%) were obtained from Fluka Chemical Corporation. Monochlorobenzene (Fisher certified, 0.02% water) was obtained from Fisher Scientific. Phosgene (> 99% pure) was obtained from Matheson Gas Products.

Instrumentation, conditions and procedures

ARC (Columbia Scientific Industries, model 851-0004)

All pressures were recorded to the nearest 0.1 psia (0.69 kPa), and all temperatures to the nearest 0.01 K. The commercial ARC was used with the only modification being the removal of the pressure-limiting valve. The sample solution is contained in a metal bomb (2.54 cm i.d. sphere) that is sealed to a pressure transducer via steel capillary (0.0254 cm i.d., 30.48 cm length). For low-pressure work (< 414 kPa), we included a 3-way ball valve between the bomb and transducer to permit degassing of the solution. The sample thermocouple is secured to the outside of the bomb and the bomb assembly is placed inside the calorimeter furnace. The pressure transducer is secured outside the heated portion of the calorimeter and remains at room temperature throughout the experiment. A complete description of the ARC can be found in the literature [9, 10]. The sample is quickly heated to the desired temperature by the calorimeter furnace. The internal bomb pressure is taken after 10 min at temperature. A Sensotec transducer model TJE/743-02 [range (0–2500) psia or (0–17.2) MPa, accuracy 0.05% full-scale] was used with a stainless steel bomb for phosgene experiments. A Sensotec transducer model TJE/713-04 [range (0–50) psia or (0–345) kPa, accuracy 0.1% full-scale] was used with a Hasteloy-C bomb for all other experiments.

Phosgene–chlorobenzene solutions were prepared in ARC bombs by the following procedure: A known chlorobenzene weight is charged to the ARC bomb, which is then connected to the phosgene cylinder (in the fume hood) and cooled in a dry ice–acetone bath to approximately 195 K before opening the cylinder valve to fill the bomb. The bomb is quickly sealed and reweighed. The bomb is secured to the pressure transducer, which was previously adjusted to read the barometric pressure in the laboratory while open to the atmosphere.

Benzene–cyclopentane solutions were made up in the ARC bomb by weight at room temperature and shaken vigorously for 5 min. The bomb was secured to the pressure transducer via a ball-valve. The solution was degassed by freeze–pump–thaw cycling using a dry–ice–acetone bath and a “roughing” vacuum pump. Charge weights were nominally 6 g total in a 25 g bomb.

Gas-Chromatography (Hewlett Packard model HP5890-FID)

Equilibrium vapors were analyzed by GC using a flame-ionization detector in line with a boiling point-type column (HP-5 capillary column, 25 m long, 0.32 mm i.d., 0.52 μm film thickness) and headspace autosampler designed to take 1 cm^3 of the headspace of a 10 cm^3 , septum-sealed glass sample vial. Detector, injection port, and sample vial temperatures were 548, 408, and 318 K, respectively. The column temperature was ramped from 338 to 373 K at 10 K min^{-1} with an initial isothermal hold at 338 K of 0.5 min. Using a carrier gas (helium) velocity of 25 cm s^{-1} , the retention times for cyclopentane and benzene were 1.98 and 2.45 min, respectively.

VLE solutions were made up by weight in the autosampler vials under room conditions. A large excess of the liquid phase was used to insure that the solution could not completely vaporize at 318 K. Each vial was sealed with a teflon-coated rubber septum, shaken vigorously for 5 min and placed in the GC oven at 318 K, where it equilibrated for no less than 3 h with gentle shaking before being sampled. For each component, the peak area counts were converted to micrograms in the headspace sample using a suitable calibration curve.

Results

Benzene-cyclopentane binary at 318 K

Barker's numerical method [1] was used to reduce experimental (ARC) PTx data to isothermal $y-x$ data. Figure 1 is an equilibrium y vs. x plot showing our calculated results, results from direct GC-headspace analysis of the equilibrium vapor and the literature [1] values. The distance (in mol fraction units) between upper and lower bounds to the experimental y -data (at the 95% confidence level) is 0.017, for any liquid composition. From $y-x$ data, the partial pressures of each component

