Vapor–Liquid Equilibrium Data at Atmospheric Pressure for the Ternary and the Subbinary Systems Containing *n*-Hexane–Benzene–1-Butanol

S. Govindaswamy, AN. Andiappan, and SM. Lakshmanan*

Department of Technology, Annamalai University, Annamalainagar-608101, Tamilnadu, India

Vapor–liquid equilibrium (VLE) data at 760 mmHg pressure are reported for the binary systems *n*-hexane–benzene and *n*-hexane–1-butanol and for the ternary system *n*-hexane–benzene–1-butanol. The VLE data for *n*-hexane–benzene compared well with the literature values. The VLE data for *n*-hexane–1-butanol were found to be thermodynamically consistent when Herington's test was applied. The ternary data were tested for thermodynamic consistency by the Li and Lu method. Both the binary and ternary data were correlated with the Wilson equations.

The binary mixture, *n*-hexane–benzene, obtained from the petroleum industry poses the problem of complete separation. Even after prolonged distillation in very efficient columns it is impossible to obtain pure *n*-hexane containing less than 2.5% by volume benzene (*17*). Apart from the chemical method, the separation is to be effected in the presence of a third component. The effect of different compounds on the separation of *n*-hexane–benzene mixtures had been reported by Deal and Derr (*3*). Tassios (*16*) analyzed the effect of pyridine, furfural, nitromethane, and diethylene glycol on the separation of *n*-hexane from benzene and reported the relative volatilities and separation factors.

McCracken and Smith (*11*) suggested methyl alcohol to be a good solvent for the separation of the above binary mixture.

Ho and Lu (*6*) and Waldo and Weber (*18*) studied the effect of ethyl alcohol while Prabhu and Van Winkle (*13*) reported the role of 1-propanol on the separation of *n*-hexane–benzene mixtures. Belknap and Weber (*1*) discussed the importance of methyl cyclopentane on the separation of the mixture.

With a view to continue the study of the effect of polar compounds like alcohols on the separation of *n*-hexane–benzene mixtures a program has been made to use 2-propanol and all the butanols as entrainers. As vapor–liquid equilibrium data are necessary to test the solvent selectivity this paper reports the VLE (vapor–liquid equilibrium) data of the ternary system *n*-hexane (1)–benzene (2)–1-butanol (3) and relevant binaries.

The VLE data for the system benzene–1-butanol had been reported by Mann, Shemilt, and Waldichuk (*10*) and Yerazunis, Plowright, and Smola (*21*). The work had been repeated by Kesavaraj (*7*) in this laboratory and the data compared well with the published values. The vapor–liquid equilibrium data for the system benzene–1-butanol reported by Kesavaraj (*7*) had been used in this paper for the computation of the ternary data.

The vapor–liquid equilibrium data were collected for the system *n*-hexane–benzene. The results conform to the earlier observations made by Tongberg and Johnston (*17*) and Prabhu and Van Winkle (*13*). This also tests the suitability of the equilibrium still.

The vapor–liquid equilibrium data for the binary *n*-hexane–1-butanol and the ternary had been measured and are reported in this paper.

Experimental Section

"Analar" grade benzene and 1-butanol supplied by B.D.H. India and guaranteed Reagent grade *n*-hexane, Japan make, were dried and distilled. The fractions boiling within ±0.1 °C were collected and used. The physical properties of the liquids together with the literature values (*19*) are reported in Table I.

The vapor–liquid equilibrium data were determined on a still similar to the one designed by Othmer, Gilmont, and Conti (*12*). It differed from the original still in having the condensate receiver (vapor hold-up) as an integral part of the still. The description and working procedure are found elsewhere (*12, 15*).

Temperature was measured using a mercury-filled-in thermometer with an accuracy to read ±0.05 °C and manufactured by E' mil, England. All boiling points were measured at atmospheric pressure and corrected to 760 mmHg. The compositions of the binary mixtures consisting of *n*-hexane–benzene were determined by the measurement of their refractive indices and those of *n*-hexane–1-butanol by the measurement of densities. An Abbe refractometer (Erma, Japan) provided with thermoprisms and which had a measuring provision of 0.0002 was used. The temperature of the prisms was controlled at 35 ± 0.05 °C by circulating water from an immersion Thermostat, Type E 3 E (German make). Illumination was provided by a sodium vapor lamp. Densities were measured at 35 °C using a 10-ml specific gravity bottle whose volume was ascertained by weighing double distilled water at that temperature and assuming the density from literature (*7*). Calibration diagrams for composition as a function of density and refractive index were prepared by measuring those properties for samples of known composition.

