898 *J. Chem. Eng. Data* **2000,** *45,* 898−901

Liquid−Liquid Equilibria of the System Water + 2-Propanol + 2,2,4-Trimethylpentane at 25 °C

J. J. Otero, J. F. Comesaña, J. M. Correa,* and A. Correa

Department of Chemical Engineering, University of Vigo, 36200 Vigo, Spain

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Liquid−liquid equilibria of the system water + 2-propanol + 2,2,4-trimethylpentane at 25 °C were obtained to evaluate 2,2,4-trimethylpentane as an extraction agent in aqueous solutions of 2-propanol. The experimental data were fitted using the NRTL and UNIQUAC equations. Equilibria predictions, applying the UNIFAC method, were also made with the use of liquid−liquid equilibria specific parameters.

Introduction

To design the extraction equipment for the separation of a homogeneous liquid mixture of two components, using a third component, it is necessary to know the liquid−liquid equilibria data of the ternary system formed by these components. These data are also useful for mixtures of three liquid components and when the immiscibility region is to be avoided.

In this work the system water + 2-propanol + 2,2,4-trimethylpentane at 25 °C has been studied. A prior analysis of the viability of different solvents as extraction agents of 2-propanol from its aqueous solutions,[1] and even of the actual 2,2,4-trimethylpentane at 20 °C,[2] was performed. This system is of interest, since 2-propanol is an alkanol that can be added to fuels, however having the disadvantage that it is hygroscopic even when dissolved in gasoline.[3−8]

Experimental Section

2,2,4-Trimethylpentane and 2-propanol were from Panreac. They were not purified further. The purities specified by the manufacturer were as follows: 2,2,4-trimethylpentane, 99.5%; 2-propanol, 99.8%. Distilled water was obtained from the MILLI-Q 185 PLUS system, with a resistivity of 18.2 MΩ·cm.

The Solubility curve was determined by the cloud point method,[9] using a thermostated cell, with two top orifices and one lateral, equipped with a magnetic stirrer. The temperature inside the cell was measured with a PT-100 probe that was introduced through the lateral orifice of the cell, connected to a Yokogawa 7563 thermometer (precision ± 0.01 °C). This temperature was considered stable when no changes greater than ±0.05 °C were observed during the determination of each curve section.

Tie lines were determined by introducing into the same cell approximately 40 mL of a mixture of the three components at the immiscibility region. This mixture was mixed vigorously for 0.5 h. After the mixing was completed, two needles were introduced, one through the lateral orifice and another through one of the two top orifices, while the PT-100 probe was introduced through the other. After a rest period of 3 h, samples were withdrawn from both phases. The syringes used were preheated to avoid phase separation during sample withdrawal. The densities of both phases at equilibrium were measured to later determine their compositions.

The analytical technique followed to determine the composition of the phases at equilibrium consists of preparing binary mixtures by weight, using a Mettler AT261 balance with a precision of $\pm 10^{-4}$ g. These mixtures are miscible with those to which the third component is added, until reaching compositions corresponding to the binodal curve. The maximum error in the calculation of the compositions of the binodal curve is estimated to be $\pm 10^{-4}$. Next, the densities of these ternary mixtures are measured using an Anton Paar DMA 60/602 densimeter with a nominal precision of 10^{-5} g·cm^{-3}. The temperature of the densimeter is controlled with a stability of ±0.01 °C. Each measurement was taken on three occasions, with a precision of $\pm 10^{-5}$. Figure 1 shows density as a function of the compositions of water, 2-propanol, and 2,2,4-trimethylpentane for these ternary mixtures. From the experimental data two density−composition calibration curves were constructed for water and 2,2,4-trimethylpentane (Figure 1).

Once the calibration curves are constructed, this technique allows us to determine the compositions of the mixtures, corresponding to end tie lines, whose densities were measured previously, with an estimated precision of ±0.002 in mass fraction.

Results and Discussion

The compositions defining the binodal curve of the ternary mixture water + 2-propanol + 2,2,4-TMP at 25 °C are listed in Table 1, while compositions corresponding to end tie lines are shown in Table 2. Note that both solubilities obtained are similar to those reported in the literature.[10]

Experimental data were fitted using the NRTL equation 11 and the UNIQUAC equation 12. A computer program[13] was used, where the parameter α_{ij} of the NRTL equation was successively assigned the values 0.1, 0.2, and 0.3. The other parameters were determined for both equations, by minimizing the objective function

$$F_x = \sum^{k} \min \sum^{i} \sum^{j} (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum^{n} P_n{}^2 + \left[\ln\left(\frac{\hat{\gamma}^{\mathrm{I}}_{\mathrm{S}\infty}}{\hat{\gamma}^{\mathrm{II}}_{\mathrm{S}\infty}} \beta_\infty \right) \right]^2 \qquad (1)$$

where x is the experimental mole fraction, $\hat{x}$ is the mole

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* To whom correspondence should be addressed. E-mail: jcorrea@uvigo.es.

