LIQUID-VAPOUR EQUILIBRIUM. IL.*

PHASE EQUILIBRIA IN THE TERNARY SYSTEM ETHYL ACETATE-ETHANOL-WATER

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The vapour–liquid and liquid–liquid equilibria were measured in the ternary system ethyl acetate–ethanol–water and pertaining binary systems at 70, 55 and 40°C as a part of a broader study examining the possibility of prediction of behaviour of polycomponent systems from the binary data.

The title system with three binary and one ternary azeotrope and a limited solubility of the components in the liquid phase was selected as a model system to test the adequacy of the classic III and IV suffix Margules equation[1] as well as the recent Renon–Prausnitz[2] NRTL equation for prediction of phase equilibria in multicomponent systems with several liquid phases from the binary data[3]. The experimental equilibrium data of this system have been published[4,5]. The data, however, were measured by different authors at different temperatures (and most likely with different accuracies) and their use could misrepresent the results of prediction.

EXPERIMENTAL

Materials

Ethyl acetate was prepared from a product of laboratory grade purity (Lachema, Brno) by triple distillation with acetic anhydride[6] in a laboratory 40-plate bubble-cap glass column. Ethanol was distilled from a 96% product in a 40-plate column. The distillate (about 96% weight water azeotrope) was partly distilled once again and used, partly desiccated by azeotropic distillation with benzene[6]. The residual moisture was removed by adsorption on a molecular sieve Nalsit 3 A in a 150 cm long glass column. Measured physical constants of chemicals are summarized in Table I.

The temperature dependence of the vapour pressure of ethyl acetate and ethanol was measured in an equilibrium still and correlated by the empirical Antoine equation[7]

$$\log P_i^0 = A_i - B_i/(t + C_i)\,, \tag{1}$$

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TABLE I

Physical Constants of Compounds

Constant		Found	Literature
		Ethyl acetate	
d_4^{20}		0·90057	0·90063[6]
n_D^{20}		1·37242	1·37239[6]
norm. b.p., °C		77·06	77·114[6]
Antoine	A	7·08520	7·10233[9]
const.	B	1 231·470	1 245·239[9]
	C	215·84	217·911[9]
		Ethanol	
d_4^{20}		0·78942	0·78934[6]
n_D^{20}		1·36132	1·36139[6]
norm. b.p., °C		78·28	78·325[6]
Antoine	A	8·27621	8·16290[9]
const.	B	1 685·632	1 623·220[9]
	C	234·15	228·980[9]
		Water	
n_D^{20}		1·3330	1·33296[6]

TABLE II

Density and Refractive Index along Solubility Line in the System Ethyl Acetate–Ethanol–Water at 20°C

w_1, %	w_2, %	d_4^{20}	n_D^{20}	w_1,%	w_2,%	d_4^{20}	n_D^{20}
7·31	0	0·9981	1·3383	38·79	20·45	0·9330	—
7·04	2·74	0·9935	1·3394	41·90	20·30	0·9295	1·3646
6·83	4·09	0·9924	1·3406	43·09	20·17	0·9285	—
6·99	6·83	0·9869	1·3427	50·00	19·66	0·9213	1·3663
7·94	9·03	0·9840	1·3499	54·90	18·99	0·9171	1·3678
11·94	15·47	0·9711	1·3511	58·34	18·14	0·9146	1·3685
14·61	17·36	0·9653	—	67·26	15·61	0·9090	1·3699
16·44	18·25	0·9619	1·3545	77·86	11·09	0·9048	1·3700
23·00	20·00	0·9515	1·3582	87·81	6·22	0·9030	1·3716
28·14	20·41	0·9450	—	93·18	3·19	0·9020	1·3719
32·06	20·62	0·9402	1·3615	97·04	0	0·9057	1·3724

