

Vapor Pressures of Methyl *tert*-Butyl Ether, Ethyl *tert*-Butyl Ether, Isopropyl *tert*-Butyl Ether, *tert*-Amyl Methyl Ether, and *tert*-Amyl Ethyl Ether

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The vapor pressures of methyl *tert*-butyl ether, ethyl *tert*-butyl ether, isopropyl *tert*-butyl ether, *tert*-amyl methyl ether, and *tert*-amyl ethyl ether were measured by ebulliometry or the static method in the pressure ranges 14–102 and 3–835 kPa (methyl *tert*-butyl ether), respectively. The data were correlated using the Antoine and Wagner equations. The experimental data of methyl *tert*-butyl ether and ethyl *tert*-butyl ether were compared with data available in the literature.

Introduction

Vapor pressures are most important for the design of rectification processes. They are also used for the calculation of phase equilibria using g^E models or group contribution methods and to derive the required enthalpy of vaporizations using the Clausius–Clapeyron equation. Ambrose et al. (1) have published reliable vapor pressures for some ethers. For ethers used as gasoline additives only a limited number of vapor pressure measurements are available. With a view to the synthesis and design of processes for reactive distillation, vapor pressure data for methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), isopropyl *tert*-butyl ether (IPTBE), *tert*-amyl methyl ether (TAME), and *tert*-amyl ethyl ether (TAEE) have been measured.

Apparatus

The ethers were obtained from the different suppliers indicated in Table 1 with purities between 92 and 97%. They were purified by washing several times with bidistilled water to remove the alcohols, dried with molecular sieves 4A, and distilled at low pressure. After the purification steps the purities given in Table 1 were obtained by GLC analysis. The normal boiling points available in the literature for some of these ethers are also presented in Table 1 for comparison with the boiling points obtained in this work from eq 1 and the constants given in Table 3.

The vapor pressure measurements were carried out with ebullimeters of the Eckert type connected in series to the same pressure controller. A manometer filled with mercury was used to read the absolute pressure by means of a Digimatic Scale Unit. The temperatures in the two ebullimeters were read from a quartz thermometer connected to a microcomputer for automatic recording of the temperatures. The thermometers were calibrated at the triple

point of water. A detailed description of the apparatus has been given by Dallinga et al. (2).

The measurements of the vapor pressure of MTBE were done by a static method described by Kolbe and Gmehling (3). That method allowed measurements above atmospheric pressure up to 835 kPa, corresponding to the maximum temperature that could be read.

The accuracy of temperature measurements is estimated to be ± 0.01 K. The accuracy of pressure measurements is $5.00 + 0.01P_i^s$ Pa for the static apparatus and $1.00 + 0.01P_i^s$ Pa for the dynamic apparatus.

Results and Discussion

Temperatures measured on IPTS-68 were converted to ITS-90. The results are given in Table 2. The coefficients of the equations fitted to the experimental vapor pressures are given in Tables 3 and 4. The equations used for the correlation are the Antoine equation (4) (Table 3)

$$\log(P_i^s/\text{kPa}) = A + \frac{B}{(T/K) + C} \quad (1)$$

and the Wagner equation (5) (Table 4) in the form

$$\ln(P_r^s) = (a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^{5.0})/T_r \quad (2)$$

In these equations P_i^s is the vapor pressure, T the absolute temperature, P_r^s the reduced vapor pressure equal to P_i^s/P_c (P_c = critical pressure), T_r the reduced temperature equal to T/T_c (T_c = critical temperature), $\tau = (1 - T_r)$, and A , B , C , a , b , c , and d are adjustable coefficients.

The critical temperatures for the substances for which no experimental values were available were estimated by the Joback (6) and Ambrose (7, 8) methods. For further processing, an average value was used. Ambrose (5) has

Table 1. Purities, Normal Boiling Points (T_B) at 101.325kPa, and Published Data

substance/supplier	purity/(mol %)	T_B /K (obtained)	T_B /K (lit.)
MTBE/Hüls AG, Marl, FRG	99.99	328.32	328.15, ^a 328.21, ^b 328.31, ^c 328.55 ^d
ETBE/Veba Öl AG, Gelsenkirchen, FRG	99.90	345.86	346.06 ^e
IPTBE/Veba Öl AG	99.82	360.43	
TAME/EC Erdölchemie GmbH, Köln, FRG	99.96	359.39	359.26, ^f 359.45, ^g 359.58 ^h
TAEE/Phillips Petroleum Co., Oklahoma	99.95	374.70	

^a Reference 14. ^b Reference 11. ^c Reference 15. ^d Reference 16. ^e Reference 12. ^f Reference 17. ^g Reference 18. ^h Reference 19.

