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Liquid-Liquid Equilibrium for the Ternary Systems Composed of Diethyl Phenylmalonate + Acetic Acid + Water and Diethyl Methylmalonate + Acetic Acid + Water at 294, 298, and 308 K

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Liquid-liquid equilibrium measurements for the systems diethyl phenylmalonate + acetic acid + water and diethyl methylmalonate + acetic acid + water were made at 294, 298, and 308 K. The mole fraction composition along the binodal curves was fit to a correlation equation, and tie-line results were fit by the Bachman, Hand, Othmer-Tobias, and selectivity methods. We conclude that diethyl phenylmalonate and diethyl methylmalonate can be used as solvents for extracting acetic acid from its aqueous solutions.

Introduction

The recovery of acetic acid from aqueous solution is of great economic importance to industries which utilize acetic acid as a raw material or solvent for reaction. Various methods of recovering acetic acid have been reviewed in the *Encyclopedia of Chemical Technology* (*1*) and by Shreve (*2*), Othmer (*3*), and Garcia (*4*). Comparative economics for processes to recover acetic acid from aqueous solutions of various solvents and the factors affecting the selection of extractants for acetic acid have been reviewed by Brown (*5*). Many systems containing acetic acid + water and different solvents have been published (*6*). Diethyl phenylmalonate + acetic acid + water and diethyl methylmalonate + acetic acid + water have not been studied previously.

In this study, liquid-liquid equilibrium measurements on diethyl phenylmalonate + acetic acid + water and diethyl methylmalonate + acetic acid + water have been made.

Experimental Section

Purity of Components. The diethyl phenylmalonate, diethyl methylmalonate, and acetic acid used in this study were pure grade materials obtained from Fluka Chemie AG, CH-9470 Buchs, Switzerland. Water was deionized and distilled in an all-glass distillation unit. The physical constants for the materials appear in Table I together with literature (*7*) values.

Binodal Curve Determination. Depending upon the region of the binodal curve (i.e., diethyl phenylmalonate-, diethyl methylmalonate-, or water-rich phase), homogeneous samples of known compositions of the binary mixtures of acetic acid + water, acetic acid + diethyl phenylmalonate, and acetic acid + diethyl methylmalonate were titrated, respectively, with the third component in a thermostated glass-stoppered bottle. The addition of appropriate amounts of diethyl phenylmalonate and diethyl methylmalonate to a one-phase solution of acetic acid + water and that of water to a one-phase solution of acetic acid + diethyl phenylmalonate and acetic acid + diethyl methylmalonate rendered the systems immiscible. The titrant was added in small amounts from a Kimax microburet with an accuracy of ±0.01 cm^3. The contents of the glass-stoppered bottles were shaken vigorously to obtain proper mixing and equilibrium. The number of moles of titrant added was calculated from its volume and density. The binodal curve results for the ternary systems at 294, 298, and 308 K are reported in Tables II and III and Figure 1. The thermostatic bath temperature was maintained to within ±0.1 K of the required temperature.

Table I. Refractive Index n_D and Density of Components

component	n_D(20°C) lit.	n_D(20°C) measd	ρ(20°C)/(g cm^{-3}) lit.	ρ(20°C)/(g cm^{-3}) measd
diethyl phenylmalonate	1.4977	1.4910	1.0950	1.0955
diethyl methylmalonate	1.4126	1.4130	1.0225	1.0200
acetic acid	1.3716	1.3720	1.0492	1.0500
water	1.3333	1.3332	0.9982	0.9984

Tie-Line Data Determination. To obtain tie-line data, the global mixture (see Tables IV and V) was directly weighed at room temperature into screw-capped Pyrex tubes, sealed, and placed in a thermostated shaking bath set at 294 and 298 K. Each tube contained about 10 cm^3 liquid and 8 cm^3 gas phase (air and solution vapor). After 2 h, the shaker was stopped and the samples were allowed to separate at the temperature. Samples of the lower and upper layers were taken with long-needled syringes and weighed. The acetic acid was determined in each phase by a titrimetric method; water was determined in each phase by Karl-Fisher solutions. Diethyl phenylmalonate and diethyl methylmalonate were determined by measuring the refractive index of both phases.

The mole fraction of each component along the binodal curve was correlated as a function of the refractive index. The spline-fit technique extended by Klaus and Van Ness (*8*) was used for this correlation. The measurement of the refractive index of both phases at equilibrium gives the tie-line composition. The results are presented in Tables IV and V and Figures 2 and 3.

