Thermal Conductivity Measurements and Molecular Association in a Series of Alcohol Vapors: Methanol, Ethanol, Isopropanol, and t-Butanol

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Thermal conductivity measurements on the vapors of methanol, ethanol, isopropanol, and t-butanol are reported as a function of temperature (330–420 K) and pressure (11–240 kPa). The thermal conductivity versus pressure isotherms for all four alcohols exhibit upward curvatures at the lower temperatures and nearly linear increases at higher temperatures. This behavior is indicative of a dimeric species and one or more polymeric clusters in the vapor in addition to the monomer. Quantum mechanical calculations have indicated that tetramers are the most likely polymeric species. Detailed analyses of the data provide thermodynamic data $(\Delta H, \Delta S)$ for the dimerization and tetramerization reactions and show interesting correlations with the size of the monomer unit.

KEY WORDS: Alcohol; hydrogen bonding; thermal conductivity; thermodynamics.

1. INTRODUCTION

The importance of developing an understanding of hydrogen bonding between molecules has long been recognized as a prerequisite for attacking many fundamental questions on the structure of liquids (such as water) and on nucleation and condensation. Consequently there have been a large number of experimental studies of species which form hydrogen bonds in the vapor phase [1]. A great deal of this work has been directed toward the study of alcohol vapors; a review of such studies through 1973 is given in Ref. 2. In a study of methanol vapor from this laboratory [3], the thermal conductivity isotherms exhibited a strong upward curvature with pressure. Measurements

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of the thermal conductivities of molecules which tend to form hydrogen bonds can provide information on large associated species which cannot be readily obtained by other types of measurements. It was found that the methanol thermal conductivity data could be fit very well assuming the presence of a tetrameric associated species in addition to the monomer.

In this paper we report thermal conductivity measurements on the series of alcohol vapors: methanol, ethanol, isopropanol, and t-butanol. The data were taken in the temperature range 330–420 K and the pressure range 80–1800 Torr (11–240 kPa). Data on methanol and ethanol were acquired over a larger range of temperature and pressure than that reported previously [3, 5]. In each case the lower-temperature isotherms exhibit upward curvatures with increasing pressure, while at the higher temperature the isotherms show essentially linear increases with pressure. All of the alcohol thermal conductivity isotherms were fit quite well using the Butler–Brokaw theory [6–8] assuming the presence of a dimer and one higher associated species in addition to the monomer. In Section 2 details of the thermal conductivity measurements are given. In Section 3 the data are fit to the Butler–Brokaw theory assuming various possible associated species. Finally, in Section 4 the thermodynamic quantities for the associated species are discussed.

2. EXPERIMENTAL METHOD

The thermal conductivity, k, of each alcohol vapor was measured as a function of pressure at a minimum of six temperatures in the range 330–420 K. All measurements were made with a thick hot-wire cell using a relative technique in which the cell was calibrated with high-purity reference gases (e.g., N_2, Ar, Kr). Details of the apparatus, experimental procedure, and reference gas thermal conductivities have been given in other publications. [9, 10]. The reagent-grade alcohol samples were dried (Linde molecular seive, 15A) and degassed *in vacuo* prior to use. Due to the so-called "temperature-jump" effect [11], no data were recorded at pressures below 80 Torr (11 kPa).

For the cell used in this study [12], the measured cell voltages, V, at a constant input current, were empirically found to be related to the reference gas thermal conductivities by the relation

$$V = A + B/k, \tag{1}$$

where A and B are constants dependent only on the temperature. Because of this linear relationship, it was sufficient to calibrate the cell with only two

Table I. Experimental Thermal Conductivities (cal · cm^{-1} · s^{-1} · K^{-1}) of Methanol Vapor[a]

| T = 337.6 K | | T = 352.2 K | | T = 366.6 K | | T = 381.7 K | | T = 400.3 K | | T = 419.9 K | |
p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$
105	4.505	99	4.799	109	5.107	112	5.415	115	5.875	105	6.384
127	4.525	109	4.808	145	5.126	123	5.430	139	5.880	137	6.390
171	4.569	176	4.838	184	5.150	200	5.456	187	5.905	182	6.403
219	4.627	190	4.855	241	5.178	231	5.477	273	5.939	259	6.430
264	4.690	263	4.899	273	5.192	299	5.498	328	5.959	331	6.457
302	4.768	264	4.909	318	5.217	326	5.514	391	5.969	391	6.484
345	4.858	347	4.981	382	5.251	375	5.525	441	5.989	479	6.497
374	4.937	375	4.999	456	5.295	457	5.573	518	6.011	587	6.545
429	5.098	433	5.065	493	5.310	497	5.584	619	6.054	645	6.538
460	5.238	433	5.056	551	5.356	541	5.606	621	6.044	779	6.580
493	5.403	509	5.153	594	5.387	588	5.623	701	6.085	788	6.573
533	5.627	561	5.227	680	5.449	640	5.651	755	6.088	944	6.629
543	5.690	599	5.285	714	5.476	696	5.679	819	6.117	1013	6.643
584	5.973	686	5.454	779	5.530	757	5.713	916	6.151	1102	6.665
593	6.050	702	5.490	796	5.546	777	5.719	932	6.155	1205	6.701
629	6.380	724	5.544	888	5.641	847	5.753	1044	6.187	1264	6.694
637	6.436	779	5.681	946	5.710	869	5.771	1097	6.203	1394	6.744
648	6.567	863	5.939	990	5.763	946	5.800	1181	6.239	1465	6.781
654	6.618	998	6.483	1046	5.834	971	5.818	1210	6.242	1535	6.789
		1088	6.970	1102	5.914	1057	5.878	1235	6.259	1616	6.804
				1159	6.009	1146	5.927	1333	6.295	1781	6.849
				1227	6.114	1180	5.945	1468	6.342	1812	6.864
				1287	6.229	1279	6.008	1616	6.411		
				1291	6.236	1317	6.033	1777	6.474		
				1361	6.385	1351	6.059				
				1356	6.363	1391	6.091				
				1431	6.729	1419	6.117				

[a] 1 cal · cm^{-1} · s^{-1} · K^{-1} = 4.184 × 10^{-2} J · m^{-1} · s^{-1} · K^{-1}.

