INVESTIGATION ON THE SYSTEM TRIETHYL AMINE—ACETIC ACID

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Introduction

Gardner [1] was the first to call attention to the system triethyl amine-acetic acid. After a fairly long time, this mixture of special behaviour, was investigated by van Klooster and Douglas [2] who pointed out that the system has only partial miscibility and at a concentration of 21 mole % of triethyl amine it forms a negative azeotrope. It is worth mentioning that the region of limited mixing lies between the concentration of 40 and 95 mole % of triethyl amine, consequently the development of the azeotrope is not directly connected with the formation of the two liquid phases. The anomalistic trend of the equilibrium curve suggests the extreme case of the negative homoazeotropes and at the same time, it can be considered as being the opposite analogue of the positive heteroazeotropes developing in case of components absolutely insoluble in each other [3].

Van Klooster and Douglas strived to explain this phenomenon with the dimerization of the acetic acid and by supposing the formation of a compound to be characterized by the composition $4CH_3COOH \cdot N(C_2H_5)_3$; otherwise, the existence of ionic compounds of such a type developing between aromatic amines and acetic acid was observed by others, too [4, 5].

In this Institute the vapour—liquid equilibria of carboxylic acids were investigated recently. The association taking place in these systems certainly plays a role also in case of the acetic acid; therefore, besides its general interest, the system triethyl amine—acetic acid was considered to be suitable for studying simultaneously the general behaviour of the carboxylic acids, too.

Experimental

During the investigations chemicals of analytical purity were used.

For analysis of the system measurements of refractivity were employed obtaining suitable accuracy with a relative error of 1%. In case of heterogeneous mixtures, acetic acid of known quantity was added to a definite quantity of the sample and the refractive index of the homogeneous mixture developed
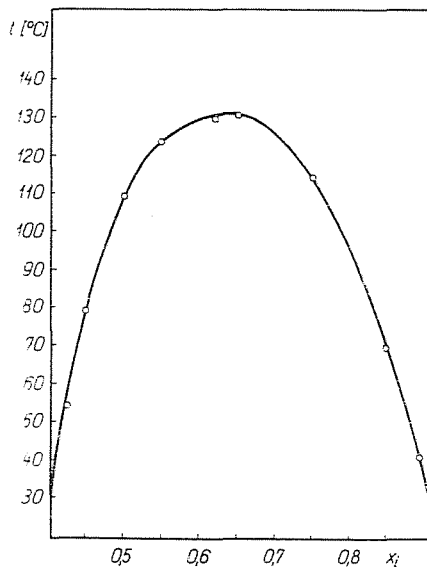
Fig. 1. Solubility diagram of the system triethyl amine—acetic acid as a function of the triethyl amine concentration
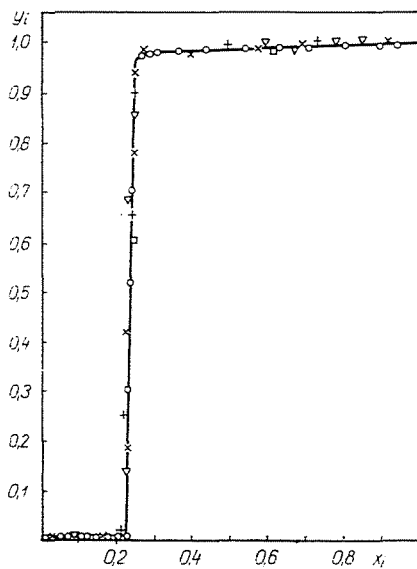

Fig. 2. Equilibrium diagram of the system triethyl amine — acetic acid

○ 760 torr
▽ 380 torr
× 190 torr
□ 95 torr
+ 47.5 torr

in such way was determined; from this value the original composition could be determined.

A modified WILLIAMS-type apparatus was used for the equilibrium measurements. The function of this apparatus was described in detail previously [6]. The solubility of the system was determined, in the usual way, using sealed ampoules. At higher temperatures the determination was also performed in
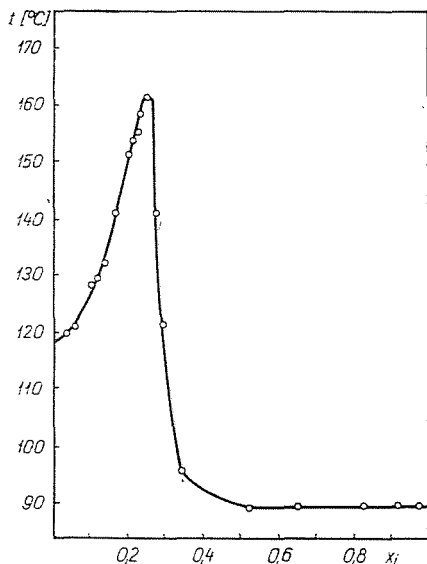

Fig. 3. Boiling-point diagram of the system triethyl amine—acetic acid

an open vessel, in order to eliminate the possible error due to the vapour pressure of the system itself, but the so obtained results were identical with those gained by the other method.

