

LIQUID-VAPOUR EQUILIBRIUM. LIV.*

THE SYSTEMS ETHYL ACETATE-BENZENE, ETHYL ACETATE-TOLUENE AND ETHYL ACETATE-ETHYLBENZENE

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Vapour-liquid equilibria have been measured in the systems ethyl acetate-benzene, ethyl acetate-toluene, and ethyl acetate-ethylbenzene at 50, 60, and 70°C. The modified circulation still of the Gillespie type has been used for the measurements. The measured data have been correlated by means of the equations expressing the dependence of activity coefficients on the composition of the liquid phase.

As part of a systematic study of thermodynamic properties of binary mixtures whose components belong to various groups of Ewell's classification of liquids¹, the isothermal vapour-liquid equilibria have been measured for binary systems of ethyl acetate with three aromatic hydrocarbons.

EXPERIMENTAL

Preparation of pure substances and criteria of purity. Ethyl acetate, the reagent grade chemical (Lachema, Brno), was twice rectified on a 40 plate column after adding acetic anhydride (50 ml per 1 l of ester). The physical constants of ethyl acetate prepared in this way were: d_4^{20} 0.90063 g/cm³ (ref.² 0.90063), n_D^{20} 1.37242 (ref.² 1.37243), b.p. 77.13°C (ref.² 77.15). The purification of benzene, toluene, and ethylbenzene and their physical constants were given in the preceding paper³.

Apparatus and procedure. The apparatus and equipment used for measuring the vapour-liquid equilibria was described previously³. The samples of equilibrium phases were analyzed refractometrically at 20°C. For the system ethyl acetate-benzene, a refractometer with interchangeable prisms (Zeiss, Jena) enabling to read the fifth decimal place was used. For the other systems, the refractive indices were measured by an Abbe refractometer with an accuracy of ± 0.0001 . On the basis of calibration binary mixtures (Table I), interpolation tables were computed for reading off the composition from the measured values of refractive indices of the equilibrium samples.

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TABLE I

Refractive Indices of the Binary Solutions of Ethyl Acetate with Aromatic Hydrocarbons at 20°C

Ethyl acetate(1)-benzene(2)		Ethyl acetate(1)-toluene(2)		Ethyl acetate(1)-ethylbenzene(2)	
x_1	n_D^{20}	x_1	n_D^{20}	x_1	n_D^{20}
0.0934	1.4871	0.1227	1.4822	0.1449	1.4804
0.1219	1.4829	0.1893	1.4741	0.1964	1.4749
0.1934	1.4729	0.2877	1.4621	0.3292	1.4603
0.2606	1.4636	0.3219	1.4586	0.4299	1.4486
0.3160	1.4560	0.4703	1.4402	0.5178	1.4381
0.3795	1.4473	0.5924	1.4250	0.6067	1.4265
0.4786	1.4346	0.5984	1.4243	0.6928	1.4151
0.5784	1.4220	0.7672	1.4029	0.7779	1.4040
0.6838	1.4091	0.8138	1.3964	0.8620	1.3930
0.7816	1.3972	0.9056	1.3843	0.9276	1.3830
0.8904	1.3849				

TABLE II

Antoine Vapour Pressure Constants

Compound	<i>A</i>	<i>B</i>	<i>C</i>	Ref.
Ethyl acetate	7.10233	1 245.239	217.911	4
Benzene	6.90565	1 211.033	220.790	5
Toluene	6.95334	1 343.943	219.377	5
Ethylbenzene	6.95719	1 424.255	213.206	5

RESULTS

The measured vapour-liquid equilibrium data were correlated by the third and fourth order Margules equations, the Wilson equation, and by the second order expansion of relative volatility relation. The procedure and relations used are given in the preceding paper³. The constants of the Antoine vapour pressure equation for the pure substances were taken over from the literature (Table II). The experimental vapour-liquid equilibrium data, the constants of the above-mentioned equations and mean deviations of the calculated and experimental values are given in Tables III-V.

