Liquid−Liquid Equilibria of the System Water + Acetic Acid + 2-Hexanone at 25 °C and 35 °C

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Liquid−liquid equilibria of the system water + acetic acid + 2-hexanone at 25 °C and 35 °C were studied to evaluate 2-hexanone as an extraction agent in aqueous solutions of acetic acid. The experimental data were fitted using the NRTL and UNIQUAC equations. Equilibrium predictions, applying the UNIFAC method, were also made with the use of liquid−liquid equilibrium specific parameters for both temperatures.

Introduction

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

In this work, liquid−liquid equilibrium data of the system water + acetic acid + 2-hexanone have been determined at 25 °C and 35 °C in order to analyze the viability of 2-hexanone as an extraction agent. The use of ketones in the recovery of acetic acid from its aqueous solutions has been previously studied,[1−3] using other ketones of shorter carbon chain.

Experimental Section

2-Hexanone was supplied by Merck and acetic acid by Carlo Erba. None of the reagents underwent further purification. Purities specified by the manufacturers were the following: 2-hexanone, 98%; acetic acid, 99.9%. Distilled water was obtained from the Milli-Q 185 Plus system, with a resistivity of 18.2 MΩ·cm.

The experimental technique followed to determine the binodal curve and tie-lines has been previously described.[4] The refractive index and density of the phases at equilibrium corresponding to end tie-lines are measured in order to be able to determine their compositions later on. Methods based on measurements of physical properties to determine liquid−liquid equilibrium have been used by other authors.[5−9]

The analytical technique followed to determine the composition of the phases at equilibrium involves preparing binary mixtures by weight, using a Scaltec SBA31 balance with a precision of $\pm 10^{-4}$ g. The third component is added to these miscible binary mixtures until compositions corresponding to the binodal curve are reached. The maximum error in the calculation of the compositions of the binodal curve was estimated to be $\pm 10^{-4}$. Next, the refractive index

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and density of these ternary mixtures are measured by using a Dr. Kernchen ABBEMAT-HP automatic refractometer with a precision of $\pm 10^{-5}$ and an Anton Paar DMA 60/602 densimeter with a precision of $\pm 10^{-5}$ g·cm^{-3}. Densimeter temperature is controlled with a stability of ± 0.01 °C. Each measurement was taken on three occasions, with a precision of $\pm 10^{-5}$. In the treatment of experimental data, the refractive index was used instead of density, because in this case the latter is not considered to be appropriate as it presents maximum values at points corresponding to intermediate locations of the binodal curve. Figure 1 shows the refractive index as a function of the compositions of water, acetic acid, and 2-hexanone for these ternary mixtures. From the experimental data, two refractive index−composition calibration curves were constructed for water and 2-hexanone (Figure 1).

Once the calibration curves are constructed, this technique allows one to determine the composition of mixtures corresponding to end tie-lines, for which the refractive index was measured previously, with an estimated precision of ± 0.003 in mass fraction.

Given that the measurement of two physical properties is available, as an alternative method for the determination of compositions from the property values, the simultaneous fitting of each property to a Redlich−Kister expression[10] (eq 1) was attempted using

$$Q = \sum_{i=1}^{3}\sum_{j=1}^{4} A_{ij} w_i^j \tag{1}$$
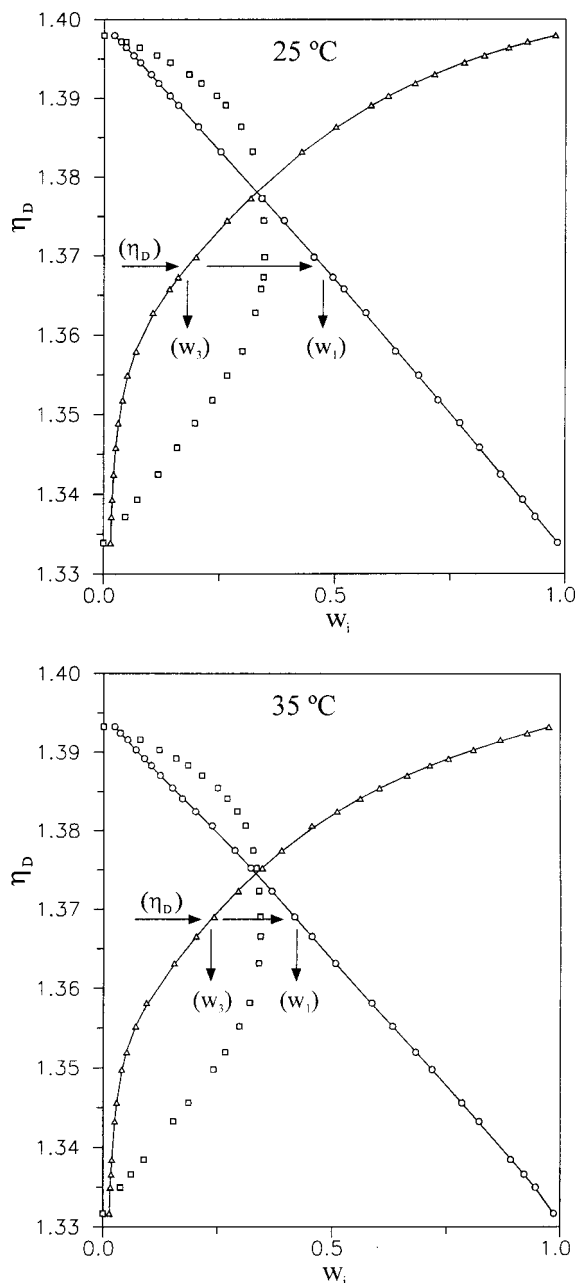
where Q is n_D or ρ^{-1} and w_i is the mass fraction of component i. Compositions of end tie-lines are obtained by solving both equations simultaneously, using density and refractive index values.

