ported while a more significant difference is observed in the case of density. The latter is likely to be due to using a more accurate instrument here than in previous work.

Glossary

A, B, C	coefficients (eq 1)
w_{eq}	solubility, kg of K_2SO_4/kg of H_2O
x	concentration of 2-propanol, kg of 2-propanol/kg of H_2O
ρ	density of saturated solution, kg/m^3

Registry No. K_2SO_4, 7778-80-5; 2-propanol, 67-63-0.

Literature Cited

(1) Mullin, J. W. *Crystallization*, 2nd ed.; Butterworths: London, 1972; Chapter 8, pp 263-265.
(2) Karpinski, P. H.; Budz, J.; Mydlarz, J. International Symposium-Workshop on Particulate and Multi-Phase Processes and 16th Annual Meeting of the Fine Particle Society, Miami Beach, FL, 1985.
(3) Mydlarz, J.; Jones, A. G. *Chem. Eng. Res. Dev.*, in press.
(4) Mullin, J. W.; Gaska, C. *J. Chem. Eng. Data* **1973**, *18*, 217.
(5) Ishii, T.; Fujita, S. *J. Chem. Eng. Data* **1978**, *23*, 19.
(6) Broul, M.; Nývlt, J.; Söhnel, O. *Solubility in Inorganic Two-Component Systems*; Academia: Prague; Elsevier: Amsterdam, 1981; pp 89, 94.

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Isobaric Vapor–Liquid Equilibria for 6-Methyl-5-hepten-2-one + Bis(3-methyl-2-butenyl) Ether, Bis(3-methyl-2-butenyl) Ether + 3,3-Dimethyl-2-propen-1-ol, 3,3-Dimethyl-2-propen-1-ol + 6-Methyl-5-hepten-2-one, and 6-Methyl-5-hepten-2-one + 6-Methyl-3-isopropenyl-5-hepten-2-one Binary Systems

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Isobaric vapor–liquid equilibria (VLE) data and UNIQUAC parameters of four binary systems, 6-methyl-5-hepten-2-one + bis(3-methyl-2-butenyl) ether, bis(3-methyl-2-butenyl) ether + 3,3-dimethyl-2-propen-1-ol, 3,3-dimethyl-2-propen-1-ol + 6-methyl-5-hepten-2-one, and 6-methyl-5-hepten-2-one + 6-methyl-3-isopropenyl-5-hepten-2-one at 50, 100, and 150 mmHg are presented. The vapor pressure data and Antoine constants for pure components are also reported.

Introduction

6-Methyl-5-hepten-2-one is an important organic intermediate for synthesizing vitamins A, E, and K_1 as well as some kinds of perfumes and fine chemicals. For the design and operation of separation processes for manufacturing 6-methyl-5-hepten-2-one with high purity, it is necessary to obtain precise VLE data at low pressures for various combinations of components concerning these processes. In this work, the isobaric $p-t-x$ data for 6-methyl-5-hepten-2-one + bis(3-methyl-2-butenyl) ether, bis(3-methyl-2-butenyl) ether + 3,3-dimethyl-2-propen-1-ol + 6-methyl-5-hepten-2-one, and 6-methyl-5-hepten-2-one + 6-methyl-3-isopropenyl-5-hepten-2-one binary systems at low pressures and vapor pressures of corresponding pure components were presented. The vapor compositions were calculated by a direct method based on the Gibbs–Duhem equation developed previously (*1*). The experimental data sets were also correlated with UNIQUAC model (*2*) for practical purposes.

Experimental Section

All chemicals prepared from other laboratories using the methods provided by literature (*3*) were further purified by rectification in an Auto Annular Still (Perkin-Elmer Model 251) under vacuum with approximately 100 theoretical plates. The purity of all chemicals as tested by gas chromatography was greater than 99.9 wt %. Vapor–liquid equilibria and vapor pressures were measured by an Eckert ebulliometer (*4*) connected with a constant-pressure control unit (sensitivity ±0.02 mmHg) and charged with liquid mixture of known amount and composition. After the steady state was established, the pressure readings were taken from a mercury manometer by a cathetometer (accuracy ±0.02 mm) and corrected for standard density and gravitation acceleration. The temperatures were measured by using a calibrated mercury thermometer (accuracy ±0.01 °C). The equilibrium composition of liquid