The measured solubility diagram of the system is shown in Fig. 1. The full line is traced on the basis of VAN KLOOSTER's and DOUGLAS' measurements, while the points inscribed represent the authors' measuring results.

The equilibrium data obtained at a pressure of 760 torr are summarized in Table I as well as in Figs. 2 and 3. For the sake of comparison, in Fig. 2 the equilibrium data gained at pressures of 380, 190, 95, and 47.5 torr are also shown. The trend of the equilibrium curve is very similar to the above-mentioned authors' results [2] but, according to our results, the steep portion of the curve appears at a triethyl amine concentration of 24 mole %, and not at 21 mole %.

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Table I

Vapour—liquid equilibrium of the system triethyl amine—acetic acid at 760 torr

x_i	y_i	$t(°C)$
0,037	0,001	120,0
0,052	0,001	121,2
0,108	0,002	128,1
0,112	0,002	129,0
0,141	0,003	132,5
0,179	0,004	142,0
0,205	0,006	152,9
0,219	0,011	155,3
0,226	0,348	156,0
0,235	0,519	158,9
0,260	0,983	162,0
0,275	0,983	142,1
0,299	0,984	122,5
0,345	0,987	96,8
0,525	0,991	89,7
0,650	0,990	89,8
0,825	0,995	89,6
0,910	0,998	89,5
0,951	0,999	89,5

Evaluation of the experimental results

From the vapour—liquid equilibrium data and the steep portion of the curve, respectively, the conclusion can be drawn that, in contrast to VAN KLOOSTER's and DOUGLAS' statements, the establishment of the triethyl amine—acetic acid complex is closer to the molar ratio of 1 to 3 (25 mole % of triethyl amine).

The results of the measurements carried out in vacuum refer to the fact that the complex having a molar ratio of 1 : 3 can be revealed at each pressure and that its composition, respectively, undergoes practically no change. This statement points to the presence of a compound, because in case of an azeotrope the composition ought to be shifted by such a considerable change in pressure.

Mention must be made of the fact that the existence of this complex having the composition of $3CH_3COOH \cdot N(C_2H_5)_3$ can more easily be explained with the formation of hydrogen-bonds than the existence of the ionic compound containing 4 moles of acetic acid.

As was shown by several authors, in the vapour phase, the acetic acid is present in oligomeric form. By measuring the vapour density, in acetic acid vapour the presence of trimeric and tetrameric molecules was proved, besides the dimeric ones [7, 8, 9, 10], while in equilibrium measurements it was stated recently [11, 12, 13] that, in accordance with the results of infrared and Raman spectroscopy [14], it is sufficient to take only the dimerization into consideration.

In compliance with the afore-said, to correlate the vapour—liquid equilibrium data obtained in the experimental way, the Raoult—Dalton law corrected only with the activity coefficient cannot be used, and the introduction of other correction factors seems also to be necessary.

The consistency of selected points on the smoothed equilibrium curve drawn on the basis of the measuring data was controlled by the following general equation:

$$P y_i z_i \zeta_i = P_i d_i x_i \gamma_i \lambda_i \tag{1}$$

where P = total pressure of the system

y_i = molar fraction of component i in the vapour phase

z_i = correction factor for the behaviour of component i in the vapour phase (z factor)

ζ_i = correction factor for association of component i in the vapour phase

P_i = vapour pressure of component i

d_i = correction factor for the vapour pressure of component i partly dimerized

x_i = molar fraction of component i in the liquid phase

γ_i = activity coefficient of component i and

λ_i = correction factor for association of component i in the liquid phase.

With this general equation also the association can be taken into account; thus the validity of the equation comprises the non-hildebrandian mixtures too.

During the computations the vapour pressure of the acetic acid partly dimerized was considered on the basis of MAREK's data [15]; the literature data concerning the vapour pressure of triethyl amine are partly contradictory and partly incorrect [16, 17]. The relation

$$\log P_{\text{triethyl amine}} = 6.8264 - \frac{1161.4}{(205+t)}$$

was found to be the most correct [18].

