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Vapor–Liquid Equilibria of Hydrocarbons and Fuel Oxygenates

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We report here the pure component vapor pressures of methyl *tert*-butyl ether (MTBE), 2,2,4-trimethylpentane (TMP), and methylcyclohexane (MCH) and P–T–x–y data for MTBE separately with TMP and MCH, for MTBE with four- and eleven-component simulated gasoline mixtures, and for ethanol (ETOH) with the eleven-component simulated gasoline mixture over a temperature range from 15 to 60 °C. In addition we report static cell (P–T–x) data at -6.7 °C for the same mixtures. The data we report here are useful for developing activity coefficient and equation of state models to predict the shift in equilibrium pressures and vapor compositions when oxygenates, such as ethers or alcohols, are added to gasoline in order to increase the octane rating and/or decrease pollution emissions on combustion.

Introduction

Presently there is interest in adding oxygenated compounds, such as ethers and alcohols, to gasolines because of their octane-enhancing and pollution-reducing capabilities. However, there are relatively few vapor–liquid equilibrium data on oxygenate + binary and oxygenate + multicomponent hydrocarbon mixtures. Such data are of importance in deciding, for example, how the Reid vapor pressure of a (real or synthetic) gasoline mixture would change with additions of various oxygenated compounds and more generally in predicing the vapor-phase composition that would be in equilibrium with different hydrocarbon liquids. Also, such data are needed for developing and testing equation of state and activity coefficient models that could be used to predict these effects when no experimental data are available.

For this reason the American Petroleum Institute commissioned the measurements we report here of the vapor–liquid of methyl *tert*-butyl ether (MTBE) separately with 2,2,4-trimethylpentane (TMP), methylcyclohexane (MCH), and a four-component and an eleven-component simulated gasoline mixture and of ethanol (ETOH) with the eleven-component simulated gasoline over a range of temperatures from -6.7 to +60.0 °C. In this paper we report the results of this study, as well as our measurements of the vapor pressures of MTBE, TMP, and MCH.

Equipment and Materials Used

All the chemicals used in this work were purchased from Aldrich, except for 200 proof ethanol obtained from the U.S. Industrial Chemical Co., and all were used as received. The hexylbenzene was of 97% purity, and the butane had a purity of 98%. The 2-methylpentane, MCH, 2-heptene, and undecane had a reported purity of 99%, and isopentane had a purity of 99.8%. The remaining chemicals had a purity of 99.9% or better.

Table I. Experimental Vapor Pressures P of the Pure Components as a Function of Temperature t, and Antoine Constants A, B, and C [$\log (P/\text{kPa}) = A - B/[t/°\text{C}) + C]$]

2,2,4-trimethylpentane		methyl *tert*-butyl ether		methylcyclohexane	
t/°C	P/kPa	t/°C	P/kPa	t/°C	P/kPa
15.70	4.000	14.00	20.750	21.70	4.960
16.00	4.050	15.00	21.720	24.10	5.690
18.00	4.440	16.00	22.800	25.00	5.960
21.08	5.240	17.00	23.730	30.62	7.900
25.02	6.412	18.00	24.800	34.68	9.535
30.50	8.408	19.70	26.640	38.00	11.140
35.50	10.530	21.60	28.885	45.72	15.450
38.00	11.815	24.00	32.000	50.62	18.830
49.35	19.012	28.14	37.972	55.36	22.695
60.00	28.595	30.33	41.473	60.00	27.125
		31.16	42.735		
		35.61	50.916		
		40.40	60.850		
		44.76	71.330		
		49.00	82.990		
		53.09	95.750		
A = 5.428 82		A = 6.625 62		A = 5.266 03	
B = 990.390		B = 1454.276		B = 916.554	
C = 189.3107		C = 260.0056		C = 179.0968	

