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Calculation of Bubble and Dew Points of Ideal Multicomponent Mixtures by Using Statistical Methods. Part II. The Olefinic and Alkylbenzene Series

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Abstract

The results obtained by using derived equations prove to be equally accurate and more economic to simulate if applied to the olefinic and some selected members of the alkylbenzene series as they were for the paraffinic series. A large number of mixtures with a temperature span of 5.9 to 30.5°C are involved in this study. Satisfactory results are also obtained when these equations, slightly modified by appropriate pressure correction factors, are applied to hydrocarbon mixtures at nonatmospheric pressures. The proposed approach is, however, not recommended for nonideal hydrocarbon mixtures. The statistical approach can save up to 60% of computer CPU time for mixtures containing up to 10 components. Computed bubble and dew points are compared with both the conventional iterative method and some VLE experimental data.

INTRODUCTION

In Part I of this work (*1*), the basic equations used to develop a statistical method for computing bubble and dew points were derived for the paraffinic series. This approach eliminates the need for Antoine's constants and requires only the mole fraction of each component in the mixture and the normal boiling temperatures. The results obtained by using this noniterative algorithm were quite accurate. For instance, compared with the conventional trial-and-error method, the average relative error in bubble point calculations ranged from 0.008% for binary mixtures to 0.091% for 10-component mixtures. The corresponding average error values for dew-point calculations were 0.009 and 0.255% for binary and 10-component mixtures, respectively. It was also shown that the relative error in both bubble and dew-point calculations was higher for mixtures containing lighter components (C_6 and C_7) and decreased considerably for mixtures containing heavier components (C_{16} and above). The efficiency of the proposed method was also demonstrated by a considerable saving in computer CPU time consumption.

In Part II, the applicability of statistical method is investigated for two more homologous series: the olefinic series and selected members of the alkylbenzene series. The algorithm developed is also used to test mixtures at total pressures different from atmospheric and mixtures containing cross-fertilized components randomly chosen from all three homologous series. The computed results in all cases are compared with the conventional trial-and-error algorithm as well as with experimental values for multicomponent mixtures whose VLE data are available.

EXTENSION OF THE STATISTICAL METHOD TO OTHER HOMOLOGOUS SERIES

In order to test the validity of the proposed algorithm to other ideal multicomponent hydrocarbon mixtures, the olefinic series and some selected members of the alkylbenzene series are used. The olefins are slightly polar hydrocarbons with a dipole moment ranging from 0.3 to 0.5 debyes (*2*). At total pressures near atmospheric, the olefinic mixtures are therefore assumed to behave ideally. The olefinic components investigated in this study covered the range C_6H_{12} to $C_{17}H_{34}$. Four different composition profiles were used, as described in Part I.

Nine alkylbenzene compounds were selected with dipole moment ranging from 0.0 to 0.5 debyes (*2*). These compounds are approximately of similar size and have the same chemical nature. It was therefore assumed that the chosen compounds would form ideal mixtures in the total pressure range investigated.

The basic equations originally derived in Part I (*1*) for computing the bubble point, t_B, and the dew point, t_D, of multicomponent paraffinic mixtures were as follows:

$$t_B = t_{av} - \Delta t_B$$

$$t_D = t_{av} + \Delta t_D$$

where t_{av} is the average boiling point of the mixture, calculated from the given mole fractions and normal boiling points, and Δt_B and Δt_D are temperature increments given by the following equations (*3*):

$$\Delta t_B = \alpha_B B \exp(-BS/1.8\sigma) \qquad (1)$$

TABLE 1
Constants A_i in Equation (3)

A_i	Homologous series Paraffinic	Olefinic	Alkylbenzenes
A_1	7.8	7.8	7.5
A_2	400	400	400
A_3	1.0	1.0	1.0
A_4	1.5	1.5	1.5
A_5	0.004	0.005	0.002
A_6	0.0005	0.004	0.01

and

$$\Delta t_D = \alpha_D D \exp (DS/1.5\sigma) \tag{2}$$

where

$$\alpha_B = 1 + 0.002BE$$

$$\alpha_D = 1 + 0.004(DE + 0.0005\sigma^2)$$

$$B = 6.8\mu_2/(\mu_1 + 400)$$

$$D = 7.8\mu_2/(\mu_1 + 400)$$

$$\sigma = \text{standard deviation} = \pm\sqrt{\mu_2}$$

$$S = \text{skewness} = \mu_3/\mu_2^{3/2}$$

$$E = \text{excess} = \mu_4/\mu_2^2 - 3$$

$$\mu_r = \text{statistical moments} = \sum_{i=1}^{n} x_i(t_{bi} - \mu_1)^r$$

For bubble-point calculations, Eq. (1) was found to be applicable with the same degree of accuracy to all three homologous series. On the other hand, Eq. (2) for dew-point calculations was slightly modified to fit the olefinic and alkylbenzene series. For this purpose, Eq. (2) can be generalized as

$$\Delta t_D = \alpha_D D \exp (A_3 DS/A_4 \sigma) \tag{3}$$

where

$$\alpha_D = 1 + A_5(DE + A_6\sigma^2)$$

$$D = A_1\mu_2/(\mu_1 + A_2)$$

The constants A_i are given in Table 1 for the three homologous series investigated in this work.

VALIDITY OF THE STATISTICAL METHOD AT PRESSURES DIFFERENT FROM ATMOSPHERIC

If the developed algorithm, based on the statistical approach, is to be applied at a total pressure different from atmospheric, the boiling points of the individual components should be available at the required pressure. Emperical equations were therefore developed to express Antoine constants in terms of the normal boiling points for members of the three homologous hydrocarbon series. The curve-fitting technique proposed by Said and Al-Ameeri (*4*) was utilized.

Antoine constants A, B, and C for both paraffinic and olefinic series can be expressed in terms of the normal boiling point, t_{bn}, as follows:

$$A = 15.85 + 0.0027\beta_1/(1 + 0.002\beta_1) \tag{4}$$

$$B = 2700 + 6.7\beta_1 \tag{5}$$

$$C = 223 - 0.36\beta_1 \tag{6}$$

where

$$\beta_1 = t_{bn} - 70$$

For the selected members of the alkylbenzene series, the following Antoine constants were derived:

$$A = 15.9 + 0.002\beta_2 \tag{7}$$

$$B = 2800 + 8.0\beta_2 \tag{8}$$

$$C = 222.2 - 0.2038\beta_2/(1 - 0.0007\beta_2) \tag{9}$$

where

$$\beta_2 = t_{bn} - 80$$

Several computer runs were performed to test the applicability of Eqs. (1) and (3) to mixtures at total pressures different from atmospheric. The pressure range investigated was between 0.5 and 1.5 atm in order not to violate the validity of the pressure range for the Antoine constants used in the conventional trial-and-error algorithm. It was found that the right-hand sides of Eqs. (1) and (3) must be multiplied by appropriate pressure correction factors. These factors were determined as $P^{-0.11}$ for bubble-point calculations using Eq. (1), and $P^{0.16}$ for dew-point calculations using Eq. (3), where P is expressed in atmospheres.

