Table II. Summary of Crystallographic Data

Solid no.	Dimensions, Å			Unit cell
	a	b	c	
1, 2, 3, 10, 11, 12	16.58	22.11	17.27	Orthorhombic
4, 5, 13	16.47	21.98	17.13	Orthorhombic
6, 7, 8	15.80	21.38	16.50	Orthorhombic

Discussion

Although the tie-lines are converging to three different centers on the line AB (except one), ternary compound formation was not confirmed by x-ray studies, and isothermal invariant points were not found on the diagram. This is another support for the opinion that ternary compounds are not formed in this system. We believe that solid solutions between $ZrO(NO_3)_2 \cdot 5H_2O$ and $ZrOCl_2 \cdot 8H_2O$ are crystallized at 0 °C, at least for a total acidity close to 8.2 N. Although formation of solid solutions between two hydrates with differing degrees of hydration seems to be rather unusual, we were not able to prove the formation of any ternary compound of known composition. Similarly, existence of isothermal invariant points was not detected on the phase diagram, at least in the regions that we studied.

Pure zirconyl chloride octahydrate and pure zirconyl nitrate hydrates were similarly studied by the x-ray diffraction method. For zirconyl chloride octahydrate we have obtained the following parameters (mean value of four measurements): $a = 12.9$ Å, $b = 12.9$ Å, $c = 10.6$ Å.

They are very close to literature data. Accordingly, this salt belongs to the tetragonal system.

We have also prepared pure zirconyl nitrate dihydrate $Zr(NO_3)_2 \cdot 2H_2O$ and measured the crystallographic dimensions: $a = 9.44$ Å, $b = 12.85$ Å, $c = 9.85$ Å (mean value of four measurements).

According to the above results, this salt belongs to the orthorhombic system.

As for the zirconyl nitrate pentahydrate, we were not able to prepare crystals corresponding exactly to $Zr(NO_3)_2 \cdot 5H_2O$ and having a constant composition (4). It appears that the pentahydrated nitrate is stable only in the form of solid solutions.

When the total acid was increased to 9.4 N, we were able to prepare solutions more concentrated than shown by the line AB. Solid phases which crystallized from these mixtures at 0 °C were apparently mixed salts formed between zirconyl chloride octahydrate and hydrates of zirconyl nitrate with water molecules less than five (4, 3, and 2). X-Ray results were more difficult to interpret, and it was not possible to show the existence of a ternary compound.

Glossary

X_i mole percent of species i
W_1 weight percent of NO_3^-
W_2 weight percent of Cl^-
N normality
S solubility curve

Literature Cited

(1) Burns, E. A., Muraca, R. F., *Anal. Chim. Acta*, **23**, 136–44 (1960).
(2) Delaunay, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **84** (1963).
(3) Kieselbach, R., *Ind. Eng. Chem. Anal. Ed.*, **16**, 76 (1944).
(4) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 7, Longmans, Green and Co., London, 1957.
(5) "Reagent Chemicals ACS Specifications", 4th ed, American Chemical Society, Washington, D.C., 1968.
(6) Rosin, J., "Reagent Chemicals and Standards", 3d ed, D. Van Nostrand, New York, N.Y., 1955.
(7) Swift, E. H., Arcand, G. M., Lutwack, R., Meier, D. J., *Anal. Chem.*, **22**, 306–308 (1950).

Thermodynamic Properties of the System Toluene–1,2-Dichloroethane

S. Sundaram[†] and D. S. Viswanath*

Department of Chemical Engineering, Indian Institute of Science, Bangalore-560 012, India

Data on heats of mixing at 30 °C, vapor–liquid equilibrium, latent heats of vaporization at 686 mmHg, and vapor pressures for the system toluene–1,2-dichloroethane are presented.

This paper presents the experimental data on vapor–liquid equilibrium, latent heats of vaporization, vapor pressure, and heats of mixing of mixtures of toluene and 1,2-dichloroethane. Earlier work from this laboratory has been reported (17, 18). A literature survey revealed that the system toluene–1,2-dichloroethane has been studied and Table I shows the extent of study on the system. In addition to these available data, Barker (2) has reported activity coefficients for the system at 30, 40, and 50 °C determined by gas–liquid chromatographic techniques.

[†] On deputation from Regional Engineering College, Tiruchirapalli, India.