The experimental results of the systems studied (Tables II and III) were used to predict the binodal curve results. It was observed that the phase boundary lines of Figure 1 could be correlated by eq 1 using a least-squares method (*9*), for the

$$x_{2,k} = \sum_{i=0}^{n} C_i x^{i}_{3,k} \qquad (1)$$

n = number of parameters

k = E or R (extract or raffinate phase)

x_2 = mole fraction of acetic acid

x_3 = mole fraction of water

solvent-rich lines and water-rich lines at different temperatures. The parameters for each phase are presented in Tables VI and VII along with the standard deviations.

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Table II. Binodal Curve Results for Diethyl Phenylmalonate (1) + Acetic Acid (2) + Water (3)[a]

$T/\mathrm{K} = 294.0$				$T/\mathrm{K} = 298.4$				$T/\mathrm{K} = 308.0$			
$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$
0.0000	0.0987	0.0000	1.0000	0.0000	0.1350	0.0000	0.1000	0.0000	0.2432	0.0000	1.0000
0.1963	0.1771	0.0609	0.9387	0.1525	0.1786	0.1061	0.8929	0.1625	0.2753	0.0521	0.9455
0.2401	0.2035	0.1305	0.8685	0.2420	0.2240	0.1650	0.8333	0.2460	0.2991	0.0765	0.9203
0.2768	0.2317	0.1594	0.8389	0.3370	0.3080	0.2161	0.7798	0.2500	0.3000	0.1025	0.8948
0.3040	0.2515	0.3064	0.6772	0.3675	0.3537	0.2713	0.7188	0.3090	0.3250	0.1255	0.8719
0.3410	0.2991	0.3068	0.6780	0.3825	0.4010	0.3011	0.6838	0.3485	0.3540	0.1477	0.8498
0.3700	0.3450	0.3215	0.6580	0.3915	0.4346	0.3268	0.6493	0.3620	0.3710	0.1674	0.8304
0.3883	0.3863	0.3500	0.6127	0.3917	0.4679	0.3638	0.5823	0.3754	0.4077	0.1876	0.8093
0.4004	0.4486	0.3578	0.5952	0.3899	0.4978	0.3838	0.5267	0.3811	0.4540	0.2059	0.7902
0.3825	0.5213	0.3587	0.5966	0.3871	0.5111					0.2308	0.7632
		0.3851	0.5124	0.3840	0.5258					0.2486	0.7439
		0.3863	0.5139	0.3810	0.5368					0.2645	0.7257
				0.3777	0.5496					0.2870	0.6986
										0.3141	0.6626
										0.3250	0.6451
										0.3351	0.6282
										0.3455	0.6084
										0.3488	0.6000
										0.3730	0.5010

[a] $x_{i,E}$ is mole fraction in extracted phase; $x_{i,R}$ is mole fraction in raffinate phase.

Table III. Binodal Curve Results for Diethyl Methylmalonate (1) + Acetic Acid (2) + Water (3)[a]

$T/\mathrm{K} = 294.0$				$T/\mathrm{K} = 298.0$				$T/\mathrm{K} = 308.0$			
$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$
0.0000	0.1550	0.0000	0.9970	0.0000	0.1710	0.0000	0.9980	0.0000	0.1940	0.0000	0.9990
0.0555	0.1863	0.0227	0.9762	0.0490	0.1961	0.0227	0.9759	0.0221	0.2026	0.0229	0.9764
0.1124	0.2253	0.0383	0.9616	0.0968	0.2274	0.0372	0.9616	0.0469	0.2136	0.0379	0.9613
0.1430	0.2500	0.0637	0.9365	0.1400	0.2611	0.0625	0.9365	0.0815	0.2313	0.0625	0.9366
0.1740	0.2792	0.1324	0.8589	0.1780	0.3000	0.1295	0.8617	0.1144	0.2520	0.1293	0.8614
0.2123	0.3250	0.1561	0.8274	0.2040	0.3331	0.1572	0.8262	0.1639	0.2945	0.1563	0.8248
0.2411	0.3737	0.1847	0.7844	0.2320	0.3800	0.1865	0.7834	0.2042	0.3490	0.1845	0.7818
0.2609	0.4264	0.2280	0.7017	0.2445	0.4114	0.2281	0.7005	0.2181	0.3741	0.2262	0.6937
0.2704	0.4747	0.2551	0.6255	0.2599	0.4635	0.2438	0.6579	0.2295	0.4000	0.2345	0.6688
0.2723	0.5000	0.2645	0.5847	0.2648	0.5250	0.2608	0.5799	0.2425	0.4349	0.2455	0.6277
		0.2699	0.5547					0.2539	0.4760	0.2532	0.5847
								0.2586	0.5263		

[a] $x_{i,E}$ is mole fraction in extracted phase; $x_{i,R}$ is mole fraction in raffinate phase.