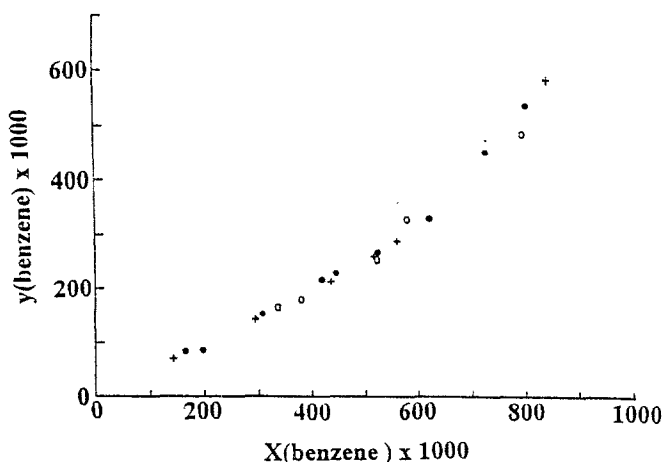


Fig. 1 Equilibrium y vs. x plot for the benzene-cyclopentane binary (318 K) showing literature [1] PTx values (+), ARC PTx values (o) and GC-headspace values (•)

were calculated along with the total pressure. Molar volumes and second virial coefficients required for the calculation were taken from the literature [1]; the required pure component vapor pressures were measured using ARC. Figure 2 shows the results of ARC-PTx analysis in the form of a pressure-composition diagram. Positive deviation from Raoult's law is observed. The ARC pressure data are within ± 2 kPa of the literature [1] experimental values. Calculated pressures are within ± 1.5 kPa of the same literature values.

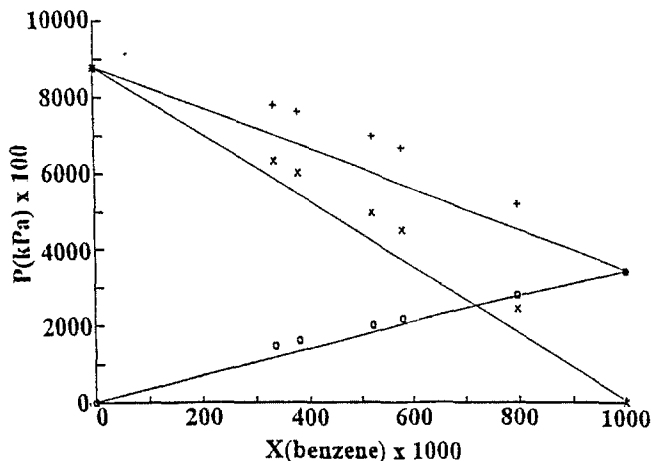


Fig. 2 Pressure-composition diagram for the benzene-cyclopentane binary (318 K) showing the partial pressures of the components (benzene (o), cyclopentane (x)), the Raoult's law lines and the total solution vapor pressure (+)

Phosgene-mcb binary at 448 K

The vapor pressure curve of phosgene between 380 and 450 K was determined by ARC. A comparison to a literature [12] curve is made in Fig. 3: ARC and literature values never differ by more than 5% over the experimental temperature range. The vapor pressure of pure chlorobenzene was determined by ARC at 448 K along with several phosgene-chlorobenzene solutions. Because of large system pressures, direct analysis of the vapor phase by the GC-headspace technique was not performed. ARC PTx data was once again reduced to $y-x$ data using Barker's method. The results from this analysis are given in Table 1. Molar volumes and second virial coefficients required for the VLE model were taken from the literature [13] except the mixed-second virial coefficient, which we approximated by the midpoint between the values of the corresponding pure compounds, having found no literature value. Pure component vapor pressures employed in the model were measured by ARC. No vapor pressure data could be found in the open scientific literature on this binary for comparison, however, Melham [3] has already shown the applicability of ARC to high-pressure VLE using the acetone-water binary. Calculated and experimental pressures differ by no more than 3% except at the 0.5552 chlorobenzene

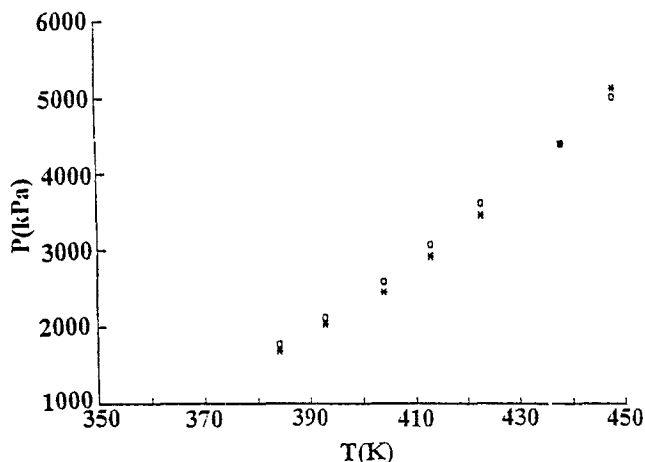


Fig. 3 Phosgene vapor pressure curve (ARC data (o), literature [12] data (*))