COMPARISON WITH EXPERIMENTAL DATA

A literature search, done to collect experimental VLE data for the three homologous hydrocarbon series investigated in this work (*n*-alkanes–*n*-

TABLE 2
Experimental Data for Some Binary Hydrocarbon Mixtures

	Composition profiles, mole fractions			
Mixtures	1	2	3	4
Benzene (1)	0.90	0.70	0.50	0.10
Toluene (2)	0.10	0.30	0.50	0.90
Benzene (1)	0.936	0.771	0.576	0.144
n-Heptane (2)	0.064	0.229	0.424	0.856
Benzene (1)	0.91	0.764	0.512	0.113
n-Octane (2)	0.09	0.236	0.488	0.887
n-Hexane (1)	0.962	0.792	0.585	0.172
Benzene (2)	0.038	0.208	0.415	0.828
n-Hexane (1)	0.869	0.707	0.508	0.10
Toluene (2)	0.131	0.293	0.492	0.90
n-Heptane (1)	0.9112	0.7268	0.5320	0.1124
n-Octane (2)	0.0888	0.2732	0.4673	0.8876
n-Heptane (1)	0.90	0.50	0.30	0.10
Toluene (2)	0.10	0.50	0.70	0.90
n-Octane (1)	0.909	0.72	0.516	0.15
Ethylbenzene (2)	0.091	0.28	0.484	0.85

TABLE 3
Comparison between Conventional and Statistical Methods for Binary Olefinic Mixtures at Atmospheric Pressure

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B^a	E_D^b
C_6, C_7	I	66.450	65.481	68.269	0.993	65.457	1.795	68.245	−0.037	−0.035
	II	78.513	75.329	81.866	3.189	75.324	3.497	82.010	−0.007	+0.176
	III	84.545	81.605	87.154	2.925	81.620	2.602	87.147	+0.018	−0.008
	IV	90.577	89.180	91.578	1.382	89.195	1.022	91.599	+0.017	+0.023
C_8, C_9	I	123.792	123.147	124.884	0.665	123.127	1.066	124.858	−0.016	−0.020
	II	134.025	131.986	136.354	2.066	131.959	2.282	136.307	−0.020	−0.034
	III	139.141	137.303	140.905	1.854	137.287	1.743	140.884	−0.012	−0.015
	IV	144.257	143.408	144.947	0.855	143.402	0.695	144.952	−0.004	+0.003
C_{10}, C_{11}	I	172.727	172.273	173.446	0.467	172.260	0.693	173.42	−0.008	−0.015
	II	181.571	180.175	183.195	1.421	180.150	1.575	183.146	−0.014	−0.027
	III	185.993	184.753	187.246	1.257	184.736	1.226	187.219	−0.009	−0.014
	IV	190.415	189.852	190.913	0.570	189.845	0.494	190.909	−0.004	−0.002
C_{12}, C_{13}	I	215.252	214.919	215.759	0.342	214.910	0.482	215.734	−0.004	−0.010
	II	223.022	222.016	224.212	1.025	221.997	1.142	224.162	−0.009	−0.020
	III	226.907	226.023	227.838	0.899	226.008	0.898	227.805	−0.007	−0.014
	IV	230.792	230.395	231.166	0.403	230.389	0.365	231.157	−0.003	−0.004

[a] $\% E_B = [(\text{statistical } t_B - \text{conventional } t_B)/\text{conventional } t_B] \times 100$.

[b] $\% E_D = [(\text{statistical } t_D - \text{conventional } t_D)/\text{conventional } t_D] \times 100$.

TABLE 4

Comparison between Conventional and Statistical Methods for Tertiary and Quaternary Olefinic Mixtures at Atmospheric Pressure

Mixture	Composition profile		Conventional method (°C)		Statistical method (°C)				Relative error (%)	
		t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
C_6, C_7, C_8	I	78.262	73.604	85.581	4.743	73.519	7.424	85.686	−0.115	+0.123
	II	97.752	85.215	100.783	7.584	85.178	8.031	100.783	−0.043	0.000
	III	93.089	80.397	98.148	4.672	80.417	5.006	98.095	+0.025	−0.050
	IV	107.161	101.446	111.593	5.699	101.462	4.498	111.659	+0.016	+0.059
C_1, C_9, C_{10}	I	133.836	130.725	138.511	3.188	130.648	4.620	138.456	+0.017	−0.040
	II	146.187	141.261	151.660	4.998	141.189	5.396	151.583	−0.005	−0.050
	III	146.439	143.417	149.823	3.051	143.388	3.317	149.756	−0.020	−0.040
	IV	158.478	154.864	161.591	3.645	154.833	3.116	161.594	−0.020	+0.002
C_{11}, C_{12}, C_{13}	I	202.842	200.971	205.540	1.921	200.921	2.595	205.437	−0.025	−0.050
	II	212.888	209.985	216.251	2.960	209.928	3.244	216.132	−0.027	−0.055
	III	213.058	211.294	215.109	1.795	211.260	1.973	215.031	−0.016	−0.036
	IV	222.896	220.824	224.876	2.105	220.791	1.937	224.833	−0.015	−0.020
C_6, C_7, C_8, C_9	I	92.380	82.843	105.461	9.687	82.693	13.675	105.863	−0.180	+0.381
	II	106.269	93.617	119.217	12.777	93.492	12.995	119.264	−0.130	+0.039
	III	106.727	97.830	115.987	8.903	97.824	9.256	115.983	−0.006	−0.003
	IV	120.158	109.099	128.935	11.109	109.049	8.885	129.043	−0.046	+0.084
C_8, C_9, C_{10}, C_{11}	I	145.904	139.464	154.773	6.579	139.325	8.857	154.751	−0.100	−0.014
	II	157.798	149.375	166.875	8.550	149.248	8.982	166.780	−0.085	−0.057
	III	158.145	152.300	164.527	5.908	152.237	6.290	164.435	−0.040	−0.056
	IV	169.692	162.250	175.973	7.253	162.439	6.273	175.965	−0.050	−0.005
C_{10}, C_{11}, C_{12}, C_{13}		191.929	187.352	198.196	4.686	187.243	6.114	198.043	−0.058	−0.077
	II	202.296	196.369	208.928	6.033	196.263	6.481	208.755	−0.054	−0.083
	III	202.565	198.481	207.481	4.149	198.416	4.481	207.046	−0.030	−0.065
	IV	212.663	207.699	217.335	5.041	207.662	4.593	217.256	−0.018	−0.036

