of the id_2 term of eq 1. However, gold capillaries with the smaller diameter were very difficult to fabricate properly. Furthermore, it was hard to keep a constant, slow rate of bubble formation with these capillaries. Failure to maintain a constant and fairly slow rate of bubble formation (~2/min) can cause erroneous results (*12*).

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Thermodynamic Properties of the Systems Methylcyclohexane–Toluene, *n*-Heptane–Toluene, and Methylcyclohexane–Toluene–*n*-Heptane

Jaime Wisniak* and Abraham Tamir

Department of Chemical Engineering, Ben Gurion University of the Negev, Beer-Sheva, Israel

Enthalpy–concentration data and boiling point–composition correlations have been determined for the binary systems methylcyclohexane–toluene and *n*-heptane–toluene. New vapor–liquid equilibrium data are presented for the ternary methylcyclohexane–*n*-heptane–toluene. The system behaves almost ideally, and its activity coefficients are well correlated by the Redlich–Kister equation.

The hydrocarbon systems methylcyclohexane–toluene, *n*-heptane–toluene, and methylcyclohexane–toluene–*n*-heptane have been used normally for testing the efficiency of fractionating columns. These systems are near ideal and easy to analyze and their boiling point range is small enough to neglect the temperature effect on the activity coefficients. Extensive information is available on the vapor–liquid equilibrium of the binaries (*2–5, 7, 9, 11–13, 17, 18*), but the data on the ternary system are meager (*3, 6*). Bromiley and Quiggle (*3*) have reported the vapor–liquid equilibrium compositions at atmospheric pressure without indicating the boiling point of the mixture nor the activity coefficient of its components. Katayama et al. (*7*) have determined the isothermal activity coefficients at 25 °C. Holzhauer and Ziegler (*6*) have recently reported the heat capacity of the pure components and the excess heat capacity and excess enthalpy of the binary mixtures over a wide temperature range.

All the necessary thermodynamic information is now available to calculate the enthalpy–concentration diagram of the binaries and correlate their boiling points. These new data should increase the calibration power of the systems as well as help in the determination of point to point plate efficiencies.

Experimental Section

Purity of Materials. Analytical grade reagents (+99%) purchased from Merck and Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities. Properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik (*1*) recirculation still was used in the equilibrium determinations. The equipment and operating techniques have been described elsewhere (*19*). All analysis were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with OV-17 on 80–100 mesh Supelcoport and was operated isothermally at 60 °C. Injector and detector temperatures were 180 °C. Calibration analyses were carried out to convert the peak area ratio to weight composition. Concentration measurements were generally accurate to within ±0.3%.

Results and Discussion

Boiling Point Correlation. The boiling points of the binary systems were correlated with their compositions using the equation suggested by Wisniak and Tamir (*20*)

$$T = x_1T_1^0 + x_2T_2^0 + \omega + x_1x_2 \sum_{k=0}^{l} C_k(x_1 - x_2)^k \qquad (1)$$

where T_1^0 and T_2^0 are the boiling points of the pure components, l is the number of terms in the series expansion of $(x_1 - x_2)$ and

$$\omega = x_1 \ln y_1/x_1 + x_2 \ln y_2/x_2 \qquad (2)$$

The contribution of ω was found to be negligible and the term was dropped from eq 1.

The data of ref 5 and 9 were judged to be thermodynamically consistent and used to determine the constants in eq 1. The

Table I. Physical Properties of Pure Compounds

Index	Compd	Refractive index at 25 °C	Bp, °C (760 mmHg)
1	*n*-Heptane	1.38505	98.38
		1.38511[a]	98.43[a]
2	Methylcyclohexane	1.41935	100.92
		1.42058[a]	100.93[a]
3	Toluene	1.49255	110.65
		1.49413[a]	110.62[a]

[a] Reference 14.

