Table II. Common Ion Effect on Lithium Fluoride Solubility

Description	Molarity		
	Li^+	F^-	K^+
From Table I 30.8°C	0.0528	0.0528	...
Satd LiF + KF 30.4°C	0.028	0.0925	0.066
Satd LiF + LiCl 30.5°C	0.113	0.025	...

For determinations in the presence of excess lithium, 10.0 grams of LiF and 6.4 grams of LiCl were added to about 1500 ml of nitrogen-purged distilled water. The solution was equilibrated at 30.5°C for 96 hr after approaching the temperature from the high side. Samples were withdrawn in duplicate and analyzed for lithium and fluoride as before. The results are presented in Table II.

DISCUSSION

The solubility values of Payne are essentially verified by our measurements. The values up to 81.8°C show a slight increase in solubility.

An estimate of the heat of solution from the values at 23.7° and 81.8°C yields a value of 920 cal/mol ± 100 cal/mol.

The solubility products based on measurements from Table I are:

at 25°C	2.6×10^{-3}
at 80°C	3.3×10^{-3}

The data from Table II yields the following solubility products at temperatures between 30.4 and 30.8°C:

$$2.8 \times 10^{-3},\ 2.6 \times 10^{-3},\ \text{and}\ 2.8 \times 10^{-3}$$

These results show that within the range explored (doubling the cation or anion concentration), the counterion concentration can be calculated with reasonable accuracy and that knowledge of activity coefficients is not required.

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RECEIVED for review April 3, 1972. Accepted June 26, 1972.

Vapor-Liquid Equilibria in Systems *n*-Hexane–Benzene and *n*-Pentane–Toluene

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Total vapor pressures of binary mixtures *n*-hexane–benzene and *n*-pentane–toluene were determined as functions of temperature and composition using a static method. The experimental results were correlated in terms of the Antoine equation. The interpolated isothermal P-x values were employed to compute equilibrium vapor compositions by means of an indirect method, in which the Redlich-Kister equation was used to represent the liquid activity coefficients. The P-x-y values thus obtained are presented for the *n*-hexane–benzene system at 30, 40, 50, and 60°C and for the *n*-pentane–toluene system at 20, 25, 30, 35, and 40°C.

Vapor-liquid equilibrium data for aromatic-saturated hydrocarbon mixtures are of interest to petroleum and petrochemical industries. These hydrocarbons are important constituents of the products from the catalytic reforming process. In this investigation, total vapor pressures for the binary systems *n*-hexane–benzene and *n*-pentane–toluene were experimentally determined by means of a static method. Vapor-liquid equilibrium data for the system *n*-hexane–benzene are available in the literature (*1*, *5*, *9*, *11*). However, isothermal data for the system were reported only at 25°C (*9*). The experimental results obtained were correlated by means of the Antoine equation from which isothermal *P*-*x* values were obtained. The equilibrium vapor compositions were then computed by an indirect method. The *P*-*x*-*y* values are presented at 30, 40, 50, and 60°C for the *n*-hexane–benzene system, and at 20, 25, 30, 35, and 40°C for the *n*-pentane–toluene system.

EXPERIMENTAL DETAILS

The arrangement of the apparatus is schematically shown in Figure 1. The main parts of the apparatus consist of an equilibrium cell and a solution reservoir. The equilibrium cell is made of a 100-ml flat-bottomed pyrex flask containing two small magnetic stirrers. The cell is connected to the manometer by a U-tube mercury seal-off valve (valve 1). This valve can be bypassed to the vacuum manifold or to the atmosphere by a three-way stopcock so that the mercury level in the U-tube can be manipulated. The solution reservoir is made of a 100-ml round-bottomed pyrex flask which can be isolated from the system by means of two U-tube mercury seal-off valves (valves 2 and 3). A capillary tube is connected to the upper