Table II. Experimental Thermal Conductivities (cal · cm⁻¹ · s⁻¹ · K⁻¹) of Isopropanol Vapor[a]

Table II. Experimental Thermal Conductivities ($cal \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1}$) of Isopropanol Vapor[a]

$T = 340.3$ K		$T = 348.4$ K		$T = 367.8$ K		$T = 385.1$ K		$T = 400.0$ K		$T = 419.5$ K	
p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$
124	4.516	129	4.699	117	5.125	137	5.557	109	5.902	115	6.420
136	4.520	163	4.725	139	5.149	168	5.595	130	5.920	149	6.460
156	4.549	192	4.747	195	5.163	244	5.617	182	5.926	227	6.480
171	4.562	228	4.777	217	5.187	281	5.639	215	5.950	296	6.521
186	4.588	272	4.826	274	5.201	285	5.634	301	5.985	378	6.542
204	4.609	305	4.858	302	5.225	328	5.655	411	6.023	440	6.590
219	4.635	356	4.917	340	5.230	357	5.683	413	6.047	536	6.590
229	4.643	400	4.981	399	5.283	401	5.700	505	6.065	600	6.640
246	4.683	448	5.061	424	5.283	411	5.706	562	6.109	690	6.654
256	4.691			470	5.317	446	5.717	610	6.122	771	6.683
275	4.740			501	5.352	487	5.740	682	6.141	826	6.683
288	4.754			553	5.387	529	5.757	725	6.160	915	6.697
306	4.794			592	5.407	552	5.757	753	6.166	989	6.726
308	4.803			650	5.457	576	5.779	801	6.193	1068	6.755
				694	5.482	625	5.814	832	6.195	1179	6.755
				724	5.518	657	5.808	884	6.224	1275	6.792
				786	5.554	699	5.848	918	6.237	1292	6.827
				808	5.591	737	5.842	975	6.264	1394	6.830
				899	5.681	775	5.877	1012	6.270	1416	6.860
				901	5.675	782	5.877	1080	6.297	1624	6.883
				995	5.822	823	5.866	1115	6.317	1558	6.893
				1002	5.827	876	5.924	1192	6.344	1664	6.914
						914	5.942	1229	6.344	1720	6.929
						919	5.930	1352	6.399	1833	6.960
						979	5.988	1488	6.441	1900	6.984
						1022	5.982	1637	6.511		7.007
						1027	5.995	1798	6.575		
						1097	6.037				
						1144	6.082				
						1145	6.062				
						1208	6.117				
						1210	6.117				
						1212	6.104				

[a] $1 \; cal \cdot cm^{-1} \cdot s^{-1} \cdot K^{-1} = 4.184 \times 10^{-2} \; J \cdot m^{-1} \cdot s^{-1} \cdot K^{-1}$.
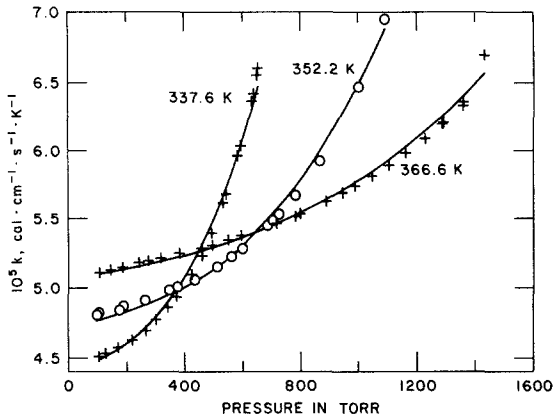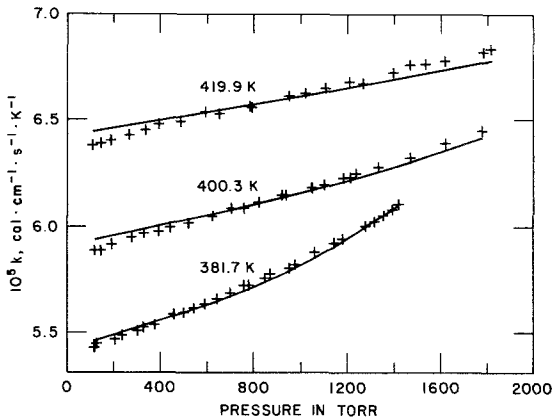
Fig. 1. Methanol vapor thermal conductivity versus the total pressure at the three lowest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.

gases (N_2 and Ar) in order to determine A and B. We estimate that the absolute error in the calculated thermal conductivities is less than 1% and the relative error less than 0.5%. The uncertainty in the measured pressure is estimated to be ± 4 Torr (0.5 kPa) over the entire range. The experimental thermal conductivity data for ethanol has been tabulated in a previous publication [4]. The experimental data for methanol, isopropanol, and t-butanol are given in Tables I–III, respectively. The thermal conductivity

Fig. 2. Methanol vapor thermal conductivity versus the total pressure at the three highest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.

