and ψ values capable of reproducing the individual γ_1 values for different compositions at the same (constant) (and also different) total molalities. The extent to which eq 12 or an analogous eq 13 for the second component is successful in doing

$$-2.303\alpha_{21} = f(\phi^0) + \theta + \frac{1}{2}(m + m_2) \qquad (13)$$

this is measured by the magnitude of the standard deviation σ of Table VII. Further, the magnitude of the parameter ψ as found for any particular electrolyte in a binary mixture measures how far the more elaborate eq 12 is necessary for reproducing the observed γ values for the electrolyte component showing deviations from Harned rule behavior (eq 9) in mixtures, in contrast to the Harned rule obeying component, whose behavior is adequately described by eq 9 (for which $\psi = 0$). (See first referee's remark at beginning of section.)

Acknowledgment

The award of a Senior Research Fellowship, C.S.I.R., Government of India, to one of the authors (P.M.) is gratefully acknowledged. The authors are thankful to Dr. N. G. Mukherjee, Department of Chemistry, Calcutta University, for help in computer programming.

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Received for review July 28, 1976. Resubmitted November 14, 1977. Accepted May 12, 1978.

Supplementary Material Available: Table IV, concerning the evaluation of $f(\phi^0)$, θ, and ΔG^E, and Tables V and VI, containing the values of α_{12} and α_{21} for the systems $HCl-(CH_3)_4NCl$ and $HCl-(C_2H_5)_4NCl$ at 25 °C (2 pages). Ordering information is given on any current masthead page.

Vapor–Liquid Equilibria of the Ternary System Chloroform–Methanol–Benzene

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New data of the vapor–liquid equilibria of the system chloroform–methanol–benzene were obtained at 760 mmHg. The activity coefficients were satisfactorily correlated according to the Redlich–Kister equation and could be predicted by considering only the binary data. Boiling points of the ternary mixture were predicted by an empirical correlation with a mean error of ±1.12%. The system probably exhibits azeotropic behavior.

Introduction

This ternary system for which no vapor equilibrium data are available was chosen for two reasons: (a) to confirm whether the ternary system exhibits an azeotrope, as the binary chloroform–methanol and the methanol–benzene form a minimum boiling point azeotrope, and (b) to examine whether ternary

Table I. Physical Constants of Compounds at 25 °C

Compound	Density	Refractive index
Chloroform	1.485	1.440
	1.480[a]	1.443[a]
Methanol	0.791	1.360
	0.787[b]	1.326[b]
Benzene	0.880	1.497
	0.874[a]	1.498[a]

[a] Reference 4. [b] Reference 5.

0021-9568/78/1723-0287$01.00/0

Table II. Ternary Vapor-Liquid Equilibrium Data for Chloroform (1) -Methanol (2) -Benzene (3) at 760 mmHg

