Excess Gibbs Energies of Mixing for Some Binary Mixtures

Buta R. Sharma[1] **and Prem P. Singh**[2]
Department of Chemistry and Biochemistry, Panjab Agricultural University, Ludhiana, India

Total vapor pressures of pyridine–bromoform, pyridine–chloroform, *n*-hexane–bromoform, *n*-hexane–chloroform, and benzene–bromoform at 303.15 and 313.15K were determined by a static method and were used to calculate excess Gibbs energies of mixing for these mixtures.

This paper reports excess Gibbs energies of mixing for mixtures A + B thought to have specific A–B interactions: pyridine–bromoform, pyridine–chloroform, *n*-hexane–bromoform, *n*-hexane–chloroform, and benzene–bromoform.

Experimental

Method. Benzene, *n*-hexane, pyridine, chloroform, and bromoform were purified as suggested by Vogel (*9*). Purities of the final samples were checked by measuring their densities; the results agreed to within 0.00002 g cm^{-3} with those in the literature as reported earlier (6). Vapor pressures were measured by a modified static method (7). The apparatus (excluding the manometric part) was placed in a water thermostat which, in turn, was placed in another water thermostat. The temperature of the outer thermostat was controlled to ±0.01K, and the temperature drift in the inner thermostat was of the order of ±0.002K. The manometric part was maintained at a higher temperature (323.15 ± 0.01)K to avoid condensation. All pressure measurements were reproducible to better than ±0.02 torr. The equilibrium mole fraction in the liquid phase was determined (1) from refractive index measurements as described earlier. An uncertainty of 0.0001 in refractive index leads to an error of about 0.0003 in x_1.

Results

Total vapor pressures P, refractive indices n_D, partial pressures P_1, P_2, activity coefficients γ_1, γ_2, and residual pressures R, together with the excess Gibbs energies G^E computed by Barker's method (*2*) for different mole fractions x_1 of component 1, are recorded in Table I. The second virial coefficients of the pure substances were evaluated from the Berthelot equation (*5*) by use of critical constant data (*8*). The critical constants V_c, P_c, and T_c of bromoform were evaluated, respectively, from the Lyderson method, Riedel method, and modified Guldberg rule as reported (*4*). It was further assumed that $B_{12} = (B_{11} + B_{22})/2$. The excess Gibbs energies were assumed to have the form:

$$G^E/RT = x_1(1 - x_1)(G_0 + G_1(2x_1 - 1) + G_2(2x_1 - 1)^2) \quad (1)$$

where G_0, G_1, and G_2 were chosen by the method of least squares and are recorded in Table II. The three terms of Equation 1 were sufficient to give results in agreement with the experimental vapor pressures. All calculations were made on an IBM 1620 computer. Although no color was observed in the pyridine–bromoform mixture at first, it gradually became yellow on standing. In several cases, $x_2 > 0.75$ the liquid mixture was opaque at the conclusion of the experiment. Because of this, no attempt was made to determine G^E for this mixture at $x_2 > 0.75$. The results in Table I correspond to those compositions in which opacity was not apparent. An interesting feature of this mixture is that a mixture containing $x_2 > 0.75$, after several hours of slow cooling in the dark, yields yellowish crystals (mp > 200°C). Further work on these crystals is in progress. Following a similar observation (*3*) for carbon tetrachloride-triethylamine, light was excluded from the experiment in a number of measurements but with no effect on color change.

Discussion

Examination of Table I shows that the activity coefficients of bromoform in pyridine–bromoform and *n*-hexane–bromoform are always greater than the activity coefficients of chloroform in its mixtures with pyridine and *n*-hexane.

The excess Gibbs energies of mixing for *n*-hexane–chloroform and *n*-hexane–bromoform are all positive at 303.15K and become more positive at 313.15K. G^E for the system pyridine–chloroform is negative at 303.15K and its temperature coefficient is positive. On the other hand, for pyridine–bromoform, G^E is negative at 303.15K but becomes still more negative at 313.15K.

An interesting feature is the observation that when chloroform is replaced by bromoform in its mixture with *n*-hexane, the excess Gibbs energy acquires a much more positive character. The G^E data for pyridine–chloroform and pyridine–bromoform support these observations.