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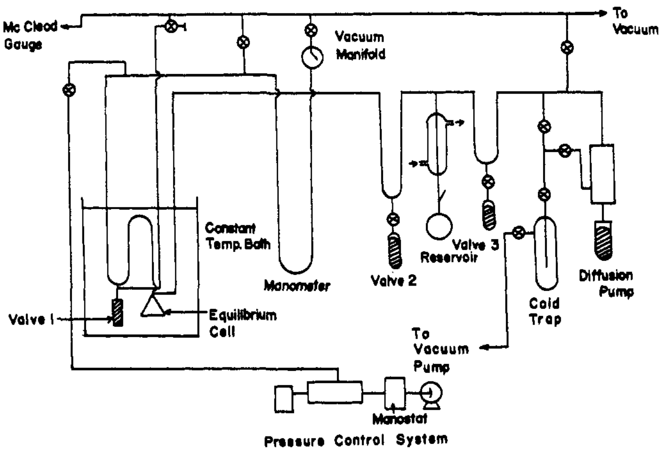

Figure 1. Schematic diagram of apparatus

part of the reservoir through which the liquid solution is introduced. A Liebig condenser is built above the reservoir to condense and reflux vaporized materials from the reservoir.

As soon as a liquid solution of known composition, about 80 ml, was introduced into the reservoir through a capillary tube by means of a hypodermic syringe; the reservoir was immersed into liquid nitrogen in a Dewar flask. After the liquid sample was frozen, the capillary was sealed off, and the degassing procedure followed. Valve 3 was opened and all the noncondensable gas was evacuated. Then Valve 3 was closed and the reservoir was heated to expel the dissolved or trapped gas in the solution, which was then again frozen and the noncondensable gas evacuated. The process was repeated until no change of the vapor pressure could be detected.

When the whole apparatus was evacuated, valve 2 was opened and the degassed solution was transferred into the equilibrium cell, which was then totally immersed with valve 1 into a constant temperature bath. The mercury levels of the two arms of the U-tube were adjusted to about the same level by introducing helium gas through the pressure control system. After equilibrium was established, the pressure difference between the manometer and that of the U-tube mercury valve were measured with a cathetometer. Total vapor pressure measurements were made and recorded from 25–60°C for the *n*-hexane–benzene system and from 20–40°C for the *n*-pentane–toluene system. Refractive index and density measurements were made for each of the solutions before the degassing procedure and after the total vapor pressure measurement to determine the compositions of the solutions. Precision of the temperature measurements is estimated to be ±0.01°C, of the pressure measurements, ±0.05 mm Hg, and of the composition measurements, ±0.0005 in terms of mole fractions.

Research grade *n*-hexane, benzene, *n*-pentane, and toluene, supplied by Phillips Petroleum Co., were used without further purification. Physical properties of these materials used in this investigation are summarized in Table I.

RESULTS AND DATA REDUCTION

The experimentally determined vapor pressures of *n*-hexane, benzene, and their mixtures are listed in Table II, and the experimentally determined vapor pressures of *n*-pentane, toluene, and their mixtures are listed in Table III. These results were correlated by means of the Antoine equation. The correlated constants obtained are reported in Table IV and are used to obtain the isothermal total vapor pressure–liquid composition relationship.

At low pressures, the liquid activity coefficient for com-

(*Continued on page 497*)

Table I. Physical Properties of Materials Used

Material	Temp, °C	Exptl	Lit.
	Refractive Index		
Benzene	25	1.49787	1.49792 (*2*)
n-Hexane	25	1.37230	1.37226 (*3*)
Toluene	25	1.49417	1.49414 (*2*)
n-Pentane	25	1.35474	1.35472 (*3*)
	Density		
Benzene	20.0	0.87868	0.87903 (*2*)
n-Hexane	20.0	0.65839	0.65937 (*3*)
Toluene	20.0	0.86655	0.86696 (*2*)
n-Pentane	20.0	0.62564	0.62624 (*3*)
Benzene	25.0	0.87386	0.87380 (*2*)
n-Hexane	25.0	0.65490	0.65481 (*3*)

Table II. Vapor Pressure of *n*-Hexane–Benzene Mixtures

x_1 = 1.000		x_1 = 0.774		x_1 = 0.587		x_1 = 0.440		x_1 = 0.303	
t, °C	P_{obs}, mm Hg	*t*, °C	P_{obs}, mm Hg	*t*, °C	P_{obs}, mm Hg	*t*, °C	P_{obs}, mm Hg	*t*, °C	P_{obs}, mm H
28.19	174.05	30.26	186.89	26.96	158.87	26.26	147.04	25.24	133.87
32.92	211.60	31.88	200.22	35.35	224.77	29.08	167.92	30.08	164.66
37.62	254.51	37.27	248.91	38.30	251.36	31.46	184.92	35.45	204.71
41.49	295.02	41.71	294.61	39.80	267.16	36.92	229.54	40.22	247.17
44.58	331.96	46.55	354.23	41.98	290.90	41.49	273.92	46.67	315.80
49.66	399.63	53.26	450.08	47.65	359.26	46.86	335.44	51.70	379.91
51.51	427.37	61.52	596.98	52.99	434.06	51.79	400.64	56.01	442.17
57.79	531.74			57.01	499.83	59.38	519.25	60.33	512.57
63.09	634.63			61.28	577.87				

