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Experimental and Predicted (Vapor + Liquid) Equilibrium Data of Ternary Mixtures of Methanol, Water, and Propan-1,2,3-triol at 96 kPa

J. Soujanya,[†] B. Satyavathi,[*,†] and T. Sankarshana[‡]

[†]Chemical Engineering Division, Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500007, Andhra Pradesh, India

[‡]College of Technology, Osmania University, Hyderabad 500007, Andhra Pradesh, India

ABSTRACT: Experimental vapor−liquid equilibrium (VLE) measurements of the methanol (1) + water (2) + propan-1,2,3-triol (3) ternary system were carried out at various compositions at the local atmospheric pressure. The experiments were carried out using a modified Sweitoslawsky ebulliometer. The experimental temperatures were compared with the predictions made using Wilson and nonrandom two-liquid (NRTL) models. These predictions were made using only binary parameters. The Wilson model represented this ternary system better than the NRTL model. Experimental temperatures were found to be in good agreement with the predicted values.

INTRODUCTION

The biodiesel industry produces effluent streams containing large quantities of methanol, water, and propan-1,2,3-triol.[1] These are also found in propan-1,2,3-triol processing industries.[2] The experimental vapor−liquid equilibrium (VLE) data of the constituent binaries have been reported in our previous work,[3] at various subatmospheric pressures and at the local atmospheric pressure of 95.3 kPa using the Wilson equation. In the present work, the methanol (1) + water (2) + propan-1,2,3-triol (3) ternary system's VLE behavior has been studied experimentally at the local atmospheric pressure of 96 kPa. The bubble-point temperature predictions of the ternary mixtures at the experimentally studied compositions were predicted using the binary systems' parameters obtained from experimental data using nonrandom two-liquid (NRTL) and Wilson models. Corresponding Wilson parameters were taken from ref 3, while the NRTL binary parameters are from the present paper. Density measurements were made at 293.15 K and are reported here.

EXPERIMENTAL SECTION

Materials. The methanol (≥ 0.995 mass fraction, gas chromatograph) and propan-1,2,3-triol (0.995 mass fraction, AOCS official method Ea. 6-51[4]) provided by SD Fine Chemicals, India and double-distilled water (100 % pure, gas chromatograph) were used for experimentation. The densities and refractive indices of the pure components were also measured using a Rudolph Research analytical automatic densitometer (model DDM2911) and (Schmidt and Haensch) refractometer (model DSR λ) and are reported in Table 1 along with literature values.[5] The uncertainties of these instruments are determined to be 0.1 kg·m^{-3} and 0.00001, respectively. Propan-1,2,3-triol and methanol were stored in desiccators prior to the experiments to prevent the absorption of moisture.

Apparatus. A Sweitoslawsky-type ebulliometer, similar to the one described by Hala et al.,[6] was used for VLE measurements. The details of the construction of the ebulliometer used in the present study are as described by Vittal Prasad et al.[7] The ebulliometer is connected to a vacuum pump and nitrogen gas cylinder, along with a closed end manometer in line to maintain the pressure to within ± 0.05 kPa of the desired value of 96 kPa. This is done by adjusting the opening of the needle valve of the gas cylinder or by opening the bypass line of the vacuum pump. A K-type thermocouple with a digital indicator calibrated by a point-to-point comparison with a platinum resistance thermometer (certified by the National Institute of Standards and

Table 1. Comparison of Density, ρ, and Refractive Index, n_D, Data with Literature Data

		ρ/kg·m^{-3}		n_D	
chemical	T/K	exp.	lit.[4]	exp.	lit.[4]
methanol	293.15	791.03	791.04	1.328	1.32840
water	293.15	998.20	998.2058	1.333	1.332988
propan-1,2,3-triol	293.15	1261.3	1261.34	1.474	1.4746

Table 2. Experimental VLE Data and Densities, ρ, at 293.15 K of Methanol (1) + Water (2) + Propan-1,2,3-triol (3) Ternary Mixtures at 96 kPa

sample no.	x_1[a]	x_2[a]	T/K	ρ/kg·m^{-3}
1	0.705	0.245	341.65	0.8502
2	0.6	0.35	342.90	0.9175
3	0.57	0.08	345.82	1.0793
4	0.385	0.605	347.76	0.9397
5	0.284	0.67	350.62	0.9525
6	0.2	0.38	363.49	1.1699
7	0.08	0.82	364.10	1.0852
8	0.04	0.9	367.50	1.0618

[a] Liquid-phase mole fractions of components 1 and 2.

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Table 3. Representation and Comparison of Ternary VLE Data Using Wilson and NRTL Models

model	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	α_{12}	α_{13}	α_{23}	$\sigma(T)^c$
Wilson[a]	0.8941	0.6116	0.9182	0.6829	1.2875	1.9025	-	-	-	0.779285
NRTL[b]	0.6326	0.024	0.7252	−0.0494	−0.5989	−0.3401	0.4	0.3	0.4	1.834277

[a] $A_{ij} = \Lambda^{ij}$. [b] $A_{ij} = \tau^{ij}$. [c] $\sigma(T) = [\Sigma(T_{exp} - T_{cal})/n]^{0.5}$, where n is the number of data points.