Table III. Experimental Thermal Conductivities (cal · cm^{-1} · s^{-1} · K^{-1}) of t-Butanol Vapor[a]

$T = 347.7$ K		$T = 358.0$ K		$T = 370.7$ K		$T = 384.0$ K		$T = 400.2$ K		$T = 419.6$ K	
p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$	p (Torr)	$10^5 k$
81	4.608	105	4.863	89	5.136	99	5.435	106	5.844	93	6.319
85	4.634	123	4.863	102	5.136	104	5.446	188	5.873	128	6.305
120	4.638	157	4.891	154	5.175	155	5.482	275	5.896	152	6.339
124	4.656	194	4.905	180	5.180	174	5.472	319	5.926	261	6.385
155	4.687	231	4.938	223	5.200	180	5.477	415	5.950	313	6.398
159	4.669	271	4.957	234	5.220	231	5.514	473	5.986	411	6.425
184	4.705	301	4.986	308	5.241	270	5.520	556	6.009	458	6.465
198	4.701	339	5.005	315	5.256	307	5.547	628	6.041	569	6.466
217	4.732	378	5.044	385	5.281	344	5.552	675	6.047	609	6.520
234	4.741	401	5.054	394	5.302	385	5.584	762	6.090	711	6.551
252	4.778	443	5.088	462	5.338	434	5.584	803	6.071	757	6.564
276	4.778	472	5.113	480	5.333	488	5.628	917	6.128	849	6.590
282	4.801	524	5.169	545	5.390	517	5.623	964	6.134	889	6.601
309	4.815	555	5.194	595	5.405	548	5.655	1052	6.179	939	6.614
316	4.838	612	5.266	644	5.438	579	5.655	1108	6.179	1043	6.641
347	4.866	647	5.302	704	5.470	613	5.688	1142	6.290	1087	6.652
353	4.890	675	5.339	715	5.491	673	5.689	1159	6.205	1194	6.677
374	4.909	680	5.339	785	5.524	685	5.711	1212	6.218	1196	6.678
389	4.923			800	5.540	758	5.728	1278	6.231	1340	6.710
395	4.942			892	5.617	766	5.745	1334	6.257	1386	6.720
418	4.981			925	5.628	850	5.762	1463	6.297	1496	6.743
432	4.981			978	5.662	856	5.785	1497	6.304	1554	6.756
456	5.035			995	5.690	954	5.814	1662	6.378	1661	6.777
				1051	5.741	959	5.837	1860	6.469	1790	6.801
				1108	5.781	1071	5.877			1891	6.819
						1072	5.889				
						1133	5.912				
						1202	5.942				
						1203	5.954				

[a] 1 cal · cm^{-1} · s^{-1} · K^{-1} = 4.184 × 10^{-2} J · m^{-1} · s^{-1} · K^{-1}.
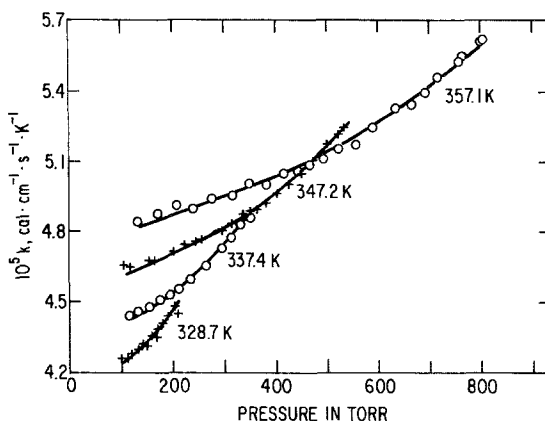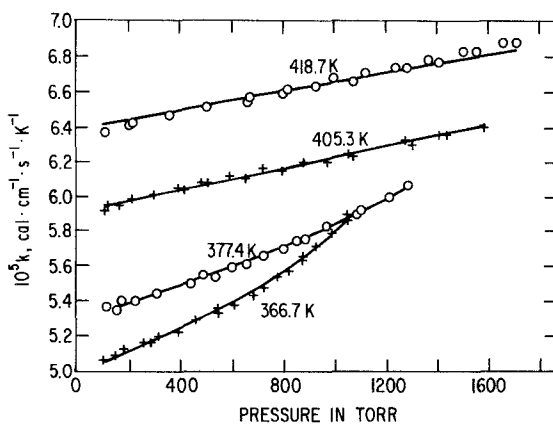
Fig. 3. Ethanol vapor thermal conductivity versus the total pressure at the four lowest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.

data of methanol reported in Table I were remeasured over the entire temperature range 338–420 K using the present apparatus. This is due to a slight inconsistency in the data in the present work as compared to the previously reported methanol results [3]. It was found that the present data fall below the previous results by a maximum of 10% at the lower pressures (<500 Torr). The final thermodynamic results for the methanol tetramerization reaction in Ref. 3 are not significantly affected by this discrepancy. Values of the presently measured thermal conductivity extrapolated to zero

