



Experimental (vapour + liquid) equilibrium data of (methanol + water), (water + glycerol) and (methanol + glycerol) systems at atmospheric and sub-atmospheric pressures

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ABSTRACT

Experimental (vapour + liquid) equilibrium results for the binary systems, (methanol + water) at the local atmospheric pressure of 95.3 kPa and at sub-atmospheric pressures of (15.19, 29.38, 42.66, 56.03, and 67.38) kPa, (water + glycerol) system at pressures (14.19, 29.38, 41.54, 54.72, 63.84, and 95.3) kPa and the (methanol + glycerol) system at pressures (32.02 and 45.3) kPa were obtained over the entire composition range using a Sweitoslwasky-type ebulliometer. The relationship of the liquid composition (x_1) as a function of temperature (T) was found to be well represented by the Wilson model. Computed vapour phase mole fractions, activity coefficients and the measured values along with optimum Wilson parameters are presented.

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1. Introduction

Bio-diesel is a possible important substitute for fossil fuel in the near future and is a much researched topic in present times. Glycerol is a by product of biodiesel processing and binary and ternary systems containing methanol, water, and glycerol are found in the downstream of bio-diesel manufacturing process [1]. In order to recover methanol from this aqueous glycerol solution, distillation is the preferred separation technique for which (vapour + liquid) equilibrium (VLE) data are required. This investigation of the binary systems formed by methanol, water, and glycerol is a continuation of our previous studies on the phase equilibria of binary systems containing alcohols, hydrocarbons and halogenated organics [2,3]. These binary systems and their ternary systems are found in various industrial streams, namely in the bio-diesel post-production process. {Methanol (1)+ water (2)}, {water (1) + glycerol (2)} and {methanol (1) + glycerol (2)} binary systems are studied at the local atmospheric and sub-atmospheric pressures over the entire composition range. In an extensive survey of the available literature, we did not find any experimental information for these binary systems at the pressures studied in the present work.

2. Experimental

2.1. Materials

The chemicals used in this work were purified according to the methods suggested by Riddick et al. [4]. Analytical grade vacuum-distilled glycerol (Qualigens, India) is used in the experiments. Methanol of analytical grade (SD Fine Chemicals, India) was fractionally distilled to ensure complete removal of water. These distillations were done a few hours before the VLE experimentation. Both methanol and glycerol were stored in dessicators to prevent absorption of moisture. Double distilled water for the purpose of experimentation was prepared in the laboratory itself and checked for any impurities in a Shimadzu GC. The properties of water, methanol and glycerol such as density and refractive index were determined and compared with the available literature values. A Rudolph Research Analytical automatic densitometer (Model DDM 2911) and (Schmidt + Haensch) refractometer (Model DSR χ) were used for the determination of properties of the substances. The accuracy of these instruments has been determined to be $0.1 \text{ kg} \cdot \text{m}^{-3}$ and 0.00001, respectively. The refractive index measurements were done at $T = 293.15 \text{ K}$ employing the sodium D line and the density measurements were also done at this temperature. The experimentally determined and the literature values [4] of density and refractive index are presented in table 1.

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TABLE 1
Comparison of density (ρ) and refractive index (n_D) results with the literature data.

| Chemical | T/K | $\rho/(\text{kg} \cdot \text{m}^{-3})$ | | n_D | |
|----------|--------|--|----------------|--------------|----------------|
| | | Present work | Literature [4] | Present work | Literature [4] |
| Methanol | 293.15 | 791.03 | 791.04 | 1.328 | 1.32840 |
| Water | 293.15 | 998.20 | 998.2058 | 1.333 | 1.332988 |
| Glycerol | 293.15 | 1261.3 | 1261.34 | 1.474 | 1.4746 |

2.2. Method

A Sweitoslawsky-type ebulliometer, very similar to the one described by Hala *et al.* [5], was used. The details of the construction of our ebulliometer are given in an earlier publication [2]. The ebulliometer is connected to a vacuum pump and a nitrogen gas cylinder, along with a closed-end manometer to enable the measurement and maintenance of the total pressure of the system at the desired level. The total pressure is maintained at the desired value by opening or closing the needle valve attached to the gas cylinder or the opening of the bypass line of the vacuum pump. The reading of the manometer and application of the needed corrective action are frequently carried out to maintain the total pressure to within ± 0.05 kPa of the desired value. A long-stemmed mercury-in-glass thermometer calibrated by means of point to point comparison with a platinum resistance thermometer certified by National Institute of Standards and Technology, Gaithersburg (USA), is used for temperature measurement with an accuracy of ± 0.05 K. The thermometer is placed in the thermo-well filled with glycerol to note the steady-state temperature of the (vapour + liquid) mixture impinging on the Cottrell tube. The mixture samples to be studied are prepared gravimetrically by weighing the required amounts of the pure liquids and stirring them well before charging the mixtures into the still. A Mettler balance, capable of recording weights to the accuracy ± 0.0001 g is used.