G^E for benzene–bromoform is positive at 303.15K and $\partial G^E/\partial T$ is negative for this mixture. Whereas the curve of G^E against the mole fraction x_1 of *n*-hexane is almost symmetrical about $x_1 = 0.5$ in *n*-hexane–chloroform, this is not so in the case of *n*-hexane–bromoform at 303.15K. For pyridine–chloroform the curve of G^E against the mole fraction at 303.15K is skewed slightly toward the chloroform-rich end of the mole fraction scale. It becomes almost symmetrical at 313.15K. For pyridine–bromoform the curve of G^E against the mole fraction at 303.15K is skewed toward the pyridine-rich end of the mole fraction scale, but the maximum shifts toward low mole fraction of pyridine at 313.15K.

---

[1] Present address, Department of Chemistry, D.A.V. College, Jullundur, India.

[2] To whom correspondence should be addressed.

Table I. Refractive Indices n_D, Total Vapor Pressures P, Partial Pressures P_1, P_2, Activity Coefficients γ_1, γ_2, Residual Pressures R, and Excess Gibbs Energies of Mixing of Various Systems at 303.15 and 313.15K for Different Mole Fractions x_1 of Component 1

x_1	n_D	P, torr	P_1, torr	P_2, torr	γ_1	γ_2	$R = P_{expt} - P_{calc}$	G^E, J mol^{-1}
Pyridine(1)–bromoform(2), 303.15K								
0.0000	1.5895	9.21	0.00	9.21	0.6426	1.0000	0.00	. . .
0.2503	1.5715	12.30	5.53	6.77	0.7604	0.9807	−0.00	−209
0.3702	1.5618	14.07	8.47	5.60	0.7877	0.9653	−0.00	−278
0.4398	1.5558	15.16	10.27	4.91	0.8039	0.9519	−0.03	−311
0.5500	1.5460	17.15	13.36	3.79	0.8359	0.9157	−0.01	−348
0.6701	1.5347	19.83	17.19	2.55	0.8823	0.8398	0.08	−356
0.7797	1.5237	22.72	21.14	1.47	0.9323	0.7244	0.10	−316
0.8399	1.5175	24.22	23.43	0.94	0.9591	0.6414	−0.16	−267
0.9102	1.5100	26.41	26.08	0.43	0.9851	0.5309	−0.11	−177
1.0000	1.4998	29.10	29.10	0.00	1.0000	0.3803	0.00	. . .
Pyridine(1)–bromoform(2), 313.15K								
0.0000	1.5858	11.37	0.00	11.37	0.3974	1.0000	0.00	. . .
0.2399	1.5684	14.55	6.54	8.09	0.6688	0.9365	−0.09	−380
0.3297	1.5613	16.90	10.12	6.81	0.7524	0.8938	−0.03	−439
0.4502	1.5513	20.75	15.48	5.20	0.8425	0.8320	0.06	−463
0.5098	1.5462	22.82	18.26	4.47	0.8778	0.8011	0.07	−455
0.6499	1.5335	27.85	24.95	2.90	0.9400	0.7294	−0.00	−391
0.7600	1.5230	31.79	30.17	1.84	0.9719	0.6738	−0.22	−303
0.8101	1.5181	33.67	32.51	1.40	0.9822	0.6482	−0.24	−251