Table II. Correlation of Boiling Points, Eq 1 and 2

System	C_0	C_1	C_2	C_3	Rmsd	Dif % [a]
n-Heptane (1)–methylcyclohexane (2)	−1.1724	−2.2118	−1.5167	5.3001	0.045	0.035
n-Heptane (1)–toluene (3)	−8.1192	−2.5067	0.58453	3.8842	0.079	0.059
Methylcyclohexane (2)–toluene (3)	−9.2962	2.7314	−2.9556	1.1784	0.063	0.038

System	A	B	C	Rmsd	Dif % [a]
n-Heptane (1)–methylcyclohexane (2)–toluene (3)	−6.5465	−21.256	63.740	0.336	0.256

[a] Dif % = $100/n \sum_{i=1}^{n} (|T_{exptl} - T_{calcd}|/T_{exptl})$.

Table III. Enthalpy–Concentration Data for the System *n*-Heptane (1)–Toluene (2) at 760 mmHg

Enthalpy of Unsaturated Liquid, cal/(g mol)

	Mole fraction, x_1										
Temp, K	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.00
185	0	92	150	183	196	195	182	158	122	71	0
195	325	429	500	546	575	589	593	586	567	534	428
205	652	768	852	913	955	985	1005	1014	1012	997	963
215	982	1111	1208	1282	1339	1384	1419	1445	1460	1462	1444
225	1316	1457	1567	1655	1726	1786	1837	1879	1910	1929	1928
235	1654	1807	1931	2033	2119	2194	2260	2318	2366	2400	2416
245	1996	2162	2300	2415	2516	2606	2688	2762	2826	2877	2910
255	2343	2523	2674	2804	2919	3025	3122	3212	3293	3360	3409
265	2695	2889	3054	3198	3329	3449	3563	3669	3766	3850	3915
275	3053	3260	3440	3599	3744	3881	4010	4133	4246	4347	4428
285	3417	3638	3832	4006	4167	4319	4465	4604	4734	4851	4949
295	3787	4023	4231	4421	4597	4765	4927	5083	5230	5363	5478
305	4163	4414	4637	4842	5035	5219	5398	5570	5734	5884	6015
315	4546	4812	5051	5272	5480	5681	5876	6066	6246	6414	6562
325	4936	5218	5472	5709	5935	6152	6365	6571	6769	6954	7119
335	5333	5631	5902	6156	6398	6633	6863	7087	7303	7505	7688
345	5736	6051	6340	6611	6871	7124	7372	7615	7849	8069	8269
355	6147	6480	6787	7077	7356	7627	7894	8156	8408	8647	8865
365	6564	6917	7244	7553	7852	8144	8430	8711	8984	9242	9478
375	6988	7363	7711	8042	8362	8675					

Enthalpy of Saturated Liquid and Vapor (total vaporization), cal/(g mol)

	$x_1 = y_1$										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.00
T, K	383.8	381.8	380.1	378.5	377.0	375.6	374.3	373.3	372.6	372.0	371.5
$H°_{L1}$	7365	7672	7955	8218	8466	8706	8945	9187	9431	9670	9887
$H°_{V1}$	15296	15568	15815	16042	16255	16460	16663	16869	17078	17282	17463

Enthalpy of Superheated Vapor, cal/(g mol)

	Mole fraction, y_1										
Temp, K	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.00
400	15826	16191	16529	16848	17156	17457	17753	18047	18334	18610	18864
410	16163	16545	16900	17237	17562	17881	18195	18505	18810	19103	19374
420	16508	16907	17280	17635	17977	18313	18645	18973	19296	19606	19895
430	16859	17277	17668	18040	18401	18754	19104	19450	19790	20119	20425
440	17219	17654	18063	18454	18832	19204	19571	19936	20294	20641	20965
450	17585	18039	18466	18875	19272	19662	20048	20430	20807	21172	21515
460	17959	18431	18877	19304	19720	20128	20533	20934	21329	21713	22074
470	18339	18830	19295	19741	20175	20603	21026	21446	21860	22262	22642
480	18727	19237	19720	20186	20639	21085	21527	21966	22399	22821	23220
490	19121	19650	20153	20638	21110	21575	22037	22495	22947	23388	23806
500	19522	20071	20593	21097	21589	22074	22555	23032	23504	23964	24402

results reported in Table II were obtained by a Simplex optimization technique.

