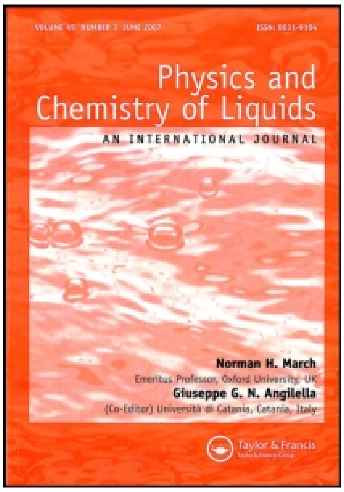

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Liquid-Liquid Equilibria for Water Nitromethane (1-Propanol, or Acetone, or *p*-Dioxane) Ternary Systems at 303.15 *K*

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LIQUID-LIQUID EQUILIBRIA FOR WATER + NITROMETHANE + (1-PROPANOL, OR + ACETONE, OR + *p*-DIOXANE) TERNARY SYSTEMS AT 303.15 *K*

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Liquid-liquid equilibria, distribution coefficients, and selectivities of ternary systems of the type: (water + K + nitromethane), where K is 1-propanol, acetone, or *p*-dioxane, have been determined at (303.15 ± 0.05) K, in order to evaluate the suitability of nitromethane for extracting preferentially the second components from their aqueous solutions. The line data were satisfactorily correlated by the Othmer and obias method, and the plait point coordinates for the three systems were estimated. The experimental data were compared with values calculated using the NRTL and UNIQUAC models, and with those predicted by the UNIFAC group contribution method. This last method predicts qualitative and quantitative behaviour which are in disagreement with experimental results, while the values calculated using the other two models are in agreement but only when the concentration of component K is low. The three ternary systems studied have distribution coefficients higher than unity, and high selectivities. Therefore, nitromethane could be considered as a potential solvent for the extraction of K from its aqueous solutions.

Keywords: Liquid-liquid equilibria; ternary systems; aqueous solutions

1. INTRODUCTION

Liquid-liquid equilibria (LLE) studies have become increasing important in chemical technology. Liquid-liquid extraction provides

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*Corresponding author. Fax: 154-381-4243909, e-mail: hsolimo@herrera.unt.edu.ar an alternative to distillation for the recovery of chemicals from aqueous solutions, which needs reliable LLE data for the design of the extraction equipment.

The main purposes of this study are: (i) to report experimental data on the phase equilibria of ternary mixtures of the type: (water + K + nitromethane) where K is 1-propanol (P), acetone (A) or *p*-dioxane (D), at (303.15 ± 0.05) K; (ii) to evaluate the potential of nitromethane (N) for the recovery of K from its aqueous solutions from the dependence of the distribution coefficients and selectivities with the mass fraction of K in the extract phase; (iii) to verify the suitability of the NRTL [1] and UNIQUAC [2] activity coefficient models and of the UNIFAC [3] group contribution method (using the liquid–liquid equilibrium interaction parameters reported by Magnussen *et al.* [4]) for these three ternary systems; (iv) to correlate experimental equilibrium data with the Othmer and Tobias' method [5] in order to obtain the plait point coordinates for each ternary system.

2. EXPERIMENTAL SECTION

2.1. Materials

Nitromethane (Baker, A. R.), 1-propanol, acetone, and *p*-dioxane (Merck, p.a.) with purities greater than 99.5 mass% obtained by gas chromatography were used without any further purification. Bidistilled water (W) was used throughout this work. All organic chemicals were stored over activated molecular sieves to prevent water absorption.

2.2. Procedure

The procedure for the determination of binodal curves and tie lines data for these ternary systems at (303.15 ± 0.05) K was similar to that previously described [6] but, in this case, a vibrating tube densimeter KEM, DA300 with an accuracy of $\pm 0.1\,\mathrm{kg\,m^{-3}}$ was used in order to build a calibration curve: density against mass fraction of K in both phases. When the equilibrium was reached for each tie line, samples of both conjugated phases were drawn with hypodermic syringes and their densities measured in order to obtain their compositions with the aid of the calibration curve. Since the composition of the binodal curves were obtained by mass, the uncertainly throughout the binodal curve is lesser than that for tie line data. They were estimated to be within ± 0.0005 and ± 0.001 of mass fraction, respectively.