Material Used and Purification

Analar toluene and laboratory grade 1,2-dichloroethane supplied by British Drug House, Bombay, were purified by the methods described by Weissberger (30) and Riddick and Bunger (19). The purities were checked against refractive index and density, and are reported in Table II. Vapor phase chromatographs were obtained for the liquids using an AIMIL-NCL dual column gas chromatograph using Silicone gum rubber S.E. 30 as column material. A single peak was obtained for all the liquids.

Vapor Pressure Data

Vapor pressures of 1,2-dichloroethane were obtained up to laboratory pressure in a Brown still and at higher pressures in a Swietoslawsky type still. The present values together with data

Table I. Literature Survey on Toluene-1,2-Dichloroethane System

Data on	Pressure, (mmHg)	Comments	Ref
Vapor–liquid equilibrium	760	Colburn still	4, 5, 7, 11, 12, 16
	200	Othmer still	14
Heats of mixing	—	—	27

Table II. Properties of Toluene and 1,2-Dichloroethane

Material	η_D Present work	Lit. (6)	Density 30 °C Present work	Lit. (6)
Toluene	1.491 42	1.491 29	0.8578	0.8576
1,2 Dichloro-ethane	1.439 14	1.439 2	1.2386	1.2390

Table III. Vapor Pressure Data for 1,2-Dichloroethane

t, °C	P_D (exptl)	% deviation[a] Eq 1	Eq 2	Eq 3
70[b]	493.0	−0.003	0.16	−0.65
70.52	500.0	0.06	0.60	−0.15
71.10	507.5	0.54	1.02	0.35
71.93	523.5	0.25	0.68	0.09
74.43	571.0	−0.08	0.18	−0.09
76.15	605.5	−0.27	−0.13	−1.19
78.10	648.0	−0.24	−0.22	−0.03
80.00[b]	678.2	0.83	0.63	1.06
80.20	687.0	0.19	0.08	0.55
79.60	678.5	−0.50	−0.56	−0.16
84.20	782.5	−0.20	−0.59	0.44
83.70[c]	760.0	1.14	0.65	1.74
88.20	880.5	0.25	−0.37	1.25
90.35	942.5	−0.08	−0.84	1.12
95.10	1082.5	0.05	−1.00	1.72
99.10	1215.0	−0.05	−1.30	2.06
102.35	1335.5	−0.40	−1.90	2.07
105.60	1453.5	0.04	−1.60	2.90
108.32	1559.0	0.37	−1.40	3.50
108.10[c]	1520.0	2.20	0.39	5.20
% av abs deviation		0.22	0.78	1.08

[a] $(P_{calcd} - P_{expd}) \times 100/P_{cal}$. [b] Literature value from ref 28. [c] Literature value from ref 25.

available in literature (25, 28) are tabulated in Table III. The present data fitted an Antoine form of equation:

$$\log P_D = 7.039\ 93 - \frac{1274.078\ 86}{223.0 + t} \quad (1)$$

with an average absolute deviation of 0.2% and maximum deviation of 0.5%.

The Antoine equation for 1,2-dichloroethane available in literature (6) is

$$\log P_D = 6.952\ 22 - \frac{1247.8}{223 + t} \quad (2)$$

Equation 2 fits the present data with an average absolute deviation of 0.8% and maximum deviation of 1.8%.

Gallangher (10) has fitted his data up to 1000 mmHg to the following equation:

$$\log P_D = 7.8462 - \frac{1769.4}{273.16 + t} \quad (3)$$

Equation 3 fits the present data with an average absolute deviation of 1% and a maximum of 3%. The present data given by eq 1 are also better at higher pressures.

Table IV. t–x–y Data at 686 mmHg for the System: Toluene-1,2-Dichloroethane

t	x_T	y_T	γ_T	γ_D	γ_T/γ_D	x_T ideal
82.90	0.140	0.067	1.020	1.003	1.017	0.143
84.12	0.188	0.090	0.980	0.998	0.981	0.184
87.35	0.318	0.180	1.040	0.972	1.070	0.331
88.58	0.380	0.210	0.976	0.994	0.980	0.371
90.05	0.435	0.255	0.987	0.985	1.002	0.429
90.55	0.450	0.275	1.012	0.970	1.040	0.456
91.85	0.485	0.310	1.015	0.949	1.070	0.493
93.00	0.546	0.330	0.926	1.010	0.916	0.506
95.60	0.630	0.450	1.008	0.945	1.067	0.635
99.50	0.765	0.600	0.957	1.060	0.903	0.751
102.4	0.850	0.730	0.985	0.947	1.040	0.837
104.5	0.925	0.847	0.987	1.013	0.970	0.913
105.5	0.957	0.912	0.997	0.989	1.008	0.955
106.15	0.975	0.945	0.995	1.040	0.950	0.970

The experimental vapor pressures of toluene were compared with the values obtained from the Antoine equation taking the constants from A.P.I. tables (22):

$$\log P_T = 6.954\ 64 - \frac{1344.8}{219.482 + t} \quad (4)$$

The present data fitted the above equation with an average absolute deviation of 0.1% and maximum deviation of 0.25%.