x_1 = 0.241		x_1 = 0.154		x_1 = 0.077		x_1 = 0.049		x_1 = 0.000	
31.03	165.97	27.62	134.56	31.32	143.71	27.84	119.25	29.47	117.59
33.68	185.19	32.34	163.11	37.00	182.13	31.97	142.22	33.57	139.47
36.89	210.54	36.06	190.23	40.85	212.52	37.49	179.33	36.19	156.17
41.15	248.84	40.27	224.78	45.03	249.82	43.13	224.94	39.49	179.06
45.23	290.82	45.32	273.28	49.94	301.28	49.32	285.58	41.86	196.11
50.36	351.48	51.15	339.52	56.38	380.74	54.91	350.52	43.59	210.54
55.69	424.68	55.28	393.21	60.06	433.59	60.15	420.79	43.98	214.47
61.05	509.07	60.83	476.66					47.39	244.78
								52.30	299.61
								66.00	485.73
								67.30	505.14

Table III. Vapor Pressure of *n*-Pentane–Toluene Mixtures

$x_1 = 1.000$		$x_1 = 0.898$		$x_1 = 0.766$		$x_1 = 0.694$		$x_1 = 0.630$		$x_1 = 0.494$	
t, °C	P_{obs}, mm Hg	t, °C	P_{obs}, mm Hg	t, °C	P_{obs}, mm Hg	t, °C	P_{obs}, mm Hg	t, °C	P_{obs}, mm Hg	t, °C	P_{obs} mm Hg
20.03	424.24	20.75	403.16	20.85	354.00	20.10	322.74	19.69	297.03	20.10	249.51
22.31	463.78	24.62	465.89	24.00	406.16	25.11	389.60	25.02	363.88	22.48	274.24
25.24	518.34	29.45	555.04	26.68	442.14	27.45	424.41	28.73	415.66	25.90	311.93
28.63	586.96	34.36	656.73	28.50	471.91	31.32	487.16	34.55	509.65	29.63	356.50
31.54	650.55	39.87	788.12	32.54	537.61	35.29	558.39	39.73	607.06	31.78	385.57
35.00	734.21					39.22	637.94			34.75	427.64
37.72	804.85									37.78	475.36
										40.04	511.76

$x_1 = 0.392$		$x_1 = 0.306$		$x_1 = 0.185$		$x_1 = 0.140$		$x_1 = 0.000$	
20.85	227.84	20.77	188.54	22.58	145.77	20.66	110.44	21.68	24.77
25.18	267.22	23.48	210.05	25.50	162.25	23.72	126.77	25.06	29.81
28.43	299.60	26.83	237.65	28.52	180.91	26.52	140.76	28.47	34.74
31.60	334.82	29.65	263.58	31.27	199.27	30.20	160.99	30.28	38.93
34.65	371.07	32.87	294.73	36.03	235.29	32.87	176.92	33.60	44.52
37.75	411.71	35.50	321.72	38.30	249.27	36.04	197.80	36.25	50.66
40.46	449.43	37.92	350.00			38.40	214.31	40.67	60.99
		41.12	388.13			39.94	226.33		

Table IV. Antoine Equation Constants

x_1	a	b	c	x_1	a	b	c
	n-Hexane(1)–Benzene System				*n*-Pentane(1)–Toluene System		
1.000	6.87773	1171.530	224.366	1.000	6.85221	1064.630	232.000
0.774	6.98329	1228.016	230.391	0.898	6.21933	788.727	197.500
0.587	6.88363	1181.814	225.391	0.766	5.95742	715.672	189.375
0.440	6.95059	1232.173	231.582	0.694	6.28242	848.341	204.688
0.303	6.46135	979.436	200.625	0.630	6.57456	1004.891	225.313
0.241	6.28876	898.958	189.844	0.494	6.42540	957.336	217.578
0.154	6.45651	986.165	200.078	0.392	6.19298	902.683	214.492
0.077	6.67304	1092.724	210.625	0.306	6.01840	835.391	202.500
0.049	6.85479	1190.399	221.250	0.185	5.54055	707.181	186.875
0.000	6.89745	1206.350	220.237	0.140	5.15610	546.229	155.000
				0.000	6.95334	1343.943	219.377