All vapor pressure and vapor–liquid equilibrium measurements at 15 °C and above were made with a Stage-Muller dynamic still described previously (*1*). Temperatures were measured with a platinum resistance thermometer (Rosemount Model 162N) and a Fluke Model 8520A programmable digital multimeter with an accuracy to ±0.02 °C. Pressures were measured with a Wallace and Tiernan Model FA-187 precision mercury manometer to an accuracy of ±1.3 Pa. Samples from the binary mixture vapor–liquid equilibrium measurements were analyzed with a Hewlett-Packard Model 5730A gas chromatograph with a Model 3390A integrator. A stainless steel column (6-ft length × $^1/_4$-in.-i.d.) packed with 200 mesh Porapak Q, operated isothermally, was used in the analysis with a thermal conductivity detector. Analyses of systems involving the close-boiling four- and eleven-component simulated gasoline mixtures were done with a Hewlett-Packard Model 5880 gas chromatograph, Model 5880A integrator, and Model 7673A autosampler and autoinjector. A DB-S-60N, 60-m capillary column with a 1.0-μm film thickness of bonded methyl 5% phenyl silicone was used for analysis with a flame ionization detector. The temperature programs used in the analyses were as follows: MTBE + four-component system, 40 °C for 25 min, thereafter increasing by 10 °C/min up to 150 °C, which was then maintained for another 10 min, oxygenates + simulated gasoline mixture and all the static cell measurements, 40 °C for 10 min, thereafter increasing by 10 °C/min up to 250 °C, which was then maintained for another 25 min. In all cases 1-μL samples were used with a split ratio of approximately 55:1. The GC-integrator results were analyzed by the response-factor method with response factors determined from the analysis of gravimetrically prepared mixtures run at the same conditions as the later samples.

Since reliable measurements at -6.7 °C could not be made with our dynamic still because of the difficulty in controlling the low pressures involved while containing the butane, static cell measurements were made at this temperature. The equipment we use, shown in Figure 1, was made for us at the Technical University of Berlin and includes glass cells with injection ports, temperature-control equipment, temperature measurement with a platinum resistance thermometer, and differential pressure measurement with an MKS Model 223B pressure transducer (range of ±13 kPa) and digital readout, which we calibrated against a water-filled manometer read with a cathetometer.

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Table II. Experimental Vapor Pressures P, Liquid Mole Fractions $x(1)$, and Vapor Mole Fractions $y(1)$ at Constant Temperature t of the Binary Mixtures

methyl *tert*-butyl ether (1) + 2,2,4-trimethylpentane (2)			methyl *tert*-butyl ether (1) + methylcyclohexane (2)		
P/kPa	$x(1)$	$y(1)$	P/kPa	$x(1)$	$y(1)$
t = −6.63 °C[a]			t = −6.64 °C[a]		
1.06	0.0000		0.95	0.0000	
1.65	0.0750		1.57	0.0570	
2.15	0.1390		2.06	0.1070	
2.47	0.1940		2.37	0.1530	
2.86	0.2430		2.72	0.1960	
t = 15.00 °C					
6.62	0.0608	0.2879	5.40	0.0476	0.3333
7.45	0.1190	0.4609	5.90	0.0639	0.3850
9.50	0.2222	0.6202	8.80	0.1803	0.6126
			10.80	0.2716	0.7022
t = 25.00 °C					
11.13	0.1144	0.4584	9.55	0.0725	0.3752
11.85	0.1242	0.4794	11.10	0.1179	0.4847
15.03	0.2261	0.6082	12.07	0.1422	0.5282
			15.51	0.2467	0.6737
t = 38.00 °C					
18.22	0.0774	0.3180	18.66	0.1092	0.4389
22.91	0.1756	0.5327	23.78	0.2235	0.6111
23.92	0.1915	0.5551			
27.72	0.2562	0.6354			
t = 60.00 °C					
37.24	0.0702	0.2583	41.00	0.1014	0.3795
47.99	0.1842	0.5005	51.33	0.2190	0.5648
62.44	0.3353	0.6863			

[a] Static cell, vapor-phase mole fractions not measured.