Enthalpy–Concentration Data. Calculation of enthalpy–concentration data is a simple procedure when the following information is available: (1) the specific heat of the pure components both in the liquid and vapor phases at various temperatures, (2) the latent heat of vaporization between the two phases at known temperatures for different concentrations, (3) vapor–liquid equilibrium data, and (4) excess enthalpies as a function of temperature and composition.

(1) Enthalpy of the Pure Liquids. The reference temperature for $H = 0$ was taken as 185 K for the system *n*-heptane–toluene and 180 K for the binary methylcyclohexane–toluene. These temperatures are the integer values immediately above the melting point of the pure components. The specific heat data, $(c_L)_i$, for the pure liquid were taken from Holzhauer and Ziegler (*6*).

The enthalpy $(H_L°)_i$ at any temperature T is

$$(H_L°)_i = \int_{T_0}^{T} (c_L)_i \, dT \qquad (3)$$

Table IV. Enthalpy–Concentration Data for the System Methylcyclohexane (2)–Toluene (3) at 760 mmHg

Enthalpy of Unsaturated Liquid, cal/(g mol)
Mole fraction, x_2

Temp, K	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.00
180	0	85	135	161	173	176	172	159	133	84	0
190	324	411	462	489	503	509	508	499	477	432	352
200	650	739	791	821	837	845	848	843	825	785	710
210	979	1070	1124	1156	1175	1187	1193	1192	1179	1144	1074
220	1310	1404	1461	1496	1518	1533	1543	1547	1539	1510	1445
230	1646	1743	1803	1840	1865	1884	1899	1908	1906	1882	1823
240	1986	2086	2149	2190	2219	2242	2262	2276	2279	2262	2209
250	2330	2434	2501	2546	2579	2606	2631	2651	2660	2649	2602
260	2680	2788	2859	2907	2945	2977	3008	3034	3049	3044	3004
270	3035	3147	3223	3276	3318	3356	3392	3424	3446	3448	3415
280	3396	3513	3593	3651	3699	3742	3784	3823	3852	3860	3834
290	3763	3886	3971	4034	4087	4136	4185	4230	4266	4282	4263
300	4136	4265	4355	4424	4483	4539	4594	4646	4690	4713	4701
310	4516	4651	4747	4822	4887	4950	5012	5072	5123	5154	5150
320	4902	5044	5147	5228	5300	5369	5439	5507	5566	5606	5610
330	5295	5444	5554	5642	5721	5798	5875	5951	6019	6067	6080
340	5695	5851	5969	6064	6150	6235	6321	6405	6482	6540	6562
350	6102	6266	6391	6494	6588	6681	6776	6870	6956	7024	7055
360	6516	6688	6821	6932	7035	7137	7240	7344	7441	7519	7560
370	6937	7118	7259	7378	7490	7601	7715	7829	7937	8026	8078
380	7364	7554									

Enthalpy of Saturated Liquid and Vapor (total vaporization), cal/(g mol)
$x_2 = y_2$

	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.00
T, K	383.8	381.5	379.8	378.5	377.5	376.6	375.8	375.1	374.6	374.2	374.0
H°_{L1}	7526	7621	7697	7765	7835	7910	7994	8082	8169	8244	8290
H°_{V1}	15457	15503	15529	15549	15570	15596	15630	15669	15707	15733	15730

Enthalpy of Superheated Vapor, cal/(g mol)
Mole fraction, y_2

Temp, K	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.00
400	15988	16125	16229	16316	16398	16483	16571	16662	16748	16816	16850
410	16325	16473	16589	16687	16781	16877	16977	17079	17177	17257	17302
420	16669	16829	16957	17067	17173	17281	17393	17507	17616	17708	17765
430	17021	17193	17333	17456	17574	17693	17818	17944	18065	18169	18239
440	17380	17565	17717	17853	17983	18115	18252	18391	18525	18642	18724
450	17747	17945	18110	18258	18401	18546	18696	18848	18995	19124	19219
460	18120	18331	18510	18671	18828	18986	19149	19314	19474	19617	19725
470	18501	18726	18917	19093	19263	19435	19611	19790	19964	20120	20242
480	18889	19127	19333	19522	19706	19892	20082	20275	20462	20633	20769
490	19283	19536	19756	19959	20157	20357	20562	20769	20971	21155	21306
500	19684	19951	20186	20404	20617	20831	21051	21272	21488	21688	21852

where T_0 is the reference temperature. Equation 3 is valid up to the boiling point of the pure component.

