

LIQUID-VAPOUR EQUILIBRIUM. LXI.*

THE SYSTEMS ISOPRENE-2-METHYL-2-BUTENE-EXTRACTION SOLVENT

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Vapour-liquid equilibrium in the systems isoprene-2-methyl-2-butene-aniline, isoprene-2-methyl-2-butene-N,N-dimethylformamide, isoprene-2-methyl-2-butene-nitromethane at 20 and 30°C and saturated vapour pressures of isoprene and 2-methyl-2-butene in the pressure range of 90–740 Torr were measured. For measuring the vapour-liquid equilibria, a static semi-microstill was used which enabled to work with an accuracy of 1–2%.

Measuring the vapour-liquid equilibrium of the ternary systems was meant to contribute to the rational selection of a suitable extraction solvent which would make it possible to separate isoprene and 2-methyl-2-butene on distillation columns on industrial scale.

EXPERIMENTAL

Substances Used

Aniline (an analytical grade reagent) was, after a few days' drying over KOH, distilled under reduced pressure on a forty-plate column¹. n_D^{20} 1.5860 (ref.² 1.5862), d_4^{20} 1.0218 (ref.² 1.02173). *Nitromethane* (an analytical grade reagent) was dried with CaCl₂ and distilled over on a forty-plate column¹. n_D^{20} 1.3819 (ref.³ 1.38195), d_4^{25} 1.1306 (ref.³ 1.1307). *N,N-Dimethylformamide* (an analytical grade reagent) was dried with anhydrous MgSO₄ and distilled under vacuum on a forty-plate column¹. n_D^{20} 1.4304 (ref.² 1.43047), d_4^{20} 0.9487 (ref.² 0.94873). *Isoprene* (a technical reagent from Kaučuk, Kralupy, stabilized with 0.02% tert-butylcatechol) was twice distilled under nitrogen atmosphere¹ on an 1.5 m long packed column filled with stainless steel helices. n_D^{20} 1.4218 (ref.² 1.4219), d_4^{20} 0.6811 (ref.² 0.68095). (The pure isoprene was stored in the dark and cold and used up at the latest within three weeks.) *2-Methyl-2-butene* was prepared by the following synthesis: At first 2-methyl-2-butanol was prepared⁴ from ethyl magnesium bromide and acetone. On dehydrating it with concentrated sulphuric acid at 80°C, a mixture of 2-methyl-2-butene with small amounts of 2-methyl-1-butene was formed⁵ which was separated by distillation on a sixty-plate column. n_D^{20} 1.3873 (ref.² 1.3874), d_4^{20} 0.6621 (ref.² 0.6623).

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Measurement and Apparatus

The saturated vapour pressures of isoprene and 2-methyl-2-butene were measured by means of the Swietoslowski ebulliometer⁶ connected to a vacuum station. The pressure was measured by a thermostated closed U-manometer, provided with calibrated sealed tungsten contacts, in which mercury closes the electric circuit of the magnetic valve connecting the pressure reservoir with the vacuum supply⁷. The pressure in the equipment was maintained with an accuracy of 0.05 Torr. Temperature was measured by a resistance platinum thermometer connected to the Mueller bridge (Leeds and Northrup) with an accuracy of 10^{-3} °C.

The binodal curve of the nitromethane solubility in the isoprene-2-methyl-2-butene system was determined by titration at 20 and 30°C with the aim of delimiting the single-phase region in which the vapour-liquid equilibrium of the ternary system was then measured. The other extractive solvents are completely miscible with isoprene and 2-methyl-2-butene.

