Part I

PHASE EQUILIBRIA

MOLECULAR TRANSPORT

THERMODYNAMICS

Isobaric Vapor-Liquid Equilibria for the Ternary System Acetone-Benzene-Chlorobenzene

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For studies in the behavior of multicomponent mixtures subjected to distillation, complete vapor-liquid data for a ternary system were required. The system acetone-benzene-chlorobenzene was chosen because available data indicated that it would be a totally miscible system, having no azeotrope but giving relatively large values of $y - x$, and could be relatively easily analyzed by specific gravity and refractive index measurements.

EXPERIMENTAL

Purity of the Components. Relatively pure liquids from the British Drug House were used. The acetone was of analytical reagent grade and was treated by drying over calcium sulfate and subsequent distillation in a small column, packed with 7 feet of glass helices and operated at a reflux ratio of 4 to 1. The benzene, also of analytical reagent grade, was purified by twice freezing out four fifths and rejecting the remainder. The chlorobenzene, which was of laboratory reagent quality, was distilled in the packed column in the same way as acetone. The cut taken for these two liquids had a boiling range of less than 0.1° C.

The properties of the purified liquids and some corresponding values collected by Timmermans (*14*) are tabulated in Table I. The results he reported are a selection of the more reliable figures published before 1950 and indicate the range of results obtained in careful studies.

Analytical Method. Mixtures of acetone, benzene, and chlorobenzene can be easily analyzed by means of specific gravity and refractive index measurements. Lines of constant specific gravity and refractive index do not meet at right angles on equilateral triangular graph paper, which is the optimum condition for ease of analysis. However, because of the large changes of properties within the system, the relatively acute meetings of these lines do not prevent satisfactorily accurate analysis. In the worst case, uncertainty of ±0.0001 in specific gravity and refractive index means an uncertainty of 0.0012, 0.0018 and 0.0006 in the values of x_A, x_B, and x_C, respectively.

Refractive indices were determined using an Abbe refractometer, and values could be reproduced to within ±0.0001. Specific gravities were determined using 5-ml. pycnometers with graduated arms; measurements were reproducible tc within ±0.0001. The small sample needed made this measurement nearly as economical in terms of material as in the measurement of refractive index.

Table II give specific gravity and refractive index information from which an analytical diagram can be constructed, such as Figure 1, using the right triangle which has several advantages as pointed out by Hatta (*5*). The calibration mixtures were made up by weighing. The values for the ternary mixtures were obtained by adding acetone to selected mixtures of benzene and chlorobenzene; hence the data can be plotted in series against increasing x_a and values for the lines of constant property found by interpolation.

Table I. Properties of Pure Compounds Used

Property	Literature Values	Experimental
	Acetone	
Sp. gr., d_4^{25}	0.7846–0.78503	0.7846 ± 0.0001
Ref. index, n_D^{25}	1.35662[a]	1.3560 ± 0.0001
Boiling point, ° C.	56.1–56.3	56.1 ± 0.1
	Benzene	
Sp. gr., d_4^{25}	0.87360–0.87376	0.8734 ± 0.0001
Ref. index, n_D^{25}	1.49790–1.4981	1.4978 ± 0.0001
Boiling point, ° C.	80.07–80.106	80.0 ± 0.1
	Chlorobenzene	
Sp. gr., d_4^{25}	1.10085–1.10110	1.1010 ± 0.0001
Ref. index, n_D^{25}	1.5219–1.5220[b]	1.5219 ± 0.0001
Boiling point, ° C.	131.687–132.00	131.8 ± 0.1

[a] The only value reported by Timmermans was determined in 1914 by by Rosanoff, Bacon, and White (*10*) and is probably not as reliable as the figure of 1.35596 found by Thomas and McAllister in 1957 (*13*) whose value for the specific gravity of pure acetone is 0.78438.

[b] Estimated by extrapolating data obtained at lower temperatures.

The present data can be used with confidence if, instead of the values of p_M measured by the authors, the values of p_M' are used where

$$p_M' = p_M + \Sigma x_i(p_i' - p_i) \qquad (1)$$

in which $p_i' - p_i$ is the difference between the experimental value of a property listed in Table I and the corresponding value for the component being used.