(2) Enthalpy of the Liquid Mixture. The enthalpy of the liquid mixture at any temperature and composition was calculated according to

$$H_L = x_1 H_{L1}^\circ + x_2 H_{L2}^\circ + \Delta H^E \quad (4)$$

where ΔH^E is the excess enthalpy at the specific temperature. Data on ΔH^E have been reported by Holzhauer and Ziegler (*6*) in the form of a Redlich–Kister expansion, with temperature-dependent coefficients. Equation 4 is assumed valid up to the boiling point of the mixture, the latter being calculated with eq 1.

(3) Enthalpy of Saturated Pure Vapor. This parameter was calculated by adding the heat of vaporization to the enthalpy of the pure liquid at the boiling point. The heats of vaporization taken from ref 14 were 7576 cal/mol for *n*-heptane, 7931 cal/mol for toluene, and 7440 cal/mol for methylcyclohexane.

(4) Enthalpy of Vapor Mixtures. Heats of vaporization of the solutions were assumed to be a linear molar combination of the heat of vaporization of the pure components. Excess enthalpies of mixing in the vapor phase were assumed to be negligible. These two assumptions are reasonable on the basis of the low pressure involved and the almost ideal behavior of the system. Specific heat data for the pure components were taken from ref 14.

Complete enthalpy–concentration data for both systems appear in Tables III and IV.

Ternary Vapor–Liquid Equilibrium. Vapor–liquid equilibrium measurements were made at 760 mmHg for the ternary *n*-heptane–methylcyclohexane–toluene and are reported in Table V. Liquid activity coefficients were calculated according to

$$\ln \gamma_i = \ln (Py_i/P_i^0 x_i) + (B_i - V_i^0)(P - P_i^0)/RT + (P/RT)[(1 - y_i)(y_j\delta_{ij} + y_k\delta_{ik}) - y_j y_k \delta_{jk}] \quad (5)$$

where

$$\delta_{ij} = 2B_{ij} - B_i - B_j \quad (6)$$

Vapor pressures P_i^0 were calculated using Antoine's equation

Table V. Ternary Vapor–Liquid Equilibrium Data for *n*-Heptane (1)–Methylcyclohexane (2)–Toluene (3) at 760 mmHg

