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Vapor-Liquid Equilibrium for Formic Acid-Triethylamine System Examined by the Use of a Modified Still. Formic Acid-Trialkylamine Azeotropes

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In order to shed light on the previous confused data reported for the constant-boiling liquids for the formic acid-trialkylamine system, vapor-liquid equilibria for a representative formic acid-triethylamine system under a number of pressures were examined by the use of a modified still designed for this purpose. The diagrams obtained and the pressure dependence of the azeotropic compositions clearly indicate azeotropic features. Precise composition of the maximum azeotrope was determined for this system as well as for other formic acid-trialkylamine systems.

Keywords——azeotrope; azeotropic compn; boiling point diagram; continuous distn still; dynamic flow method; formic ac trialkylamine azeotrope; formic ac triethylamine azeotrope; vapor compn binary azeotrope; vapor liq equil

There are many reports on the constant-boiling liquids composed of formic acid and trialkylamines. Their high-boiling and polar properties have developed versatile utilization for organic reactions[2] as a reducing reagent, formylating reagent, and others. However, there remains some uncertainty as to their compositions. Some references show compositions different from the others, and all the previously reported compositions are of compond-like integral ratios of formic acid and trialkylamine. The constant-boiling liquid for formic acid-triethylamine was reported as $3HCO_2H \cdot NEt_3$ in a Netherlands patent[3] and by Wagner,[4] $11HCO_2H \cdot 5NEt_3$ by Poziomek and Pankau,[5] $5HCO_2H \cdot 2\ NEt_3$ by André[6] and by Ito,[7] and $2HCO_2H \cdot NEt_3$ by Wagner[4]; that for formic acid–trimethylamine as $3HCO_2H \cdot NMe_3$ in a Netherlands patent[3] and by Wagner,[4] $5HCO_2H \cdot 2NMe_3$ by André[6] and by Sekiya and Ito[8]; that for formic acid–tributylamine, as $3HCO_2H \cdot NBu_3$ by Wagner,[4] and $7HCO_2H \cdot 3NBu_3$ by Sekiya, *et al.*[9] These confused data prompted us to determine vapor-liquid equilibria of the homogeneous liquid systems of formic acid–trialkylamine.

The continuous distillation stills available today[10] or proposed in the literatures[11] are not suited for the study of the liquid systems comprised of formic acid, which is susceptible to partial decomposition at elevated temperatures, because of longer refluxing time to reach equilibrium and requirement of a larger volume of the sample. It became necessary to develop a continuous distillation still capable of rapid attainment of equilibrium using a rather small volume of the sample. We have newly designed a small and compact still that can reach

1) Location: *2–2–1 Oshika, Shizuoka.*
2) M. Sekiya, *Yuki Gosei Kagaku Kyokai Shi*, **34**, 67 (1976).
3) Farbenfabriken Bayer A.G., Dutch Patent 6503120, 6504228 (1965) [*C.A.*, **64**, 6501, 17477 (1966)].
4) K. Wagner, *Angew. Chem.*, **82**, 73 (1970).
5) E.J. Poziomek and M.D. Pankau, *J. Chem. Eng, Data*, **8**, 627 (1963).
6) M.G. André, *Compt. Rend.*, **126**, 1105 (1898).
7) K. Ito, *Yakugaku Zassi*, **86**, 1166 (1966).
8) M. Sekiya and K. Ito, *Chem. Pharm. Bull.* (Tokyo), **12**, 677 (1964).
9) M. Sekiya, S. Takayama, K. Ito, J. Suzuki, K. Suzuki, and Y. Terao, *Chem. Pharm. Bull.* (Tokyo), **20**, 2661 (1972).
10) Other types of vapor-liquid equilibrium stills are commercially available from Shibata Chemical Apparatus Mfg. Co., Ltd., Asahi P and C Glass Ind. Co., Ltd., *etc.*
11) O.F. Othmer, *Anal. Chem.*, **20**, 763 (1948); L. Garwin and P.O. Haddad, *Ind. Eng. Chem.*, **45**, 1558 (1953); R.G. Harper and J.C. Moore, *Ind. Eng. Chem.*, **49**, 411 (1957).

equilibrium rapidly (5 min) and using a small volume of the sample (20 ml). Results obtained with the test samples, benzene-ethanol and acetic acid–water, were satisfactory and stable, being in good agreement with the equilibrium data in the literature.[12)]

After success of these results, formic acid–triethylamine, selected as a representative binary system, was submitted to the measurement of vapor-liquid equilibrium under ordinary and a number of reduced pressures. Data obtained indicated equilibrium diagrams involving azeotropes. A number of azeotropes of the binary systems comparised of other aliphatic tertiary amines were found with analogy.

