PHASE EQUILIBRIA IN THE ACETALDEHYDE–DIETHYL ETHER–WATER SYSTEM

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Vapour–liquid and liquid–liquid phase equilibria in the ternary acetaldehyde–diethyl ether–water system were determined at isothermal conditions. Experimental vapour–liquid equilibrium data were correlated by the Renon–Prausnitz equation.

The production of synthetic ethanol by direct hydration of ethylene yields a whole series of side products: acetaldehyde, diethyl ether, propionaldehyde, acetone, vinyl acetate, ethyl acetate, diethoxyethane, 2-butanone, 2-methyl-3-pentanone, isopropanol, sec-butanol, tert-butanol, isobutanol, 3-methyl-2-pentanone and some hydrocarbons. All of these substances are present in traces, only the concentration of water (2·6 vol.%) and diethyl ether (0·85 vol. %) is somewhat higher. As long as the resulting ethanol is further processed as an intermediate (in Czechoslovakia still for the production of 1,3-butadiene), the present impurities are usually harmless, because the resulting butadiene undergoes before polymerization an efficient purification cycle. At present, however, attempts are being made to use the excess of ethanol, which should constantly increase due to changes in the technology of the production of butadiene from butane, in food industry. During the rectification of synthetic ethanol, the forerun is formed by a mixture of acetaldehyde, diethyl ether and water. Thus, one of the tasks is the development of such a separation equipment which could separate this mixture to its pure components. The given problem can presumably be solved by adding further water to the separated mixture of acetaldehyde and diethyl ether (in this process, water would act as an extracting agent). For the design of an extractive rectification equipment we must know the phase vapour–liquid and liquid–liquid equilibria in the acetaldehyde–diethyl ether–water system as well as in the corresponding binary systems.

EXPERIMENTAL

Preparation of pure substances and their physico-chemical parameters have been described earlier[1].

Measurements of vapour–liquid equilibrium data in the ternary system were performed in a static semimicroapparatus proposed by Wichterle and Hála[2]. The most important concentration regions from operational aspects are those in which the mole fraction of acetaldehyde in the ternary liquid mixture does not exceed the value of 0·3 on both sides of the solubility curve in the direction of the concentration ends (Fig. 1). The measurements were performed only in these concentration regions. The equilibrium apparatus was connected to a Chrom 3 chromatograph with thermal conductivity detection. The 1 m-long chromatographic column with the diameter of 0·5 cm was filled with Porapac Q. The temperature of separation was 443·2 K. The carrier gas was electrolytic hydrogen with the over-pressure at the column inlet of ~150 kPa and the rate of flow of 3 l/h. The analysis of one sample was repeated at least 3 times to increase the accuracy. The accuracy of the analytical method was estimated as 1·5% on samples with known composition. The accuracy in the determination of composition of the liquid mixture was given by the accuracy of weighing. With respect to a high volatility of diethyl ether and, especially, acetaldehyde, it was necessary to use precooled laboratory vessels, syringes, *etc.*

Solubility data (solubility curve) in the ternary system were measured by a turbidity method. The homogeneous mixture of acetaldehyde and water in a thermostated vessel (the temperature of its jacket was being maintained at 288·2 K) was titrated by diethyl ether (from a burette with the water jacket maintained also at 288·2 K) till the solution became turbid. The tie lines were constructed by analysing two phases of the heterogeneous three-component mixture after shaking for 2 h in a thermostat at 288·2 K. The method and accuracy of this analysis were the same as in the case of the measurement of vapour–liquid equilibrium data.

TABLE I

The Vapour–Liquid Equilibrium in the Acetaldehyde(1)–Diethyl Ether(2)–Water(3) System at 308·2 K

x_1	x_2	y_1	y_2	α_{213}	Δy_1[a]	Δy_2[b]
0·292	0·016	0·727	0·216	5·42	—0·014	0·011
0·273	0·033	0·595	0·375	5·21	—0·011	0·011
0·252	0·027	0·616	0·372	5·64	0·007	0·013
0·205	0·024	0·546	0·422	6·60	—0·009	0·011
0·150	0·018	0·483	0·455	7·25	—0·012	—0·009
0·094	0·016	0·355	0·601	9,95	—0·011	0·014
0·277	0·677	0·461	0·512	0·45	0·006	—0·009
0·237	0·694	0·411	0·582	0 48	0·005	0·022
0·212	0·771	0·385	0·602	0·43	—0·010	0·010
0·183	0·770	0·352	0 611	0·41	0·006	—0·011
0·111	0·848	0·252	0·707	0·37	0·014	—0·017
0·055	0·922	0·125	0·825	0·39	—0·012	—0·010

[a] $\Delta y_1 - y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}$; [b] $\Delta y_2 - y_{2,\mathrm{exp}} - y_{2,\mathrm{calc}}$.