Fig. 4. Ethanol vapor thermal conductivity versus the total pressure at the four highest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.
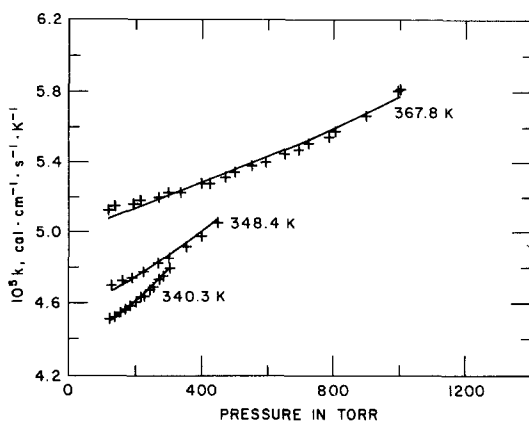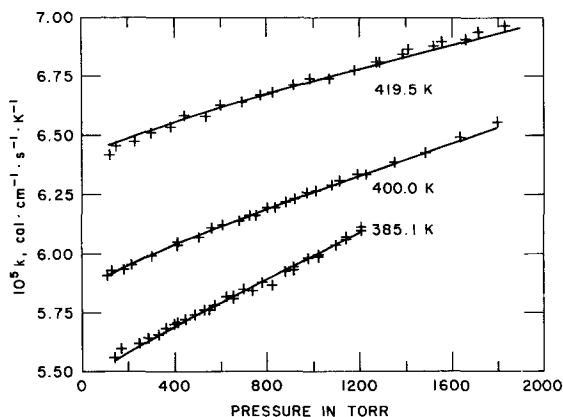
Fig. 5. Isopropanol vapor thermal conductivity versus the total pressure at the three lowest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.

pressure are in close agreement with those of other experimental studies [13–15].

Plots of the experimental k data for the four alcohols versus the total pressure are given in Figs. 1–8. It is apparent that at the lowest temperatures the $k-p$ isotherms for each alcohol exhibit strong upward curvature, whereas at the highest temperatures the thermal conductivity increases nearly linearly with the pressure.

Fig. 6. Isopropanol vapor thermal conductivity versus the total pressure at the three highest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.
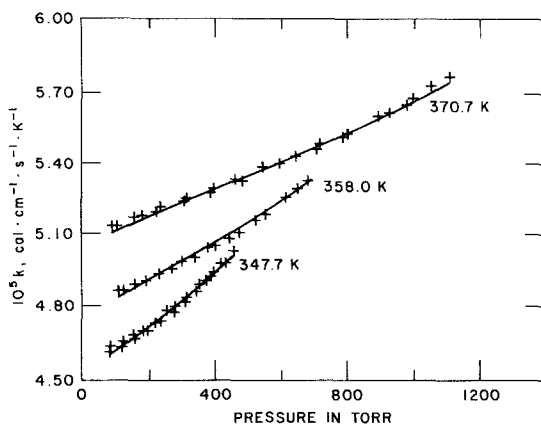
Fig. 7. t-Butanol vapor thermal conductivity versus the total pressure at the three lowest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.

3. DATA ANALYSIS

The thermal conductivity of an associating gas can be expressed as

$$k = k_f + k_c + k_R, \tag{2}$$

where k_f is the thermal conductivity of a frozen (nonreacting) composition of all the vapor species, k_c is the enhancement of the thermal conductivity due to
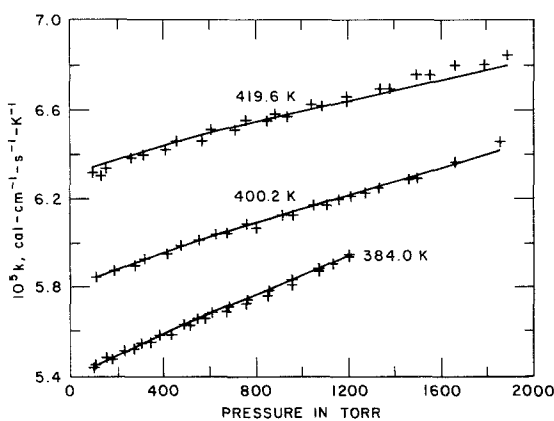

Fig. 8. t-Butanol vapor thermal conductivity versus the total pressure at the three highest temperatures. The solid lines are the best fits to the experimental data using the Butler–Brokaw theory assuming a monomer–dimer–tetramer model.

"collisional transfer," and k_R is the contribution to the thermal conductivity from the transport of association enthalpy in a thermal gradient. Generally, k_f and k_c are very weakly dependent on pressure, whereas k_R is strongly dependent on pressure if there are associated species in the vapor.

A general expression for k_R when there are associated species present in the vapor has been given by Butler and Brokaw [6, 7] and is discussed in detail elsewhere [8]. An approximate equation for k_R when there are only small amounts of associated species present is given by

$$k_R = \sum_n (pD_{1n}/RT)\,(\Delta H_n^2/RT^2)\,K_n p_1^{n-1}, \tag{3}$$

where n is the cluster size, T is the temperature in degrees kelvin, pD_{1n} is the pressure–binary diffusion coefficient, R is the gas constant, K_n is the equilibrium constant for $nA \rightleftharpoons A_n$, ΔH_n is the association reaction enthalpy change, and p_1 is the partial pressure of the monomer. Equation (3) indicates that the effect on the thermal conductivity of the presence of a small amount of dimer ($n = 2$) in the vapor is a nearly linear increase in the thermal conductivity with pressure at constant temperature (pD_{1n} is pressure independent). Equation (3) also illustrates the p^{n-1} dependence of k_R which leads to the upward curvature of thermal conductivity versus pressure plots when there is a sufficient concentration of higher polymers ($n > 2$) present.

The experimental isotherms for the alcohols shown in Figs. 1–8 change in overall shape with temperature in a very interesting manner. The lower-temperature isotherms show strong upward curvatures indicative of one or more polymeric species larger than the dimer. At the higher temperatures, however, the isotherms increase linearly with pressure, indicative of a dimeric contribution to k_R. Thus, in light of the above discussion, it qualitatively appears that there are indeed at least two association reactions occurring simultaneously in this series of alcohols vapors. The temperature dependence of the terms in Eq. (3) apparently cause the dimeric reaction to dominate the thermal conductivity enhancement at high temperatures and the higher polymers to dominate at low temperatures.