10.1021/je000055g CCC: $19.00

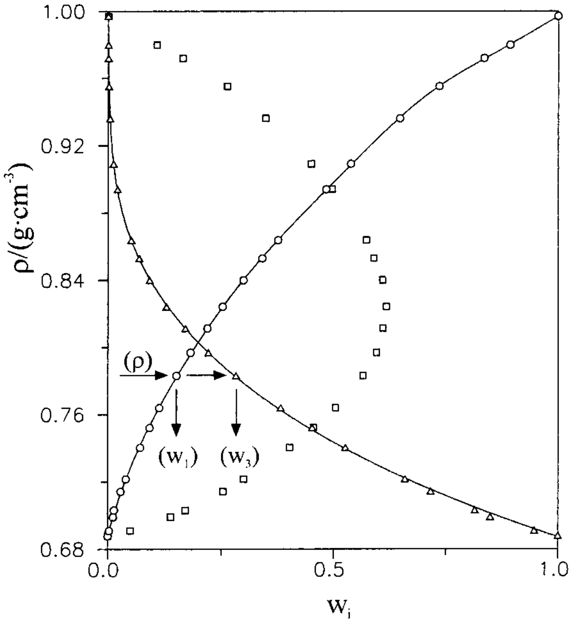

Figure 1. Densities for the system water + 2-propanol + 2,2,4-trimethylpentane: ○, water; □, 2-propanol; △, 2,2,4-trimethylpentane. The solid lines represent calibration curves.

Table 1. Compositions that Determine the Binodal Curve, Expressed as Mass Fraction (w_i), for the System Water (1) + 2-Propanol (2) + 2,2,4-Trimethylpentane (3), at 25 °C

w_1	w_2	w_3	ρ/(g·cm^{-3})
0.0001	0.0000	0.9999	0.687 78
0.0029	0.0500	0.9471	0.690 84
0.0118	0.1388	0.8494	0.699 00
0.0140	0.1708	0.8152	0.702 97
0.0286	0.2545	0.7169	0.714 21
0.0401	0.3001	0.6598	0.721 55
0.0715	0.4020	0.5265	0.740 30
0.0923	0.4552	0.4525	0.752 09
0.1135	0.5041	0.3824	0.763 92
0.1512	0.5654	0.2834	0.783 09
0.1826	0.5954	0.2220	0.796 86
0.2194	0.6095	0.1711	0.811 28
0.2534	0.6171	0.1295	0.824 22
0.2995	0.6089	0.0916	0.840 04
0.3412	0.5897	0.0691	0.853 03
0.3759	0.5727	0.0514	0.863 87
0.4828	0.4963	0.0209	0.894 08
0.5385	0.4495	0.0120	0.909 12
0.6475	0.3482	0.0043	0.936 16
0.7353	0.2632	0.0015	0.955 19
0.8348	0.1646	0.0006	0.972 05
0.8927	0.1067	0.0006	0.979 95
1.0000	0.0000	0.0000	0.997 05

Table 2. Compositions that Determine Ends of Tie Lines, Expressed as Mass Fraction (w_i), for the System Water (1) + 2-Propanol (2) + 2,2,4-Trimethylpentane (3), at 25 °C

aqueous phase				organic phase			
w_1	w_2	w_3	ρ/(g·cm^{-3})	w_1	w_2	w_3	ρ/(g·cm^{-3})
0.907	0.093	0.000	0.982 49	0.000	0.011	0.989	0.688 10
0.762	0.237	0.001	0.960 03	0.001	0.024	0.975	0.689 32
0.685	0.312	0.003	0.945 27	0.004	0.050	0.946	0.691 99
0.602	0.392	0.007	0.925 31	0.006	0.066	0.928	0.693 61
0.537	0.450	0.013	0.908 39	0.007	0.080	0.913	0.695 06
0.425	0.541	0.034	0.877 87	0.011	0.107	0.882	0.697 94
0.284	0.611	0.105	0.835 12	0.019	0.172	0.809	0.705 25

Table 3. Residual F and $\Delta\beta$ of the NRTL and UNIQUAC Equations (25 °C) for the System Water (1) + 2-Propanol (2) + 2,2,4-Trimethylpentane (3)

model	β_∞	F (%)	$\Delta\beta$ (%)
NRTL (α_{ij} = 0.3)	0.65	0.5871	11.9
UNIQUAC	0.66	0.5198	12.0