TABLE III
Vapour-Liquid Equilibrium in the Ethyl Acetate(1)-Benzene(2) System

50°C			60°C			70°C		
x_1	y_1	P, Torr	x_1	y_1	P, Torr	x_1	y_1	P, Torr
0.1497	0.1641	277.49	0.5702	0.5822	417.37	0.1486	0.1595	567.14
0.3346	0.3519	281.34	0.6338	0.6428	418.30	0.3302	0.3538	579.65
0.4580	0.4696	282.70	0.6841	0.6908	419.00	0.5650	0.5835	591.63
0.5697	0.5783	283.71	0.7595	0.7646	419.61	0.6523	0.6643	594.50
0.8545	0.8549	285.79	0.8200	0.8205	419.92	0.6519	0.6638	594.50
0.6289	0.6342	284.57	0.1225	0.1422	399.77	0.6995	0.7083	596.50
0.6708	0.6746	284.81	0.3124	0.3302	409.85	0.6974	0.7070	596.50
0.7170	0.7182	285.02	0.3904	0.4079	412.88	0.7510	0.7578	597.94
0.7629	0.7646	285.42	0.4724	0.4900	415.39	0.7765	0.7807	598.43
0.7599	0.7616	285.42	—	—	—	0.8029	0.8058	598.71
0.8162	0.8162	285.60	—	—	—	0.8282	0.8295	599.80
0.8637	0.8637	285.83	—	—	—	0.8545	0.8558	599.91
0.8976	0.8976	285.95	—	—	—	—	—	—

Equation Order	Temperature °C	A_{12}	A_{21}	D_{12}	Dev. ^a
Margules 3	50	0.0388	0.0283	—	0.0006
	60	0.0450	0.0298	—	0.0016
	70	0.0378	0.0399	—	0.0018
Margules 4	50	0.0300	0.0213	—0.0240	0.0006
	60	0.0824	0.0678	0.1032	0.0010
	70	0.0138	0.0222	—0.0609	0.0018
Wilson	50	0.7243	1.2313	—	0.0007
	60	0.6390	1.3362	—	0.0016
	70	1.0009	0.9117	—	0.0015
Alpha 2	50	0.1276	0.0311	—	0.0010
	60	0.1564	0.0261	—	0.0016
	70	0.1542	0.0030	—	0.0015

^a Mean deviation in the vapour phase composition.

TABLE IV
Vapour-Liquid Equilibrium in the Ethyl Acetate(1)-Toluene(2) System

50°C			60°C			70°C		
x_1	y_1	P , Torr	x_1	y_1	P , Torr	x_1	y_1	P , Torr
0.029	0.064	273.6	0.029	0.064	400.9	0.029	0.064	577.2
0.047	0.107	266.7	0.044	0.107	389.9	0.052	0.114	560.4
0.071	0.154	258.9	0.069	0.153	380.2	0.075	0.145	548.1
0.084	0.192	253.2	0.086	0.199	369.0	0.095	0.196	527.4
0.108	0.243	244.3	0.108	0.237	360.1	0.113	0.228	520.0
0.137	0.283	236.7	0.131	0.283	347.9	0.138	0.285	498.7
0.170	0.352	225.2	0.162	0.345	332.5	0.159	0.334	482.5
0.183	0.385	219.4	0.186	0.391	321.4	0.190	0.393	459.9
0.228	0.464	206.0	0.226	0.454	304.2	0.264	0.488	425.0
0.294	0.559	188.8	0.301	0.556	277.9	0.301	0.544	404.4
0.397	0.658	168.9	0.399	0.660	247.9	0.407	0.675	356.3
0.489	0.758	149.2	0.478	0.749	223.4	0.471	0.737	329.9
0.536	0.794	141.1	0.552	0.801	207.4	0.561	0.802	299.1
0.560	0.818	131.9	0.575	0.828	198.2	0.583	0.828	292.9
0.575	0.822	131.3	0.588	0.834	197.9	0.604	0.843	286.4
0.649	0.862	125.7	0.639	0.853	189.4	0.646	0.846	280.3
0.734	0.904	116.4	0.735	0.904	172.7	0.752	0.909	250.8
0.795	0.928	109.2	0.786	0.921	162.4	0.780	0.918	245.5
0.851	0.951	104.4	0.860	0.951	152.7	0.869	0.953	224.6