In order to fit the alcohol vapor thermal conductivity data to Eq. (2), values for pD_{ij}, k_c, and k_f are necessary. We now proceed to explain how equations for these quantities were obtained. The pressure binary diffusion coefficient product, pD_{ij}, can be expressed [9] in terms of the monomer self-diffusion coefficient by the semiempirical relation

$$pD_{ij} = pD_{11}\,[(i + j)/2ij]^{1/2}\,[2/(i^{1/3} + j^{1/3})]^2. \tag{4}$$

The term pD_{11} is evaluated from gaseous viscosity data and the Lennard-Jones potential parameters, ϵ/k_B and σ, using a procedure described in Ref. 9. The form of pD_{11} is

$$10^5 pD_{11} = aT^2 + bT (\text{cal} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}), \tag{5}$$

where a and b are constants $(1 \text{ cal} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} = 4.184 \times 10^{-2}$ $\text{J} \cdot \text{m}^{-1} \cdot \text{s}^{-1})$. For methanol [16] and ethanol [17], experimental gaseous viscosities were used. For isopropanol and t-butanol the estimated viscosities of Gallant [18] were used. Lennard-Jones potential parameters for methanol were taken from Monchick and Mason [19]; those for ethanol, from Ref. 20; and those for isopropanol and t-butanol were estimated using the method of Ref. 21. Table IV lists these potential parameters and the resulting constants, a and b, in Eq. (5) for each alcohol.

The k_f and k_c terms are also somewhat pressure dependent (although to a much smaller extent than the k_R term) and must be included in the complete data analysis. In calculating these terms for the alcohol vapors the assumption is made that the equilibrium composition can be represented in terms of a monomer–dimer mixture only, i.e., the partial pressures of the higher polymers are negligible compared to those of the monomer or dimer. This assumption will be seen to be justified by the final results.

Using the scheme outlined in Ref. 9, the k_f term can be represented by the expression

$$k_f = k_1 \left[\frac{1}{1 + 1.57\, K_2 p_1} + \frac{k_2/k_1}{1 + 0.699/K_2 p_1} \right], \tag{6}$$

where k_1 is the value of the thermal conductivity at zero pressure and is taken to be a fitting parameter for each isotherm. The k_2 term is the hypothetical dimer thermal conductivity at zero pressure. The k_2/k_1 ratio was determined in a similar manner as in Ref. 9 except that Hirschfelder's formulation of the Eucken factor, E, was used [22]. This can be written as

Table IV. Values of the Lennard-Jones Potential Parameters, ϵ/k_B, and σ; Constants a and b from Eq. (5); the Dimer to Monomer Thermal Conductivity Ratio, k_2/k_1; and the Collision Parameter, B_c

	ϵ/k_B (K)	σ (Å)	$10^3 a$	$10^3 b$	k_2/k_1	B_c
Methanol	452	3.67	2.66	12.48	0.936	2.31
Ethanol	391	4.46	1.58	39.43	0.920	3.25
Isopropanol	391	4.93	1.17	−7.08	0.915	3.60
t-Butanol	350	5.48	0.94	−9.61	0.910	4.47

$$E = (1 - \delta_f) + 2\delta_f C_p/5R, \tag{7}$$

where δ_f was assumed to be 0.667 for both the monomer and the dimer of each alcohol. Using the heat capacities reported by Gallant [18] for methanol, isopropanol, and t-butanol and by Touloukian and Makita [23] for ethanol, we obtained the values of k_2/k_1 listed in Table IV. At 373 K, and at 1-atm pressure (101 kPa), the k_f contribution results in decreases in the total thermal conductivity of 0.4, 0.9, 1.6, and 1.6% for methanol, ethanol, isopropanol, and t-butanol, respectively.

The k_c term was obtained using the scheme outline in Ref. 24 (using the Lennard-Jones parameters in Table IV) and can be written as

$$k_c = B_c k_1 p/T, \tag{8}$$

with p in atmospheres and T in degrees kelvin. The constant B_c is given for each alcohol in Table IV. At 373 K and at 1-atm pressure, the k_c contribution results in increases in the total thermal conductivity of 0.6, 0.9, 1.0, and 1.2% for methanol, ethanol, isopropanol, and t-butanol, respectively. Note the near-cancellation of the k_f and k_c terms.

Using a least-squares fitting procedure described in detail in Ref. 9, the measured thermal conductivities for each alcohol were fit to Eq. (2) with k_f defined by Eq. (6), k_c defined by Eq. (8), and k_R given by the complete Butler–Brokaw expression. The complete form of the Butler–Brokaw equations is given in Refs. 6–8. In these fits, various models for the form of k_R were chosen. Consistent with the qualitative analysis of the k–p isotherms presented earlier, it was assumed that the alcohol dimer and *one* higher polymer were present in the vapor. The higher n-mers tested were the trimer ($n = 3$) through the octamer ($n = 8$). The variables in the fitting procedure were ΔH_2, K_2, ΔH_n, K_n, and one k_1 value for each isotherm.