To calculate the correction factor z_i including the non-ideal behaviour of the vapour phase, SCHEIBEL's following equation [19] was used:

$$\log z_i = \frac{(P_i - P)(V_i - \beta_i)}{2.3\, RT}$$

where V_i = volume of component i corrected to the appropriate temperature with WATSON's equation [20] and

β_i = second virial coefficient of component i calculated for the individual points with BERTHELOT's relation [3] judged to be the most suitable:

$$\beta_i = \frac{9R\tau_i}{128} = \frac{27\,R\tau_i^3}{64\,\pi_i\,T^2}$$

where R = universal gas constant

τ_i = critical temperature of component i

τ_i = critical pressure of component i and

T = prevailing temperature.

The value taking the association occurring in the vapour phase into account was calculated for the associating component (acetic acid) with MAREK's following equation:

$$\varrho_2 = \frac{[\sqrt{1 + 4KPy_2(2 - y_2)} - 1]\,K_2 P_2}{[\sqrt{1 + 4K_2 P_2} - 1]\,KPy_2(2 - y_2)}$$

where K = equilibrium constant for the associating reaction of acetic acid in case of pure acetic acid and

K_2 = the same value in the given mixture.

The remaining signs are the same as stated above.

For calculating the correction factor relating to the non-associating component (triethyl amine) and valid because of the association of the acetic acid occurring in the vapour phase, MAREK's equation was employed [12] as well, according to which

$$\varrho_1 = \frac{2\left[1 - y_2 + \sqrt{1 + 4KPy_2(2 - y_2)}\right]}{(2 - y_2)\left[1 + \sqrt{1 + 4KPy_2(2 - y_2)}\right]} \quad .$$

The association equilibrium constants were taken into account on the basis of literature data [15].

The values obtained after substitutions for the products of multiplication γ_i and λ_i are shown in Table II. The change of the products with composition is shown in Fig. 4.

Table II

Values of the correction factors for the vapour—liquid equilibrium of the system triethyl amine —acetic acid as a function of the concentration

x_1	y_1	t	z_1	z_2	ξ_1	ξ_2	$\gamma_1\lambda_1$	$\gamma_2\lambda_2$
0,050	0,001	120,9	1,0837	1,0017	1,61	0,38	0,014	1,011
0,100	0,002	127,0	1,1380	1,0063	1,57	0,43	0,013	1,009
0,200	0,004	152,5	1,2450	1,0396	1,27	0,72	0,006	0,708
0,220	0,201	155,5	1,2335	1,0369	1,06	0,76	0,229	0,676
0,230	0,520	160,0	1,2042	1,0300	1,00	0,97	0,552	0,600
0,260	0,983	162,5	1,1246	1,0114	1,00	0,94	1,354	0,038
0,310	0,985	115,1	1,0348	0,9900	1,00	0,78	1,793	0,081
0,410	0,988	90,0	1,0001	0,9807	1,00	0,63	2,376	0,109
0,520	0,991	89,7	1,0000	0,9806	1,00	0,69	1,880	0,112
0,650	0,993	89,6	0,9999	0,9805	1,00	0,72	1,522	0,124
0,800	0,995	89,5	0,9998	0,9804	1,00	0,76	1,246	0,165
0,950	0,999	89,5	0,9998	0,9804	1,00	0,90	1,050	0,154

From the Figure it appears that the function of the composition of the activity coefficients (more correctly speaking, the values gained from the product of the association factor valid in the liquid phase and of the corresponding activity coefficient) is formed in conformity with a minimum and a
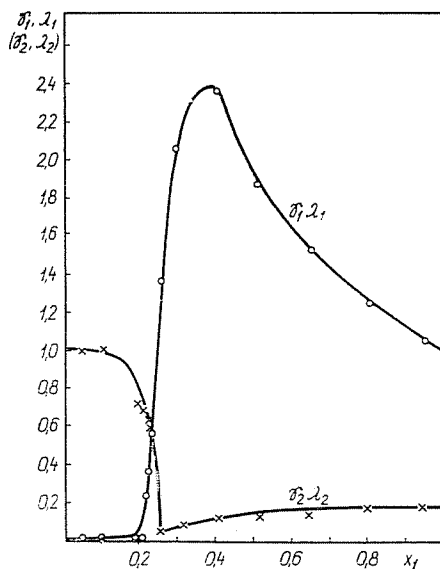

Fig. 4. Values of the products $\gamma_i\lambda_i$ as a function of the triethyl-amine concentration

maximum curve, respectively, thus, with this method thermodynamically inconsistent data are obtained. It is worth mentioning that, in spite of this fact, the curves satisfy the requirement of approaching 1 in case of the limiting concentrations.