TABLE I

Vapour Pressures of Isoprene and 2-Methyl-2-butene

Isoprene		2-Methyl-2-butene	
<i>t</i> °C	<i>P</i> _{exp} Torr	<i>t</i> °C	<i>P</i> _{exp} Torr
-16.204	90.35	-12.102	90.35
-12.508	109.13	- 8.421	109.13
- 8.291	134.42	- 4.158	134.42
- 4.649	159.87	- 0.487	159.87
- 0.541	193.37	3.643	193.37
2.793	224.44	7.001	224.44
6.725	266.22	10.974	266.22
10.416	311.05	14.692	311.05
14.852	372.81	19.185	372.81
20.211	459.75	24.567	459.75
26.339	578.49	30.739	578.49
33.257	739.40	37.723	740.15

Antoine vapour pressure constants

6.92587	A	6.93402
1 091.747	B	1 104.007
235.860	C	233.891

Standard deviation

0.18

0.12

Vapour-liquid equilibrium was measured in the static semi-microstill^{8,9} which in combination with a gas chromatograph¹⁰ enables to determine quickly the concentration dependence of relative volatility or of the ratio of activity coefficients. Prior to the measuring, the function of the chromatograph (with the thermal conductivity detection) and the equilibrium semi-microstill was tested, which led to the finding of the optimum conditions for measuring the vapour-liquid equilibrium of the given systems, *i.e.* flow rate of carrier gas-hydrogen, temperature of the column and detector cell, heating current of the detector filament, saturation of the feeding space of the eight-way stopcock of the equilibrium still. As a filling of the chromatographic column (3 m long and 4 mm in diameter) 5% ethylene-bis-oxypionitrile on Chromosorb W was chosen. An integrator, which worked with an accuracy of 1%, was connected to the chromatograph. The use of the semi-microstill has, in comparison with classical types (*e.g.* the Gillespie still⁶) these advantages: 1) For measuring the vapour-liquid equilibrium in the entire concentration range, a small amount of pure substances (about 50 ml of each component for a ternary system) is needed. 2) With regard to the small amount of sample in the still (3 ml) establishing equilibrium is very quick. A disadvantage is, for a change, the fact that the total pressure above the liquid phase cannot be measured. The composition of the liquid phase was determined by weighing the sample. With regard to the small volume of the analyzed vapour phase (about 1.2 ml) one can assume that the composition of the liquid and vapour phase does not change during 5–10 repeated analyses. This fact was experimentally verified, too. The result of the chromatographic analysis of the vapour phase of the given systems were two integral curves, corresponding to the

TABLE II

Solubility of Nitromethane in the Isoprene(1)–2-Methyl-2-butene(2)–Nitromethane(3) System

x_1	x_2	x_1	x_2
	20°C	0.113	0.698
		0.070	0.762
—	0.146	—	0.872
0.015	0.149		
0.043	0.159		30°C
0.048	0.160		
0.064	0.164	—	0.198
0.096	0.184	0.028	0.211
0.117	0.202	0.060	0.244
0.135	0.217	0.071	0.259
0.164	0.265	0.080	0.288
0.185	0.319	0.097	0.337
0.210	0.406	0.104	0.375
0.209	0.471	0.116	0.446
0.198	0.513	0.119	0.490
0.176	0.577	0.116	0.533
0.166	0.594	0.097	0.597
0.135	0.656	0.062	0.684
		—	0.813

areas of two peaks, whose ratio is directly proportional to the ratio of concentrations of isoprene and 2-methyl-2-butene in this phase (the extraction solvent did not have to be analyzed in the vapour phase owing to its low vapour pressure at 20 and 30°C), thus $(d_1/d_2)_v = f(y_1/y_2)$. Similarly, by analyzing the liquid sample, we obtain the ratio of concentrations of isoprene and 2-methyl-2-butene in the liquid phase, thus $(d_1/d_2)_l = f(x_1/x_2)$, where f is proportionality factor, y_i denotes the mole fraction of the component i in the gas phase, x_i the mole fraction of the component i in the liquid phase and d_i the height of the integral curve for the component i . As the proportionality factors are identical in both cases, the relative volatility α_{12} or α_{123} is to be determined directly from the ratio of the integral curve heights, *i.e.*

$$\alpha_{12} = (y_1/x_1)/(y_2/x_2) = (d_1/d_2)_v (d_2/d_1)_l \quad (1)$$

To attain a better reproducibility of experimental data each experimental point was repeated 5–10 times and, from it, then the average value of α_{12} or α_{123} was determined.

