

Isothermal and Isobaric Vapor-Liquid Equilibrium Data and Excess Free Energies by the Total Pressure Method

Systems: 2,2,4-Trimethylpentane-Toluene, Cyclohexane-1-Butanol, and Ethanol-*n*-Heptane

R. S. RAMALHO and JEAN DELMAS

Department of Chemical Engineering, Laval University, Quebec 10, P.Q., Canada

Isothermal vapor-liquid equilibrium data were obtained by the total pressure method for systems 2,2,4-trimethylpentane-toluene at 100°C., cyclohexane-1-butanol at 110°, 100°, 90°, and 80° C., and ethanol-*n*-heptane at 90°, 80°, and 70° C. Isobaric data was obtained at several pressures by cross-plotting of isothermal data. Excess free energy values were also calculated. A numerical method was employed for all calculations.

THE total pressure method for obtaining vapor-liquid equilibrium data consists in the determination of the bubble point temperatures of mixtures of known compositions as a function of pressure. The main advantages of the method are elimination of the analysis of vapor and liquid phases at equilibrium, which usually introduce appreciable error in the data, and a considerable reduction of the time required to obtain the data.

In a previous paper by the same authors (4), a numerical method for calculating excess free energies and activity coefficients for binary systems, from total pressure measurements, has been developed. This method has been used in performing the calculations needed in this investigation. This paper presents isothermal and isobaric vapor-liquid equilibrium data and excess free energies for the systems 2,2,4-trimethylpentane-toluene, cyclohexane-1-butanol, and ethanol-*n*-heptane.

EXPERIMENTAL

Apparatus. The experimental apparatus was, with some modifications, that employed by Prengle and Palm (2). Three ebulliometers were operated concurrently at the same pressure, so as to speed up the collection of data. Detailed drawings of the equipment and operating procedure are available from the authors (1). A discussion of the probable uncertainties in each of the primary variables for this type of experimental determination is presented by Prengle and Palm (2).

2,2,4-Trimethylpentane-Toluene. The operation of the equipment, as well as the numerical method of calculation proposed by the authors (4), was tested by comparison with the data from Prengle and Pike (3) for the system 2,2,4-trimethylpentane-toluene at 100°C. The experimental data taken are essentially identical to those of Prengle and Pike (3). The calculated results are, however, appreciably different. As pointed out by the authors (4), the values of the total pressure recalculated from the Prengle and Pike data (3), utilizing their final results for the correction coefficients for nonideality of the vapor phase (ϕ) and activity coefficients (γ), deviate considerably from their own experimental values. Figure 1 illustrates this fact; for the present data, excellent agreement between the recalculated and experimental total pressure values was obtained.

The data for system 2,2,4-trimethylpentane-toluene are summarized in Table I and plotted in Figures 1 and 2. The experimental measurements of total pressure were made

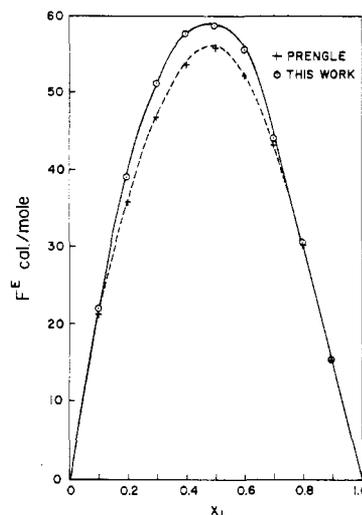


Figure 1. Excess Gibbs free energy for system 2,2,4-trimethylpentane-toluene at 100°C.

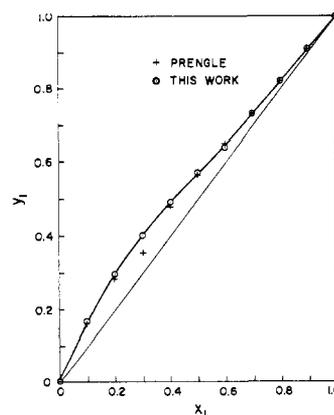


Figure 2. Isothermal vapor-liquid equilibrium data for system 2,2,4-trimethylpentane-toluene at 100°C.

