

## LIQUID-VAPOUR EQUILIBRIUM. LIII.\*

## THE SYSTEMS BENZENE-DIISOPROPYL ETHER, DIISOPROPYL ETHER-TOLUENE, DIISOPROPYL ETHER-ETHYLBENZENE, BENZENE-DIPROPYL ETHER, DIPROPYL ETHER-TOLUENE AND DIPROPYL ETHER-ETHYLBENZENE

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Vapour-liquid equilibria have been measured in the systems benzene-diisopropyl ether, diisopropyl ether-toluene, diisopropyl ether-ethylbenzene, benzene-dipropyl ether, dipropyl ether-toluene and dipropyl ether-ethylbenzene at 50, 60 and 70°C. The modified circulation still of the Gillespie type has been used for the measurement. The measured data have been correlated by means of equations expressing the dependence of activity coefficients on the composition of the liquid phase.

As part of a systematic study of thermodynamic properties of binary mixtures whose components belong to various groups of Ewell's classification of liquids<sup>1</sup>, the isothermal vapour-liquid equilibria have been measured in binary systems of aromatic hydrocarbons with two symmetrical ethers.

## EXPERIMENTAL

*Preparation of pure substances and criteria of purity.* Diisopropyl ether, a commercially available reagent (Shell, Holland), was treated with acidified ferrous sulphate solution (to remove peroxides), 0.5%  $\text{KMnO}_4$  (to remove aldehydes), then with 5% NaOH and finally with water. On drying with calcium sulphate, it was twice distilled with sodium on a 40-plate column. Dipropyl ether, a commercially available reagent (Lachema, Brno), was purified in the same way. Benzene (Standard, Urxovy závody, Valašské Meziříčí) was used without further purification. Toluene, an analytical grade reagent (Urxovy závody, Valašské Meziříčí), was freed from sulphur-containing impurities by treating with concentrated  $\text{H}_2\text{SO}_4$ , washed with water, dried with sodium and three times rectified on a 50 plate column<sup>2</sup>. Ethylbenzene, a technical grade reagent (Kaučuk, Kralupy), was twice rectified on a 40 plate column. The comparison of the measured and published values of physical constants of the substances used is given in Table I.

*Apparatus and procedure.* For measuring the vapour-liquid equilibria, a modified Gillespie circulation apparatus<sup>1</sup> was used. Temperature was measured by mercury standards calibrated

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TABLE I  
Physical Constants of Pure Compounds

Compound	Constant	Measured	Published
Diisopropyl ether	$d_4^{20}$ , g/cm <sup>3</sup>	0.72565	0.7257 <sup>3</sup>
	$n_D^{20}$	1.3682	1.36823 <sup>3</sup>
	b.p., °C	68.34	68.293 <sup>3</sup>
Dipropyl ether	$d_4^{20}$ , g/cm <sup>3</sup>	0.75168	0.75178 <sup>4</sup>
	$n_D^{20}$	1.3802	1.3803 <sup>4</sup>
	b.p., °C	89.96	90.14 <sup>4</sup>
Benzene	$d_4^{20}$ , g/cm <sup>3</sup>	0.8790	0.8789—0.8791 <sup>5</sup>
	$n_D^{20}$	1.5011	1.5009—1.50115 <sup>5</sup>
	b.p., °C	80.05	80.07—80.11 <sup>5</sup>
Toluene	$d_4^{20}$ , g/cm <sup>3</sup>	0.8669	0.8669—0.8672 <sup>5</sup>
	$n_D^{20}$	1.4967	1.4966—1.49693 <sup>5</sup>
	b.p., °C	110.625	110.606—110.75 <sup>5</sup>
Ethylbenzene	$d_4^{20}$ , g/cm <sup>3</sup>	0.8670	0.86696—0.8672 <sup>5</sup>
	$n_D^{20}$	1.4959	1.4958—1.49593 <sup>5</sup>
	b.p., °C	136.26	136.1—136.4 <sup>5</sup>

TABLE II  
Refractive Indices of the Binary Solutions of Diisopropyl Ether with Aromatic Hydrocarbons at 20°C

