

LIQUID-VAPOUR EQUILIBRIUM. XLVII.*
THE SYSTEM CYCLOHEXANE-1-HEXANOL

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In a connection with a more detailed study of the vapour-liquid phase equilibria in binary systems alcohol-cyclohexane¹⁻⁵, the isothermal equilibrium at 50, 60, 70 and 81.2°C, as well as the isobaric equilibrium at 70 and 100 Torr have been measured for the system cyclohexane-1-hexanol.

EXPERIMENTAL

Purification of Substances

Cyclohexane. The reagent grade chemical was purified by rectification on a forty-plate bubble-cup column. Formaldehyde test for benzene was negative. *1-Hexanol.* The reagent grade chemical was purified by the vacuum distillation at 30 Torr on a 1.5 m long column packed by stainless

TABLE I
Physical Constants of Pure Substances

Component	Reference	B.p., °C	n_D^{25}	d_4^{20}	d_4^{25}
Cyclohexane	9,10	80.70—80.85	1.42354—1.42358	0.7783—0.77853	—
	this work	80.8	1.42354	0.77831	—
1-Hexanol	16	157.5	1.41607	—	0.81531
	this work	157.38	1.4161	—	0.81526

TABLE II
Constants of the Antoine Equation

Component	A	B	C
Cyclohexane	6.85875	1 212.014	223.956
1-Hexanol	8.16353	1 903.290	205.046

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TABLE III

Vapour-Liquid Equilibrium in the System Cyclohexane(1)-1-Hexanol(2) at 50°C

Experimental				$(y_{\text{exp}} - y_{\text{calc}})$			
x_1	y_1	P	$\log(y_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.9238	0.9908	265.5	-0.761	-0.0008	-0.0012	-0.0013	-0.0008
0.8987	0.9898	263.0	-0.671	-0.0004	-0.0005	-0.0006	-0.0002
0.8360	0.9875	258.0	-0.520	-0.0002	0.0001	0.0001	0.0000
0.7947	0.9853	254.8	-0.472	-0.0012	-0.0009	-0.0008	-0.0011
0.7471	0.9842	249.0	-0.387	-0.0014	-0.0010	-0.0009	-0.0014
0.6495	0.9819	238.4	-0.245	-0.0022	-0.0022	-0.0021	-0.0024
0.6475	0.9819	235.7	-0.241	-0.0022	-0.0022	-0.0021	-0.0024
0.5190	0.9830	215.9	0.016	0.0006	-0.0001	-0.0001	0.0002
0.4989	0.9842	214.9	0.084	0.0020	0.0013	0.0013	0.0017
0.4317	0.9808	199.8	0.114	-0.0004	-0.0014	-0.0014	-0.0007
0.2996	0.9787	163.3	0.315	0.0005	-0.0004	-0.0006	0.0006
0.2607	0.9697	148.3	0.241	-0.0071	-0.0078	-0.0079	-0.0069
0.1505	0.9608	100.5	0.422	-0.0080	-0.0067	-0.0067	-0.0074
<i>Mean deviation</i>				<i>0.0021</i>	<i>0.0020</i>	<i>0.0020</i>	<i>0.0020</i>
Constants of correlation equations							
		A_{12}	A_{21}	D			
Wilson		0.3602	0.2102				
Laar 2		0.6706	0.8659				
Margules 3		0.6590	0.8514				
Margules 4		0.7703	0.9208	0.3246			

TABLE IV

Vapour-Liquid Equilibrium in the System Cyclohexane(1)-1-Hexanol(2) at 60°C

Experimental				$(y_{\text{exp}} - y_{\text{calc}})$			
x_1	y_1	P	$\log(y_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.9632	0.9915	384.6	-0.929	-0.0014	-0.0020	-0.0027	-0.0009
0.8770	0.9853	374.7	-0.606	-0.0014	-0.0009	-0.0011	-0.0008
0.7697	0.9830	359.2	-0.342	-0.0007	-0.0001	0.0007	-0.0011
0.7651	0.9819	358.8	-0.358	-0.0017	-0.0011	0.0003	-0.0021
0.6667	0.9808	343.4	-0.173	-0.0009	-0.0009	-0.0001	-0.0016
0.5672	0.9775	320.8	-0.061	-0.0023	-0.0029	-0.0022	-0.0022
0.5648	0.9764	319.2	-0.078	-0.0034	-0.0040	-0.0032	-0.0033
0.4679	0.9743	293.2	0.052	-0.0031	-0.0041	-0.0038	-0.0015

TABLE IV
 (Continued)

