PHASE EQUILIBRIA IN BINARY SYSTEMS CONTAINING ACETALDEHYDE

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The vapour–liquid equilibrium in binary acetaldehyde–diethyl ether, acetaldehyde–ethanol and acetaldehyde–water systems was measured at the pressure of 101·32 kPa. The experimental data were correlated by the two- and three-constant Redlich–Kister equation.

During the production of ethanol by direct hydration of ethylene, we can find among reaction products a mixture of ethanol, water, acetaldehyde and diethyl ether. For the rectification of synthetic ethanol by extractive distillation it is necessary to know the equilibrium data in all of the corresponding binary systems.

EXPERIMENTAL AND RESULTS

Materials used: acetaldehyde, a product of "The British Drug Houses Ltd.", was used without further purification, since the chromatographic analysis indicated at least 99·9% purity. Denaturated ethanol was dehydrated by azeotropic rectification with an additional portion of benzene. Before the measurement itself, ethanol was refluxed with freshly annealed CaO and then rectified again. Diethyl ether was shaken subsequently with an acidified solution of $FeSO_4$ to remove peroxides, with a 0·5% solution of $KMnO_4$ to remove aldehydes and finally with a 5% solution of KOH. Then it was dried with $CaSO_4$ and rectified with sodium. Redistilled water was employed with a specific conductivity of $\sim 4 \cdot 10^{-6} \Omega^{-1} cm^{-1}$. The physico-chemical constants of the substances used are given in Table I. The saturated vapour pressures of pure substances were taken from the literature[1] and their Antoine equation constants are also reported in Table I.

The method of measurements. The modified Gillespie recirculation still was used. The measurements were performed at a constant pressure of 101·32 kPa, the boiling point temperature of the mixture was determined by calibrated Anschütz thermometers. The recirculation vessels containing the liquid and condensed vapour phases were efficiently cooled with a mixture of solid CO_2 and acetone to reduce losses of extremely volatile diethyl ether and acetaldehyde. The low-boiling mixture of acetaldehyde and diethyl ether was heated only by a 250 W infrared lamp. The analysis of samples of both vapour and liquid phases was performed in the following manner; 0·5—1·0 g of the analyzed solution in a sealed ampoule was weighed and broken inside an excess amount of an 0·5M aqueous solution of hydroxylamine hydrochloride. After 30 minutes, this solution was back titrated by an 0·1M solution of NaOH in the presence of bromophenol blue. The maximum error of this analytical method was determined as ±0·3 wt.% on samples with a known composition.

Experimental data are given in Table II and in Fig. 1. The data were correlated by the two- and three-constant Redlich–Kister equation

$$Q = g^E/(2\cdot303RT) = x_1x_2[b + c(x_1 - x_2) + d(x_1 - x_2)^2 + \ldots], \quad (1)$$

$$\log \gamma_1 = x_2^2[b + c(3x_1 - x_2) + d(x_1 - x_2)(6x_1 - 1) + \ldots], \quad (2)$$

$$\log \gamma_2 = x_1^2[b + c(x_1 - 3x_2) + d(x_1 - x_2)(1 - 6x_2) + \ldots]. \quad (3)$$

Constants in this equation for the systems investigated are given in Table III and they were obtained by minimizing the function

$$F = \sum_{i=1}^{N} (y_{1,\text{exp}} - y_{1,\text{vyp}})^2, \quad (4)$$

where N is the number of experimental points. The calculated constants were used for calculating back the vapour phase composition and differences between experimental and calculated values can be found in Table II.

TABLE I

Physico-Chemical Properties of Pure Components

Property[a]	Exp.	Literature	Ref.	Property[a]	Exp.	Literature	Ref.
		Acetaldehyde				Ethanol	
$d_{277.2}^{288.2}$	0·7847	0·7846	1	$d_{277.2}^{293.2}$	0·7895	0·7893—5	2
n.b.p.	293·4	293·4	1	$n_D^{293.2}$	1·3613	1·3614	2
A	—	8·00552	3	n.b.p.	351·5	351·4—6	2
B	—	1 600·017	3	A	—	8·11220	3
C	—	291·809	3	B	—	1 592·864	3
				C	—	226·184	3
		Diethyl ether			Water		
$d_{277.2}^{288.2}$	0·7193	0·7193	2	A	—	7·96681	4
$n_D^{288.2}$	1·3556	1·35555	2	B	—	1 668·2	4
A	—	6·92032	3	C	—	228·0	4
B	—	1 064·066	3				
C	—	228·799	3				

[a] A, B, C are constants in the Antoine equation $\log P = A - B/(T - 273\cdot2 + C)$, where P is in Torr and T in K.