Vapor–Liquid Equilibrium Data

A Brown still (3) was used to determine the equilibrium data. The still required 230 cm^3 of feed and took about 3–4 h to reach equilibrium. The data taken at 686 mmHg are shown in Figures 1 and 2 and Table IV. Data from literature (5, 11, 12, 14, 16) are also shown in Figures 1 and 2. A plot of log (γ_T/γ_D) vs. mole fraction of toluene showed a uniform scatter about the $y = 0$ axis. This type of behavior is typical of ideal solutions. This conclusion agrees with other workers (4, 5, 7, 11, 12, 14, 16).

The analysis of the mixture was done using refractive index and the calibration chart prepared in terms of mole fraction of the toluene fitted equation (5) with an average absolute deviation of 0.02% and maximum deviation of 0.05%:

$$\eta_D = 1.439\ 147 + 0.065\ 986 x_T - 0.013\ 766 x_T^2 \quad (5)$$

Higher order polynomials tried gave deviations of the same order.

Heats of Mixing

The calorimeter used in the present study was similar to those used by Vold (29), Tsao and Smith (26), and Ruiter (20) in that all these calorimeters have vapor space. The calorimeter is a cylindrical Dewar flask of 7.0 cm height and 4.5 cm diameter. The total volume of the calorimeter is 145 cm^3. The space between the walls of the calorimeter was evacuated to 10^{-3} mmHg. The calorimeter has four inlet ports, two for feeding the pure liquids through jacketed burettes, one for introducing the heater and temperature sensing element, and the fourth for a stirrer. The sensing element was a thermopile of eight copper–constantan thermocouples with its reference junction in ice. This thermopile was used in conjunction with a Wheatstone Bridge manufactured by Bajaj Electricals, Bombay, and a spot galvanometer manufactured by Cambridge Measuring Instruments Company Limited, England. Power for the heater made of fine nichrome wire was supplied by a 2 V battery. A voltmeter and ammeter manufactured by Bajaj Electricals, Bombay, along with a standard of 1 Ω resistance was used to measure the power supplied to the heater. The meters were calibrated in the Electrical Engineering Department of this institute. The voltmeter was
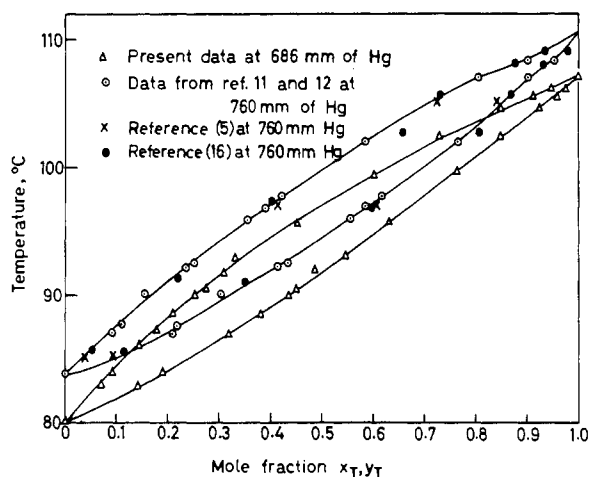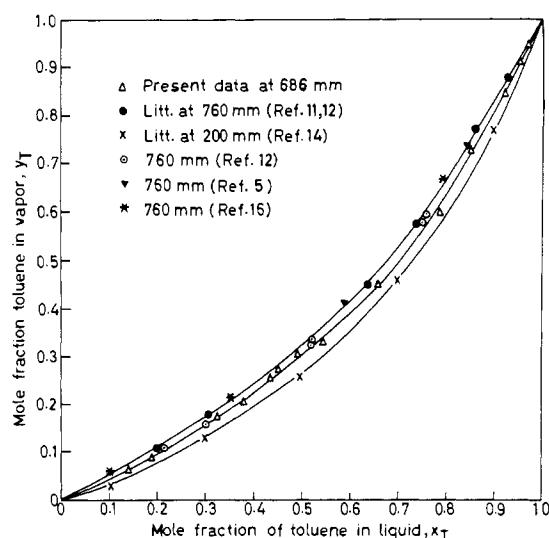
Figure 1. $t-x-y$ data for toluene-1,2-dichloroethane.