TABLE III

Vapour–Liquid Equilibrium Data in System Ethyl Acetate–Ethanol

x_1 mol %	y_1 mol %	P Torr	x_1 mol %	y_1 mol %	P Torr	x_1 mol %	y_1 mol %	P Torr
$t = 70°C$			$t = 55°C$			$t = 40°C$		
0·65	1·75	548·6	0·55	1·85	284·3	0·60	2·20	136·6
1·8	4·6	559·4	3·7	10·4	302·5	4·4	14·4	150·9
13·1	23·7	633·6	8·3	20·1	325·2	8·4	22·7	163·1
21·0	32·1	664·6	15·1	29·7	349·7	18·7	37·0	183·0
26·3	36·7	680·4	19·6	34·8	360·3	24·2	42·8	191·9
38·7	45·4	703·8	24·3	38·9	371·6	32·0	48·4	199·7
45·2	49·3	710·0	34·0	45·3	386·4	45·4	56·0	208·3
48·8	51·7	712·2	46·4	52·1	397·5	49·5	57·4	210·2
62·5	59·7	711·2	59·2	60·1	402·0	55·2	60·7	211·8
69·1	64·1	706·4	68·2	65·2	400·9	66·3	66·4	213·2
75·5	68·1	697·8	71·5	67·4	399·5	74·9	71·6	212·1
82·2	74·7	679·2	85·3	78·6	385·2	88·5	82·9	204·6
90·3	83·9	651·6	89·8	83·9	376·5	92·0	87·1	200·6
93·2	88·8	635·4	94·4	90·2	365·0	96·0	92·8	195·3
97·5	94·8	615·6	—	—	—	—	—	—

TABLE IV

Vapour–Liquid Equilibrium in System Ethyl Acetate–Water

x_1 mol %	y_1 mol %	P Torr	x_1 mol %	y_1 mol %	P Torr	x_1 mol %	y_1 mol %	P Torr
$t = 70°C$			$t = 55°C$			$t = 40°C$		
0·004	0·15	233·9	0·012	0·52	118·85	0·011	0·38	55·66
0·010	0·56	234·9	0·017	0·81	119·25	0·012	0·54	55·84
0·015	0·84	235·7	0·018	0·81	119·30	0·012	0·55	55·84
0·016	0·85	235·7	96·95	90·93	372·0	96·48	90·22	202·7
96·76	90·59	646·3	96·99	90·85	371·7	97·46	92·46	199·5
97·23	91·73	641·1	97·80	93·82	364·7	98·07	94·31	197·3
97·88	93·95	630·6	98·94	96·76	358·0	98·79	96·49	193·9
98·55	96·30	623·1	99·27	98·46	352·2	99·42	98·84	190·5
99·27	98·26	610·3	—	—	—	—	—	—

TABLE V

Vapour–Liquid Equilibrium Data in System Ethanol–Water

x_1 mol %	y_1 mol %	P Torr	x_1 mol %	y_1 mol %	P Torr	x_1 mol %	y_1 mol %	P Torr
	$t = 70°C$			$t = 55°C$			$t = 40°C$	
6·2	37·4	362·5	5·1	33·6	173·35	6·2	37·4	75·14
9·5	43·9	399·0	8·5	42·8	197·8	7·7	40·6	89·00
13·1	48·2	424·0	10·6	46·1	207·5	9·8	45·0	94·60
19·4	52·4	450·9	18·0	52·4	227·3	12·8	48·8	101·50
25·2	55·2	468·0	23·0	55·5	236·3	18·1	54·3	109·00
33·4	58·3	485·5	32·4	58·9	248·2	31·9	59·8	116·90
40·1	61·1	497·6	42·9	62·8	258·0	39·9	62·8	121·05
59·3	69·1	525·9	55·3	68·0	267·0	51·1	67·6	125·50
68·0	73·9	534·3	68·5	74·6	274·9	68·3	74·6	130·40
79·3	81·6	542·7	77·4	80·1	278·4	77·4	80·9	132·50
81·0	82·6	543·1	81·0	82·9	279·4	81·0	82·9	132·80
94·3	94·1	544·5	89·4	89·8	280·6	87·5	87·9	133·50
94·7	94·5	544·5	95·4	95·2	280·5	95·7	95·6	133·80