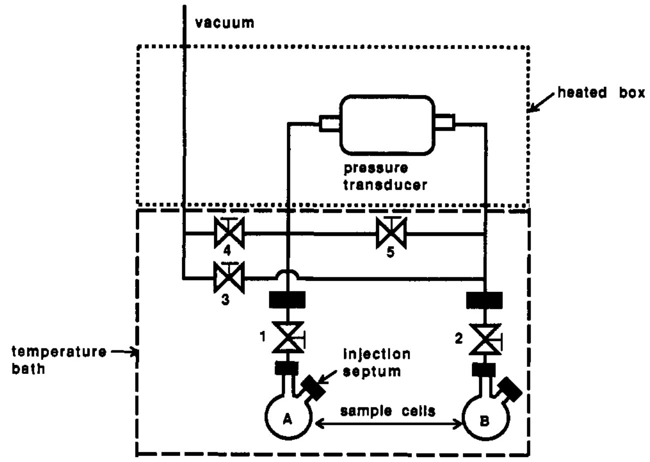

Figure 1. Schematic diagram of the static cell apparatus showing cells, injection ports, and locations of temperature bath and heated pressure transducer box. Valve 5 is open only to zero the pressure transducer. Cell A contained mixture under study while cell B was either evacuated or contained the reference solvent.

Pressures were measured relative to absolute vacuum and/or heptane (which is available in high purity and whose vapor pressure is well-known). Since we used a static cell, only the liquid composition, temperature, and bubble point pressure are reported for the measurements at −6.7 °C.

The static cell was operated in two different manners, depending on the mixture. In one way all components, in the proper relative proportions, were added to the cell. This mixture was then degassed under vacuum while an ultrasonic bath was simultaneously used at least three times, its bubble point pressure measured, and then the mixture composition determined by GC analysis. This analysis is necessary since, during the degassing step, the more volatile components are preferentially lost. However, for the MTBE + simulated gasoline mixtures all components, other than MTBE and butane, were placed in the cell in the proportions required. This mixture was then degassed, as was the MTBE separately. An excess of butane was then added to the simulated gasoline, and the mixture was further degassed by freezing with liquid nitrogen and evacuating. A freeze–evacuate–thaw cycle was repeated two additional times. A sample was then withdrawn from the mixture cell and analyzed, and then the contents of the cell were weighed.

Following this, gravimetric additions of the degassed MTBE were made by injection through a septum into the cell, and the bubble point of the new mixture was then measured. As a precaution against air leaks into the cell during the injections,

Table III. Experimental Vapor Pressures P, Liquid Mole Fractions $x(i)$, and Vapor Mole Fractions $y(i)$ at Temperatures t of the Mixture Methyl *tert*-Butyl Ether (1) + 2,2,4-Trimethylpentane (2) + Heptane (3) + MCH (4) + Toluene (5)

t/°C	P/kPa	$x(1)$	$x(2)$	$x(3)$	$x(4)$	$y(1)$	$y(2)$	$y(3)$	$y(4)$
−6.73[a]	0.91	0.000	0.387	0.152	0.104				
−6.76[a]	1.46	0.036	0.373	0.146	0.100				
−6.76[a]	1.67	0.070	0.360	0.141	0.097				
−6.74[a]	1.85	0.103	0.348	0.136	0.093				
−6.82[a]	2.04	0.133	0.336	0.131	0.090				
−6.78[a]	2.21	0.161	0.325	0.127	0.087				
−6.76[a]	2.38	0.187	0.315	0.123	0.085				
15.00	5.15	0.043	0.354	0.133	0.092	0.203	0.350	0.118	0.084
15.00	6.45	0.098	0.335	0.125	0.087	0.359	0.285	0.096	0.068
15.00	8.53	0.203	0.297	0.112	0.077	0.548	0.202	0.068	0.049
25.00	6.09	0.000	0.340	0.135	0.099	0.000	0.415	0.147	0.109
25.00	7.11	0.030	0.354	0.125	0.094	0.156	0.367	0.117	0.089
25.00	10.12	0.101	0.316	0.124	0.088	0.360	0.266	0.097	0.069
25.00	12.90	0.192	0.267	0.109	0.077	0.513	0.196	0.074	0.053
38.00	10.95	0.000	0.353	0.136	0.099	0.000	0.420	0.148	0.106
38.00	13.32	0.047	0.321	0.127	0.093	0.215	0.321	0.117	0.084
38.00	15.62	0.078	0.318	0.127	0.090	0.294	0.282	0.108	0.074
38.00	17.65	0.117	0.309	0.122	0.087	0.385	0.252	0.096	0.066
38.00	18.40	0.126	0.308	0.120	0.086	0.398	0.250	0.091	0.065
38.00	21.71	0.179	0.279	0.113	0.080	0.474	0.219	0.080	0.054
60.00	26.45	0.000	0.345	0.138	0.099	0.000	0.404	0.153	0.105
60.00	31.25	0.049	0.329	0.125	0.092	0.198	0.332	0.118	0.084
60.00	43.15	0.163	0.286	0.115	0.081	0.467	0.212	0.084	0.055
60.00	45.00	0.186	0.286	0.113	0.080	0.499	0.204	0.078	0.053
60.00	48.06	0.213	0.275	0.109	0.077	0.540	0.184	0.071	0.049

