

Isothermal vapour-liquid equilibria for 11 examples of (an ether + a hydrocarbon)

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A recirculating still was used in the determination of isothermal vapour-liquid equilibria for eight examples of (an aliphatic ether + an alkane) and three of (an aliphatic ether + benzene) at a total of 14 isothermal conditions. Activity coefficients and excess molar Gibbs free energies were evaluated and then correlated.

1. Introduction

There is evidence that vapour-liquid equilibrium (VLE) values for (an ether + a hydrocarbon) have not been systematically investigated.^(1, 2)

For (a monoether + a hydrocarbon), isothermal VLE values have been reported for (*n*-propyl ether + *n*-heptane),⁽³⁾ (*n*-propyl ether + benzene),⁽⁴⁾ (*n*-butyl ether + *n*-hexane),⁽⁵⁾ (isopropyl ether + an aromatic hydrocarbon), and (*n*-propyl ether + an aromatic hydrocarbon).⁽⁶⁾ The aromatic hydrocarbons used in the work of Linek *et al.*⁽⁶⁾ were benzene, toluene, and ethyl benzene. The reported isobaric VLE values include those for (isopropyl ether + *n*-heptane),^(7, 8) and (isopropyl ether + benzene).⁽⁹⁾ Maczynski *et al.*⁽¹⁾ pointed out that the available VLE values for (isopropyl + a hydrocarbon) might not be reliable.

{An ether containing more than one oxygen atom (poly ether) + an alkane} represents a very interesting class of mixtures. Their behaviour would make it possible to investigate the effects of induction and positions of oxygen atoms in the ether molecule on thermodynamic properties. The replacement of alkane by benzene would make it possible to estimate the n -to- π contribution to the excess molar Gibbs energy.⁽¹⁰⁾

' The purpose of this VLE study is further to investigate (a poly ether + a hydrocarbon), and to provide reliable isothermal values for (isopropyl ether + a hydrocarbon) and (a straight chain monoether + a hydrocarbon), for evaluating

the effects of chain length and branching as well as the number and positions of oxygen atoms in the ether molecule on VLE values.

In an earlier article,⁽¹⁰⁾ limited VLE values were determined for 10 mixtures for evaluating the steric and inductive effects of oxygen atoms in ethers on excess Gibbs energies for (an ether + a hydrocarbon). However, no numerical values of equilibrium compositions and pressure were reported. In this work, experimental details and equilibrium values (temperature-pressure-compositions, activity coefficients, and excess molar Gibbs energies) over the complete composition range are reported for eight examples of (an aliphatic ether + an alkane) and three examples of (an aliphatic ether + benzene) at a total of 14 isothermal conditions.

2. Experimental

A modified Dvorak and Boublik recirculating still⁽¹¹⁾ was used to establish vapour-liquid equilibrium values for (methyl *n*-butyl ether + *n*-heptane) at 323.15 and 343.15 K; (isopropyl ether + *n*-heptane) at 323.15 and 343.15 K; (isopropyl ether + 2,4-dimethylpentane) at 343.15 K; (*n*-pentyl ether + *n*-undecane) at 403.15 K; (dimethoxymethane + *n*-hexane) at 313.15 K; (diethoxymethane + *n*-heptane) at 323.15 and 343.15 K; (1,2-dimethoxyethane + 2,4-dimethylpentane) at 343.15 K; (2,5,8,11-tetraoxadodecane + *n*-dodecane) at 435.26 K; (methyl *n*-butyl ether + benzene) at 343.15 K; (isopropyl ether + benzene) at 343.15 K; and (diethoxymethane + benzene) at 343.15 K.