TABLE 5
Comparison between Conventional and Statistical Methods for 5- and 10-Component Olefinic Mixtures at Atmospheric Pressure

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
C_6, C_7, C_8, C_9, C_{10}	I	105.749	90.647	125.086	15.334	90.415	19.337	125.819	−0.256	+0.586
	II	119.118	100.886	137.046	18.462	100.656	17.928	137.065	−0.228	+0.014
	III	119.970	108.352	131.662	11.595	108.375	11.692	131.701	+0.021	+0.030
	IV	132.488	115.204	145.990	17.486	115.002	13.502	146.127	−0.175	+0.094
C_8, C_9, C_{10}, C_{11}, C_{12}	I	157.402	147.052	170.880	10.559	146.843	13.478	170.955	−0.142	+0.044
	II	168.900	156.559	181.802	12.533	156.367	12.902	181.668	−0.123	−0.074
	III	169.549	161.864	177.747	7.752	161.797	8.198	177.642	−0.041	−0.059
	IV	180.398	168.960	190.277	11.599	168.799	9.879	190.254	−0.095	−0.012
C_9, C_{10}, C_{11}, C_{12}, C_{13}	I	180.469	171.740	191.892	8.909	171.560	11.423	191.806	−0.105	−0.045
	II	191.200	180.842	202.286	10.522	180.672	11.086	202.090	−0.091	−0.097
	III	191.770	185.366	198.752	6.477	185.293	6.982	198.606	−0.039	−0.073
	IV	201.932	192.408	210.487	9.663	192.269	8.550	210.403	−0.072	−0.040
C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}	I	138.112	105.392	181.246	32.996	105.116	46.379	184.491	−0.260	+1.790
	II	175.371	127.122	215.766	48.958	126.413	37.295	212.666	−0.558	−1.437
	III	179.303	158.909	198.259	20.331	158.972	19.205	198.508	+0.040	+0.126
	IV	212.631	177.907	233.963	35.730	176.901	22.594	235.225	−0.565	+0.539
C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}	I	185.557	162.003	217.642	23.933	161.624	33.352	218.909	−0.234	+0.582
	II	218.119	183.436	249.578	35.112	183.004	29.952	248.070	−0.236	−0.604
	III	221.248	207.058	235.484	14.275	206.973	14.100	235.348	−0.041	−0.058
	IV	250.682	226.582	267.427	24.643	226.039	17.280	267.962	−0.240	+0.200

TABLE 6

Comparison between Conventional and Statistical Methods for Binary Alkylbenzene Mixtures at Atmospheric Pressure

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture[a]	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
A–B	I	83.122	82.137	84.836	0.986	82.136	1.699	84.821	+0.001	−0.018
	II	95.324	92.077	98.729	3.153	92.171	3.489	98.813	+0.102	+0.085
	III	101.425	98.418	103.953	2.886	98.539	2.579	104.004	+0.123	+0.049
	IV	107.526	106.091	108.500	1.361	106.165	0.987	108.513	+0.070	+0.012
B–C	I	113.133	112.469	114.215	0.676	112.457	1.060	114.193	−0.011	−0.019
	II	123.360	121.251	125.671	2.105	121.255	2.328	125.688	−0.003	+0.014
	III	128.473	126.565	130.225	1.892	126.581	1.765	130.238	+0.013	+0.010
	IV	133.587	132.701	134.273	0.873	132.714	0.689	134.276	+0.010	+0.002
C–D	I	136.965	136.894	137.059	0.073	136.892	0.090	137.055	−0.002	−0.003
	II	140.250	140.043	140.492	0.212	140.038	0.234	140.484	−0.004	−0.006
	III	141.892	141.715	142.088	0.182	141.710	0.190	142.082	−0.004	−0.004
	IV	143.535	143.457	143.616	0.080	143.455	0.079	143.614	−0.001	−0.001
D–E	I	144.955	144.912	144.997	0.039	144.916	0.046	145.001	+0.003	+0.003
	II	147.349	147.225	147.460	0.111	147.238	0.123	147.472	+0.009	+0.008
	III	148.546	148.440	148.637	0.095	148.451	0.101	148.647	+0.007	+0.007
	IV	149.743	149.697	149.781	0.041	149.702	0.042	149.785	+0.003	+0.003
E–F	I	151.224	151.146	151.331	0.083	151.141	0.102	151.326	−0.003	−0.003
	II	154.755	154.528	155.029	0.239	154.516	0.263	155.018	−0.008	−0.007
	III	156.521	156.327	156.743	0.205	156.316	0.214	156.735	−0.007	−0.005
	IV	158.286	158.201	158.378	0.090	158.196	0.089	158.375	−0.003	−0.002

[a] A = benzene, B = toluene, C = ethylbenzene, D = *o*-xylene, E = isopropylbenzene, F = *n*-propylbenzene.

TABLE 7
Comparison between Conventional and Statistical Methods for Tertiary Alkylbenzene Mixtures at Atmospheric Pressure

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
A–B–C	I	94.830	90.289	101.369	4.515	90.315	6.750	101.580	+0.029	+0.208
	II	108.929	101.799	116.083	6.998	101.931	7.461	116.390	+0.130	+0.264
	III	109.589	105.109	114.020	4.338	150.251	4.459	114.048	+0.135	+0.025
	IV	122.866	117.645	126.750	5.066	117.800	3.960	126.826	+0.132	+0.060
B–C–D	I	121.624	119.322	124.484	2.316	119.308	2.874	124.498	−0.012	+0.010
	II	130.357	127.571	133.045	2.781	127.575	2.708	133.065	+0.003	+0.015
	III	132.673	130.799	134.311	1.860	130.813	1.640	134.313	+0.010	+0.002
	IV	138.514	137.031	139.681	1.474	137.040	1.165	139.679	+0.007	−0.001
C–D–E	I	140.027	139.717	140.392	0.310	139.717	0.364	140.391	0.000	0.000
	II	143.612	143.177	144.065	0.426	143.186	0.462	144.074	+0.006	+0.006
	III	143.991	143.646	144.182	0.259	143.652	0.277	144.188	+0.004	+0.006
	IV	147.126	146.846	147.382	0.266	146.860	0.268	147.394	+0.010	+0.008
D–E–F	I	147.633	147.363	147.944	0.261	147.372	0.319	147.952	+0.006	+0.005
	II	151.287	150.830	151.794	0.452	150.835	0.510	151.797	+0.003	+0.002
	III	150.910	150.634	151.223	0.272	150.638	0.312	151.222	+0.003	0.000
	IV	155.040	154.686	155.412	0.355	154.689	0.369	155.409	0.000	−0.002