This second method would be applied if both properties present maximum values at intermediate points of the binodal curve, as occurs with density in this system. Results obtained from both methods are similar; the largest differences observed being ± 0.003 unit mass fraction.

Results and Discussion

The compositions defining the binodal curve of the ternary mixture water + acetic acid + 2-hexanone at 25

Figure 1. Refractive indices for the system water + acetic acid + 2-hexanone at 25 and 35 °C: ○, water; □, acetic acid; △, 2-hexanone. 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) + Acetic Acid (2) + 2-Hexanone (3)

w_1	w_2	w_3	$\rho/(\text{g·cm}^{-3})$	n_D
		$T = 25$ °C		
0.9843	0.0000	0.0157	0.99501	1.33389
0.9354	0.0471	0.0175	1.00103	1.33715
0.9080	0.0730	0.0190	1.00439	1.33932
0.8597	0.1181	0.0222	1.00968	1.34247
0.8139	0.1593	0.0268	1.01404	1.34583
0.7707	0.1973	0.0320	1.01755	1.34891
0.7231	0.2351	0.0418	1.01969	1.35178
0.6814	0.2669	0.0517	1.02066	1.35491
0.6303	0.2992	0.0705	1.01946	1.35794
0.5662	0.3272	0.1066	1.01320	1.36277
0.5183	0.3394	0.1423	1.00532	1.36577
0.4944	0.3449	0.1607	1.00091	1.36726
0.4536	0.3466	0.1998	0.99137	1.36979
0.3891	0.3448	0.2661	0.97497	1.37447
0.3406	0.3420	0.3174	0.96283	1.37727
0.2522	0.3206	0.4272	0.93622	1.38320
0.2038	0.2953	0.5009	0.91786	1.38638
0.1607	0.2624	0.5769	0.90003	1.38911
0.1426	0.2432	0.6142	0.89126	1.39030
0.1178	0.2097	0.6725	0.87805	1.39189
0.1015	0.1835	0.7150	0.86828	1.39303
0.0779	0.1426	0.7795	0.85405	1.39454
0.0640	0.1129	0.8231	0.84468	1.39543
0.0473	0.0765	0.8762	0.83296	1.39644
0.0365	0.0469	0.9166	0.82421	1.39717
0.0222	0.0000	0.9778	0.81116	1.39797
		$T = 35$ °C		
0.9859	0.0000	0.0141	0.99261	1.33168
0.9456	0.0380	0.0164	0.99645	1.33496
0.9205	0.0615	0.0180	0.99906	1.33661
0.8910	0.0897	0.0193	1.00218	1.33845
0.8207	0.1536	0.0257	1.00833	1.34327
0.7831	0.1868	0.0301	1.01110	1.34559
0.7178	0.2410	0.0412	1.01422	1.34978
0.6818	0.2662	0.0520	1.01422	1.35194
0.6311	0.2976	0.0713	1.01226	1.35521
0.5860	0.3196	0.0944	1.00786	1.35815
0.5059	0.3391	0.1550	0.99470	1.36314
0.4548	0.3427	0.2025	0.98300	1.36653
0.4167	0.3419	0.2414	0.97287	1.36901
0.3670	0.3390	0.2940	0.96009	1.37230
0.3208	0.3331	0.3461	0.94737	1.37524
0.2861	0.3257	0.3882	0.93712	1.37750
0.2369	0.3094	0.4537	0.92069	1.38065
0.2005	0.2907	0.5088	0.90766	1.38244
0.1717	0.2692	0.5591	0.89591	1.38407
0.1501	0.2488	0.6011	0.88519	1.38545
0.1235	0.2145	0.6620	0.87156	1.38704
0.1041	0.1842	0.7117	0.86031	1.38831
0.0893	0.1579	0.7528	0.85085	1.38922
0.0707	0.1216	0.8077	0.83854	1.39030
0.0527	0.0797	0.8676	0.82608	1.39161
0.0364	0.0363	0.9273	0.81338	1.39244
0.0246	0.0000	0.9754	0.80270	1.39326