T, °C	X_1	X_2	X_3	Y_1	Y_2	Y_3	γ_1	γ_2	γ_3
54.37	0.528	0.401	0.071	0.380	0.588	0.032	0.9321	2.2783	1.0149
54.75	0.625	0.281	0.094	0.577	0.377	0.046	1.1736	2.0607	1.0981
54.85	0.454	0.451	0.095	0.491	0.441	0.068	1.3738	1.4910	1.5964
55.10	0.526	0.411	0.063	0.421	0.543	0.036	1.0105	1.9897	1.2570
55.16	0.339	0.556	0.105	0.331	0.614	0.055	1.2346	1.6553	1.1474
55.24	0.542	0.377	0.081	0.437	0.530	0.033	1.0127	2.1051	0.8922
55.29	0.455	0.464	0.081	0.377	0.579	0.044	1.0413	1.8617	1.1856
55.32	0.290	0.603	0.107	0.298	0.633	0.069	1.2943	1.5614	1.4045
55.35	0.579	0.342	0.079	0.456	0.513	0.031	0.9850	2.2365	0.8566
55.36	0.439	0.456	0.105	0.375	0.576	0.049	1.0711	1.8786	1.0164
55.47	0.269	0.622	0.109	0.288	0.641	0.071	1.3425	1.5226	1.4111
55.50	0.320	0.644	0.036	0.353	0.625	0.022	1.3778	1.4343	1.3210
55.65	0.298	0.591	0.111	0.299	0.636	0.065	1.2501	1.5779	1.2606
55.75	0.221	0.663	0.116	0.250	0.667	0.083	1.4079	1.4674	1.5345
55.77	0.646	0.286	0.068	0.500	0.475	0.025	0.9535	2.4342	0.7922
55.89	0.425	0.433	0.142	0.350	0.580	0.070	1.0160	1.9452	1.0546
56.06	0.588	0.177	0.235	0.528	0.350	0.122	1.0952	2.8602	1.1154
56.20	0.570	0.210	0.220	0.516	0.366	0.118	1.0995	2.5050	1.1459
56.26	0.436	0.307	0.257	0.415	0.431	0.154	1.1575	2.0064	1.2750
56.37	0.718	0.219	0.063	0.552	0.426	0.022	0.9275	2.7818	0.7386
56.45	0.281	0.620	0.099	0.382	0.510	0.108	1.6450	1.1660	2.2972
56.47	0.343	0.586	0.071	0.341	0.577	0.082	1.2040	1.3939	2.4230
56.50	0.477	0.343	0.180	0.377	0.547	0.076	0.9549	2.2564	0.8857
56.55	0.255	0.531	0.214	0.297	0.511	0.192	1.4094	1.3545	1.8866
56.55	0.363	0.361	0.276	0.363	0.451	0.186	1.2069	1.7604	1.4195
56.80	0.291	0.428	0.281	0.302	0.490	0.208	1.2453	1.5937	1.5446
56.82	0.226	0.525	0.249	0.204	0.613	0.183	1.0872	1.6229	1.5265
56.90	0.619	0.224	0.157	0.465	0.453	0.082	0.8933	2.8176	1.0846
56.95	0.211	0.565	0.224	0.254	0.533	0.213	1.4404	1.3038	1.9720
57.00	0.234	0.553	0.213	0.276	0.529	0.195	1.4078	1.3201	1.8946
57.15	0.245	0.506	0.249	0.186	0.659	0.155	0.9054	1.7852	1.2758
57.16	0.144	0.588	0.268	0.139	0.685	0.176	1.1535	1.5952	1.3458
57.17	0.200	0.478	0.322	0.174	0.645	0.181	1.0375	1.8472	1.1527
57.35	0.166	0.636	0.198	0.211	0.571	0.218	1.5042	1.2191	2.2503
57.40	0.165	0.509	0.326	0.176	0.543	0.281	1.2619	1.4432	1.7629
57.47	0.160	0.529	0.311	0.176	0.545	0.279	1.2984	1.3897	1.8302
57.50	0.525	0.148	0.327	0.472	0.344	0.184	1.0482	3.1509	1.1513
57.50	0.119	0.647	0.234	0.152	0.584	0.264	1.5082	1.2162	2.2965