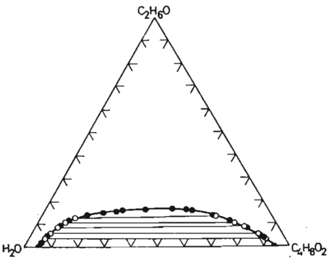

FIG. 1

Liquid–Liquid Equilibrium (weight fraction) of the System Ethyl Acetate(1)–Ethanol(2)–Water(3) at 70°C

● Data from solubility curve, ○—○ conjugated liquid phases.

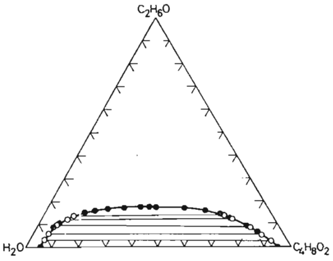

FIG. 2

Liquid–Liquid Equilibrium (weight fraction) of the System Ethyl Acetate(1)–Ethanol(2)–Water(3) at 55°C

● Data from solubility curve, ○—○ conjugated liquid phases.

where P_i^0 is the vapour pressure of substance i in Torr, t is the temperature in °C and A_i, B_i and C_i are empirical parameters. The values of these parameters are summarized in Table I. The mean deviation of the experimental values of the vapour pressure calculated from (*1*) was ±0·16 Torr (ethyl acetate), respectively ±0·18 Torr (ethanol), *i.e.* ±0·07% rel. in both cases.

TABLE VI

Vapour–Liquid Equilibrium Data in System Ethyl Acetate–Ethanol–Water

x_1 mol %	x_2 mol %	y_1 mol %	y_2 mol %	P Torr
		$t = 70$°C		
30·2	46·4	43·3	38·8	710·8
3·5	92·3	8·7	86·3	577·8
1·2	56·2	5·5	66·2	538·4
16·2	48·2	32·6	42·6	664·8
73·8	24·6	69·4	25·6	742·8
16·3	19·0	50·3	18·6	702·2
3·4	23·1	26·0	39·6	572·0
79·8	12·6	71·3	16·2	722·5
30·4	65·7	41·2	56·0	695·9
		$t = 55$°C		
27·4	51·2	44·1	38·7	385·2
2·0	93·9	7·3	91·0	295·3
1·0	60·5	3·7	69·3	277·2
15·6	44·6	39·4	39·0	267·7
67·3	21·0	65·5	21·4	416·4
13·7	21·3	50·5	22·6	384·7
2·4	22·3	25·4	40·7	295·3
0·13	5·7	1·43	35·1	177·4
84·9	9·1	76·7	12·8	404·8
34·4	60·3	46·1	48·0	374·9
		$t = 40$°C		
21·1	50·8	44·8	38·1	194·7
0·32	61·8	3·4	73·1	161·5
15·2	46·8	41·4	38·0	185·9
70·0	19·9	68·9	20·1	219·6
10·3	20·0	50·1	22·9	197·8
1·9	20·6	21·7	40·0	142·3
0·01	6·42	1·2	37·5	84·45
88·0	7·4	78·9	10·1	215·0
30·7	61·4	48·8	44·9	200·7

Vapour–Liquid Equilibria

The equilibria between liquid and gas phases were measured in a modified Gillespie still[8]. The construction of the apparatus necessitates that both the liquid phase and the condensate of the gas phase be homogeneous. The boiling point temperature was measured by a mercury thermometer with an accuracy ±0·01°C. The pressure was measured indirectly by the boiling point of water in a connected ebulliometer; the boiling point of water was measured by mercury thermometers calibrated by means of a platinum resistance thermometer and Mueller resistance bridge (Leeds & Northrup) with an accuracy ±0·01°C. The corresponding error of the total pressure is about ±0·05% rel. The total volume of the sample in the equilibrium still was 150 ml. The sampling, *i.e.* venting the apparatus into the atmosphere and taking samples by syringes, took place after at least two hours of boiling.