3. RESULTS AND DISCUSSION

Densities and refractive indices of the pure liquids were in good agreement with published values [7]. They are listed in Table I along with literature values for comparison. Mutual solubilities are also included.

The experimental values for the binodal curves and equilibrium data for $(W+P+N)$, $(W+A+N)$, and $(W+D+N)$ ternary systems at (303.15 ± 0.05) K are given in Tables II, III and IV, respectively.

Figures 1, 2, and 3 show the experimental LLE diagrams at (303.15 ± 0.05) K, containing binodal curves, tie lines, and the plait points (PP) for the $(W+P+N)$, $(W+A+N)$, and $(W+D+N)$ ternary systems, respectively. Predicted LLE by the UNIFAC method, and calculated NRTL and UNIQUAC values fitted to the experimental results are also included. A solutropic behaviour can be observed in Figure 1 for the $(W+P+N)$ ternary system.

The tie line data for these ternary systems were satisfactority correlated with the Othmer and Tobias' method [5]. The empirical equation:

$$\log[(1-w_{1R})/w_{1R}] = a\log[(1-w_{3E})/w_{3E}] + b \qquad (1)$$

can represent all tie-line data with adequate precision, where w_{1R} and w_{3E} are the mass fraction of water (component 1) in the water-rich layer (raffinate, R) and the mass fraction of nitromethane (component 3) in the nitromethane-rich layer (extract, E), respectively. In our case, the best values of the parameters, a and b, in Eq. (1) are given in Table V for the three ternary systems with their corresponding linear correlation coefficients. Table V also lists the experimental and calculated plait

TABLE I Density (ρ) and refractive index (n_D) of pure components and mutual solubility[a] at (303.15 ± 0.05) *K*

Compound	$\rho/kg\,m^{-3}$		n_D	
	Exptl.	*Lit.*	*Exptl.*	*Lit.*
Water (W)	995.4	995.67[b]	1.3319	1.33192[b]
Nitromethane (N)	1123.2	1124.39[c]	1.3778	1.37738[c]
1-propanol (P)	801.8	799.6[c,d]	1.3815	1.38370[c,d]
Acetone (A)	779.4	780.33[c]	1.3538	1.35596[c,d]
p-dioxane (D)	1022.1	1027.97[c,d]	1.4180	1.42025[c,d]

[a] Experimental mutual solubility of partially miscible binary system ($W + N$): water in nitromethane: 1.50 mass%; nitromethane in water: 12.00 mass%.

[b] Weast, R. C. CRC Handbook of Chemistry and Physics (CRC Press, Inc., Boca Raton, 1988-1989), 69th edition.

[c] Riddick, J. A., Bunger, W. B. and Sakano, T. K. Organic Solvents (Wiley & Sons, New York, Chichester, Brisbane, Toronto and Singapore, 1986), 4th edn.

[d] Measured at 298.15 *K*.

TABLE II Binodal curve and equilibrium data for: water(1) + 1-propanol(2) + nitromethane ternary system at (303.15 ± 0.05) *K*. Densities ($\rho/\mathrm{kg\,m^{-3}}$) of the equilibrium phases are also included

$100w_1$	$100w_2$	$100w_1$	$100w_2$
(a) Binodal curve			
88.00	0.00	35.30	24.20
82.15	5.65	33.95	24.00
81.50	5.90	31.85	24.35
79.85	7.10	27.00	24.15
78.75	8.20	23.40	23.80
77.75	9.20	22.15	23.35
73.75	12.00	20.35	22.55
72.60	12.75	17.35	21.25
67.55	15.75	16.75	20.35
63.20	18.15	13.90	18.95
58.55	19.45	12.60	16.70
55.40	20.35	11.30	16.55
51.05	21.55	10.00	15.40
46.45	22.35	9.00	11.70
44.45	22.95	6.90	10.10
39.05	23.50	6.60	8.60
38.35	23.75	5.75	6.40
37.30	23.85	4.70	5.00
		1.50	0.00