Experimental

Apparatus of Modified Continuous Distillation Still and Procedure——An apparatus shown in Fig. 1 was designed and used. The still consists of three parts; a boiler, a condensing region, and a condensate-recycling region. The boiler (A) is a cylindrical flask, near the bottom of which are fitted the two side tubes (B and C) which serve for determination of boiling point of the liquid in A. Relatively large diameter of B and C is suited for proper mixing of the liquid. B is fitted with an enclosed scale thermometer (D) having 0.1 degree graduation corrected by the boiling point of water, while C is fitted with a glass rod, the end of which is connected with a disposable small capillary tube (1×10 mm) (E) closed at the upper end and bent to the bottom of A. The liquid in A can be heated externally in an appropriate bath and stirred vigorously with a magnetic stirrer. The vapor travels up to the condensing region through the outlet vapor tube (F) of a relatively wide diameter and short length, which satisfactorily serves to prevent entrainment of splashed liquid into the vapor and to eliminate significant pressure rise in A. The vapor phase temperature can be measured by the fitted long thermometer (G), the mercury-filled bulb of which is located at the upper part of F and is wrapped with a platinum foil to eliminate the effect of heat radiation. The condensing region consists of an inclined collective gutter (H) and the Liebig condenser (I). The vapor is condensed in H and the condensate enters into the receiver cup (J) through the U-tube and flows over through the nozzle (K) into the return tube (L). J is fitted with the ground-glass stopper to permit sampling of the cold condensate, and K can act as a drop counter for estimation of the recycling rate. L is fitted with an internal cold finger and is connected with A through a heavy-walled capillary tube. Thus, the cold condensate can be returned back into the bottom of A. J and L have a small volume of 0.5 ml and 1.0 ml, respectiviely, so that the

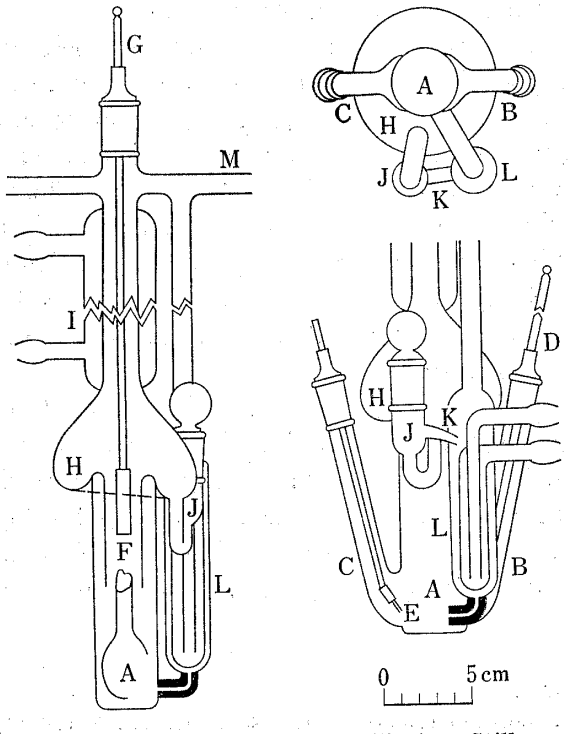

Fig. 1. Vapor-Liquid Equilibrium Still

left, front view; top right, base view; bottom right, side view

A, boiler; B, side tube for thermometer; C, side tube for capillary tube; D, G, thermometers; E, capillary tube; F, outlet vapor tube; H, sloped collective gutter; I, condenser; J, condensate receiver cup; K, nozzle for drop counter; L, return tube; M, connection to atomosphere or vacuum