TABLE 8
Comparison between Conventional and Statistical Methods for Quaternary Alkylbenzene Mixtures at Atmospheric Pressure

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture[a]	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
A–B–C–D	I	106.866	99.128	115.576	7.648	99.218	9.181	116.047	+0.091	+0.408
	II	117.787	108.840	125.500	8.793	108.994	8.058	125.845	+0.141	+0.275
	III	120.016	113.394	125.558	6.456	113.560	5.686	125.702	+0.146	+0.115
	IV	128.708	122.037	133.272	6.512	122.196	4.668	133.376	+0.130	+0.078
B–C–D–E	I	128.979	125.808	132.267	3.163	125.849	3.344	132.323	+0.033	+0.042
	II	135.354	132.157	138.170	3.165	132.189	2.875	138.229	+0.024	+0.043
	III	137.313	135.150	139.115	2.137	135.176	1.820	139.133	+0.019	+0.013
	IV	141.730	139.717	143.362	1.974	139.756	1.562	143.292	+0.028	−0.049
C–D–E–F	I	143.749	143.071	144.546	0.675	143.074	0.801	144.550	+0.002	+0.003
	II	147.503	146.662	148.469	0.875	146.628	0.972	148.475	+0.004	+0.004
	III	147.441	146.862	148.069	0.570	146.871	0.634	148.078	+0.006	+0.006
	IV	151.256	150.520	152.012	0.729	150.527	0.759	152.015	+0.005	+0.002
D–E–F–G	I	151.189	150.582	151.924	0.608	150.581	0.724	151.913	0.000	−0.007
	II	154.743	153.979	155.622	0.777	153.966	0.858	155.601	−0.008	−0.013
	III	154.748	154.198	155.387	0.562	154.186	0.620	155.368	−0.008	−0.012
	IV	158.296	157.678	158.975	0.639	157.657	0.654	158.950	−0.013	−0.016

[a] G = 1-methyl-2-ethylene.

TABLE 9

Comparison between Conventional and Statistical Methods for 5- and 8-Component Alkylbenzene Mixtures at Atmospheric Pressure

Mixture[a]	Composition profile	t_{av} (°C)	Conventional method (°C)		Statistical method (°C)				Relative error (%)	
			t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
A–B–C–D–E	I	115.582	105.914	124.713	9.530	106.052	9.678	125.260	+0.130	+0.439
	II	124.298	114.334	131.952	9.786	114.512	8.035	132.333	+0.156	+0.285
	III	128.485	121.816	133.143	6.491	121.994	4.774	133.259	+0.146	+0.087
	IV	133.014	125.163	138.013	7.663	125.351	5.175	138.189	+0.150	+0.128
B–C–D–E–F	I	134.548	130.699	138.294	3.828	130.720	3.819	138.367	+0.016	+0.053
	II	140.117	136.309	143.443	3.772	136.345	3.388	143.505	+0.026	+0.043
	III	142.014	139.836	143.813	2.145	139.869	1.812	143.826	+0.024	+0.009
	IV	145.686	142.829	147.964	2.815	142.871	2.307	147.993	+0.029	+0.020
C–D–E–F–G	I	147.386	146.258	148.737	1.136	146.250	1.337	148.723	−0.006	−0.009
	II	151.023	149.725	152.479	1.310	149.713	1.437	152.460	−0.008	−0.012
	III	150.966	150.177	151.858	0.792	150.174	0.877	151.843	−0.002	−0.010
	IV	154.660	153.515	155.869	1.161	153.499	1.186	155.846	−0.010	−0.015
A–B–C–D–E–F–G–H	I	128.707	116.219	138.964	12.320	116.387	10.809	139.516	+0.145	+0.397
	II	139.881	127.073	148.696	12.629	127.252	9.205	149.086	+0.141	+0.262
	III	143.472	136.142	148.347	7.129	136.343	4.944	148.466	+0.148	+0.080
	IV	151.666	143.807	156.426	7.143	144.012	4.862	156.528	+0.143	+0.065
B–C–D–E–F–G–H–I	I	144.103	138.598	149.595	5.484	138.619	5.572	149.675	+0.015	+0.053
	II	152.775	146.675	158.331	6.072	146.703	5.649	158.424	+0.019	+0.059
	III	153.954	150.653	157.037	3.269	150.685	3.072	157.026	+0.021	−0.007
	IV	161.604	157.413	165.235	4.163	157.441	3.647	165.251	+0.018	+0.010

[a] H = *sec*-butylbenzene, I = butylbenzene.

alkanes, alkenes–alkenes, and alkylbenzenes–alkylbenzenes) confirmed that such VLE data are very scarce for these mixtures. For the investigated pressure range, experimental data are available for the mixtures shown in Table 2. Data are not available for any alkene–alkene mixture. It should be noticed that Table 2 contains some mixtures which are cross-fertilized from both paraffinic and alkylbenzene series.