[a] Static cell, vapor-phase mole fractions not measured.

Table IV. Experimental Vapor Pressures P, Liquid Mole Fractions $x(i)$, and Vapor Mole Fractions $y(i)$ at Temperatures t of the Mixture Methyl *tert*-Butyl Ether (1) with Simulated Gasoline [Butane (2) + 2-Methylbutane (3) + 2-Methylpentane (4) + Benzene (5) + TMP (6) + 1-Heptene (7) + MCH (8) + Toluene (9) + *p*-Xylene (10) + Undecane (11) + Hexylbenzene (12)]

i	$x(i)$[a]	$x(i)$[a]	$x(i)$	$y(i)$	$x(i)$	$y(i)$	$x(i)$	$y(i)$
	$t = -6.69$ °C	$t = -6.69$ °C	$t = 25.00$ °C		$t = 25.00$ °C		$t = 38.00$ °C	
	$P = 11.54$ kPa	$P = 11.84$ kPa	$P = 30.20$ kPa		$P = 32.60$ kPa		$P = 53.80$ kPa	
1	0.000	0.121	0.000	0.000	0.112	0.172	0.186	0.227
2	0.051	0.045	0.018	0.123	0.028	0.182	0.028	0.171
3	0.228	0.200	0.202	0.627	0.126	0.378	0.119	0.395
4	0.055	0.048	0.052	0.068	0.055	0.077	0.048	0.057
5	0.023	0.020	0.024	0.018	0.022	0.018	0.021	0.014
6	0.144	0.127	0.166	0.057	0.154	0.060	0.141	0.047
7	0.091	0.081	0.104	0.038	0.095	0.039	0.087	0.032
8	0.064	0.056	0.073	0.024	0.068	0.025	0.062	0.020
9	0.105	0.092	0.121	0.029	0.113	0.031	0.102	0.024
10	0.182	0.160	0.183	0.016	0.173	0.018	0.157	0.013
11	0.034	0.030	0.035	0.000	0.033	0.000	0.030	0.000
12	0.023	0.020	0.022	0.000	0.021	0.000	0.019	0.000
	$t = -6.69$ °C	$t = -6.68$ °C	$t = 38.00$ °C		$t = 25.00$ °C		$t = 60.00$ °C	
	$P = 11.65$ kPa	$P = 11.94$ kPa	$P = 49.00$ kPa		$P = 35.90$ kPa		$P = 90.90$ kPa	
1	0.043	0.154	0.000	0.000	0.180	0.231	0.105	0.152
2	0.049	0.043	0.016	0.105	0.023	0.148	0.021	0.143
3	0.218	0.192	0.221	0.672	0.150	0.414	0.139	0.435
4	0.052	0.046	0.058	0.063	0.038	0.050	0.063	0.079
5	0.022	0.019	0.026	0.016	0.020	0.014	0.025	0.019
6	0.138	0.122	0.165	0.049	0.137	0.050	0.154	0.059
7	0.088	0.077	0.102	0.033	0.085	0.033	0.096	0.041
8	0.061	0.054	0.072	0.020	0.061	0.021	0.067	0.024
9	0.100	0.089	0.117	0.026	0.101	0.025	0.110	0.031
10	0.174	0.154	0.172	0.014	0.156	0.014	0.168	0.017
11	0.033	0.029	0.031	0.000	0.030	0.000	0.032	0.000
12	0.022	0.020	0.020	0.000	0.019	0.000	0.020	0.000
	$t = -6.69$ °C		$t = 60.00$ °C		$t = 38.00$ °C		$t = 60.00$ °C	
	$P = 11.80$ kPa		$P = 92.50$ kPa		$P = 51.90$ kPa		$P = 99.70$ kPa	
1	0.083		0.000	0.000	0.109	0.151	0.191	0.237
2	0.047		0.010	0.068	0.023	0.143	0.043	0.280
3	0.209		0.216	0.652	0.146	0.494	0.081	0.252
4	0.050		0.060	0.073	0.053	0.063	0.053	0.064
5	0.021		0.026	0.020	0.023	0.015	0.022	0.016
6	0.132		0.166	0.063	0.151	0.047	0.144	0.052
7	0.084		0.103	0.043	0.093	0.031	0.089	0.036
8	0.058		0.073	0.026	0.067	0.019	0.063	0.021
9	0.096		0.118	0.034	0.111	0.024	0.104	0.026
10	0.167		0.174	0.021	0.172	0.013	0.159	0.016
11	0.032		0.033	0.000	0.032	0.000	0.031	0.000
12	0.021		0.021	0.000	0.020	0.000	0.020	0.000