It is more convenient to carry out the preliminary interpolation of d_4^{25} and n_D^{25} by plotting values of Δp rather than actual values of p_M where

$$\Delta p = 10^4(p_M - \Sigma x_i p_i) \qquad (2)$$

For this reason, values of Δd_4^{25} and Δn_D^{25} are listed in Table II. The relationship

$$p_M' = \Sigma x_i p_i + 10^{-4}\Delta p \qquad (3)$$

can now be used in constructing plots of p_M'.

Procedure. For the determination of the vapor-liquid equilibria, a still was constructed and operated as described by Ellis (*3*). The pressure in the apparatus was controlled at 760 ± 1 mm. of mercury by means of a simple manostat. Mercury thermometers, divided to 0.1° C. and which were compared with instruments which had been checked by the National Physical Laboratory, were used for all temperature measurements.

Results. Table III gives the results obtained for the three binaries and for 54 points in the ternary region. The results are plotted in Figure 2 where smoothed curves give the vapor in equilibrium with the liquid represented on the triangular grid.

TESTING THE DATA

Consistency of the Binary System. The consistency of the binaries has been tested in the way discussed by Thijssen (*12*). The activity coefficients have been corrected for nonideality in the vapor phase by the method described by Perry (*9*). This correction is important for this system because of the wide boiling point range. Plots of log γ_1/γ_2 against x_1 are given in Figure 3.

As shown by Thijssen, the data for a binary system are consistent if

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} dx_1 = -\int_0^1 \left[x_1 \frac{d \log \gamma_1}{dx_1} + x_2 \frac{d \log \gamma_2}{dx_1} \right] dx_1 \qquad (4)$$

$$= \frac{1}{2.3} \int_0^1 \frac{\Delta H_m}{RT^2} \frac{dT}{dx_1} dx_1 \qquad (5)$$

Values of the integrals concerned for the three binary systems have been obtained graphically and are given in Table IV. The data of Tallmadge and Canjar (*11*) have been used to evaluate the right side of Equation 5 for the acetone—benzene system. Equation 4 must be used to test the consistency of the other two binaries because of the lack of heat of mixing data for them, though it is less accurate than Equation 5 because the heat of mixing and dT/dx can be more accurately determined than can the slopes of the log γ plots.

Table II. Data for Analysis of the System Acetone-Benzene-Chlorobenzene

Acetone	Benzene	Δd_4^{25}	Δn_D^{25}
0.0980	0.9020	16.0	20.0
0.2025	0.7975	31.0	38.0
0.3115	0.6885	41.5	51.5
0.3899	0.6001	48.0	57.0
0.5070	0.4930	49.0	59.0
0.6099	0.3901	47.5	56.0
0.7062	0.2938	41.0	49.5
0.7952	0.2048	33.0	39.5
0.8937	0.1063	18.5	20.5
0.1102	0	100.5	52.0
0.2079	0	176.0	88.0
0.3059	0	233.0	116.5
0.4169	0	276.0	141.5
0.5138	0	291.5	147.5
0.6081	0	286.0	144.0
0.6997	0	260.0	129.0
0.7963	0	207.5	103.0
0.8990	0	120.5	58.5
0	0.0967	24.0	3.0
0	0.2456	52.0	5.0
0	0.4015	70.0	7.0
0	0.5004	74.0	6.5
0	0.6304	70.0	6.0
0	0.7203	61.5	5.5
0	0.7924	48.5	4.0
0	0.8973	27.0	3.0
0.1078	0.1115	114.0	48.5
0.1933	0.1008	169.0	78.0
0.3020	0.0872	223.0	110.0
0.3939	0.0758	255.0	125.5
0.5803	0.0525	268.5	135.5
0.8210	0.0224	172.5	90.5
0.1057	0.2245	126.5	46.5
0.1962	0.2018	175.0	77.0
0.3050	0.1744	215.0	103.0
0.4910	0.1278	250.5	127.5
0.6779	0.0808	224.0	117.0
0.1050	0.3343	125.0	46.0
0.2150	0.2932	171.5	77.5
0.3024	0.2606	200.0	96.5
0.4182	0.2173	221.0	112.0
0.6185	0.1425	211.5	112.5
0.8230	0.0661	133.5	72.5
0.1028	0.4459	121.0	41.0
0.2037	0.3958	155.5	68.5
0.2939	0.3509	179.5	86.0
0.5039	0.2466	196.5	107.5
0.6973	0.1504	163.5	92.0
0.8546	0.0723	98.5	56.0
0.1031	0.5592	108.0	38.0
0.1988	0.4995	134.0	61.0
0.2906	0.4423	153.0	78.5
0.4035	0.3719	164.0	91.0
0.5915	0.2547	157.0	93.5
0.7906	0.1306	108.5	66.0
0.1020	0.6717	86.5	34.0
0.2016	0.5972	107.0	56.5
0.3111	0.5153	123.0	71.5
0.5127	0.3645	131.0	87.5
0.6865	0.2345	108.0	74.5
0.1030	0.7813	57.0	28.0
0.1973	0.6992	72.5	47.0
0.3096	0.6013	87.0	61.5
0.4033	0.5197	92.0	69.5
0.6066	0.3427	88.5	70.0
0.8038	0.1709	58.0	45.5