A Texas Instrument pressure gauge (type 144-01) together with a Bourdon capsule (0 to 175 kPa) were used for pressure measurements. The gauge was calibrated by measuring the vapour pressure of demineralized and distilled water at a number of temperatures using a Świętosławski-type ebulliometer. The pressure was controlled by a two-liquid manostat. A calibrated Hewlett-Packard quartz thermometer (Model 2801 A) was used to measure the temperature. It is estimated that the pressures are accurate to ± 0.013 kPa and temperatures to ± 0.01 K. The compositions of the condensed vapour and liquid samples for (an ether + an alkane) were analysed using an Anton-Paar digital densimeter (Model DMA 02A) with its temperature maintained at (298.15 ± 0.01) K. For (an ether + benzene), a Bausch and Lomb Abbé-3L precision refractometer was used with its temperature also maintained at (298.15 ± 0.01) K. The accuracy of the determined mole fraction is estimated to be ± 0.008 for (an ether + an alkane), and ± 0.001 for (an ether + benzene).

In the determination, Phillips Research-Grade *n*-hexane, *n*-heptane, and benzene were used as supplied. Fluka pure-grade dimethoxymethane, diethoxymethane, and methyl butyl ether were purified by a preparative g.l.c. (F & M Model 775). After purification, the purity of the products was estimated, by the chromatograph using a flame ionization detector, to be better than 99.9 moles per cent. Isopropyl ether (Aldrich, 99 moles per cent), 1,2-dimethoxyethane (Aldrich, 99 moles per cent), *n*-pentyl ether (Eastman Kodak), 2,5,8,11-tetraoxadodecane (Aldrich, 99 moles per cent), 2,4-dimethylpentane (Albany International Chemical Division, 99 moles per cent), *n*-dodecane (Matheson Coleman & Bell, 99 moles per cent), and *n*-undecane

(Aldrich, 99 moles per cent) were purified by fractionating over sodium through a packed column at a reflux ratio of 40. The middle portions of the distillates were analysed chromatographically, were found to be free from impurities, and were used in this work. The densities, refractive indices, and vapour pressures of the chemicals agree reasonably well with the values given in the literature.⁽¹²⁻¹⁷⁾

3. Results and discussion

The experimentally determined values of pressure p , temperature T , liquid mole fraction x , and vapour mole fraction y were used to calculate activity coefficients f_i and excess molar Gibbs energies G_m^E .

The $\ln f_1$ values were obtained from

$$\ln f_1 = \ln(y_1 p/x_1 p_1^*) + (B_{11} - V_1^*)(p - p_1^*)/RT + y_2^2 p \delta_{12}/RT, \quad (1)$$

and similarly for $\ln f_2$, where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}. \quad (2)$$

p_i^* , V_i^* , and B_{ii} are the vapour pressure, liquid molar volume, and second virial coefficient of component i , respectively. The quantity B_{12} is the cross second virial coefficient. All the second virial coefficients were calculated by the method of Hayden and O'Connell.⁽¹⁸⁾ The calculated pure-component and cross second virial coefficients are reported in tables 1 and 2, respectively. The values of V_i (either obtained from the literature or determined in this work) at the temperature investigated and used in the calculation of f are also reported in table 1. The p , T , x , y , f_i , and G^E values for (an ether + an alkane) are reported in table 3, and for (an

TABLE 1. Values of liquid molar volume V_m^* and second virial coefficient B

	T/K	$V_m^*/(\text{cm}^3 \cdot \text{mol}^{-1})$	$B/(\text{cm}^3 \cdot \text{mol}^{-1})$
$\text{CH}_3\text{OC}_4\text{H}_9$	323.15	125	-1389
	343.15	128	-1185
$(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$	323.15	148	-1524
	343.15	152	-1299
$\text{C}_5\text{H}_{11}\text{OC}_3\text{H}_7$	403.15	228	-3078
$\text{CH}_3\text{OCH}_2\text{OCH}_3$	313.15	92	-937
$\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5$	323.15	131	-1507
	343.15	134	-1276
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	343.15	105	-1183
$\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3$	435.26	209	-2103
C_6H_{14}	313.15	134	-1634
C_7H_{16}	323.15	152	-2275
	343.15	157	-1896
$(\text{CH}_3)_3\text{CHCH}_2\text{CH}(\text{CH}_3)_2$	343.15	160	-1575
$\text{C}_{11}\text{H}_{24}$	403.15	238	-3704
$\text{C}_{12}\text{H}_{26}$	435.26	249	-4067
C_6H_6	343.15	95	-1019