Table IV. Tie-Line Results and Distribution Coefficients of Acetic Acid α for Diethyl Phenylmalonate (1) + Acetic Acid (2) + Water (3)[a]

$T/\mathrm{K} = 294.0$							$T/\mathrm{K} = 298.4$						
$x_{2,I}$	$x_{3,I}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	α	$x_{2,I}$	$x_{3,I}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	α
0.0586	0.6630	0.0738	0.1205	0.0541	0.9430	1.36	0.0555	0.5609	0.0680	0.1550	0.0505	0.9465	1.35
0.1129	0.6518	0.1410	0.1486	0.1020	0.8942	1.38	0.1073	0.5582	0.1250	0.1660	0.0870	0.9094	1.44
0.1640	0.6499	0.2050	0.1812	0.1530	0.8424	1.34	0.1604	0.5453	0.1920	0.1895	0.1340	0.8617	1.43
0.1854	0.5558	0.2305	0.1930	0.1653	0.8298	1.39	0.2129	0.5407	0.2571	0.2248	0.1872	0.8078	1.37
0.2193	0.6367	0.2768	0.2277	0.2160	0.7785	1.28							
0.2563	0.5452	0.3040	0.2465	0.2304	0.7625	1.32							
0.3036	0.5306	0.3472	0.3064	0.2852	0.7040	1.22							
0.3328	0.5330	0.3715	0.3460	0.3080	0.6802	1.21							

[a] $x_{i,I}$ is mole fraction of initial solution; $x_{i,E}$ is mole fraction in extracted phase; $x_{i,R}$ is mole fraction in raffinate phase.

Table V. Tie-Line Results and Distribution Coefficients of Acetic Acid α for Diethyl Methylmalonate (1) + Acetic Acid (2) + Water (3)[a]

$T/\mathrm{K} = 294.0$							$T/\mathrm{K} = 298.0$						
$x_{2,I}$	$x_{3,I}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	α	$x_{2,I}$	$x_{3,I}$	$x_{2,E}$	$x_{3,E}$	$x_{2,R}$	$x_{3,R}$	α
0.0368	0.6364	0.0560	0.1850	0.0262	0.9704	2.14	0.0370	0.6432	0.0548	0.2004	0.0257	0.9707	2.13
0.0680	0.6470	0.0978	0.2200	0.0473	0.9480	2.07	0.0775	0.6246	0.1154	0.2426	0.0506	0.9442	2.28
0.0882	0.6706	0.1330	0.2550	0.0665	0.9276	2.00	0.0975	0.6333	0.1432	0.2603	0.0627	0.9314	2.28
0.1247	0.6478	0.1767	0.2901	0.0955	0.8970	1.85	0.1126	0.6598	0.1660	0.2797	0.0767	0.9164	2.16
0.1571	0.6375	0.2089	0.3250	0.1182	0.8712	1.76	0.1359	0.6525	0.1904	0.3005	0.0944	0.8969	2.02
0.1877	0.6458	0.2350	0.3834	0.1351	0.8534	1.74	0.1562	0.6331	0.2150	0.3400	0.1063	0.8335	2.01
0.2105	0.6492	0.2640	0.4565	0.1673	0.8156	1.58	0.1863	0.6487	0.2500	0.4200	0.1381	0.8496	1.81
0.2568	0.6209	0.2758	0.5407	0.1995	0.7605	1.38	0.2100	0.6522	0.2677	0.4730	0.1579	0.8244	1.71

[a] $x_{i,I}$ is mole fraction of initial solution; $x_{i,E}$ is mole fraction in extracted phase; $x_{i,R}$ is mole fraction in raffinate phase.