Table I. Data for the Binary Systems

x_1	γ_1	γ_2	$\log(\gamma_1/\gamma_2)$	y_1	ϕ_1	ϕ_2	π , Mm. of Hg	P^s , Mm. of Hg	F^s , Cal./Mole
2,2,4-TRIMETHYLPENTANE-TOLUENE AT 100° C.									
0.0	1.4151	1.0000	0.14076	0.0000			556.30	0.0	0.0
0.1	1.3372	0.9998	0.12604	0.1700	0.9896	1.0020	604.42	26.09	21.45
0.2	1.2534	1.0090	0.09406	0.2999	0.9920	1.0037	643.87	43.51	38.81
0.3	1.1819	1.0271	0.06101	0.4049	0.9939	1.0051	675.73	53.34	51.08
0.4	1.1210	1.0552	0.02628	0.4945	0.9954	1.0062	701.08	56.65	57.83
0.5	1.0720	1.0927	-0.01731	0.5754	0.9966	1.0070	720.98	54.53	58.70
0.6	1.0200	1.1701	-0.05962	0.6437	0.9975	1.0076	736.52	48.04	55.44
0.7	1.0099	1.1926	-0.07322	0.7319	0.9983	1.0080	748.78	38.27	44.34
0.8	1.0028	1.2159	-0.08472	0.8201	0.9989	1.0084	758.83	26.28	30.69
0.9	1.0003	1.2279	-0.08907	0.9102	0.9994	1.0087	767.74	13.17	15.47
1.0	1.0000	1.2300	-0.0900	1.0000			776.60	0.0	0.0
CYCLOHEXANE-1-BUTANOL AT 110° C.									
0.0	4.0813	1.0000	0.6107	0.0			583.20	0.0	0.0
0.1	2.2831	1.0030	0.3572	0.4117	0.9835	1.0151	908.38	216.95	64.905
0.2	2.0030	1.0178	0.2939	0.5779	0.9888	1.0259	1154.32	354.68	116.651
0.3	1.7801	1.0937	0.2118	0.6563	0.9941	1.0309	1339.02	431.15	179.107
0.4	1.5642	1.2167	0.1093	0.7017	0.9945	1.0347	1476.84	460.74	225.557
0.5	1.4310	1.2930	0.440	0.7522	0.9964	1.0376	1578.49	454.17	234.263
0.6	1.2902	1.5035	0.0661	0.7792	0.9979	1.0394	1651.06	418.52	240.652
0.7	1.1647	1.8799	-0.2076	0.7984	0.9988	1.0408	1698.04	357.27	225.480
0.8	1.0638	2.4889	-0.3689	0.8261	0.9996	1.0418	1719.23	270.24	176.604
0.9	1.0009	3.5167	-0.5457	0.8750	0.9998	1.0426	1710.84	153.62	96.43
1.0	1.0000	4.5631	-0.6592	1.0			1665.44	0.0	0.0
CYCLOHEXANE-1-BUTANOL AT 100° C.									
0.0	4.6123	1.0000	0.6639	0.0			393.54	0.0	0.0
0.1	2.4955	1.1020	0.3922	0.4681	0.9860	1.0150	683.99	199.71	75.81
0.2	2.1639	1.0232	0.3254	0.6283	0.9905	1.0241	887.53	312.53	127.98
0.3	1.8481	1.1085	0.222	0.6952	0.9931	1.0286	1030.41	364.66	189.84
0.4	1.6136	1.2198	0.1219	0.7376	0.9952	1.0323	1132.97	376.49	230.09
0.5	1.4588	1.2960	0.0514	0.7818	0.9967	1.0352	1209.70	362.68	236.20
0.6	1.3127	1.5105	-0.0607	0.8057	0.9981	1.0372	1269.18	331.23	243.39
0.7	1.1937	1.8619	-0.1925	0.8263	0.9990	1.0388	1314.15	285.46	230.08
0.8	1.0889	2.5494	-0.3769	0.8445	0.9997	1.0396	1341.43	222.00	191.94
0.9	1.0009	4.1859	-0.6213	0.8723	0.9999	1.0404	1341.98	131.82	106.81
1.0	1.0000	5.0817	-0.7060	1.0			1300.90	0.0	0.0
CYCLOHEXANE-1-BUTANOL AT 90° C.									
0.0	5.3603	1.0000	0.7292	0.0			255.70	0.0	0.0
0.1	2.5101	1.0147	0.3932	0.5112	0.9878	1.0120	483.26	153.48	76.09
0.2	2.1819	1.0270	0.3273	0.6677	0.9916	1.0203	645.71	241.86	127.99
0.3	1.8700	1.1255	0.2207	0.7290	0.9938	1.0251	762.13	284.21	195.01
0.4	1.6469	1.2294	0.1271	0.7712	0.9956	1.0282	847.35	295.36	263.07
0.5	1.4903	1.30186	0.589	0.8117	0.9970	1.0317	911.93	285.86	257.79
0.6	1.3413	1.5283	-0.0467	0.2321	0.9984	1.0340	962.17	262.03	242.78
0.7	1.2085	1.9881	-0.2166	0.8421	0.9992	1.0355	1000.09	225.88	244.23
0.8	1.1024	2.8985	-0.4195	0.8752	0.9997	1.0364	1023.48	175.19	210.18
0.9	1.0012	4.8274	-0.6832	0.8752	0.9999	1.0372	1015.84	103.48	114.25
1.0	1.0000	5.7614	-0.7605	1.0			996.43	0.0	0.0
CYCLOHEXANE-1-BUTANOL AT 80° C.									
0.0	4.0520	1.0000	0.6077	0.0			159.25	0.0	0.0
0.1	2.2733	1.0012	0.3514	0.5419	0.9893	1.0088	316.01	98.01	65.49
0.2	2.0770	1.0290	0.3150	0.6982	0.9924	1.0156	440.87	164.12	105.72
0.3	1.8101	1.1975	0.1796	0.7475	0.9945	1.0203	539.44	203.93	213.25
0.4	1.6120	1.3972	0.0622	0.7782	0.9960	1.0239	616.28	222.03	274.82
0.5	1.4863	1.4861	0.0	0.8200	0.9973	1.0267	674.96	221.95	277.97
0.6	1.3635	1.6470	-0.0822	0.8497	0.9985	1.0287	717.96	206.20	270.47
0.7	1.2068	2.0181	-0.2232	0.8548	0.9994	1.0303	746.74	176.23	240.24
0.8	1.1277	2.68310	-0.3764	0.8843	0.9998	1.0318	761.72	132.45	205.99
0.9	1.0130	3.3920	-0.5246	0.8921	0.9999	1.0328	762.29	74.27	93.83
1.0	1.0000	3.4700	-0.6405	1.0			746.77	0.0	0.0
ETHANOL- <i>n</i> -HEPTANE AT 90° C.									
0.0	22.1003	1.000	1.344	0.0			595.52	0.0	0.0
0.1	7.3139	1.0908	0.8263	0.5942	0.9861	1.0109	1456.39	803.07	200.07
0.2	4.1747	1.1851	0.5469	0.6292	0.9886	1.0195	1552.46	839.35	304.09
0.3	2.9247	1.2511	0.3689	0.6581	0.9908	1.0245	1563.17	791.27	345.47
0.4	2.1828	1.4898	0.1659	0.6525	0.9967	1.0282	1575.14	744.45	397.97
0.5	1.7620	1.7013	0.0153	0.6556	0.9979	1.0317	1563.07	673.07	395.98