TABLE 2. Values of cross second virial coefficient B_{12}

	T K	B_{12} $\text{cm}^3 \cdot \text{mol}^{-1}$	T K	B_{12} $\text{cm}^3 \cdot \text{mol}^{-1}$
$\text{CH}_3\text{OC}_4\text{H}_9\text{-C}_7\text{H}_{16}$	323.15	-1741	343.15	-1470
$(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2\text{-C}_7\text{H}_{16}$	323.15	-1825	343.15	-1540
$(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2\text{-(CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$	343.15	-1413		
$\text{C}_5\text{H}_{11}\text{OC}_5\text{H}_{11}\text{-C}_{11}\text{H}_{24}$	403.15	-3361		
$\text{CH}_3\text{OCH}_2\text{OCH}_3\text{-C}_6\text{H}_{14}$	313.15	-1213		
$\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5\text{-C}_7\text{H}_{16}$	323.15	-1832	343.15	-1540
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3\text{-(CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$	343.15	-1315		
$\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3\text{-C}_{12}\text{H}_{26}$	435.26	-2972		
$\text{CH}_3\text{OC}_4\text{H}_9\text{-C}_6\text{H}_6$	343.15	-1086		
$(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2\text{-C}_6\text{H}_6$	343.15	-1141		
$\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5\text{-C}_6\text{H}_6$	343.15	-1135		

TABLE 3. Isothermal vapour-liquid equilibrium results for (an aliphatic ether + an alkane): pressure p , liquid mole fraction x , vapour mole fraction y , activity coefficients f_1 and f_2 , and excess molar Gibbs energies G_m^E

$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J} \cdot \text{mol}^{-1}}$	$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J} \cdot \text{mol}^{-1}}$
{(1-x)CH ₃ OC ₄ H ₉ +xC ₇ H ₁₆ } at 323.15 K											
18.91	0	0				40.34	0.631	0.808	1.020	1.091	120
26.26	0.192	0.408	1.111	1.011	78	41.67	0.674	0.834	1.018	1.099	116
30.49	0.312	0.566	1.098	1.008	93	42.04	0.688	0.842	1.104	1.108	113
33.90	0.417	0.633	1.068	1.024	110	43.33	0.732	0.866	1.010	1.124	105
36.57	0.502	0.725	1.046	1.052	127	48.84	0.925	0.965	1.001	1.184	38
38.14	0.555	0.760	1.034	1.069	130	50.94	1	1			
39.84	0.610	0.795	1.026	1.089	132						
{(1-x)CH ₃ OC ₄ H ₉ +xC ₇ H ₁₆ } at 343.15 K											
40.57	0	0				77.26	0.565	0.753	1.030	1.057	116
44.79	0.058	0.144	1.128	1.001	22	81.39	0.640	0.803	1.020	1.072	107
55.02	0.203	0.401	1.100	1.009	75	85.11	0.710	0.843	1.009	1.102	98
69.00	0.427	0.645	1.047	1.035	112	86.58	0.733	0.864	1.017	1.055	77
74.25	0.515	0.716	1.034	1.049	116	96.06	0.911	0.953	0.998	1.214	45
76.38	0.552	0.742	1.029	1.059	118	100.99	1	1			
{(1-x)(CH ₃) ₂ CHOCH(CH ₃) ₂ +xC ₇ H ₁₆ } at 323.15 K											
18.91	0	0				38.85	0.552	0.762	0.997	1.075	83
23.37	0.117	0.277	1.041	1.008	32	42.12	0.649	0.827	0.990	1.112	83
25.74	0.180	0.385	1.033	1.016	49	45.45	0.746	0.880	0.994	1.111	60
27.51	0.228	0.453	1.022	1.024	66	48.35	0.830	0.927	0.999	1.075	30
34.39	0.422	0.664	1.009	1.044	77	49.34	0.859	0.935	0.994	1.163	43
36.46	0.482	0.722	1.015	1.023	54	50.55	0.894	0.956	0.998	1.090	21
37.31	0.507	0.742	1.002	1.021	50	54.26	1	1			
{(1-x)(CH ₃) ₂ CHOCH(CH ₃) ₂ +xC ₇ H ₁₆ } at 343.15 K											
40.58	0	0				76.99	0.543	0.747	1.009	1.025	46
58.14	0.254	0.461	1.016	1.023	59	85.52	0.676	0.826	0.992	1.096	70
60.01	0.284	0.499	1.015	1.020	53	92.64	0.786	0.895	0.996	1.087	43
63.45	0.334	0.553	1.007	1.034	70	93.61	0.801	0.902	0.996	1.096	43