[a] Static cell, vapor-phase mole fractions not measured.

the cell is heated to a temperature at which the bubble point of its contents is approximately 100 kPa before each injection. Also, as a further precaution, the cell was inverted before and during the oxygenate addition so that an air leak would be visible as bubbles. At the end of a run (two or more injections) a sample of the mixture was withdrawn and analyzed as a consistency check. The amount of each of the hydrocarbons and the added oxygenate were determined by GC analysis, at the end of a run, and compared with the initial cell composition and the known amount of the oxygenate which had been added. If there had been a significant discrepancy, the run would have been rejected and repeated.

Since we used a static cell for measurements at −6.7 °C, we report only temperature, liquid composition, and bubble point pressure. For the MTBE + simulated gasoline mixture, one has a direct measure of how the bubble point pressure of the mixture changes as a result of MTBE addition. However, to assure the proper total pressure, the ethanol + simulated gasoline mixture run was slightly different since some butane, together with ethanol, was added at the first injection.

Experimental Results

The vapor pressures of 2,2,4-trimethylpentane from 15.7 to 60 °C, of MTBE from 14.0 to 53.09 °C, and of MCH from 21.7 to 60 °C are given in Table I. These measurements are in good agreement with published data for these systems (*2*–*4*). We performed $P-T-x-y$ measurements for the MTBE + TMP mixture at 15, 25, 38, and 60 °C, using at least two and sometimes three or four compositions at each temperature. The data for these measurements are in Table II, as are the results of the static cell ($P-T-x$) measurements which were made at −6.7 °C and four different MTBE compositions. We also made $P-T-x-y$ and $P-T-x$ measurements for the MTBE + MCH mixture following the same protocol as above. The results also appear in Table II.

We performed $P-T-x-y$ measurements for the MTBE + four-component simulated gasoline mixture at 15, 25, 38, and 60 °C. The data for these measurements appear in Table III. To obtain data at lower temperatures, we did static cell ($P-T-x$) measurements at −6.7 °C, and these data appear in the table. We also performed $P-T-x-y$ measurements at 15, 25, 38, and 60 °C for a MTBE + the eleven-component simulated gasoline mixture, and static cell ($P-T-x$) measurements for this system are given at −6.7 °C. The results appear in Table IV. As the relative proportions of the hydrocarbons in the static cell measurements were unchanged with the MTBE additions, our results directly show the effect on the bubble point pressure of MTBE additions to this gasoline mixture.