57.55	0.124	0.626	0.250	0.152	0.579	0.269	1.4450	1.2435	2.1870
57.57	0.200	0.373	0.427	0.186	0.515	0.299	1.0935	1.8537	1.4253
57.60	0.117	0.561	0.322	0.130	0.568	0.302	1.3088	1.3572	1.9053
57.65	0.220	0.341	0.439	0.203	0.502	0.295	1.0812	1.9701	1.3643
57.65	0.151	0.434	0.415	0.148	0.531	0.321	1.1514	1.6359	1.5705
57.67	0.113	0.566	0.321	0.125	0.568	0.307	1.3003	1.3410	1.9385
57.73	0.784	0.140	0.076	0.629	0.344	0.027	0.9248	3.3210	0.7198
57.77	0.102	0.471	0.427	0.101	0.557	0.342	1.1613	1.5721	1.6198
57.85	0.109	0.539	0.352	0.117	0.561	0.322	1.2548	1.3797	1.8438
57.88	0.177	0.708	0.115	0.261	0.576	0.163	1.7117	1.0814	2.8400
57.90	0.336	0.273	0.391	0.227	0.592	0.181	0.7848	2.8783	0.9270
58.00	0.086	0.744	0.170	0.126	0.630	0.244	1.7045	1.1172	2.8677
58.01	0.006	0.595	0.399	0.007	0.610	0.383	1.3642	1.3479	1.9266
58.01	0.236	0.322	0.442	0.169	0.611	0.220	0.8311	2.5040	0.9937
58.03	0.021	0.731	0.248	0.039	0.611	0.350	2.1670	1.0988	2.8275
58.03	0.033	0.685	0.282	0.041	0.627	0.332	1.4498	1.2038	2.3569
58.05	0.023	0.576	0.401	0.024	0.603	0.373	1.2175	1.3743	1.8639
58.05	0.010	0.592	0.398	0.011	0.608	0.381	1.2843	1.3480	1.9186
58.05	0.019	0.583	0.398	0.021	0.602	0.377	1.2897	1.3554	1.8983
58.05	0.032	0.632	0.336	0.037	0.610	0.353	1.3484	1.2677	2.1036
58.07	0.016	0.584	0.400	0.017	0.605	0.378	1.2393	1.3587	1.8926
58.08	0.017	0.654	0.329	0.019	0.622	0.359	1.3033	1.2474	2.1828
58.09	0.011	0.653	0.336	0.012	0.623	0.365	1.2722	1.2507	2.1727
58.10	0.277	0.313	0.410	0.215	0.615	0.170	0.8964	2.5860	0.8239
58.10	0.017	0.691	0.292	0.021	0.533	0.346	1.4396	1.2009	2.3674
58.10	0.135	0.338	0.527	0.119	0.526	0.355	1.0216	2.0393	1.3481
58.10	0.193	0.279	0.528	0.167	0.502	0.331	1.0007	2.3596	1.2543
58.11	0.007	0.682	0.311	0.008	0.627	0.365	1.3322	1.2042	2.3457
58.12	0.086	0.423	0.491	0.080	0.540	0.380	1.0794	1.6703	1.5486
58.15	0.053	0.720	0.227	0.061	0.637	0.302	1.3366	1.1584	2.6494
58.16	0.034	0.711	0.255	0.043	0.636	0.321	1.4695	1.1702	2.5077
58.19	0.090	0.308	0.602	0.068	0.546	0.386	0.8752	2.3123	1.2800
58.22	0.023	0.744	0.233	0.030	0.653	0.317	1.5138	1.1454	2.7038
58.22	0.028	0.740	0.232	0.038	0.652	0.310	1.5744	1.1500	2.6548
58.22	0.042	0.400	0.558	0.037	0.568	0.395	1.0211	1.8495	1.4117
58.28	0.036	0.455	0.509	0.050	0.542	0.408	1.6053	1.5469	1.5963
58.30	0.012	0.751	0.237	0.015	0.661	0.324	1.4481	1.1446	2.7098
58.32	0.027	0.730	0.243	0.035	0.649	0.316	1.4991	1.1553	2.5755
58.33	0.007	0.758	0.235	0.008	0.660	0.332	1.3231	1.1307	2.7983