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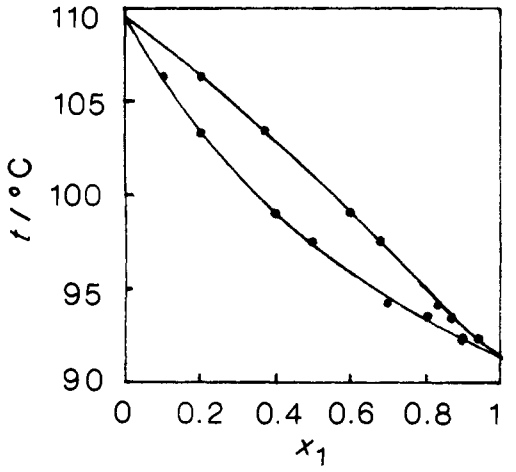

Figure 1. $t-x-y$ diagram of 6-methyl-5-hepten-2-one (1) + bis(3-methyl-2-butenyl) ether (2) system at 50 mmHg: (●) experimental; (—) UNIQUAC.

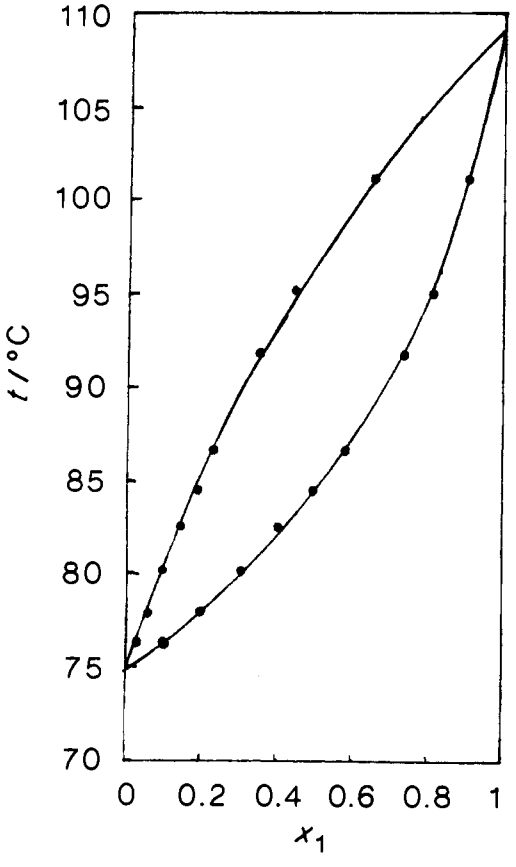

Figure 2. $t-x-y$ diagram of bis(3-methyl-2-butenyl) ether (1) + 3,3-dimethyl-2-propen-1-ol (2) system at 50 mmHg: (●) experimental; (—) UNIQUAC.

phase in the ebulliometer was calculated from the original composition by means of the material balance equation (*5*).

Results

Boiling points as a function of liquid compositions and pressures were measured for 6-methyl-5-hepten-2-one + bis(3-methyl-2-butenyl) ether, bis(3-methyl-2-butenyl) ether + 3,3-dimethyl-2-propen-1-ol, 3,3-dimethyl-2-propen-1-ol + 6-methyl-5-hepten-2-one, and 6-methyl-5-hepten-2-one + 6-methyl-3-isopropenyl-5-hepten-2-one binary systems at 50–150 mmHg.

