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Vapor–Liquid Equilibrium for Binary Mixtures of 1,4-Diazabicyclo[2.2.2]octane with Ethylenediamine, Ethanolamine, and Ethylene Glycol

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Abstract Vapor–liquid equilibria of mixtures of 1,4-diazabicyclo[2.2.2]octane with ethylenediamine, ethanolamine, and ethylene glycol were studied. Ideal behavior in the ethylenediamine and 1,4-diazabicyclo[2.2.2]octane mixture was observed. Ethanolamine and 1,4-diazabicyclo[2.2.2]octane form an azeotrope with a minimum boiling point whereas ethylene glycol and 1,4-diazabicyclo[2.2.2]octane form an azeotrope with a maximum boiling point. Non-ideal behavior of the mixtures was described by the NRTL equation, and the corresponding constants were calculated.

Keywords Amine · Azeotrope · NRTL · Vapor–liquid equilibrium

1 Introduction

1,4-Diazabicyclo[2.2.2]octane (DABCO) is a well-known compound, and it is widely used as a basic catalyst for polyurethane substances. In addition to other raw materials [1–3], the synthesis of DABCO from ethylenediamine [4] (EDA) and ethanolamine (EA) [5] has been described in the literature. The synthesis is mostly carried out over an acidic zeolite catalyst ZSM-5 at temperatures above 300 °C in the presence of water. At these conditions, hydrolysis of EDA and EA to form ethylene glycol (EG) can occur; hence, the three substances can be in the reaction mixture simultaneously (Scheme 1). Therefore, it is necessary to understand the vapor–liquid equilibrium of all these substances in the separation process.

Besides the technological importance of this process, it is interesting in terms of the behavior of the substances. EDA, EA, and EG have a similar structure where an

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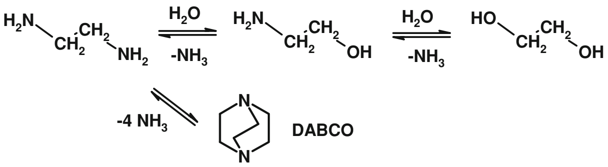

Scheme 1 DABCO reaction pathway

amino functional group is replaced by the hydroxyl group from EDA up to EG. DABCO itself is a white crystalline substance with interesting physical properties, that is, the small difference between the melting (161.1 °C) and boiling points (174.3 °C) [6]. We experimentally measured the binary vapor–liquid equilibrium for the DABCO–EDA, DABCO–EA, and DABCO–EG mixtures by differential distillation. We observed that a small difference in the structure leads to larger differences in the behavior of the substances.

2 Experimental

2.1 Chemicals

All the substances were obtained from commercial suppliers (EDA 99.9 %, EA 99.9 % Sigma–Aldrich, EG–Penta, DABCO–BC-MCHZ). EG was purified before equilibrium measurements to 99.9 % by distillation on a column with 5 TP. DABCO was re-crystallized using methyl-tert-butylether to 99.99 %.

2.2 Apparatus

The apparatus was composed of a three-necked 500 mL distillation flask equipped with a thermometer with an uncertainty of 0.1 °C and a sensor with an injection needle for sampling (Fig. 1). A distillation box with separate routes for the vapors and recurrent liquid was placed on the distillation flask and the route for the liquid enabled the sampling. The upper part of the distillation flask and the route for the vapor was colored in black and exposed to infrared light. Thus, neither condensation nor separation of the compounds on the walls of the distillation flask and the vapor routes took place. The vapors generated in the flask condensed in the cooler and the resultant liquid was directed below the level of the liquid in the flask. The route for the liquid was kept at constant temperature due to the solidification of DABCO from the vapors at high concentration. A steady state was assumed after 30 min, and simultaneous sampling from the flask and the recurrent condensed distillate was carried out. Under those steady-state conditions, the concentration of the substances in the samples corresponded to one theoretical stage. The validity of those assumptions was verified by use of a model mixture of C9, C10, and C11 linear hydrocarbons because of the similar boiling-point temperature range as our reaction mixture. Validity of Raoult's law was assumed, and for illustration, the vapor–liquid data obtained for the C10–C11 measurements are given in Fig. 2. Atmospheric pressure was measured with a mercury manometer to within an uncertainty of 0.1 kPa.