The compositions of the ternary mixtures were deduced from the density and refractive index measurement. For estimation of ternary compositions it was necessary to prepare curves of constant densities and refractive indices as a function of composition. These curves for the system *n*-hexane–benzene–1-butanol are shown in Figure 1.

Vapor pressures of pure components for the entire range of experimental temperatures were calculated using Antoine equations obtained from Weissberger (*19*). The liquid phase activity coefficients were computed using the equation,

$$\gamma_i = \frac{\pi y_i}{p_i^0 x_i} \exp \frac{(\pi - p_i^0)(B_i - v_i)}{RT} \tag{1}$$

The second virial coefficient, B_i, was calculated by the method described by Hala (*4*).

The activity coefficients of the pure components in the liquid phases of the binary and ternary mixtures were correlated through the Wilson equation (*20*). For binary mixtures:

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \tag{2}$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \tag{2A}$$

where

$$\Lambda_{ij} = v_j/v_i \exp \left[\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right] \tag{2B}$$

For ternary mixtures:

Table I. Physical Properties of Pure Components

Component	Density, g/cm³ (35 °C) Obsd	Density, g/cm³ (35 °C) Lit.	Refractive index (35 °C) Obsd	Refractive index (35 °C) Lit.	Bp, °C Obsd	Bp, °C Lit.
n-Hexane	0.6469	0.6470	1.3680	1.3670	68.70	68.70
Benzene	0.8630	0.8633	1.4916	1.4915	80.10	80.10
1-Butanol	0.7989	0.7984	1.3940	1.3950	117.50	117.70

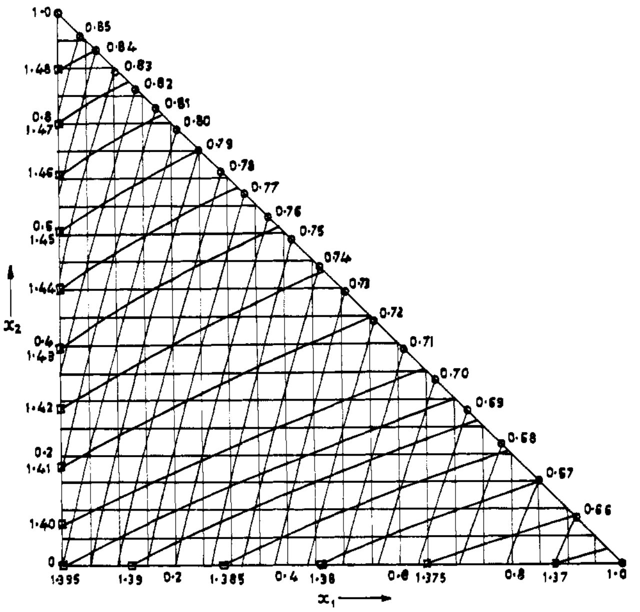

Figure 1. Refractive index and density curves for system *n*-hexane (1)–benzene (2)–1-butanol (3) at 35 °C.

$$\ln \gamma_1 = -\ln(x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}) + 1 - \left[\frac{x_1}{x_1 + x_2\Lambda_{12} + x_3\Lambda_{13}} + \frac{x_2\Lambda_{21}}{x_1\Lambda_{21} + x_2 + x_3\Lambda_{23}} + \frac{x_3\Lambda_{31}}{x_1\Lambda_{31} + x_2\Lambda_{32} + x_3}\right] \quad (3)$$

Results and Discussion

Binary Systems. The vapor–liquid equilibrium data for the system *n*-hexane (1)–benzene (2) collected by the authors were in good agreement with previously published values by Prabhu and Van Winkle (*13*). The data were correlated through the Wilson equation and the following binary parameter values were obtained:

$$\lambda_{12} - \lambda_{11} = 30.567 \text{ cal/(g mol)}$$

$$\lambda_{21} - \lambda_{22} = 256.45 \text{ cal/(g mol)}$$

The data were found thermodynamically consistent using Herington's test (*5*). The value of $(D - J)$ was found to be 6.91.