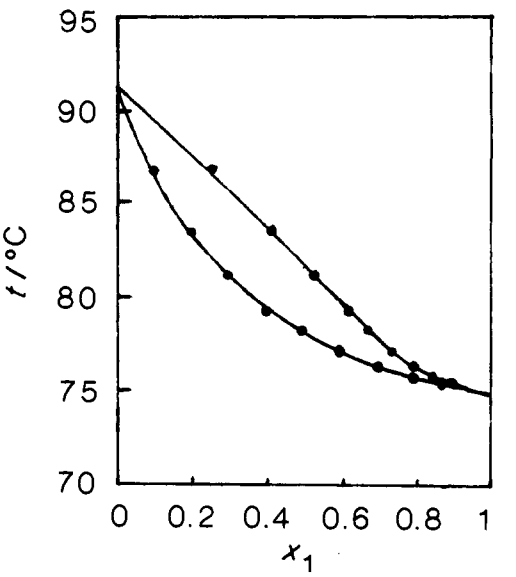

Figure 3. $t-x-y$ diagram of 3,3-dimethyl-2-propen-1-ol (1) + 6-methyl-5-hepten-2-one (2) system at 50 mmHg: (●) experimental; (—) UNIQUAC.

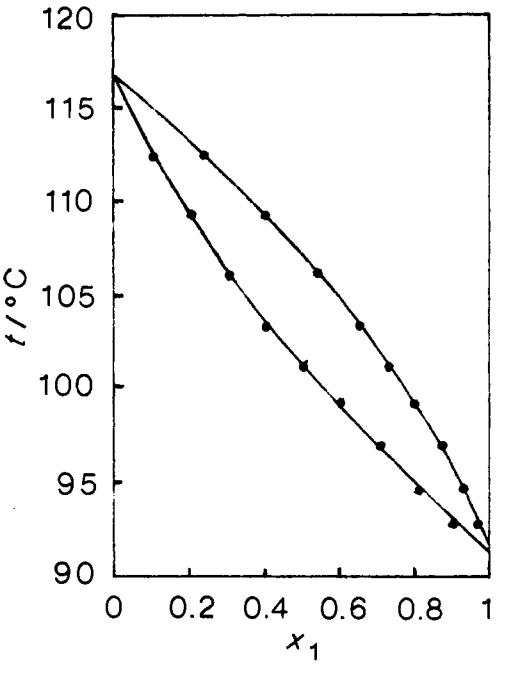

Figure 4. $t-x-y$ diagram of 6-methyl-5-hepten-2-one (1) + 6-methyl-3-isopropenyl-5-hepten-2-one (2) system at 50 mmHg: (●) experimental; (—) UNIQUAC.

In order to obtain complete VLE data, the equilibrium vapor compositions were calculated by a direct thermodynamic method developed previously (*1*). The results are listed in Table I.

The experimental $p-t-x$ data of four binary systems were also correlated with the UNIQUAC equation. The model parameters were estimated by means of a maximum likelihood method (*6*) developed previously with the use of the objective function S;

$$S = \sum_{i=1}^{N} (p_{i,\text{calcd}} - p_{i,\text{exptl}})^2 / \sigma_p^2 \qquad (1)$$

The required volume parameters r_i and area parameters q_i for

Table I. Isobaric VLE Data of Four Binary Systems Compared with Bubble-Point-Calculation Values by UNIQUAC at 50, 100, and 150 mmHg[a]