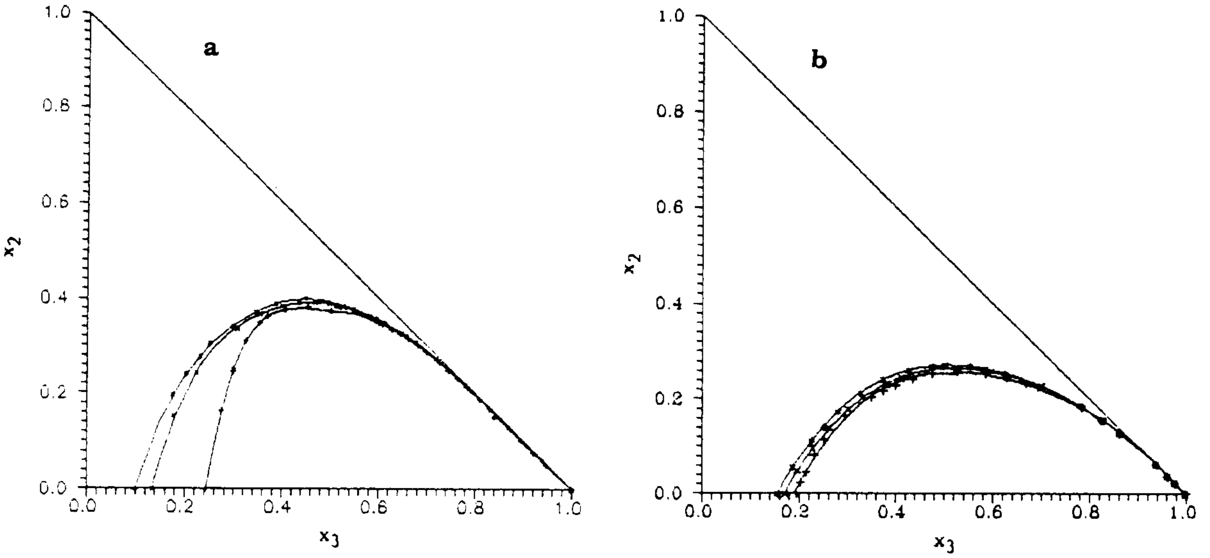

Figure 1. (a) Binodal curves of diethyl phenylmalonate (1) + acetic acid (2) + water (3): *, 294.0 K; ×, 298.4 K; +, 308.0 K; —, predicted. (b) Binodal curves of diethyl methylmalonate (1) + acetic acid (2) + water (3): *, 294.0 K; ×, 298.0 K; +, 308.0 K; —, predicted.