RESULTS AND DISCUSSION

Results of measurements of the vapour–liquid equilibrium at 308·2 K are presented in Table I, whereas liquid–liquid equilibrium data at 288·2 K are in Tables II and III and in Fig. 1.

The vapour–liquid equilibrium data were correlated by the Renon–Prausnitz equation (the NRTL equation)[3] and we assumed that, in comparison with other existing equations approximating the concentration dependence of activity coefficients in the solution, this one could be most appropriate for a quantitative description of the ternary system studied. For a N-component system, Renon had proposed the following relation for the concentration dependence of the molar excess Gibbs free energy

$$Q = g^E/(RT) = \sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j T_{ji} G_{ji} \, . \, [\sum_{k=1}^{N} x_i G_{ki}]^{-1} \, , \qquad (1)$$

TABLE II

The Solubility Curve in the Acetaldehyde(1)–Diethyl Ether(2)–Water(3) System at 288·2 K

x_1	x_2	x_1	x_2	x_1	x_2
0·106	0·019	0·393	0·077	0·497	0·318
0·188	0·025	0·454	0·116	0·450	0·400
0·253	0·039	0·493	0·160	0·343	0·538
0·347	0·060	0·516	0·224	0·208	0·710

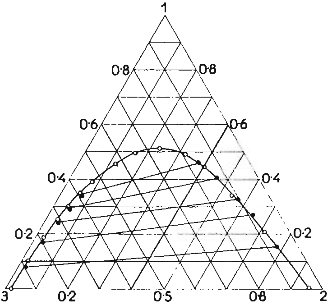

FIG. 1

The Liquid–Liquid Equilibrium in the Acetaldehyde(1)–Diethyl Ether(2)–Water(3) System at 288·2 K with

$$G_{ji} = \exp(-\alpha T_{ji}) \qquad (2)$$

and

$$T_{ji} = (g_{ji} - g_{ii})/(RT)\,. \qquad (3)$$

Other thermodynamic functions activity coefficients, resp. their ratio, can be defined through this molar excess Gibbs free energy Q as

$$\ln \gamma_i = Q - (\partial Q/\partial x_i)_{T,P,x_{l \neq j}} - \sum_{i=1}^{N} x_i (\partial Q/\partial x_i)_{T,P,x_{l \neq j}}\,. \qquad (4)$$

By connecting Eqs (*1*) and (*4*), we obtain, *e.g.*, the following relation for the activity coefficient of the first component in an N-component system

$$\begin{aligned} \ln \gamma_1 = {} & \sum_{j=1}^{N} x_j T_{j1} \exp(-\alpha_{j1} T_{j1}) \,.\, \Big[\sum_{j=1}^{N} x_j \exp(-\alpha_{j1} T_{j1})\Big]^{-1} + \\ & + \sum_{j=1}^{N} \Big\{x_j \exp(-\alpha_{1j} T_{1j})\, T_{1j} \,.\, \Big[\sum_{k=1}^{N} x_k \exp(-\alpha_{kj} T_{kj})\Big]^{-1} \,. \\ & .\, \Big\{T_{1j} - \sum_{l=1}^{N} x_1 T_{1j} \exp(-\alpha_{1j} T_{1j}) \,.\, \Big[\sum_{k=1}^{N} x_k \exp(-\alpha_{kj} T_{kj})\Big]^{-1}\Big\}\Big\}\,. \end{aligned} \qquad (5)$$

Expressions for other activity coefficients can be obtained by a cyclic change of the indices.

TABLE III

Tie Lines in the Acetaldehyde(1)–Diethyl Ether(2)–Water(3) System at 288·2 K (upper and lower figures refer to the aqueous and ether phases, resp.)

x_1	x_2	x_3	x_1	x_2	x_3
0·083	0·025	0·892	0·295	0·057	0·648
0·155	0·773	0·078	0·406	0·461	0·133
0·175	0·033	0·792	0·346	0·070	0·584
0·274	0·637	0·089	0·461	0·373	0·166
0·238	0·045	0·717			
0·327	0·566	0·107			

The behaviour of ternary systems is above all affected by binary interactions and therefore it was necessary to know the set of binary constants of the corresponding binary systems. The data for these binary systems were taken from the literature and correlated by the NRTL equation. The basic acetaldehyde (1)–diethyl ether (2) system was measured in previous work[1]. This system forms an azeotropic mixture at $x_{az} = 0{\cdot}837$ and $T_{az} = 292{\cdot}8$ K. Constants in the NRTL equation were calculated by minimizing deviations in the vapour phase composition ($T_{12} = 1{\cdot}0784$, $T_{21} = -0{\cdot}0478$, $\alpha_{12} = 0{\cdot}47$). The relative volatility of diethyl ether with respect to acetaldehyde, as a measure of separability of both components, was calculated from experimental data[1] as

$$\alpha_{21} = y_2 x_1 / y_1 x_2 = \gamma_2 P_2^0(T) / \gamma_1 P_1^0(T) \,. \tag{6}$$