(Continued)

Table I. Data for the Binary Systems (Continued)

x_1	γ_1	γ_2	$\log(\gamma_1/\gamma_2)$	y_1	ϕ_1	ϕ_2	π , Mm. of Hg	P^E , Mm. of Hg	F^E , Cal./Mole
ETHANOL- <i>n</i> -HEPTANE AT 90° C.									
0.6	1.5959	2.1556	-0.1306	0.6807	0.9983	1.0333	1661.87	665.68	424.23
0.7	1.3907	2.8409	-0.3101	0.6868	0.9990	1.0342	1675.84	615.15	392.66
0.8	1.2253	4.0042	-0.5143	0.7015	0.9996	1.0344	1652.95	587.08	317.38
0.9	1.1382	7.0406	-0.7915	0.7364	0.9998	1.0365	1645.24	520.58	226.82
1.0	1.0000	21.7827	-1.3381	1.0			1183.46	0.0	0.0
ETHANOL- <i>n</i> -HEPTANE AT 80° C.									
0.0	20.8711	1.0000	1.3195	0.0			31.52	0.0	0.0
0.1	7.5682	1.1578	0.8153	0.5746	0.9894	1.0072	1063.70	593.76	234.64
0.2	4.0646	1.1779	0.5379	0.6153	0.9938	1.0131	1070.96	562.60	288.77
0.3	2.8218	1.2516	0.3530	0.6413	0.9964	1.0182	1072.93	526.16	328.85
0.4	2.1566	1.4282	0.1791	0.6500	0.9978	1.0224	1080.17	494.98	365.69
0.5	1.7535	1.7032	0.0126	0.6545	0.9987	1.0261	1091.30	467.69	383.79
0.6	1.5911	2.0769	-0.1158	0.6786	0.9988	1.0276	1146.16	484.13	400.76
0.7	1.3850	2.7430	-0.2968	0.6842	0.9992	1.0278	1155.21	454.76	372.48
0.8	1.1919	3.9093	-0.4785	0.69155	0.9998	1.0281	1124.52	385.66	338.22
0.9	1.1021	7.0291	-0.8043	0.7217	0.9998	1.0283	1120.83	343.55	198.12
1.0	1.0000	20.5083	-1.3120	1.0			815.70	0.0	0.0
ETHANOL- <i>n</i> -HEPTANE AT 70° C.									
0.0	20.1321	1.0000	1.3038	0.0			304.73	0.0	0.0
0.1	7.1507	1.1126	0.8079	0.5323	0.9912	1.0053	687.80	358.98	199.73
0.2	3.9130	1.1682	0.5251	0.5962	0.9948	1.0103	712.50	359.60	270.70
0.3	2.7994	1.2024	0.3963	0.6319	0.9974	1.0138	723.26	346.26	312.16
0.4	2.1116	1.4343	0.1681	0.6330	0.9984	1.0171	726.85	325.77	351.41
0.5	1.7578	1.6606	0.0250	0.6502	0.9991	1.0187	736.82	311.65	365.07
0.6	1.5137	2.0682	-0.1345	0.6579	0.9993	1.0215	752.74	303.48	367.90
0.7	1.2921	2.7391	-0.3263	0.6582	0.9994	1.0227	749.28	275.93	328.49
0.8	1.1785	3.7509	-0.5029	0.6874	0.9997	1.0232	748.18	250.74	269.60
0.9	1.0695	6.7786	-0.8021	0.7128	0.9999	1.0238	736.47	214.94	77.25
1.0	1.0000	20.1237	-1.3036	1.0			545.62	0.0	0.0