Experimental				$(y_{\text{exp}} - y_{\text{calc}})$			
x_1	y_1	P	$\log(\gamma_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.3982	0.9708	269.4	0.117	-0.0043	-0.0054	-0.0055	-0.0015
0.3623	0.9719	253.3	0.200	-0.0017	-0.0028	-0.0030	0.0017
0.2920	0.9643	222.6	0.230	-0.0053	-0.0061	-0.0067	-0.0013
0.2116	0.9553	176.8	0.312	-0.0067	-0.0065	-0.0075	-0.0039
0.1500	0.9463	138.6	0.409	-0.0044	-0.0026	-0.0037	-0.0054
0.1322	0.9366	124.8	0.395	-0.0090	-0.0065	-0.0075	-0.0120
<i>Mean deviation</i>				0.0033	0.0033	0.0034	0.0028
Constants of correlation equations		A_{12}	A_{21}	D			
Wilson		0.5928	0.1407				
Laar 2		0.5341	0.9226				
Margules 3		0.5236	0.8455				
Margules 4		0.8312	1.0319	0.9568			

steel helices. The measured physical constants of the pure substances were in good agreement with published data (see Table I).

Apparatus and Analytical Method

The Gillespie-type circulation still, as modified by Otsuki and Williams was used for measurements. Temperature was measured by means of a calibrated platinum resistance thermometer. Its resistance was determined by a Wheatstone bridge MLL, Metra Blansko, which was tempered by an air thermostat. For indicating the zero position, a galvanometer DG 20, Metra Blansko was used.

Pressure was measured by the closed manometer with a firmly adjustable mercury level in one arm⁶. The height of the mercury level was read off by means of a cathetometer with an accuracy of ± 0.1 mm.

The composition of equilibrium mixtures was determined by measuring dielectric constants by a dielectrometer in resonant connection. The composition of the mixtures was then read from a calibration curve. The maximum error of the method amounted to ± 0.05 per cent.

RESULTS

The measured isothermal and isobaric values on the vapour-liquid equilibrium were correlated by the second order van Laar equation⁷, the third and fourth order Margules equations⁷ and by the Wilson equation⁸. The equilibrium data together with the deviations of the experimental and calculated values of mole fractions in the vapour phase and the values of constants of the correlation equations are summarized in Tables III–VIII.

TABLE V
Vapour-Liquid Equilibrium in the System Cyclohexane(1)-1-Hexanol(2) at 70°C

Experimental				$(y_{\text{exp}} - y_{\text{calc}})$			
x_1	y_1	P	$\log(\gamma_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.9954	0.9975	543.9	-1.190	0.0004	-0.0000	-0.0008	-0.0003
0.9842	0.9908	538.5	-1.218	-0.0021	-0.0022	-0.0037	-0.0026
0.9675	0.9897	538.1	-0.947	-0.0003	0.0008	-0.0003	0.0007
0.9398	0.9897	526.8	-0.667	0.0018	0.0039	0.0050	0.0046
0.8795	0.9875	515.2	-0.423	0.0017	0.0033	0.0083	0.0044
0.7200	0.9852	493.5	-0.045	0.0032	0.0021	0.0069	0.0015
0.6893	0.9798	474.4	-0.119	-0.0014	-0.0028	0.0012	-0.0036
0.5604	0.9775	436.7	0.072	0.0006	-0.0014	-0.0014	-0.0020
0.3727	0.9632	360.7	0.180	-0.0024	-0.0039	-0.0101	-0.0003
0.3143	0.9597	317.4	0.250	0.0001	-0.0007	-0.0088	0.0047
0.1882	0.9367	225.7	0.335	0.0021	0.0044	-0.0066	0.0099
0.1586	0.9250	196.0	0.345	0.0015	0.0052	-0.0056	0.0082
0.0990	0.8868	131.6	0.379	0.0035	0.0121	0.0045	0.0015
0.0592	0.8288	99.1	0.411	0.0095	0.0248	0.0256	-0.0098
0.0588	0.8319	95.2	0.424	0.0136	0.0290	0.0299	-0.0060
<i>Mean deviation</i>				<i>0.0030</i>	<i>0.0064</i>	<i>0.0079</i>	<i>0.0040</i>
Constants of correlation equations		A_{12}	A_{21}	D			
Wilson		1.0149	0.0452				
Laar 2		0.3517	1.2281				
Margules 3		0.2887	1.0513				
Margules 4		0.5748	1.1645	1.3113			

TABLE VI
Vapour-Liquid Equilibrium in the System Cyclohexane(1)-1-Hexanol(2) at 81.2°C

Experimental				$(y_{\text{exp}} - y_{\text{calc}})$			
x_1	y_1	P	$\log(\gamma_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.9103	0.9808	741.9	-0.627	-0.0021	-0.0025	-0.0030	-0.0020
0.8755	0.9798	732.3	-0.491	0.0001	0.0002	-0.0001	0.0005
0.8204	0.9743	716.1	-0.411	-0.0018	-0.0012	-0.0011	-0.0012
0.7351	0.9720	692.0	-0.234	-0.0000	0.0007	0.0013	0.0004
0.6838	0.9687	672.8	-0.176	-0.0012	-0.0007	0.0000	-0.0011