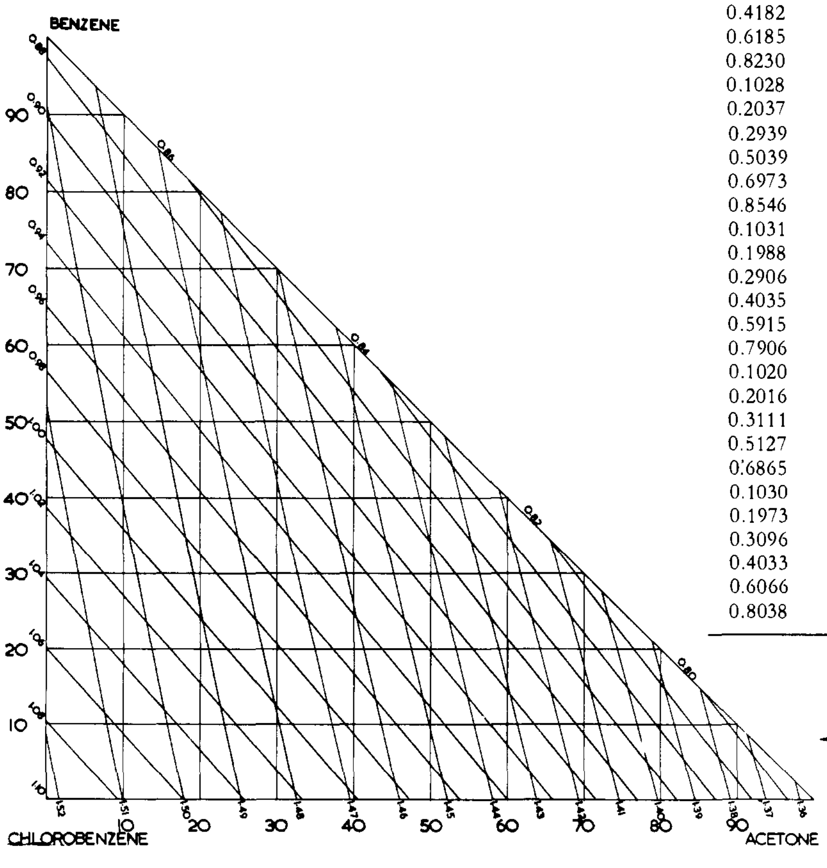

Figure 1. Lines of constant density and refractive index for the ternary system

The consistency of the results is shown by the small quantities in the difference column of Table IV. The points in the $\log \gamma_1/\gamma_2$ *vs.* x_1 (Figure 3) lie on smooth curves, showing that the data are reasonably free from random errors.

The vapor-liquid equilibria for the acetone—benzene binary have been reported several times. Canjar, Horni, and Rothfus (*1*) give an activity coefficient plot in which five series of results are compared. The authors' results agree well with those of Tallmadge and Canjar (*11*).

Othmer (*8*) reported the system acetone—chlorobenzene but not his experimental data; a graph indicates that there were relatively few of these. This may account for the rather large discrepancy between his smoothed data and the present results at higher concentrations of acetone.

The benzene-chlorobenzene binary is not reported in the collection of Chu (*3*), except for the isothermal data of Martin and Collie (*7*).

The relative volatility of acetone with respect to chlorobenzene (for the binary) is substantially constant. An $x - y$ diagram constructed with $y_A/y_C \times x_C/x_A = 10.2$ deviates by no more than 0.001 mole fraction from the best curve through the experimental points.