Table V. Summary of Correlation

t, °C	B	C	Std dev, mm Hg	Av % dev	$\ln \gamma_1^\infty$	$\ln \gamma_2^\infty$
			n-Hexane (1)-Benzene System			
30°C	0.58345	−0.11143	0.42	0.19	0.69488	0.47202
40°C	0.54523	−0.11679	0.46	0.14	0.66202	0.42844
50°C	0.50682	−0.10441	0.65	0.13	0.61123	0.40241
60°C	0.46698	−0.07816	0.86	0.13	0.54514	0.38882
			n-Pentane(1)-Toluene System			
20°C	0.59274		3.91	1.16	0.59274	0.59274
25°C	0.57876		3.93	0.88	0.57876	0.57876
30°C	0.56209		3.80	0.78	0.56209	0.56209
35°C	0.54296		3.84	0.73	0.54296	0.54296
40°C	0.52031		4.72	0.74	0.52031	0.52031

Table VI. Calculated Isothermal Vapor-Liquid Equilibrium Values for *n*-Hexane(1)–Benzene System

P_{exptl}, mm Hg	P_{calcd}, mm Hg	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$	G^E, cal/mol
			30°C			
187.10		1.000	1.000	0.0000	0.4720	0.000
185.03	185.61	0.774	0.794	0.0179	0.3431	55.055
180.37	180.25	0.587	0.656	0.0739	0.2261	82.380
173.83	173.30	0.440	0.555	0.1564	0.1397	88.579
163.86	163.95	0.303	0.453	0.2716	0.0720	79.802
158.38	158.28	0.241	0.398	0.3384	0.0471	70.661
148.02	148.16	0.154	0.303	0.4482	0.0201	51.821
135.47	136.00	0.077	0.185	0.5628	0.0052	28.996
130.88	130.56	0.049	0.128	0.6087	0.0022	19.227
119.30		0.000	0.000	0.6949	0.0000	0.000

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Table VI. *(Continued)*

P_{exptl}, mm Hg	P_{calcd}, mm Hg	x_1	y_1	ln γ_1	ln γ_2	G^E, cal/mol
40°C						
279.50		1.000	1.000	0.0000	0.4284	0.000
276.48	276.91	0.774	0.794	0.0153	0.3199	52.356
269.48	269.24	0.587	0.656	0.0661	0.2141	79.165
259.16	259.31	0.440	0.555	0.1432	0.1336	85.761
246.02	245.95	0.303	0.453	0.2525	0.0694	77.706
238.56	237.88	0.241	0.398	0.3165	0.0455	68.952
223.28	223.50	0.154	0.303	0.4223	0.0195	50.733
205.61	206.32	0.077	0.185	0.5333	0.0051	28.481
198.72	198.64	0.049	0.128	0.5780	0.0021	18.866
182.80		0.000	0.000	0.6620	0.0000	0.000
50°C						
405.30		1.000	1.000	0.0000	0.4024	0.000
401.46	401.53	0.774	0.793	0.0147	0.2976	50.493
391.05	390.61	0.587	0.648	0.0624	0.1981	76.055
375.58	376.47	0.440	0.540	0.1341	0.1232	82.189
357.59	357.54	0.303	0.433	0.2351	0.0638	74.296
347.27	346.21	0.241	0.377	0.2941	0.0418	65.884
325.91	326.24	0.154	0.281	0.3914	0.0179	48.428
302.23	302.79	0.077	0.167	0.4933	0.0047	26.187
292.57	292.43	0.049	0.115	0.5343	0.0019	17.981
271.30		0.000	0.000	0.6112	0.0000	0.000
60°C						
572.70		1.000	1.000	0.0000	0.3888	0.000
568.14	567.74	0.774	0.794	0.0155	0.2753	49.129
552.84	552.11	0.587	0.647	0.0617	0.1785	72.778
530.61	532.00	0.440	0.537	0.1278	0.1092	77.707
505.04	505.38	0.303	0.426	0.2185	0.0558	69.574
490.56	489.69	0.241	0.367	0.2706	0.0364	61.461
462.09	462.57	0.154	0.270	0.3557	0.0155	44.943
431.78	431.61	0.077	0.158	0.4439	0.0040	25.071
419.05	418.23	0.049	0.107	0.4792	0.0016	16.551
391.40		0.000	0.000	0.5451	0.0000	0.000