Table 2. Experimental Vapor Pressures and Deviations^a

T/K	P _i ^s /kPa	ΔP_i^s /Pa		T/K	P _i ^s /kPa	ΔP_i^s /Pa		T/K	P _i ^s /kPa	ΔP_i^s /Pa	
		I	II			I	II			I	II
Methyl <i>tert</i>-Butyl Ether^b											
300.956	37.417	-96	34	362.544	276.150	-101	-59	391.469	552.645	-333	1
304.397	42.944	-51	50	362.542	276.128	-108	-66	391.462	552.567	-326	9
307.896	49.188	-24	46	362.539	276.112	-103	-61	391.461	552.547	-334	0
312.707	58.733	-182	-158	366.959	309.586	-7	101	391.457	552.515	-317	17
318.586	72.841	59	28	366.993	309.862	1	118	396.436	615.633	-252	-37
323.633	86.748	99	24	367.129	310.919	-16	103	396.431	615.571	-248	-33
323.666	86.855	109	34	367.265	312.027	15	136	396.424	615.485	-242	-27
328.498	102.046	132	22	367.285	312.162	-9	113	396.419	615.415	-246	-31
328.528	102.133	119	9	367.295	312.282	32	154	396.410	615.308	-234	-19
333.387	119.445	137	1	371.791	349.410	-76	125	396.405	615.243	-233	-18
333.386	119.444	140	4	371.818	349.639	-80	121	401.997	692.608	220	158
338.224	138.873	150	2	371.827	349.717	-80	121	402.002	692.708	248	185
338.229	138.893	149	1	371.834	349.795	-62	139	402.015	692.817	171	107
338.232	138.905	148	0	376.779	394.265	-344	-62	402.016	692.804	144	80
342.570	158.286	98	-48	376.775	394.231	-340	-58	402.015	692.800	154	90
342.592	158.403	111	-34	376.771	394.199	-334	-52	402.014	692.784	153	89
342.652	158.699	125	-21	376.765	394.147	-330	-48	402.016	692.792	132	68
347.361	182.115	82	-51	381.877	444.696	-409	-65	406.172	754.575	349	-53
347.359	182.110	87	-45	381.877	444.698	-407	-62	406.174	754.610	353	-49
347.367	182.158	93	-34	381.877	444.722	-383	-38	406.174	754.633	376	-26
347.370	182.174	94	-39	386.469	494.239	-343	25	406.174	754.647	390	-12
352.709	211.877	48	-39	386.469	494.239	-343	25	406.177	754.685	383	-20
352.710	211.877	42	-45	386.468	494.219	-352	16	411.236	835.491	977	-31
357.669	242.704	18	-11	386.468	494.224	-347	21	411.235	835.486	989	-19
357.672	242.734	28	-1	386.476	494.099	-561	-194	411.232	835.431	983	-25
357.676	242.757	25	-4	386.478	494.127	-556	-188	411.233	835.431	967	-41
357.680	242.778	20	-9	386.481	494.169	-547	-180	411.232	835.451	1003	-5
362.550	276.190	-104	-62	391.707	555.357	-522	-192				
362.546	276.170	-95	-53	391.478	552.755	-333	1				
abs mean deviations:										242	56
Ethyl <i>tert</i>-Butyl Ether^c											
305.552	23.264	35	33	314.862	33.996	33	27	330.257	60.236	5	-16
306.951	24.641	5	3	316.979	36.843	-47	-55	333.401	67.196	3	-19
308.714	26.502	-6	-9	317.198	37.205	0	-9	336.438	74.498	-13	-33
309.523	27.394	-12	-15	318.893	39.774	64	54	339.135	81.543	17	1
311.248	29.403	3	-1	322.770	45.905	-48	-62	341.283	87.437	-44	-53
312.893	31.401	-10	-15	323.651	47.557	81	66	343.620	94.330	-12	-11