Consistency of Ternary Systems. Checking the consistency of binary equilibria is a well developed process, but there is no wholly satisfactory method for checking the thermodynamic consistency of ternary vapor-liquid data for systems with wide boiling point ranges. Compare, for example, the relationship derived by Krishnamurty and Venkata Rao (*6*) neglecting temperature variations, and that by Chao and Hougen (*2*), considering temperature variations. We suggest the following technique.

From the definition of excess free energy

$$\frac{F^E}{RT} = \Sigma x_i \ln \gamma_i \tag{6}$$

on differentiating,

$$\frac{\partial \dfrac{F^E}{RT}}{2.3\, \partial x_1} = \sum \frac{\partial x_i}{\partial x_1} \log \gamma_i + \sum x_i \frac{\partial \log \gamma_i}{\partial x_1} \tag{7}$$

Differentiation is carried out at constant pressure along a curve given by x_2 = function of x_1 and under the equilibrium conditions, denoted by P, C, and e.

For the ternary system along C

$$d \log \gamma_j = \left(\frac{\partial \log \gamma_j}{\partial x_i}\right)_{(T,P,C)} dx_i + \left(\frac{\partial \log \gamma_j}{\partial T}\right)_{(x_i,P,C)} dT \tag{8}$$

hence

$$\sum x_i \left(\frac{\partial \log \gamma_i}{\partial x_1}\right)_{(P,C,e)} = \sum x_i \left(\frac{\partial \log \gamma_i}{\partial x_1}\right)_{(T,P,C)} + \left(\frac{\partial T}{\partial x_1}\right)_{(P,C,e)} \sum x_i \left(\frac{\partial \log \gamma_i}{\partial T}\right)_{(x_i,P,C)} \tag{9}$$

$$= - \frac{\Delta H_m \partial T}{2.3 RT \partial x_1}_{(P,C,e)} \tag{10}$$

since, from the Gibbs-Duhem theorem,

$$\sum x_i \left(\frac{\partial \log \gamma_i}{\partial x_1}\right)_{(T,P,C)} = 0$$

Thus Equation 7 gives

$$\frac{\partial \left(\dfrac{F^E}{RT}\right)}{2.3\, \partial x_1}_{(P,C,e)} = \sum \left(\frac{\partial x_i}{\partial x_1}\right)_C \log \gamma_i - \frac{\Delta H_m}{2.3 RT^2} \left(\frac{\partial T}{\partial x_1}\right)_{(P,C,e)} \tag{11}$$

Integrating along a suitably defined path from one pure component to another, the left side of Equation 11 gives zero. In the absence of heat of mixing data, Equation 7 may be integrated directly. Thus, for the path defined by the lines $x_2 = kx_1$ and $x_3 = 0$,