Table II. Vapor–Liquid Equilibrium Data for *n*-Hexane (1)–1-Butanol (3) at 760 mmHg

t, °C	x_1	y_1	y_1 (calcd)[a]	Activity coefficients γ_1	Activity coefficients γ_3
107.40	0.0450	0.3350	0.3571	2.7276	1.0083
100.50	0.0825	0.5200	0.5250	2.7091	0.9827
96.40	0.1030	0.6070	0.5928	2.7953	0.9674
92.90	0.1300	0.6530	0.6572	2.5976	1.0155
88.00	0.1670	0.7320	0.7241	2.5676	1.0069
82.80	0.2240	0.8000	0.7894	2.3995	1.0135
80.70	0.2550	0.8250	0.8136	2.3008	1.0157
79.35	0.2900	0.8350	0.8334	2.1249	1.0691
75.80	0.3530	0.8750	0.8634	2.0198	1.0494
73.20	0.4420	0.8975	0.8887	1.7820	1.1303
72.10	0.5100	0.9025	0.9013	1.6032	1.2918
70.90	0.5860	0.9125	0.9124	1.4611	1.4556
70.40	0.6730	0.9220	0.9213	1.3045	1.6834
69.05	0.8000	0.9300	0.9331	1.1520	2.6431
69.00	0.8250	0.9310	0.9352	1.1200	2.9850
68.90	0.8480	0.9340	0.9374	1.0963	3.3038
68.60	0.8850	0.9400	0.9415	1.0667	4.0302
68.50	0.9225	0.9475	0.9478	1.0346	5.2591
68.30	0.9650	0.9680	0.9621	1.0165	7.1701
68.30	0.9750	0.9730	0.9685	1.0113	8.4696
68.50	0.9900	0.9870	0.9833	1.0043	10.0924

Wilson parameters: $\lambda_{13} - \lambda_{11} = -60.3038$ cal/(g mol), $\lambda_{31} - \lambda_{33} = 1968.857$ cal/(g mol).

[a] Mean error in y_1 = 0.0060.

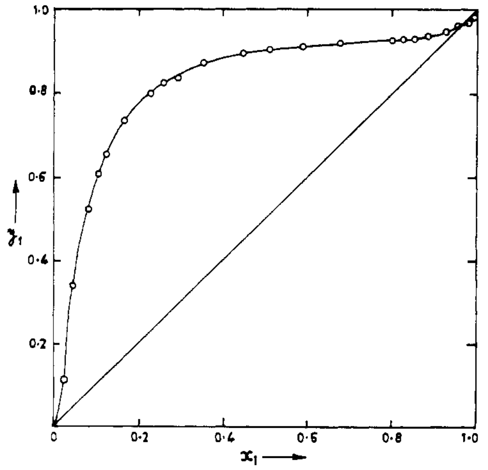

Figure 2. Vapor–liquid equilibrium for *n*-hexane (1)–1-butanol (3) at 760 mmHg pressure.

The vapor–liquid equilibrium data for the system *n*-hexane (1)–1-butanol (3) are presented in Table II and shown graphically in Figure 2. It is observed from Figure 2 that this system forms an azeotrope which boils at 68.2 °C having 0.9667 mole fraction of *n*-hexane. From a plot of log γ_1/γ_2 vs. liquid composition for this system the thermodynamic consistency of the data had been established using Herington's test. The value of $(D - J)$ was found to be −19.28 which is less than 10 as required by the method. Table II also presents the calculated vapor composition for the system through the Wilson equation. It is observed from Table II that the calculated vapor compositions compare well with the experimental values. The mean error is reported as 0.0060 mole fraction of *n*-hexane in the vapor phase composition. The Wilson parameters for the system *n*-hexane (1)–1-butanol (3) were

$$\lambda_{13} - \lambda_{11} = -60.30 \text{ cal/(g mol)}$$

$$\lambda_{31} - \lambda_{33} = 1968.86 \text{ cal/(g mol)}$$

The binary data for *n*-hexane–1-butanol were also computed through the Wilson equation by the nomographical method suggested by Sabarathinam et al. (*14*). The mean error was 0.0055 mole fraction of *n*-hexane in the vapor phase. The Wilson parameters were $\Lambda_{13} = 0.7489$ and $\Lambda_{31} = 0.083$.