°C and 35 °C are listed in Table 1, whereas compositions corresponding to end tie-lines are shown in Table 2. Note that both solubilities obtained are similar to those reported in the literature.[11]

Experimental data were fitted using the NRTL equation[12] and UNIQUAC equation.[13] A computer program[14] was used, in which 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

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

(2)

where x is the experimental mole fraction, $\hat{x}$ is the mole fraction of the calculated tie-line closest to the experimental tie-line considered, i represents the components of the mixture, j represents the phases, and k represents 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 $\hat{\gamma}_{S\infty}^I$ and $\hat{\gamma}_{S\infty}^{II}$ 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.[1-3]
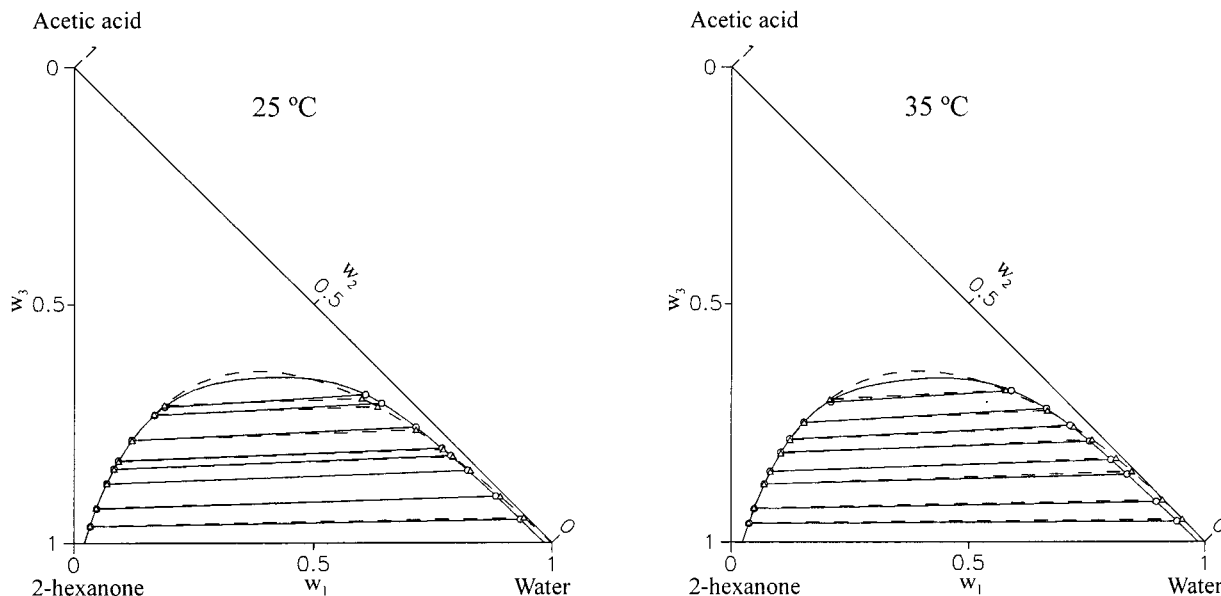
Figure 2. Binodal curve and tie-lines, experimental (solid line) and calculated using the UNIQUAC equation (dashed line).

Table 2. System Water (1) + Acetic Acid (2) + 2-Hexanone (3): Compositions That Determine Ends of Tie-Lines, Expressed as Mass Fraction (w_i)

