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Cohesive Energies in Polar Organic Liquids. 4. *n*-Alkyl Acetates

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Liquid densities and vapor pressures over a range of temperature have been measured for several *n*-alkyl acetates. The former have been fitted to power series, the latter to Antoine and Cox equations. Overall averages for $\Delta p/p$ are 8×10^{-5} and 5×10^{-5}, respectively, for the vapor pressure equations. Evaluation of the contributions of orientation, induction, and dispersion energies to total cohesion in the liquid leads to results consistent with previous studies on other homologous series with greater dipole moments. Evidence exists to suggest that the polarizability of an electric dipole plays a role in determining the magnitude of dipole–dipole interaction energies. Second virial coefficients are calculated for methyl and propyl acetates.

Introduction

The first paper in this series (*9*) was an attempt to provide quantitative estimates of the contributions of dispersion, induction, and orientation energies to total cohesion (defined as the energy of vaporization to the ideal gas state) in the 2-ketones up to 2-tridecanone. It was based on the postulate that the dispersion energy per CH_2 group is constant at a constant volume per CH_2 group in the liquid state and can be measured by using enthalpies of vaporization and coefficients of thermal expansion for the *n*-alkanes. Similar data for a homologous series containing a polar entity allows isolation of the polar contribution to cohesion. The approach has since been applied to *n*-alkyl nitriles and chlorides (*8*) and cyclic ketones (*6*) with results that appear consistent with qualitative ideas concerning the influence of a permanent dipole on molecular interactions.

Table I. Antoine Constants[a]

acetate	temp range, °C	A	B	C	T_{bp}, K	$10^4(\Delta p/p)_{av}$
methyl (1)	39-67	6.177 365	1215.148	225.9523	330.017	0.68
methyl (2)	35-65	6.087 563	1165.799	220.2459	330.030	0.33
propyl	49-110	6.019 889	1284.670	208.8604	374.666	0.58
butyl	53-131	6.026 542	1368.051	203.9298	399.211	0.25
hexyl	105-186	6.017 152	1496.817	190.9355	444.085	1.42
heptyl	114-205	6.018 648	1558.502	184.3141	465.483	0.86
decyl	172-257	6.041 787	1722.354	165.3775	521.706	1.45

[a] $\log p(\text{cmHg})^{-1} = A - B/(C + t)$. To convert to kPa, add 0.124903 to A.

The *n*-alkyl acetates provide an interesting analogy to the 2-ketones, being structurally identical except for the substitution of an oxygen atom for the CH_2 adjacent to the carbonyl group. The results of the substitution include a drastic difference in the way the densities of the members of the series vary with the length of the *n*-alkyl side chain. Methyl acetate is considerably more dense than 2-butanone, and, as the alkyl side chains of the two series are lengthened, their densities approach a common value. Another effect of the substitution is a redistribution of electronic charge in the carbonyl group, lowering the dipole moment in the acetate series. Because the change in density (i.e., molar volume) with side-chain length lies at the heart of the approach in question, and because the qualitative effect on the results of changing the dipole moment of the polar group is predictable, its application to the alkyl acetates provides a good test of the validity of its postulates (*9*).

Experimental Section

Vapor pressures (*7*) and densities (*12*) as functions of temperature were measured by using the apparatus previously described. In all cases those compounds which were not 99.9% pure by gas chromatography were distilled to this purity on a spinning band column. All samples except that used for the second methyl acetate vapor pressure were stored over a molecular sieve before use. This sample, designated "methyl (2)" in Tables I, II, and III, was certified to contain less than 0.05% water and was transferred directly from the bottle to the ebulliometer under a stream of helium.

The suppliers of the acetates used for the vapor pressure measurements were as follows: methyl, propyl, and decyl, Matheson Coleman and Bell; butyl and hexyl, Chemical Samples Co.; heptyl, Pfaltz and Bauer.

The density measurements were carried out several years ago at the U.S. Army Coating and Chemical Laboratory, Ab-

Table II. Cox Constants[a]

acetate	a	$-b \times 10^3$	$c \times 10^6$	T_{bp}	$10^4 \times (\Delta p/p)_{av}$
methyl (1)	0.765 175	0.164 724	−0.097 129	330.016	0.70
methyl (2)	0.762 784	0.102 581	−0.267 888	330.028	0.16
propyl	0.921 167	0.955 022	0.964 123	374.667	0.64
butyl	0.912 843	0.831 893	0.748 312	399.312	0.20
hexyl[b]	0.962 408	0.945 875	0.827 587	444.089	1.16
	0.975 789	1.011 471	0.907 583	444.091	3.58
heptyl[b]	0.960 445	0.864 851	0.695 989	465.484	0.52
	0.959 752	0.861 679	0.692 378	465.484	0.69
decyl[b]	1.046 217	1.058 904	0.831 570	521.705	0.45
	0.989 381	0.821 191	0.583 540	521.703	4.74

[a] $\log p(\text{atm})^{-1} = A'(1 - T_{bp}/T)$, where $\log A' = a + bT + cT^2$. T_{bp} was treated as a parameter in fitting the data. To convert atm to kPa, multiply by 101.325. [b] Lower row of figures includes oil manometer data over extended temperature range. See Table III.