		direct method	UNIQUAC			
system, press.	x_1	t_{expt}/°C	$y_{1,calcd}$	t_{calcd}/°C	$y_{1,calcd}$	Δt/°C	Δy_1
A, 50 mmHg	0.0000	109.36	0.0000	109.36	0.0000	0.00	0.0000
	0.0956	106.44	0.1986	106.31	0.1977	−0.13	−0.0009
	0.1993	103.37	0.3787	103.51	0.3636	0.14	−0.0151
	0.4020	99.14	0.5949	99.14	0.5967	0.00	0.0018
	0.4977	97.61	0.6741	97.46	0.6799	−0.15	0.0058
	0.6983	94.22	0.8296	94.54	0.8218	0.32	−0.0078
	0.8004	93.43	0.8713	93.30	0.8838	−0.14	0.0125
	0.9004	92.34	0.9415	92.20	0.9418	−0.15	0.0003
	1.0000	91.20	1.0000	91.20	1.0000	0.00	0.0000
rms						0.17	0.0083
B, 50 mmHg	0.0000	74.73	0.0000	74.73	0.0000	0.00	0.0000
	0.0984	76.24	0.0257	76.31	0.0263	0.07	0.0006
	0.1998	77.88	0.0527	78.07	0.0570	0.19	0.0043
	0.3054	80.01	0.0881	80.08	0.0938	0.07	0.0057
	0.4022	82.59	0.1387	82.14	0.1337	−0.45	−0.0050
	0.5033	84.61	0.1818	84.59	0.1842	−0.02	0.0024
	0.5835	86.72	0.2282	86.82	0.2335	0.10	0.0053
	0.7379	91.89	0.3529	92.21	0.3682	0.32	0.0153
	0.8043	95.11	0.4408	95.21	0.4541	0.10	0.0133
	0.9014	101.26	0.6445	100.85	0.6413	−0.41	−0.0032
	1.0000	109.36	1.0000	109.36	1.0000	0.00	0.0000
rms						0.24	0.0077
C, 50 mmHg	0.0000	91.20	0.0000	91.20	0.0000	0.00	0.0000
	0.0991	86.76	0.2522	86.54	0.2569	−0.22	0.0047
	0.1992	83.37	0.4187	83.34	0.4171	−0.03	−0.0016
	0.2990	81.03	0.5229	81.06	0.5277	0.03	−0.0022
	0.3950	79.08	0.6211	79.42	0.6086	0.34	−0.0125
	0.4963	78.11	0.6711	78.09	0.6783	−0.02	0.0072
	0.6030	77.14	0.7351	77.00	0.7424	−0.14	0.0073
	0.6991	76.16	0.8037	76.21	0.7970	0.05	−0.0067
	0.7987	75.56	0.8525	75.56	0.8549	0.00	0.0024
	0.8985	75.38	0.9103	75.06	0.9197	−0.32	0.0094
	1.0000	74.73	1.0000	74.73	1.0000	0.00	0.0000
rms						0.18	0.0069
D, 50 mmHg	0.0000	116.65	0.0000	116.65	0.0000	0.00	0.0000
	0.0992	112.48	0.2365	112.54	0.2344	0.06	−0.0021
	0.2000	109.28	0.3981	109.09	0.4074	−0.19	0.0093
	0.2984	106.07	0.5413	106.17	0.5383	0.10	−0.0030
	0.3966	103.26	0.6488	103.56	0.6436	0.30	−0.0052
	0.4980	101.13	0.7250	101.10	0.7333	−0.03	0.0083
	0.5983	99.11	0.7961	98.84	0.8073	−0.27	0.0112
	0.6996	96.94	0.8653	96.71	0.8699	−0.23	0.0046
	0.7990	94.51	0.9268	94.76	0.9213	0.25	−0.0055
	0.9006	92.59	0.9662	92.89	0.9649	0.30	−0.0013
	1.0000	91.20	1.0000	91.20	1.0000	0.00	0.0000
rms						0.22	0.0065
A, 100 mmHg	0.0000	127.85	0.0000	127.85	0.0000	0.00	0.0000
	0.0954	124.01	0.2149	124.19	0.2055	0.18	−0.0094
	0.1994	121.02	0.3704	121.10	0.3668	0.08	−0.0036
	0.4022	116.99	0.5781	116.68	0.5864	−0.31	0.0083
	0.4977	115.11	0.6715	115.04	0.6665	−0.07	−0.0050
	0.6984	112.02	0.8157	112.16	0.8110	0.14	−0.0047
	0.8003	110.70	0.8805	110.89	0.8771	0.18	−0.0034
	0.9004	109.52	0.9408	109.73	0.9395	0.21	−0.0013
	1.0000	108.65	1.0000	108.65	1.0000	0.00	0.0000
rms						0.18	0.0057
B, 100 mmHg	0.0000	89.66	0.0000	89.66	0.0000	0.00	0.0000
	0.0984	91.10	0.0251	91.34	0.0269	0.24	0.0018
	0.1999	92.95	0.0523	93.19	0.0571	0.25	0.0048
	0.3054	95.23	0.0872	95.33	0.0928	0.10	0.0056
	0.4023	97.82	0.1315	97.55	0.1313	−0.27	−0.0002
	0.5033	100.45	0.1817	100.21	0.1802	−0.24	−0.0015
	0.5836	102.47	0.2212	102.67	0.2285	0.21	0.0073
	0.7379	108.64	0.3557	108.69	0.3623	0.05	0.0066
	0.8043	111.99	0.4397	112.06	0.4489	0.07	0.0092
	0.9015	118.54	0.6346	118.41	0.6386	−0.13	0.0040
	1.0000	127.85	1.0000	127.85	1.0000	0.00	0.0000
rms						0.19	0.0054
C, 100 mmHg	0.0000	108.65	0.0000	108.65	0.0000	0.00	0.0000
	0.0991	104.09	0.2438	103.77	0.2516	−0.32	0.0078
	0.1992	100.28	0.4184	100.18	0.4180	−0.10	−0.0004
	0.2989	97.51	0.5365	97.47	0.5364	−0.04	−0.0001
	0.3949	95.19	0.6318	95.43	0.6234	0.24	−0.0084
	0.4959	93.43	0.7044	93.74	0.6967	0.32	−0.0077
	0.6028	92.49	0.7502	92.35	0.7613	−0.14	0.0111
	0.6990	91.33	0.8153	91.37	0.8130	0.04	−0.0023
	0.7987	90.69	0.8570	90.58	0.8650	−0.11	0.0080
	0.8985	90.29	0.9171	89.99	0.9223	−0.31	0.0052
	1.0000	89.66	1.0000	89.66	1.0000	0.00	0.0000
rms						0.21	0.0068