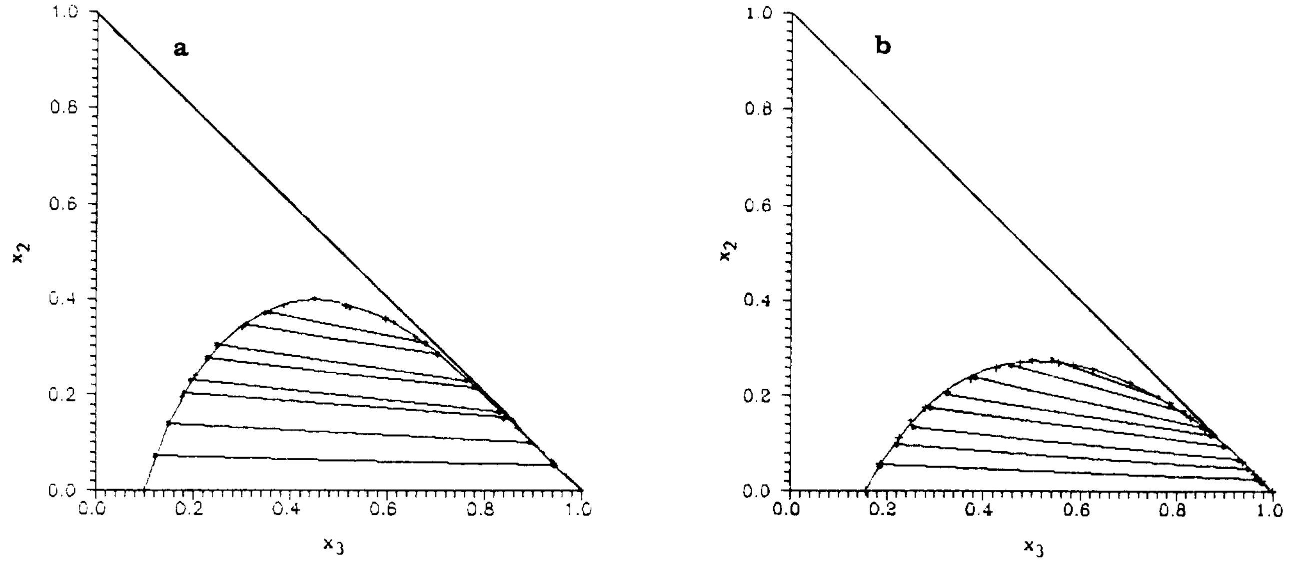

Figure 2. (a) Equilibrium data of the diethyl phenylmalonate (1) + acetic acid (2) + water (3) at 294.0 K: *, experimental equilibrium data; +, experimental binodal curve data; —, predicted. (b) Equilibrium data of the diethyl methylmalonate (1) + acetic acid (2) + water (3) at 294.0 K: *, experimental equilibrium data; +, experimental binodal curve data; —, predicted.

Table VI. Polynomial Approximation Parameters of the Binodal Curves for Diethyl Phenylmalonate (1) + Acetic Acid (2) + Water (3)

T/K	phase	n	C_0	C_1	10^2C_2	10^4C_3	10^5C_4	std dev
294.0	extract	4	−46.1666	6.3480	−19.8428	31.8739	−2.1500	0.1381
	raffinate	3	−40.0490	3.7627	−5.3810	2.0188		0.0872
298.4	extract	4	−92.3137	10.5961	−34.0570	51.5960	−3.0719	0.2775
	raffinate	3	−37.5942	3.6873	−5.3183	2.0071		0.0791
308.0	extract	3	−428.3899	32.7579	−76.9600	60.4330		0.0622
	raffinate	3	−64.3628	4.6632	−6.5051	2.4865		0.0480

Table VII. Polynomial Approximation Parameters of the Binodal Curves for Diethyl Methylmalonate (1) + Acetic Acid (2) + Water (3)

T/K	phase	n	C_0	C_1	10^2C_2	10^4C_3	10^6C_4	std dev
294.0	extract	4	−40.8599	3.4886	−6.1051	4.1127	−0.8163	0.02176
	raffinate	4	5.9610	0.8928	−0.9664	0.1481	−0.1378	0.01444
	both	4	−41.1072	3.5390	−6.4671	5.1524	−1.8182	0.05332
298.0	extract	4	−60.9629	5.5621	−14.7224	19.8682	−11.3565	0.05039
	raffinate	4	36.1087	−1.0985	3.6042	−4.2809	1.4113	0.04119
	both	4	−45.4708	3.6762	−6.6576	5.3111	−1.8804	0.19846
308.0	extract	4	−131.5566	12.8318	−42.4372	65.6629	−39.0581	0.04298
	raffinate	4	−13.6850	1.3982	−1.1544	−0.2511	0.1421	0.06743
	both	4	−61.5648	4.7660	−9.4417	8.3321	−3.0472	0.46588