TABLE 3—continued

$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J}\cdot\text{mol}^{-1}}$	$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J}\cdot\text{mol}^{-1}}$
64.79	0.355	0.583	1.104	1.022	48	95.25	0.826	0.915	0.996	1.109	41
66.49	0.381	0.603	1.009	1.032	65	96.25	0.842	0.923	0.996	1.115	38
67.42	0.395	0.614	1.003	1.042	74	106.56	1	1			
73.63	0.491	0.699	1.000	1.051	72						
$\{(1-x)(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2 + x(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2\}$ at 343.15 K											
73.29	0	0				93.91	0.544	0.627	1.021	1.034	77
77.01	0.082	0.124	1.102	1.001	26	94.41	0.566	0.644	1.011	1.046	73
78.36	0.115	0.167	1.081	1.003	34	95.39	0.599	0.671	1.006	1.055	71
82.05	0.207	0.283	1.062	1.008	53	97.66	0.674	0.736	1.004	1.063	64
86.23	0.316	0.407	1.053	1.012	69	101.11	0.792	0.834	1.000	1.083	47
89.32	0.402	0.496	1.040	1.019	77	105.07	0.934	0.947	0.999	1.126	18
91.48	0.469	0.559	1.029	1.026	77	106.82	1	1			
$\{(1-x)\text{C}_5\text{H}_{11}\text{OC}_5\text{H}_{11} + x\text{C}_{11}\text{H}_{24}\}$ at 404.15 K											
14.42	0	0				17.93	0.681	0.733	0.995	1.038	28
14.85	0.079	0.097	0.940	1.010	13	18.23	0.759	0.806	0.998	1.012	5
15.54	0.199	0.255	1.028	1.001	22	18.70	0.827	0.856	0.997	1.075	34
16.26	0.329	0.398	1.015	1.010	39	18.78	0.868	0.889	0.991	1.087	12
17.41	0.572	0.633	0.995	1.031	34	19.42	1	1			
$\{(1-x)\text{CH}_3\text{OCH}_2\text{OCH}_3 + x\text{C}_6\text{H}_{14}\}$ at 315.15 K											
37.32	0	0				87.99	0.655	0.792	1.133	1.382	502
45.02	0.053	0.206	1.900	1.006	104	88.53	0.670	0.797	1.123	1.410	498
65.60	0.248	0.539	1.534	1.058	386	89.78	0.719	0.819	1.090	1.498	457
74.24	0.365	0.636	1.388	1.115	490	90.26	0.731	0.826	1.085	1.518	448
79.28	0.451	0.691	1.300	1.164	525	91.53	0.786	0.855	1.056	1.644	389
85.36	0.579	0.757	1.190	1.284	536	93.78	0.919	0.930	1.009	2.104	147
85.39	0.580	0.757	1.189	1.289	535	94.06	1	1			
87.46	0.634	0.782	1.149	1.356	520						
$\{(1-x)\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 + x\text{C}_7\text{H}_{16}\}$ at 323.15 K											
18.90	0	0				25.71	0.521	0.601	1.101	1.127	289
21.94	0.162	0.266	1.340	1.015	160	26.15	0.589	0.652	1.075	1.164	283
22.52	0.203	0.316	1.302	1.020	187	26.82	0.730	0.757	1.032	1.268	235
24.39	0.366	0.476	1.178	1.063	264	27.08	0.828	0.835	1.013	1.366	173
24.49	0.370	0.480	1.181	1.065	271	27.07	0.839	0.844	1.011	1.377	162
24.87	0.408	0.512	1.160	1.073	275	26.95	1	1			
24.88	0.417	0.518	1.151	1.081	279						
$\{(1-x)\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 + x\text{C}_7\text{H}_{16}\}$ at 343.15 K											
40.58	0	0				55.18	0.613	0.667	1.060	1.058	264
43.78	0.082	0.143	1.362	1.005	84	55.88	0.688	0.725	1.039	1.202	238
48.01	0.222	0.326	1.250	1.020	185	56.74	0.808	0.820	1.015	1.299	177
51.38	0.360	0.463	1.169	1.054	257	56.83	0.828	0.836	1.013	1.316	165
52.57	0.430	0.522	1.129	1.077	269	56.90	0.942	0.939	1.001	1.443	63
52.59	0.431	0.523	1.130	1.076	269	56.71	1	1			
53.44	0.489	0.570	1.102	1.098	271						
$\{(1-x)\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 + x(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2\}$ at 343.15 K											
73.29	0	0				79.77	0.656	0.566	1.115	1.370	512
79.03	0.143	0.191	1.711	1.015	255	78.20	0.723	0.614	1.076	1.483	464
82.31	0.396	0.397	1.339	1.114	516	75.25	0.306	0.686	1.038	1.668	369
82.07	0.485	0.455	1.248	1.179	548	70.66	0.893	0.786	1.011	1.933	230