Benzene(1)—diisopropyl ether(2)		Diisopropyl ether(1)—toluene(2)		Diisopropyl ether(1)—ethylbenzene(2)	
$x_1$	$n_D^{20}$	$x_1$	$n_D^{20}$	$x_1$	$n_D^{20}$
0.2322	1.39010	0.1315	1.38215	0.0904	1.48310
0.2423	1.39115	0.2561	1.39105	0.1631	1.47330
0.3174	1.39905	0.2831	1.39905	0.2479	1.46205
0.4652	1.41605	0.4423	1.41805	0.3314	1.45120
0.6060	1.43420	0.4435	1.41815	0.4486	1.43610
0.6435	1.43955	0.5220	1.42805	0.5566	1.42220
0.7387	1.45390	0.6531	1.44530	0.6390	1.41205
0.8078	1.46505	0.7399	1.45730	0.7095	1.40330
0.8538	1.47305	0.8555	1.47410	0.7856	1.39410
		0.9038	1.48130	0.8696	1.38405

by means of a Mueller bridge with platinum resistance thermometer (Leeds and Northrup). The accuracy of the temperature measurements was  $\pm 0.01^\circ\text{C}$ . Pressure was measured indirectly by measuring the boiling point of water in an ebulliometer connected in parallel. The samples of the equilibrium phases were analyzed refractometrically at  $20^\circ\text{C}$ . Refractive indices were measured by an Abbe-type refractometer with an accuracy of  $\pm 0.0001$ . Refractive indices of calibration mixtures (Tables II, III) were found to conform to the equation

$$n_D = x_1 n_{D1} + x_2 n_{D2} + x_1 x_2 (A_1 x_1 + A_2 x_2 - A_3 x_1 x_2), \quad (1)$$

where  $x_1, x_2$  are mole fractions and  $n_{D1}, n_{D2}$  refractive indices of pure compounds 1 and 2, resp.,  $n_D$  is refractive index of the mixture and  $A_1, A_2, A_3$  are empirical constants determined

TABLE III

Refractive Indices of the Binary Solutions of Dipropyl Ether with Aromatic Hydrocarbons at  $20^\circ\text{C}$

Benzene(1)-dipropyl ether(2)		Dipropyl ether(1)-toluene(2)		Dipropyl ether(1)-ethylbenzene(2)	
$x_1$	$n_D^{20}$	$x_1$	$n_D^{20}$	$x_1$	$n_D^{20}$
0.1617	1.39410	0.0785	1.48540	0.0833	1.48490
0.3062	1.40710	0.1611	1.47420	0.1421	1.47830
0.4497	1.42180	0.2329	1.46500	0.2197	1.46910
0.5488	1.43290	0.2918	1.45760	0.3622	1.45200
0.6189	1.44190	0.3701	1.44800	0.4233	1.44540
0.6907	1.45140	0.4970	1.43260	0.5308	1.43280
0.8015	1.46750	0.5716	1.42430	0.5882	1.42570
0.8786	1.47980	0.7195	1.40830	0.6734	1.41610
0.9417	1.49000	0.8204	1.39800	0.7992	1.40240
		0.9138	1.38880	0.8540	1.39620

TABLE IV

Antoine Vapour Pressure Constants

Compound	A	B	C	Ref.
Diisopropyl ether	6.84159	1135.034	218.230	6
Dipropyl ether	6.94461	1254.781	218.820	6
Benzene	6.90565	1211.033	220.790	7
Toluene	6.95334	1343.943	219.377	7
Ethylbenzene	6.95719	1424.255	213.206	7

from experimental data by the least square method. On the basis of Eq. (1), interpolation tables were computed for reading the composition from measured values of refractive indices of the equilibrium mixtures.

TABLE V  
Vapour-Liquid Equilibrium in the Benzene(1)-Diisopropyl Ether(2) System

50°C			60°C			70°C		
$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr
0.065	0.049	407.2	0.171	0.138	563.5	0.053	0.041	799.9
0.120	0.094	402.1	0.210	0.169	556.2	0.122	0.095	784.2
0.169	0.130	396.9	0.249	0.200	549.1	0.169	0.134	775.9
0.190	0.150	395.3	0.288	0.230	541.9	0.191	0.151	773.1
0.258	0.201	387.1	0.317	0.255	538.6	0.261	0.210	756.8
0.289	0.230	384.0	0.363	0.297	529.1	0.290	0.233	753.5
0.343	0.275	378.6	0.451	0.370	513.6	0.352	0.282	740.7
0.416	0.328	369.6	0.495	0.412	506.1	0.423	0.344	727.8
0.451	0.365	367.7	0.553	0.464	496.1	0.458	0.375	721.0
0.533	0.434	358.3	0.575	0.486	490.8	0.535	0.448	705.3
0.586	0.483	353.7	0.624	0.533	483.3	0.589	0.497	694.1
0.666	0.560	342.8	0.706	0.616	465.9	0.666	0.569	678.9
0.728	0.620	337.1	0.929	0.886	411.8	0.728	0.634	663.8
0.844	0.759	312.1	0.988	0.981	393.0	0.842	0.771	620.4
0.915	0.859	293.5	—	—	—	0.915	0.864	589.0
0.963	0.934	282.0	—	—	—	0.967	0.940	566.7
0.992	0.986	273.1	—	—	—	0.992	0.986	553.0