Equation Order	Temperature °C	A_{12}	A_{21}	D_{12}	Dev. ^a
Margules 3	50	-0.1279	-0.0230	—	0.0045
	60	-0.1196	0.0035	—	0.0044
	70	-0.1441	-0.0118	—	0.0059
Margules 4	50	-0.1202	-0.0128	0.0309	0.0046
	60	-0.0696	0.0702	0.2003	0.0043
	70	-0.1341	0.0019	0.0401	0.0058
Wilson	50	2.9952	0.0817	—	0.0070
	60	2.9637	0.0656	—	0.0052
	70	3.0386	0.0694	—	0.0086
Alpha 2	50	1.6922	-0.8239	—	0.0095
	60	1.6989	-0.8097	—	0.0076
	70	1.5532	-0.8128	—	0.0110

^a Mean deviation in the vapour phase composition.

TABLE V
Vapour-Liquid Equilibrium in the Ethyl Acetate(1)-Ethylbenzene(2) System

50°C			60°C			70°C		
x_1	y_1	P , Torr	x_1	y_1	P , Torr	x_1	y_1	P , Torr
0.016	0.101	38.3	0.016	0.088	59.8	0.016	0.073	90.7
0.028	0.168	41.7	0.033	0.204	67.3	0.024	0.123	95.9
0.047	0.294	48.9	0.054	0.330	77.8	0.035	0.208	104.4
0.102	0.515	58.5	0.102	0.498	99.6	0.056	0.320	119.7
0.118	0.558	70.8	0.189	0.665	138.6	0.094	0.455	140.7
0.211	0.703	98.7	0.227	0.713	153.0	0.169	0.610	187.6
0.282	0.764	118.3	0.260	0.735	166.3	0.205	0.671	211.7
0.311	0.800	126.1	0.291	0.777	178.4	0.230	0.703	223.4
0.389	0.844	143.7	0.370	0.829	207.7	0.264	0.742	240.8
0.529	0.899	176.8	0.514	0.885	257.5	0.495	0.870	361.2
0.631	0.919	202.0	0.617	0.921	291.1	0.601	0.904	413.1
0.678	0.941	212.3	0.665	0.933	305.2	0.633	0.925	425.9
0.770	0.961	232.1	0.761	0.953	336.7	0.748	0.949	480.7
0.821	0.968	243.1	0.815	0.968	355.0	0.807	0.962	505.9

Equation Order	Temperature °C	A_{12}	A_{21}	D_{12}	Dev. ^a
Margules 3	50	0.0725	0.0627	—	0.0104
	60	0.0647	0.0985	—	0.0072
	70	0.0590	0.0978	—	0.0105
Margules 4	50	0.0235	-0.0540	-0.2779	0.0088
	60	0.0324	0.0273	-0.1662	0.0065
	70	-0.0055	-0.0363	-0.3256	0.0079
Alpha 2	50	8.1748	-0.7313	—	0.0100
	60	7.6930	-0.7392	—	0.0071
	70	7.1123	-0.7226	—	0.0107

^a Mean deviation in the vapour phase composition.

REFERENCES

- Hála E., Pick J., Fried V., Vilím O.: *Vapour-Liquid Equilibrium*, 2nd Ed. Pergamon Press, London 1967.
- Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Vol. II. Elsevier, New York 1965.
- Linek J., Wichterle I., Polednová J.: *This Journal* 37, 2820 (1972).
- Polák J., Mertl I.: *This Journal* 30, 3526 (1965).
- Dreisbach R. R.: *Physical Properties of Chemical Compounds*. Adv. Chem. Series 15. American Chemical Society 1955.

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