mole fraction where the difference was 10%. The activity coefficients given in Table 1 refer to the standard state as the pure components at the same temperature and pressure as those of the mixture. The chlorobenzene activity coefficients at mole fractions 0.7063, 0.5330 and 0.5552 are inconsistent with the Gibbs-Duhem equa-

Table 1 Phosgene-chlorobenzene VLE at 448 K. Compositions, total (*P*) and partial (*p*) pressures and activity coefficients (γ) (1=chlorobenzene, 2=phosgene, exp.=experimental, calc.=calculated)

VLE model results using ARC experimental vapor pressures for pure components (3.0337 bar for chlorobenzene, 50.3523 bar for phosgene)							
X_1	y_1	$\frac{P_{exp}}{bar}$	$\frac{P_{calc}}{bar}$	γ_1	γ_2	$\frac{p_1}{bar}$	$\frac{p_2}{bar}$
0.7063	0.2091	13.4999	13.4810	0.9827	1.0752	2.8226	10.6577
0.5330	0.1269	20.3119	20.8781	0.9823	1.0785	2.5765	18.3032
0.5552	0.1242	23.7765	21.0842	0.9809	1.0803	2.9530	18.1315
0.3554	0.0780	29.4509	29.4725	1.0175	1.0504	2.2983	27.1720
0.2816	0.0628	33.1775	33.1719	1.0492	1.0356	2.0842	31.0890
0.1750	0.0420	40.6859	39.7035	1.1205	1.0159	1.7068	37.9972
VLE model results using 2.8889 bar for chlorobenzene vapor pressure and 48.9672 bar for phosgene vapor pressure in order to bring the γ_1 values at large X_1 values closer to unity							
0.7063	0.2003	13.4999	13.6213	0.9848	1.1156	2.7045	10.9169
0.5330	0.1224	20.3119	21.0258	0.9913	1.1067	2.4860	18.5418
0.5552	0.1197	23.7765	21.2408	0.9986	1.1102	2.8743	18.3952
0.3554	0.0765	29.4509	29.4482	1.0428	1.0649	2.2521	27.1952
0.2816	0.0622	33.1775	33.0350	1.0857	1.0451	2.0622	30.9733
0.1750	0.0423	40.6859	39.3757	1.1807	1.0198	1.7196	37.6557

tion by being (slightly) less than unity: We expect, considering the positive deviation from Raoult's law by the phosgene partial pressures at these concentrations, positive deviations by the chlorobenzene component. The Raoult's law partial pressures depend upon the vapor pressures of the pure components: One possible cause for the observed inconsistency in the chlorobenzene mole fraction is the experimental uncertainty in these vapor pressures.

Table 1 shows the VLE model data obtained by adjusting the values for the vapor pressures of the pure components in order to bring the chlorobenzene activity coefficient closer to unity at the standard state. The values employed in this calculation differ from the ARC experimental vapor pressures by 5 and 3% for chlorobenzene and phosgene, respectively. (This phosgene value differs from the most recently published value [14] by less than 1%.)

Discussion

The selection of an experimental method depends upon many factors including availability, cost, and requirements on the quality of the data. For those laboratories fortunate to already possess an ARC, the second criteria (cost) will not likely rule out this technique for acquisition of PTx data: We cannot think of a simpler or faster method provided that the physical property data (molar volume and second virial coefficients) required to support the VLE model are available.

Determination of the composition of the vapor phase by GC-headspace analysis, although presently limited (in our laboratory) to relatively low-pressures, is both cost and time effective and provides an excellent check on the VLE model predictions.

Use of the VLE model is an excellent way to make a critical examination of the quality of the experimental PTx data.

Finally, it must be pointed out that the application of ARC for the determination of VLE data did not originate with us; along with Melham's article already mentioned [3] we know, from our search of the literature, one other [15], which treats the determination of critical properties in a novel application. The present work extends the ARC technique into the sub-ambient pressure regime.

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