LIQUID–LIQUID EQUILIBRIUM IN THE SYSTEM GLYCEROL–WATER–ACETONE AT 25°C

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ABSTRACT

Krishna, R., Low, C.Y., Newsham, D.M.T., Olivera-Fuentes, C.G. and Paybarah, A., 1989. Liquid–liquid equilibrium in the system glycerol–water–acetone at 25°C. *Fluid Phase Equilibria*, 45: 115–120.

Liquid–liquid equilibrium for the glycerol–water–acetone system has been determined at 25°C and the data were correlated using UNIQUAC and NRTL models with good accuracy. The plait point of the system was determined from thermodynamic stability considerations; the value obtained agrees reasonably well with that obtained from the conventional Hand plot.

INTRODUCTION

In a recent study Krishna et al. (1985) reported interphase mass transfer measurements in the glycerol(1)–water(2)–acetone(3) system in a Lewis stirred cell and showed that multicomponent diffusional interaction effects are significant for this system. As support for the above mass transfer study, accurate measurements of liquid–liquid equilibrium data were required, especially in the region of the plait point; these data are reported in the present communication.

EXPERIMENTAL DETAILS

The three components were each weighed in a stoppered separating funnel (capacity 100 ml) in the sequence glycerol, water and acetone in order

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to minimize evaporation losses because of increasing volatility. After weighing one sample,' the separating funnel containing the mixture was closed at once with the stopper and sealed quickly with Teflon tape, so that the loss of sample by evaporation, especially of acetone, would be minimized. The sealed separating funnel was shaken vigorously for about 15 min and then allowed to settle for 2 h with intermittent shaking in a constant-temperature thermostat bath which was maintained at $25 \pm 0.01°C$. After this period, the separating flask was returned to its stand in order to allow the mixture to settle for a period of two days in a room maintained at a constant temperature of $25°C$. When two sharply defined layers were formed, the lower aqueous layer was run off and separated as completely as possible. Aliquots of each liquid layer were then withdrawn for analysis using a pipette.

Analysis of the phase compositions was carried out by measurement of the refractive index and density. The refractive indices were measured using a Zeiss dipping refractometer with a set of thermostated prisms. Densities of acetone-rich samples were measured by means of Lipkin U-tube pycnometers and that of glycerol-rich samples were measured using capped bottle-type pycnometers. Further details of the experimental procedure are available elsewhere (Low, 1979). The standard deviation in the refractive index determinations was found to be 0.000019 and the average standard deviation for the density determinations was found to be 0.14 kg m^{-3}.

In order to determine the compositions of the phases from measurements of refractive index and density, standard mixtures of known compositions were prepared and the compositions x_1 and x_2 fitted as functions of the density and refractive index by a fifth-order polynomial (Low, 1979); the resultant standard deviations of the composition determinations, as found from analyses of mixtures of known compositions, were

$$\sigma_{x_1} = 0.0015; \qquad \sigma_{x_2} = 0.0041; \qquad \sigma_{x_3} = 0.0044$$

RESULTS AND DATA CORRELATION

The experimental tie-line data are presented in Table 1. The UNIQUAC and NRTL parameters were determined from the tie-line data using the procedure and program given by Sørensen (1980); these parameters are given in Table 2. The root mean square deviation (RMSD) for the fits were found to be 0.01013 and 0.010138 for the UNIQUAC and NRTL models respectively.

A further important aspect of the present study was the determination of the plait point of the system. This information was required for interpretation of the mass transfer measurements in the region of the plait point; in

TABLE 1

Experimental tie-line compositions at 25 °C for the system glycerol(1)–water(2)–acetone(3)

Acetone-rich phase		Glycerol-rich phase	
x_1	x_2	x_1	x_2
0.0373	0.0000	0.8379	0.0000
0.0384	0.0099	0.7748	0.0597
0.0378	0.0206	0.7228	0.1186
0.0391	0.0301	0.6780	0.1600
0.0397	0.0435	0.6196	0.2196
0.0404	0.0788	0.4924	0.3387
0.0438	0.0638	0.5490	0.2818
0.0455	0.0940	0.4762	0.3492
0.0468	0.1208	0.4096	0.4038
0.0472	0.1102	0.4234	0.3902
0.0490	0.1308	0.3895	0.4196
0.0496	0.1481	0.3602	0.4421
0.0532	0.1645	0.3415	0.4562
0.0582	0.1889	0.3145	0.4768
0.0601	0.2057	0.2904	0.4865
0.0602	0.2212	0.2751	0.4968
0.0680	0.2415	0.2570	0.4970
0.0750	0.2655	0.2370	0.4970
0.0840	0.2990	0.2212	0.4953
0.0897	0.3208	0.2076	0.4913
0.0972	0.3340	0.1962	0.4867
0.1115	0.3651	0.1800	0.4709
0.1136	0.3680	0.1772	0.4676
0.1183	0.3866	0.1693	0.4608
0.1260	0.3918	0.1650	0.4530

our earlier paper we showed that the understanding of the mass transfer behaviour rested heavily on arguments based on irreversible thermodynamics and phase stability (Krishna et al., 1985). From thermodynamic stability arguments, it follows that the determinant of the Hessian matrix [G] vanishes (Modell and Reid, 1983), i.e.

$$|G| = 0 \tag{1}$$

where the elements of the matrix [G] are

$$G_{ij} = \partial^2 G / \partial x_i \, \partial x_j = G_{ji} \tag{2}$$

The matrix [G] can be determined from the UNIQUAC or NRTL model parameters determined above. A search algorithm allows the determination of the compositions that satisfy eqn. (1). The compositions that satisfy eqn. (1) define the spinodal curve. Figure 1 shows a plot of both the binodal and