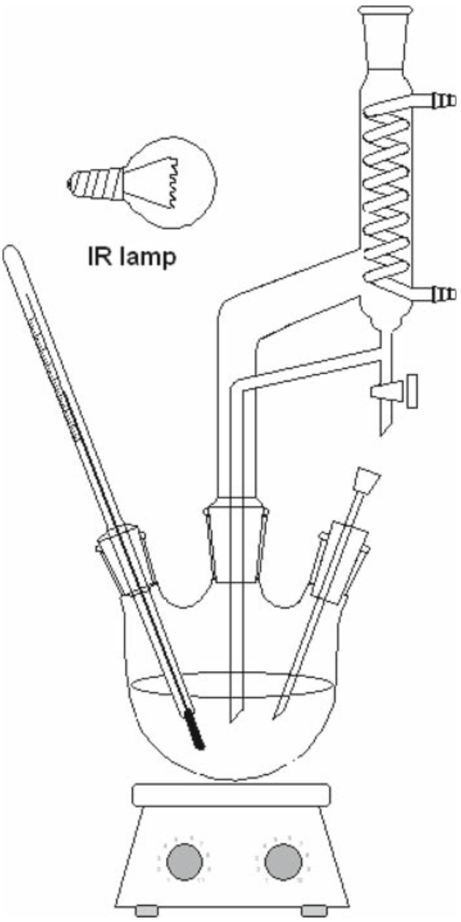

Fig. 1 Apparatus for the vapor–liquid measurements

2.3 Analytical

For accurate determination of the substance concentrations, the internal standard method was used. The obtained samples were dissolved in methanol and analyzed by gas chromatographic instrument Shimadzu GC-2010 equipped with a flame ionization detector (FID). The corresponding correction factors were obtained by the analysis of a series of standards prepared from pure substances. The uncertainties of the reported mole fractions for the liquid and vapor phases are within ±0.001.

2.4 Calculation

For computation of the ideal behavior of the EDA–DABCO binary, AspenPlus software was used. The constants of the NRTL equation for the description of the non-ideal behavior of EA–DABCO and EG–DABCO were computed by the correlation of the

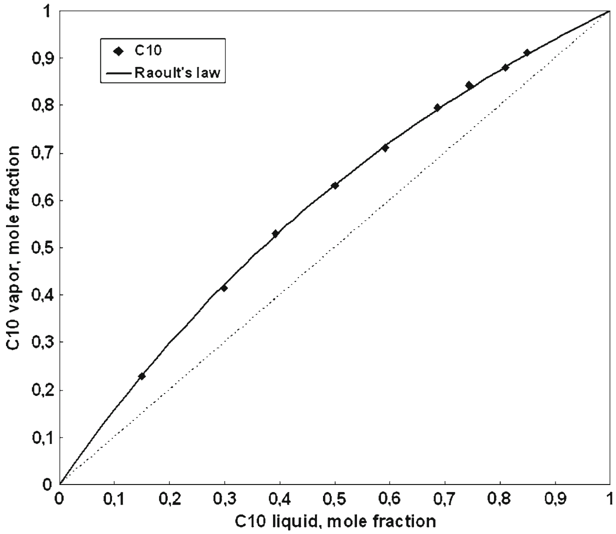

Fig. 2 Vapor–liquid equilibrium for C10–C11 mixture at 99.8 kPa

Table 1 Constants for calculation of the vapor pressures of the pure substances

Components	C10	C11	EDA	EA	EG	DABCO
A	112.73	131	73.51	92.624	84.09	137.63
B	−9,750	−11,143	−7,573	−10,367	−10,411	−11,428

experimental data using methods incorporated in the AspenPlus software. Vapor pressures of the pure substances were not experimentally measured because they are sufficiently and accurately described in the literature [7–10]. An equation for calculation of the vapor pressures of the pure substances was used as follows, and the constants are given in Table 1.