TABLE VI
 (Continued)

Experimental				$(y_{\text{exp}} - y_{\text{calc}})$			
x_1	y_1	P	$\log(\gamma_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.6226	0.9675	651.1	-0.076	0.0001	0.0003	0.0009	-0.0000
0.5625	0.9632	621.3	-0.025	-0.0016	-0.0017	-0.0013	-0.0019
0.4793	0.9575	574.5	0.053	-0.0030	-0.0035	-0.0034	-0.0032
0.4526	0.9575	557.1	0.099	-0.0013	-0.0020	-0.0020	-0.0015
0.4348	0.9564	548.9	0.119	-0.0012	-0.0019	-0.0021	-0.0014
0.3926	0.9542	519.7	0.171	-0.0003	-0.0010	-0.0014	-0.0002
0.3112	0.9474	457.2	0.261	0.0013	0.0006	0.0000	0.0018
0.2967	0.9432	436.5	0.254	-0.0010	-0.0016	-0.0016	-0.0004
0.2665	0.9376	412.9	0.275	-0.0020	-0.0024	-0.0030	-0.0012
0.2450	0.9366	397.2	0.316	0.0010	0.0008	0.0002	0.0019
0.1992	0.9204	336.4	0.323	-0.0043	-0.0038	-0.0042	-0.0032
0.1775	0.9148	312.4	0.351	-0.0028	-0.0019	-0.0020	-0.0017
0.1003	0.8590	215.1	0.389	-0.0117	-0.0075	-0.0055	-0.0116
<i>Mean deviation</i>				<i>0.0020</i>	<i>0.0019</i>	<i>0.0019</i>	<i>0.0019</i>
Constants of correlation equations							
	A_{12}	A_{21}	D				
Wilson	0.6891	0.1879					
Laar 2	0.4792	0.7729					
Margules 3	0.4537	0.7229					
Margules 4	0.5340	0.8037	0.2846				

 TABLE VII
 Vapour-Liquid Equilibrium in the System Cyclohexane(1)-1-Hexanol(2) at 70 Torr

Experimental				$y_{\text{exp}} - y_{\text{calc}}$			
x_1	y_1	$T, ^\circ\text{C}$	$\log(\gamma_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.9708	0.9964	18.30	-1.283	-0.0020	-0.0008	-0.0016	-0.0008
0.9608	0.9953	18.45	-1.264	-0.0028	-0.0013	-0.0021	-0.0014
0.8604	0.9952	18.90	-0.666	-0.0016	-0.0003	0.0002	-0.0005
0.7871	0.9942	19.60	-0.515	-0.0021	-0.0014	-0.0005	-0.0018
0.7265	0.9942	20.00	-0.364	-0.0017	-0.0016	-0.0006	-0.0020
0.6211	0.9943	20.85	-0.132	-0.0009	-0.0014	-0.0007	-0.0017
0.5762	0.9942	21.70	-0.044	-0.0006	-0.0013	-0.0007	-0.0015

TABLE VII
 (Continued)

Experimental				$(y_{\text{exp}} - y_{\text{calc}})$			
x_1	y_1	$T, ^\circ\text{C}$	$\log(\gamma_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.4808	0.9908	23.30	-0.052	-0.0029	-0.0039	-0.0038	-0.0038
0.3936	0.9864	25.65	-0.031	-0.0056	-0.0070	-0.0073	-0.0062
0.2995	0.9842	29.20	0.141	-0.0045	-0.0063	-0.0073	-0.0046
0.2951	0.9842	29.70	0.158	-0.0041	-0.0060	-0.0070	-0.0043
0.2052	0.9759	35.50	0.270	-0.0048	-0.0073	-0.0093	-0.0046
0.1206	0.9563	46.70	0.437	-0.0000	-0.0039	-0.0075	-0.0021
0.0943	0.9377	52.35	0.469	0.0015	-0.0032	-0.0075	-0.0039
0.0564	0.8780	63.30	0.526	0.0099	0.0036	-0.0017	-0.0092
0.0311	0.7430	75.40	0.538	0.0140	0.0065	0.0021	-0.0325
0.0053	0.2535	90.40	0.543	0.0035	0.0050	0.0050	-0.0609
<i>Mean deviation</i>				0.0039	0.0035	0.0038	0.0083
Constants of correlation equations				D			
	A_{12}	A_{21}					
Wilson	0.7280	0.0960					
Laar 2	0.5370	1.3683					
Margules 3	0.5305	1.1358					
Margules 4	0.6860	1.3470		1.1872			

Activity coefficients of the components were calculated from the relation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - \gamma_i^1)(P - P_i^0)}{RT} \quad (1)$$

The temperature dependence of the molar volumes γ_i^1 of both pure components was expressed as a quadratic relation, using the tabular data^{9,10}. Second virial coefficients of cyclohexane were taken from Hajjar's paper¹¹. For the purpose of calculating, their temperature dependence was changed into the analytical form

$$B_{ii} = A - B/T^2 \quad (2)$$

Second virial coefficients of hexanol were estimated using the relation proposed by Pitzer¹². For this estimation, critical values given by Jefremov¹³ were used.