TABLE 3—continued

$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J}\cdot\text{mol}^{-1}}$	$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J}\cdot\text{mol}^{-1}}$
81.04	0.584	0.518	1.164	1.276	543	65.67	0.957	0.897	1.002	2.185	101
80.28	0.641	0.555	1.126	1.354	527	61.26	1	1			
80.27	0.645	0.558	1.123	1.362	526						
$\{(1-x)\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3 + x\text{C}_{12}\text{H}_{26}\}$ at 435.26 K											
22.76	0	0				25.04	0.628	0.508	1.178	1.450	872
25.39	0.307	0.337	1.624	1.063	691	24.77	0.669	0.530	1.141	1.543	837
25.49	0.462	0.420	1.345	1.204	858	23.93	0.740	0.579	1.089	1.701	727
25.43	0.518	0.448	1.279	1.274	885	22.12	0.854	0.680	1.025	2.136	477
25.05	0.586	0.484	1.202	1.369	861	17.13	1	1			

TABLE 4. Isothermal vapour-liquid equilibrium results for (an aliphatic ether + benzene): pressure p , liquid mole fraction x , vapour mole fraction y , activity coefficients f_1 and f_2 , and excess molar Gibbs energies G_m^E

$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J}\cdot\text{mol}^{-1}}$	$\frac{p}{\text{kPa}}$	$1-x$	$1-y$	f_1	f_2	$\frac{G_m^E}{\text{J}\cdot\text{mol}^{-1}}$
$\{(1-x)\text{CH}_3\text{OC}_4\text{H}_9 + x\text{C}_6\text{H}_6\}$ at 343.15 K											
73.52	0	0				88.18	0.4887	0.5642	1.0138	1.0168	43
79.65	0.1948	0.2515	1.0284	1.0047	26	90.53	0.5819	0.6503	1.0064	1.0235	38
81.63	0.2627	0.3279	1.0180	1.0090	32	92.53	0.6585	0.7207	1.0064	1.0224	33
83.38	0.3209	0.3904	1.0126	1.0142	39	94.38	0.7315	0.7837	1.0040	1.0264	28
85.53	0.3959	0.4704	1.0134	1.0153	41	98.90	0.9064	0.9289	1.0041	1.0127	14
86.89	0.4411	0.5168	1.0139	1.0173	45	101.03	1	1			