$$P = \exp\left(A + \frac{B}{T}\right) \quad P\,[\text{bar}]\,,\, T\,[K]$$

The equation for the NRTL model of the activity coefficients was used in the following form:

$$\ln\gamma_i = \frac{\sum_j x_j\tau_{ji}G_{ji}}{\sum_k x_kG_{ki}} + \sum_j \frac{x_jG_{ij}}{\sum_k x_kG_{kj}}\left(\tau_{ij} - \frac{\sum_m x_m\tau_{mj}G_{mj}}{\sum_k x_kG_{kj}}\right)$$

where

$$G_{ij} = \exp\left(-c_{ij}\tau_{ij}\right)$$
$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$$

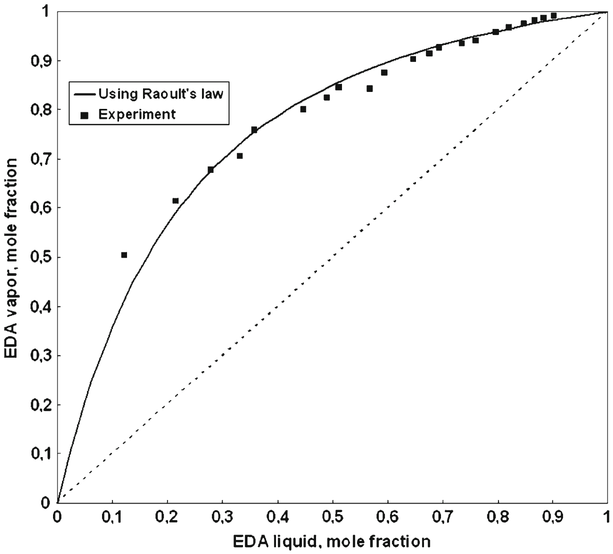

Fig. 3 Vapor–liquid equilibrium for EDA–DABCO mixture at 99.6 kPa

Table 2 Vapor–liquid equilibrium data for EDA–DABCO system at 99.6 kPa

t (°C)	x_{EDA}	y_{EDA}
152.5	0.122	0.505
142.6	0.215	0.614
139.1	0.278	0.677
135.9	0.332	0.706
134.2	0.357	0.759
132.3	0.447	0.8
130.1	0.49	0.825
128.5	0.511	0.846
127.5	0.568	0.843
126.7	0.595	0.876
125.6	0.646	0.902
125.1	0.676	0.914
124.5	0.693	0.927
124.0	0.735	0.934
123.5	0.76	0.94
122.9	0.797	0.958
122.4	0.821	0.967
122.1	0.848	0.974
121.7	0.868	0.982
121.3	0.884	0.987
121.0	0.902	0.991