TABLE III

Vapour-Liquid Equilibrium in the Isoprene(1)–2-Methyl-2-butane(2) System at 20 and 30°C

20°C			30°C		
x_1	y_1	α_{12}	x_1	y_1	α_{12}
0.217	0.253	1.219	0.217	0.248	1.192
0.221	0.253	1.195	0.223	0.255	1.190
0.375	0.421	1.210	0.375	0.410	1.160
0.376	0.417	1.185	0.376	0.415	1.175
0.511	0.553	1.184	0.520	0.558	1.165
0.521	0.565	1.195	0.521	0.560	1.168
0.662	0.699	1.188	0.662	0.692	1.146
0.666	0.702	1.184	0.666	0.692	1.125
0.676	0.708	1.165	0.676	0.699	1.114
0.825	0.841	1.118	0.814	0.831	1.122
0.827	0.844	1.131	0.825	0.837	1.091
0.814	0.836	1.165	0.827	0.840	1.095

Equation order	t °C	A_{12} g_{11}	A_{21} g_{22}	g_{12}	Standard dev.
Alpha	20	0.2369	−0.1125		0.017
2	30	0.2254	−0.0723		0.013
Margules	20	0.0115	0.0275		0.016
3	30	0.0418	0.0213		0.022
Wilson-	20	−5.976.21	−6.153.13	−6.044.63	0.016
Tassios	30	−5.894.70	−6.065.05	−5.952.50	0.024

TABLE IV

Vapour-Liquid Equilibrium in the Isoprene(1)-2-Methyl-2-butene(2)-N,N-Dimethylformamide (3) System at 20 and 30°C

x_1	x_3	20°C		30°C	
		y_1	α_{123}	y_1	α_{123}
0.041	0.802	0.156	0.709	0.170	0.785
0.083	0.607	0.172	0.777	0.177	0.803
0.122	0.393	0.184	0.891	0.180	0.871
0.165	0.212	0.208	0.992	0.204	0.986
0.060	0.845	0.301	0.682	0.324	0.759
0.157	0.593	0.334	0.800	0.342	0.826
0.240	0.382	0.363	0.899	0.362	0.894
0.310	0.199	0.384	0.988	0.382	0.979
0.102	0.800	0.434	0.737	0.452	0.792
0.205	0.597	0.450	0.791	0.461	0.826
0.303	0.400	0.473	0.880	0.477	0.893
0.398	0.205	0.506	1.023	0.495	0.978
0.137	0.795	0.583	0.693	0.611	0.781
0.265	0.602	0.608	0.778	0.626	0.841
0.409	0.396	0.649	0.881	0.656	0.910
0.529	0.207	0.666	0.995	0.661	0.973
0.122	0.852	0.762	0.681	0.781	0.761
0.284	0.657	0.788	0.770	0.799	0.826
0.493	0.404	0.805	0.864	0.807	0.874
0.674	0.185	0.831	1.028	0.826	0.992

Equation order	t °C	A_{13} g_{33}	A_{31} g_{13}	A_{23} g_{23}	A_{32}	Standard dev.
Alpha	20	0.2041	—	0.8548	—	0.018
2	30	1.2376	—	1.9698	—	0.020
Margules	20	-0.0896	-0.0986	0.1667	0.2684	0.016
3	30	-0.0706	-0.0678	0.1061	0.3232	0.017
Wilson-	20	-11 179.96	-6 530.27	-6 392.64		0.021
Tassios	30	-10 889.71	-6 818.62	-6 762.87		0.023

RESULTS

The measured vapour pressures of isoprene and 2-methyl-2-butene (Table I) were correlated by means of the Antoine equation⁶

$$\log P = A - B/(t + C), \quad (2)$$

TABLE V

Vapour-Liquid Equilibrium in the Isoprene(1)-2-Methyl-2-butene(2)-Aniline(3) System at 20 and 30°C