Temp, °C		Liquid compn			Vapor compn			Activity coeff		
Obsd	Calcd	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
101.93	101.76	0.411	0.134	0.455	0.468	0.143	0.389	1.03422	1.03909	1.09060
105.87	106.23	0.089	0.126	0.785	0.129	0.158	0.713	1.18458	1.10076	1.03589
101.90	101.43	0.374	0.212	0.414	0.420	0.217	0.363	1.02078	0.99746	1.11948
107.15	107.66	0.055	0.086	0.859	0.101	0.097	0.802	1.45114	0.95785	1.02738
106.55	106.93	0.072	0.106	0.822	0.120	0.146	0.734	1.33794	1.18795	0.99918
101.90	101.47	0.370	0.211	0.419	0.424	0.222	0.354	1.04165	1.02528	1.07870
101.70	101.24	0.315	0.325	0.360	0.355	0.336	0.309	1.02996	1.01286	1.10225
102.22	102.08	0.449	0.073	0.478	0.515	0.079	0.406	1.03363	1.04561	1.07447
101.60	101.18	0.266	0.427	0.307	0.283	0.421	0.296	0.97494	0.96852	1.24176
107.95	108.34	0.039	0.069	0.892	0.076	0.101	0.823	1.50810	1.21779	0.99298
108.45	108.83	0.029	0.056	0.915	0.059	0.083	0.858	1.55415	1.21741	0.99533
107.63	107.61	0.023	0.123	0.854	0.049	0.173	0.778	1.66251	1.17979	0.98919
101.23	101.24	0.088	0.720	0.192	0.102	0.729	0.169	1.07284	1.00451	1.14587
100.70	100.85	0.234	0.600	0.166	0.278	0.576	0.146	1.11574	0.96605	1.16265
102.68	102.20	0.223	0.291	0.486	0.281	0.311	0.408	1.12143	1.02009	1.04813
103.12	103.48	0.154	0.243	0.603	0.200	0.283	0.517	1.14212	1.09873	1.05706
102.70	103.14	0.188	0.232	0.580	0.173	0.307	0.520	0.81846	1.26239	1.11874
104.00	105.06	0.122	0.161	0.717	0.159	0.190	0.651	1.11938	1.08783	1.09169
102.20	101.66	0.303	0.263	0.434	0.351	0.279	0.370	1.04443	1.02554	1.07915
101.50	101.13	0.218	0.531	0.251	0.231	0.535	0.234	0.97365	0.99238	1.20417
105.10	105.59	0.145	0.108	0.747	0.213	0.138	0.649	1.22531	1.14438	1.01257
101.15	101.14	0.431	0.187	0.382	0.472	0.188	0.340	1.01598	0.99953	1.16126
100.90	101.09	0.170	0.628	0.202	0.187	0.635	0.178	1.02739	1.01208	1.15814
100.95	101.05	0.141	0.685	0.174	0.156	0.688	0.156	1.03193	1.00396	1.17664
103.89	104.44	0.231	0.099	0.670	0.311	0.118	0.571	1.15985	1.10188	1.02788
101.75	100.95	0.477	0.163	0.360	0.531	0.166	0.303	1.01605	0.99637	1.07922
103.40	103.34	0.180	0.224	0.596	0.234	0.258	0.508	1.13471	1.07862	1.04248
101.00	100.98	0.112	0.748	0.140	0.122	0.751	0.127	1.01458	1.00225	1.18882
101.04	100.96	0.100	0.773	0.127	0.109	0.776	0.115	1.01414	1.00104	1.18531
100.98	100.97	0.096	0.776	0.128	0.107	0.777	0.116	1.03871	1.00006	1.18834
102.70	102.61	0.151	0.341	0.508	0.189	0.379	0.432	1.11327	1.06029	1.06113
101.08	100.98	0.095	0.775	0.130	0.105	0.778	0.117	1.02722	0.99996	1.17673
102.57	102.37	0.139	0.395	0.466	0.170	0.432	0.398	1.09162	1.04695	1.06972
101.10	100.97	0.095	0.777	0.128	0.105	0.781	0.114	1.02666	1.00069	1.16380
101.10	100.97	0.095	0.777	0.128	0.105	0.781	0.114	1.02666	1.00069	1.16380
103.10	103.00	0.119	0.343	0.538	0.140	0.375	0.485	1.03515	1.03199	1.11209
101.12	100.94	0.095	0.785	0.120	0.103	0.784	0.113	1.00655	0.99377	1.22978
101.00	100.94	0.075	0.819	0.106	0.084	0.820	0.096	1.04318	0.99946	1.18689
103.90	103.85	0.095	0.290	0.615	0.125	0.338	0.537	1.13315	1.07719	1.05286
103.15	103.15	0.079	0.394	0.527	0.102	0.445	0.453	1.13451	1.06470	1.05889
101.01	100.92	0.065	0.841	0.094	0.071	0.842	0.087	1.01710	0.99916	1.21258
101.07	100.90	0.053	0.870	0.077	0.059	0.870	0.071	1.03487	0.99637	1.20596
102.70	102.71	0.070	0.470	0.460	0.085	0.514	0.401	1.07998	1.04329	1.08779
100.77	100.69	0.128	0.800	0.072	0.170	0.770	0.060	1.24488	0.96676	1.09939
102.30	102.46	0.059	0.529	0.412	0.072	0.573	0.355	1.09715	1.04437	1.08762
100.29	100.37	0.294	0.645	0.061	0.310	0.634	0.056	1.00146	1.00011	1.22811
102.10	102.28	0.053	0.571†	0.376	0.062	0.603	0.335	1.05743	1.02364	1.13110
101.47	101.79	0.403	0.139	0.458	0.449	0.146	0.405	1.02464	1.03538	1.14311
101.88	102.07	0.044	0.623	0.333	0.054	0.655	0.291	1.11601	1.02510	1.11647
100.03	100.52	0.338	0.533	0.129	0.359	0.524	0.117	1.01601	1.00732	1.22253
100.72	101.14	0.493	0.120	0.387	0.547	0.120	0.333	1.04152	1.00573	1.13671
101.65	101.94	0.039	0.656	0.305	0.047	0.686	0.267	1.10273	1.02589	1.12588
99.97	100.32	0.399	0.482	0.119	0.436	0.461	0.103	1.04704	0.98156	1.16870
99.40	100.05	0.665	0.083	0.252	0.691	0.070	0.239	1.01145	0.87894	1.30199
101.50	101.68	0.029	0.725	0.246	0.034	0.749	0.217	1.07718	1.01757	1.13943
100.60	100.60	0.380	0.412	0.208	0.408	0.409	0.183	1.01115	1.00165	1.16637
99.25	99.63	0.742	0.065	0.193	0.760	0.066	0.174	1.00116	1.06249	1.24306
100.61	100.85	0.265	0.547	0.188	0.286	0.546	0.168	1.01607	1.00690	1.18438
101.20	100.98	0.339	0.354	0.307	0.376	0.360	0.264	1.02755	1.00972	1.12037
100.20	100.40	0.430	0.389	0.181	0.457	0.382	0.161	1.01194	1.00157	1.19301
100.82	100.62	0.426	0.310	0.264	0.448	0.310	0.242	0.98446	1.00305	1.20748
99.95	100.15	0.495	0.345	0.160	0.523	0.336	0.141	1.01296	1.00002	1.19056
99.22	99.44	0.677	0.221	0.102	0.696	0.213	0.091	1.00570	1.00935	1.23121
101.10	100.11	0.579	0.196	0.225	0.614	0.192	0.194	0.98520	0.97518	1.12650
99.60	99.99	0.679	0.074	0.247	0.709	0.075	0.216	1.01081	1.05054	1.19349
99.00	99.26	0.729	0.185	0.086	0.744	0.179	0.077	1.00448	1.01935	1.24359
100.10	100.10	0.541	0.270	0.189	0.571	0.264	0.165	1.00774	0.99992	1.17426
99.33	99.64	0.743	0.062	0.195	0.767	0.059	0.174	1.00679	0.99360	1.22742
98.90	99.37	0.796	0.050	0.154	0.835	0.043	0.122	1.03532	0.90846	1.10352
100.18	100.50	0.339	0.535	0.126	0.357	0.529	0.114	1.00323	1.00904	1.21423
99.15	99.53	0.684	0.188	0.128	0.706	0.180	0.114	1.01167	1.00460	1.23162
99.60	99.68	0.602	0.285	0.113	0.624	0.275	0.101	1.00341	1.00017	1.21988