RESULTS AND DISCUSSION

The modified algorithm was tested through a large number of computer runs on the olefinic and alkylbenzene series. The computed bubble and dew points were compared with those calculated by the conventional iterative algorithm. Tables 3–9 display some samples from both homologous series. Each table depicts the components comprising the mixture, the four composition profiles, the average boiling temperatures (t_{av}), the bubble points (t_B), and the dew points (t_D) computed using both statistical and

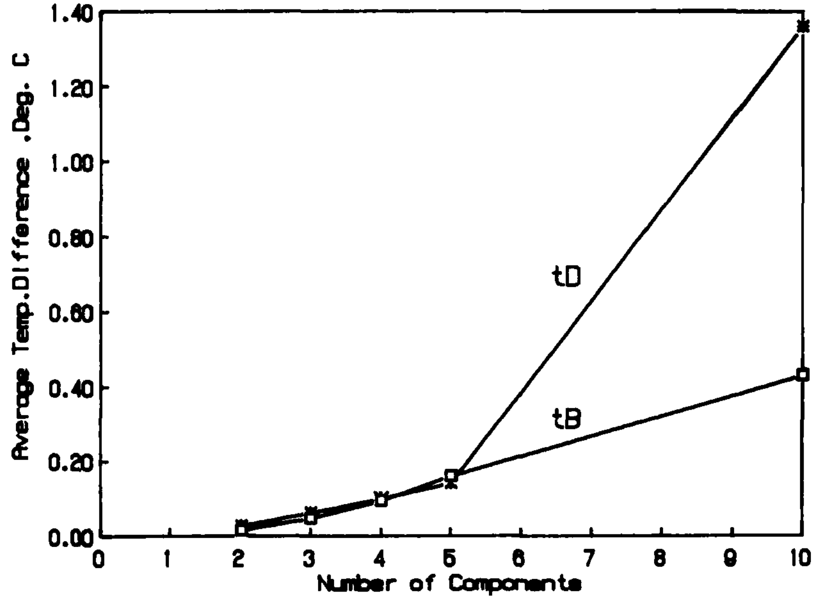

FIG. 1. Average temperature difference as a function of the number of components for the olefinic mixtures.

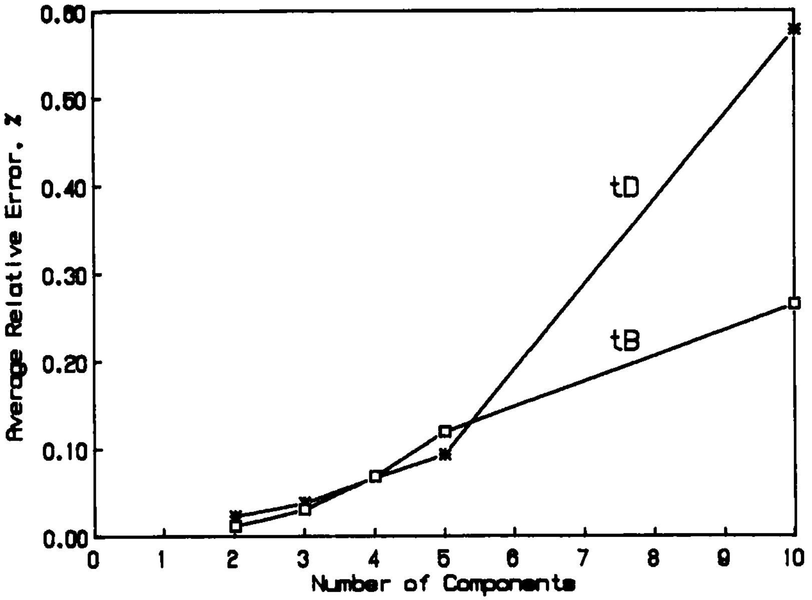

FIG. 2. Average relative error as a function of the number of components for the olefinic mixtures.

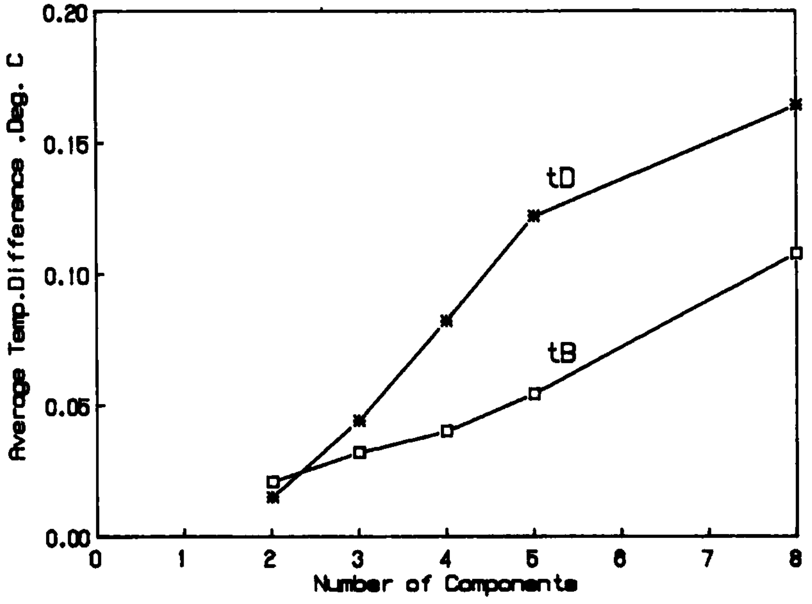

FIG. 3. Average temperature difference as a function of the number of components for the alkylbenzene mixtures.

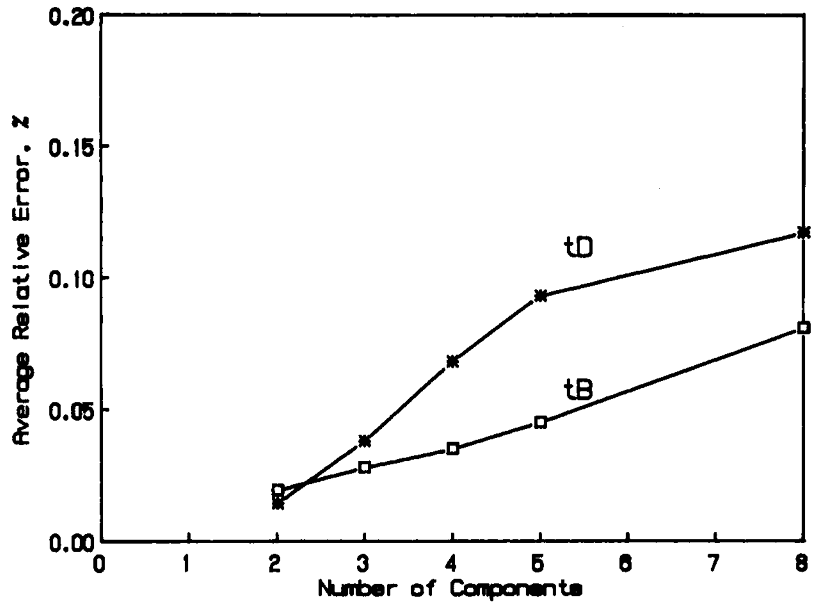

FIG. 4. Average relative error as a function of the number of components for the alkylbenzene mixtures.

conventional methods, and the relative errors, E_B and E_D. The temperature increments Δt_B, calculated using Eq. (1), and Δt_D, calculated using Eq. (3), are also shown for convenience.