x_1	x_3	20°C		30°C	
		y_1	α_{123}	y_1	α_{123}
0.040	0.814	0.178	0.788	0.176	0.780
0.085	0.602	0.194	0.883	0.201	0.926
0.127	0.414	0.209	0.953	0.209	0.953
0.172	0.216	0.233	1.078	0.226	1.039
0.071	0.812	0.319	0.771	0.324	0.789
0.152	0.595	0.342	0.863	0.346	0.878
0.223	0.409	0.372	0.977	0.378	1.004
0.292	0.218	0.382	1.039	0.386	1.053
0.103	0.800	0.461	0.807	0.461	0.805
0.210	0.598	0.495	0.895	0.496	0.901
0.310	0.404	0.514	0.974	0.518	0.992
0.407	0.221	0.535	1.051	0.529	1.028
0.135	0.795	0.603	0.787	0.605	0.793
0.266	0.597	0.630	0.878	0.630	0.878
0.390	0.411	0.650	0.946	0.651	0.953
0.517	0.220	0.672	1.044	0.670	1.032
0.166	0.797	0.777	0.775	0.783	0.802
0.326	0.600	0.792	0.862	0.796	0.887
0.485	0.405	0.807	0.949	0.808	0.954
0.640	0.215	0.816	1.007	0.818	1.016

Equation order	t °C	A_{13} g_{33}	A_{31} g_{13}	A_{23} g_{23}	A_{32}	Standard dev.
Alpha	20	-0.0380	—	0.3319	—	0.015
2	30	-0.1959	—	0.1059	—	0.021
Margules	20	-0.0620	-0.0687	0.1514	0.1698	0.015
3	30	-0.2613	-0.2218	-0.0560	-0.0181	0.022
Wilson-	20	-13 130.49	-6 221.91	-6 142.93		0.016
Tassios	30	-12 692.44	-6 135.21	-6 060.18		0.025

where P is saturated vapour pressure in Torr, A , B , C are constants determined by the weighted least square method and t is temperature in °C.

The measured points of the binodal curve of the nitromethane solubility in the isoprene-2-methyl-2-butene system at 20 and 30°C are presented in Table II.

TABLE VI

Vapour-Liquid in the Isoprene(1)-2-Methyl-2-butene(2)-Nitromethane(3) System at 20 and 30°C

20°C			30°C		
x_1	x_3	α_{123}	x_1	x_3	α_{123}
0.070	0.814	0.751	0.071	0.812	0.795
0.232	0.384	0.975	0.149	0.604	0.820
0.304	0.196	1.041	0.234	0.378	0.973
0.104	0.801	0.751	0.299	0.204	1.046
0.213	0.591	0.842	0.197	0.614	0.816
0.325	0.379	0.993	0.297	0.420	0.946
0.417	0.199	1.042	0.395	0.225	1.008
0.130	0.804	0.728	0.101	0.798	0.792
0.260	0.607	0.841	0.200	0.600	0.858
0.397	0.400	0.953	0.384	0.231	1.039
0.539	0.185	1.050	0.133	0.798	0.783
0.160	0.806	0.709	0.268	0.592	0.868
0.334	0.596	0.806	0.399	0.395	0.921
0.492	0.403	0.887	0.512	0.222	1.003
0.647	0.214	1.029	0.166	0.797	0.777
—	—	—	0.330	0.598	0.849
—	—	—	0.487	0.405	0.927
—	—	—	0.618	0.244	1.014

Equation order	t °C	A_{13} g_{33}	A_{31} g_{13}	A_{23} g_{23}	A_{32}	Standard dev.
Alpha	20	-0.2564	—	0.1451	—	0.021
2	30	-0.0148	—	0.3706	—	0.019
Margules	20	-0.1138	-0.1605	0.1425	0.0726	0.023
3	30	-0.0702	-0.0520	0.1397	0.2047	0.018
Wilson-	20	-8 700.65	-6 421.84	-6 283.98		0.021
Tassios	30	-8 569.09	-6 570.21	-6 492.59		0.021

