this test. All other data points that satisfy the $T/T_{cb} < 0.95$ or $T/T_{cm} < 1.00$ criterion were included.

This method for estimating the volumes or densities of liquid mixtures of aliphatic hydrocarbons is strictly applicable only to bubble-point mixtures. At temperatures not close to T_{cb}—e.g., $T/T_{cb} < 0.8$—the method can also be used at higher pressures, because at low temperatures the compressibility of liquids is quite small. This method should not be used, however, at extremely high pressures at any temperature.

NOMENCLATURE

b = weighting factor in T_{cb} determination
c = adjustment coefficient in weighting-factor determination
M = molecular weight
n = number of components in the mixture
T = temperature, °K
V = molar bubble-point volume
x = mole fraction of a component of the mixture
Z_c = critical compressibility factor
ρ = density

Subscripts

b = weighted mole average
c = critical
i, j = components of a multicomponent mixture
m = mole average
1, 2 = components of a binary mixture

LITERATURE CITED

(1) Akers, W. W., Kehn, D. M., Kilgore, C. H., *Ind. Eng. Chem.*, **46**, 2536 (1954).
(2) American Petroleum Institute, "Technical Data Book—Petroleum Refining," Chap. 6, pp 35-9, 1966.
(3) Berry, V. M., Sage, B. H., *J. Chem. Eng. Data*, **4**, 204 (1959).
(4) Deam, J. R., PhD Thesis, Figure 18, Oklahoma State University, Stillwater, Okla., 1969.
(5) Glanville, J. W., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **42**, 508 (1950).
(6) Harmens, A., *Chem. Eng. Sci.*, **20**, 813 (1965).
(7) Harmens, A., *ibid.*, **21**, 725 (1966).
(8) Kay, W. B., *Ind. Eng. Chem.*, **30**, 459 (1938).
(9) Kay, W. B., *ibid.*, **32**, 353 (1940).
(10) Kay, W. B., *ibid.*, **40**, 1459 (1948).
(11) Lu, B. C.-Y., *Chem. Eng.*, **66** (9), 137 (1959).
(12) McKay, R. A., Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **43**, 2112 (1951).
(13) Natural Gas Processors Suppliers Assn., "Engineering Data Book," pp 165, 167, 169, 1966.
(14) Nysewander, C. N., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **32**, 118 (1940).
(15) Olds, R. H., Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, **41**, 475 (1949).
(16) Olds, R. H., Sage, B. H., Lacey, W. N., *ibid.*, **34**, 1008 (1942).
(17) Rackett, H. G., *J. Chem. Eng. Data*, **15**, 514 (1970).
(18) Rackett, H. G., SM thesis, Massachusetts Institute of Technology, Cambridge, Mass, 1960.
(19) Reamer, H. H., Sage, B. H., *J. Chem. Eng. Data*, **9**, 24 (1964).
(20) Reamer, H. H., Sage, B. H., *ibid.*, **10**, 49 (1965).
(21) Reamer, H. H., Sage, B. H., *ibid.*, **11**, 17 (1966).
(22) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **38**, 986 (1946).
(23) Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, **39**, 77 (1947).
(24) Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, **42**, 534 (1950).
(25) Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, **43**, 976 (1951).
(26) Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, **43**, 2515 (1951).
(27) Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.*, **45**, 1805 (1953).
(28) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem., Chem. Eng. Data Series*, **1**, 29 (1956).
(29) Reamer, H. H., Sage, B. H., Lacey, W. N., *J. Chem. Eng. Data*, **5**, 44 (1960).
(30) Reamer, H. H., Selleck, F. T., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **45**, 1810 (1953).
(31) Sage, B. H., Lacey, W. N., *ibid.*, **32**, 992 (1940).
(32) Sage, B. H., Lavender, H. M., Lacey, W. N., *ibid.*, **32**, 743 (1940).
(33) Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., *ibid.*, **34**, 1108 (1942).
(34) Weise, H. C., Reamer, H. H., Sage, B. H., *J. Chem. Eng. Data*, **15**, 75 (1970).
(35) Yen, L. C., Woods, S. S., *AIChE J.*, **12**, 95 (1966).