The general behavior at atmospheric pressure of both the olefinic series, represented by 100 tested mixtures, and the alkylbenzene series, represented by 84 tested mixtures, is similar to that observed for the paraffinic series investigated in Part I of this work (*1*). This means that the relative error in calculating t_D is slightly higher than that for t_B, and it decreases considerably within each group of mixtures as the number of carbon atoms increases. The relative error increases, however, as the number of components in the mixture increases. This is clearly demonstrated in Figs. 1–5 which represent the average values of the temperature differences, relative errors, and computer CPU time consumption for the tested mixtures in each homologous series.

As can be seen from Figs. 1 and 2, both bubble and dew-point calculations for the olefinic series gave the same level of accuracy for binary, tertiary, quaternary, and 5-component mixtures. For these mixtures the range of the average temperature difference was 0.01–0.16°C, corresponding to an average relative error range of 0.01–0.12%. For olefinic mixtures

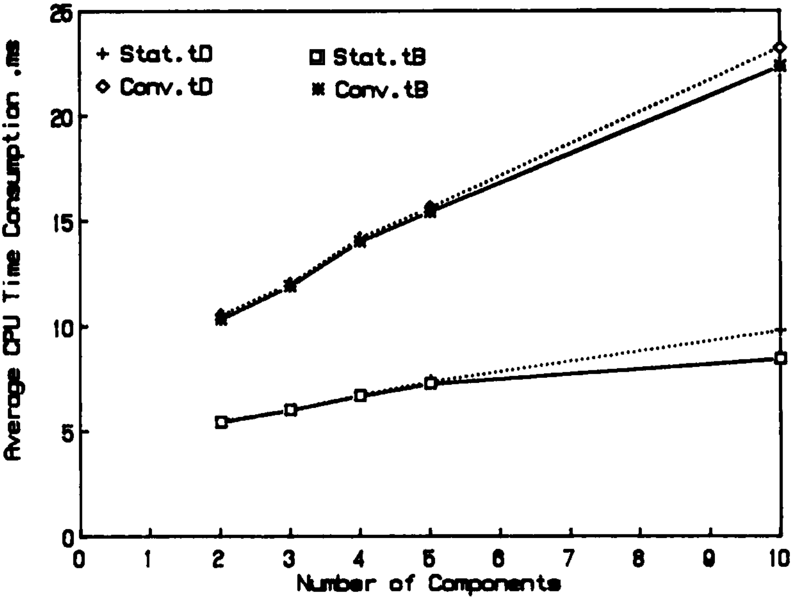

FIG. 5. Average computer CPU time as a function of the number of components at atmospheric pressure.

containing more than 5 components, the relative error increases for both t_B and t_D. Thus, for the twelve 10-component mixtures tested, the average temperature difference was 0.43°C for t_B corresponding to an average relative error of 0.22%, while the corresponding values for t_D were 1.36°C and 0.58%, respectively.

The selected members of the alkylbenzene series behaved more ideally compared to the olefinic series, especially as the number of components increased. As Figs. 3 and 4 clearly show, the average temperature difference for t_B for mixtures containing up to 5 components had a range of 0.02–0.05°C, resulting in an average error range of 0.02–0.04%. For the eight 8-component mixtures investigated in this series, the corresponding values increased to 0.11°C and 0.08%, respectively. The dew-point calculations gave an average temperature difference range of 0.02–0.16°C, corresponding to an average relative error range of 0.01–0.12%, respectively.

The maximum, minimum, and average relative error in calculating both bubble and dew points for the olefinic and alkylbenzene series were consistently higher whenever the lighter components C_6 and C_7 were involved. The same behavior was observed with the paraffinic series [1].

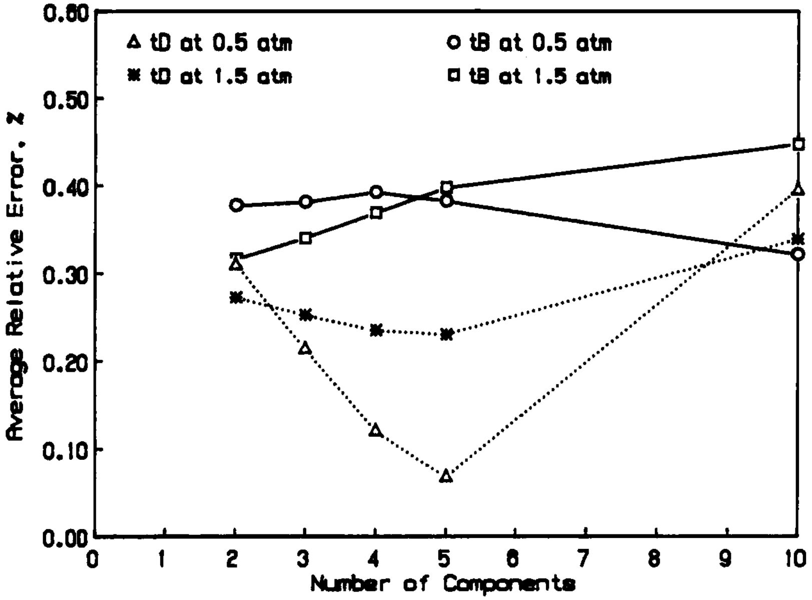

FIG. 6. Average relative error as a function of the number of components for the paraffinic mixtures at a total pressure different from atmospheric.

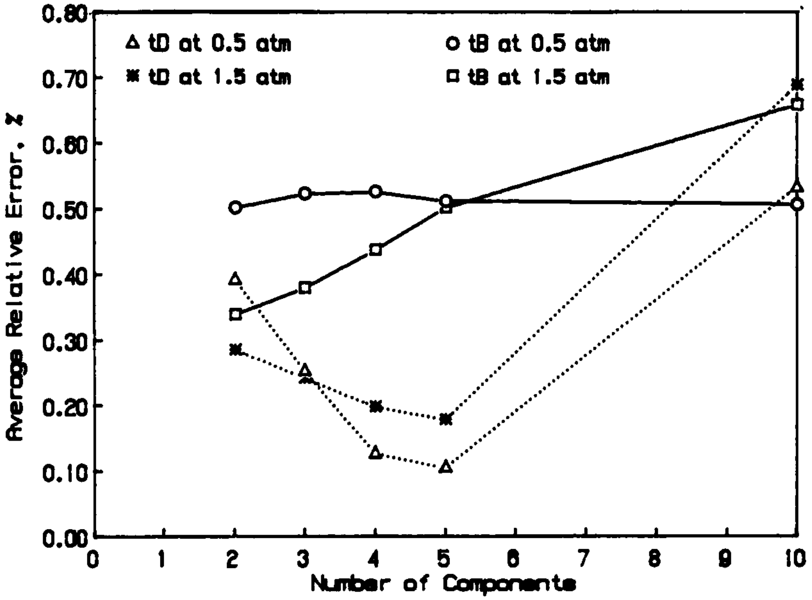

FIG. 7. Average relative error as a function of the number of components for the olefinic mixtures at a total pressure different from atmospheric.