Legend for Figure 1:
- △ Present data at 686 mm of Hg
- ⊙ Data from ref. 11 and 12 at 760 mm of Hg
- × Reference (5) at 760 mm Hg
- ● Reference (16) at 760 mm Hg

Figure 2. $x-y$ data for toluene-1,2-dichloroethane.

Legend for Figure 2:
- △ Present data at 686 mm
- ● Litt. at 760 mm (Ref. 11,12)
- × Litt. at 200 mm (Ref. 14)
- ⊙ 760 mm (Ref. 12)
- ▼ 760 mm (Ref. 5)
- ✻ 760 mm (Ref. 16)

compared with an AVO 8 multimeter in the range 0–15 V and the ammeter with an Elliot 86 standard ammeter in the range 0–2 A. The jacketed burettes were of 50 cm³ capacity, graduated in steps of 0.1 cm³. An ultrathermostat Type U10 manufactured by VEB Prufgerate-Werk Medigen, East Germany, was used to maintain the temperature within ±0.02 °C. After both liquids attained 30 °C a known amount of the liquid was fed to the calorimeter. About 5 cm³ of the second liquid was added and the deflection in the galvanometer noted. Since the present system was exothermic, the mixture was allowed to cool down to its initial temperature. The quantity of heat added and the time taken to bring the system to the original temperature were noted. The heat of mixing of that composition is given by:

$$\Delta H_m = \frac{EIt'}{\dfrac{V_T \rho_T}{M_T} + \dfrac{V_D \rho_D}{M_D}} \quad (6)$$

and the composition given by

$$x_T = \frac{V_T \rho_T / M_T}{\dfrac{V_T \rho_T}{M_T} + \dfrac{V_D \rho_D}{M_D}} \quad (7)$$

The heats of mixing for the whole range of composition were determined by taking the second liquid in the calorimeter and adding the first liquid.

The calorimeter was checked with systems reported in lit-

Table V. Heats of Mixing of Systems Used for Calibration of the Apparatus

System	% max devn	% min devn	% av abs devn
Benzene—Methanol	2.6	0.3	1.4
Benzene—2-propanol	4.0	0.0	2.1
Toluene—2-propanol	2.7	0.2	1.6
Toluene—1-butanol	3.1	0.0	1.8

Table VI. Heats of Mixing Data of Toluene—1,2-Dichloroethane

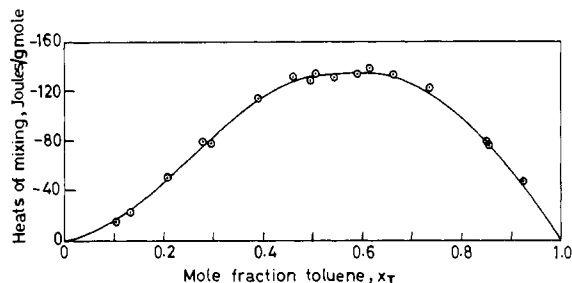| V_T	V_D	x_T	$\Delta H_m / \mathrm{J\ mol^{-1}}$
5.0	34.6	0.096	−15.100
7.0	34.6	0.131	−23.340
11.9	34.6	0.204	−51.020
18.0	34.6	0.279	−80.240
20.0	35.1	0.297	−78.680
30.0	35.1	0.389	−116.810
40.0	35.1	0.459	−132.105
40.0	30.7	0.492	−129.260
48.4	35.1	0.506	−132.829
40.0	25.3	0.540	−130.690
40.0	20.7	0.589	−135.960
40.0	18.4	0.617	−139.250
40.0	15.3	0.660	−134.660
40.0	10.7	0.735	−122.540
40.0	5.2	0.851	−78.000
40.0	5.0	0.856	−77.320
40.0	3.0	0.912	−49.000

Figure 3. Heats of mixing data for toluene-1,2-dichloroethane at 30 °C and 686 mmHg.

erature (31). Table V shows the systems studied and their deviations from literature value after making vapor space correction as suggested by McGlashan (15).