After the mixture is charged in to the ebulliometer, vacuum is applied gradually and then the heating rate is slowly increased and adjusted to produce the required boil-up rate so that a drop count of about 30 drops per minute is achieved. This is in accordance with the suggestion of Hala *et al.* [5]. The equilibrium temperature is recorded after steady-state conditions, judged by the constancy of the equilibrium temperature and uniformity of the drop rate is maintained at least for 30 min. The VLE experiment is first done at the lowest pressure. After the measurement of the equilibrium temperature at this pressure, vacuum is released and the pressure increased to the next higher value to be studied.

A Gas Chromatograph (GC-17A, Shimadzu) is used to verify the constancy of composition of the binary mixtures both at the beginning and at the end of each experiment for (water + methanol) system. The GC analysis is carried out using a TCD detector fitted with SE-30 column. The analysis of the (glycerol + methanol) and (glycerol + water) systems for the same purpose is carried out according to the American Oil Chemists' Society (AOCS) official method Ea-6-51 [6], by estimating concentration of glycerol by the sodium periodate oxidation method.

3. Results and discussion

The $T-x_1$ results for the {methanol (1) + water (2)} system at pressures (15.19, 29.38, 42.66, 56.03, 67.38, and 95.3) kPa, {water (1) + glycerol (2)} system at pressures (14.19, 29.38, 41.54, 54.72, 63.84, and 95.3) kPa and {methanol (1) + glycerol (2)} system at pressures (32.02 and 45.3) kPa were obtained experimentally and are presented in tables 2 to 4 along with the derived phase equilibrium information. The experimental results were fitted to the Wil-

TABLE 2
Experimental $T-x$ results and derived phase equilibrium information of {methanol (1) + water (2)} binary system at various pressures.