For every alcohol except ethanol, the best fits were obtained assuming a monomer–dimer–tetramer model. In the ethanol case a 1–2–6 model gave an equivalent fit to the 1–2–4 case. These best fits are shown as the solid lines in Figs. 1–8 and are seen to do a good job in reproducing the data at both high and low temperatures. Only in the two highest-temperature isotherms of methanol are there significant deviations from the experimental data points. It should be pointed out that for every alcohol, the 1–2–n fits for $4 \leq n \leq 8$ were essentially indistinguishable by visual inspection. That is to say although the standard deviations of the fits for $n > 4$ were larger than the $n = 4$ fit, the increase was in many cases too small to be detectable by eye in the actual plots. On the other hand, the 1–2–3 fits in each alcohol had significantly larger standard deviations and the quality of the fits was obviously inade-

quate. In every case, the addition of a second higher polymer to the 1–2–4 fits did not produce a significantly better fit.

The zero-pressure thermal conductivities, $k_1(T)$, taken from the 1–2–4 fits, are given in Table V. Over the temperature range of these experiments, the k_1 values were essentially linear with temperature. Parameters from least-squares linear fits to the $k_1(T)$ data are also given in Table V.

4. RESULTS AND DISCUSSION

The best-fit thermodynamic quantities obtained for the various assumed polymerization reactions are given in Table VI. For each alcohol, note the relative constancy of the dimerization thermodynamic parameters, ΔH_2 and ΔS_2, from the 1–2–n fits as n increases from 4 to 8. The reason for this is that the fitting procedure extracts the dimerization thermodynamic data mainly from the higher-temperature isotherms where there is little contribution from the higher-polymer association reaction. This also indicates that the dimerization thermodynamic parameters are relatively insensitive to the choice of higher polymer, which gives us confidence in the dimer values. The dimerization data obtained from the 1–2–3 fit deviate significantly from the other values because of the poorer quality of the fits.

Due to the essential equivalence in quality of the various 1–2–n fits for $n > 3$, we cannot unambiguously conclude that only one particular n-mer is responsible for the thermal conductivity enhancement. Certainly the actual

Table V. Zero-Pressure Thermal Conductivities,[a] $k_1(T)$, and Linear Least-Squares Fitting Coefficients,[b] a' and b', from the 1–2–4 Fits

Methanol		Ethanol		Isopropanol		t-Butanol	
T (K)	$10^5 k_1$	T (K)	$10^5 k_1$	T (K)	$10^5 k_1$	T (K)	$10^5 k_1$
337.6	4.41	328.7	4.11	340.3	4.33	347.7	4.52
352.2	4.71	337.4	4.31	348.4	4.52	358.0	4.75
366.6	5.06	347.2	4.53	367.8	4.98	370.7	5.05
381.7	5.41	357.1	4.73	385.1	5.46	384.0	5.39
400.3	5.90	366.7	5.00	400.0	5.85	400.2	5.80
419.9	6.42	377.4	5.29	419.5	6.42	419.6	6.31
		405.3	5.91				
		418.7	6.39				
$a' = -3.92$		$a' = -4.10$		$a' = -4.66$		$a' = -4.19$	
$b' = 0.0245$		$b' = 0.0249$		$b' = 0.0263$		$b' = 0.0250$	

[a] cal $\cdot$ cm^{-1} $\cdot$ s^{-1} $\cdot$ K^{-1} (1 cal $\cdot$ cm^{-1} $\cdot$ s^{-1} $\cdot$ K^{-1} = 4.184 $\times$ 10^{-2} J $\cdot$ m^{-1} $\cdot$ s^{-1} $\cdot$ K^{-1}).
[b] $10^5 k_1 = a' + b'T$.

Table VI. Thermodynamic Parameters (ΔH_2, ΔS_2, ΔH_n, ΔS_n)[a] Obtained for Alcohol Association Reactions from the 1–2–n-mer Fits to the Thermal Conductivity Data

Fit	Methanol	Ethanol	Isopropanol	t-Butanol
	$\Delta H_2, \Delta H_n$	$\Delta H_2, \Delta H_n$	$\Delta H_2, \Delta H_n$	$\Delta H_2, \Delta H_n$
$n = 3$	−3.46, −12.94	−3.20, −12.99	−4.04, −12.91	−4.07, −13.03
4	−3.51, −23.01	−3.70, −22.15	−4.09, −21.65	−4.26, −21.27
5	−3.50, −26.85	−3.92, −27.14	−4.17, −27.76	−4.38, −27.11
6	−3.89, −35.10	−3.86, −35.87	−4.13, −37.24	−4.37, −34.50
7	−3.99, −49.86	−3.88, −48.11	−4.29, −49.46	−4.30, −48.17
8	−4.07, −56.04	−3.90, −55.09	−4.28, −58.16	−4.31, −55.55
	$\Delta S_2, \Delta S_n$	$\Delta S_2, \Delta S_n$	$\Delta S_2, \Delta S_n$	$\Delta S_2, \Delta S_n$
$n = 3$	−18.88, −46.99	−16.09, −46.62	−16.99, −46.24	−16.38, −46.31
4	−17.42, −78.22	−16.36, −74.65	−16.15, −72.37	−16.67, −71.23
5	−17.13, −89.92	−16.88, −89.43	−16.48, −90.17	−16.48, −88.46
6	−17.70, −114.9	−16.43, −114.7	−16.27, −117.2	−16.29, −120.7
7	−17.82, −159.1	−16.31, −149.9	−16.59, −152.1	−16.18, −147.9
8	−17.31, −177.2	−16.33, −169.8	−16.46, −176.5	−16.23, −168.5

[a] Units of ΔH_n are kcal · mol^{-1}; units of ΔS_n are cal · mol^{-1} · K^{-1} (1 cal = 4.184 J).