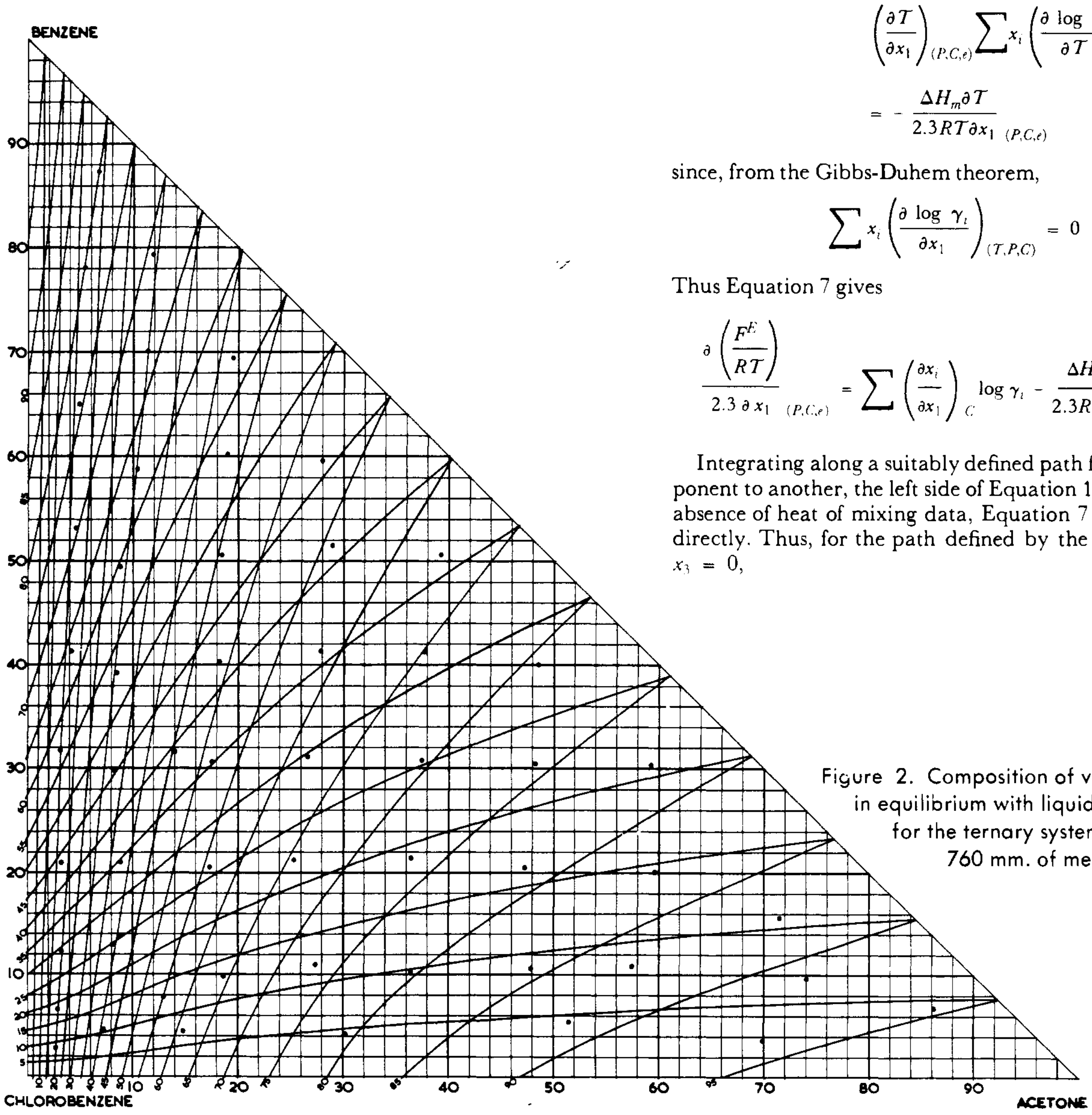

Figure 2. Composition of vapor (curved lines) in equilibrium with liquid (straight lines) for the ternary system boiling at 760 mm. of mercury

Table III. Isobaric Vapor-Liquid Equilibrium Data for System Acetone-Benzene-Chlorobenzene

(Pressure = 760 mm. Hg)