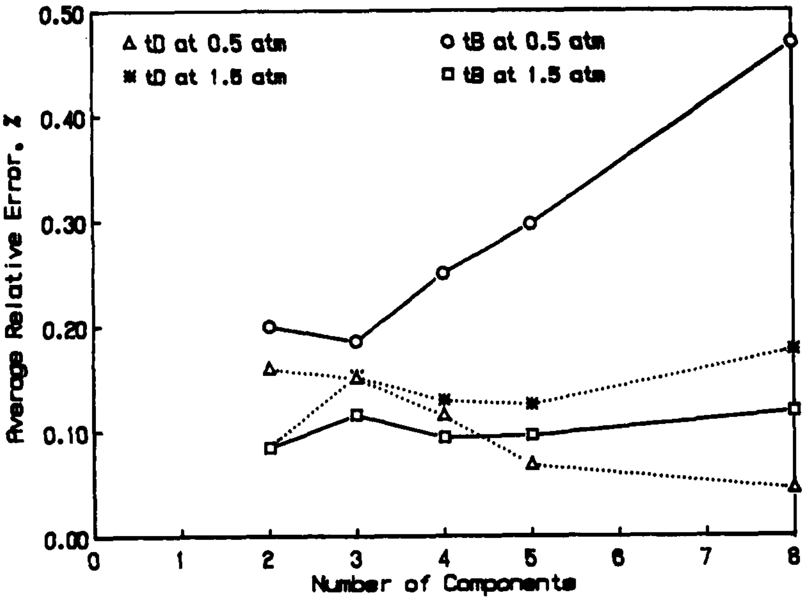

FIG. 8. Average relative error as a function of the number of components for the alkylbenzene mixtures at a total pressure different from atmospheric.

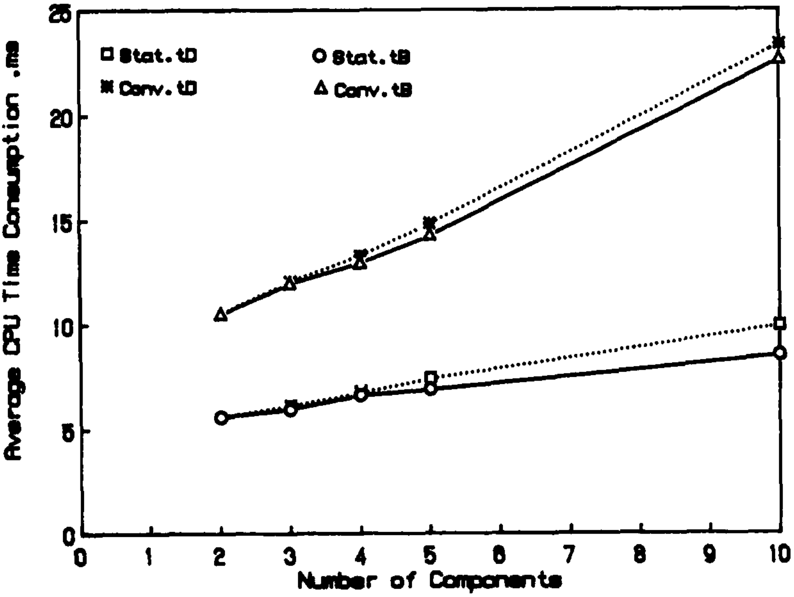

FIG. 9. Average computer CPU time as a function of the number of components at a pressure different from atmospheric.

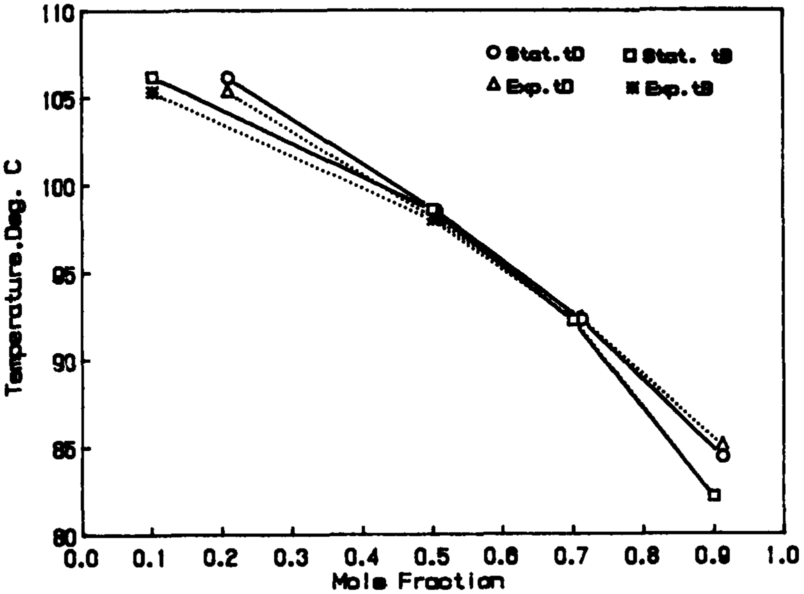

FIG. 10. Statistical and experimental values of bubble and dew points for benzene (1)–toluene (2) mixtures.