TABLE 2

UNIQUAC and NRTL parameter representation of the liquid–liquid equilibrium data

UNIQUAC parameters
Glycerol(1): $r = 3.5857$; $q = 3.060$
Water(2): $r = 0.9200$; $q = 1.400$
Acetone(3): $r = 2.5735$; $q = 2.336$
Binary interaction parameters

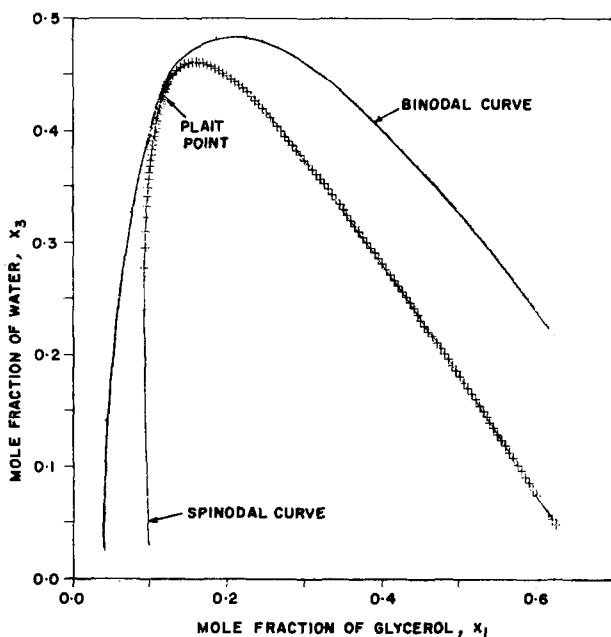| $i-j$	a_{ij}	a_{ji}	
1–2	30.029	−403.230	
1–3	162.610	191.620	
2–3	146.200	−23.520	
RMSD = 0.01013			
NRTL parameters			
	a_{ij}	a_{ji}	α_{ij} [1]
1–2	−385.510	−453.180	0.200
1–3	258.790	735.360	0.200
2–3	624.750	−198.330	0.200
RMSD = 0.010138			

[1] Value fixed by Sørensen's program at 0.2.

Fig. 1. Binodal and spinodal curves for the system glycerol(1)–acetone(2)–water(3) calculated with the NRTL parameters as given in Table 2.
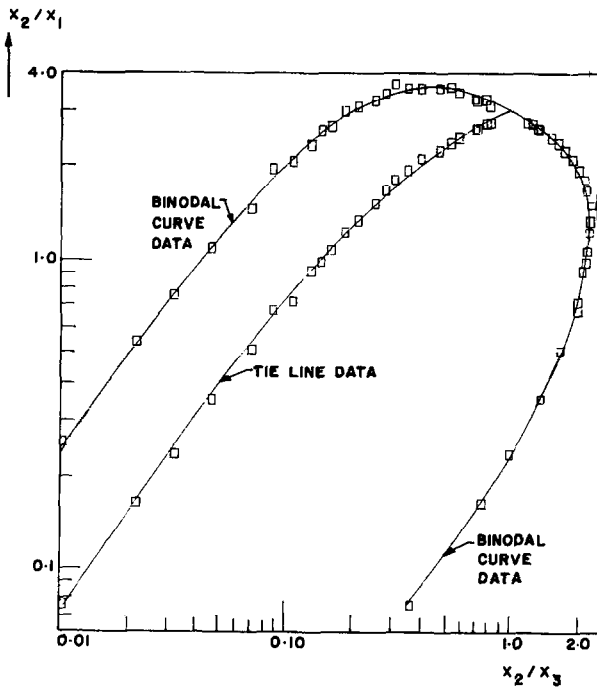
Fig. 2. Hand plot for determination of the plait point. The tie-line data are those given in Table 1.

spinodal curves using the NRTL parameter set; the spinodal curve intersects the binodal curve tangentially at only one point, the plait point, and the composition at this intersection was determined to be

$$x_1 = 0.1245; \qquad x_2 = 0.4440; \qquad x_3 = 0.4315$$

The corresponding results obtained with the UNIQUAC model were indistinguishable from the values given above.

The more conventional Hand plot for the determination of the plait point directly from the tie-line data is shown in Fig. 2. The plait point determined from this method is

$$x_2/x_3 = 1.047; \qquad x_2/x_1 = 2.95$$

or

$$x_1 = 0.1477; \qquad x_2 = 0.4360; \qquad x_3 = 0.4163$$

which is in reasonable agreement with that determined from thermodynamic considerations.

CONCLUSIONS

The liquid–liquid equilibrium tie-line data for the glycerol–water–acetone system could be correlated with good and comparable accuracy by both the NRTL and UNIQUAC models. The plait point for this system was determined from thermodynamic stability arguments and the value agreed reasonably well with that obtained using the conventional Hand plot.

LIST OF SYMBOLS

a_{ij} interaction energies in UNIQUAC and NRTL models (K)
G molar Gibbs free energy (J mol^{-1})
G_{ij} second partial derivative of G with respect to composition (J mol^{-1})
[G]   two dimensional Hessian matrix with elements G_{ij} (J mol^{-1})
$|G|$ determinant of the Hessian matrix [G]
x_1 mole fraction of glycerol
x_2 mole fraction of water
x_3 mole fraction of acetone

Greek letters

α_{ij} non-randomness parameter in the NRTL model

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