Table II (*Continued*)

T, °C	X_1	X_2	X_3	Y_1	Y_2	Y_3	γ_1	γ_2	γ_3
58.34	0.054	0.376	0.570	0.046	0.557	0.397	0.9830	1.9195	1.3835
58.35	0.068	0.334	0.598	0.059	0.520	0.421	0.9998	2.0150	1.3995
58.36	0.080	0.334	0.586	0.068	0.539	0.393	0.9791	2.0894	1.3314
58.38	0.113	0.837	0.050	0.189	0.749	0.062	1.9157	1.1648	2.4240
58.41	0.059	0.495	0.446	0.053	0.591	0.356	1.0344	1.5441	1.5792
58.42	0.086	0.348	0.566	0.075	0.535	0.390	1.0022	1.9855	1.3651
58.48	0.173	0.274	0.553	0.148	0.504	0.348	0.9780	2.3724	1.2433
58.50	0.047	0.359	0.594	0.040	0.541	0.419	0.9771	1.9383	1.3947
58.60	0.049	0.356	0.595	0.042	0.510	0.448	0.9803	1.8332	1.4853
58.61	0.026	0.805	0.169	0.040	0.681	0.279	1.7625	1.0867	3.2320
58.62	0.112	0.344	0.544	0.099	0.529	0.372	1.0082	1.9703	1.3449
58.67	0.092	0.824	0.084	0.163	0.681	0.156	2.0136	1.0614	3.6128
58.68	0.546	0.213	0.241	0.429	0.434	0.137	0.8833	2.6259	1.1125
58.70	0.070	0.275	0.655	0.056	0.539	0.405	0.9119	2.5006	1.2137
58.75	0.033	0.332	0.635	0.028	0.555	0.417	0.9669	2.1278	1.2871
58.83	0.223	0.275	0.502	0.180	0.569	0.251	0.9117	2.6355	0.9724
58.85	0.029	0.699	0.272	0.035	0.635	0.330	1.3718	1.1539	2.3613
58.85	0.066	0.436	0.498	0.060	0.566	0.374	1.0314	1.6471	1.4649
58.90	0.060	0.252	0.688	0.049	0.525	0.426	0.9249	2.6341	1.2080
58.94	0.106	0.300	0.594	0.092	0.522	0.386	0.9800	2.1986	1.2648
58.96	0.053	0.260	0.687	0.035	0.522	0.443	0.7469	2.5309	1.2561
58.96	0.120	0.229	0.651	0.098	0.511	0.391	0.9211	2.8167	1.1685
58.90	0.044	0.313	0.643	0.037	0.532	0.431	0.9530	2.1488	1.3078
59.00	0.096	0.333	0.571	0.093	0.399	0.508	1.0894	1.5044	1.7356
59.00	0.280	0.162	0.558	0.242	0.437	0.321	0.9676	3.4076	1.1174
59.03	0.625	0.179	0.196	0.515	0.402	0.083	0.9138	2.8594	0.8192
59.05	0.840	0.098	0.062	0.723	0.255	0.022	0.9496	3.3347	0.6902
59.10	0.090	0.357	0.553	0.079	0.536	0.385	0.9867	1.8844	1.3474
59.15	0.158	0.217	0.625	0.130	0.497	0.373	0.9211	2.8695	1.1533
59.20	0.076	0.857	0.067	0.142	0.718	0.140	2.0895	1.0521	3.9875
59.30	0.064	0.331	0.605	0.054	0.546	0.400	0.9435	2.0522	1.2712
59.38	0.110	0.202	0.688	0.089	0.496	0.415	0.9005	3.0431	1.1578
59.45	0.100	0.263	0.637	0.085	0.509	0.406	0.9442	2.3921	1.2200
59.58	0.865	0.082	0.053	0.778	0.201	0.021	0.9751	3.0778	0.7591
59.62	0.066	0.308	0.626	0.060	0.451	0.489	1.0043	1.7925	1.4905
59.65	0.022	0.879	0.099	0.039	0.747	0.214	1.9643	1.0459	4.0723
59.66	0.110	0.177	0.713	0.089	0.490	0.421	0.8923	3.3902	1.1228
59.97	0.093	0.222	0.685	0.076	0.500	0.424	0.8930	2.7224	1.1647
60.05	0.084	0.222	0.694	0.067	0.518	0.415	0.8699	2.8117	1.1216
60.19	0.053	0.902	0.045	0.112	0.774	0.114	2.2926	1.0336	4.6672
60.20	0.081	0.205	0.714	0.066	0.498	0.436	0.8841	2.9073	1.1404
60.32	0.148	0.150	0.702	0.123	0.460	0.417	0.8959	3.6536	1.1049
60.45	0.031	0.956	0.013	0.073	0.892	0.035	2.5370	1.1121	4.8916
60.65	0.707	0.102	0.191	0.634	0.285	0.081	0.9422	3.3334	0.7804
61.13	0.282	0.190	0.528	0.223	0.529	0.248	0.8285	3.2209	0.8459
61.30	0.733	0.088	0.179	0.694	0.226	0.080	0.9737	2.9872	0.8068
61.32	0.038	0.930	0.032	0.083	0.833	0.084	2.2888	1.0293	4.6478
61.37	0.457	0.194	0.349	0.423	0.390	0.187	0.9557	2.3112	0.9596
61.40	0.853	0.038	0.109	0.828	0.118	0.054	0.9935	3.6161	0.8961
61.40	0.128	0.115	0.757	0.104	0.447	0.449	0.8468	4.4235	1.0647
61.66	0.764	0.073	0.163	0.744	0.181	0.075	0.9896	2.8460	0.8223
61.75	0.436	0.132	0.432	0.385	0.410	0.205	0.9020	3.5115	0.8388
61.78	0.350	0.160	0.490	0.289	0.478	0.233	0.8454	3.3671	0.8386
62.00	0.189	0.177	0.634	0.145	0.550	0.305	0.7844	3.4620	0.8424
62.15	0.029	0.948	0.023	0.063	0.874	0.063	2.2194	1.0236	4.7122
62.30	0.111	0.109	0.780	0.091	0.434	0.475	0.8307	4.3630	1.0613
62.66	0.022	0.960	0.018	0.050	0.902	0.048	2.2861	1.0215	4.5070
62.77	0.162	0.088	0.750	0.144	0.401	0.455	0.8856	4.9008	1.0408
65.50	0.243	0.053	0.704	0.243	0.280	0.477	0.9116	5.0860	1.0644
66.50	0.477	0.042	0.481	0.538	0.186	0.276	0.9911	4.1323	0.8735
69.30	0.204	0.065	0.731	0.219	0.276	0.505	0.8734	3.5151	0.9601
69.70	0.241	0.051	0.708	0.287	0.226	0.487	0.9555	3.6151	0.9444
71.50	0.264	0.022	0.714	0.342	0.130	0.528	0.9837	4.4952	0.9607
71.60	0.077	0.025	0.898	0.086	0.203	0.711	0.8502	6.1161	1.0252