Experimental data on the vapour-liquid equilibrium of the systems measured were adjusted by means of the third-order Margules equation⁶, the relative volatility expansion of the second order¹¹ and the Wilson-Tassios equation¹² using the following assumptions: a) the vapour phase behaves ideally, b) the concentration of the extraction solvent in the vapour phase is negligible. On the basis of the second assumption then $y_3 = 0$, $\alpha_{32} = 0$, $\alpha_{31} = 0$. Whereas the first assumption is justified

for all systems studied, the second one is justified only with the systems containing aniline and N,N-dimethylformamide as an extractive solvent (with respect to their high boiling points). However, nitromethane has a relatively high vapour pressure at the temperatures of 20 and 30°C. Considering that it was not possible to determine the coefficients of relative volatility α_{31} and α_{32} for the isoprene-2-methyl-2-butene-nitromethane system (for analytical reasons), the experimental data x_i, α_{123} do not describe fully the vapour-liquid equilibrium. Notwithstanding these data give sufficient information on the effect of the extraction solvent on the separability of isoprene and 2-methyl-2-butene.

The third-order Margules equation has the form for a binary system

$$\log \gamma_i = x_j^2(A_{ij} + 2x_i(A_{ji} - A_{ij})) \quad (3)$$

and for a ternary system

$$\begin{aligned} \log \gamma_i = & x_j^2(A_{ij} + 2x_i(A_{ji} - A_{ij})) + x_k^2(A_{ik} + 2x_i(A_{ki} - A_{ik})) + \\ & + x_j x_k (A_{ji} + A_{ik} - A_{kj} + 2x_i(A_{ki} - A_{ik}) + 2x_k(A_{kj} - A_{jk}) + \\ & - C_i(1 - 2x_i)), \end{aligned} \quad (4)$$

from which by a cyclic permutation, the equations for $\log \gamma_j$ and $\log \gamma_k$ are obtained. In the relations (3) and (4), A_{ij} are binary constants and C_i is a ternary constant which can be estimated from the binary constants by the method proposed by Colburn and Wohl⁶:

$$C_i = \frac{1}{2}(A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23}). \quad (5)$$

The expansion of the relative volatility of the second order has the form for a binary system

$$\alpha_{12} = (1 + A_{12}x_2)/(1 + A_{21}x_1) \quad (6)$$

and for a ternary system

$$\alpha_{ij} = (1 + A_{ij}x_j + A_{ik}x_k)/(1 + A_{ji}x_i + A_{jk}x_k), \quad (7)$$

where A_{ij} are binary constants.

The multicomponent form of the Wilson-Tassios equation is given by

$$\ln \gamma_i = 1 - \ln \sum_j^n x_j G_{ji} - \sum_j^n (x_j G_{ij} / \sum_k^n x_k G_{kj}), \quad (8)$$

in which for the parameter G_{ji} the relation holds

$$G_{ji} = (V_j/V_i) \exp [-(g_{ji} - g_{ii})/RT], \quad (9)$$

where V_i is the molar volume of the component i (at a given temperature), g_{ji} is an adjustable parameter (for which it holds $g_{ji} = g_{ij}$) and the parameter for the pure component i , g_{ii} , is determined from vaporization energy

$$g_{ii} = -\Delta U_{\text{vap}} = RT - \Delta H_{\text{vap}} = RT - 2.303RT^2B/(C + t)^2, \quad (10)$$

where B , C are constants of the Antoine equation, t is temperature in $^{\circ}\text{C}$, T is absolute temperature and R is gas constant.

When correlating the experimental data according to the above-said relations, the weighted least square method^{13,14} was used. The composition of the vapour phase was calculated from the adjusted values of α_{12} or α_{123} , *i.e.* from the relation

$$y_1 = (\alpha_{12}x_1/x_2)/(1 + \alpha_{12}x_1/x_2). \quad (11)$$

In Tables III–VI, the experimental data are presented together with the evaluated constants of correlation relations used and the standard deviations, S , in relative volatility calculated from the equation

$$S = \left(\sum_i^n (\alpha_{12}^{\text{exp}} - \alpha_{12}^{\text{calc}})^2 / (n - k) \right)^{0.5}, \quad (12)$$

where n is the number of experimental points and k the number of constants which are to be determined in the correlation relation used.

In the studied series of extraction solvents, the relative volatility of isoprene and 2-methyl-2-butene is most influenced by N,N -dimethylformamide.

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