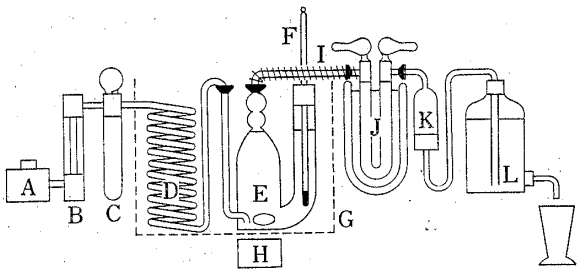

Fig. 2. Schematic Diagram of Apparatus for Dynamic Flow Method

A, air pump; B, flowmeter; C, purification tube; D, prewarmer; E, vapor saturator; F, thermometer; G, thermostat; H, magnetic stirrer; I, outlet tube; J, cooled trap; K, guard tube; L, Mariotte flask

12) *a*) A. Niini, *Ann. Acad. Fenn.*, *A*, **55**, No. 8 (1940); *b*) R. Gilmont and D.F. Othmer, *Ind. Eng. Chem.*, **36**, 1061 (1944).

content can be rapidly and continuously recycled. As occasions demand, M is opened into air through a guard tube or connected with a vacuum system.

By the use of this still, sampling of the vapor-phase condensate and the boiling temperature determination are made separately as follows: about 20 ml of a sample liquid is placed in A, and E is put into place with the aid of a Teflon tubing. A is mounted in a heating bath and heated with vigorous stirring of the liquid under atmospheric or reduced pressure regulated by a Manostat[13] connected with the vacuum system. The bath temperature is raised about 30° above the expected boiling point and, after refluxing for 5 min, the cold condensate is sampled quickly from J for analysis. Then the bath temperature is gradually lowered, whereupon the bubbling from the lower open end of E ceases and then the liquid begins to be sucked into E. The temperature of D at this moment indicates the boiling point of the liquid in A, and the liquid in A is sampled for analysis.

Dynamic Flow Method——Schematic diagram of the apparatus used for the dynamic equilibrium method is shown in Fig. 2. About 100 ml of a sample liquid is placed in the vapor saturator (E), fitted with a thermometer (F), and air inlet tube and outlet tube having a double vapor bulb. E is heated at a required temperature in the thermostat (G) with vigorous stirring by a magnetic stirrer (H). Dry air, prewarmed in the spiral tube (D) immersed in G, is bubbled through the liquid in E. Stream of air is supplied from the air pump (A) through the flowmeter (B) and purification tube (C) packed with silica gel, Ascarite, and Anhydron, and its flow rate is regulated to the limit of 40 ml/min. The air flow saturated with the vapor is warmed in the outlet tube (I) equipped with an electric heater, and then introduced into the U-trap (J) cooled with Dry Ice–acetone mixture. Through the guard tube (K), J is connected with the Mariotte flask (L), where volume of the flowing air is measured. After a requisite volume of the air is passed, the condensate in J, which is weighed, and the residual liquid in E are subjected to analysis.

Materials and Reagents——For the determination of equilibria for formic acid–triethylamine system 99% formic acid and triethylamine of special grade were used. The chemicals used for analysis were of JIS special reagent grade.

Six formic acid–trialkylamine azeotropes listed in Table II were prepared by the following procedures. A mixture of 80% formic acid and trialkylamine, roughly in the azeotropic molar proportion, was carefully distilled under a reduced pressure. After removal of a lower boiling distillate, a fraction at constant higher boiling temperature was collected. This distillate was dried over anhydrous $MgSO_4$ and redistilled. Analytically pure sample was obtained by further redistillation.

Analytical Method——For the determination of the composition of the vapor and liquid phases, the refractive index method was adopted for the benzene–ethanol system and titrimetric method for the acetic acid–water and formic acid–trialkylamine systems. In the case of the formic acid–trialkylamine system, the amine content was measured by the potentiometric titrimetry in AcOH using 0.1N $HClO_4$ in AcOH–Ac_2O. When formic acid in the sample was present in excess over equivalent of the trialkylamine, the excess amount was measured titrimetrically using 0.1N NaOH. In the case of smaller content of formic acid, the redox titration method[14] with 0.1N $KMnO_4$ was adopted, after removal of trialkylamine by concentration of the sample solution basified with Na_2CO_3.