$\{(1-x)(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2 + x\text{C}_6\text{H}_6\}$ at 343.15 K											
73.49	0	0				88.40	0.3435	0.4343	1.0588	1.0307	113
75.17	0.0307	0.0507	1.1845	1.0011	18	90.72	0.4137	0.5026	1.0428	1.0406	116
78.02	0.0859	0.1311	1.1344	1.0074	50	92.76	0.4784	0.5646	1.0346	1.0461	114
80.31	0.1353	0.2020	1.1409	1.0059	65	94.27	0.5302	0.6117	1.0270	1.0521	108
82.11	0.1775	0.2539	1.1164	1.0102	80	95.32	0.5654	0.6449	1.0261	1.0513	104
84.15	0.2287	0.3136	1.0956	1.0149	92	97.16	0.6293	0.6972	1.0149	1.0706	99
84.31	0.2327	0.3172	1.0911	1.0167	94	98.19	0.6719	0.7323	1.0085	1.0804	89
86.42	0.2875	0.3780	1.0775	1.0216	105	106.58	1	1			
$\{(1-x)\text{CH}_3\text{OCH}_2\text{OCH}_3 + x\text{C}_6\text{H}_6\}$ at 343.15 K											
73.49	0	0				64.62	0.5121	0.4480	0.9952	0.9984	-9
72.64	0.0415	0.0308	0.9457	0.9998	-7	63.20	0.5965	0.5354	0.9993	0.9943	-8
71.68	0.0989	0.0741	0.9425	1.0029	-9	63.09	0.6005	0.5399	0.9993	0.9929	-9
70.67	0.1605	0.1271	0.9826	1.0010	-6	61.91	0.6718	0.6150	0.9990	0.9929	-9
70.22	0.1849	0.1495	0.9970	0.9983	-6	60.68	0.7471	0.6984	1.0004	0.9899	-7
68.75	0.2661	0.2189	0.9938	0.9975	-10	59.43	0.8232	0.7853	1.0004	0.9878	-5
67.72	0.3247	0.2706	0.9921	0.9976	-12	58.04	0.9111	0.8869	0.9974	1.0112	-3
66.75	0.3830	0.3236	0.9919	0.9984	-12	56.59	1	1			
60.95	0.4295	0.3670	0.9915	0.9987	-13						

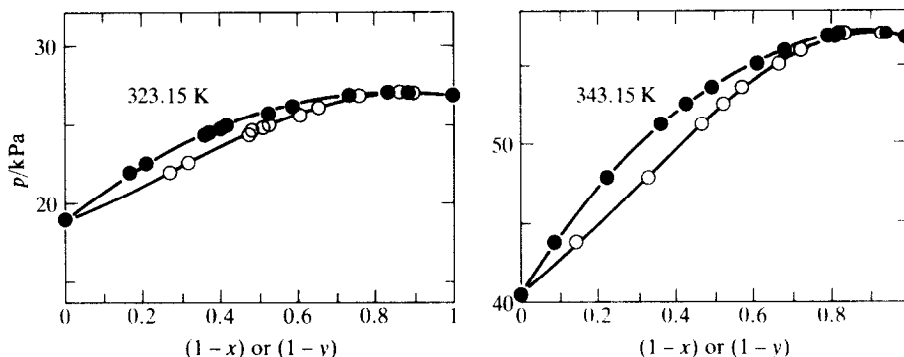


FIGURE 1. Experimental results for $\{(1-x)\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 + x\text{C}_7\text{H}_{16}\}$ at two temperatures.

ether + benzene) in table 4. To serve as an example, the results obtained for (diethoxymethane + *n*-heptane) are presented in figure 1.