Ternary System. The ternary vapor–liquid equilibrium data are presented in Table III. The data had been tested for thermodynamic consistency by the Li and Lu method (*9*), selecting groups of points. The deviations were within the experimental

Table III. Vapor–Liquid Equilibrium Data for *n*-Hexane (1)–Benzene (2)–1-Butanol (3) at 760 mmHg

		Liquid composition		Vapor composition (EX)		Calcd values[a]		
No.	Temp, °C	x_1	x_2	y_1	y_2	Temp, °C	y_1	y_2
1.	91.00	0.9133	0.2833	0.0468	0.6432	92.89	0.0597	0.6570
2.	93.90	0.0233	0.1920	0.1234	0.5134	96.21	0.1210	0.5295
3.	92.10	0.0300	0.2040	0.1590	0.5150	94.58	0.1470	0.5307
4.	87.60	0.0375	0.3050	0.1432	0.5870	89.31	0.1466	0.6189
5.	85.50	0.0434	0.3665	0.1485	0.6420	86.89	0.1503	0.6513
6.	83.90	0.0600	0.3465	0.2150	0.5968	86.03	0.2019	0.6061
7.	83.15	0.0600	0.3950	0.1868	0.6232	84.89	0.1882	0.6375
8.	81.80	0.0700	0.3900	0.2370	0.6033	84.27	0.2140	0.6172
9.	80.20	0.0833	0.3768	0.2850	0.5620	83.62	0.2484	0.5874
10.	80.70	0.0868	0.4000	0.2668	0.5700	82.95	0.2483	0.5965
11.	79.40	0.0943	0.4133	0.2720	0.5800	82.27	0.2592	0.5933
12.	78.30	0.1200	0.4120	0.3300	0.5333	80.85	0.3068	0.5581
13.	77.70	0.1433	0.3967	0.3655	0.5120	79.89	0.3500	0.5215
14.	77.00	0.1467	0.4134	0.3668	0.5167	79.54	0.3483	0.5279
15.	76.50	0.1720	0.3868	0.4133	0.4700	78.72	0.3943	0.4859
16.	76.30	0.1900	0.3467	0.4480	0.4400	78.40	0.4359	0.4431
17.	79.50	0.1900	0.1900	0.5468	0.2867	80.81	0.5348	0.3067
18.	77.90	0.1934	0.1934	0.5590	0.2934	80.54	0.5364	0.3079
19.	75.20	0.2268	0.3533	0.4800	0.4170	76.95	0.4729	0.4186
20.	76.65	0.2280	0.2033	0.5800	0.2800	78.64	0.5678	0.2951
21.	74.40	0.2500	0.3450	0.5200	0.3933	76.25	0.4992	0.3972
22.	74.50	0.2700	0.2668	0.5668	0.3100	76.25	0.5620	0.3273
23.	73.80	0.2800	0.3250	0.5332	0.3832	75.49	0.5353	0.3653
24.	73.70	0.2834	0.2750	0.5734	0.3300	75.75	0.5675	0.3266
25.	75.30	0.2900	0.1590	0.6630	0.2185	76.71	0.6573	0.2185
26.	73.30	0.3068	0.2633	0.5967	0.3100	75.15	0.5922	0.3058
27.	72.85	0.3400	0.2500	0.6200	0.2800	74.37	0.6224	0.2808
28.	72.60	0.3400	0.3600	0.5850	0.3333	73.87	0.5583	0.3589
29.	72.50	0.3520	0.2400	0.6350	0.2667	74.13	0.6361	0.2682
30.	72.80	0.3867	0.1532	0.7200	0.1968	73.85	0.7181	0.1813
31.	72.00	0.4028	0.2250	0.6667	0.2468	73.11	0.6723	0.2392
32.	71.50	0.4100	0.2934	0.6300	0.2950	72.75	0.6326	0.2880
33.	71.60	0.4220	0.2120	0.6868	0.2267	72.79	0.6897	0.2233
34.	72.00	0.4233	0.1800	0.7080	0.2050	72.90	0.7132	0.1963
35.	71.20	0.4550	0.2068	0.6935	0.2200	72.24	0.7065	0.2109
36.	71.10	0.4667	0.2000	0.7165	0.1940	72.07	0.7155	0.2028
37.	70.40	0.5200	0.2400	0.7032	0.2433	71.27	0.7071	0.2222
38.	70.60	0.5233	0.1900	0.7434	0.1833	71.29	0.7408	0.1837
39.	70.40	0.5333	0.1532	0.7582	0.1585	71.23	0.7698	0.1521
40.	70.40	0.5367	0.1600	0.7568	0.1650	71.17	0.7657	0.1573
41.	70.30	0.5575	0.1615	0.7610	0.1567	70.92	0.7701	0.1555
42.	70.20	0.5690	0.1500	0.7733	0.1468	70.80	0.7812	0.1445
43.	69.80	0.6150	0.1432	0.7882	0.1350	70.34	0.7964	0.1336
44.	69.35	0.6200	0.2033	0.7500	0.1930	70.27	0.7573	0.1800
45.	69.60	0.6400	0.1285	0.8100	0.1234	70.12	0.8119	0.1191
46.	69.45	0.6700	0.1168	0.8200	0.1070	69.87	0.8259	0.1071
47.	69.40	0.6933	0.0900	0.8435	0.0815	69.70	0.8494	0.0830
48.	68.80	0.7167	0.1450	0.8030	0.1432	69.53	0.8148	0.1268
49.	69.10	0.7190	0.1120	0.8310	0.0910	69.51	0.8375	0.1000
50.	68.85	0.7567	0.1068	0.8412	0.0900	69.28	0.8473	0.0940
51.	68.70	0.7733	0.0833	0.8500	0.0833	69.12	0.8662	0.0739
52.	68.70	0.7933	0.0800	0.8534	0.0734	69.05	0.8715	0.0705
53.	68.60	0.8050	0.1218	0.8434	0.1033	68.99	0.8474	0.1055
54.	68.70	0.8100	0.0715	0.8567	0.0700	68.96	0.8800	0.0630
55.	68.60	0.8100	0.1167	0.8434	0.1000	68.96	0.8515	0.1012
56.	68.40	0.8200	0.1068	0.8567	0.1000	68.91	0.8596	0.0928
57.	68.60	0.8320	0.0690	0.8760	0.0634	68.85	0.8854	0.0606