aqueous phase				organic phase			
w_1	w_2	w_3	n_D	w_1	w_2	w_3	n_D
			$T = 25\ °C$				
0.933	0.049	0.018	1.33744	0.034	0.035	0.931	1.39730
0.882	0.097	0.021	1.34100	0.047	0.073	0.880	1.39649
0.823	0.151	0.026	1.34512	0.069	0.125	0.806	1.39512
0.787	0.183	0.030	1.34757	0.084	0.156	0.760	1.39415
0.769	0.198	0.033	1.34882	0.093	0.173	0.734	1.39356
0.714	0.243	0.043	1.35258	0.121	0.216	0.663	1.39170
0.642	0.292	0.066	1.35744	0.169	0.268	0.563	1.38860
0.609	0.310	0.081	1.35970	0.190	0.285	0.525	1.38720
			$T = 35\ °C$				
0.941	0.043	0.016	1.33526	0.038	0.039	0.923	1.39241
0.896	0.085	0.019	1.33824	0.050	0.070	0.880	1.39170
0.834	0.142	0.024	1.34229	0.070	0.122	0.808	1.39036
0.800	0.172	0.028	1.34452	0.083	0.148	0.769	1.38957
0.755	0.211	0.034	1.34743	0.105	0.188	0.707	1.38820
0.713	0.244	0.043	1.35006	0.124	0.216	0.660	1.38705
0.664	0.279	0.057	1.35317	0.154	0.251	0.595	1.38526
0.590	0.316	0.094	1.35782	0.210	0.294	0.496	1.38197

Table 3. Residuals F and $\Delta\beta$ of the UNIQUAC and NRTL Equations Fitted to Liquid−Liquid Equilibrium Data for the System Water (1) + Acetic Acid (2) + 2-Hexanone (3)

model	β_∞	$\Delta\beta$ (%)	F (%)
	$T = 25\ °C$		
UNIQUAC	3.04	1.6	0.1676
NRTL ($\alpha_{ij} = 0.2$)	3.21	1.2	0.1367
	$T = 35\ °C$		
UNIQUAC	5.76	1.5	0.2190
NRTL ($\alpha_{ij} = 0.2$)	4.24	2.3	0.1972

In Table 3 the values of residual F (eq 3) and the mean error of the solute distribution ratio $\Delta\beta$ (eq 4) obtained using optimum values of the solute distribution ratio at infinite dilution, β_∞, for both equations are given by

$$F = 100\sqrt{\frac{\sum^{k}\min\sum^{i}\sum^{j}(x_{ijk} - \hat{x}_{ijk})^2}{6M}} \quad (3)$$

$$\Delta\beta = 100\sqrt{\frac{\sum^{k}\left[\dfrac{\hat{\beta}_k - \beta_k}{\beta_k}\right]^2}{M}} \quad (4)$$

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. For the NRTL equation, the best results are obtained for $\alpha_{ij} = 0.2$.

The specific parameters for the two equations (fitted individually for each set of data at a given temperature) 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 Figure 2 the tie-lines calculated using the UNIQUAC equation are compared with the experimental values.

For the system studied, both equations, NRTL and UNIQUAC, fit the experimental data with high precision at both temperatures, and only small deviations exist in the upper part of the binodal curves with respect to the experimental data.

Equilibrium compositions were calculated using a computer program[15] that utilizes predicted activity coefficients applying the UNIFAC method[16] and parameters of group interactions specific for liquid−liquid equilibria.[17] Calculated tie-lines are compared with experimental ones in Figure 3.

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

$$F_P = 100\sqrt{\frac{\sum^{i}\sum^{j}\sum^{k}(w_{ijk} - \hat{w}_{ijk})^2}{6M}} \quad (5)$$

where the subscripts i, j, and k are the components, the phases, and the tie-lines, respectively, whereas w is the experimental mass fraction, $\hat{w}$ the calculated mass fraction,
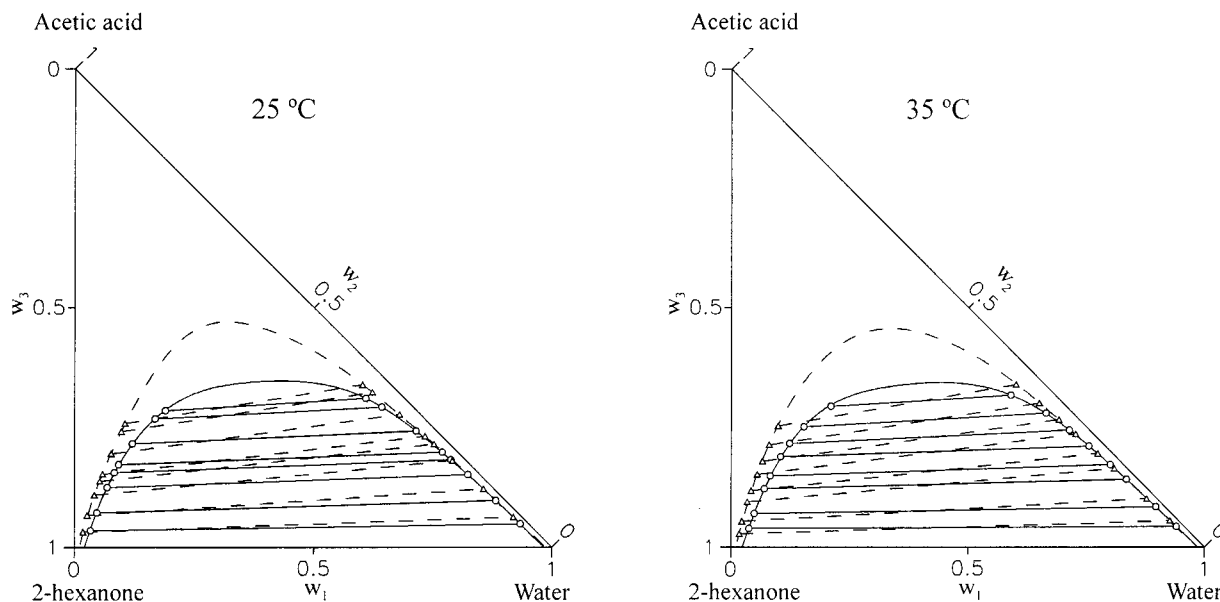
Figure 3. Binodal curve and tie-lines, experimental (solid line) and calculated using the UNIFAC method (dashed line).