The concentration dependence of the relative volatility is illustrated in Fig. 2. Since this system forms an azeotropic mixture, it cannot be separated to its pure components by a common rectification. An addition of water to the separated mixture brings about an increase in the relative volatility of diethyl ether with respect to acetaldehyde in comparison with the binary system (and, consequently, also a possibility of separating the mixture)

$$\alpha_{213} = [\gamma_{23}/\gamma_{13}]_{123} \cdot P_2^0(T)/P_1^0(T) \,, \tag{7}$$

since deviations of the behaviour of the diethyl ether–water system from Raoult's law are substantially higher than those of the acetaldehyde–water system.

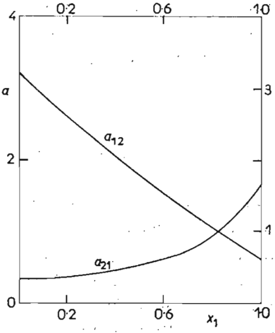

FIG. 2

The Concentration Dependence of the Relative Volatility in the Acetaldehyde(1)–Diethyl Ether(2) System at 101·32 kPa

The ratio of relative volatilities in a ternary and a binary system at a constant ratio of separated components 2 and 1 is denoted as the selectivity of the extracting agent

$$S = \alpha_{213}/\alpha_{21} = (\gamma_2/\gamma_1)_{123}/(\gamma_2/\gamma_1)_{12}\,[x_2/x_1]\,. \tag{8}$$

An addition of the extracting agent to the separated mixture leads to an increase in the ratio of activity coefficients to the limiting value

$$\alpha^0_{123} = P^0_2/P^0_1 \lim_{x_3\to 1} (\gamma_2/\gamma_1)_{123} = P^0_2/P^0_1(\gamma_2/\gamma_1)^0_{123}\,. \tag{9}$$

The diethyl ether(2)–water(3) system exhibits a limited miscibility of both components[4,8]. The mutual solubility of both components decreases with an increasing temperature in the temperature range 273 – 363 K. This indicates that this system possesses a lower critical solubility temperature (of course, deep below the melting point of pure water). The aqueous solution of diethyl ether forms a heterogeneous azeotropic mixture with the following parameters[7]: n.b.p. = 307·3 K and 1·3 wt % water. The vapour–liquid equilibrium data have been measured several times[4–6] but the indirect data by Signer[5] seem to be most reliable. The values of constants $T_{23} = 2{\cdot}5412$, $T_{32} = 3{\cdot}4060$, $\alpha_{23} = 0{\cdot}35$ were obtained by minimizing the total vapour pressure above the solution. The optimum value of the parameter α is somewhat higher than the generalized value recommended by Renon for heterogeneous systems.

The acetaldehyde(1)–water(3) system has also been measured many times[1,9–15], however, no all of the available data are sufficiently reliable. For the correlation of our ternary system, we selected the data by Morozov[11] ($T_{13} = 1{\cdot}8887$, $T_{31} = 0{\cdot}7036$, $\alpha_{13} = 0{\cdot}65$), where the value of the parameter α is also higher than the recommended one. With the above set of the binary constants, we calculated back the vapour phase composition.

$$y_{1,\text{calc}} = 1/(1 + \gamma_2 P^0_2 x_2/(\gamma_1 P^0_1 x_1) + \gamma_3 P^0_3 x_3/(\gamma_1 P^0_1 x_1))\,, \tag{10}$$

$$y_{2,\text{calc}} = 1/(1 + \gamma_1 P^0_1 x_1/(\gamma_2 P^0_2 x_2) + \gamma_3 P^0_3 x_3/(\gamma_2 P^0_2 x_2))\,. \tag{11}$$

Deviations between the calculated and experimental vapour phase compositions are also given in Table I.

In the concentration region experimentally investigated – where the concentration of water lies in the range 0·7 – 0·9 mole fraction, *i.e.*, to the left from the solubility curve – the values of the relative volatility of diethyl ether with respect to acetaldehyde reach 5 – 10 in comparison with values of 0·3 – 1·0 in the binary mixtures.

In these cases, a considerable increase in the relative volatility is observed. It is obvious that to the right from the solubility curve, where the concentration of water is extremely low, no substantial changes in the relative volatility are encountered. No azeotropic mixture was observed in the ternary system.

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