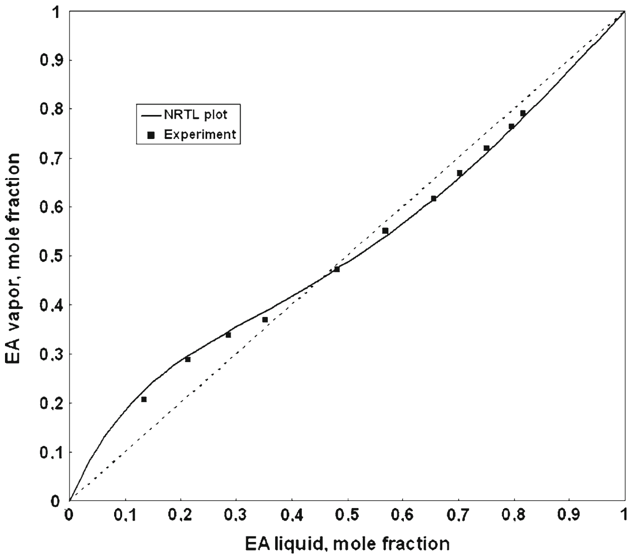

Fig. 4 Vapor–liquid equilibrium for EA–DABCO mixture at 98.9 kPa

Table 3 Vapor–liquid equilibrium data for EA–DABCO system at 98.9 kPa

Experimental data			NRTL equation			
t (°C)	x_{EA}	y_{EA}	$t_{cal.}$ (°C)	Δt	$y_{EAcal.}$	Δy_{EA}
169.5	0.134	0.207	168.0	1.5	0.232	−0.025
167.6	0.213	0.288	166.6	1.0	0.301	−0.013
166.5	0.286	0.338	165.8	0.7	0.347	−0.009
165.9	0.352	0.369	165.5	0.4	0.387	−0.018
165.8	0.482	0.472	165.3	0.5	0.470	0.002
165.9	0.569	0.55	165.5	0.4	0.537	0.013
166.5	0.655	0.616	166.0	0.5	0.611	0.005
166.6	0.703	0.669	166.4	0.2	0.659	0.010
167.2	0.751	0.719	166.8	0.4	0.706	0.013
167.5	0.796	0.764	167.2	0.3	0.755	0.009
167.7	0.817	0.791	167.4	0.3	0.777	0.014

3 Results

EDA and DABCO have the largest difference in boiling points at normal pressure (EDA: 117.1 °C and DABCO: 174.3 °C) in relation to all the investigated compounds. EDA as a primary amine and DABCO as a tertiary amine are both relatively non-polar. In a mixture of amines in the liquid phase, it can be assumed that they do not mutually interact; hence, they can be described by Raoult's law for ideal mixtures. This assumption was experimentally verified, and from the results it is apparent that the

Table 4 Constants of the NRTL equation for the binary mixtures EA–DABCO and EG–DABCO

Component *i* Component *j* Temperature units	EA DABCO (K)	EG DABCO (K)
a_{ij}	−9.85433	4.030891
a_{ji}	−5.7283	0.884255
b_{ij}	4018.48	−1862.21
b_{ji}	3411.652	−761.04
c_{ij}	0.3	0.3

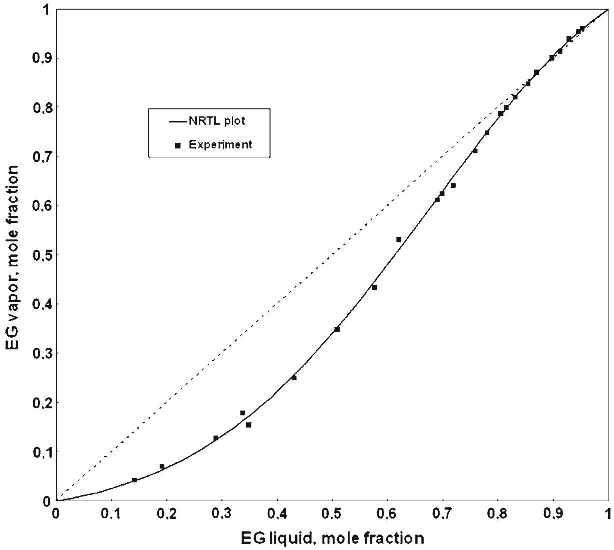

Fig. 5 Vapor–liquid equilibrium for EG–DABCO mixture at 98.9 kPa

vapor–liquid equilibrium calculations based on the vapor pressures of pure substances were well described by the experimental points (Fig. 3, Table 2).

The boiling point of EA at normal pressure is 169.7 °C, which is close to that of DABCO (174.3 °C). The substitution of an amino molecule in EDA for a hydroxyl molecule to EA results in increased polarity. EA can form hydrogen bonds with the free electron pair of nitrogen in DABCO. If compounds have closer boiling points and differ considerably in polarity, it can be assumed that they would show non-ideal behavior. That was demonstrated by the behavior of the DABCO–EA binary mixture where an azeotrope with a minimum boiling point at 165.3 °C, 98.9 kPa, and a composition of 45.2 mol% was observed (Fig. 4 Table 3). The calculated constants of the NRTL equation for the non-ideal behavior of the DABCO–EA mixture are given in Table 4.