physical picture is one in which many different polymers exist in the vapor and one cannot separate their individual contributions to the thermal conductivity in the data analysis. However, we believe that the results of the 1–2–4 model giving the best fit for every alcohol is certainly strong evidence for the presence of a tetrameric species in the alcohol vapors. Theoretical *ab initio* molecular orbital calculations by Curtiss [25] indicate that for a series of methanol polymers $2 \le n \le 6$, the largest increase in binding energy occurred in the tetrameric species, leading us to believe that the tetramers are the most likely species larger than dimer in the vapor. This apparently occurs due to a favorable hydrogen bonding arrangement in the cyclic tetrameric structure. In a PVT study by Kretschmer and Wiebe [26], it was found that a monomer–dimer–tetramer model fit the data best for methanol, ethanol, and isopropanol. This is also consistent with heat capacity studies of Barrow [27] and Weltner and Pitzer [28]. Note, however, that in none of these studies were any higher polymer models ($n > 4$) tested.

The results of the various 1–2–n fits allow us to set definitive upper limits to the concentration of the associated species for $n = 3, 4, 5, 6, 7, 8$. In other words, the best-fit values of K_n at any temperature in the experimental range represent the largest possible values consistent with the thermal conductivity data. From the thermodynamic results in Table VI, we calculated the n-mer partial pressures at 373 K and 1-atm pressure. Generally, the polymer pressures are of the order of 10^{-3} atm (10^{-1} kPa) for the trimer; 10^{-4} atm

(10^{-2} kPa) for the tetramer, pentamer, and hexamer; and 10^{-5} atm (10^{-3} kPa) for the heptamer and octamer.

Keeping in mind the uncertainties in the thermodynamic data obtained from the 1–2–4 fit, we can explore various trends that appear in the data on the dimer and tetramer as the alcohol size is increased (see Table VI). For example, as one proceeds from methanol through t-butanol, the quantities ΔS_2, ΔH_4, and ΔS_4 all become less negative, whereas, ΔH_2 becomes more negative. (The only exception to these trends is the decrease in ΔS_2 in going from isopropanol to t-butanol.) The dimerization and tetramerization constants mostly increase in going from methanol to t-butanol. Because of the large decrease in pD_{1n}, the net effect of these patterns in the individual parameters is to cause the numerical value of the quantity ($pD_{12}K_2\Delta H_2^2$) at 373 K to increase by a factor of 2, while the quantity ($pD_{14}K_4\Delta H_4^2$) decreases slightly (~7%) when one proceeds through the series methanol–t-butanol. Thus from Eq. (3) we see that the contribution to λ_R from the tetramer relative to the dimer decreases as one increases in the alcohols complexity.

There have been numerous successful attempts to correlate the hydrogen bond strength of heteroassociated species (i.e., AOH $\cdots$ $\overset{H}{O}$B) in solution to the relative acidities of the proton donor and acceptor. It is found that the hydrogen bond strength is enhanced as the relative acidities of the two species become increasingly disparate. However, these same correlations for self-association (i.e., one component) are not as successful. Since the same molecule acts as both proton donor and proton acceptor, this tends to cancel any effects due to acidities. Davis et al. [29] found that dimerization enthalpies became less negative in the series methanol, ethanol, isopropanol, and t-butanol in CCl_4 solution. One might predict on the basis of these results that decreasing the acidity of the monomer (i.e., by the addition of methyl groups to the alcohol) causes the dimerization enthalpy to become less negative. Singh and Rao [30] found that, in solution, fluorinated alcohols have less negative values of ΔH_2 than the corresponding unfluorinated alcohols, which in terms of relative acidities, implies the opposite. If we assume that trends in gas phase acidities parallel the condensed phase acidities, then our dimerization enthalpies go in the opposite direction from that found in CCl_4 solution, but in the same direction as the fluorinated species.

If the observed trend in dimerization enthalpies is indeed real, then one might expect a similar trend in the tetramer enthalpies. In fact the opposite trend is observed (Table VI). Hence, it appears that no simple explanation in terms of acidities can be given.

Quantum mechanical results by Curtiss [25] for methanol polymers indicate that cooperative effects in the bonding cause the binding energy in

the n-mers to be significantly larger than $n-1$ times the dimerization energy. The results in Table VI indicate that the experimental tetramer enthalpies are 8.5 kcal $\cdot$ mol^{-1} (35.6 kJ $\cdot$ mol^{-1}) to 12.5 kcal $\cdot$ mol^{-1} (52.3 kJ $\cdot$ mol^{-1}) more negative than the simple addition of dimer enthalpies would indicate.

The trend in polymerization entropies is also interesting. For both dimer and tetramer, the value of ΔS_n° tends to become less negative as the alcohol complexity increases. In order to investigate this effect in more detail, we calculated the translational and rotational entropies for the monomers and tetramers of each alcohol using standard statistical mechanical relations [31]. The rotational calculation was simplified by assuming that the CH$_n$ groups were point masses. The hydrogen bonds were arranged in a square planar, cyclic array [25] with linear O–H $\cdots$ O bonds set at 2.50 Å (1 Å = 10^{-10} m), r(CC) = 1.43 Å, < (HOC) = 104°, < (OCC) = 107.7°, and < (CCC) = 109.5°. In the methanol tetramer each methyl group was situated such that the H–O–C(H$_3$) bond angle was 104° and the H $\cdots$ O–C(H$_3$) bond angle was 166°. In the ethanol tetramer, the methyl groups were added to the methanol tetramer in the hydrogen bond plane such that the C(H$_3$)–C(H$_2$)–O–H dihedral angle was 180°. The next sets of methyl groups were added out of the plane (forming the isopropanol and the t-butanol tetramers). The results of this calculation are given in Table VII. Both the translational and the rotational contributions to ΔS_4 go in a direction opposite to that observed experimentally, i.e., they become more negative from methanol through t-butanol. Therefore, it must be the vibrational contribution of ΔS_4 which causes the observed trend. Estimates of this contribution were made by subtracting the calculated $\Delta S_{4,\text{trans}}$ and $\Delta S_{4,\text{rot}}$ from the total experimental enthalpy, $\Delta S_{4,\text{total}}$, and the results are given in Table VII. Assuming that only the 18 new intermolecular vibrations contribute significantly to $\Delta S_{4,\text{vib}}$ we

