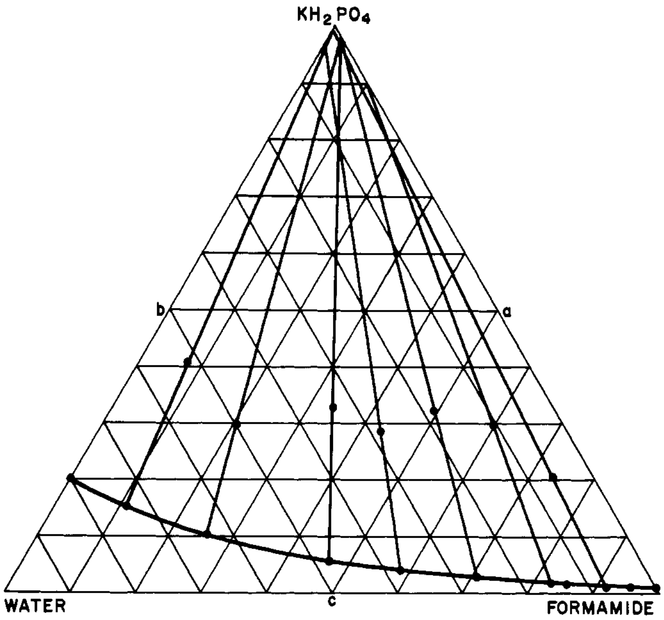

Figure 3. System formamide–H_2O–KH_2PO_4 at 25° C. (weight %)

was used without further purification, since it had a melting point of 2.5° ± 0.1° C., which was in good agreement with the literature value of 2.55° C. (*5*).

A known excess of salt was added to a selected mixture of water and formamide in a 100-ml. volumetric flask. Each flask was attached to the arm of a mechanical shaker and immersed in a water bath which was maintained at 25° C. After vigorous shaking for at least 24 hours, the saturated liquid phase was removed through a fine fritted glass filter on the end of a tube by applying a slight pressure to the system.

Amide nitrogen was determined by the Kjeldahl procedure. After the formamide had been removed by evaporating an aqueous solution of the sample to dryness, potassium was determined by the Perrin method and phosphorus was determined gravimetrically by the quinoline molybdate method. Water was calculated by difference.

RESULTS AND DISCUSSION

The complete system was determined for each of the following salts: KCl, KNO_3, and KH_2PO_4. The data are listed in Table I. The salt itself is the only solid phase in each of these systems at 25° C. The solubility of both potassium chloride and potassium nitrate decreased almost linearly with addition of formamide (Figures 1 and 2). The solubility of monopotassium phosphate decreased somewhat more rapidly at low formamide concentrations (Figure 3). Tie lines were established from the known initial composition and the analysis of the saturated liquid phase. The wet residue was not analyzed. This method was sufficiently accurate, since the systems were relatively simple and none of the solutions were unduly viscous. The data of Linke and Seidell (*4*) were used for the solubility of the pure salts in water—26.4, 27.5, and 20.0 grams per 100 grams of saturated solution of KCl, KNO_3, and KH_2PO_4, respectively.

LITERATURE CITED

(1) Colton, E., Brooker, R.E., *J. Phys. Chem.* **62**, 1595–6 (1958).
(2) Gopal, R., Husain, M.M., *J. Indian Chem. Soc.* **40**, 272–4 (1963).
(3) Jones, T.M., Lewis, H.T., Jr., Getsinger, J.G., *J. Agr. Food Chem.* **14**, 20–3 (1966).
(4) Linke, W.F., Seidell, A., "Solubilities, Inorganic and Metal-Organic Compounds," 4th ed., Vol. II, pp. 114, 250, 287, American Chemical Society, Washington, D. C., 1965.
(5) Smith, G. F., *J. Chem. Soc.* **1931**, p. 3257.

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Vapor-Liquid Equilibria of 1,3-Butadiene Systems

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Vapor-liquid equilibrium data at 25° C. are reported for solutions of 1,3-butadiene in benzene, ethyl acetate, ethyl ether, carbon tetrachloride, carbon disulfide, dichloromethane, and nitromethane at concentrations up to 20 to 30% butadiene in the liquid. Measurements were made by a static technique. The results are compared with several expressions for excess Gibbs energy.