314.412	33.325	-40	-46	326.709	53.209	129	110	345.802	101.127	1	14
314.783	33.848	-9	-15	328.761	57.161	34	13	345.823	101.214	22	35
abs mean deviations:										29	29
Isopropyl <i>tert</i>-Butyl Ether^c											
306.719	14.260	10	0	317.647	22.699	-6	-5	340.405	53.149	-135	-139
306.718	14.260	10	0	317.747	22.773	-26	-23	343.735	59.600	-75	-82
307.563	14.791	-3	-12	319.530	24.515	10	13	343.706	59.600	-17	-24
307.552	14.791	4	-5	319.562	24.515	-22	-18	346.889	66.401	129	118
309.337	16.013	21	14	321.590	26.607	3	7	346.953	66.401	-11	-22
309.366	16.013	1	-6	321.631	26.607	-41	-36	350.254	73.929	-2	-16
311.361	17.452	-3	-7	327.731	33.784	48	53	350.251	73.929	5	-9
311.383	17.452	-20	-24	327.705	33.784	81	86	352.774	80.257	150	135
313.032	18.752	9	7	330.206	37.038	28	32	352.843	80.257	-25	-40
313.048	18.752	-4	-6	330.262	37.038	-49	-45	355.510	87.409	145	130
314.658	20.057	-12	-13	332.334	40.030	5	8	355.584	87.409	-55	-70
314.679	20.057	-30	-30	332.377	40.030	-58	-54	357.712	93.324	-53	-67
316.504	21.709	43	44	336.391	46.426	112	113	360.603	101.860	-45	-55
316.569	21.709	-15	-14	336.497	46.426	-62	-62	360.571	101.860	52	42
317.558	22.699	76	78	340.327	53.149	8	4				
abs mean deviations:										39	40
<i>tert</i>-Amyl Methyl Ether^c											
306.236	14.544	-17	-32	320.272	26.201	20	27	335.479	46.280	-38	-17
306.258	14.544	-31	-47	320.263	26.201	30	36	339.768	53.739	-79	-59
308.654	16.153	-29	-41	323.735	29.957	-22	-11	342.786	59.653	-2	15
308.672	16.153	-42	-54	323.710	29.957	7	18	346.151	66.750	2	14
309.323	16.694	38	27	326.308	33.058	-24	-10	349.527	74.535	14	18
309.330	16.694	33	22	326.280	33.058	11	26	352.385	81.674	26	20
313.237	19.683	19	14	330.840	39.176	0	20	354.389	86.915	-45	-59
313.256	19.683	3	-1	330.853	39.176	-18	1	356.219	92.039	-6	-29
317.304	23.285	40	42	331.019	39.369	-64	-45	359.252	101.076	90	49
317.307	23.285	37	39	332.949	42.275	-28	-8				
abs mean deviations:										28	27
<i>tert</i>-Amyl Ethyl Ether^c											
319.901	14.657	-11	-23	340.481	33.160	-1	4	360.861	66.586	53	55
319.889	14.657	-4	-16	345.466	39.759	72	79	360.860	66.586	55	57
323.578	17.131	-1	-9	345.511	39.759	8	15	366.561	79.458	-35	-40
323.539	17.131	27	19	350.111	46.664	9	16	366.540	79.458	16	13
327.153	19.833	-7	-11	350.121	46.664	-7	0	369.285	86.280	-67	-72
327.151	19.833	-5	-9	354.306	53.696	-57	-52	369.237	86.280	58	53
331.129	23.235	-15	-16	354.275	53.696	-2	4	371.837	93.076	-103	-109
331.116	23.235	-4	-4	357.763	60.154	-70	-66	371.796	93.076	10	4
334.377	26.365	-10	-8	357.723	60.154	8	12	374.390	100.494	65	57
334.346	26.365	21	23	361.077	66.916	-76	-75	374.392	100.494	59	51
340.480	33.160	0	6	361.036	66.916	11	13				
abs mean deviations:										30	30