The intersection to be seen in Fig. 4 of the activity coefficients and the results of multiplication $\gamma_i \lambda_i$, respectively, the corresponding abscissa value of which, according to HÖGFELDT [21], furnishes, in the case of formation of a compound, information concerning the composition of the compound, appears at a concentration of 24 mole % of triethyl amine. This value approaches well
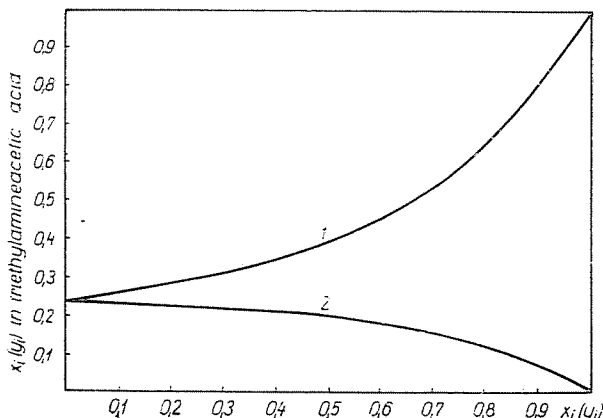

Fig. 5. Reduction of the apparent triethyl amine concentration appearing in the pseudobinary system triethyl amine—acetic acid to real binary molar fractions
Abscissa pertaining to curve 1: molar fraction of triethyl amine in the system triethyl amine
—$3CH_3COOH \cdot N(C_2H_5)_3$
Abscissa pertaining to curve 2: molar fraction of acetic acid in the system acetic acid—
$3CH_3COOH \cdot N(C_2H_5)_3$

the composition of the compound postulated above and characterized with the formula $3CH_3COOH \cdot N(C_2H_5)_3$.

It is here to be mentioned that the determination of the degree of association in the liquid phase would be very complicated and would be equivalent to the separated determination of γ_i from the results $\gamma_i \lambda_i$.

Unfortunately, the trend of the curves of Fig. 4 cannot substantially be influenced by this separated determination and the separation of the correction factor for the association in the liquid phase, from the result of multiplication mentioned above, does not render the values consistent of the activity coefficients.

Further, investigations were carried out in connection with the question whether the pseudobinary system triethyl amine—acetic acid can be considered as the mixture of two binary systems, namely of the system triethyl amine —$3CH_3COOH \cdot N(C_2H_5)_3$ and of the system acetic acid—$3CH_3COOH \cdot$

$\cdot$ N(C$_2$H$_5$)$_3$. Starting from the given experimental data, to decide this question, calculations were carried out in connection with the equilibrium of the two systems. The diagrams making possible the conversion from the pseudobinary system to the two binary systems were plotted (Fig. 5), and determining ebulliometrically the vapour pressure of the compound 3CH$_3$COOH $\cdot$ $\cdot$ N(C$_2$H$_5$)$_3$ (Fig. 6), the values of the activity coefficients were calculated for different liquid compositions. In case of the system acetic acid—3CH$_3$COOH $\cdot$ $\cdot$ N(C$_2$H$_5$)$_3$, the curves giving the change of the activity coefficients with the composition show a minimum—maximum trend; in case of the system triethyl
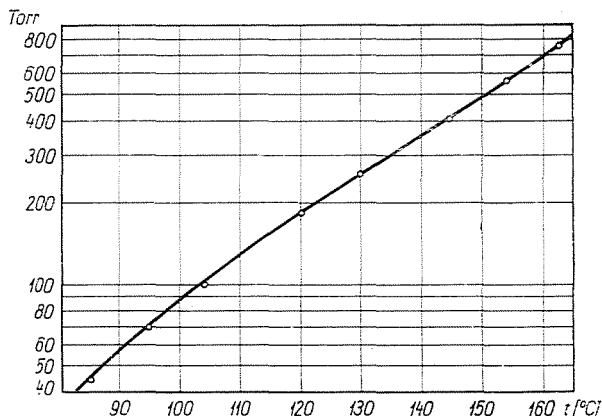

Fig. 6. Vapour pressure of the compound 3CH$_3$COOH$\cdot$N (C$_2$H$_5$)$_3$

amine—3CH$_3$COOH $\cdot$ N(C$_2$H$_5$)$_3$, the curves showed no extreme value, while the activity coefficient of the compound 3CH$_3$COOH $\cdot$ N(C$_2$H$_5$)$_3$ converged to zero instead of 1 at the triethyl amine concentration of zero, which fact cannot be physically interpreted.

Summary

Investigations were carried out in connection with the vapour-liquid equilibrium of the system triethyl amine—acetic acid. After determining the equilibrium curve of the extremely non-ideal system, with the aid of an extremely general equation, computations were carried out to determine the thermodynamical consistency of the experimental results. The calculations closed with a negative result, and the authors only succeeded in giving the probable formation of the compound 3CH$_3$COOH $\cdot$ N(C$_2$H$_5$)$_3$.

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