VAPOR-LIQUID equilibrium data are useful not only in the design of separation processes, but also as a key to the understanding of intermolecular forces in solution. The authors report experimental results for the interactions of a conjugated π-bond structure, 1,3-butadiene, with seven varied solvents.

Although many experimenters use circulation stills for direct measurements of vapor-liquid equilibria (*3*), they usually obtain isobaric data which are inadequate for rigorous thermodynamic analysis without information on the heat of mixing. In this work, a static technique was used to obtain isothermal vapor pressures of butadiene solutions. This method avoided the necessity of sampling either phase, thus eliminating one frequent source of error, but it did require precautions to prevent condensation of the vapor outside the cell and adequate degassing of solvents. Recently, other authors have reported using similar techniques (*2, 18*).

EXPERIMENTAL

Reagents used were:

Benzene, Baker, thiophene-free spectrophotometric reagent.
n-Butane, Phillips Petroleum, research grade, purity >99.90%.
1,3-Butadiene, Phillips Petroleum, research grade, purity >99.97%.

n-Decane, Eastman, practical grade.
Carbon tetrachloride, Baker, GC-spectrophotometric.
Ethyl acetate, Baker, GC-spectrophotometric.
Ethyl ether, Eastman, spectrophotometric grade.
Nitromethane, Eastman, spectrophotometric grade.
Carbon disulfide, Fischer, IR-grade.
Dichloromethane, Mallinckrodt, reagent.

All solvents were dried with Linde 4A molecular sieves. The carbon disulfide and dichloromethane were both purified according to Perrin *et al.* (*10*), and distilled before use. All solvents were degassed by alternate freezing and pumping, followed by refluxing in a degassing still, with periodic removal of vapor to vacuum for several days, as was found effective by Hermsen and Prausnitz (*4*). Measured solvent vapor pressures are compared with the literature values in Table I.

A schematic diagram of the apparatus is shown in Figure 1. The equilibrium cell was a Morton flask with stopcock, removable for weighing. A 1-mm. glass capillary, wrapped with heating tape to prevent condensation, connected the cell to a fused quartz precision pressure gage (Model 140, Texas Instruments). The bourdon tube inside (range, 0 to 1000 mm. of Hg) was maintained at 43.8° C. with a built-in thermostat. The gage was calibrated by the manufacturer with a primary standard dead weight tester to 0.010% of reading, with occasional deviations of 0.05 mm. of Hg or less. All the calibrations have traceability to the National Bureau of Standards. The gage had been checked to ± 0.05 mm. of Hg up to 1 atm. with a large-bore mercury manometer and a cathetometer. The reference side of the gage was evacuated. The cell volume was calibrated by filling with water and weighing. The cell was thermostated in a bath maintained by a Hallikainen Thermotrol temperature controller at 25.00° ± 0.01° C., as measured by an extended-scale thermometer calibrated against standard N.B.S.-calibrated thermometers. The variation in bath temperature at the equilibrium cell was verified to be less than ±0.001° C. by a Beckmann thermometer. A magnetic stirrer mounted beneath the bath drove a teflon-coated magnet inside the cell.

Table I. Vapor Pressure of Pure Components

	Temp., °C.	Vapor Pressure, Mm. of Hg		
		This work	Lit.	Ref.
1,3-Butadiene	25	. . .	2133	(*17*)
Benzene	25.00	95.6	95.20	(*20*)
	40	182.8	182.7	(*15*)
Ethyl acetate	25.00	94.6	94.6	(*9*)
Ethyl ether	25.0	536.2	537.0	(*6*)
Carbon tetrachloride	25.00	115.7	114.9 ± 0.2	(*23*)
	40	213.1	213.3	(*15*)
Dichloromethane	25	433.2	433.9 ± 0.4	(*8*)
Nitromethane	25.3	36.8	37.1	(*5*)
Carbon disulfide	25.00	361.0	360.9	(*19*)

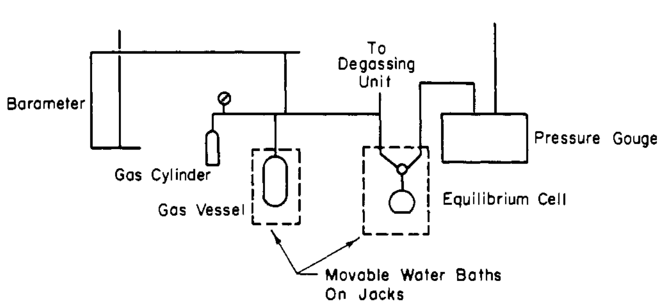

Figure 1. Schematic diagram of apparatus for vapor-liquid equilibrium studies

The gas vessel was merely a calibrated volume, also immersible in a temperature bath, to be used for measuring in the amounts of butadiene gas. The high-vacuum system included a mercury diffusion pump and a McLeod gage. The vacuum achieved was better than 10^{-7} mm. of Hg. Further details of the apparatus are available elsewhere (*22*).