Table VII. Calculated Isothermal Vapor-Liquid Equilibrium Values for *n*-Pentane(1)–Toluene System

P_{exptl}, mm Hg	P_{calcd}, mm Hg	x_1	y_1	ln γ_1	ln γ_2	G^E, cal/mol
20°C						
424.10		1.000	1.000	0.0000	0.5927	0.000
391.75	385.74	0.898	0.990	0.0062	0.4777	31.626
346.34	340.87	0.766	0.978	0.0326	0.3474	61.899
321.21	317.76	0.694	0.931	0.0556	0.2852	73.713
300.75	297.58	0.630	0.964	0.0811	0.2353	80.476
248.79	253.82	0.494	0.948	0.1518	0.1446	86.303
220.53	218.82	0.392	0.932	0.2188	0.0913	82.297
183.59	185.91	0.306	0.912	0.2855	0.0555	73.326
132.48	132.13	0.185	0.861	0.3938	0.0203	52.075
108.34	109.23	0.140	0.824	0.4381	0.0117	41.589
21.82		0.000	0.000	0.5927	0.0000	0.000
25°C						
512.50		1.000	1.000	0.0000	0.5787	0.000
472.60	466.22	0.898	0.990	0.0061	0.4664	31.430
416.12	411.93	0.766	0.976	0.0318	0.3392	61.455
388.13	383.92	0.694	0.969	0.0543	0.2785	72.814
363.10	359.45	0.630	0.962	0.0792	0.2297	79.912
301.23	306.39	0.494	0.944	0.1482	0.1412	85.702
265.36	264.03	0.392	0.926	0.2137	0.0891	81.724
222.00	224.32	0.306	0.905	0.2788	0.0542	72.828
159.52	159.73	0.185	0.850	0.3845	0.0198	51.702
132.28	132.35	0.140	0.811	0.4278	0.0114	41.091
28.44		0.000	0.000	0.5788	0.0000	0.000
30°C						
614.80		1.000	1.000	0.0000	0.5621	0.000
565.46	559.32	0.898	0.989	0.0059	0.4530	31.025
495.80	494.05	0.766	0.975	0.0309	0.3295	60.703
465.23	460.31	0.694	0.966	0.0527	0.2705	71.892
435.16	430.81	0.630	0.959	0.0769	0.2231	78.908

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Table VII. (*Continued*)

P_{exptl}, mm Hg	P_{calcd}, mm Hg	x_1	y_1	ln γ_1	ln γ_2	G^E, cal/mol
			30°C (*Contd*)			
361.91	366.88	0.494	0.940	0.1440	0.1371	84.639
316.89	315.96	0.392	0.921	0.2075	0.0865	80.678
266.27	268.39	0.306	0.897	0.2707	0.0526	71.887
190.45	191.43	0.185	0.838	0.3734	0.0192	51.038
159.78	158.98	0.140	0.797	0.4154	0.0111	40.782
36.65		0.000	0.000	0.5621	0.0000	0.000
			35°C			
732.40		1.000	1.000	0.0000	0.5430	0.000
671.37	666.32	0.898	0.988	0.0057	0.4376	30.465
586.14	588.31	0.766	0.973	0.0298	0.3183	59.584
553.44	547.90	0.694	0.964	0.0509	0.2613	70.589
517.90	512.56	0.630	0.956	0.0743	0.2155	77.485
431.66	435.98	0.494	0.935	0.1391	0.1324	83.097
375.75	375.16	0.392	0.915	0.2004	0.0836	79.225
316.93	318.57	0.306	0.890	0.2615	0.0508	70.584
225.56	227.60	0.185	0.826	0.3607	0.0186	50.141
191.08	189.46	0.140	0.782	0.4013	0.0107	40.036
46.78		0.000	0.000	0.5430	0.0000	0.000
			40°C			
867.20		1.000	1.000	0.0000	0.5203	0.000
791.37	788.88	0.898	0.987	0.0054	0.4193	29.630
687.90	696.08	0.766	0.971	0.0286	0.3050	58.042
653.72	647.90	0.694	0.962	0.0488	0.2504	68.752
612.35	605.74	0.630	0.953	0.0712	0.2065	75.455
511.35	514.44	0.494	0.931	0.1333	0.1269	80.931
442.57	442.18	0.392	0.908	0.1921	0.0801	77.161
374.54	375.27	0.306	0.881	0.2506	0.0487	68.747
265.16	268.49	0.185	0.813	0.3457	0.0178	48.823
226.43	224.03	0.140	0.767	0.3845	0.0102	38.954
59.15		0.000	0.000	0.5203	0.0000	0.000