0.8998	1.5089	38.16	36.58	0.68	0.9949	0.6011	0.88	−144
1.0000	1.4985	40.88	40.88	0.00	1.0000	0.5451	0.00	. . .
Pyridine(1)–chloroform(2), 303.15K								
0.0000	1.4395	241.51	0.00	241.51	0.1945	1.0000	0.00	. . .
0.0801	1.4458	215.52	0.71	217.87	0.3038	0.9821	−3.06	−281
0.1596	1.4513	190.52	2.00	189.95	0.4250	0.9387	−1.43	−478
0.2849	1.4596	151.97	5.10	145.78	0.6097	0.8485	1.07	−651
0.3502	1.4638	133.16	7.11	124.77	0.6921	0.8001	1.26	−689
0.4398	1.4695	109.05	10.10	99.07	0.7842	0.7379	−0.12	−698
0.5150	1.4739	92.12	12.70	80.20	0.8433	0.6907	−0.79	−673
0.6298	1.4806	71.69	16.70	55.41	0.9082	0.6260	−0.43	−589
0.7200	1.4854	58.57	19.83	38.63	0.9442	0.5775	0.09	−491
0.8501	1.4924	42.76	24.29	17.96	0.9811	0.5014	0.49	−301
0.9103	1.4956	36.21	26.30	9.85	0.9925	0.4603	0.04	−193
1.0000	1.4998	29.10	29.10	0.00	1.0000	0.3900	0.00	. . .
Pyridine(1)–chloroform(2), 313.15K								
0.0000	1.4354	316.50	0.00	316.50	0.4564	1.0000	0.00	. . .
0.0798	1.4416	288.95	1.82	288.67	0.5484	0.9926	−1.54	−142
0.1698	1.4482	258.14	4.53	254.29	0.6423	0.9707	−0.67	−259
0.2500	1.4539	230.59	7.40	223.05	0.7143	0.9439	0.12	−331
0.3297	1.4594	203.84	10.57	192.63	0.7744	0.9134	0.62	−377
0.4401	1.4667	168.22	15.28	152.58	0.8409	0.8678	0.35	−404
0.5499	1.4737	135.41	20.20	115.59	0.8920	0.8192	−0.38	−396
0.6302	1.4785	114.16	23.90	90.38	0.9225	0.7805	−0.12	−370
0.7598	1.4860	83.02	29.99	53.18	0.9625	0.7082	−0.15	−291
0.8200	1.4892	70.49	32.83	37.60	0.9772	0.6687	0.04	−237
0.9301	1.4950	51.17	37.90	12.74	0.9960	0.5841	0.52	−107
1.0000	1.4985	40.88	40.88	0.00	1.0000	0.5217	0.00	. . .
n-Hexane(1)–bromoform(2), 303.15K								
0.0000	1.5895	9.21	0.00	9.21	2.5975	1.0000	0.00	. . .
0.0802	1.5700	42.65	35.47	8.53	2.3606	1.0040	−1.36	182
0.1999	1.5415	85.32	77.58	7.62	2.0636	1.0264	0.10	417
0.2797	1.5230	107.77	99.60	7.08	1.8896	1.0554	1.08	546
0.3298	1.5126	118.79	111.20	6.75	1.7875	1.0814	0.82	615
0.4503	1.4849	138.46	132.88	6.06	1.5619	1.1798	−0.48	734
0.5399	1.4654	147.71	144.21	5.60	1.4125	1.3027	−2.11	776
0.6298	1.4463	156.97	152.65	5.18	1.2807	1.4965	−0.87	768
0.7400	1.4238	166.83	160.91	4.63	1.1480	1.9020	1.27	678
0.8502	1.4019	176.69	169.73	3.75	1.0531	2.6688	3.20	481
0.9401	1.3845	184.94	179.97	2.17	1.0091	3.8576	2.79	225
1.0000	1.3732	189.78	189.78	0.00	1.0000	5.2083	0.00	. . .