Temp., °C.	X_A	X_B	Y_A	Y_B	Temp., °C.	X_A	X_B	Y_A	Y_B
76.5	0.054	0.946	0.155	0.845	77.2	0.067	0.874	0.189	0.799
74.9	0.084	0.916	0.218	0.782	109.9	0.072	0.046	0.404	0.106
71.8	0.156	0.844	0.338	0.662	103.8	0.080	0.129	0.385	0.250
69.1	0.237	0.763	0.440	0.560	102.0	0.088	0.138	0.419	0.251
68.8	0.240	0.760	0.444	0.556	98.4	0.088	0.210	0.383	0.342
66.4	0.335	0.665	0.541	0.459	95.0	0.082	0.298	0.329	0.455
64.2	0.432	0.568	0.623	0.377	91.0	0.085	0.392	0.312	0.529
62.4	0.532	0.468	0.698	0.302	86.6	0.088	0.494	0.293	0.595
60.6	0.647	0.353	0.774	0.226	82.2	0.104	0.588	0.300	0.628
59.6	0.709	0.291	0.813	0.187	78.0	0.114	0.701	0.298	0.664
59.1	0.758	0.242	0.845	0.155	75.3	0.119	0.794	0.292	0.692
57.7	0.869	0.131	0.915	0.085	98.2	0.148	0.045	0.622	0.068
122.6	0.031	0	0.238	0	99.2	0.129	0.078	0.554	0.127
114.5	0.064	0	0.409	0	91.2	0.186	0.098	0.644	0.132
102.8	0.130	0	0.607	0	88.6	0.173	0.206	0.561	0.264
94.1	0.208	0	0.726	0	84.8	0.175	0.306	0.519	0.350
82.6	0.334	0	0.836	0	87.6	0.140	0.316	0.449	0.393
74.5	0.466	0	0.900	0	80.8	0.182	0.403	0.492	0.414
69.8	0.572	0	0.929	0	77.7	0.184	0.506	0.456	0.482
65.8	0.683	0	0.954	0	75.2	0.190	0.602	0.432	0.528
62.7	0.772	0	0.966	0	72.6	0.195	0.694	0.414	0.568
62.4	0.784	0	0.973	0	83.2	0.302	0.042	0.793	0.043
59.4	0.884	0	0.986	0	83.1	0.273	0.110	0.729	0.122
126.4	0	0.053	0	0.174	81.2	0.253	0.212	0.657	0.223
121.8	0	0.104	0	0.311	77.8	0.266	0.311	0.618	0.298
115.1	0	0.192	0	0.480	74.2	0.278	0.413	0.586	0.358
108.2	0	0.295	0	0.628	71.4	0.289	0.515	0.555	0.413
108.2	0	0.296	0	0.629	70.1	0.280	0.596	0.524	0.456
102.7	0	0.399	0	0.731	77.5	0.364	0.103	0.793	0.099
97.1	0	0.514	0	0.816	74.4	0.364	0.214	0.736	0.189
93.9	0	0.591	0	0.860	71.7	0.374	0.308	0.694	0.254
90.3	0	0.684	0	0.904	69.4	0.377	0.412	0.652	0.314
89.5	0	0.703	0	0.912	67.0	0.392	0.506	0.623	0.362
86.7	0	0.786	0	0.942	70.9	0.514	0.054	0.884	0.042
86.1	0	0.804	0	0.950	71.5	0.478	0.106	0.841	0.089
83.5	0	0.884	0	0.971	69.5	0.472	0.205	0.786	0.162
121.8	0.026	0.028	0.185	0.088	67.3	0.482	0.305	0.740	0.227
117.9	0.028	0.066	0.182	0.192	65.2	0.485	0.400	0.705	0.279
113.0	0.032	0.122	0.198	0.293	67.5	0.574	0.108	0.870	0.081
107.3	0.032	0.210	0.178	0.438	65.0	0.596	0.200	0.826	0.145
101.5	0.031	0.317	0.152	0.564	63.1	0.592	0.303	0.779	0.206
95.5	0.042	0.413	0.168	0.638	64.6	0.699	0.036	0.936	0.024
90.0	0.046	0.532	0.173	0.701	62.1	0.740	0.096	0.910	0.067
85.4	0.049	0.650	0.166	0.757	61.8	0.714	0.156	0.875	0.106
81.0	0.054	0.781	0.164	0.798	59.1	0.861	0.067	0.944	0.046

$$\underset{x_2 = kx_1}{\int_0^{\frac{1}{k+1}}} \log \frac{\gamma_1 {\gamma_2}^k}{{\gamma_3}^{k+1}}\, dx_1 + \underset{x_3 = 0}{\int_{\frac{1}{k+1}}^{1}} \log \frac{\gamma_1}{\gamma_2}\, dx_1 =$$

$$\underset{x_2 = kx_1}{\int_0^{\frac{1}{k+1}}} \frac{\Delta H_m}{2.3RT^2} \left(\frac{\partial T}{\partial x_1}\right)_{(P,C,e)} dx_1 +$$

$$\underset{x_3 = 0}{\int_{\frac{1}{k+1}}^{1}} \frac{\Delta H_m}{2.3RT^2} \left(\frac{\partial T}{\partial x_1}\right)_{(P,C,e)} dx_1 \qquad (12)$$

$$= - \underset{x_2 = kx_1}{\int_0^{\frac{1}{k+1}}} \sum x_i \left(\frac{\partial \log \gamma_i}{\partial x_1}\right)_{(P,C,e)} dx_1 - \underset{x_3 = 0}{\int_{\frac{1}{k+1}}^{1}} \sum x_i \left(\frac{\partial \log \gamma_i}{\partial x_1}\right)_{(P,C,e)} dx_1 \qquad (13)$$

Table IV. Integrals of Equation 13 Evaluated from Chlorobenzene Point to Acetone Point

	Left Side, Equations 4,5 or 12,13	Right Side, Equations 4,5 or 12,13	Difference
Acetone/ Benzene	-0.0027	-0.0041[a] -0.006[b]	+0.0014 +0.003
Benzene/ Chlorobenzene	-0.0171	-0.014[b]	- 0.003
Acetone/ Chlorobenzene	-0.0304	-0.024[b]	- 0.006
Ternary path	-0.034	-0.028[b]	- 0.006

[a] Calculated from heats of mixing.