constants are needed in the calculation of the ternary vapor–liquid equilibria from data on the binary systems.

Analytical grade reagents were used. The chloroform contained 1% ethanol that was extracted with water washes followed by drying with calcium chloride. Gas chromatography analysis of the dried product failed to show any significant impurities. The properties of the pure compounds are listed in Table I with reliable literature values. The determinations were made in a modified all-glass Dvorak and Boublik recirculation still (*1*) and the experimental features have been described previously (*13*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Minigrator type of electronic integrator. The column was 200 cm long and 0.32 cm in diameter and was packed with Chromosorb 101 and operated isothermally at 165 °C. Injector temperature was 210 °C and the detector operated at 150 mA and 210 °C. Calibration analyses were carried out to convert the peak area ratio to the actual weight composition of the mixture. Concentration measurements were generally accurate to ±0.003 mole fraction.

Table III. Redlich-Kister Correlation for Chloroform (1)-Methanol (2)-Benzene (3)

System	Binary constants in eq (6, 7) B_{ij}	C_{ij}	D_{ij}	RMSD γ_i	γ_j
1-2	1.3138	1.2471×10^{-3}	2.2070×10^{-5}	0.3079	0.4905
1-3	−0.1207	5.7009×10^{-5}	4.3638×10^{-6}	0.0811	0.0212
2-3	1.9159	1.1929×10^{-3}	9.2230×10^{-4}	0.6316	0.1747
Chloroform				Overall RMSD in γ	Y
Methanol		$C_1 = 0$		0.2937	0.0426
Benzene		$C_1 = -0.30588$		0.2679	0.0418

$$\left(\frac{Y_{obsd} - Y_{calcd}}{Y_{obsd}}\right)100 = y^a$$

Maximum			Mean[b]		
Chloroform	Methanol	Benzene	Chloroform	Methanol	Benzene
47.0	49.5	50.5	11.03	8.58	12.99

[a] Y_{calcd} is based on computed values of the activity coefficients. [b] Mean = $\Sigma^m Y/m$.

Results and Discussions

The temperature-concentration measurements at 760 mmHg for the ternary system are reported in Table II. The liquid activity coefficients were calculated from the equation

$$\ln \gamma_i = \ln \frac{Y_i P}{X_i P_i^0} + \frac{(B_{ii} - V_i^0)(P - P_i^0)}{RT} + \frac{P}{2RT} \sum_{j=1}^{N} \sum_{k=1}^{N} Y_i Y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

Vapor pressures P^0 were calculated according to the Antoine equation (2) where the constants are reported elsewhere (2, 10). The virial coefficients B_{ii} and the mixed virial coefficient B_{ij} were estimated by the method of Tsonopoulos (11, 12) using the molecular parameters suggested by the author.