Equation	Order	Temperature	$A_{12}$	$A_{21}$	$D_{12}$	Dev. <sup>a</sup>
Margules	3	50	0.0612	0.0990	—	0.0016
		60	0.0219	0.1144	—	0.0028
		70	0.0426	0.0851	—	0.0015
Margules	4	50	0.0544	0.0924	-0.0206	0.0015
		60	0.0273	0.1194	0.0140	0.0028
		70	0.0492	0.0915	0.0197	0.0015
Wilson	50	50	1.3080	0.5781	—	0.0017
		60	1.7542	0.3295	—	0.0028
		70	1.4627	0.5059	—	0.0015
Alpha	2	50	-0.1651	0.7347	—	0.0034
		60	-0.1760	0.5803	—	0.0017
		70	-0.1741	0.6226	—	0.0028

<sup>a</sup> Mean deviation in the vapour phase composition.

## RESULTS

The mutual dependence of the equilibrium compositions of the liquid and vapour phases in a binary system is given by

$$y_1 = [\alpha_{12}(x_1/x_2)]/[1 + \alpha_{12}(x_1/x_2)], \quad y_2 = 1/[1 + \alpha_{12}(x_1/x_2)], \quad (2a, b)$$

TABLE VI  
Vapour-Liquid Equilibrium in the Diisopropyl Ether(1)-Toluene(2) System

50°C			60°C			70°C		
$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr
0.057	0.228	113.9	0.044	0.171	161.7	0.044	0.163	234.4
0.080	0.298	122.5	0.085	0.292	183.2	0.060	0.213	245.6
0.108	0.371	133.5	0.190	0.501	234.9	0.086	0.281	264.9
0.193	0.518	161.5	0.260	0.589	268.8	0.186	0.478	333.2
0.248	0.592	181.8	0.280	0.610	278.3	0.266	0.577	382.6
0.287	0.638	193.2	0.302	0.635	288.5	0.270	0.585	384.1
0.298	0.648	198.7	0.380	0.708	324.4	0.290	0.607	398.3
0.380	0.718	226.1	0.447	0.753	352.6	0.378	0.692	451.4
0.448	0.766	245.9	0.548	0.815	395.9	0.436	0.733	485.1
0.549	0.825	278.0	0.599	0.842	417.7	0.535	0.797	543.5
0.600	0.851	292.9	0.711	0.896	463.5	0.603	0.833	578.1
0.807	0.938	357.9	0.810	0.933	506.1	0.800	0.933	695.9
0.892	0.965	386.1	0.892	0.964	547.4	0.888	0.962	753.0

Equation	Order	Temperature	$A_{12}$	$A_{21}$	$D_{12}$	Dev. <sup>a</sup>
Margules	3	50	0.1049	-0.0589	—	0.0059
		60	0.1178	-0.0647	—	0.0079
		70	0.1011	-0.0858	—	0.0069
Margules	4	50	0.0691	-0.1194	-0.1568	0.0038
		60	0.0596	-0.1477	-0.2140	0.0057
		70	0.0450	-0.1776	-0.2366	0.0043
Wilson		50	0.2092	2.1580	—	0.0081
		60	0.1864	2.1832	—	0.0101
		70	0.1847	2.2668	—	0.0096
Alpha	2	50	3.6848	-0.5898	—	0.0046
		60	3.3086	-0.5962	—	0.0035
		70	3.0173	-0.5856	—	0.0052

<sup>a</sup> Mean deviation in the vapour phase composition.