(b) Equilibrium data

Water rich-phase			*Nitromethane rich-phase*		
$100w_{1R}$	$100w_{2R}$	$\rho/kg\,m^{-3}$	$100w_{1E}$	$100w_{2E}$	$\rho/kg\,m^{-3}$
85.5	2.6	1013.3	3.1	2.0	1107.6
80.0	7.1	1006.0	5.8	6.6	1085.4
78.6	8.6	1003.4	7.0	9.2	1073.3
75.5	10.6	1000.1	8.7	12.2	1059.0
72.5	13.0	996.1	12.3	17.0	1036.4
70.0	14.3	994.4	14.7	19.3	1025.1
67.0	16.0	991.4	19.7	22.2	1012.0

TABLE III Binodal curve and equilibrium data for: water(1) + acetone(2) + nitromethane ternary system at (303.15 ± 0.05) *K*. Densities (ρ/kg m^{-3}) of the equilibrium phases are also included

$100w_1$	$100w_2$	$100w_1$	$100w_2$
(a) Binodal curve			
88.00	0.00	30.15	39.10
80.75	8.15	29.55	39.30
76.65	12.30	26.70	39.85
75.85	12.95	23.05	40.45
71.40	17.05	22.40	40.40
67.30	20.50	17.80	40.20
62.45	23.90	15.35	39.15
60.35	25.45	13.00	37.40
52.80	29.80	10.75	34.40
48.95	31.65	8.20	28.70
43.80	33.95	8.05	27.40
39.70	35.50	6.60	23.65
36.05	37.05	6.35	17.35
34.95	37.35	4.90	13.95
34.30	37.60	4.45	9.80
		1.50	0.00

(b) Equilibrium data

Water rich-phase			*Nitromethane rich-phase*		
$100w_{1R}$	$100w_{2R}$	$\rho/kg\,m^{-3}$	$100w_{1E}$	$100w_{2E}$	$\rho/kg\,m^{-3}$
85.0	3.6	1010.8	4.5	9.3	1075.6
83.6	5.1	1008.4	4.8	11.6	1065.4
82.3	6.7	1005.6	5.3	15.2	1049.1
80.3	8.6	1002.0	6.0	19.5	1032.2
76.8	12.3	995.5	7.4	26.0	1005.9
67.5	20.4	980.9	9.0	30.6	988.1

points (UNIFAC, NRTL, and UNIQUAC methods) for these systems at (303.15 ± 0.05) *K*.

In selecting solvents, it is necessary to take into account the effect of the aqueous *K* concentration on the *K* distribution coefficients and the selectivity for *K* over water. As shown in Figure 4, the *K* distribution coefficients (*m*) defined as the ratio of the *K* mass fraction in the organic phase (w_{KE}) to that in the aqueous one (w_{KR}) are not constant. Additionally, the system ($W + P + N$) presents a different qualitative behaviour than the other two systems: the distribution coefficient increases when the mass fraction of *P* in the organic phase increases, while the opposite can be observed for the two ternary systems:

TABLE IV Binodal curve and equilibrium data for: water(1) + *p*-dioxane(2) + nitromethane ternary system at (303.15 ± 0.05) *K*. Densities (ρ/kg m^{-3}) of the equilibrium phases are also included

(a) Binodal curve

$100w_1$	$100w_2$	$100w_1$	$100w_2$
88.00	0.00	18.30	38.95
78.80	8.95	15.00	38.20
74.65	12.75	12.80	37.40
68.65	17.85	12.65	37.15
64.15	21.35	10.00	33.80
58.55	25.35	8.00	31.10
54.95	28.05	6.80	27.65
47.25	31.85	6.50	24.10
39.65	34.95	5.10	19.45
31.50	37.00	4.30	14.20
25.90	38.95	4.15	9.40
21.80	39.10	3.70	5.10
21.40	39.15	1.50	0.00