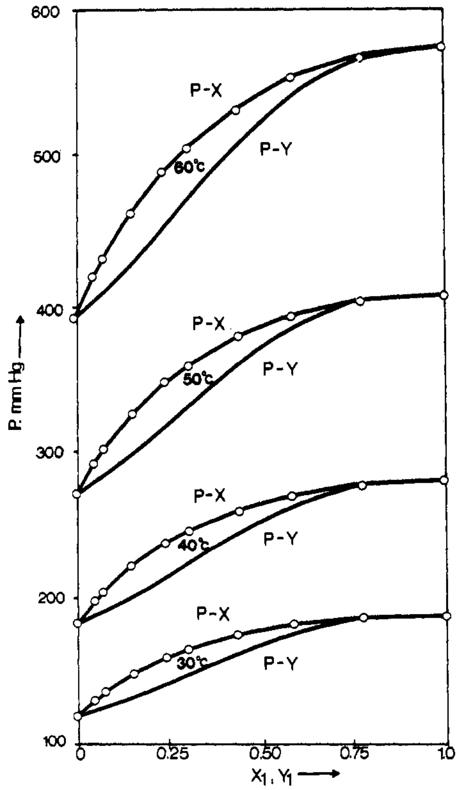

Figure 2. P-x-y diagram for the system n-hexane–benzene at four isothermal conditions

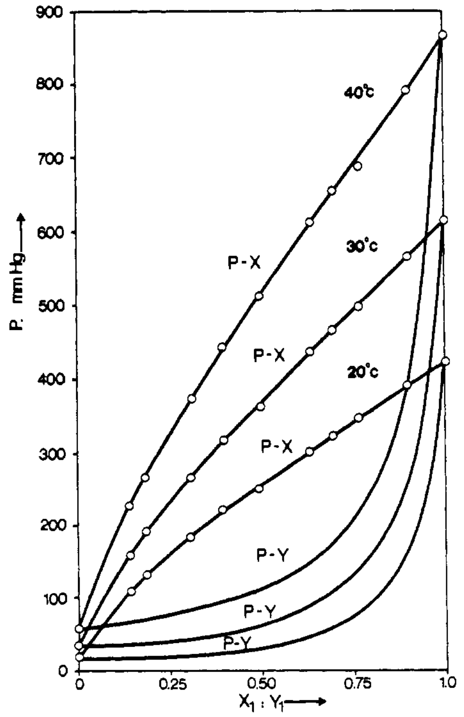

Figure 3. P-x-y diagram for the system n-pentane–toluene at three isothermal conditions

ponent i in a binary solution, based on the Raoult's law convention, may be calculated from the following equation *(10)*:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i p_i} + \frac{(\beta_{ii} - V_i)(P - p_i)}{RT} + \frac{P\delta_{12} y_j^2}{RT} \quad (1)$$