where  $x_1, x_2$  are mole fractions of the components 1, 2 in the liquid phase and  $y_1, y_2$  those in the vapour phase. The relative volatility  $\alpha_{12}$  is defined by

$$\alpha_{12} = (y_1/y_2)/(x_1/x_2), \quad (3)$$

TABLE VII  
Vapour-Liquid Equilibrium in the Diisopropyl Ether(1)-Ethylbenzene(2) System

50°C			60°C			70°C		
$x_1$	$y_1$	$P, \text{Torr}$	$x_1$	$y_1$	$P, \text{Torr}$	$x_1$	$y_1$	$P, \text{Torr}$
0.050	0.411	58.2	0.048	0.345	83.3	0.063	0.393	137.7
0.075	0.517	71.0	0.067	0.432	96.7	0.069	0.406	139.3
0.085	0.527	72.8	0.077	0.470	102.1	0.120	0.559	184.1
0.142	0.646	96.2	0.130	0.608	133.5	0.126	0.580	187.6
0.155	0.656	100.2	0.209	0.728	176.5	0.255	0.743	285.2
0.281	0.785	151.0	0.268	0.777	210.4	0.336	0.803	343.0
0.360	0.820	183.0	0.471	0.884	318.1	0.457	0.867	430.2
0.399	0.840	197.1	0.560	0.915	367.0	0.549	0.901	497.4
0.479	0.878	225.1	0.662	0.943	417.9	0.663	0.933	569.3
0.574	0.919	261.4	0.738	0.958	457.1	0.740	0.951	628.0
0.672	0.948	296.4	0.827	0.974	504.1	0.805	0.972	683.6
0.745	0.961	325.9	0.903	0.984	544.8	0.901	0.984	748.8
0.845	0.977	364.3	0.949	0.992	565.0	0.977	0.998	809.4
0.900	0.986	388.9	0.977	0.999	585.2	—	—	—
0.950	0.993	401.5	—	—	—	—	—	—
0.977	0.999	411.0	—	—	—	—	—	—

  

Equation	Order	Temperature	$A_{12}$	$A_{21}$	$D_{12}$	Dev. <sup>a</sup>
Margules	3	50	0.1593	-0.4147	—	0.0077
		60	0.0778	-0.1561	—	0.0085
		70	0.0917	-0.2137	—	0.0084
Margules	4	50	0.1015	-0.5435	-0.3379	0.0059
		60	0.0096	-0.3149	-0.4018	0.0042
		70	-0.0079	-0.4344	-0.5729	0.0050
Wilson		50	0.2359	2.2362	—	0.0164
		60	0.1819	2.4110	—	0.0100
		70	0.0738	2.7621	—	0.0135
Alpha	2	50	9.7521	-0.5935	—	0.0179
		60	9.3481	-0.7417	—	0.0046
		70	8.1391	-0.7131	—	0.0067

<sup>a</sup> Mean deviation in the vapour phase composition.

TABLE VIII  
Vapour-Liquid Equilibrium in the Benzene(1)-Dipropyl Ether(2) System

50°C			60°C			70°C		
$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr
0.039	0.051	187.48	0.058	0.078	282.62	0.060	0.085	408.80
0.118	0.161	195.51	0.059	0.082	281.78	0.080	0.105	412.86
0.223	0.284	204.95	0.151	0.201	293.53	0.104	0.140	415.81
0.249	0.318	207.54	0.181	0.244	296.22	0.128	0.174	422.63
0.292	0.372	211.79	0.293	0.365	312.39	0.166	0.219	429.39
0.364	0.447	217.89	0.313	0.384	313.23	0.175	0.231	431.31
0.440	0.530	224.68	0.352	0.430	319.69	0.216	0.274	438.43
0.514	0.594	230.23	0.400	0.484	323.92	0.245	0.311	444.09
0.565	0.634	234.37	0.465	0.554	331.86	0.248	0.317	441.95
0.600	0.677	236.35	0.478	0.563	334.03	0.345	0.422	460.74
0.666	0.735	241.29	0.518	0.604	338.50	0.415	0.487	468.15
0.707	0.768	244.43	0.614	0.691	348.78	0.433	0.513	474.79
0.726	0.783	246.67	0.643	0.714	352.76	0.465	0.537	479.47
0.762	0.814	248.68	0.661	0.724	353.62	0.525	0.603	488.86
0.822	0.860	253.32	0.725	0.779	360.17	0.546	0.620	492.62
0.863	0.895	256.15	0.753	0.800	364.41	0.580	0.652	496.51
0.900	0.923	258.46	0.780	0.822	366.87	0.606	0.674	500.17
0.934	0.956	261.24	0.812	0.851	370.26	0.619	0.688	498.39
0.965	0.971	262.35	0.848	0.878	373.84	0.637	0.700	502.90
0.979	0.985	263.35	0.895	0.918	377.96	0.719	0.773	513.27
—	—	—	0.925	0.940	380.69	0.720	0.774	515.32
—	—	—	0.960	0.969	384.51	0.828	0.860	526.48
—	—	—	—	—	—	0.883	0.903	533.21
—	—	—	—	—	—	0.940	0.952	540.64
—	—	—	—	—	—	0.957	0.967	543.10
—	—	—	—	—	—	0.979	0.984	544.84