| x_1^a | T/K ^b | γ_1^c | γ_2^d | y_1^e | $G^E/(\text{J} \cdot \text{mol}^{-1})^f$ |
|----------------------|------------------|--------------|--------------|----------|--|
| <i>P</i> = 15.19 kPa | | | | | |
| 0 | 327.4 | 1.606042 | 1 | 0 | 0 |
| 0.1 | 318.05 | 1.483868 | 1.004199 | 0.433386 | 114.3289 |
| 0.2 | 312.4 | 1.378775 | 1.017334 | 0.62119 | 202.5571 |
| 0.3 | 308.55 | 1.288843 | 1.04051 | 0.725289 | 266.587 |
| 0.4 | 305.7 | 1.212544 | 1.075326 | 0.79242 | 306.6749 |
| 0.5 | 303.5 | 1.148704 | 1.124061 | 0.840656 | 322.456 |
| 0.6 | 301.7 | 1.096488 | 1.189948 | 0.87856 | 313.1177 |
| 0.7 | 300.1 | 1.0554 | 1.277601 | 0.910835 | 277.5458 |
| 0.8 | 298.7 | 1.025321 | 1.393705 | 0.940365 | 214.5586 |
| 0.9 | 297.4 | 1.006563 | 1.548131 | 0.969404 | 122.622 |
| 1 | 296.1 | 1 | 1.755839 | 1 | 0 |
| <i>P</i> = 29.38 kPa | | | | | |
| 0 | 341.75 | 2.45739 | 1 | 0 | 0 |
| 0.1 | 329.5 | 1.93843 | 1.012246 | 0.479956 | 125.8029 |
| 0.2 | 324. | 1.611825 | 1.045444 | 0.633507 | 223.344 |
| 0.3 | 320.75 | 1.397867 | 1.095969 | 0.71447 | 294.9369 |
| 0.4 | 318.4 | 1.254011 | 1.161658 | 0.769848 | 340.3327 |
| 0.5 | 316.5 | 1.156114 | 1.241205 | 0.814265 | 358.7403 |
| 0.6 | 314.85 | 1.08975 | 1.333832 | 0.85364 | 349.0856 |
| 0.7 | 313.3 | 1.045907 | 1.439083 | 0.890791 | 310.0188 |
| 0.8 | 311.9 | 1.018743 | 1.55671 | 0.927078 | 240.115 |
| 0.9 | 310.5 | 1.004342 | 1.686593 | 0.963351 | 137.4669 |
| 1 | 309.2 | 1 | 1.82869 | 1 | 0 |
| <i>P</i> = 42.66 kPa | | | | | |
| 0 | 350.6 | 1.706597 | 1 | 0 | 0 |
| 0.1 | 340.4 | 1.56327 | 1.004659 | 0.41357 | 138.2823 |
| 0.2 | 334.3 | 1.440576 | 1.019296 | 0.598483 | 245.4145 |
| 0.3 | 330.15 | 1.335973 | 1.045287 | 0.702982 | 323.6261 |
| 0.4 | 327.1 | 1.247446 | 1.084672 | 0.77136 | 373.1334 |
| 0.5 | 324.8 | 1.17345 | 1.140428 | 0.821163 | 393.3805 |
| 0.6 | 322.9 | 1.112883 | 1.216898 | 0.861004 | 383.0767 |
| 0.7 | 321.3 | 1.065096 | 1.320502 | 0.89567 | 340.7202 |
| 0.8 | 319.85 | 1.029928 | 1.460918 | 0.928488 | 264.3395 |
| 0.9 | 318.5 | 1.007819 | 1.65315 | 0.962243 | 151.6725 |
| 1 | 317.15 | 1 | 1.921295 | 1 | 0 |
| <i>P</i> = 56.03 kPa | | | | | |
| 0 | 357.35 | 1.671714 | 1 | 0 | 0 |
| 0.1 | 347.25 | 1.535669 | 1.004507 | 0.400566 | 135.3171 |
| 0.2 | 341.05 | 1.419041 | 1.018645 | 0.585914 | 240.0016 |
| 0.3 | 336.8 | 1.319504 | 1.04369 | 0.692578 | 316.2321 |
| 0.4 | 333.7 | 1.235209 | 1.081525 | 0.763113 | 364.3152 |
| 0.5 | 331.3 | 1.16474 | 1.134872 | 0.814907 | 383.6663 |
| 0.6 | 329.3 | 1.107087 | 1.207663 | 0.856497 | 373.1637 |
| 0.7 | 327.6 | 1.06165 | 1.305642 | 0.892694 | 331.4559 |
| 0.8 | 326.1 | 1.028281 | 1.437342 | 0.926805 | 256.8076 |
| 0.9 | 324.7 | 1.007367 | 1.615767 | 0.961601 | 147.1294 |
| 1 | 323.35 | 1 | 1.861367 | 1 | 0 |
| <i>P</i> = 67.38 kPa | | | | | |
| 0 | 362.1 | 1.782389 | 1 | 0 | 0 |
| 0.1 | 351.35 | 1.623431 | 1.004965 | 0.408929 | 90.78876 |
| 0.2 | 344.9 | 1.487694 | 1.020617 | 0.591988 | 164.0267 |
| 0.3 | 340.65 | 1.372172 | 1.048554 | 0.695447 | 220.3343 |
| 0.4 | 337.55 | 1.274486 | 1.091179 | 0.763268 | 258.8257 |
| 0.5 | 335.2 | 1.192816 | 1.152064 | 0.812859 | 278.0438 |
| 0.6 | 333.3 | 1.125869 | 1.236535 | 0.85276 | 275.9942 |
| 0.7 | 331.7 | 1.072884 | 1.352672 | 0.887901 | 250.2951 |
| 0.8 | 330.25 | 1.033692 | 1.513059 | 0.921845 | 198.0729 |
| 0.9 | 328.9 | 1.008866 | 1.737989 | 0.957859 | 115.9826 |
| 1 | 327.65 | 1 | 2.061682 | 1 | 0 |
| <i>P</i> = 95.3 kPa | | | | | |
| 0 | 371.45 | 1.649278 | 1 | 0 | 0 |
| 0.1 | 361.2 | 1.517319 | 1.004426 | 0.381845 | 137.1455 |
| 0.2 | 354.85 | 1.40428 | 1.018278 | 0.566476 | 243.085 |
| 0.3 | 350.4 | 1.307894 | 1.042748 | 0.6755 | 319.951 |
| 0.4 | 347.1 | 1.22636 | 1.079585 | 0.748836 | 368.1293 |
| 0.5 | 344.55 | 1.158295 | 1.131307 | 0.803301 | 387.1822 |
| 0.6 | 342.45 | 1.102709 | 1.201525 | 0.847367 | 376.1008 |
| 0.7 | 340.65 | 1.059 | 1.295456 | 0.885926 | 333.5914 |
| 0.8 | 339.05 | 1.026994 | 1.420761 | 0.922327 | 258.0599 |
| 0.9 | 337.55 | 1.007009 | 1.588931 | 0.959379 | 147.595 |
| 1 | 336.1 | 1 | 1.817709 | 1 | 0 |

^a Mole fractions of component 1 in the liquid phase.

^b Temperature.

^c Activity coefficients of component 1.

^d Activity coefficients of component 2.

^e Mole fractions of component 1 in the vapour phase.

^f Excess Gibbs free energy.

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