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A Ternary Positive-Negative Azeotrope: Acetone–Chloroform–Ethanol

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The ternary positive-negative system composed of acetone, chloroform, and ethanol was investigated at 710 mm Hg by a combined ebulliometric-distillation method. In this system a positive-negative (saddle) azeotrope is formed. The azeotrope contains acetone 33.4, chloroform 48.3, and ethanol 18.3% by mole and boils at 61.17° C. The azeotropic parameters of the ternary saddle system were also computed from binary azeotropic data assuming that the components form a regular solution.

Saddle azeotropic systems, called also positive-negative systems, exhibit a hyperbolic point which is neither a minimum nor maximum in either boiling temperature or vapor pressure and are characterized by the presence of the "top-ridge line." They also exhibit some peculiar properties called distillation anomalies. The first ternary positive-negative (saddle) azeotrope, in spite of the fact that its existence was predicted by W. Ostwald at the end of last century, was found in 1945 by Ewell and Welch (*2*) in the system acetone–chloroform–methanol.

Since then Bushmakin and Kiss (*1*) and Molodenko and Bushmakin (*5*) have described two other saddle azeotropes obtained by replacing one of the constituents by another substance. In other similar systems, only ternary positive azeotropes were found. Historical outline of azeotropy with special emphasis on saddle azeotropes is given in Swietoslawski's book (*8*). The purpose of this work was to confirm a suggestion that replacement of methanol by ethanol in the system examined by Ewell and Welch would result in the formation of the saddle azeotrope and to determine by a combined ebulliometric-distillation method the composition and boiling temperature of this azeotrope.

EXPERIMENTAL

Ethanol, chloroform, and acetone were all from Analar, BDH, London. Ethanol was dehydrated with benzene on a laboratory fractionating column (10 t.p.); dehydration of acetone was carried out on the column in the presence of phosphorus pentoxide. Chloroform was also subjected to fractional distillation. Then the density d^{20}, refractive index n_D^{20}, and the ebulliometric degree of purity, defined by Swietoslawski (*7*) as the difference between the boiling and the condensation temperatures, were determined for each of the substances mentioned. Physical properties of the substances are listed in Table I.

The method consisted at first in finding the minimum, M, of boiling temperature on the isobaric boiling temperature surface formed by the negative azeotrope [(−)1,2] and ethanol, 3, then the shape of the sections 1′–1″, 2′–2″, 3′–3″, etc., of the boiling temperature isobar surface was found by successive dosing of the main line mixtures with the binary mixtures as shown in Figure 1. In this way the shape of the top-ridge line (maxima on these isobars) was determined, and the composition of the saddle azeotrope was found by extrapolation. Full details regarding the examination of a positive-negative (saddle) azeotrope by this method are described in Swietoslawski's monograph (*8*). This method was employed for examining ternary systems as well as the three binary systems acetone–chloroform, acetone–ethanol, and chloroform–ethanol. Swietoslawski's differential ebulliometer served for this purpose. To observe small changes in atmospheric pressure during measurements, Swietoslawski's simple ebulliometer filled with double-distilled water was used. Temperature was measured with the aid of calibrated mercury-in-glass thermometers (0.1° division) and of Beckmann 5° thermometers (0.01° division).

RESULTS

In Table II are presented binary azeotropic data. These data differ slightly from those reported in the literature (*6*), which were obtained almost exclusively by fractional distillation.

The main line obtained by dosing negative azeotrope [(−)1,2] with pure ethanol exhibits the minimum of the boiling temperature amounting to 61.00° C. The mixture characterized by that minimum contains approximately 8.5% of ethanol and 91.5% by weight of the negative azeotrope.