TABLE VII

Solubility Lines (w. %) in System Ethyl Acetate–Ethanol–Water

40°C		55°C		70°C	
w_1	w_2	w_1	w_2	w_1	w_2
6·27	0	5·49	0	5·14	0
6·12	1·18	5·76	6·09	5·36	2·45
5·80	2·14	6·36	8·93	5·65	4·73
6·03	6·90	7·57	10·52	8·85	9·34
7·21	9·10	10·24	12·09	11·56	11·70
11·58	14·23	15·39	15·32	13·20	12·39
13·00	15·14	18·94	16·08	13·90	12·40
16·21	16·44	21·79	16·43	17·15	13·69
19·13	17·22	22·86	16·81	23·07	15·41
25·17	18·18	24·14	16·81	24·07	15·57
27·60	18·45	29·08	17·38	27·21	15·79
30·84	18·66	35·12	18·05	28·40	16·09
35·73	18·81	38·40	18·05	32·08	16·34
39·91	18·84	40·71	17·89	36·81	16·60
44·73	18·82	51·96	17·50	41·14	16·84
49·51	18·64	60·60	15·71	47·72	17·03
55·92	17·71	67·04	14·06	53·72	16·62
62·49	16·48	67·76	13·73	55·40	16·22
68·98	14·00	70·61	13·01	62·91	14·72
71·70	13·33	79·07	9·16	64·60	14·17
78·49	10·07	84·28	6·74	72·71	11·47
83·73	7·49	87·39	5·11	82·38	7·23
87·01	5·95	95·24	0	86·77	5·07
91·73	3·31	—	—	88·59	3·89
96·12	0	—	—	94·39	0

Table VIII

Liquid–Liquid Equilibrium Data in System Ethyl Acetate–Ethanol–Water

Water phase				Ester phase			
w_1	w_2	x_1	x_2	w_1	w_2	x_1	x_2
w. %		mol %		w. %		mol %	
t = 70°C							
5·9	3·1	1·3	1·3	89·3	3·3	67·8	4·7
7·9	5·8	1·8	2·7	85·4	5·9	61·2	7·9
8·9	9·1	2·1	4·1	78·3	9·3	50·0	11·3
9·8	10·9	2·3	5·0	72·7	11·3	42·1	12·5
13·2	12·9	3·3	6·2	64·9	14·2	33·4	14·0
t = 55°C							
5·5	3·9	1·2	1·7	91·7	2·5	73·5	3·7
6·1	6·1	1·4	2·6	86·0	6·1	63·2	8·6
7·6	9·7	1·8	4·3	80·9	8·8	54·6	11·4
10·0	12·5	2·4	5·8	73·0	11·9	43·1	13·4
12·0	13·4	3·0	6·4	68·1	13·7	37·2	14·5
t = 40°C							
5·9	4·7	1·3	2·0	92·4	2·7	76·0	4·3
6·6	7·4	1·5	3·2	87·5	5·8	66·8	8·5
7·8	10·3	1·8	4·6	81·5	9·2	56·3	12·1
11·3	13·6	2·8	6·4	72·7	12·5	43·2	14·4
16·2	16·7	4·3	8·5	62·1	16·3	31·2	15·7

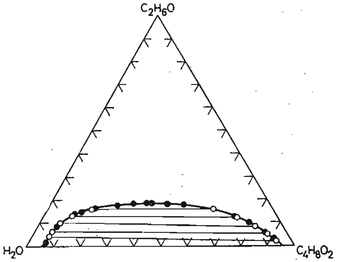

Fig. 3

Liquid–Liquid Equilibrium (weight fraction) of the System Ethyl Acetate(1)–Ethanol(2)–Water(3) at 40°C

● Data from solubility curve, o—o conjugated liquid phases.