(b) Equilibrium data

Water rich-phase			*Nitromethane rich-phase*		
$100w_{1R}$	$100w_{2R}$	$\rho/kg\,m^{-3}$	$100w_{1E}$	$100w_{2E}$	$\rho/kg\,m^{-3}$
82.2	5.6	1022.6	4.2	11.4	1105.9
75.7	11.6	1026.6	5.3	19.2	1097.2
70.5	16.2	1029.7	6.0	24.1	1090.5
64.5	21.1	1034.0	7.8	30.2	1082.8
58.9	24.9	1037.6	10.2	34.3	1077.4
52.3	29.3	1041.4	13.8	37.4	1072.0

$(W+A+N)$ and $(W+D+N)$. Figure 4 also shows the selectivity ($\beta = m\, w_{1R}/w_{1E}$, where w_{1R} and w_{1E} are the mass fractions of water in the raffinate and extract phase, respectively) against the mass fraction of *K* in the extract phase (w_{KE}). As can be seen, this property decreases when w_{KE} increases for the three ternary systems. Consequently, the distribution coefficient and selectivity trends are as follows:

$$m_A > m_D > m_P$$

$$\beta_A > \beta_D > \beta_P$$

From the analysis of Figure 4, we conclude that both extraction properties have values that are high enough to consider nitromethane as a potential solvent for the extraction of *K* from its aqueous solutions.

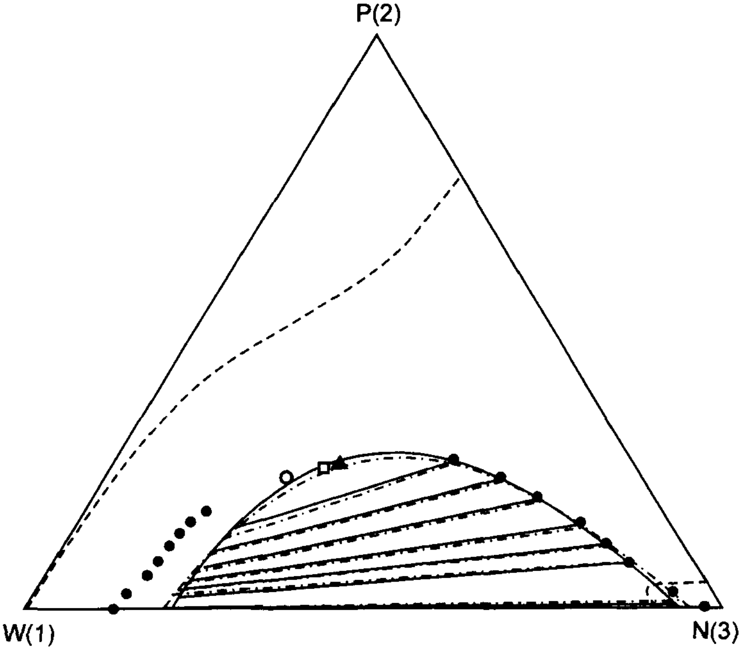

FIGURE 1 Experimental binodal curve and tie lines (●) for the system water + 1-propanol + nitromethane at 303.15 *K*. (----) UNIFAC predictions, (–·–·–) UNIQUAC tie lines, and (—) NRTL tie lines. ○, □, ▲, Experimental, UNIQUAC, and NRTL plait points, respectively.

4. CORRELATION OF THE EXPERIMENTAL DATA

Thermodynamic models, such as the NRTL [1] and UNIQUAC [2], were used to correlate the LLE for these systems. This was done with the help of an iterative computer program developed by Sørensen [8]. In order to minimize the values of the two objective functions in terms of activity and molar fractions, a penalty term, designed to reduce the risk of multiple solutions associated with high parameter values, was included, Figures 1, 2, and 3 show the LLE calculations using these models for $(W+P+N)$, $(W+A+N)$, and $(W+D+N)$ ternary systems, respectively.