Result and Discussion

For testing the modified apparatus preliminary experiments were conducted with the sample, benzene–ethanol and acetic acid–water. The capillary method[15] by the use of the still indicated precision in the boiling point determination by premeasurement of the boiling point of water, which showed 100.00° with standard deviation of 0.038° throughout 15 runs in three days. With the use of benzene–ethanol system the still was operated to know the time required for reaching the equilibrium between vapor and liquid with respect to the bath temperature. Stable equilibrium was confirmed to exist after the sample was boiled for 5 min at the bath temperature, 30° higher than the boiling liquid temperature. Plots of temperatures and compositions of the vapor phase at varied bath temperatures measured after a 5-min boiling are shown in Fig. 3.

13) Manostat, model HV-1 (Shibata Chemical Apparatus Mfg. Co., Ltd.) was used for pressure regulation in the present work.

14) F.P. Treadwell and W.T. Hall, "Analytical Chemistry," Vol. 2, John Wiley and sons, Inc., New York, 1958, p. 560.

15) A. Steyermark, "Quantitative Organic Microanalysis," 2nd Ed., Academic Press, New York, 1961, p. 552.

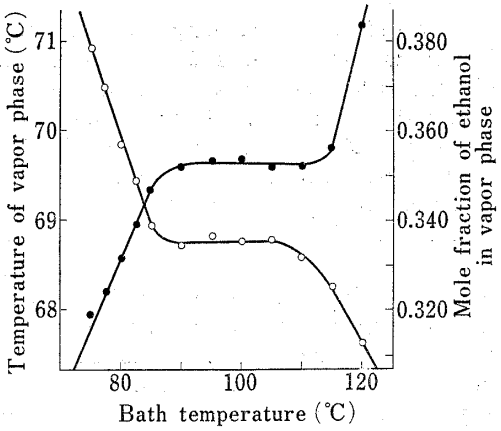

Fig. 3. Dependences on Bath Temperatures for Benzene–Ethanol System

(Meassured after 5-min boiling)
—●—: temperature of vapor phase
—○—: composition of vapor phase

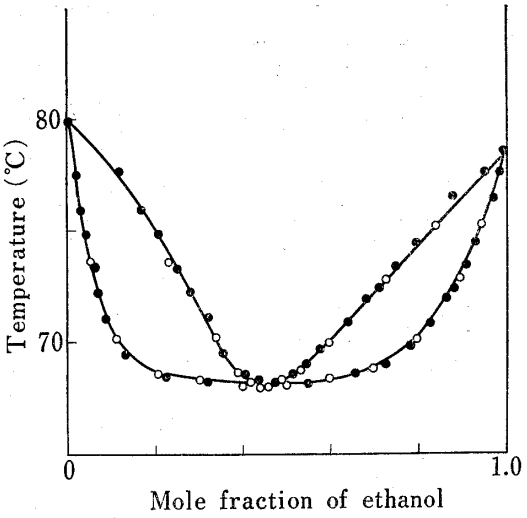

Fig. 4. Boiling Point Diagram for Benzene–Ethanol System

—●—: this work, —○—: literature[12a]

Curves of temperature *vs.* compositions of the liquids and vapors determined for the benzene–ethanol system gave the boiling point diagram shown in Fig. 4. The diagram determined for the acetic acid–water system in the same way is shown in Fig. 5. As can be seen in these two graphs, these data are in good agreement with those in the literatures.[12] Test for the thermodynamic consistency of the equilibrium data by Herington method[16] was

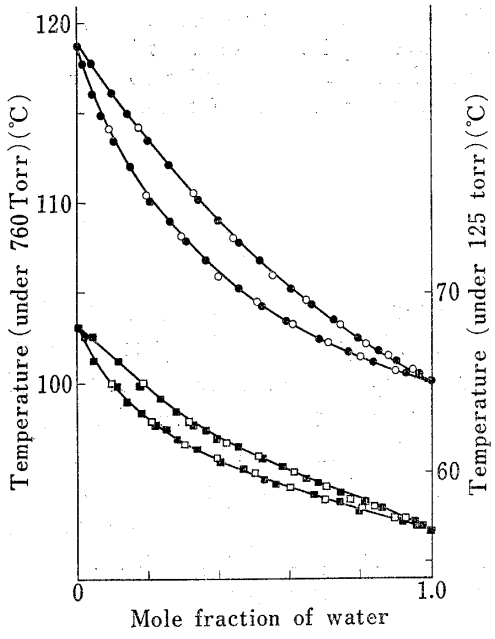

Fig. 5. Boiling Point Diagram for Acetic Acid–Water System

upper diagram, under 760 Torr
lower diagram, under 125 Torr
—●—■—: this work, —○—□—: literature[12b]