Table 4. Optimized System Specific Parameters (25 °C) of the UNIQUAC and NRTL Equations for the System Water (1) + 2-Propanol (2) + 2,2,4-Trimethylpentane (3)[a]

equation	β_∞	$i-j$	b_{ij}/K	b_{ji}/K
UNIQUAC	0.66	1−2	135.07	−132.74
		1−3	162.73	1311.0
		2−3	92.717	8.1065
equation	β_∞	$i-j$	a_{ij}/K	a_{ji}/K
NRTL (α = 0.3)	0.65	1−2	222.13	−48.334
		1−3	1708.6	1146.6
		2−3	623.65	−0.65286

[a] $b_{ij} = (u_{ij} - u_{jj})/R$; $a_{ij} = (g_{ij} - g_{jj})/R$.

fraction of the calculated tie line closest to the experimental tie line considered, i are the components of the mixture, j are the phases, and k are the tie lines. This function includes a penalization term to reduce the risks of multiple solutions associated with parameters of high value, in which Q is a constant and P_n are the (NRTL or UNIQUAC) parameters. It also includes a term to attempt to correctly reproduce experimental results when working with low solute concentrations, in which $\hat{\gamma}^{\mathrm{I}}_{\mathrm{S}\infty}$ and $\gamma^{\mathrm{II}}_{\mathrm{S}\infty}$ represent the solute activity coefficients calculated at infinite dilution in both phases and β_∞ is the solute molar distribution ratio at infinite dilution. The procedure necessary for using the program and for obtaining the optimum β_∞ value has been described in previous works.[14,15]

In Table 3 the values of residual F (eq 2) and the mean error of the solute distribution ratio $\Delta\beta$ (eq 3) obtained using optimum values of the solute distribution ratio at infinite dilution, β_∞, for both equations are given

$$F = 100\sqrt{\frac{\sum^{k}\min\sum^{i}\sum^{j}(x_{ijk} - \hat{x}_{ijk})^2}{6M}} \tag{2}$$

$$\Delta\beta = 100\sqrt{\frac{\sum^{k}\left[\frac{\hat{\beta}_k - \beta_k}{\beta_k}\right]^2}{M}} \tag{3}$$

where β and $\hat{\beta}$ are the experimental and calculated solute mole distribution ratios, respectively. The latter two parameters represent the coefficient between the solute mole fractions in the organic phase and in the aqueous phase.

The parameters for the two equations using the optimal values of β_∞ are listed in Table 4, where g_{ij}, g_{ji}, u_{ij}, and u_{ji} are the interaction parameters between molecules $i-j$ and $j-i$ for the NRTL and UNIQUAC equations, respectively. In Figures 2 and 3 the tie lines calculated using these parameters are compared with experimental values.

The NRTL equation fits the experimental data of the equilibria with good precision, although a clear deviation is observed at the top of the binodal curve. The UNIQUAC equation also gives a good fit of the experimental data and gives a calculated binodal curve that is closer to the experimental one.

Equilibrium compositions were calculated using a computer program,[16] that utilizes predicted activity coefficients

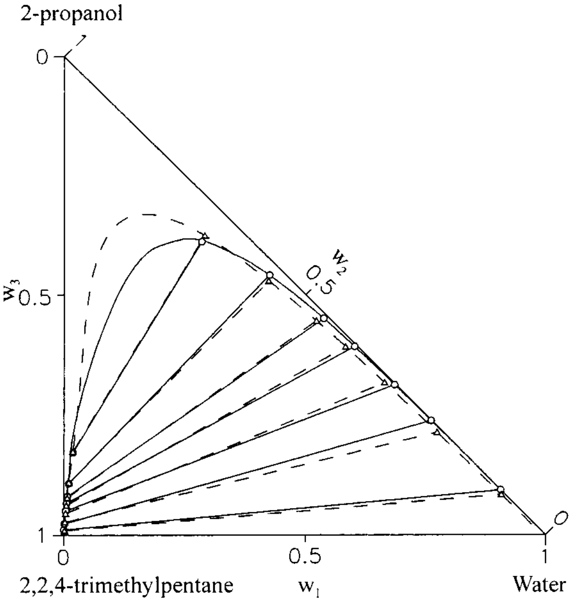

Figure 2. Binodal curve and tie lines: experimental (solid line) and calculated using the NRTL equation (dashed line).

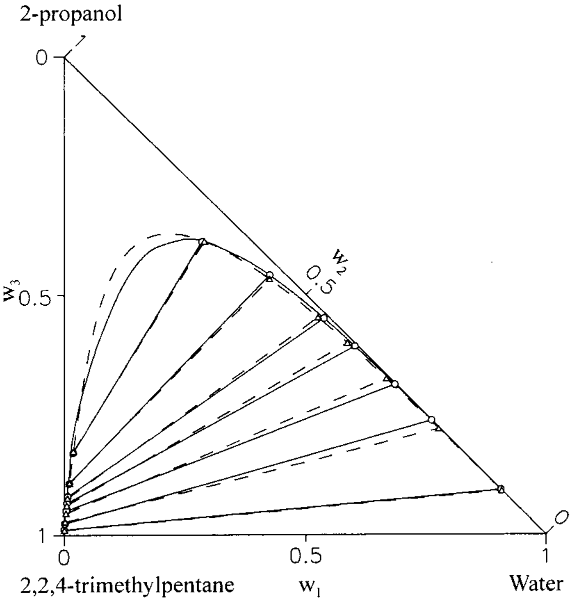

Figure 3. Binodal curve and tie lines: experimental (solid line) and calculated using the UNIQUAC equation (dashed line).

applying the UNIFAC method,[17] and parameters of group interactions specific for liquid−liquid equilibria.[18] Calculated tie lines are compared with experimental ones in Figure 4.