Table VII. Analysis of the Alcohol Tetramerization Entropy[a]

Alcohol	$\Delta S_{4,\text{trans}}$	$\Delta S_{4,\text{rot}}$	$\Delta S_{4,\text{total}}$	$\Delta S_{4,\text{vib}}$[b]	Average ν in cm^{-1} at 373 K[c]
Methanol	−108.2	−43.0	−78.2	73.0	92
Ethanol	−111.4	−57.8	−74.7	94.6	50
Isopropanol	−113.8	−66.7	−72.4	108.4	34
t-Butanol	−115.7	−70.8	−71.2	115.3	28

[a]Units of cal $\cdot$ mol^{-1} $\cdot$ K^{-1} (1 cal = 4.184 J).

[b]$\Delta S_{4,\text{vib}} = \Delta S_{4,\text{total}}^{\text{expt.}} - \Delta S_{4,\text{trans}}^{\text{theory}} - \Delta S_{4,\text{rot}}^{\text{theory}}$.

[c]Calculated from $S_{4,\text{vib}} = 18R \left[(\bar{u}/e^{\bar{u}} - 1) - \ln(1 - e^{-\bar{u}}) \right]$, where $\bar{u} = (h\bar{\nu}/k_B T)$ and $\bar{\nu}$ is the average intermolecular frequency.

calculated "average" values of the intermolecular frequencies for each alcohol, and these are also given in Table VII. Note that although this analysis must lead to substantial uncertainties, the magnitudes of the frequencies are reasonable and also there is a steady decrease in the average frequency as one proceeds from methanol tetramer to t-butanol tetramer. This is what one might predict a priori, due to the increased mass of the alcohols as one proceeds down the group. Curtiss and Pople found decreased intermolecular frequencies in the D_2O dimer as compared to the H_2O dimer [32]. It is worthy of note that this trend of less negative entropies with increasing size is found for the association of ionic halides both experimentally and theoretically [33].

An estimate of the uncertainties in the dimer and tetramer thermodynamic parameters was made using a procedure similar to that in Ref. 24. The resulting uncertainties for each alcohol are given by: ΔH_2, ± 0.9 kcal $\cdot$ mol^{-1} (± 3.4 kJ $\cdot$ mol^{-1}); ΔS_2, ± 0.7 cal $\cdot$ mol^{-1} $\cdot$ K^{-1} (± 2.9 J $\cdot$ mol^{-1} $\cdot$ K^{-1}); ΔH_4, ± 3 kcal $\cdot$ mol^{-1} (± 12.6 kJ $\cdot$ mol^{-1}); ΔS_4, ± 5 cal $\cdot$ mol^{-1} $\cdot$ K^{-1} (± 21 J $\cdot$ mol^{-1} $\cdot$ K^{-1}).

5. CONCLUSIONS

The following conclusions can be drawn from this study of association in the alcohol vapors:

(1) Vapor phase polymerization leads to large enhancements in the thermal conductivity. The effect is most pronounced in the lighter alcohols at the lower temperatures.

(2) A monomer–dimer–tetramer model appears to fit the experimental data best for the four alcohols. The thermodynamic quantities are the following (1 cal = 4.184 J): $\Delta H_2 = -3.51$ kcal $\cdot$ mol^{-1}, $\Delta S_2 = -17.42$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1}, $\Delta H_4 = -23.01$ kcal $\cdot$ mol^{-1}, and $\Delta S_4 = -78.22$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1} for methanol; $\Delta H_2 = -3.70$ kcal $\cdot$ mol^{-1}, $\Delta S_2 = -16.36$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1}, $\Delta H_4 = -22.15$ kcal $\cdot$ mol^{-1}, and $\Delta S_4 = -74.65$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1} for ethanol; $\Delta H_2 = -4.09$ kcal $\cdot$ mol^{-1}, $\Delta S_2 = -16.15$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1}, $\Delta H_4 = -21.65$ kcal $\cdot$ mol^{-1}, and $\Delta S_4 = -72.37$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1} for isopropanol; and $\Delta H_2 = -4.26$ kcal $\cdot$ mol^{-1}, $\Delta S_2 = -16.67$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1}, $\Delta H_4 = -21.27$ kcal $\cdot$ mol^{-1}, and $\Delta S_4 = -71.23$ cal $\cdot$ mol^{-1} $\cdot$ K^{-1} for t-butanol.

(3) Upper limits to the amounts of polymers through the octamer can be deduced from the thermal conductivity data. The limits are ca. 10^{-3} atm (10^{-1} kPa) for the trimer, 10^{-4} atm (10^{-2} kPa) for the tetramer, pentamer, and hexamer, and 10^{-5} atm (10^{-3} kPa) for the heptamer and octamer, all at 373 K and 1-atm pressure (10^2 kPa).

(4) The average hydrogen bond enthalpy per monomer unit in the

tetramer decreases as the monomer complexity increases, while in the dimer the opposite is true.

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