[b] Calculated from slopes of log activity coefficient plots.

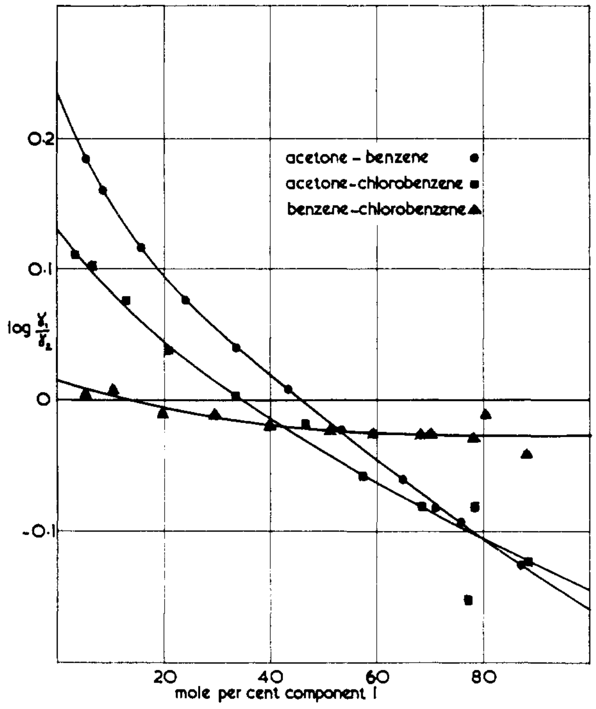

Figure 3. Activity coefficient plots for the three binary systems

The integrals in Equation 13 have been evaluated for the ternary from the chlorobenzene point to the acetone point along the path defined by the lines $x_B = x_A$ and $x_C = 0$, and are given in Table IV.

The small difference term indicates the consistency of the results and demonstrates the practicality of the method, but a drawback is that smoothed data must be used, giving no indication of the magnitude of random errors in the data.

NOMENCLATURE

F^E = excess free energy per mole of solution
d_4^{25} = specific gravity at 25° C. with respect to water at 4° C.
n_D^{25} = refractive index for sodium D line at 25° C.
p_M = property (either d_4^{25} or n_D^{25}) of a mixture as recorded in this work
p_M' = property of mixture as determined in other situations
Δp = $10^4(p_M - \Sigma x_i p_i)$
x = mole fraction in liquid
y = mole fraction in vapor in equilibrium with liquid of composition x
γ = activity coefficient
ΔH_m = isobaric and isothermal heat of mixing

SUBSCRIPTS

A = acetone
B = benzene
C = chlorobenzene

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Phase Equilibria in 1-Butanol–Water–Lactic Acid System

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Purification of lactic acid by liquid-liquid extraction has been investigated by several investigators, and the results have been summarized recently by Weiser and Geankoplis (*8*). They found that 3-methyl-1-butanol appeared to be the best selective solvent to extract lactic acid from aqueous solutions. They obtained a complete ternary equilibrium and phase diagram for the system 3-methyl-1-butanol–water–lactic acid at 25.0° C. and some data at 49.5° C.

However, they found that the butyl alcohols were also good extracting agents for lactic acid. The amyl alcohols are somewhat less soluble in dilute lactic acid–water solutions than the butyl alcohols and should give lower solvent losses in an extraction process.

To make a more complete study of extraction of lactic acid it was felt that ternary data using a butyl alcohol would be useful. As a result complete solubility and tie line data were obtained for the system 1-butanol–water–lactic acid at 25.0° C. Also the tie line data for the 3-methyl-1-butanol and 1-butanol systems were correlated by two methods.

EXPERIMENTAL PROCEDURES

The lactic acid and 1-butanol used in the experiments were Baker analyzed reagent grade. The lactic acid solution was 85% lactic acid and contained a mixture of free lactic acid and the self-polymer. To break up the mixture into the simple monomeric lactic acid, solutions containing about 20% acid were prepared and refluxed for 24 hours. This was analyzed by

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