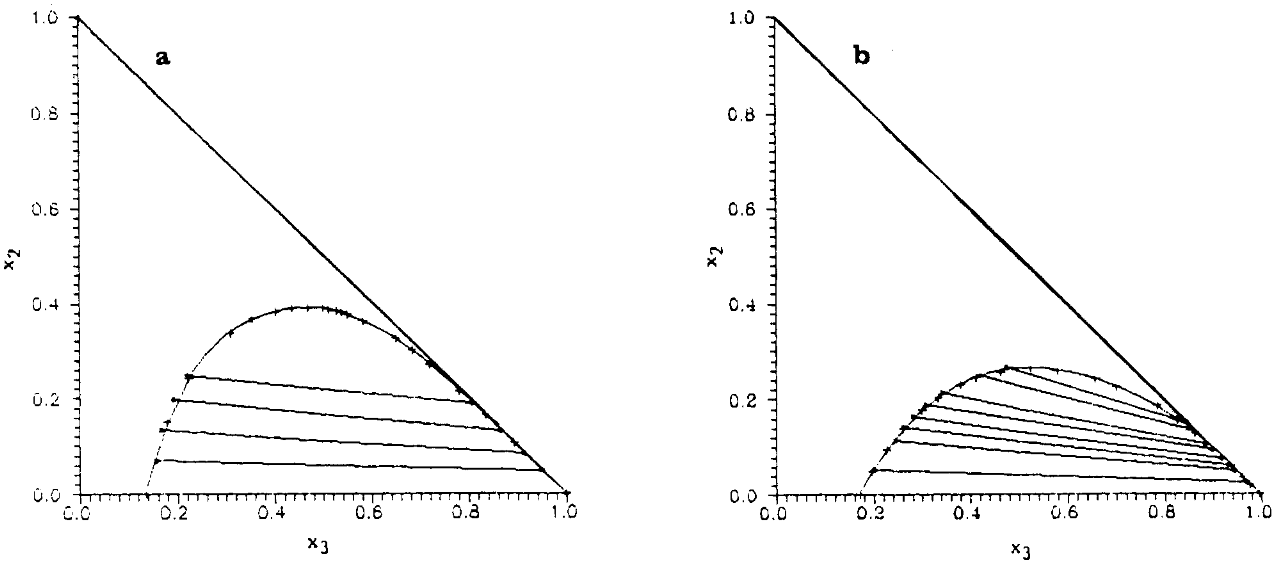

Figure 3. (a) Equilibrium data of the diethyl phenylmalonate (1) + acetic acid (2) + water (3) at 298.4 K: *, experimental equilibrium data; +, experimental binodal curve data; —, predicted. (b) Equilibrium data of the diethyl methylmalonate (1) + acetic acid (2) + water (3) at 298.0 K: *, experimental equilibrium data; +, experimental binodal curve data; —, predicted.

Table VIII. Results of the Least-Squares Analysis for Diethyl Phenylmalonate (1) + Acetic Acid (2) + Water (3) at 294.0 and 298.4 K

			T/K = 294.0			T/K = 298.4		
correlation	eq	i	a_i	b_i	R_i^2	a_i	b_i	R_i^2
Bachman	2	1	113.4442	−20.2957	0.8897	142.6270	−39.9709	0.9861
Othmer–Tobias	3	2	1.5540	1.1217	0.9694	1.0456	0.8143	0.9876
Hand	4	3	−0.9041	0.7875	0.9919	−0.8706	0.8472	0.9999
selectivity	5	4	0.6806	0.6061	0.9970	0.5117	0.6379	0.9852

Table IX. Results of the Least-Squares Analysis for Diethyl Methylmalonate (1) + Acetic Acid (2) + Water (3) at 294.0 and 298.0 K

			T/K = 294.0			T/K = 298.0		
correlation	eq	i	a_i	b_i	R_i^2	a_i	b_i	R_i^2
Othmer–Tobias	3	2	2.5063	1.1186	0.9510	2.1699	0.9612	0.8847
Hand	4	3	−1.5109	0.7592	0.9842	−1.5873	0.7659	0.9896
selectivity	5	4	0.0690	0.6552	0.9975	−0.4372	0.7273	0.9688

The tie-line data of the mixture diethyl phenylmalonate + acetic acid + water and diethyl methylmalonate + acetic acid + water were correlated by the Bachman, Hand, Othmer–Tobias, selectivity, and regression methods.

Bachman method

$$x_{3,\mathrm{R}} = a_1 + b_1(x_{3,\mathrm{R}}/x_{1,\mathrm{E}}) \tag{2}$$

Othmer–Tobias method

$$\ln \frac{1 - x_{1,\mathrm{E}}}{x_{1,\mathrm{E}}} = a_2 + b_2 \ln \frac{1 - x_{3,\mathrm{R}}}{x_{3,\mathrm{R}}} \tag{3}$$

Hand method

$$\ln (x_{2,\mathrm{R}}/x_{3,\mathrm{R}}) = a_3 + b_3 \ln (x_{2,\mathrm{E}}/x_{1,\mathrm{E}}) \tag{4}$$

selectivity method

$$\ln (x_{2,\mathrm{R}}x_{1,\mathrm{E}}/x_{1,\mathrm{R}}x_{2,\mathrm{E}}) = a_4 + b_4 \ln (x_{1,\mathrm{E}}x_{3,\mathrm{R}}/x_{3,\mathrm{E}}x_{1,\mathrm{R}}) \tag{5}$$

The parameters a_j and b_j (j = 1–4) of eqs 2–5 were obtained by using the least-squares method starting from experimental tie-line data in Tables IV and V. The parameters and the correlation coefficients are given in Tables VIII and IX.