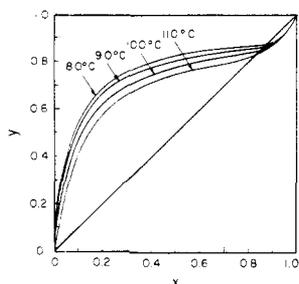


Figure 3. Isothermal vapor-liquid equilibrium data for system cyclohexane-1-butanol at 110°, 100°, 90°, and 80° C.

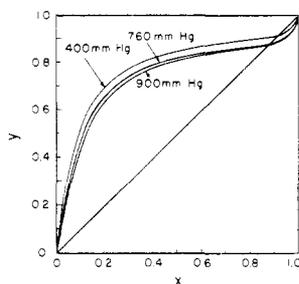


Figure 4. Isobaric vapor-liquid equilibrium data for system cyclohexane-1-butanol at total pressures at 400, 760, and 900 mm. of Hg

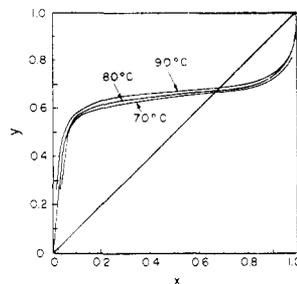


Figure 5. Isothermal vapor-liquid equilibrium data for system ethanol-*n*-heptane at 90°, 80°, and 70° C.

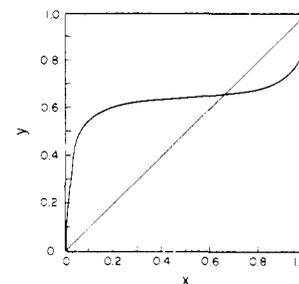


Figure 6. Isobaric vapor-liquid equilibrium data for system ethanol-*n*-heptane at total pressure of 760 mm. of Hg

at the molar concentrations indicated in Table I. The reported values of the temperatures and pressures were obtained by the procedure which is described in detail in the previous paper (4).

Cyclohexane-1-Butanol. Isothermal data at 110°, 90°, and 80° C. are presented in Table I and Figure 3. Isobaric vapor-liquid equilibrium data, at pressures of 400, 760, and 900 mm. of mercury, were obtained by cross-plotting of the isothermal data and are presented in Figure 4.

Ethanol-*n*-Heptane. Isothermal data at 90°, 80°, and 70° C. are presented in Table I and Figure 5. Isobaric vapor-liquid equilibrium data, at 760 mm. of mercury, obtained by cross-plotting of the isothermal data, are presented in Figure 6.