Apiezon L and N greases were used, except where direct contact of organic solvents was encountered. In those cases, the inside of the stopcocks or ground glass joints were covered with a mannitol starch grease (*7*).

For each run, the solvent was distilled under vacuum from the degassing still and frozen into the equilibrium cell. The amount so used was found by weighing, with appropriate buoyancy corrections. The butadiene was frozen into the gas vessel and evacuated; the vessel was then placed in the bath and the quantity of butadiene determined by a *P-V-T* measurement, with appropriate corrections for gas-phase nonideality. The excess butadiene in the line to the pressure gage was pumped out, and then the measured amount of butadiene was transferred quantitatively into the equilibrium cell by freezing with liquid nitrogen.

The water bath, on a jack, was raised to thermostat the cell, and after one to two hours of stirring, the pressure was constant to better than 0.01 mm. of Hg. Subsequent portions of butadiene were added and the procedure repeated. Six to eight points were taken for each solvent, the two limitations being the upper limit of the pressure gage—1000 mm. of Hg—and the volume of material in the cell. At the end of the run, the final solution was weighed as an independent check of the total amount of butadiene added. The zero for the pressure gage was checked before and after each run; drift was always less than the precision of the calibration.

As a check on the experimental technique, two systems for which literature data are available were run first. For the benzene–carbon tetrachloride system, two degassing stills were used, and portions of each solvent were vacuum-distilled into the cell and weighed. For a system more closely approximating the butadiene mixtures, the butane-decane system was run by the same procedure as used for the butadiene systems.

DATA REDUCTION

The experimental data actually taken along the 25° C. isotherm were the total pressure of the system as a function of the total contents of the cell, liquid plus vapor. An iterative computer procedure, similar to those described by Prausnitz *et al.* (*11*), was used to calculate the compositions of the liquid and vapor phases. Since the vapor space is small and the pressures relatively low, the liquid compositions were quite close to the over-all compositions. Moreover, use of a truncated virial equation (*11*) for the vapor phase rendered the small correction for the amount of material in the vapor most accurate. The liquid phase compositions thus calculated were used to obtain the parameters in an expression for the excess Gibbs energy by a least square fit to the total pressures. Details of the calculation are available elsewhere (*22*).

Various expressions for the excess Gibbs energy were used to fit each set of data, using a nonlinear regression technique and fitting the experimental vapor pressures. The Scatchard (*14*) equation, an enthalpic expression, gives activity coefficients, γ, for a binary mixture in terms of one parameter, A

$$RT \ln \gamma_1 = Av_1 \left(\frac{x_2 v_2}{x_1 v_1 + x_2 v_2} \right)^2$$

$$RT \ln \gamma_2 = Av_2 \left(\frac{x_1 v_1}{x_1 v_1 + x_2 v_2} \right)^2 \qquad (1)$$

Also fit were two other enthalpic expressions, the two-parameter van Laar equation

$$\ln \gamma_1 = \frac{A_{12}}{\left(1 + \frac{A_{12}}{A_{21}} \frac{x_1}{x_2}\right)^2}$$

$$\ln \gamma_2 = \frac{A_{21}}{\left(1 + \frac{A_{21}}{A_{12}} \frac{x_2}{x_1}\right)^2} \qquad (2)$$

and a three-parameter Redlich-Kister (*13*) equation

$$RT \ln \gamma_1 = x_2^2 [B - C(1 - 4x_1) + D(1 - 8x_1 + 12x_1^2)]$$

$$RT \ln \gamma_2 = x_1^2 [B + C(1 - 4x_2) + D(1 - 8x_2 + 12x_2^2)] \qquad (3)$$

In addition, a recent entropic expression suitable for a large variety of nonideal mixtures suggested by Wilson (*21*) was used. The two-parameter Wilson equation is a semiempirical generalization of the Flory-Huggins equations. It has a built-in temperature dependence and can be rigorously extended to multicomponent systems (*11*) without additional parameters. The activity coefficients for a binary are given by