For the evaluation of the plait point at 294 and 298 K, the Hand, Othmer–Tobias, and Bachman equations were taken and the system of these independent nonlinear equations was solved in the unknowns $x_{3,\mathrm{R}}$, $x_{2,\mathrm{R}}$, and $x_{2,\mathrm{E}}$, with $x_{3,\mathrm{E}}$ chosen as the independent variable. The composition of the mixture must be the same at the plait point: $x_{1,\mathrm{E}} = x_{1,\mathrm{R}}$, $x_{2,\mathrm{E}} = x_{2,\mathrm{R}}$, and $x_{3,\mathrm{R}} = x_{3,\mathrm{R}}$. Practically the same plait value was obtained.

The distribution coefficients of acetic acid for diethyl methylmalonate + acetic acid + water are drawn and smoothed by using a polynomial approximation. The coefficients of the polynomials are given in Table X. The plait point is calculated by the extrapolation of this polynomial at $x_{2,\mathrm{E}} = x_{2,\mathrm{R}}$. The experimental data, plait point and smoothed curve are presented in Figure 4. The mean values of plait point composition are given in Table XI.

The distribution coefficients of the acetic acid were calculated from eq 6.

$$\alpha = x_{2,\mathrm{E}}/x_{2,\mathrm{R}} \tag{6}$$

Results and Discussion

The binodal curve results are reported in Tables II and III at 294, 298, and 308 K. Binodal curve results can be calculated within ±0.2 K by using the parameters given in Tables VI and VII.

The tie-line results are given in Tables IV and V at 294 and 298 K. The liquid–liquid equilibrium data for the systems

Table X. Polynomial Approximation Parameters of the Distribution of Acetic Acid Obtained from Equilibrium Data for Diethyl Methylmalonate + Acetic Acid + Water

T/K	n	C_0	C_1	C_2	10^2C_3	10^4C_4	std dev
294.0	4	−0.8240	2.7983	−0.1535	0.9049	−2.4106	0.134 39
298.0	4	−3.4118	4.1125	−0.2919	1.5175	−3.4648	0.213 46

Table XI. Plait Point Compositions Obtained from the Hand, Othmer–Tobias, and Bachman Equations

	diethyl phenylmalonate (1) + acetic acid (2) + water (3)		diethyl methylmalonate (1) + acetic acid (2) + water (3)	
T/K	x_2	x_3	x_2	x_3
294.0	0.3865	0.4640	0.2369	0.6788
298.0			0.2344	0.6803
298.4	0.3757	0.4805		

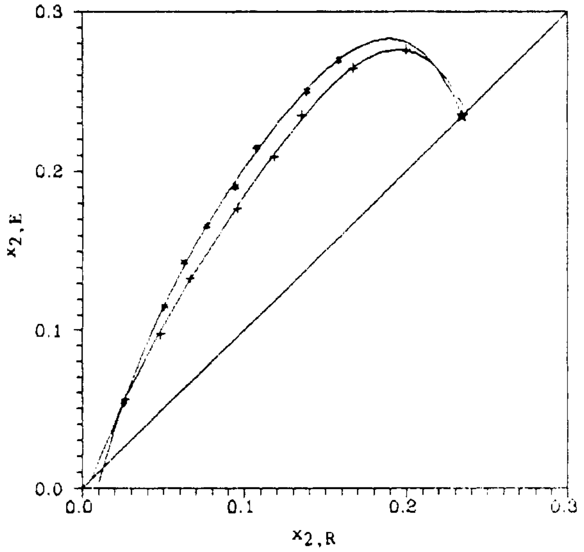

Figure 4. Distribution curve of acetic acid for diethyl methylmalonate (1) + acetic acid (2) + water (3): *, 294.0 K; +, 298.0 K; —, predicted. $x_{2,R}$ = mole fraction of acetic acid in raffinate phase; $x_{2,E}$ = mole fraction of acetic acid in extract phase.

under consideration can be obtained by using the parameters given in Tables VIII and IX. The tie-line data at 294 K are correlated by the selectivity, Hand, Othmer–Tobias, and Bachman methods. Tables VIII and IX also contain the correlation coefficients for the four methods and show that the selectivity method fits the data better than the other correlations at 294 K.

The distribution coefficients of the acetic acid were calculated and are given in Tables IV and V. Diethyl phenylmalonate and diethyl methylmalonate can be used as solvents for the extraction of acetic acid from its aqueous solution.

Glossary

a_j, b_j	parameters of eqs 2–5
C	parameters in polynomial approximation eq 1
n	number of parameters
T	temperature
$x_{i,k}$	molar fraction of components in k phase
α	distribution coefficient of the acetic acid

Subscripts

E	extract phase
i	number of components
R	raffinate phase
j	number of parameters

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