^a $\Delta P_i^s = (P_{\text{exp}}^s - P_{\text{calc}}^s)_i$ where P_{calc}^s has been obtained from I, eq 1, and II, eq 2. ^b Static apparatus. ^c Ebulliometer.

Table 3. Coefficients of the Antoine Equation^a

	A	B	C
MTBE	6.070 343	-1158.912	-43.200
ETBE	6.073 724	-1206.874	-49.190
IPTBE	5.899 486	-1164.675	-61.300
TAME	6.067 822	-1256.258	-50.100
TAAE	5.926 451	-1218.389	-63.940

^a The range of validity of eq 1 is the same as the temperature range presented in Table 2.

Table 4. Coefficients of the Wagner Equation

	a	b	c	d	T _c /K	ln(P _c /kPa)
MTBE	-7.000 83	0.746 099	-1.039 04	-6.040 79	497.10 ^a	8.14175 ^a
ETBE	-7.999 60	3.343 69	-5.064 35	0.346 046	514.00 ^b	8.03606 ^b
IPTBE	-8.668 56	4.731 07	-6.257 40	-0.081 435	528.40 ^b	7.93868 ^b
TAME	-7.088 46	0.848 877	-2.075 12	-2.370 182	534.41 ^b	8.03770 ^b
TAAE	-7.225 16	1.496 581	-3.188 41	-2.947 836	552.67 ^b	7.93868 ^b

^a Reference 1. ^b Average of predicted critical properties by the Ambrose and Joback methods.

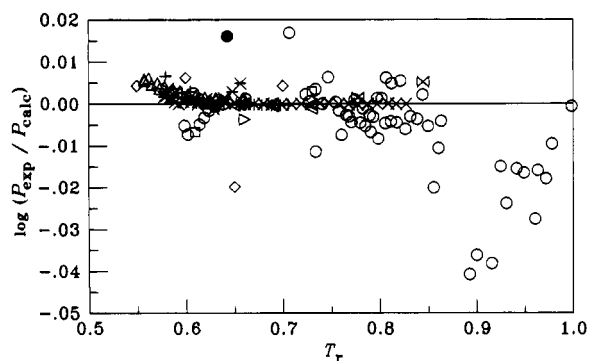


Figure 1. Residuals for methyl *tert*-butyl ether, $\Delta \log P_i^s (= \log(P_i^s \text{exp}/P_i^s \text{calc}))$, versus $T_r (=T/T_c)$ from eq 2 and values given by other researchers: +, Ambrose et al. (1); *, Wu et al. (9); ○, Daubert et al. (10); △, Aim and Ciprian (11); ◆, Zigmundova et al. (15); >, Zong et al. (16); ■, Mato et al. (20), (21); ●, Acosta et al. (22); ◊, Jin et al. (23); □, Wilding et al. (24); ◐, Leu et al. (25); ∞, Wang et al. (26); ×, this work.

shown that if no reliable value for the critical pressure is available, the missing information can also be fitted as an additional parameter. This was done when fitting the coefficients for the substances with estimated critical temperature and pressure, but no better results were obtained. The coefficients of the Wagner equation were obtained by constrained fit so that the curve $\Delta h/\Delta z (=RT^2 d \ln P_i^s/dT)$ presents a minimum between $0.8 < T_r < 1.0$. No other constraint was introduced. This was done to assure an extrapolation of the vapor pressure from the range given in Table 2 to the critical point with fair accuracy. Table 2 shows that the quality of the Wagner equation is superior to that of the Antoine equation in almost all the cases.

The residuals $\Delta P_i^s (=P_i^s \text{exp} - P_i^s \text{calc})_i$ in Table 2 are based on eqs 1 and 2 with the parameters presented in Tables 3 and 4, respectively.

No vapor pressure data of IPTBE and TAAE were found in the literature. Therefore, only the measured vapor pressure data of MTBE, TAME, and ETBE can be compared with the results of other researchers. The residuals given as $\Delta \log P_i^s (= \log(P_i^s \text{exp}/P_i^s \text{calc}))$ from eq 2 using the coefficients of Table 4 versus T_r are plotted in Figures 1–3 for MTBE, ETBE, and TAME, respectively.

In all the cases, except for the discrepancy with the values of Daubert et al. (10) and Daubert (12), good agreement is obtained with the results of other researchers especially for MTBE and TAME. For ETBE only the

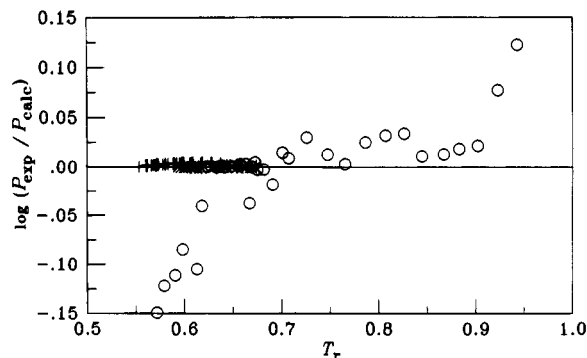


Figure 2. Residuals for ethyl *tert*-butyl ether, $\Delta \log P_i^s (= \log(P_i^s \text{exp}/P_i^s \text{calc}))$, versus $T_r (=T/T_c)$ from eq 2 and values given by other researchers: ○, Daubert (12); +, Rarey (13); ×, this work.