Results of the ebulliometric doses aimed at establishing the shape of the top-ridge line and the location of the azeotropic point (±)Az in the ternary positive system acetone–chloroform–ethanol are listed in Table III.

In Figure 1 the projection of the top-ridge line in the Gibbs concentration triangle and the point (±)Az are shown. Approximate composition of the ternary positive-negative azeotrope was graphically estimated from the results of ebulliometric doses. The azeotrope contains 22.7% of acetone, 67.3% of chloroform, and 10.0% by weight of ethanol. Owing to the fact that the boiling temperature surface in the neighborhood of the azeotropic point is very flat, supplementary measurements appear to be necessary for the accurate determination of the azeotropic composition.

For this purpose the fractional distillation method was chosen. The ternary mixture, composition of which was estimated from the ebulliometric measurements, was subjected to fractional distillation, and the main fraction of the distillate, as well as the initial mixture, was analyzed by measuring viscosity at 30° C. In addition, four other mixtures, compositions of which differed only slightly from the above mixture, were prepared and their viscosities determined in a similar way. About 90% of the distillate was collected at the constant temperature of 61.15° C at 710 mm Hg. Viscosity of the azeotrope at 30° C was 0.56 cP. In Table IV are listed azeotropic parameters (boiling temperature and composition) of ternary positive-negative system acetone–chloroform–ethanol. The values of boiling temperature and composition of the ternary saddle azeotrope are reliable to ±0.1° C and ±0.5 mol %, respectively.

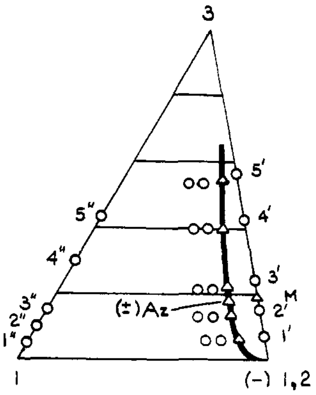

Figure 1. A portion of the Gibbs concentration triangle limited by points 1, [(−)1,2], and 3

Table I. Physical Constants of Acetone, Chloroform, and Ethanol

Substance	T^{710}, °C	T^{760}, °C[a]	d^{20}	n_D^{20}	Ebull. degree of purity[b]
Acetone, 1	54.23	56.13	0.7906	1.3590	IV
Chloroform, 2	58.47	61.00	1.4890	1.4454	IV
Ethanol, 3	76.54	78.25	0.7894	1.3614	IV

[a] Estimated values which were calculated (obtained) by assuming that the mean coefficients (*dt/dp*) for the pure acetone, chloroform, and ethanol are 0.038, 0.05, and 0.0342, respectively. [b] A substance is characterized by IV ebulliometric degree of purity when the difference between the boiling and the condensation temperatures is in the range of 0.02–0.005° C.

Table II. Azeotropic Parameters of Binary Systems Acetone–Chloroform, Chloroform–Ethanol, and Acetone–Ethanol

System	T^{710}, °C	T^{760}, °C[a]	Composition, mol % 1	2	3	δ, °C[b]
Acetone–chloroform (12)	62.12	64.4	(20.10)	(79.90)[c]		
			34.20	65.80		−3.65
Chloroform–ethanol (23)	57.14	59.20		(93.10)	(6.90)	
				83.85	16.15	1.33
Acetone–ethanol (13)			Zeotropic			

[a] Estimated values obtained in similar way as in Table I but with the assumption that the value of (*dt/dp*) for a mixture is additive function of composition. [b] δ stands for the azeotropic depression or elevation. [c] Parentheses indicate the compositions expressed in wt %.