The heats of mixing data for the system toluene-1,2-dichloroethane are shown in Table VI and Figure 3. The data fitted the equation:

$$\frac{\Delta H_m}{x_T(1 - x_T)} = 61.69 - 14.36(2x_T - 1)$$
$$+ 7.102(2x_T - 1)^2 - 77.43(2x_T - 1)^3 \quad (8)$$

with an average absolute deviation of 1.8% and maximum deviation of 4%.

Tschametz (27) has reported the heats of mixing of this system as endo–exothermic but the present study revealed that the system is exothermic. Whereas benzene-1,2-dichloroethane is endothermic (17), it is likely that the addition of a methyl group to the benzene ring has made the system exothermic as in the case of benzene–benzyl chloride and toluene–benzyl chloride systems (15).

Heats of Vaporization

The apparatus used for the determination of latent heats is

Table VII. Latent Heat of Mixtures at 686 mmHg

x_T	L_{calcd}/kJ mol^{-1}	L_{exptl}/kJ mol^{-1}	% devn[a]
0.000	32.34	32.55	−0.6
0.100	32.83	32.78	0.1
0.185	32.99	32.99	0.0
0.305	33.14	33.11	0.1
0.485	33.35	33.20	0.5
0.660	33.40	33.26	0.4
0.770	33.43	33.30	0.4
1.000	33.50	33.34	0.5

Percent average absolute deviation = 0.3.

[a] $(P_{calcd} - P_{exptl}/P_{calcd}) \times 100$.

Figure 4. Latent heat of vaporization of toluene–1,2-dichloroethane at 686 mmHg.

the same as that used by Shettigar et al. (23) and Rao and Viswanath (18). It is a closed recirculation apparatus. The mode of operation of the apparatus is described by Shettigar et al. (23). In this experiment the power to the calorimeter was from a very well-regulated dc power supply with a ripple of not more than 0.1%. The power was measured by a calibrated voltmeter and ammeter. The volume between the two predetermined marks on the liquid meter was 5.7897 ml.

The composition of liquid was determined before feeding to the unit. After steady state was reached, which took about 3–4 h, the composition of a sample tapped from the liquid meter was determined with a stop watch of 0.1-s accuracy. However, the time used for calculation at each composition is an average of six or more readings. The latent heat was calculated using the equation

$$L = \frac{EIt'}{4.186 \times 5.7897 \times \rho_m} \tag{9}$$

Table VII and Figure 4 give the latent heat of vaporization values for the system.

Theoretical Calculation of Latent Heats

The heats of vaporization of pure toluene and 1,2-dichloro-ethane were calculated using the Clausius–Clapeyron equation and the virial equations given for toluene (1) and 1,2-dichloro-ethane (21). Density variations of liquid toluene and liquid 1,2-dichloroethane with temperature are reported (8, 9). The vapor pressure equations 1 and 4 were used in the above calculations. The calculated pure component values agree well with the experimental values as seen in Table VII.

The heats of vaporization of the binaries whose pure component ideal gas specific heat variation with temperature is small is given by Shettigar et al. (23):

$$L = \Sigma L_i x_i + \Delta H_m + \Sigma y_i C_{P_i}(T_2 - T_1) \tag{10}$$

The ideal gas specific heats of toluene and 1,2-dichloroethane are given in the literature (13, 24). The calculated and experimental latent heat values shown in Table VII reveal good agreement.

Glossary

C_P	ideal gas specific heat, J g mol^{-1} K^{-1}
E	voltage, V
I	current, A
L	latent heat of vaporization, J g mol^{-1}
M	molecular weight
P	vapor pressure, mmHg
t	temperature, °C
t'	time, s
T	temperature, K
T_1	bubble point, K
T_2	dew point, K
V	volume, cm^3
x	mole fraction in liquid phase
y	mole fraction in vapor phase
γ	activity coefficient
ρ_m	density of mixture, g cm^{-3}
ρ	density of liquid, g cm^{-3}
ΔH_m	heats of mixing, J g mol^{-1}
ηD	refractive index at 30 °C, using sodium D line
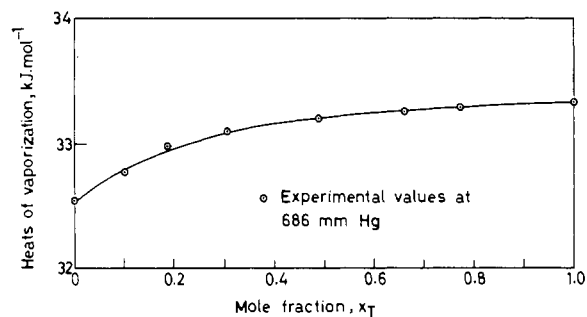
Subscripts