EG has two hydroxyl groups in its molecule which can interact with the free electron pairs of nitrogen in DABCO. The interactions are rather intense because of the

Table 5 Vapor–liquid equilibrium data for EG–DABCO system at 98.9 kPa

Experimental data			NRTL equation			
t (°C)	x_{EG}	y_{EG}	$t_{cal.}$ (°C)	Δt	$y_{EGcal.}$	Δy_{EG}
178.6	0.142	0.042	178.2	0.4	0.039	0.003
180	0.191	0.07	180.0	0.0	0.061	0.009
183.1	0.289	0.127	183.8	−0.7	0.123	0.004
184.1	0.338	0.178	185.7	−1.6	0.164	0.014
186.6	0.349	0.154	186.0	0.6	0.173	−0.019
190.1	0.431	0.25	188.9	1.2	0.254	−0.004
192.1	0.509	0.349	191.4	0.7	0.353	−0.004
193.6	0.577	0.434	193.2	0.4	0.443	−0.009
195.1	0.62	0.531	194.2	0.9	0.510	0.021
196.1	0.69	0.611	195.5	0.6	0.616	−0.005
196.6	0.699	0.624	195.7	0.9	0.631	−0.007
196.6	0.719	0.64	195.9	0.7	0.661	−0.021
197.1	0.759	0.71	196.4	0.7	0.721	−0.011
197.1	0.78	0.748	196.5	0.6	0.750	−0.002
196.1	0.805	0.787	196.7	−0.6	0.785	0.002
197.1	0.815	0.799	196.7	0.4	0.799	0.000
197.1	0.832	0.82	196.8	0.3	0.819	0.001
197.1	0.854	0.847	196.9	0.2	0.851	−0.004
197.1	0.87	0.871	196.9	0.2	0.870	0.001
197.6	0.898	0.9	196.8	0.8	0.905	−0.005
197.6	0.912	0.912	196.8	0.8	0.916	−0.004
197.1	0.929	0.938	196.7	0.4	0.937	0.001
196.6	0.945	0.953	196.7	−0.1	0.952	0.001
196.6	0.953	0.961	196.6	0.0	0.962	−0.001

cyclic nature of the DABCO molecule which causes good accessibility of the free electron pairs. These facts imply the strong non-ideal behavior of the binary mixture and lead to the formation of an azeotrope with a maximum boiling point of 196.8 °C at 98.9 kPa and a composition of 86.9 mol% EG (Fig. 5, Table 5). The EG boiling point is 196.3 °C at 98.9 kPa. The composition of the azeotrope was verified by distillation of a DABCO–EG mixture on an effective column (Sulzer EX 1.5 m. 80 TP mixture methylcyklohexane–*n*-heptane).

4 Conclusion

It was observed that the DABCO–EDA mixture behaves ideally. This can be explained by the fact that both amines have a small difference in polarity. Therefore, no considerable interaction in the liquid phase takes place. Substitution of the amino group by the hydroxyl group in the two-carbon molecule has a fundamental effect on the behavior of the substances. The DABCO–EA mixture shows strong non-ideal behavior and forms an azeotrope with a minimum boiling point. In this case, the polar effect of the substances rather than the interaction by hydrogen bonding through the hydroxyl group of the EA compound is more important. The polar EA displaces DABCO from the liquid phase and increases the DABCO partial pressure in the vapor phase. The DABCO–EG mixture also shows strong non-ideal behavior by formation of an azeotrope with a maximum boiling point. This is mainly due to the formation of hydrogen bonds between the hydroxyl group and the electron pair on nitrogen in the DABCO molecule. EG strongly bonds to DABCO in solution and therefore lowers the vapor pressure from 180 kPa to 99 kPa at the azeotropic point (196.8 °C) compared with the pure substance. From a technological point of view, it is evident that if the raw material for the synthesis of DABCO is EA, it is necessary to carry out the synthesis with total conversion. Otherwise, it would be impossible to prepare DABCO of sufficient purity by distillation due to the formation of a DABCO-EA azeotrope.

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