The inaccuracy of the predictions was evaluated using the mean quadratic deviation, F_p,

$$F_p = 100\sqrt{\frac{\sum^{i}\sum^{j}\sum^{k}(w_{ijk} - \hat{w}_{ijk})^2}{6M}} \tag{4}$$

where the subscripts *i*, *j*, and *k* are the components, the phases, and the tie lines, respectively, while *w* is the experimental mass fraction, $\hat{w}$ is the calculated mass fraction, and *M* is the number of tie lines. For the system studied in this work, the value of F_p was 0.90%.

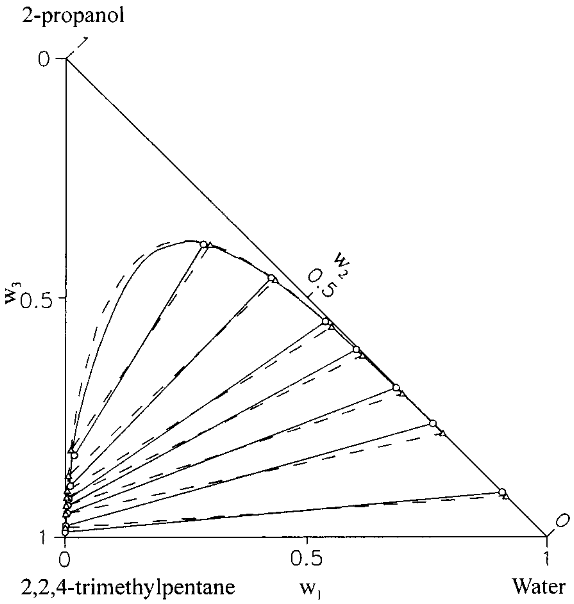

Figure 4. Binodal curve and tie lines: experimental (solid line) and calculated using the UNIFAC method (dashed line).

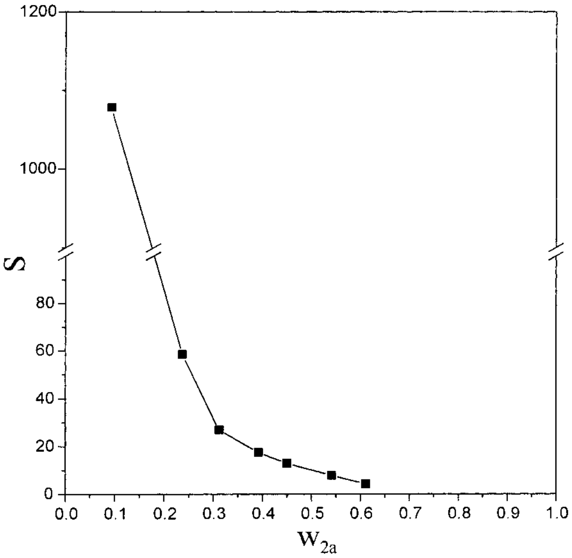

Figure 5. Separation factors, *S*, as a function of weight fraction w_{2a} of 2-propanol in the aqueous phase.

The method provides acceptable results when predicting binodal curves but shows deviations in the prediction of tie lines.

To estimate the viability of 2,2,4-trimethylpentane as an extraction agent of 2-propanol in water, distribution coefficients and separation factors[1] have been considered in the composition interval of 10 mass % to 60 mass % 2-propanol in water.

In the first part of this interval (10 mass % to 25 mass %), the distribution coefficient of 2-propanol is approximately 0.1 and the separation factor is above 50; in the second (25 mass % to 45 mass %), the distribution coefficient is between 0.1 and 0.2 and the separation factor is between 10 and 50; and in the last part (45 mass % to 60 mass %), the distribution coefficient is between 0.2 and 0.3 and the separation factor is below 10. In accordance with the criteria applied by Sayar,[1] this suggests that 2,2,4-trimethylpentane could be employed as an extraction agent of 2-propanol from dilute aqueous solutions. Furthermore, this is also observed in Figure 5, where the separation factor is presented versus mass fraction of 2-propanol in the aqueous phase.

Received for review February 14, 2000. Accepted June 12, 2000.

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