(Continued on page 362)

Table I. Continued

x_1	n_D	P, torr	P_1, torr	P_2, torr	γ_1	γ_2	$R = P_{expt} - P_{calc}$	G^E, J mol^{-1}
n-Hexane(1)–bromoform(2), 313.15K								
0.0000	1.5858	11.37	0.00	11.37	6.4861	1.0000	0.00	. . .
0.0300	1.5777	59.22	42.80	11.11	5.3128	1.0030	5.29	137
0.1303	1.5515	118.39	111.09	10.47	3.1598	1.0478	−3.18	495
0.1902	1.5363	138.10	130.03	10.19	2.5298	1.0929	−2.12	646
0.3198	1.5047	170.12	158.39	9.57	1.8282	1.2186	2.14	852
0.3999	1.4861	185.76	174.21	9.10	1.6060	1.3102	2.44	915
0.5197	1.4596	205.47	197.15	8.21	1.3964	1.4751	0.10	937
0.6501	1.4327	223.50	219.03	7.11	1.2384	1.7492	−2.64	871
0.7098	1.4209	232.20	227.49	6.57	1.1773	1.9486	−1.87	805
0.8300	1.3985	249.61	242.61	5.30	1.0726	2.6775	1.60	587
0.8999	1.3861	259.93	252.44	4.11	1.0281	3.5216	3.37	392
1.0000	1.3695	273.11	273.11	0.00	1.0000	6.1404	0.00	. . .
n-Hexane(1)–chloroform(2), 303.15K								
0.0000	1.4395	241.51	0.00	241.51	1.4437	1.0000	0.00	. . .
0.0750	1.4316	245.93	21.84	223.04	1.5273	0.9981	0.73	75
0.1598	1.4233	249.23	46.57	202.73	1.5279	0.9986	−0.07	168
0.2201	1.4178	251.12	62.37	189.48	1.4853	1.0054	−0.74	230
0.3399	1.4076	253.92	87.53	166.67	1.3494	1.0447	−0.28	329
0.4700	1.3980	253.20	107.19	145.43	1.1952	1.1354	0.56	380
0.5497	1.3927	250.06	117.35	132.30	1.1190	1.2159	0.40	377
0.6303	1.3880	244.92	127.57	117.14	1.0614	1.3117	0.20	350
0.7250	1.3831	235.00	140.76	94.79	1.0190	1.4278	−0.55	281
0.8499	1.3778	216.54	161.39	55.49	0.9983	1.5332	−0.35	157
0.9098	1.3757	206.43	172.54	33.39	0.9978	1.5362	0.49	92
1.0000	1.3732	189.78	189.78	0.00	1.0000	1.4476	0.00	. . .
n-Hexane(1)–chloroform(2), 313.15K								
0.0000	1.4354	316.50	0.00	316.50	1.9694	1.0000	0.00	. . .
0.0598	1.4294	327.89	30.37	298.33	1.8521	1.0019	−0.82	101
0.1803	1.4185	344.69	79.49	265.58	1.6054	1.0221	−0.39	268
0.2899	1.4093	351.91	111.91	239.84	1.4047	1.0651	0.14	373
0.3302	1.4061	353.17	121.68	231.03	1.3409	1.0876	0.44	398
0.4497	1.3974	352.96	146.70	205.17	1.1870	1.1757	1.08	432
0.5301	1.3920	348.49	162.04	186.36	1.1126	1.2509	0.08	421
0.6100	1.3871	341.73	177.52	164.86	1.0599	1.3338	−0.66	384
0.7498	1.3796	323.45	207.66	116.72	1.0100	1.4734	−0.93	271
0.8602	1.3745	303.18	235.22	68.00	0.9989	1.5380	−0.05	154
0.9299	1.3718	289.14	254.02	34.00	0.9989	1.5347	1.11	75
1.0000	1.3695	273.11	273.11	0.00	1.0000	1.4829	0.00	. . .
Benzene(1)–bromoform(2), 303.15K								
0.0000	1.5895	9.21	0.00	9.21	1.1189	1.0000	0.00	. . .
0.0902	1.5804	20.05	11.72	8.39	1.1043	1.0005	−0.07	23
0.1999	1.5694	33.18	25.77	7.40	1.0942	1.0020	0.00	49
0.2698	1.5625	41.44	34.65	6.77	1.0893	1.0034	0.01	64
0.3299	1.5567	48.50	42.22	6.23	1.0849	1.0051	0.04	76
0.4403	1.5462	61.13	55.88	5.24	1.0748	1.0112	0.00	95
0.5197	1.5386	69.98	65.40	4.54	1.0651	1.0198	0.03	105
0.6600	1.5256	84.59	81.44	3.32	1.0432	1.0517	−0.17	113
0.7501	1.5175	93.68	91.24	2.53	1.0276	1.0907	−0.10	106
0.8701	1.5068	105.76	104.02	1.42	1.0092	1.1804	0.30	74
0.9100	1.5033	109.73	108.34	1.02	1.0047	1.2239	0.35	56
1.0000	1.4955	118.58	118.58	0.00	1.0000	1.3584	0.00	. . .
Benzene(1)–bromoform(2), 313.15K								
0.0000	1.5858	11.37	0.00	11.37	1.0881	1.0000	0.00	. . .
0.0600	1.5799	21.26	10.64	10.70	1.0768	1.0003	−0.08	12
0.1902	1.5672	42.61	33.33	9.25	1.0626	1.0020	0.01	34
0.2599	1.5604	53.90	45.39	8.47	1.0581	1.0033	0.02	44
0.3198	1.5546	63.55	55.72	7.81	1.0549	1.0045	0.01	51
0.4397	1.5430	82.70	76.20	6.47	1.0479	1.0087	0.01	66
0.5901	1.5287	105.99	101.23	4.80	1.0356	1.0219	−0.05	76
0.6698	1.5210	117.98	114.07	3.93	1.0273	1.0361	−0.03	77
0.7200	1.5163	125.33	122.02	3.37	1.0217	1.0491	−0.07	75
0.8499	1.5041	144.38	142.28	1.90	1.0080	1.1038	0.18	56
0.9302	1.4965	156.07	154.91	0.93	1.0020	1.1597	0.22	31
1.0000	1.4900	166.32	166.32	0.00	1.0000	1.2282	0.00	. . .