Table III. Ebulliometric Doses (Sections of Boiling Temperature Isobar Surface of Mixtures 1′–1″, 2′–2″, . . . , 5′–5″)

	Composition of mixture characterized by maximum of boiling temperature, mol %			
Dose	1	2	3	T^{710}, °C
1′–1″	37.90	54.20	7.90	61.30
2′–2″	36.10	48.90	15.00	61.17
3′–3″	32.50	45.70	21.80	61.21
4′–4″	25.50	34.30	40.40	61.97
5′–5″	18.10	27.10	54.80	64.06

Table IV. Azeotropic Parameters of Ternary Positive-Negative System Acetone–Chloroform–Ethanol

Component	x_{exptl}		T^{710}, °C	T^{760}, °C[a]
Acetone, 1	33.4	±0.5	61.17 ± 0.1	63.40
Chloroform, 2	48.3			
Ethanol, 3	18.3			

[a] Estimated value.

REGULAR SOLUTIONS AND AZEOTROPIC PARAMETERS

The azeotropic parameters (boiling point and composition) in the above system were calculated with the aid of Malesinski's equations (*4*), derived on the assumption that a mixture fulfills requirements for regular solution. As it was said before (Table II), no azeotrope is formed in the acetone–ethanol system. To compute parameter x_{13}, the data for positive binary azeotrope acetone–methanol were taken from Horsley's Azeotropic Data (*3*). This is possible by assuming that the azeotropic range, Z, is constant, irrespective of component of the homologous series lying within that range, as well as of their isomers and closely related substances. In fact, slight deviations were found from this behavior. The azeotropic range parameters, z_{12}, z_{23}, and z_{13}, estimated from our binary azeotropic data, are as follows:

$$z_{12} = -22.3^\circ\text{C},\ z_{23} = 30.7^\circ\text{C, and } z_{13} = 15.2^\circ\text{C}$$

The boiling temperature and composition of the ternary saddle azeotrope composed of acetone, 1, chloroform, 2, and ethanol, 3, computed by means of Malesinski's relationships were: $T_{123}^{\text{Az}} = 60.3^\circ\text{C}$, $x_1 = 30.7\%$, $x_2 = 46.9\%$, and $x_3 = 22.4\%$ by mole. Satisfactory agreement was found between experimental and calculated boiling temperatures and composition of the azeotrope, in spite of the fact that it (azeotrope) contains associated ethanol and polar chloroform. The possible error in the composition of the ternary azeotrope for a system under isobaric conditions is due not only to the deviations of the system from regularity but also to the change of A_{ij} (regular solution constant) with temperature and to the differences in the entropies of vaporization of the pure components.

However, the effect of the differences in the vaporization entropies is usually small compared to the deviations from regularity.

For mixtures which exactly fulfill the requirements for regular solutions, the result (T_{123}^{Az}) is independent of the choice of the reference component. In our case, the reference component was chloroform. If there are deviations from regularity, however, then the values of z_{ij} and azeotropic depression or elevation δ depend on which experimentally determined quantity was used in calculation. In this case, owing to formation of no azeotrope in the acetone–ethanol system, it is impossible to show how the choice of the reference component would affect the T_{123}^{Az}.

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LITERATURE CITED

(1) Bushmakin, I. N., Kiss, I. N., *Zhur. Priklad. Khim.*, **30**, 200, 379 (1957).
(2) Ewell, R. H., Welch, L. M., *Ind. Eng. Chem.*, **37**, 1244 (1945).
(3) Horsley, L. H., Azeotropic Data, ACS monograph, Washington, D. C., 1952.
(4) Malesinski, W., "Azeotropy and Other Theoretical Problems of Vapour-Liquid Equilibrium," Interscience, Div. of John Wiley & Sons, Ltd. London, New York, Sydney, 1965.
(5) Molodenko, P. J., Bushmakin, I. N., *Vestnik*, Leningrad Univ., No. 10, 681 (1958).
(6) Röck, H., Schröder, W., *Z. Physik. Chem.*, **9**, 277 (1956).
(7) Swietoslawski, W., "Ebulliometric Measurements," Reinhold, New York, N. Y., 1945.
(8) Swietoslawski, W., "Azeotropy and Polyazeotropy," Pergamon, New York, N. Y., 1963.

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