The 141 ternary data points appearing in Table II are thermodynamically consistent and were tested by the McDermott-Ellis method (3). According to this test, two experimental points, a and b, are thermodynamically consistent if the following condition is fulfilled:

$$D < D_{max} \quad (3)$$

The local deviation D is given by (9)

$$D = \sum_{i=1}^{n} (X_{ia} + X_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \quad (4)$$

According to ref 3, a fixed value is recommended for D_{max}; however, an equation for the local value of the maximum deviation can be derived (14) which reads

$$D_{max} = \sum_{i=1}^{n} (X_{ia} + X_{ib})\left(\frac{1}{X_{ia}} + \frac{1}{Y_{ia}} + \frac{1}{X_{ib}} + \frac{1}{Y_{ib}}\right)\Delta X + 2\sum_{i=1}^{n} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta X + \sum_{i=1}^{n} (X_{ia} + X_{ib})\frac{\Delta P}{P} + \sum_{i=1}^{n} (X_{ia} + X_{ib})\beta_i \left(\frac{1}{[t_a + \delta_i]^2} + \frac{1}{[t_b + \delta_i]^2}\right)\Delta t \quad (5)$$

In the present study, the errors in the measurements were estimated to be $\Delta P = \pm 2$ mmHg, $\Delta t = \pm 0.02$ °C, and $\Delta X = 0.0030$ mole fraction units. It was found that the first term in eq 5 which accounts for the error in the concentration measurements was usually the dominant one.

The activity coefficients were correlated by the following Redlich-Kister expansions (8)

$$\ln \gamma_1 = X_2X_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2X_1 - X_2) + C_{13}(2X_1 - X_3) + 2C_{23}(X_3 - X_2) + D_{12}(X_1 - X_2)(3X_1 - X_2) + D_{13}(X_1 - X_3)(3X_1 - X_2) - 3D_{23}(X_3 - X_2)^2 + C_1(1 - 2X_1)] + X_2^2[B_{12} + C_{12}(3X_1 - X_2) + D_{12}(X_1 - X_2)(5X_1 - X_2)] + X_3^2[B_{13} + C_{13}(3X_1 - X_3) + D_{13}(X_1 - X_3)(5X_1 - X_3)] \quad (6)$$

where B_{ij}, C_{ij}, and D_{ij} are binary constants and C_1 is ternary constant. The equations for the other activity coefficients were obtained by cyclic rotation of the indices. The equations through which the binary constants were computed were

$$\ln \gamma_i = (B_{ij} + 3C_{ij} + 5D_{ij})X_j^2 - 4(C_{ij} + 4D_{ij})X_j^3 + 12D_{ij}X_j^4$$
$$\ln \gamma_j = (B_{ij} - 3C_{ij} + 5D_{ij})X_i^2 + 4(C_{ij} - 4D_{ij})X_i^3 + 12D_{ij}X_i^4 \quad (7)$$

The binary constants computed from the binary data reported (4, 6, 7) as well as parameters indicating the ability of correlating the data by the Redlich-Kister correlations are reported in Table III. Considering the values of the overall root mean square deviation for Y indicates that the ternary data can be reasonably predicted from the behavior of the different binaries that compose it without the need for interaction terms like C_1. By considering the values of the means reported in Table III in the presence of C_1, it is seen that the vapor compositions, Y, can be predicted quite accurately.

The boiling points vs. concentration of the ternary system were correlated by the following equation suggested by the writers (9, 15)

$$T = \sum_{i=1}^{3} X_i T_i^0 + \sum_{i,j=1}^{3} [X_{ij} \sum_{k=0}^{l} C_k (X_i - X_j)^k + X_1X_2X_3[A + B(X_1 - X_2) + C(X_1 - X_3) + D(X_2 - X_3) + \ldots] \quad (8)$$

where for binary mixtures it is suggested that

$$T = \sum_{i=1}^{2} X_i T_i^0 + X_1X_2 \sum_{k=0}^{l} C_k (X_i - X_j)^k \quad (8\text{-}1)$$

T^0 is the boiling point of the pure components in °C and l is the number of terms in the series expansion of $(X_i - X_j)$. C_k are the binary constants computed on the basis of the literature data

Table IV. Correlation of Boiling Points, Eq 8

System	m	C_0	C_1	C_2	C_3	RMSD	$\bar{D}$, %
Chloroform-methanol (a)	22	−35.319	1.1024	−28.087	−30.803	0.2513	0.34
Chloroform-benzene (a)	19	2.075	−2.628	0.4922	5.744	0.2146	0.16
Methanol-benzene (a)	18	−52.711	16.912	−100.44	85.852	0.9613	1.28
Methanol-benzene (b)	18	−67.981	50.488			3.441	4.69
System	m	A	B	C	D	RMSD	$\bar{D}$, %
Chloroform-methanol-benzene (c)[a]	141	−38.991	−183.83	169.10	13.698	0.901	1.12
Chloroform-ethanol-benzene (d)[b]	141	−6.803	−163.44	95.179	−65.607	1.768	2.29

[a] With binary constants a,a,a. [b] With binary constants a,a,b.