Table V (Continued)

Temp, °C		Liquid compn			Vapor compn			Activity coeff		
Obsd	Calcd	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
101.00	101.27	0.155	0.599	0.246	0.172	0.609	0.219	1.03359	1.01491	1.16666
101.68	101.77	0.132	0.518	0.350	0.154	0.545	0.301	1.06672	1.03133	1.10508
101.68	101.85	0.152	0.464	0.384	0.156	0.496	0.348	0.93839	1.04784	1.16451
99.70	99.84	0.534	0.363	0.103	0.555	0.350	0.095	1.00332	0.99674	1.25517
99.82	99.96	0.490	0.414	0.096	0.496	0.415	0.089	0.97394	1.03291	1.25725
101.63	101.54	0.139	0.558	0.303	0.160	0.581	0.259	1.05391	1.02200	1.09996
98.85	99.18	0.798	0.104	0.098	0.814	0.100	0.086	1.00814	1.01711	1.22421

Table VI. Vapor Pressure Constants, Eq 7 (*14*)

Compd	α_i	β_i	δ_i
n-Hexane	6.90240	1268.115	216.900
Methylcyclohexane	6.82689	1272.864	221.630
Toluene	6.95334	1343.943	219.377

$$\log P_i^0 = \alpha_i - \beta_i/(\delta_i + t) \tag{7}$$

where the constants appear in Table VI (*14*). The virial coefficients B_i and the mixed coefficients B_{ij} were estimated by the method of Tsonopoulos (*15, 16*) using the molecular parameters suggested by the author. In general, the contribution of the last two terms accounted for less than 1% of the activity coefficients.