Equation	Order	Temperature	$A_{12}$	$A_{21}$	$D_{12}$	Dev. <sup>a</sup>
Margules	3	50	0.0357	-0.0010	—	0.0040
		60	0.0289	0.0192	—	0.0042
		70	0.0328	0.0027	—	0.0028
Margules	4	50	0.0412	0.0042	0.0157	0.0040
		60	0.0439	0.0350	0.0463	0.0041
		70	0.0332	0.0031	0.0011	0.0028
Wilson	50	50	0.3925	1.8050	—	0.0039
		60	0.6487	1.3591	—	0.0042
		70	0.4492	1.6981	—	0.0029
Alpha	2	50	0.4425	-0.2508	—	0.0019
		60	0.4545	-0.2293	—	0.0032
		70	0.4232	-0.2153	—	0.0021

<sup>a</sup> Mean deviation in the vapour phase composition.

and for a low pressure region the relation holds

$$\alpha_{12} = (\gamma_1/\gamma_2)(P_1^0/P_2^0) \quad (* \text{ g}) \quad (4)$$

TABLE IX  
Vapour-Liquid Equilibrium in the Dipropyl Ether(1)-Toluene(2) System

50°C			60°C			70°C		
$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr	$x_1$	$y_1$	$P$ , Torr
0.033	0.060	92.75	0.033	0.065	141.52	0.033	0.065	209.27
0.039	0.076	93.79	0.039	0.076	142.48	0.039	0.073	210.29
0.045	0.081	94.06	0.045	0.081	143.15	0.045	0.081	212.01
0.098	0.179	100.04	0.103	0.184	152.15	0.103	0.187	225.69
0.134	0.238	103.81	0.134	0.233	157.29	0.134	0.235	230.33
0.160	0.281	106.61	0.164	0.286	163.34	0.149	0.256	234.01
0.193	0.327	109.86	0.193	0.312	165.99	0.186	0.312	243.23
0.230	0.360	112.89	0.238	0.377	172.36	0.246	0.382	253.88
0.249	0.391	114.65	0.255	0.389	174.75	0.260	0.405	257.69
0.312	0.453	122.10	0.319	0.468	183.80	0.310	0.463	265.86
0.385	0.540	128.61	0.394	0.549	194.21	0.400	0.557	285.59
0.457	0.611	134.95	0.457	0.607	202.87	0.450	0.611	295.18
0.538	0.684	142.98	0.541	0.681	215.76	0.541	0.694	314.91
0.592	0.723	147.40	0.586	0.716	220.48	0.584	0.722	319.82
0.690	0.799	156.38	0.695	0.792	234.22	0.695	0.801	341.06
0.812	0.882	167.77	0.810	0.879	249.22	0.810	0.882	361.04
0.872	0.919	173.30	0.880	0.922	257.58	0.880	0.930	373.46
0.954	0.972	179.60	0.954	0.972	267.50	0.953	0.972	386.40
0.980	0.985	182.02	0.982	0.985	272.06	0.981	0.985	394.16

  

Equation	Order	Temperature	$A_{12}$	$A_{21}$	$D_{12}$	Dev. <sup>a</sup>
Margules	3	50	0.0705	-0.0966	—	0.0096
		60	0.0726	-0.0736	—	0.0094
		70	0.0357	-0.0165	—	0.0048
Margules	4	50	0.0475	-0.1262	-0.0856	0.0090
		60	0.0338	-0.1233	-0.1440	0.0084
		70	0.0237	-0.0322	-0.0453	0.0046
Wilson		50	0.1482	2.4295	—	0.0121
		60	0.1752	2.3258	—	0.0109
		70	0.3543	1.9071	—	0.0049
Alpha	2	50	1.0017	-0.3749	—	0.0035
		60	0.9982	-0.3474	—	0.0027
		70	0.9928	-0.4071	—	0.0025