The nonrandomness of the liquid mixture, which is represented by the optimized third parameter in the NRTL equation (α_{ij}), is shown in

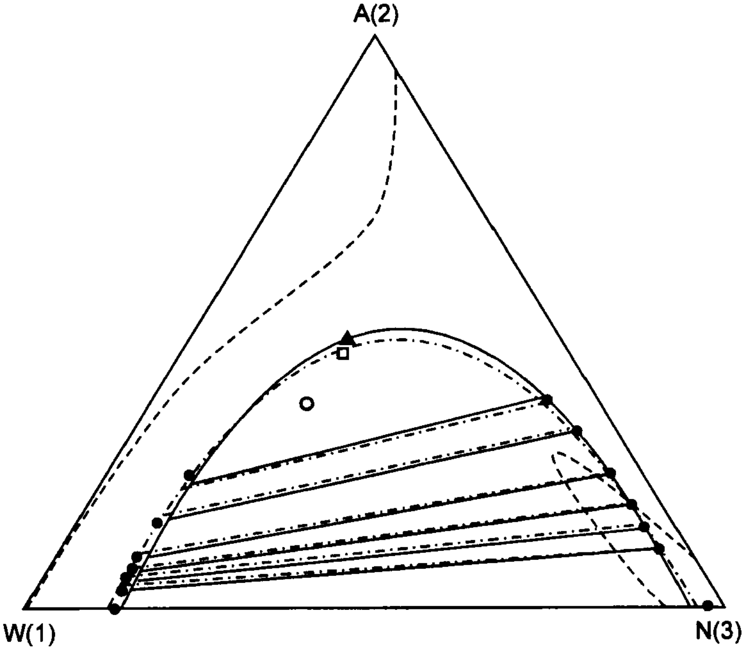

FIGURE 2 Experimental binodal curve and tie lines (●) for the system water + acetone + nitromethane at 303.15 *K*. (----) UNIFAC predictions, (- · - · -) UNIQUAC tie lines, and (—) NRTL tie lines. ○, □, ▲, Experimental, UNIQUAC, and NRTL plait points, respectively.

Table VI together with the residuals and parameter values for these two models.

The values of the residual function *F* (mol %), and of the mean error of the *K* distribution coefficient (*m*), give an idea of the goodness of fit defined as:

$$F = 100\left[\sum_k min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2/6M\right]^{1/2} \tag{2}$$

$$m = 100\left[\sum_k \left[(\hat{m}^k - m^k)/m^k\right]^2/M\right]^{1/2} \tag{3}$$

where m and $\hat{m}$ are the experimental and calculated *K* distribution coefficients, respectively; x and $\hat{x}$ are the experimental mole fractions of the liquid phase and that of the predicted tie line lying close to the