The G_m^E values of tables 3 and 4 were obtained from

$$G_m^E = RT\{(1-x)\ln f_1 + x \ln f_2\}, \quad (3)$$

where $x = x_2$, and represented by a three-parameter equation:

$$G_m^E = x(1-x) \sum_{k=1}^3 C_k(1-2x)^{k-1}, \quad (4)$$

from which it follows that

$$\ln f_i = (-1)^i(1-x_i)^2 \sum_{k=1}^3 C_k(1-2kx_i)(x_1-x_2)^{k-2}. \quad (5)$$

The values of C_k were determined by means of the maximum-likelihood principle with the objective function given by the squares of relative deviations in pressure

TABLE 5. Coefficients of equation (4) and standard deviations $s(p)$ of pressure and $s(y)$ of vapour mole fraction

	T/K	C_1	C_2	C_3	$s(p/\text{kPa})$	$s(y)$
$(1-x)\text{CH}_3\text{OC}_4\text{H}_9 + x\text{C}_7\text{H}_{16}$	323.15	0.18166	—	—	0.04	0.003
	343.15	0.15085	—	—	0.07	0.003
$(1-x)(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2 + x\text{C}_7\text{H}_{16}$	323.15	0.0707	-0.0163	—	0.02	0.007
	343.15	0.0582	-0.0128	—	0.03	0.008
$(1-x)(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2 + x(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$	343.15	0.1055	-0.0152	-0.0056	0.07	0.003
$(1-x)\text{C}_5\text{H}_{11}\text{OC}_5\text{H}_{11} + x\text{C}_{11}\text{H}_{24}$	403.15	0.0372	0.0103	-0.0258	0.04	0.006
$(1-x)\text{CH}_3\text{OCH}_2\text{OCH}_3 + x\text{C}_6\text{H}_{14}$	313.15	0.8076	0.1208	0.0371	0.08	0.006
$(1-x)\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 + x\text{C}_7\text{H}_{16}$	323.15	0.4291	-0.0108	0.0161	0.05	0.002
	343.15	0.3844	0.0016	0.0086	0.08	0.002
$(1-x)\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 + x(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CH}_3)_2$	343.15	0.7744	0.0794	0.0016	0.09	0.002
$(1-x)\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3 + x\text{C}_{12}\text{H}_{26}$	435.26	0.9736	0.1252	0.0403	0.07	0.005
$(1-x)\text{CH}_3\text{OC}_4\text{H}_9 + x\text{C}_6\text{H}_6$	343.15	0.05361	—	—	0.07	0.003
$(1-x)(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2 + x\text{C}_6\text{H}_6$	343.15	0.1555	0.2611	—	0.04	0.002
$(1-x)\text{C}_2\text{H}_5\text{OCH}_2\text{OC}_2\text{H}_5 + x\text{C}_6\text{H}_6$	343.15	0.0151	0.0045	—	0.04	0.001

TABLE 6. Azeotropic mole fractions x_{az} and pressures p_{az}

	T/K	1 - x_{az}		p_{az} /kPa	
		expt	calc.	expt	calc.
$(1-x)C_2H_5OCH_2OC_2H_5 + xC_7H_{16}$	323.15	0.895	0.907	27.1	27.05
	343.15	0.910	0.918	56.95	56.91
$(1-x)CH_3OCH_2CH_2OCH_3 + x(CH_3)_2CHCH_2CH(CH_3)_2$	343.15	0.402	0.409	82.3	82.36
$(1-x)CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OCH_3 + xC_{12}H_{26}$	435.26	0.373	0.377	25.5	25.62

and vapour mole fraction. The values obtained are listed in table 5. The standard deviations $s(p)$ in pressure and $s(y)$ in vapour mole fraction are also listed in table 5. Using the C_k values reported in table 5, the calculated vapour-liquid equilibrium values agree well with the experimental results.

Azeotropes exist in (diethoxymethane + *n*-heptane), (1,2-dimethoxyethene + 2,4-dimethylpentane), and (2,5,8,11-tetraoxadodecane + *n*-dodecane) at the temperatures studied. The azeotropic compositions and pressures estimated from the experimental results are compared in table 6 with the calculated values using equation (4).

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