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

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \qquad (4)$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp - [(\lambda_{ij} - \lambda_{ii})/RT]$$

λ_{ij} = interaction energy of ij pair

RESULTS

Experimental results for the benzene–carbon tetrachloride system at 40° C. compare well with those of Scatchard *et al.* (*15*) (Figure 2). As an additional check, a system representing extreme differences in volatility, *n*-butane–*n*-decane, was run at 37.78° C., and the results of duplicate runs are compared in Figure 3 with the data of Reamer *et al.* (*12*). Agreement in both cases is satisfactory.

The results for the seven butadiene systems are summarized in Figure 4. Each of these systems was fit with the four different expressions given above for excess Gibbs energy, and the resulting standard deviations between calculated and experimental pressures are given in Table II. These results show that a one-parameter equation is probably not sufficient to characterize these results, in spite of the limited concentration range. On the other hand, the three-parameter Redlich-Kister expression is certainly no better, and perhaps not as good as the two-parameter equations. The van Laar and Wilson equations give equally good agreement.

The experimental results are listed in Table III. The compositions of both phases were calculated as described above; the maximum probable uncertainties are 0.0001 in x and 0.001 in y. The activity coefficients presented are those calculated from the best-fit Wilson parameters listed.

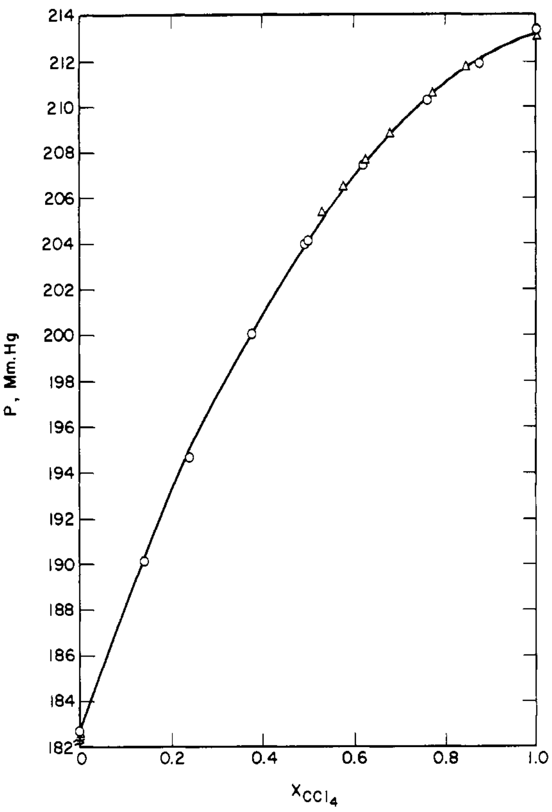

Figure 2. Vapor-liquid equilibrium data of benzene–CCl_4 system

Data at 40° C.

○ Scatchard *et al.* (1940)

△ This work

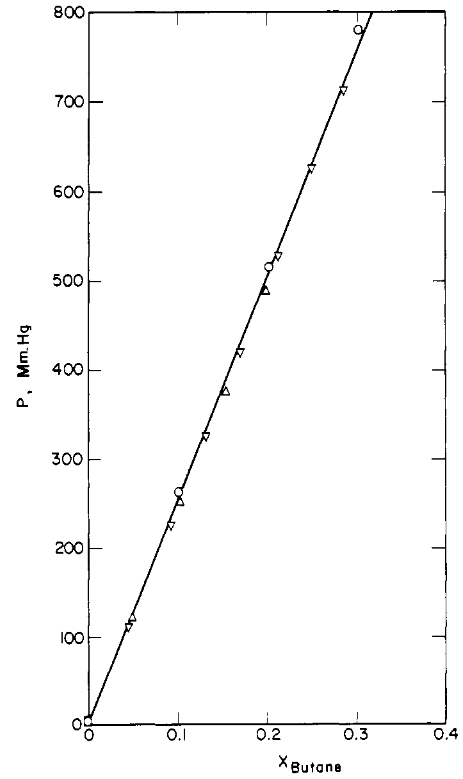

Figure 3. Vapor-liquid equilibrium data of *n*-butane–*n*-decane system

Data at 37.78° C.