The data points reported in Table V are thermodynamically consistent, as tested by the McDermott-Ellis method (*8*) modified by Wisniak and Tamir (*21*). Two experimental points a and b are considered thermodynamically consistent if the following condition is fulfilled

$$D < D_{max} \tag{8}$$

where

$$D = \sum_{i=1}^{N} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \tag{9}$$

$$D_{max} = \sum_{i=1}^{N} (x_{ia} + x_{ib}) \left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right) \Delta x + 2 \sum_{i=1}^{N} |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta x + \sum_{i=1}^{N} (x_{ia} + x_{ib}) \frac{\Delta P}{P} + \sum_{i=1}^{N} (x_{ia} + x_{ib}) \beta_i \left(\frac{1}{[t_a + \delta_i]^2} + \frac{1}{[t_b + \delta_i]^2}\right) \Delta t \tag{10}$$

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 $\Delta x = 0.0025$ mole fraction units. The first term in eq 10 was the dominant one.

The activity coefficients reported in Table V show that the ternary system behaves almost ideally. A similar behavior was found for the three binaries. The activity coefficients were correlated by the following Redlich–Kister expansion (*10*)

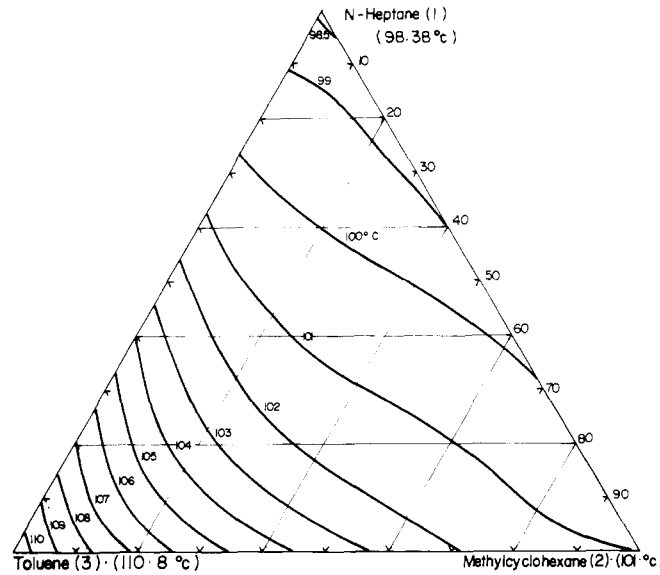

Figure 1. Isothermals of the system *n*-heptane (1)–methylcyclohexane (2)–toluene (3) at 760 mmHg.

$$\ln \gamma_1 = x_2 x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2)(3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_3) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \tag{11}$$

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

The binary and ternary Redlich–Kister coefficients were obtained by a Simplex optimization technique and are reported in Table VII. The relative values of the root mean square deviation and the ternary constant C_1, suggest that ternary data can be predicted directly from the binary systems and that the binary systems behave like regular solutions.

The boiling point of the ternary mixtures was correlated by an extension of eq 1

Table VII. Redlich–Kister Correlation of Binary and Ternary Data

System	B_{ij}	C_{ij}	D_{ij}	Rmsd γ_i	Rmsd γ_j
n-Heptane (1)–methylcyclohexane (2)	0.29958×10^{-1}	0.11949×10^{-3}	0.12337×10^{-4}	0.011456	0.069101
n-Heptane (1)–toluene (3)	0.14028	0.26630×10^{-3}	0.76142×10^{-5}	0.38918	0.37425
Methylcyclohexane (2)–toluene (3)	0.22394	0.23434×10^{-3}	0.18421×10^{-4}	0.10374	0.018893