Table I (Continued)

system, press.	x_1	t_{expt}/°C	direct method $y_{1,calcd}$	UNIQUAC t_{calcd}/°C	UNIQUAC $y_{1,calcd}$	Δt/°C	Δy_1
D, 100 mmHg	0.0000	135.10	0.0000	135.10	0.0000	0.00	0.0000
	0.0993	130.64	0.2323	130.87	0.2265	0.23	−0.0058
	0.2001	127.48	0.3841	127.27	0.3974	−0.21	0.0133
	0.2986	124.24	0.5250	124.21	0.5278	−0.03	0.0028
	0.3968	121.37	0.6332	121.48	0.6333	0.11	0.0001
	0.4981	119.00	0.7166	118.92	0.7235	−0.08	0.0069
	0.5983	116.50	0.7981	116.58	0.7984	0.08	0.0003
	0.6997	114.56	0.8565	114.38	0.8625	−0.18	0.0060
	0.7991	112.20	0.9188	112.35	0.9159	0.15	−0.0029
	0.9006	110.24	0.9623	110.42	0.9620	0.18	−0.0003
	1.0000	108.65	1.0000	108.65	1.0000	0.00	0.0000
rms						0.15	0.0059
A, 150 mmHg	0.0000	139.52	0.0000	139.52	0.0000	0.00	0.0000
	0.0953	135.06	0.2246	135.41	0.2107	0.35	−0.0139
	0.1995	132.13	0.3660	132.17	0.3680	0.04	0.0020
	0.4023	128.24	0.5684	127.76	0.5795	−0.48	0.0111
	0.4977	126.14	0.6705	126.15	0.6585	0.01	−0.0120
	0.6985	123.26	0.8071	123.26	0.8054	0.00	−0.0017
	0.8002	121.58	0.8855	121.98	0.8737	0.40	−0.0118
	0.9004	120.33	0.9405	120.79	0.9383	0.46	−0.0022
	1.0000	119.66	1.0000	119.66	1.0000	0.00	0.0000
rms						0.32	0.0094
B, 150 mmHg	0.0000	99.00	0.0000	99.00	0.0000	0.00	0.0000
	0.0984	100.39	0.0247	100.73	0.0273	0.34	0.0026
	0.1999	102.37	0.0521	102.65	0.0570	0.28	0.0049
	0.3054	104.76	0.0866	104.86	0.0918	0.10	0.0052
	0.4023	107.34	0.1276	107.19	0.1293	−0.16	0.0017
	0.5033	110.39	0.1815	110.00	0.1774	−0.39	−0.0041
	0.5836	112.33	0.2172	112.63	0.2254	0.30	0.0082
	0.7379	119.17	0.3573	119.08	0.3593	−0.09	0.0020
	0.8044	122.60	0.4390	122.70	0.4465	0.10	0.0075
	0.9016	129.41	0.6289	129.50	0.6378	0.09	0.0089
	1.0000	139.52	1.0000	139.52	1.0000	0.00	0.0000
rms						0.23	0.0056
C, 150 mmHg	0.0000	119.66	0.0000	119.66	0.0000	0.00	0.0000
	0.0992	115.03	0.2389	114.59	0.2496	−0.44	0.0107
	0.1992	110.93	0.4183	110.76	0.4186	−0.17	0.0003
	0.2988	107.88	0.5403	107.78	0.5406	−0.10	0.0003
	0.3948	105.32	0.6379	105.50	0.6306	0.18	−0.0073
	0.4958	103.02	0.7213	103.58	0.7061	0.56	−0.0152
	0.6027	102.10	0.7591	101.98	0.7716	−0.12	0.0125
	0.6990	100.82	0.8221	100.86	0.8223	0.04	0.0002
	0.7986	100.17	0.8600	99.97	0.8715	−0.20	0.0115
	0.8984	99.62	0.9218	99.32	0.9242	−0.30	0.0024
	1.0000	99.00	1.0000	99.00	1.0000	0.00	0.0000
rms						0.29	0.0088
D, 150 mmHg	0.0000	146.72	0.0000	146.72	0.0000	0.00	0.0000
	0.0993	142.09	0.2298	142.45	0.2213	0.36	−0.0085
	0.2002	138.94	0.3757	138.76	0.3912	−0.18	0.0155
	0.2987	135.70	0.5152	135.60	0.5217	−0.10	0.0065
	0.3969	132.80	0.6237	132.79	0.6276	−0.01	0.0039
	0.4981	130.26	0.7119	130.15	0.7181	−0.11	0.0062
	0.5983	127.44	0.7994	127.75	0.7934	0.31	−0.0060
	0.6997	125.66	0.8510	125.50	0.8583	−0.16	0.0073
	0.7992	123.37	0.9136	123.44	0.9126	0.07	−0.0010
	0.9006	121.37	0.9599	121.47	0.9601	0.10	0.0002
	1.0000	119.66	1.0000	119.66	1.0000	0.00	0.0000
rms						0.19	0.0074