where

$$\delta_{12} = 2\,\beta_{12} - \beta_{11} - \beta_{22} \quad (2)$$

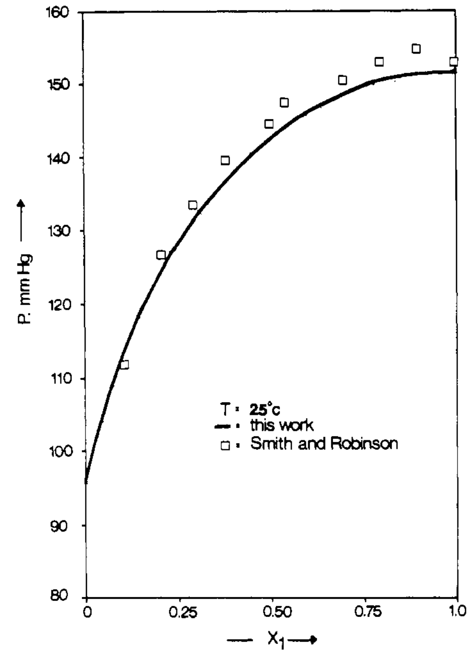

Figure 4. Total vapor pressure for the system *n*-hexane–benzene at 25°C

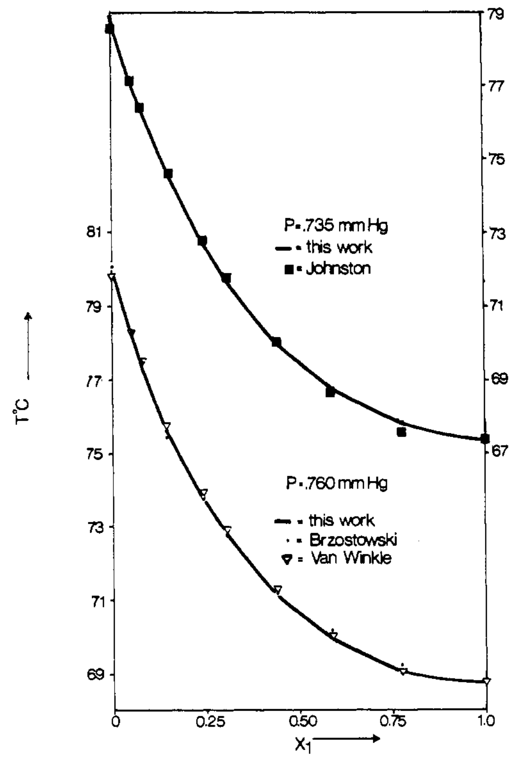

Figure 5. Bubble point temperatures for the system *n*-hexane–benzene at total pressures of 735 and 760 mm Hg

Therefore,

$$P = x_1\gamma_1 p_1 \exp\left[\frac{-(\beta_{11} - V_1)(P - p_1) - P\delta_{12}y_2^2}{RT}\right] + x_2\gamma_2 p_2 \exp\left[\frac{-(\beta_{22} - V_2)(P - p_2) - P\delta_{12}y_1^2}{RT}\right] \quad (3)$$

The liquid activity coefficients may be represented by means of the Redlich-Kister equation *(8)*:

$$\ln \gamma_1 = x_2^2[B + C(4\,x_1 - 1) + D(2\,x_1 - 1)(6\,x_1 - 1) + \,.\,.] \quad (4a)$$

$$\ln \gamma_2 = x_1^2[B + C(4\,x_1 - 3) + D(2\,x_1 - 1)(6\,x_1 - 5) + \,.\,.] \quad (4b)$$

In this investigation, the parameters of Equation 4 were evaluated by means of the nonlinear regression technique proposed previously *(4)*. The second virial coefficients β_{11} and β_{22} were calculated according to the equation of Pitzer and Curl *(7)*. The cross coefficient β_{12} was calculated according to the method of O'Connell and Prausnitz *(6)*. The third term on the right-hand side of Equation 1 was neglected in the first approximation. The y values obtained from this approximation were used in the evaluation of this term in the second approximation which was usually sufficient to provide the desired values. Calculated values of the Redlich-Kister parameters at regular temperature intervals are listed in Table V, in which the deviations of the correlation and the limiting values of the activity coefficients are also reported. The calculated P, y, $\ln \gamma$, and G^E values for the two systems are listed in Tables VI and VII in which the excess Gibbs free energies G^E were obtained from the equation

$$G^E = RT\,(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (5)$$

In addition, four isothermal P-x-y curves for the *n*-hexane–benzene systems are presented in Figure 2, and three isothermal P-x-y curves for the *n*-pentane–toluene system are presented in Figure 3.