The constants of the Antoine equation for cyclohexane¹⁴ and hexanol¹⁵ were taken over from the literature and are given in Table II.

Consistency of the measured data in the binary mixtures was checked by using the relation proposed by Redlich and Kister,

TABLE VIII
Vapour-Liquid Equilibrium in the System Cyclohexane(1)-1-Hexanol(2) at 100 Torr

Experimental				$y_{\text{exp}} - y_{\text{calc}}$			
x_1	y_1	$T, ^\circ\text{C}$	$\log(\gamma_1/\gamma_2)$	Wilson	Laar 2	Marg 3	Marg 4
0.9708	0.9954	25.70	-1.262	-0.0014	-0.0020	-0.0028	-0.0021
0.8724	0.9942	26.60	-0.662	-0.0013	-0.0005	-0.0006	-0.0008
0.7458	0.9942	27.50	-0.280	-0.0006	-0.0002	0.0007	-0.0006
0.7074	0.9928	27.95	-0.283	-0.0017	-0.0015	-0.0005	-0.0019
0.6293	0.9920	28.80	-0.162	-0.0019	-0.0019	-0.0010	-0.0022
0.5238	0.9897	30.40	-0.060	-0.0029	-0.0033	-0.0027	-0.0032
0.4803	0.9863	31.40	-0.094	-0.0056	-0.0061	-0.0056	-0.0057
0.4065	0.9842	33.60	0.007	-0.0058	-0.0065	-0.0063	-0.0055
0.3956	0.9831	34.05	0.004	-0.0066	-0.0072	-0.0071	-0.0061
0.2977	0.9798	37.90	0.171	-0.0055	-0.0062	-0.0067	-0.0040
0.1963	0.9687	45.45	0.322	-0.0048	-0.0051	-0.0068	-0.0020
0.1853	0.9675	46.85	0.355	-0.0034	-0.0037	-0.0055	-0.0005
0.1367	0.9486	53.60	0.394	-0.0053	-0.0046	-0.0076	-0.0025
0.0844	0.9103	63.90	0.496	0.0022	0.0061	0.0009	0.0015
0.0610	0.8492	70.90	0.473	-0.0083	-0.0009	-0.0076	-0.0147
0.0433	0.7822	77.90	0.511	-0.0016	0.0106	0.0025	-0.0169
0.0047	0.1643	100.00	0.450	-0.0321	-0.0174	-0.0214	-0.0653
<i>Mean deviation</i>				<i>0.0054</i>	<i>0.0049</i>	<i>0.0051</i>	<i>0.0080</i>
Constants of correlation equations		A_{12}	A_{21}	D			
Wilson		0.7418	0.0381				
Laar 2		0.5044	1.1645				
Margules 3		0.5150	0.9422				
Margules 4		0.6402	1.1411	0.9193			

$$\int_1^0 \log(\gamma_1/\gamma_2) dx_1 = 0. \quad (3)$$

For the isobaric data the procedure was used proposed by Herington⁷. The consistency of the data was better than 2 per cent.

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SOLUBILITY OF KCl, KBr, KI AND KSCN IN THE TERNARY SYSTEM WATER-ELECTROLYTE-POLY(ETHYLENE GLYCOL) (200, 1000)

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The present work is a continuation of an earlier publication¹. Solubilities of 1 : 1 electrolytes KCl, KBr, KI and KSCN in mixed solvents water-poly(ethylene glycol) (PEG) 200 and water-poly(ethylene glycol) 1000 are investigated. Homogeneous regions are delimited and empirical equations are proposed to describe solution isotherms. The mentioned solvent systems have not yet been studied.

EXPERIMENTAL

The chemicals used, KCl, KBr, KI and KSCN, of analytical reagent grade, were recrystallised from distilled water and dried to constant weight at 150°C. PEG-200 and PEG-1000 were commercial products (Chemische Werke Hüls A. G.); their mean molecular weights, as determined osmometrically in the vapour phase (with an error $\pm 5\%$) were 182 and 769, respectively. Composition of homogeneous mixture, in equilibrium with salt crystals or with the second liquid phase was established by determining two components, salt and water, whereas the third one was