[a] Systems: A, 6-methyl-5-hepten-2-one + bis(3-methyl-2-butenyl) ether; B, bis(3-methyl-2-butenyl) ether + 3,3-dimethyl-2-propen-1-ol; C, 3,3-dimethyl-2-propen-1-ol + 6-methyl-5-hepten-2-one; D, 6-methyl-5-hepten-2-one + 6-methyl-3-isopropenyl-5-hepten-2-one.

various components were calculated with the same group parameters used in UNIFAC (7). The values of r_i and q_i are reported in Table II. Table III shows the parameters of the UNIQUAC equation of four binaries. Bubble-point calculations were made with the use of these parameters. The results are also presented in Table I. It can be shown from these tables that the calculated bubble points and vapor compositions are in good agreement with the experimental values and those calculated by direct thermodynamic method.

Figures 1–4 show the $t-x-y$ diagrams of the four binary systems at 50 mmHg.

Experimental vapor pressures and corresponding Antoine constants obtained by fitting experimental data of the four pure components are listed in Tables IV and V. The rms's of fitting are 0.26, 0.35, 0.38, and 0.22 mmHg for 6-methyl-5-hepten-2-one, bis(3-methyl-2-butenyl) ether, 3,3-dimethyl-2-propen-1-ol, and 6-methyl-3-isopropenyl-5-hepten-2-one, respectively.