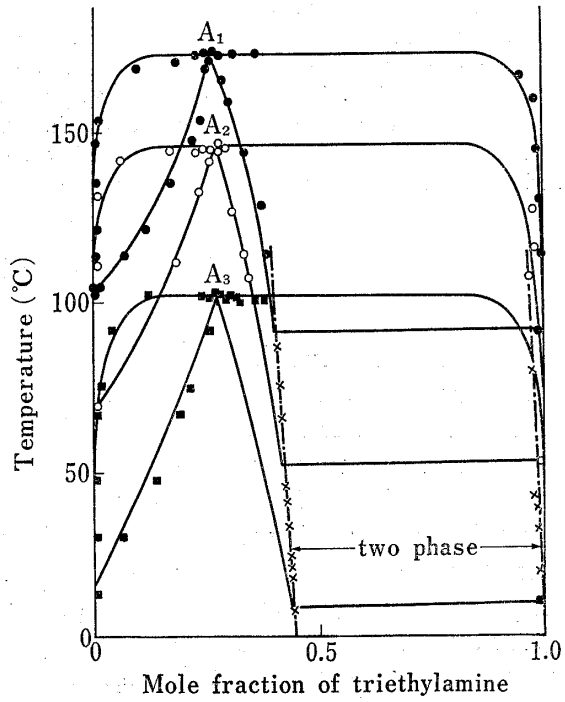

Fig. 6. Boiling Point Diagram for Formic Acid–Triethylamine System

—●—: 760 Torr, —○—: 200 Torr, —■—: 20 Torr
————×—: critical limit of solution

16) E.F.G. Herington, *J. Inst. Petrol.*, **37**, 457 (1951).

Table I. Mole Fractions of Triethylamine in Vapor–Liquid Equilibrium of Formic Acid–Triethylamine System

760 Torr[a]			200 Torr[a]			20 Torr[a]			49°[b]	
Liquid	Vapor	Temp. (°C)	Liquid	Vapor	Temp. (°C)	Liquid	Vapor	Temp. (°C)	Liquid	Vapor
0.256	0.108	167.6	0.269	0.176	144.8	0.274	0.123	101.5	0.2902	0.1563
0.259	0.189	170.4	0.273	0.233	143.2	0.273	0.247	101.6	0.2916	0.1727
0.262	0.207	172.8	0.274	0.238	144.1	0.281	0.254	100.8	0.2934	0.2348
0.264	0.238	172.9	0.275	0.262	144.2	0.283	0.281	102.7	0.2938	0.2677
0.265	0.248	172.7	0.272	0.278	146.0	0.281	0.304	101.8	0.2954	0.2852
0.264	0.268	173.2	0.278	0.279	145.9	0.286	0.313	102.3	0.2957	0.2947
0.270	0.271	173.4	0.283	0.294	146.2	0.287	0.322	100.6	0.2964	0.3866
0.279	0.320	172.6	0.279	0.320	145.0	0.296	0.360	101.3	0.2965	0.4167
0.270	0.371	172.0	0.283	0.346	144.5	0.296	0.373	100.6	0.2978	0.4822
Az. p.[c]: 0.2676		172.8	Az. p.[c]: 0.2770		144.9	Az. p.[c]: 0.2838		101.6	Az. p.[c]: 0.2944[d]	

a) Data under the constant pressure obtained by the use of the equilibrium still.
b) Data at the constant temperature obtained by the dynamic flow method.
c) Az. p.: azeotropic point
d) This mole fraction value corresponds to 0.35 Torr as the vapor pressure of the azeotrope.

satisfactory for both systems giving the D—J values less than 10, *i.e.*, —23.7 for benzene–ethanol system, and 7.5 (760 Torr) and 3.7 (125 Torr) for acetic acid–water system.