		Overall rmsd γ	Overall rmsd y
n-Heptane (1)–methylcyclohexane (2)–toluene (3)	$C_1 = -0.021444$	0.083151	0.013133
	$C_1 = 0$	0.082650	0.013103

$$T = x_1T_1^0 + x_2T_2^0 + x_3T_3^0 + \omega + \sum_{i,j=1}^{3} x_ix_j \sum_{k=0}^{l} C_K(x_i - x_j)^k + x_1x_2x_3\,[A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + \ldots] \quad (12)$$

where l is the number of terms in the series expansion of $(x_i - x_j)$ and

$$\omega = x_1 \ln (y_1/x_1) + x_2 \ln (y_2/x_2) + x_3 \ln (y_3/x_3) \quad (13)$$

Again, the contribution of ω can be neglected. The different constants of eq 12 appear in Table II and, from the value of the root mean square deviation, the correlation is good. The ternary isothermals were calculated with eq 12 and are presented in Figure 1.

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Yehudit Reizner and Kohav Ben-Zaken helped in the experimental and numerical determinations.

Glossary

α, β A, B, C	constants
B_i	second virial coefficient, cm^3/mol
B_{ij}	mixed virial coefficient, cm^3/mol
n	number of experimental points
N	number of components
P	total pressure, mmHg
P_i^0	vapor pressure of component i pure, mmHg
R	gas constant, cal/(g mol K)
rmsd	root-mean-square deviation, $[\Sigma_i^n \Sigma_j^n (y_{ji,\text{exptl}} - y_{ji,\text{calcd}})^2/3n]^{1/2}$
t, T	temperature, C, K
T_i^0	boiling temperature of component i at pressure P, K
V_i^0	molar liquid volume of component i pure, cm^3/mol
x_j, y_i	mole fraction composition of component i in the liquid and vapor phases

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Vapor–Liquid Equilibrium Data of Ethanethiol and Tetrahydrothiophene in Propane

John W. Goetzinger, Dennis W. Brinkman,* Bruce E. Poling, and Marvin L. Whisman

Bartlesville Energy Research Center, Energy Research and Development Administration, Bartlesville, Oklahoma 74003

Equilibrium K values for the odorants ethanethiol, tetrahydrothiophene, and a mixture of the two in propane were determined at −23, 0, and 35 °C. A technique was used in which samples from both the vapor and liquid phases were analyzed by gas chromatography, which gave K values to ±5%.

As part of a study to determine desired odorant concentrations in propane, the equilibrium odorant concentration in the vapor phase was measured for known concentrations in the liquid phase. This ratio of vapor concentration to liquid concentration, known as a K value (*2*), is important in obtaining proper odorant levels, yet the ratio has not been well established owing to adsorption problems and the low concentrations involved. When propane gas is released from a pressurized container, such as a consumer supply tank, the odorant–propane composition of the gas differs markedly from the composition in the liquid phase. This ratio of component concentrations is thus an important consideration in dosing the liquefied propane with the proper level of odorant for safe usage by the public. The value is also useful in fuel processing, since some mercaptans occur naturally and can cause problems by freezing out during production (*9*).

K values for various hydrocarbon mixtures have been published previously, and representative work is presented in ref 2, 6, and 9. These often have involved one alkane dissolved in another. More complicated systems, such as the sulfur-containing compounds used for odorization of natural gas and propane, have been studied only recently by Hankinson and Wilson (*2*). They found analysis by a gas chromatographic (GC) procedure to be unsatisfactory owing to adsorption of the sulfur compounds. Consequently, they based their studies on an endpoint determination by olefactory detection—when one detected an odor, a titration endpoint had been reached. It was felt that a satisfactory GC procedure could be developed, as used with methanethiol (*9*), and this report describes the successful development of such a procedure. In addition, this study looks for possible interactions when a mixture of odorants is present. Such interactions would be important if the consumer uses more than one brand of liquid propane and does not completely empty the tank before refilling.

Although it has been shown that the K value does not change with liquid concentration over a fairly wide range (*2*), it does change with temperature. Three temperatures, −23, 0, and 35 °C (−10, 32, and 95 °F), representative of conditions found at various stages of storage and distribution of LP-gas, were selected. K values for ethanethiol (ethyl mercaptan), tetrahydro-