The binary solutions were analyzed by measuring the density in modified Sprengel–Ostwald pycnometers[2] of the volume 10 and 25 ml, or by refractometry using a Zeiss refractometer (the water-rich ethyl acetate–water solutions). Concentration dependences of the density and the refractive index were determined by measuring sets of samples of known concentration. The concentration dependence of the ethanol–water solutions was taken, after verification, from the handbook[6]. The errors of analyses of the binary solutions were ±0·05% mol (ethyl acetate–ethanol and ethyl acetate–water by the density method), ±0·1% mol. (ethanol–water by the density method) and ±0·002% mol (ethyl acetate–water by refractometry). The ternary analyses were carried out by titrating until the solubility line at 20°C.

Liquid–Liquid Equilibria

The binary solubility and the solubility line in the ternary system were determined by titration in a temperature controlled vessel of the volume 30 or 60 ml with a magnetic stirrer. A reflux condenser prevented the solution from evaporation during titration. The jacket of the vessel was connected by an insulated tube with a thermostat keeping the temperature with an accuracy ±0·01°C at 20°C and ±0·05°C at 70°C. The observation of the changes inside the vessel was facilitated by shielding the vessel and its intensive illumination.

To determine the solubilities, the suitable component was added from a buret to the weighed sample in the vessel until a slight turbidity indicating the presence of two phases appeared or disappeared. To determine the composition of the conjugated phases, weighed heterogeneous solution was stirred for at least two hours and then transferred into a glass tube and placed into the thermostat. After a thorough separation of phases, samples were taken for analysis by a syringe.

The analysis of the ternary mixture was carried out by titrating the homogeneous or heterogeneous sample at 20°C until the point of turbidity. The composition of the mixture in this point was found by determining the density of the solution. The titrations were carried out so as to keep the point corresponding to the resulting composition of the mixture approximately in the middle of the solubility line where the transition between the homogeneous and heterogeneous region is in both directions most conspicious. When the composition of the sample could not be estimated in advance, a test experiment was made with 1—2 ml of the sample in a glass tube and the resulting composition was determined by the refractive index. The proper analysis was then carried out with the optimum ratio of the components added. To determine the concentration dependence of density of the solutions along the solubility line, densities and refractive indices of the mixtures resulting from the determination of the solubility line at 20°C were measured (Table II). The dependence of density on composition of the sample (resp. the weight fraction of ester) as well as the dependence of the concentration of alcohol on the concentration of ester in the middle section of the solubility line was smoothed by six-constant equation

$$d_4^{20} = 1{\cdot}00189 - 0{\cdot}35682 w_1 + 0{\cdot}93943 w_1^2 - 1{\cdot}8560 w_1^3 + 1{\cdot}8755 w_1^4 - 0{\cdot}70553 w_1^5 \qquad (2)$$

and

$$w_2 = 0{\cdot}037570 + 1{\cdot}6434 w_1 - 6{\cdot}3661 w_1^2 + 12{\cdot}474 w_1^3 - 12{\cdot}415 w_1^4 + 4{\cdot}6396 w_1^5\,, \qquad (3)$$

where w_1 and w_2 are weight fractions of ester and alcohol and d_4^{20} is the density of the mixture. Functions (*2*) and (*3*) were tabulated. The mean deviation of the calculated and experimental values is ±0·00012 g/ml and ±0·06% weight, respectively. The average error of the analysis of the ternary mixture, as was found by analysing the samples of known composition, was ±0·3% weight.

RESULTS

Experimental data of vapour–liquid equilibrium in the binary systems ethyl acetate–ethanol, ethyl acetate–water and ethanol–water are summarized in Table II through VI. All points in systems with a limited miscibility of the components in the liquid phase (*i.e.* ester–water and the ternary system) fall into the single liquid phase area. Tables VII and VIII and Figs 1 – 3 show the results of determination of the solubility line and the equilibrium between two conjugated liquid phases in the ternary system. All data were measured at 70, 55 and 40°C.

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