As the above experiments proved the possibility of using the still for reduction of heating time and amount of sample, vapor-liquid equilibria of the formic acid–trialkylamine systems were examined to know whether these binary systems involve azeotropes. We begun with the formic acid–triethylamine system selected as a representative and vapor–liquid equilibria for this binary system was examined under ordinary and a number of reduced pressures. Representative data at 760, 200, and 20 Torr are indicated in Table I. These were obtained by measurement of composition of the vapor and liquid phases in equilibria for the mixtures of different quantities of the two components. Plots of these data give diagrams of the equilibria, shown in Fig. 6, involving the liquid and vapor phases of the same composition at A_1, A_2, and A_3. In a range of larger quantities of triethylamine, two layers of the liquid phase were observed as represented by the plotted lines of the critical solution temperatures[17] in Fig. 6. The x—y diagrams between the mole fraction of triethylamine in the liquid and vapor phases gave a straight line in a range of 0.1—0.4 mole fraction of the vapor phase with the significant level less than 0.01. A_1, A_2, and A_3 in Fig. 6 were then determined as the point of intersections of the lines crossed by the tangential line passing through the origin. The boiling point at A_1, A_2, and A_3 at 760, 200, and 20 Torr, respectively, were determined from the boiling points in the range of $A_n \pm 0.05$ (n=1, 2, and 3) mole fraction, since the vapor phase lines in Fig. 6 were found to be linear and horizontal near the A_n points. The boiling points and compositions at A_1, A_2, and A_3 are listed in the bottom lines of Table I. These three compositions are close but significantly distinguished from each other by the Welch test (less than 0.01 level). The composition is altered to triethylamine-rich one with change in reducing pressure, clearly representing pressure dependence. Therefore, the liquids at A_1, A_2, and A_3 regarded as the azeotropes comprised of formic acid and triethylamine under the corresponding pressures. There was none of physical phenomena to indicate the addition compounds previously reported by the integral ratios of the components. Additional data for the composition of the azeotrope under a higher reduced pressure were obtained by the dynamic flow method at 49°. Data obtained are listed additionally in Table I, in which higher triethylamine content in the azeotrope is shown under such higher reduced pressure.

17) A. Findlay, "Practical Physical Chemistry," Longmans, Green and Co. Ltd., London, 1928, p. 267.

In view of the above data it is concluded that formic acid–triethylamine system involves an azeotrope. The molar fraction 0.2838 of triethylamine in the azeotrope at 20 Torr corresponds nearly to one of the previously reported compositions, $5HCO_2H \cdot 2NEt_3$ (molar fraction: 0.2857), but the expression by such an integral ratio appears insignificant after the clarification described in the foregoing.

Several trialkylamines, when distilled together with formic acid, have been known to give constant-boiling liquids of the constant compositions. By analogy of the formic acid–triethylamine system it can be safely said that these liquids are azeotropes, in spite of the previous reports of compound-like integral ratios of the components as described in the beginning of this paper. In order to determine accurate compositions and boiling points of the azeotropes, the constant-boiling liquids with other five trialkylamines listed in Table II were carefully prepared at 20 Torr and subjected to analysis. Reliable analytical data of these azetropes obtained by the potentiometric titration are recorded in Table II.

Table II. Formic Acid–Trialkylamine Azeotropes

Trialkylamine component	Azeotropic point [°C(20 Torr)]	Mole fraction of trialkylamine[a]	Elemental analysis (%)[b]		
			C	H	N
Trimethylamine	90.1	0.2706	37.49 (37.47)	7.99 (7.94)	7.63 (7.67)
Triethylamine	101.6	0.2838	47.16 (47.10)	9.21 (9.30)	6.57 (6.44)
Tripropylamine	97.7	0.2804	53.26 (53.34)	9.97 (10.12)	5.35 (5.39)
Tributylamine	106.5	0.3015	58.81 (58.58)	10.86 (10.86)	4.86 (4.77)
N-Methylpiperidine	102.0	0.2902	47.96 (47.95)	8.24 (8.48)	6.83 (6.62)
N-Methylmorpholine	90.0	0.2819	41.56 (41.37)	7.31 (7.40)	6.25 (6.39)
Triethylamine[c]	77.9	0.2363	51.00 (51.03)	9.70 (9.59)	4.94 (4.77)

a) Analytical data of the vapor phases obtained by the potentiometric titration, which were shown to be consistent with that of the liquid phases within ±0.001.
b) Values in parentheses are calculated from the mole fraction of the components obtained titrimetrically.
c) Acetic acid–triethylamine azeotrope, lit. [H. S. van Klooster and W. A. Douglas, *J. Phys. Chem.*, **49**, 67 (1945)] azeotropic point: 163° (760 Torr); mole fraction of triethylamine: 0.210.