Table II. Volume and Area Parameters of Four Pure Components

component	r_i	q_i
6-methyl-5-hepten-2-one	5.7120	4.9400
bis(3-methyl-2-butenyl) ether	6.9743	6.0640
3,3-dimethyl-2-propen-1-ol	4.3652	4.1120
6-methyl-3-isopropenyl-5-hepten-2-one	7.5029	6.4640

Conclusions

The experimental $p-t-x$ data of four binaries can be correlated satisfactorily by the UNIQUAC model. The UNIQUAC

Table III. UNIQUAC Parameters of Four Binary Systems

	pressure/mmHg							
	50		100		150		50–150	
system (i–j)	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$	$(u_{ij} - u_{jj})/R$	$(u_{ji} - u_{ii})/R$
6-methyl-5-hepten-2-one + bis(3-methyl-2-butenyl) ether	99.67	−75.66	−93.44	127.2	−138.5	193.7	−129.5	179.2
bis(3-methyl-2-butenyl) ether + 3,3-dimethyl-2-propen-1-ol	131.9	−101.2	70.48	−51.34	−7.393	23.20	51.52	−34.37
3,3-dimethyl-2-propen-1-ol + 6-methyl-5-hepten-2-one	32.33	7.049	186.3	−117.2	258.4	−162.7	206.4	−130.9
6-methyl-5-hepten-2-one + 6-methyl-3-isopropenyl-5-hepten-2-one	−159.7	198.4	−150.3	183.1	−135.8	161.4	−142.0	170.4

Table IV. Experimental Vapor Pressure vs Temperature Data of Four Pure Components

component	t/°C	p/mmHg
6-methyl-5-hepten-2-one	90.15	48.05
	96.41	62.03
	100.40	72.32
	104.49	85.63
	108.75	100.34
	114.95	126.09
	119.30	148.26
bis(3-methyl-2-butenyl) ether	109.10	49.25
	117.70	69.24
	123.44	84.76
	129.27	105.13
	134.90	127.90
	140.63	156.17
3,3-dimethyl-2-propen-1-ol	73.70	47.91
	80.40	65.78
	83.12	74.26
	86.48	86.15
	88.82	96.11
	91.32	108.09
	92.97	115.53
	93.28	118.01
	95.30	127.83
	97.64	141.26
6-methyl-3-isopropenyl-5-hepten-2-one	115.84	48.62
	122.74	63.36
	126.92	73.95
	129.90	82.55
	133.73	95.51
	138.05	111.21
	146.40	148.10

Table V. Antoine Constants of Four Pure Components

$$\ln (p/\text{mmHg}) = A - B/(t/°\text{C} + C)$$

component	A	B	C	press./mmHg
6-methyl-5-hepten-2-one	19.0727	5523.76	273.15	50–150
bis(3-methyl-2-butenyl) ether	18.9409	5748.66	273.15	50–150
3,3-dimethyl-2-propen-1-ol	20.7580	5860.44	273.15	50–150
6-methyl-3-isopropenyl-5-hepten-2-one	19.2544	5980.46	273.15	50–150

parameters obtained can be used in corresponding process design and development.

Glossary

A, B, C	Antoine constants
p	total vapor pressure, mmHg
q	area parameter
R	gas constant
rms	root-mean-square deviation
r	volume parameter
S	objective function
t	temperature, °C
u_{ij}	parameter of UNIQUAC equation
x	liquid mole fraction
y	vapor mole fraction
σ_p^2	estimated variance of the measured pressures

Subscripts

calcd	calculated value
exptl	experimental value
i, j	component i, j
1, 2	component 1, 2

Registry No. 6-Methyl-5-hepten-2-one, 110-93-0; bis(3-methyl-2-butenyl) ether, 26902-25-0; 3,3-dimethyl-2-propen-1-ol, 556-82-1; 6-methyl-3-isopropenyl-5-hepten-2-one, 26533-38-0.

Literature Cited

(1) Hu, Y.; Ying, X.-G. *J. Chem. Ind. Eng. (China)* **1984**, *3*, 1.
(2) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(3) Meuly, W. C.; Gradeff, P. S. U.S. Patent 3 668 255, 1972.
(4) Eckert, C. A.; Newman, B. A.; Nicolaides, G. L.; Long, T. C. *AIChE J.* **1981**, *27*, 33.
(5) Rogalski, M.; Malanowski, S. *Fluid Phase Equilib.* **1980**, *5*, 97.
(6) Hu, Y.; Ying, X.-G. *Proceedings, CIESC and AIChE Joint Meeting of Chemical Engineering, 1982*; Chemical Industry Press (China): Beijing, 1982; Vol. I, p 177.
(7) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor–Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977, pp 39–48.

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