Wilson binary energy parameters (cal/(g mol)): $\lambda_{12} - \lambda_{11} = 30.567$, $\lambda_{21} - \lambda_{22} = 256.45$, $\lambda_{23} - \lambda_{22} = 138.61$, $\lambda_{32} - \lambda_{33} = 902.61$, $\lambda_{31} - \lambda_{33} = 1968.86$, $\lambda_{13} - \lambda_{11} = -60.30$

[a] Absolute standard deviation: temp = 1.30 °C, $y_1 = 0.0097$, $y_2 = 0.0094$, $y_3 = 0.0081$.

errors. Figure 3 shows the vapor-liquid equilibrium tie-lines, the circle representing the liquid composition, and the tip of the arrow representing vapor composition. This system does not form any ternary azeotrope as seen from Table III and Figure 3.

The ternary data were computed through the Wilson equation

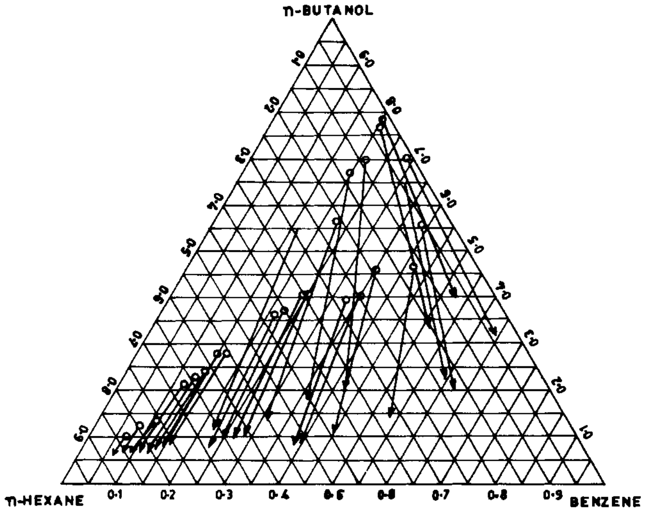

Figure 3. Vapor-liquid equilibrium tie-lines for the system *n*-hexane-benzene-1-butanol at 760 mmHg pressure.

using boiling points of the ternary mixtures and the binary Wilson parameters alone. The calculated vapor compositions are given in Table III. The binary Wilson parameters were evaluated using the data collected by the authors for *n*-hexane-benzene and *n*-hexane-1-butanol systems and the data collected by Kesavaraj (*7*) for the benzene-1-butanol system. They are given as: *n*-hexane (1)-benzene (2), $\lambda_{12} - \lambda_{11} = 30.567$ and $\lambda_{21} - \lambda_{22} = 256.45$ cal/(g mol); benzene (2)-1-butanol (3), $\lambda_{23} - \lambda_{22} = 138.61$ and $\lambda_{32} - \lambda_{33} = 902.61$ cal/(g mol); *n*-hexane (1)-1-butanol (3), $\lambda_{13} - \lambda_{11} = -60.30$ and $\lambda_{31} - \lambda_{33} = 1968.86$ cal/(g mol).