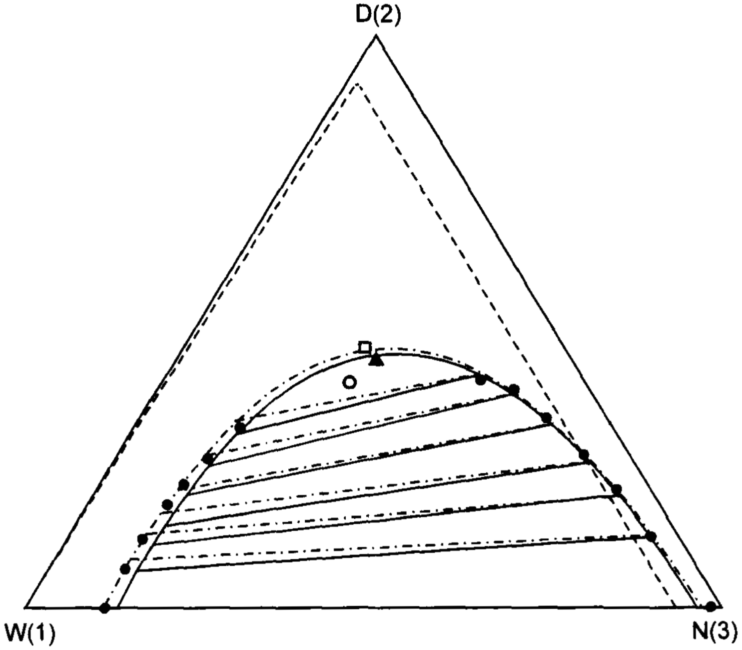

FIGURE 3 Experimental binodal curve and tie lines (●) for the system water + *p*-dioxane + nitromethane at 303.15 *K*. (----) UNIFAC predictions, (–·–·–) UNIQUAC tie lines, and (—) NRTL tie lines. ○, □, ▲, Experimental, UNIQUAC, and NRTL plait points, respectively.

considered experimental tie line, respectively; and M is the number of tie lines.

The binodal curves calculated with these two models are in good agreement with those obtained experimentally for $(W+A+N)$ and $(W+D+N)$ systems but only when the mass fraction of the component K is low, since their immiscibility regions are always larger than the experimental ones as can be seen in Figures 2, and 3. This is characterized by low values of the residuals F for these two systems. On the other hand, the agreement between experimental and calculated equilibrium data have a reasonable concordance (residuals m: ± 10 % approximately. See Tab. VI).

Figure 1 shows a poor agreement for the $(W+P+N)$ ternary system among experimental and calculated values using these two models.

TABLE V Experimental and calculated plait points, parameters of Eq. (1) and linear correlation coefficients (LCC) in the Othmer and Tobias correlation for the systems water(1) + 1-propanol(2) + nitromethane(3), water(1) + acetone(2) + nitromethane(3) and water(1) + p-dioxane(2) + nitromethane(3) at (303.15 ± 0.05) K

System		*Plait points and parameters of Eq.* (1)			
	w_i	*Exptl.*	*NRTL*	*UNIQUAC*	*UNIFAC*
$W+P+N$	w_1	0.537	0.422	0.457	predicts a type II system
	w_2	0.207	0.247	0.233	
	w_3	0.256	0.331	0.310	
	a	0.4107			
	b	−0.2555			
	LCC	0.9968			
$W+A+N$	w_1	0.448	0.287	0.312	predicts a type II system
	w_2	0.338	0.248	0.245	
	w_3	0.214	0.465	0.443	
	a	0.64			
	b	−0.2716			
	LCC	0.9097			
$W+D+N$	w_1	0.354	0.293	0.294	not calculated by program
	w_2	0.364	0.412	0.426	
	w_3	0.282	0.295	0.280	
	a	0.8272			
	b	−0.0734			
	LCC	0.9967			

This disagreement is particularly important for the aqueous phase, which is surely the responsible for both high residual values. According to both calculated residuals, the fit is better with the UNIQUAC equation than with the NRTL one.

The UNIFAC group contribution method [3] was employed by using the group interaction parameters obtained by Magnussan *et al.* [4]. The equilibrium compositions were predicted with the help of a computer program written by Frendenslund *et al.* [3] (called LLECAL), which was operated using the manual provided by Magnussen [9]. The predicted binodal curves are shown as broken lines in Figure 3. It can be seen that the UNIFAC method predicts an immiscibility region which is much larger than that experimentally determined for ($W+D+N$) ternary system, while Figures 1 and 2 show that the UNIFAC method predicts binodal bands type curves, similar to those observed for systems classified as type II by Treybal [10] for ($W+P+N$) and ($W+A+N$) systems. Therefore, this method