Table V. Binary Constants Corresponding to Best Fit in Eq 8-1

System	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	RMSD	$\bar{D}$, %
Chloroform-methanol	−36.198	−2.955	−11.464	0.4844	−29.042	−40.261			0.0923	0.13
Chloroform-benzene	2.234	−3.554	−2.122	12.362	4.806	−8.013			0.2099	0.17
Methanol-benzene	−55.699	23.254	−60.447	91.668	15.530	−170.93	−136.02	227.92	0.1669	0.23

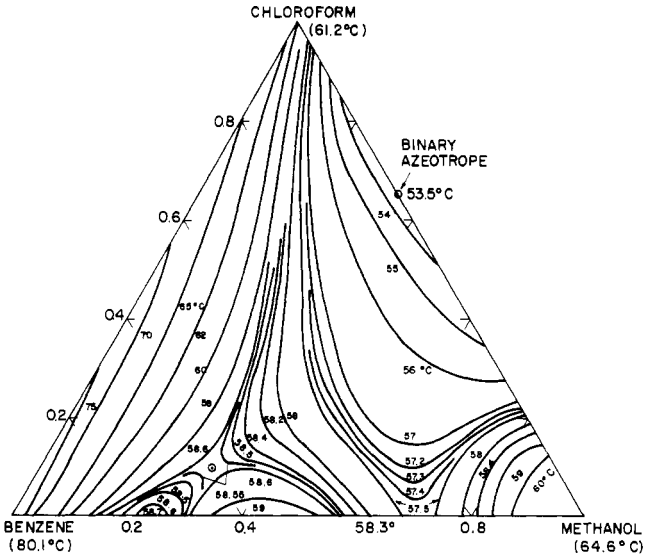

Figure 1. Isothermals for chloroform–methanol–benzene at 760 mmHg (with four binary constants for methanol–benzene).

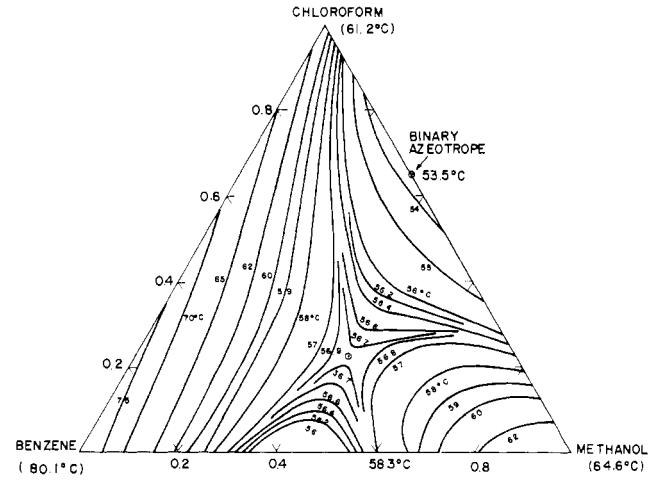

Figure 2. Isothermals for chloroform–methanol–benzene at 760 mmHg (with two binary constants for methanol–benzene).