NOMENCLATURE

- F^E = excess Gibbs free energy, cal./g. mole
- P = pressure, mm. of Hg
- P^E = excess total pressure, mm. of Hg
- x = mole fraction of the more volatile component of a binary mixture in the liquid phase
- y = mole fraction of the less volatile component of a binary mixture in the vapor phase

Greek Letters

- γ_1, γ_2 = activity coefficients for components 1 and 2, in the liquid phase

ϕ_1, ϕ_2 = coefficients of correction for nonideality of the vapor phase; components 1 and 2, respectively
 π = total pressure, mm. of Hg

Subscripts

1, 2 = denote respectively the more volatile and the less volatile components of a binary system

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Heterogeneous Phase and Volumetric Equilibrium in the Ethane-*n*-Octane System

ALLAN B. J. RODRIGUES, DAVID S. McCAFFREY, Jr.,¹ and JAMES P. KOHN

Department of Chemical Engineering and Radiation Laboratory, University of Notre Dame, Notre Dame, Ind. 46556

Vapor-liquid equilibrium composition and liquid molar volumes for the binary system of ethane and *n*-octane are presented for six isotherms between 0° and 100° C. The Flory-Huggins model for liquid solutions is shown to fit the experimental data with considerably better accuracy than the Scatchard modification of regular solution theory.

EXPERIMENTAL examination of the volumetric and phase behavior of hydrocarbon systems continues to be of interest owing to their industrial importance and the lack of a sound theoretical model for obtaining equilibrium data on such systems. The literature through 1966 shows no existing experimental data on the vapor-liquid behavior of the ethane-*n*-octane system.

The behavior of the pure components has been extensively studied. Ethane has been investigated by several groups of experimenters (1, 2, 13, 14). Barkelew, Valentine, and Hurd (1) evaluated thermodynamic properties from the PVT data of Beattie, Hadlock, and Poffenberger (2). Rodrigues (14) obtained detailed information in the critical region. Michels, Van Straaten, and Dawson (13) present data for 0° to 100° C. and to 50 atm. The properties of *n*-octane have been established by several studies (3, 8). Eduljee, Newitt, and Weale (3) presented isotherms from 0° to 60° C. to 5000 atm. Data on the liquid density, vapor pressure, critical constants, and heat of fusion are reported by Rossini *et al.* (15).

EXPERIMENTAL

The equipment and experimental techniques were described by Kohn and Kurata (11) and were the same as those used in other recent studies of binary hydrocarbon systems (9-11, 17, 18). Temperatures were obtained with a platinum resistance thermometer, which was accurate to $\pm 0.01^\circ$ C. and was frequently compared with a platinum resistance temperature standard calibrated by the National Bureau of Standards. Pressures were read on bourdon tube gages accurate to ± 0.07 atm. Each gage was frequently checked against an accurate dead weight gage. The only change in procedure from the previous studies was that the equilibrium cell was immersed in an ice bath while being purged of air. The ice bath was needed to cool

the cell to lower the vapor pressure of the octane and hence avoid its possible loss during purging. The equilibrium cells used in this study were made of borosilicate glass and were of the same type as those used in the earlier works.

Several experimental runs were taken at each isotherm to obtain a reasonably good assessment of experimental reproducibility. Compositions of ethane in the liquid and vapor phases were determined from stoichiometric analysis of the amount of pure ethane added to the cell from a thermostated reservoir. The gas was displaced from the reservoir by a manually operated mercury displacement pump. The pump has an accuracy of displacement of ± 0.01 ml. The accuracy of the measured ethane composition was dependent on the temperature and pressure of the reservoir, the delivery line volume and temperature, and the volume and temperature of the neck of the equilibrium cell. The reservoir temperature was controlled to $\pm 0.07^\circ$ C. and the pressure to ± 0.07 atm. The delivery line volume is approximately 0.7 ml., and its temperature was controlled manually to within $\pm 2^\circ$ C. Many hundreds of experimental runs with ethane in various binary and ternary systems have demonstrated that the equilibrium compositions in the cell are reliably reproduced within from 0.0005 to 0.003 mole fraction.

The ethane (Matheson Co.) was pure grade, stated by the supplier to have 99 mole % minimum purity, was purified before further use as described by Ma and Kohn (12), and was thought to have a purity of at least 99.7 mole %. Pure grade *n*-octane (Phillips Petroleum Co.) was stated by the supplier to be at least 99 mole % pure. The *n*-octane had a refractive index of 1.3971 at 20° C. in good agreement with the literature value (15) and was used as received without further purification.

RESULTS

The pressure-composition diagrams of the system in vapor-liquid equilibrium are presented in Figures 1 and

¹ Present address: U.S. Naval Academy, Annapolis, Md. 21402