From Table III it is observed that the average deviations in temperature-vapor-phase compositions are: $\Delta T = 1.30$ °C, $\Delta y_1 = 0.0097$, $\Delta y_2 = 0.0094$, $\Delta y_3 = 0.0081$. Further it is noted from Table III that the deviations are more in the dilute region than in the concentrated region. This may be due to the characteristic feature of the two-parameter Wilson equation in describing the VLE in the dilute regions as observed by Cukor and Prausnitz (*2*).

Conclusion

The vapor-liquid equilibrium data for the binary system *n*-hexane-benzene are comparable with earlier works.

The vapor-liquid equilibrium data for the binary system *n*-hexane-1-butanol showed that it was azeotropic at 0.9667 mol fraction of *n*-hexane with a boiling point 68.2 °C. The vapor-liquid equilibrium data for the ternary system *n*-hexane-benzene-1-butanol showed that there was no ternary azeotrope. The binary and ternary data were thermodynamically consistent and correlated well with the Wilson equations.

Nomenclature

B_i = second virial coefficient of component i ,
p_i^0 = vapor pressure of pure component i
R = gas constant
T = absolute temperature
v_i = molar liquid volume of component i
x_i = liquid phase mole fraction of component i
y_i = vapor phase mole fraction of component i
γ_i = activity coefficient of component i
λ_{ij} = Wilson's binary interaction energy parameter
Λ_{ij} = Wilson parameter as defined by eq 2B
π = total pressure

Literature Cited

(1) Belknap, R. C., Weber, J. H., *J. Chem. Eng. Data*, **6**, 485 (1961).
(2) Cukor, P. M., Prausnitz, J. M., *Int. Chem. Eng. Symp., Series*, **No. 32e 3**, 88 (1969).
(3) Deal, C. H., Derr, E. R., *Ind. Eng. Chem., Process Des. Dev.*, **3**, 394 (1964).
(4) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapour-Liquid Equilibrium," 2d ed, Pergamon press, New York, N.Y., 1967.
(5) Herington, E. F. G., *J. Inst. Pet., London*, **37**, 457 (1951).
(6) Ho, J. C. K., Lu, B. C.-Y., *J. Chem. Eng. Data*, **8**, 553 (1963).
(7) Kesavaraj, N., M.E.(chem) Thesis, Annamalai University, 1973.
(8) Lange, N. A., "Hand-Book of Chemistry", 10th ed, McGraw-Hill, New York, N.Y., 1961.
(9) Li, J. C. M., Lu, B. C. Y., *Can. J. Chem. Eng.*, **37**, 117 (1959).
(10) Mann, R. S., Shemilt, L. W., Waldichuk, M., *J. Chem. Eng. Data*, **8**, 502 (1963).
(11) McCracken, P. G., Smith, J. M., *AIChE. J.*, **2**, 498 (1950).
(12) Othmer, D. F., Gilmont, R., Conti, J. J., *Ind. Eng. Chem.*, **52**, 625 (1960).
(13) Prabhu, P. S., Van Winkle, M., *J. Chem. Eng. Data*, **8**, 210 (1963).
(14) Sabarathinam, PL., Andiappan, AN., Lakshmanan, SM. *Indian Chem. Eng.*, **16**, 11 (1974).
(15) Satagopan, T. M., M.E.(chem) Thesis, Annamalai University, 1972.
(16) Tassios, D. P., Azeotropic and Extractive Distillation Symposium, Division of Industrial and Engineering Chemistry, American Chemical Society, Chicago, Ill., 1970.
(17) Tongberg, C. O., Johnston, F., *Ind. Eng. Chem.*, **25**, 733 (1933).
(18) Waldo, R. A., Weber, J. H., *J. Chem. Eng. Data*, **8**, 349 (1963).
(19) Weissberger, A. "Technique of Organic Chemistry", Vol. VII, 2d ed, Interscience, New York, N.Y., 1965.
(20) Wilson, G. M., *J. Am. Chem. Soc.*, **88**, 127 (1964).
(21) Yerazunis, S., Plowright, J. D., Smola, F. M., AIChE *J.*, **10**, 660 (1964).

Received for review September 2, 1975. Accepted March 4, 1976.