(*4*, *6*, *7*) where A, B, C, and D are ternary constants computed from the ternary data in Table II. Table IV contains the binary and ternary constants which were used for calculating the azeotropic point. It was found (*9*) that sets of four binary and ternary constants gave the best result for the azeotropic point. In Table V the binary constants corresponding to the best fit in eq 8-1 are reported. The table also contains information regarding the goodness of fit of the correlation. Equation 8 was used for obtaining the isothermals shown in Figures 1 and 2. The difference between the isothermals is due to the different accuracy of fitting the data of T vs. X, with eq 8-1 for the binary system methanol–benzene. It should be noted that the same correlation was used in the determination of ternary behavior. In Figure 1, four binary constants were used and the mean deviation for the binary data was 1.28% (Table IV). However, with such a number of constants it appears that the analytical behavior of the function is oscillatory and this is reflected in the appearance of two minimum points and a maximum one. This mathematical behavior predicts several azeotropic points and is in contradiction with the experimental behavior determined by Nagata (*6*) where only one azeotrope is present. On the other hand, the T–X behavior of methanol–benzene mixtures, as shown in Figure 2, is "normal", in spite of the fact that a two-constant fit of the data with eq 8-1 is rather poor with a mean deviation of 4.69% (Table IV). In any rate, the topography

Table VI. Comparison between Observed and Calculated Values of the Azeotropic Point for the System: Chloroform-Methanol-Benzene

X_1		X_2		T, °C	
Our exptl check	Calcd	Our exptl check	Calcd	Our exptl check	Calcd
	0.102[a]		0.299[a]		58.56[a]
$X_1 = 0.110$		$X_2 = 0.242$		60.90	
$Y_1 = 0.081$		$Y_2 = 0.603$			
	0.226[b]		0.430[b]		56.72[b]
$X_1 = 0.229$		$X_2 = 0.359$		57.65	
$Y_1 = 0.219$		$Y_2 = 0.504$			

[a] Based on constants in Table IV designated by a,a,a,c. [b] Based on constants in Table IV designated by a,a,b,d.

of the curves in Figures 1 and 2 points to the existence of a saddle point azeotrope. The coordinates of the azeotrope were computed (*15*) from the simultaneous solution of two equations obtained from

$$\partial T/\partial x_1 = 0 \text{ and } \partial T/\partial x_2 = 0 \qquad (9)$$

where T is given by eq 8. Equation 9 is the Gibbs–Konovalov condition at the azeotropic point under isobaric conditions. The computed results are reported in Table VI when we considered the T–X data of Figures 1 and 2. The validity of the theoretical computations was checked experimentally as follows: A ternary solution with the predicted composition was prepared and in-

troduced in the vapor and liquid collectors of the Dvorak–Boublik recirculating still. The system was boiled until equilibrium was achieved. A gas chromatography analysis yielded the equilibrium compositions reported in Table VI. It is seen that $X_i \neq Y_i$, indicating that the computed azeotrope is a false one. On the other hand, inspection of the data in Table II indicates that few points exist where $X_i \approx Y_i$. It is therefore possible that the system contains an azeotrope in the vicinity of these points. Attempts were made to follow a prescribed path of constant composition (X_1 or X_2) on a triangular concentration diagram as Figures 1 or 2 around one of these points in order to check the existence of a true azeotrope in its vicinity. This was not successful because of very small overnight leaks which perturbed the above path.

Acknowledgment

Thanks are due to Yehudit Reizner and Kohav Ben-Zaken for their valuable contribution in the experimental and numerical work.

Glossary

A, B, C, D	constants
B_{ii}, B_{ji}	second virial coefficient of pure component and the mixed virial coefficient, respectively, in eq 1 and 2, $cm^3\ mol^{-1}$
C_1	ternary constant
D, D_{max}	local deviation and maximum local deviation defined by eq 4 and 5, respectively
$\bar{D}$	$(1/m)\sum^m\lvert(T_{obsd} - T_{calcd})/T_{obsd}\rvert 100$
m	total number of experimental points
n	number of components
P	total pressure
R	gas constant
RMSD	$(\sum^m(T_{obsd} - T_{calcd})^2/m)^{1/2}$ in eq 8 and 8-1. For Table III replace T by γ
Overall RMSD	$(\sum_{j=1}^m\sum_{i=1}^n(Y_{ji,obsd} - Y_{ji,calcd})^2/mn)^{1/2}$; similarly for γ
T	temperature, °C
V_i^0	molar volume of pure component i, $cm^3\ mol^{-1}$
X_i, Y_i	mole fraction composition of component i in the liquid and vapor phases
γ	activity coefficient
ΔX, Δp, Δt	errors in measurements of concentration, pressure, and temperature

Subscripts

calcd	calculated
obsd	observed
max	maximum
i	component i

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Received for review July 21, 1977. Accepted April 21, 1978.