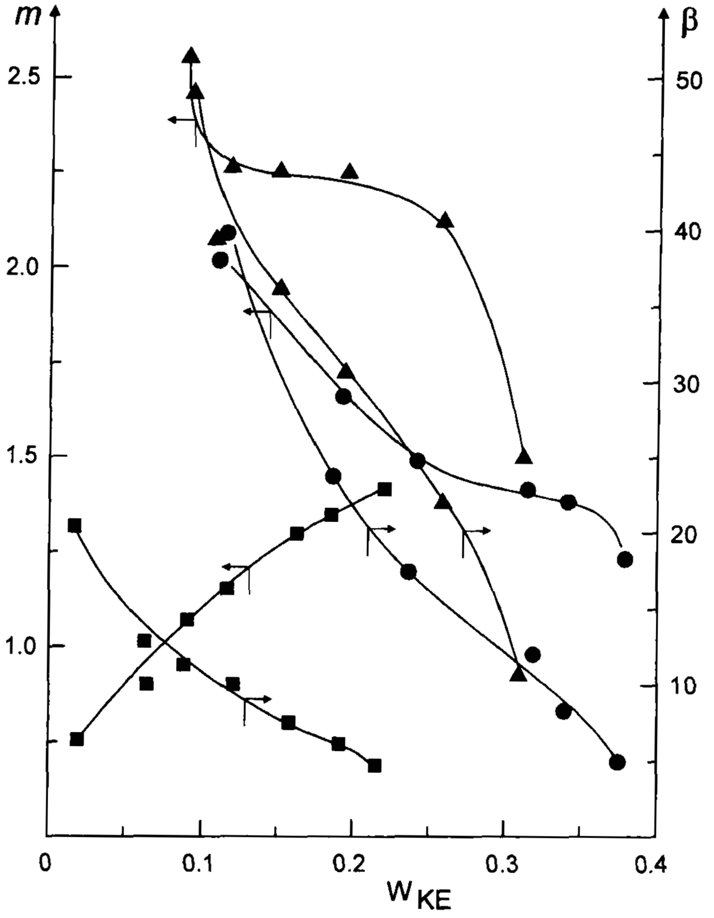

FIGURE 4 Distribution coefficients (m) and selectivities (β) against the mass fraction of the component K in the extract phase (w_{KE}) at 303.15 K for the ternary systems: (■) ($W+P+N$), ▲ ($W+A+N$), (●) ($W+D+N$).

presents both a qualitative and a quantitative disagreement with experimental results. This was also observed for other ternary systems containing the pair: water-nitromethane, (not shown in this paper) and could be due to inappropriate values for the interaction parameters for nitromethane.

TABLE VI Residual F and m, optimized parameters of the NRTL and UNIQUAC equations fitted to LLE data, and nonrandomness parameter of the NRTL equation (α_{ij}) for the $(W+P+N)$, $(W+A+N)$ and $(W+D+N)$ systems at (303.15 ± 0.05) K

System	$100F$	$100m$	i–j	a_{ij}[a]	a_{ji}[a]	α_{ij}
			NRTL equation			
$W+P+N$	1.43	86.1	1–2	628.77	−394.66	0.25
			1–3	625.62	456.61	
			2–3	−189.39	−500.47	
$W+A+N$	0.39	12.3	1–2	224.59	74.869	0.25
			1–3	770.47	403.92	
			2–3	−273.98	−192.42	
$W+D+N$	0.44	11.4	1–2	202.93	355.51	0.40
			1–3	866.14	713.88	
			2–3	−104.21	−181.22	
			UNIQUAC equation			
$W+P+N$	1.32	86.2	1–2	241.03	−116.06	
			1–3	128.97	427.06	
			2–3	104.69	−120.84	
$W+A+N$	0.35	9.8	1–2	−69.641	172.99	
			1–3	244.62	317.07	
			2–3	18.068	−105.14	
$W+D+N$	0.39	8.5	1–2	−95.538	99.440	
			1–3	215.22	379.89	
			2–3	24.076	−26.213	

[a] $a_{ij} = (g_{ij} - g_{jj})/R(K)$ for NRTL equation, where g_{ij} is the energy of interaction between and i–j pair of molecules (cal mol^{-1}). $a_{ji} = (u_{ij} - u_{jj})/R(K)$ for UNIQUAC equation, where u_{ij} is the UNIQUAC binary interaction parameter (cal mol^{-1}).

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