For purposes of comparison, total vapor pressure–liquid composition data for the system *n*-hexane–benzene obtained in this investigation were extrapolated to 25°C and compared with those reported by Smith and Robinson *(9)* in Figure 4. The agreement is poor in the region of high *n*-hexane mole fractions, perhaps due to the fact that the vapor pressure of pure *n*-hexane employed by Smith and Robinson is higher than the literature value *(3)*. On the other hand, when the extrapolated values were fitted by means of the following equation

$$P = x_1 p_1 + x_2 p_2 + x_1 x_2\,[c_1 + c_2(x_1 - x_2) + c_3(x_1 - x_2)^2] \quad (6)$$

a maximum value of P was indicated in the vicinity of the azeotropic composition reported by Smith and Robinson *(9)*.

Temperature–liquid composition data at isobaric conditions were obtained at total vapor pressures of 760 and 735 mm Hg for the system *n*-hexane–benzene by extrapolating the results obtained in this investigation. These values are compared with the literature values *(1, 5, 11)* in Figure 5. Excellent agreement was obtained.

NOMENCLATURE

a, b, c = Antoine constants
c_1, c_2, c_3 = constants, Equation 6
B, C, D = Redlich-Kister parameters
G^E = molal excess Gibbs free energy
P = total vapor pressure
p = vapor pressure of pure component
R = gas constant
T = temperature, K

t = temperature, °C
V = liquid molal volume of pure component
x = mole fraction in liquid phase
y = mole fraction in vapor phase

GREEK LETTERS

β_{11}, β_{22} = second virial coefficient of pure components 1 and 2, respectively
β_{12} = cross second virial coefficient
γ = activity coefficient
γ^{∞} = activity coefficient at infinite dilution
δ = defined in Equation 2

SUBSCRIPTS

1, 2, i, j = components

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RECEIVED for review April 11, 1972. Accepted July 3, 1972. Work supported by the National Research Council of Canada.

Vapor-Liquid Equilibria of Synthetic Seawater Solutions from 25–100°C

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The vapor pressures of synthetic seawater solutions have been measured at ionic strengths of 1.0, 2.8, and 5.8 from 25–100°C. The approximate equation for the osmotic coefficient tested by Rush and Johnson at 25°C is less accurate at higher temperatures but predicts osmotic coefficients of synthetic seawater solutions within 1.5% even at 100°C. Calculations by the "ion-component" treatment of Scatchard fit the experimental values up to 2.8*m* within a few tenths of 1% over the whole range of temperatures.

The behavior of seawater and its concentrates is of considerable practical interest at present because of its relation to desalination. Seawater is of more interest to the authors as a complex electrolyte mixture whose properties may be used to test theoretical mixture equations. A very simple equation proposed by one of us (G. S.) predicts the osmotic coefficients of synthetic sea salt solutions from those of sodium chloride solutions at the same ionic strength. Rush and Johnson (*16*) tested this isopiestically at 25°C and found that it holds remarkably well. Having already made precise vapor pressure measurements on aqueous sodium chloride (*6*) from 25–100°C, we decided to measure the vapor pressures of a few synthetic seawater solutions over the same temperature range.

EXPERIMENTAL

Materials. Reagent-grade salts were used without purification, except that powdered sodium chloride and potassium chloride were dried overnight at 165°C. Stock solutions of magnesium chloride and sodium sulfate were prepared and analyzed gravimetrically as silver chloride and barium sulfate, respectively. Triplicate analyses gave average deviations of less than 0.05% in the molality for both stock solutions. Doubly distilled conductivity water was used in the preparation of all solutions.

A stock solution of synthetic seawater containing Na^+, K^+, Mg^{2+}, Cl^-, and SO_4^{2-} ions in the proportions used by Rush and Johnson (*16*) was prepared. The relative concentrations of the ions are shown in Table I. The composition differs from that of "standard seawater" (*26*) by the replacement of bicarbonate and bromide by chloride and the replacement of calcium by magnesium.

Apparatus. The static vapor pressure apparatus used in this work resembles the apparatus of Scatchard et al. (*24*) but differs considerably from theirs in the details of its construction and operation. These details will be reported else-

Table I. Relative Proportions of Ions in Synthetic Seawater Stock Solution

Ion	m_i/m_{Na^+} (this work)	m_i/m_{Na^+} (*16*)
Na^+	1	1
Mg^{2+}	0.1313	0.1310
K^+	0.0212	0.0212
Cl^-	1.1638	1.1631
SO_4^{2-}	0.0600	0.0600

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