○ Reamer *et al.* (1946)

△ This work—Run 1

▽ This work—Run 2

Table II. Comparison of Fit with Various Equations

Solvent	% Std. Dev. in Total Pressure Scatchard	 van Laar	 Wilson	 Redlich-Kister
Benzene	1.15	0.07	0.07	0.08
Ethyl acetate	0.34	0.05	0.04	0.03
Ethyl ether	0.36	0.17	0.18	0.26
Carbon tetrachloride	1.67	0.26	0.26	0.57
Carbon disulfide	0.38	0.07	0.06	0.10
Dichloromethane	0.71	0.21	0.21	0.23
Nitromethane	5.66	0.42	0.39	0.48

The absolute accuracy of these is probably no better than ±0.2%. Only the 1,3-butadiene–ethyl ether system shows negative deviations from Raoult's law. The best-fit Wilson parameters for this mixture give a limiting activity coefficient at infinite dilution for the butadiene of 0.892, which is very close to the γ_1^∞ reported from boiling-point data *(1)* of 0.893. The negative deviations observed here are probably due to a strong interaction of the ether linkage with the π-electrons, similar to that giving rise to the same effect for the benzene–ethyl ether system *(16)*.

The butadiene-nitromethane system exhibited the strongest positive deviations from Raoult's law, with γ_1^∞ = 5.17 in this highly polar solvent. The other five solvents—benzene, ethyl acetate, carbon tetrachloride, carbon disulfide, and dichloromethane—are all a good deal less polar, or nonpolar, without being strong electron acceptors. Limiting activity coefficients for butadiene in these systems were in the range 1.16 to 2.05.

Table III. Vapor-Liquid Equilibrium Data at 25.00° C.

1,3-Butadiene (1)–Benzene (2)

x_1	y_1	P, Mm.	γ_1	γ_2
0.0000	0.000	95.6_4	1.3067	1.0000
0.0376	0.506	187.8_7	1.2835	1.0003
0.0818	0.694	292.1_2	1.2574	1.0017
0.1253	0.781	392.3_3	1.2332	1.0039
0.1650	0.828	481.0_3	1.2122	1.0068
0.2003	0.856	557.1_3	1.1945	1.0102
0.2353	0.878	632.0_9	1.1778	1.0141

$\lambda_{12} - \lambda_{11}$ = 34.14 cal./g. mole
$\lambda_{12} - \lambda_{22}$ = 142.34 cal./g. mole

1,3-Butadiene (1)–Ethyl Acetate (2)

x_1	y_1	P, Mm.	γ_1	γ_2
0.0000	0.000	94.6_2	1.1595	1.0000
0.0550	0.576	214.7_3	1.1460	1.0003
0.1091	0.737	330.9_0	1.1332	1.0013
0.1597	0.811	438.3_8	1.1214	1.0030
0.2078	0.854	538.5_8	1.1105	1.0052
0.2498	0.879	625.2_3	1.1012	1.0077
0.2881	0.897	703.6_0	1.0929	1.0105
0.3242	0.911	776.7_4	1.0854	1.0136

$\lambda_{12} - \lambda_{11}$ = –52.35 cal./g. mole
$\lambda_{12} - \lambda_{22}$ = 187.57 cal./g. mole

1,3-Butadiene (1)–Ethyl Ether (2)

x_1	y_1	P, Mm.	γ_1	γ_2
0.0000	0.000	536.2_0	0.8922	1.0000
0.0435	0.131	592.8_9	0.8986	0.9998
0.0808	0.227	642.3_2	0.9041	0.9994
0.1248	0.324	701.6_7	0.9106	0.9986
0.1677	0.405	761.2_3	0.9169	0.9974
0.2056	0.468	811.2_3	0.9223	0.9961
0.2413	0.521	866.1_0	0.9275	0.9945
0.2735	0.565	913.0_9	0.9320	0.9928

$\lambda_{12} - \lambda_{11}$ = –247.08 cal./g. mole
$\lambda_{12} - \lambda_{22}$ = 280.39 cal./g. mole