Table V. Experimental Pressures P, Liquid Mole Fractions $x(i)$, and Vapor Mole Fractions $y(i)$ at Temperatures t of the Mixture Ethanol (1) with Simulated Gasoline [Butane (2) + 2-Methylbutane (3) + 2-Methylpentane (4) + Benzene (5) + TMP (6) + 1-Heptene (7) + MCH (8) + Toluene (9) + p-Xylene (10) + Undecane (11) + Hexylbenzene (12)]

i	$x(i)^a$	$x(i)$	$y(i)$
	$t = -6.67$ °C $P = 11.40$ kPa	$t = 25.00$ °C $P = 33.00$ kPa	
1	0.000	0.089	0.178
2	0.047	0.013	0.094
3	0.198	0.083	0.264
4	0.059	0.040	0.098
5	0.025	0.023	0.029
6	0.156	0.174	0.126
7	0.099	0.107	0.080
8	0.068	0.077	0.050
9	0.111	0.131	0.053
10	0.185	0.201	0.028
11	0.032	0.038	0.000
12	0.020	0.024	0.000
	$t = -6.67$ °C $P = 11.74$ kPa	$t = 38.00$ °C $P = 54.50$ kPa	
1	0.118	0.097	0.140
2	0.042	0.011	0.077
3	0.175	0.137	0.474
4	0.052	0.052	0.087
5	0.022	0.024	0.020
6	0.137	0.162	0.075
7	0.087	0.101	0.049
8	0.060	0.071	0.030
9	0.098	0.117	0.032
10	0.163	0.175	0.016
11	0.028	0.032	0.000
12	0.018	0.020	0.000
	$t = -6.67$ °C $P = 11.79$ kPa	$t = 53.00$ °C $P = 96.70$ kPa	
1	0.212	0.100	0.000
2	0.037	0.018	0.123
3	0.156	0.164	0.509
4	0.047	0.064	0.076
5	0.019	0.025	0.016
6	0.122	0.154	0.053
7	0.078	0.095	0.036
8	0.055	0.067	0.022
9	0.088	0.108	0.024
10	0.146	0.158	0.013
11	0.025	0.029	0.000
12	0.016	0.018	0.000

[a] Static cell, vapor-phase mole fractions not measured.

Finally, we performed $P-T-x-y$ measurements at 15, 25, 38, and 60 °C for ethanol with a simulated gasoline mixture consisting of the same eleven components as were used with MTBE, and to obtain data at a lower temperature, we have made static cell ($P-T-x$) measurements at −6.7 °C. The results of these measurements appear in Table V.

Comments on Correlation of the Data

The results here represent a comprehensive data set that can be used to determine the effect of oxygenate additives to hydrocarbons and gasoline mixtures at temperatures spanning a large range around ambient conditions. Models fit to our data, for example, could then be used to predict the effects of MTBE or ethanol on the Reid vapor pressure of gasolines.

While we will not present a detailed modeling analysis of our data here, it may be useful to comment on what we found. For mixtures without either MTBE or ethanol, the $P-T-x-y$ or $P-T-x$ behavior was satisfactorily described by a cubic equation of state, such as the Peng–Robinson (*5*) or Soave version of the Redlich–Kwong (*6*) equation without the necessity of introducing a binary interaction parameter, k_{ij}. With the addition of either MTBE or ethanol, a binary interaction parameter was needed between these oxygenates and the hydrocarbons. However, when this parameter was adjusted to fit the measured vapor compositions, at fixed values of temperature and liquid compositions, the predicted pressure was systematically too low. The relative difference between the measured and predicted pressures increased with increasing oxygenate composition and decreased with increasing temperature and pressure.

Acknowledgment

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Registry No. MTBE, 1634-04-4; MCH, 108-87-2; $H_3CC(CH_3)_2CH_2CH(CH_3)CH_3$, 540-84-1; EtOH, 64-17-5; $H(CH_2)_7H$, 142-82-5; $PhCH_3$, 108-88-3; $H(CH_2)_4H$, 106-97-8; $H_3CCH(CH_3)CH_2CH_3$, 78-78-4; $H_3CCH(CH_3)(CH_2)_3H$, 107-83-5; $c\text{-}C_6H_6$, 71-43-2; $H_2C{=}CH(CH_2)_5H$, 592-78-7; $CH_3\text{-}p\text{-}C_6H_4CH_3$, 106-42-3; $H(CH_2)_{11}H$, 1120-21-4; $Ph(CH_2)_6H$, 1077-16-3.

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