<sup>a</sup> Mean deviation in the vapour phase composition.



where  $P_1^0$  and  $P_2^0$  denote the vapour pressures of pure components 1, 2 at a given temperature,  $\gamma_1, \gamma_2$  their activity coefficients and the symbol (\*g) indicates the ideal behaviour of the vapour phase. The temperature dependence of the vapour pressures of pure compounds  $P^0$  (Torr) in a form of the Antoine equation

$$\log P^0 = A - B/(t + C), \quad (5)$$

$t$  is temperature ( $^{\circ}\text{C}$ ) and  $A, B, C$  are constants, was taken over from the literature (Table IV).

TABLE X  
Vapour-Liquid Equilibrium in the Dipropyl Ether(1)-Ethylbenzene(2) System

50°C			60°C			70°C		
$x_1$	$y_1$	$P, \text{Torr}$	$x_1$	$y_1$	$P, \text{Torr}$	$x_1$	$y_1$	$P, \text{Torr}$
0.031	0.124	40.2	0.027	0.111	61.3	0.027	0.090	92.6
0.071	0.247	47.6	0.068	0.247	71.8	0.108	0.342	125.4
0.148	0.466	60.0	0.139	0.439	89.0	0.134	0.416	131.0
0.207	0.554	69.3	0.195	0.527	102.1	0.130	0.404	129.6
0.440	0.787	105.4	0.240	0.587	112.5	0.189	0.517	149.1
0.552	0.855	121.6	0.432	0.778	154.7	0.526	0.828	253.4
0.631	0.879	133.7	0.538	0.834	176.8	0.607	0.870	279.1
0.713	0.909	147.0	0.622	0.872	194.6	0.696	0.897	306.2
0.776	0.934	156.5	0.708	0.906	214.2	0.766	0.934	328.6
0.851	0.985	167.4	0.773	0.927	228.7	0.842	0.953	350.9
0.916	0.974	178.1	0.845	0.956	244.9	0.912	0.974	372.9
—	—	—	0.961	0.990	270.2	0.961	0.985	387.8

  

Equation	Order	Temperature	$A_{12}$	$A_{21}$	$D_{12}$	Dev. <sup>a</sup>
Margules	3	50	0.0542	-0.1338	—	0.0190
		60	0.0630	-0.1394	—	0.0132
		70	0.0202	-0.0410	—	0.0108
Margules	4	50	-0.1419	-0.3690	-0.7636	0.0121
		60	-0.0807	-0.3337	-0.5759	0.0080
		70	-0.1471	-0.1778	-0.6225	0.0058
Wilson		50	0.1618	2.4823	—	0.0223
		60	0.1305	2.5462	—	0.0160
		70	0.1010	2.6064	—	0.0162
Alpha	2	50	3.9428	-0.6975	—	0.0064
		60	3.8013	-0.6737	—	0.0048
		70	3.5891	-0.7038	—	0.0054

<sup>a</sup> Mean deviation in the vapour phase composition.

The concentration dependence of the activity coefficients was expressed by the relations<sup>1,8</sup>:

Margules 3rd order

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 (A_{12} - A_{21}), \quad (6)$$

Margules 4th order

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 [A_{12} - A_{21} + (x_2 - x_1) D_{12}], \quad (7)$$

Wilson

$$\ln(\gamma_1/\gamma_2) = \ln(x_2 + A_{21}x_1)/(x_1 + A_{12}x_2) + A_{12}/(x_1 + x_2 A_{12}) + \\ - A_{21}/(x_1 A_{21} + x_2), \quad (8)$$

and expansion of relative volatility 2nd order

$$\alpha_{12} = (1 + A_{12}x_2)/(1 + A_{21}x_1), \quad (9)$$

where  $A_{12}$ ,  $A_{21}$ ,  $D_{12}$  are constants characteristic for the given binary mixture and evaluated by means of the least square method using the statistical weight<sup>9</sup>. The experimental vapour-liquid equilibrium data, the constants of the above-mentioned equations and mean deviations of the calculated and experimental values are given in Tables V-X.

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