1,3-Butadiene (1)–Carbon Tetrachloride (2)

x_1	y_1	P, Mm.	γ_1	γ_2
0.0000	0.000	115.6_8	1.2111	1.0000
0.0483	0.506	225.4_7	1.1967	1.0003
0.0965	0.679	332.7_8	1.1824	1.0012
0.1409	0.762	428.7_8	1.1694	1.0027
0.1782	0.807	508.3_3	1.1586	1.0045
0.2135	0.837	583.2_5	1.1485	1.0066
0.2466	0.860	653.4_4	1.1392	1.0091
0.2771	0.876	720.5_2	1.1307	1.0118
0.3077	0.890	781.9_6	1.1223	1.0149

$\lambda_{12} - \lambda_{11}$ = 86.38 cal./g. mole
$\lambda_{12} - \lambda_{22}$ = 280.44 cal./g. mole

1,3-Butadiene (1)–Carbon Disulfide (2)

x_1	y_1	P, Mm.	γ_1	γ_2
0.0000	0.000	360.9_8	2.0469	1.0000
0.0296	0.244	466.4_2	1.9373	1.0008
0.0620	0.398	569.5_9	1.8310	1.0035
0.0948	0.497	663.7_7	1.7364	1.0081
0.1245	0.560	740.9_2	1.6600	1.0137
0.1537	0.608	811.9_4	1.5926	1.0205
0.1794	0.642	868.3_7	1.5389	1.0275
0.2041	0.669	922.0_1	1.4914	1.0351

$\lambda_{12} - \lambda_{11}$ = 152.89 cal./g. mole
$\lambda_{12} - \lambda_{22}$ = 273.81 cal./g. mole

1,3-Butadiene (1)–Dichloromethane (2)

x_1	y_1	P, Mm.	γ_1	γ_2
0.0000	0.000	433.2_1	1.2858	1.0000
0.0390	0.188	517.0_1	1.2554	1.0005
0.0807	0.327	596.6_2	1.2264	1.0020
0.1190	0.423	674.8_5	1.2016	1.0042
0.1535	0.491	739.5_1	1.1814	1.0069
0.1860	0.544	798.2_9	1.1639	1.0100
0.2175	0.588	854.0_5	1.1481	1.0135
0.2455	0.622	902.7_5	1.1351	1.0170
0.2722	0.651	948.4_5	1.1235	1.0206

$\lambda_{12} - \lambda_{11}$ = 23.54 cal./g. mole
$\lambda_{12} - \lambda_{22}$ = 128.18 cal./g. mole

1,3-Butadiene (1)–Nitromethane (2)

x_1	y_1	P, Mm.	γ_1	γ_2
0.0000	0.000	36.1_7	5.1668	1.0000
0.0258	0.869	274.1_8	4.7050	1.0012
0.0461	0.918	440.2_9	4.3861	1.0038
0.0657	0.938	574.2_6	4.1119	1.0077
0.0877	0.951	710.3_1	3.8359	1.0135
0.1099	0.958	828.3_3	3.5876	1.0210
0.1348	0.964	947.5_8	3.3393	1.0312

$\lambda_{12} - \lambda_{11}$ = 228.01 cal./g. mole
$\lambda_{12} - \lambda_{22}$ = 1155.50 cal./g. mole

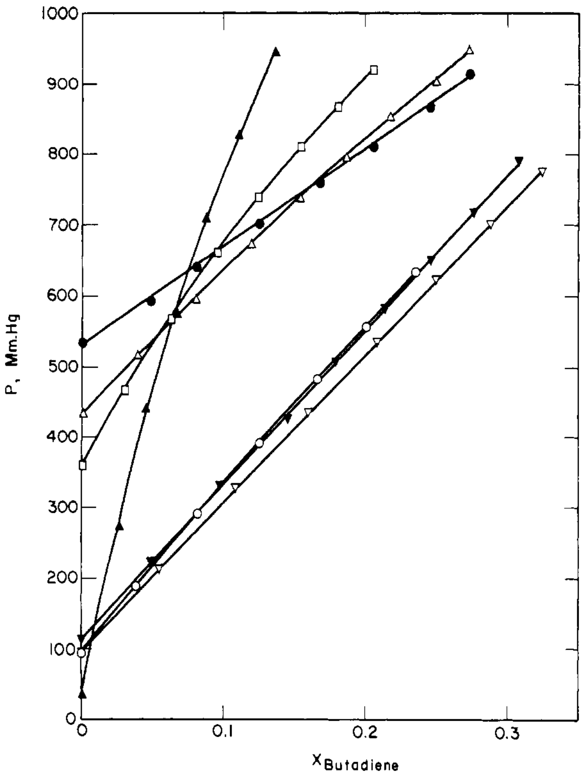

Figure 4. Vapor-liquid equilibrium data of 1,3-butadiene solutions

Data at 25.00° C.