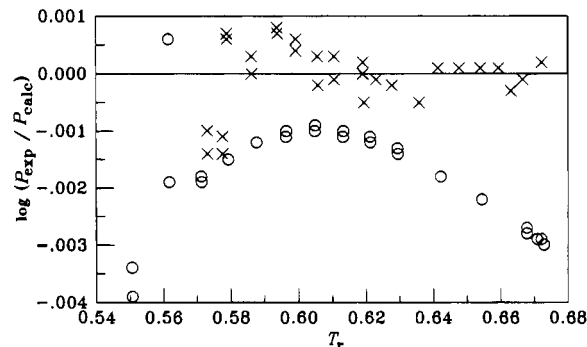


Figure 3. Residuals for *tert*-amyl methyl ether, $\Delta \log P_i^s (= \log(P_i^s \text{exp}/P_i^s \text{calc}))$, versus $T_r (=T/T_c)$ from eq 2 and values given by other researchers: ○, Cervenkova and Boublik (19); ×, this work.

results of Daubert are available. It has to be mentioned that water contamination on the order of 0.1 mol % in the ethers causes a difference in the measured pressure on the order of +20% at low temperatures (13).

The coefficients of the Wagner equation should be revised as soon as experimental values for the critical properties are available.

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Literature Cited

- (1) Ambrose, D.; Ellender, J. H.; Sprake, C. H. S.; Townsend, R. J. *Chem. Thermodyn.* **1976**, *8*, 165.
- (2) Dallinga, L.; Schiller, M.; Gmehling, J. *J. Chem. Eng. Data* **1993**, *38*, 147.
- (3) Kolbe, B.; Gmehling, J. *Fluid Phase Equilib.* **1985**, *23*, 213.
- (4) Antoine, C. C. *R. Acad. Sci.* **1888**, *107*, 681–684, 836.
- (5) Ambrose, D. *J. Chem. Thermodyn.* **1986**, *18*, 45.
- (6) Joback, K. G.; Reid, R. C. *Chem. Eng. Commun.* **1987**, *57*, 233.
- (7) Ambrose, D. *NPL Rep. Chem.* **1978**, 92.
- (8) Ambrose, D. *NPL Rep. Chem.* **1979**, 98.
- (9) Wu, H. S.; Pividal, K. A.; Sandler, S. I. *J. Chem. Eng. Data* **1991**, *36*, 418.
- (10) Daubert, T. E.; Jalowka, J. W.; Goren, V. *AIChE Symp. Ser.* **1987**, *83* (256), 128.
- (11) Aim, K.; Ciprian, M. *J. Chem. Eng. Data* **1980**, *25*, 100.
- (12) Daubert, T. E. *AIChE Data Ser.* **1991**, *1*, 80.
- (13) Rarey, J. R. (Universität Oldenburg) Private communication, 1993.
- (14) Churkin, V. N.; Gorshkov, V. A.; Pavlov, S. Yu. *Prom.-St. Sint. Kauch.* **1979**, *4*, 2.
- (15) Zigmundova, D.; Matous, J.; Novak, J. P.; Kubicek, V.; Pick, J. *Fluid Phase Equilib.* **1990**, *54*, 93.
- (16) Zong, Z.; Yang, X.; Zheng, X. *Ranliao Huaxue Xuebao* **1987**, *15*, 32.
- (17) Palczewska-Tulinska, M.; Wyrzykowska-Stankiewicz, D. *Fluid Phase Equilib.* **1990**, *54*, 57.
- (18) Pavlova, I. P.; Saraev, B. A. *Prom.-St. Sint. Kauch.* **1981**, *5*, 2.
- (19) Cervenkova, I.; Boublik, T. *J. Chem. Eng. Data* **1984**, *29*, 425.

- (20) Mato, F. A.; Berro, C.; Peneloux, A. *J. Chem. Eng. Data* **1991**, 36, 259.
- (21) Mato, F. A.; Berro, C. *J. Chem. Eng. Data* **1991**, 36, 262.
- (22) Acosta, R. G.; Rodriguez, E. R.; de la Guardia, P. M. *Rev. Inst. Mex. Petrol.* **1980**, 12, 40.
- (23) Jin, Z.-L.; Lin, H.-M.; Greenkorn, R. A. *AIChE Symp. Ser.* **1985**, 244, 1.
- (24) Wilding, W. V.; Wilson, L. C.; Wilson. *AIChE Symp. Ser.* **1987**, 256, 83.
- (25) Leu, A. D.; Chen, C. J.; Robinson, D. B. *AIChE Symp. Ser.* **1989**, 271, 85.
- (26) Wang, Y.; Ton, A.; Su Y.; Yang, Z. *Shiyu Huagong* **1989**, 18, 442.

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