TABLE II

The Vapour–Liquid Equilibrium at 101·32 kPa

x_1	y_1	T, K	δ(RK2)[a]	δ(RK3)[a]
Acetaldehyde(1)–diethyl ether(2)				
0·058	0·155	304·3	0·005	0·003
0·099	0·237	302·9	0·003	—0·002
0·194	0·381	300·25	—0·003	0·002
0·293	0·491	297·8	—0·003	0·009
0·391	0·574	295·9	—0·003	—0·006
0·539	0·674	293·9	0·002	0·001
0·658	0·739	293·2	0·004	0·004
0·801	0·814	292·8	0·002	0·007
0·842	0·838	292·8	—0·002	0·000
0·926	0·904	292·9	—0·003	0·002
Acetaldehyde(1)–ethanol(2)				
0·022	0·103	349·8	—0·009	—0·011
0·033	0·153	348·8	—0·010	—0·013
0·069	0·336	345·2	—0·025	—0·024
0·108	0·430	342·0	—0·008	—0·007
0·171	0·593	336·45	—0·002	0·000
0·208	0·670	333·25	0·005	0·007
0·263	0·739	328·4	—0·008	—0·008
0·344	0·823	323·4	—0·004	—0·006
0·456	0·911	315·3	0·011	0·007
0·531	0·937	311·5	0·008	0·004
0·743	0·991	301·6	0·014	0·014
Acetaldehyde(1)–water(2)				
0·044	0·723	328·95	0·009	0·003
0·074	0·825	320·0	—0·018	—0·011
0·091	0·883	315·5	0·000	0·008
0·140	0·934	308·7	—0·003	0·001
0·168	0·951	306·8	0·000	—0·001
0·185	0·963	305·7	0·006	0·003
0·241	0·978	303·0	0·008	—0·001
0·284	0·982	301·25	0·006	—0·004

[a] Deviations $y_{1,exp} - y_{1,calc}$.

TABLE III

Constants in the Redlich–Kister Equation for the Systems Investigated

System	b	c	d	$\delta(RK2)^a$	$\delta(RK3)^a$
Acetaldehyde	0·3230	0·0752	—	0·003	—
Diethyl ether	0·3277	0·0881	0·0520	—	0·0035
Acetaldehyde	0·0081	0·0098	—	0·009	—
Ethanol	0·0030	0·0572	0·0517	—	0·009
Acetaldehyde	0·8448	0·4387	—	0·006	—
Water	1·3702	1·9885	1·1516	—	0·005

[a] Mean deviations $y_{1,exp} - y_{1,calc}$.

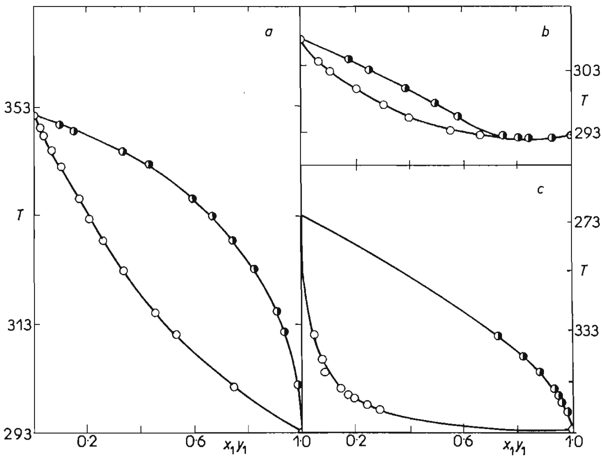

FIG. 1

T-x-y Diagrams *a* the Acetaldehyde–Ethanol, *b* Acetaldehyde–Diethyl Ether and *c* Acetaldehyde–Water Systems; x_1, y_1 Are the Mole Fractions of Acetaldehyde

Our experimental azeotropic data in the acetaldehyde—diethyl ether system, *i.e.*, $x_{az} = 0{\cdot}837$ and $T_{az} = 292{\cdot}8$ K, differ somewhat from those reported by Nycander[5], who found $x_{az} = 0{\cdot}846$ and $T_{az} = 292{\cdot}1$ K.

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