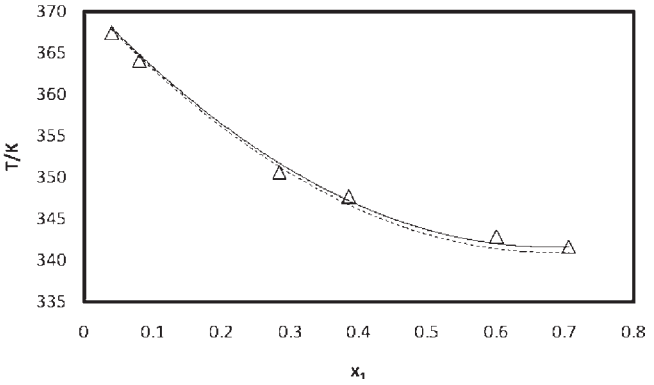

Figure 1. Comparison of experimental and predicted temperatures T/K at different mole fractions of methanol x_1. △, experimental temperature values; —, temperature predictions using the Wilson model; ---, temperature predictions using the NRTL model.

Technology, Gaithersberg, USA) is used for measuring the equilibrium temperatures with an uncertainty of ± 0.05 K. The thermometer is placed in the thermowell containing propan-1,2,3-triol to note the equilibrium temperature for the (vapor + liquid) mixture impinging on the thermowell from the Cottrell tube. The equilibrium temperature is recorded after steady-state conditions, judged by the constancy of temperature and uniformity of the drop rate maintained for at least 1800 s.

The mixtures to be studied are prepared gravimetrically by weighing the required amounts of the pure liquids and stirring them well to make homogeneous mixtures before charging the mixtures into the still. A Mettler balance, capable of recording weights to the uncertainty of ± 0.0001 g, is used. The experimentation revealed that the mixtures with propan-1,2,3-triol mole fraction >0.7 solidified upon heating. This is consistent with the report of Yong et al.,[8] who prefer vacuum distillation at 393.15 K to 399.15 K for the recovery of propan-1,2,3-triol from propan-1,2,3-triol residue to avoid polymerization, dehydration, and oxidation of propan-1,2,3-triol at higher temperatures. On the other hand, when mixtures contained a very high concentration of methanol or trace amounts of propan-1,2,3-triol, the mixtures flashed. The measured $T-x$ data are reported in Table 2 along with the densities of the mixtures.

RESULTS AND DISCUSSION

Ternary temperature predictions at 96 kPa using binary parameters were done and compared with experimental data. For the prediction of ternary VLE data, experimentally obtained binary parameters of the Wilson and NRTL models were used. Binary experimental data from ref 3 is available for the systems containing water at 95.3 kPa, while for the methanol (1) + propan-1,2,3-triol (3) system data are available only at subatmospheric pressures, and hence, parameters representing this binary system at 45.3 kPa have been used for VLE calculations of the ternary system at 96 kPa. Temperature predictions using subatmospheric binary parameters for the methanol (1) + propan-1,2,3-triol (3) system have been found to be more accurate than the predictions obtained using temperature-dependent parameters from ASPEN-LIT and ASPEN-IG at 333.15 K, 353.15 K, 373.15 K, and 563.15 K.

The multicomponent Wilson and NRTL model equations are as given in Reid et al.[9] The binary parameters of both models used in ternary calculations are listed in Table 3 along with the root-mean-square deviation (rmsd) values of temperature. The Wilson model parameters are from our previous work,[3] while the NRTL model parameters have been calculated for the same set of data. Briefly, the nonlinear methods, Powell's Dog−Leg (DL) method and Levenberg−Marquardt (LM) method as described by Madsen et al.,[10] were used for regressing the binary experimental data. In most of the cases, the DL method gave better results than the LM method. The parameters obtained by regression with the DL method are only presented. The comparison of experimental temperature values with the predictions of Wilson and NRTL models is shown in Figure 1. The rmsd of calculated temperatures from measured values indicates that the predictions of Wilson model are better suited for these aqueous alcohol systems than the NRTL model. The rmsd is expressed as $\sigma(T)$ in Table 3.

CONCLUSIONS

In this study, VLE data of the methanol (1) + water (2) + propan-1,2,3-triol (3) ternary system were experimentally determined using a modified Sweitoslawsky ebulliometer. The experimental values obtained were compared with the predictions made using the binary parameters of the Wilson and NRTL models. The Wilson activity coefficient model is better than the NRTL model in representing the behavior of the ternary system. These data will be very useful in the design of separation equipment for effluent streams.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +91-9666226355. E-mail address: drsatyavathib@gmail.com.

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