Table II. Values of Parameters of Equation 1 for Various Mixtures at 303.15 and 313.15K

System	Temp, K	G_0	G_1	G_2	σ(p), torr
Pyridine(1)–bromoform(2)	303.15	−0.5303	−0.2622	−0.1739	0.09
	313.15	−0.7037	0.1580	−0.0610	0.36
Pyridine(1)–chloroform(2)	303.15	−1.0799	0.3478	−0.2092	1.44
	313.15	−0.6219	0.0668	−0.0954	0.72
n-Hexane(1)–bromoform(2)	303.15	1.2122	0.3478	0.0901	2.02
	313.15	1.4436	−0.0273	0.3985	3.20
n-Hexane(1)–chloroform(2)	303.15	0.6077	0.0013	−0.2391	0.57
	313.15	0.6585	−0.1418	−0.1226	0.79
Benzene(1)–bromoform(2)	303.15	0.1653	0.0969	0.0440	0.19
	313.15	0.1102	0.0605	0.0348	0.12

Literature Cited

(1) Adya, A. K., Mahl, B. S., Singh, P. P., *J. Chem. Thermodyn.*, **5**, 393 (1973).
(2) Barker, J. A., *Aust. J. Chem.*, **6**, 207 (1953).
(3) Fenby, D. V., *ibid.*, **26**, 1143 (1973).
(4) Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids," McGraw-Hill, New York, N.Y., 1958.
(5) Scatchard, G., Ticknor, L. B., *J. Am. Chem. Soc.*, **74**, 3724 (1952).
(6) Sharma, B. R., Singh, P. P., *J. Chem. Thermodyn.*, **5**, 361 (1973).
(7) Taha, A. A., Grigsby, R. D., Johnson, J. R., Christian, S. D., Affsprung, H. E., *J. Chem. Educ.*, **43**, 432 (1966).
(8) Timmerman, J., "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, The Netherlands, 1950.
(9) Vogel, A., "Practical Organic Chemistry," Longmans, Green, London, England, 1968.

Received for review July 15, 1974. Accepted April 19, 1975.

Low-Temperature *K* Data for Methane–*n*-Pentane

LeRoy C. Kahre
Research and Development, Phillips Petroleum Co., Bartlesville, Okla. 74004

Phase equilibrium data are presented for the methane–*n*-pentane system at low temperatures and high pressures. Seven isotherms from 50° to −140°F and 50 to 2300 psia are obtained. A region of triple-valued dew points is observed for each of the isotherms near or below the methane critical temperature. Measured critical conditions are in good agreement with previously reported values.

The current interest in the recovery of light hydrocarbons from natural gas necessitates the obtaining of fundamental vapor-liquid equilibrium data for at least the binary systems. Data for the methane–*n*-butane system were reported previously (*4*), and this work is merely an extension to another system where literature data are not available.

Experimental

The experimental equipment (Figure 1) is the same as that used for the previous work (*4*). It consists of a vapor recirculating equilibrium cell immersed in a suitable liquid bath, a gas-liquid chromatography unit for analyses of both vapor and liquid samples, and associated temperature and pressure measuring instruments. For most of the work the samples were analyzed with the use of a component peak height (compared to a pure component at the same partial pressure) as the measure of concentration. However, near the end of the program, the output from the thermal conductivity detector was tied to a central computer so that peak areas could also be measured. No significant difference was found between the two methods of calculation. Table I presents a comparison between the pentane concentration of samples gravimetrically synthesized and that analyzed by the peak

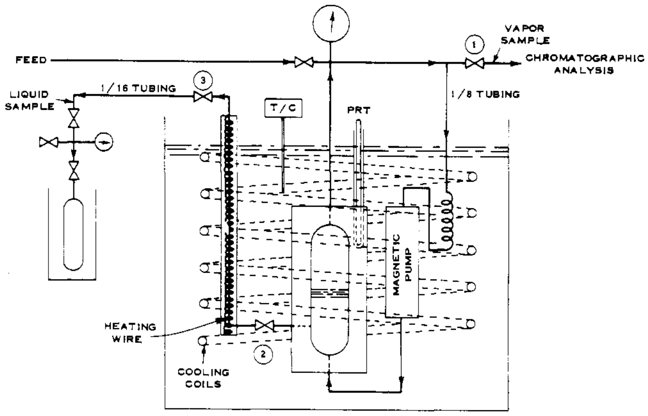

Figure 1. Schematic diagram of experimental equipment

Table I. Analyses of Synthetic Samples of Methane–*n*-Pentane

n-Pentane concn, mol %		
Synthesized	Analyzed	% Dev
86.08	85.52	0.65
51.00	50.82	0.35
28.41	28.41	0.0
13.82	13.53	2.1
0.934	0.904	3.2
0.110	0.111	0.9
0.0130[a]	0.0124	4.6

[a] Synthesized by diluting previous sample.