Table 4. Optimized System Specific Parameters of the UNIQUAC and NRTL Equations for the System Water (1) + Acetic Acid (2) + 2-Hexanone (3)[a]

equation	β_∞	$i-j$	b_{ij}/K	b_{ji}/K
		$T = 25\ °C$		
UNIQUAC	3.04	1−2	502.14	−388.26
		1−3	253.03	313.62
		2−3	−119.54	−57.328
		$T = 35\ °C$		
UNIQUAC	5.76	1−2	871.39	−492.19
		1−3	603.79	199.51
		2−3	−194.11	−64.580

equation	β_∞	$i-j$	a_{ij}/K	a_{ji}/K
		$T = 25\ °C$		
NRTL ($\alpha_{ij} = 0.2$)	3.21	1−2	169.41	−125.98
		1−3	1925.4	189.31
		2−3	−533.80	616.57
		$T = 35\ °C$		
NRTL ($\alpha_{ij} = 0.2$)	4.24	1−2	149.35	−155.57
		1−3	2013.6	168.97
		2−3	−551.50	488.47

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

and *M* the number of tie-lines. For the system studied in this work, the value of F_P was 3.75% at 25 °C and 4.77% at 35 °C. The method provides acceptable results for the prediction of binodal curves in an area of low concentrations of acetic acid, although an immiscibility region that is greater than the real is predicted. With respect to tie-lines, it has been observed that as the proportion of acetic acid increases, more discrepancies between the calculated and experimental values appear.

To estimate the viability of 2-hexanone as an extraction agent of acetic acid in water, distribution coefficients and separation factors[18] have been considered in the composition interval of 5 mass % to 30 mass % acetic acid in water. According to the criteria applied by Sayar,[18] 2-hexanone could be used as an extraction agent of acetic acid from its diluted aqueous solutions (to ~15 mass % acetic acid) as observed in Figure 4, in which the separation factor is presented versus mass fraction of acetic acid in the aqueous phase.
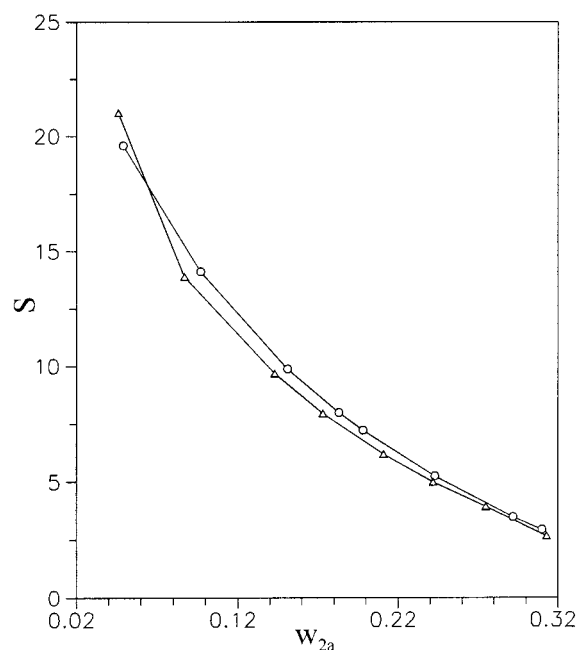

Figure 4. Separation factors, *S*, as a function of weight fraction w_{2a} of acetic acid in the aqueous phase: ○, 25 °C; △, 35 °C.

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