○ Benzene
▼ Carbon tetrachloride
△ Dichloromethane
▽ Ethyl acetate
□ Carbon disulfide
▲ Nitromethane
● Ethyl ether

ACKNOWLEDGMENT

The 1,3-butadiene used was donated by the Phillips Petroleum Co.

NOMENCLATURE

A = constant for the Scatchard equation, cal. cm.$^{-3}$
A_{12}, A_{21} = constants for the van Laar equation
B,C,D = constants for the Redlich-Kister equation
P = total pressure, mm. of Hg
R = gas constant, cal. ° K.$^{-1}$ mole^{-1}
T = absolute temperature, ° K.
v_i = liquid molar volume of component i, cm.^{3} mole^{-1}
x_i = liquid mole fraction of component i

Greek Letters

γ_i = activity coefficient of component i
λ_{ij} = interaction energy of ij pair, cal. mole^{-1}
Λ_{ij} = parameter in the Wilson equation

LITERATURE CITED

(1) Chu, J.C., "Vapor-Liquid Equilibrium Data," p. 105, J.W. Edwards, Ann Arbor, Mich., 1956.
(2) Gaw, W.J., Swinton, F.L., *Trans. Faraday Soc.* **64**, 637 (1968).
(3) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor-Liquid Equilibrium," 2nd ed., Pergamon, London, 1967.
(4) Hermsen, R.W., Prausnitz, J.M., *Chem. Eng. Sci.* **18**, 485 (1963).
(5) Joukovsky, N.I., *Bull. Soc. Chim. Belges* **43**, 397 (1934).
(6) Louder, E.A., Briggs, T.R., Browne, A.W., *Ind. Eng. Chem.* **16**, 933 (1924).
(7) Meloche, C.C., Fredrick, W.G., *J. Am. Chem. Soc.* **54**, 3264 (1932).
(8) Moelwyn-Hughes, E.A., Missen, R.W., *Trans. Faraday Soc.* **53**, 607 (1957).
(9) Mund, W., Heim, G., *Bull. Soc. Chim. Belges* **41**, 349 (1932).
(10) Perrin, D.D., Armarego, W.L.F., Perrin, D.R., "Purification of Laboratory Chemicals," pp. 104, 132, Pergamon, New York, 1966.
(11) Prausnitz, J.M., Eckert, C.A., Orye, R.V., O'Connell, J.P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," Ch. 5, Prentice-Hall, Englewood Cliffs, N. J., 1967.
(12) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **38**, 986 (1946).
(13) Redlich, O., Kister, A.T., *Ibid.*, **40**, 345 (1948).
(14) Scatchard, G., *Chem. Rev.* 8, 321 (1931).
(15) Scatchard, G., Wood, S.E., Mochel, J.M., *J. Am. Chem. Soc.* **62**, 712 (1940).
(16) Schulze, A., *Z. Physik. Chem. (Leipzig)* **97**, 388 (1921).
(17) Scott, R.B., Meyers, C.H., Rands, R.D., Jr., Brickwedde, F.G., Bekkedahl, N., *J. Res. Natl. Bur. Std.* **35**, 39 (1945).
(18) Singh, J., Benson, G.C., *Can. J. Chem.* **46**, 1249 (1968).
(19) Waddington, G., Smith, J.C., Williamson, K.D., Scott, D.W., *J. Phys. Chem.* **66**, 1074 (1962).
(20) Willingham, C.B., Taylor, W.J., Pignocco, J.M., Rossini, F.D., *J. Res. Natl. Bur. Std.* **35**, 219 (1945).
(21) Wilson, G.M., *J. Am. Chem. Soc.* **86**, 127 (1964).
(22) Wong, K.F., PhD. thesis, University of Illinois, Urbana, Ill., 1969.
(23) Wood, S.E., *J. Am. Chem. Soc.* **59**, 1510 (1937).

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