D	1,2-dichloroethane
i	component i
T	toluene

Literature Cited

(1) Andon, J. L., *Trans. Faraday Soc.*, **53**, 1078 (1957).
(2) Barker, P. E., et al., *J. Gas. Chromatgr.*, **5** (3), 119–127 (1967); *Chem. Abstr.*, **66**, 119301b (1967).
(3) Brown, I., *Aust. J. Sci. Res., Ser. A*, **3**, 306 (1950).
(4) Colburn, A. P., et al., *Ind. Eng. Chem.*, **35**, 1250 (1943).
(5) Dakshinamurthy, P., et al., *Indian J. Tech.*, **1**, 196 (1963).
(6) Dreisbach, P. G., "Physical Properties of Organic Compounds", Part I–III, American Chemical Society, Washington, D.C., 1956.
(7) Fordyce, C. R., Simonson, D. R., *Ind. Eng. Chem.*, **41**, 104 (1949).
(8) Francis, A. W., *Ind. Eng. Chem.*, **49**, 1779 (1957).
(9) Gallant, R. W., "Physical Properties of Hydrocarbons", Vol. I, Gulf Publishing Co., Houston, Texas, 1968.
(10) Gallangher, A. F., Hibbert, H., *J. Am. Chem. Soc.*, **59**, 2523 (1937).
(11) Hala, E., et al., "Vapor-Liquid Equilibrium Data", Pergamon Press, New York, N.Y., 1974, pp 130–132.
(12) Jones, C. A., Schoenburn, E. M., Colburn, A. P., *Ind. Eng. Chem.*, **35**, 666 (1943).
(13) Kobe, K. A., Harrison, R. H., *Pet. Refiner*, **36** (10), 155 (1957).
(14) Mariangles Tosi, B., *AIChE J.*, **17** (4), 854 (1971).
(15) McGlashan, M. L., "Experimental Thermochemistry", Vol. II, Skinner, H. A., Ed., Interscience, New York, N.Y., 1962, p 325.
(16) Norman, A., Elwing, P. J., *Ind. Eng. Chem.*, **41**, 2864 (1949).
(17) Patel, H. R., Ph.D. Thesis, Bangalore, India, 1974.
(18) Rao, M. V. J., Viswanath, D. S., *J. Chem. Eng. Data*, **18**, 49 (1973).
(19) Riddick, J. A., Bunger, W. S., "Techniques of Chemistry", Vol. II, "Organic Solvents", 3rd ed, Wiley-Interscience, New York, N.Y., 1970.
(20) Ruiter, L. H., *Recl. Trav. Chim. Pays-Bas*, **74**, 1131 (1955).
(21) Scott, D. W., Guthrie, G. B., Berg, W. J., *J. Phys. Chem.*, **66**, 911 (1962).
(22) "Selected Values of Properties of Hydrocarbons and Related Compounds", A.P.I. Research Project 44, Thermodynamic Research Center, Texas A&M University, College Station, Texas.
(23) Shettigar, U. R., Viswanath, D. S., Kuloor, N. R., Proceedings of the First International Conference on Calorimetry and Thermodynamics, Polish Scientific Publishers, Warsaw, 1969, p 823.
(24) Spencer, H. H., *Ind. Eng. Chem.*, **40**, 2152 (1948).
(25) Stull, D. R., *Ind. Eng. Chem.*, **39**, 517 (1947).
(26) Tsao, C. C., Smith, J. M., *Chem. Eng. Prog. Symp. Ser.*, **49** (7), 107 (1953).
(27) Tschametz, H., *Montash*, **79**, 499 (1948); *Chem. Abstr.*, **43**, 4938a (1949).
(28) Udovenku, U. U., Frid, Ts. B., *Zh. Fiz. Khim.*, **22**, 1263 (1948).
(29) Vold, R. D., *J. Am. Chem. Soc.*, **59**, 1515 (1937).
(30) Weissberger, A., Ed., "Techniques of Organic Chemistry", Vol. I, Part I, Interscience, New York, N.Y., 1949.
(31) Mrazek, R. V., Van Ness, H. C., *AIChE J.*, **7**, 190 (1961).