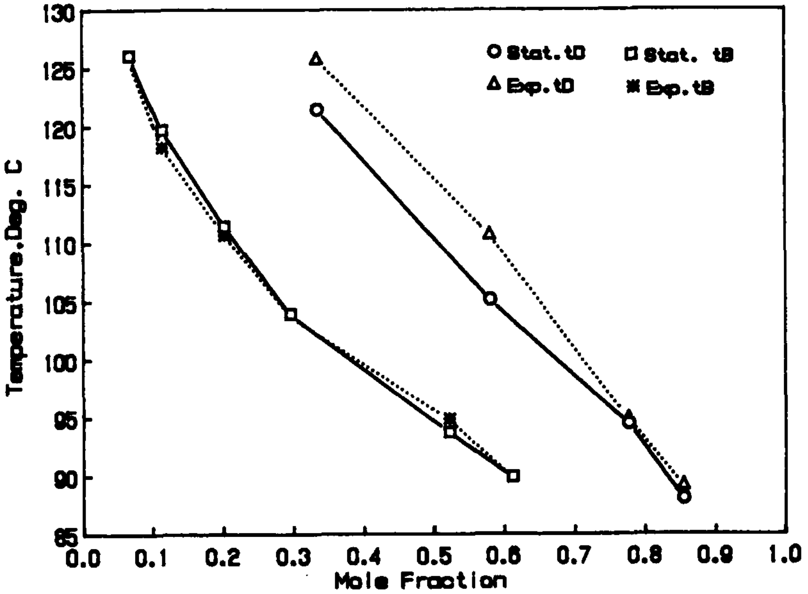

FIG. 11. Statistical and experimental values of bubble and dew points for benzene (1)–toluene (2)–ethylbenzene (3) mixtures.

TABLE 10

Comparison between Computed (statistical and conventional) and Experimental Bubble Points for Binary Hydrocarbon Mixtures at Atmospheric Pressure

	(Statistical – Experimental)		(Conventional – Experimental)		(Statistical – Conventional)	
Mixtures	°C	%	°C	%	°C	%
Benzene (1) *n*-Heptane (2)	1.80	2.09	1.78	2.09	0.02	0.03
Benzene (1) *n*-Octane (2)	1.68	1.75	1.71	1.79	0.05	0.06
n-Hexane (1) Benzene (2)	1.92	2.69	1.93	2.71	0.01	0.01
n-Hexane (1) Toluene (2)	1.92	2.29	1.94	2.31	0.03	0.04
n-Octane (1) Ethylbenzene (2)	1.16	0.90	1.15	0.90	0.01	0.10
n-Heptane (1) Toluene (2)	1.92	1.86	1.91	1.84	0.007	0.007
n-Heptane (1) *n*-Octane (2)	0.30	0.28	0.35	0.31	0.06	0.05

Regarding the validity of the proposed algorithm at total pressures different from atmospheric, a large number of computer runs were performed within a total pressure range of 0.5–1.5 atm. This range was chosen in order not to violate the validity of the pressure range specified for the Antoine constants used in the conventional trial-and-error algorithm. Figures 6–8 display some results of the average relative errors obtained for the paraffinic, olefinic, and the alkylbenzene series, respectively. As can be seen, Eqs. (1) and (3), modified by appropriate pressure correction factors, gave satisfactory results for the total pressure range investigated. The alkylbenzene series gave better results with an average relative error range of 0.05–0.47% at the lower pressures and 0.09–0.18% at the higher pressures. The corresponding values for the olefinic series are 0.39–0.53 and 0.29–0.69%, respectively, while those for the paraffinic series are 0.31–0.40 and 0.27–0.45%, respectively.

Regarding the average computer CPU time consumed, Fig. 9 shows values very similar to those depicted in Fig. 5. Incorporating the Antoine equations specifically developed for the three hydrocarbon series did not increase the CPU time consumed by the proposed algorithm. Both Figs. 5 and 9 clearly show that for mixtures containing up to 5 components, there is practically no difference in the average computer CPU time consumed in calculating t_B and t_D. The difference increases, as expected, with any further increase in the number of components. By using a UNISYS model 1172 mainframe, the average CPU time consumed in computing the bubble and dew points for 10-component mixtures with the statistical noniterative approach are 8.5 and 9.9 ms/mixture, respectively. The corresponding values using the conventional trial-and-error approach are 22.6 and 23.3 ms/mixture. Thus, about 60% of the average computer CPU time can be saved. This saving decreases as the number of components in the mixture decreases, but was always above 46%.

An attempt was made to compare the proposed noniterative method with experimental values for the three hydrocarbon series investigated. A literature search revealed that experimental VLE data are very scarce for these mixtures. Figures 10 and 11 and Table 10 show some results for those mixtures whose VLE data were available in literature.

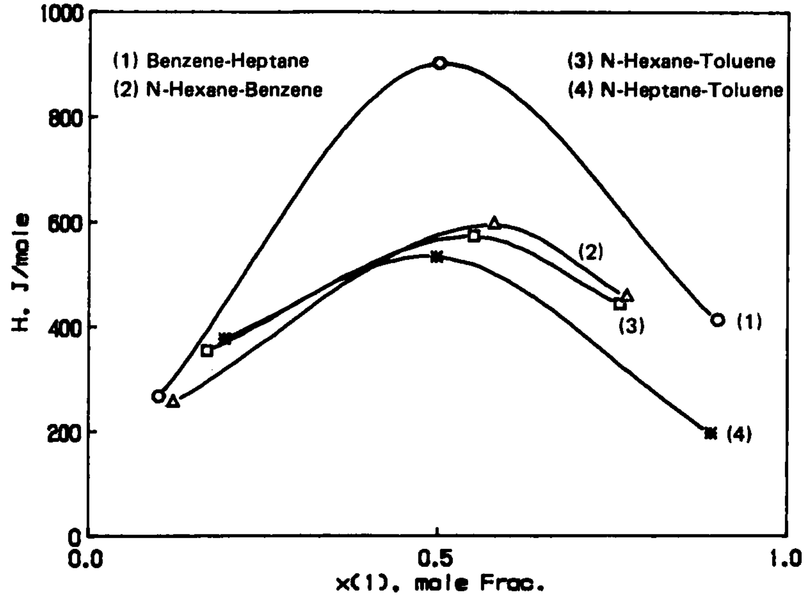

FIG. 12. Heat of mixing for hydrocarbon mixtures, at 25°C, having components from different homologous series.

It can be observed from Fig. 10 that for the binary mixture benzene-toluene, the average relative error over the concentration range investigated did not exceed 0.55%. For the tertiary mixture benzene–toluene–ethylbenzene, shown in Fig. 11, the average relative error was 0.86% for the bubble point and 2.56% for the dew point. It is noteworthy that when the experimental data were compared with those calculated by the conventional trial-and-error method, the same level of accuracy was obtained for both mixtures.

As expected, neither the statistical nor the conventional method gave satisfactory results when mixtures consisting of cross-fertilized components from paraffinic and alkylbenzene series were investigated. This is clearly shown in Table 10 where the accuracy levels of the bubble point calculations are given in terms of average temperature differences and average relative errors. The nonideal behavior of such mixtures can be demonstrated by their heats of mixing at 25°C, which are displayed in Fig. 12.

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