[†] R.E.W. is now retired, and the USACCL has been closed down.

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erdeen Proving Ground, MD, on different batches of the acetates. The laboratory has since been closed down, and attempts to locate any of the samples and the original data for methyl, ethyl, butyl, pentyl, octyl, and decyl acetates have been unsuccessful.

Results

Vapor pressure data were fitted to both Antoine (for convenient use within the range of the data) and Cox (for more reliable extrapolation to lower temperatures) equations. The constants are presented in Tables I and II; the data on which they are based are in Table III. For those data obtained by using comparative ebulliometry, the temperature of the liquid-vapor water equilibrium (t_w) is included.

Table III. Vapor Pressure Data

t	p	t_w	t	p	t_w
Methyl Acetate (1)			Methyl Acetate (2)		
67.369	108.293	110.235	64.913	99.825	107.825
63.825	96.392	106.800	61.752	89.844	104.758
61.286	88.492	104.321	57.296	77.113	100.408
58.802	81.285	101.895	52.162	64.265	95.367
56.294	74.499	99.442	46.510	52.152	89.778
53.455	67.341	96.645	41.083	42.315	84.375
39.245	39.382	82.561	35.877	34.345	79.162
49.812	59.003	93.057			
47.412	53.975	90.684			
43.640	46.775	86.942			
41.112	42.401	84.427			
Propyl Acetate			Butyl Acetate		
49.698	11.254	53.988	53.037	5.046	38.268
52.027	12.463	56.119	59.079	6.684	43.580
58.162	16.174	61.709	62.290	7.719	46.379
63.098	19.775	66.173	68.658	10.177	51.918
69.119	25.030	71.581	73.716	12.568	56.295
80.221	37.663	81.444	79.194	15.651	60.992
85.351	45.011	85.953	85.824	20.179	66.629
91.563	55.432	91.390	91.302	24.709	71.280
98.275	68.723	97.204	97.628	30.891	76.580
103.673	81.171	101.855	103.036	37.161	81.110
107.410	90.773	105.055	109.906	46.498	86.789
110.018	97.989	107.280	115.672	55.735	91.535
			122.512	68.502	97.115
			128.216	80.862	101.747
			131.837	89.546	104.662

t	p	t_w	t	p
Hexyl Acetate			Hexyl Acetate[a]	
105.944	9.488	50.407		
106.044	9.484	50.470	96.328	6.403
114.572	13.111	57.179	89.796	4.844
129.724	22.347	68.948	84.348	3.796
137.023	28.388	74.551	78.686	2.918
143.960	35.297	79.831	73.523	2.272
150.868	43.460	85.054	67.481	1.681
157.776	53.054	90.227	60.558	1.164
165.167	65.117	95.725	52.092	0.725
171.942	78.011	100.732		
178.394	92.135	105.485		
185.996	111.212	111.029		
Heptyl Acetate			Heptyl Acetate[a]	
114.460	6.345	42.580	89.601	2.1404
123.581	9.053	49.547	97.667	3.1090
123.879	9.156	49.763	106.456	4.5617
132.511	12.575	56.301	114.474	6.3485
140.118	16.399	62.011		
148.598	21.737	68.316		
155.615	27.155	73.497		
163.958	34.971	79.604		
171.042	42.951	84.754		
178.433	52.757	90.080		
185.907	64.418	95.431		
193.358	77.979	100.721		
199.733	91.320	105.228		
204.999	103.615	108.923		
Decyl Acetate			Decyl Acetate[a]	
172.831	8.894	49.190	116.452	0.869
185.040	13.388	57.633	122.477	1.162
196.031	18.888	65.142	126.397	1.394
208.504	27.239	73.571	139.907	2.523
217.252	34.706	79.419	149.186	3.696
225.050	42.687	84.598	156.924	5.000
233.043	52.329	89.867	163.407	6.368
241.386	64.188	95.334	167.837	7.473
241.392	64.199	95.339		
249.443	77.575	100.576		
256.856	91.776	105.373		

[a] Measured with oil manometer.

The density data were fitted to quadratic or cubic equations in temperature, the constants for which are presented in Table IV, along with the density at 25 °C, the average difference between observed and calculated values, and the temperature range of the measurements. Table V contains the original data for propyl, hexyl, and heptyl acetate.

Discussion

Table VI compares densities and boiling points measured in the present work with literature values. Ambrose (*1*) has measured a boiling point within 0.01 K of the present value for the methyl acetate, throwing some doubt on the value of Wojciechowski. The only other discrepancy worthy of mention is that between the present and literature boiling points for hexyl acetate. We observed a slight dependence of equilibrium temperature on time for this compound (note the higher average difference between observed and calculated vapor pressures in Tables I and II). Consequently we remeasured its vapor pressure on a fresh sample only to observe more serious evidence of decomposition. Since the apparent equilibrium temperature rose with time, and the first sample had the lower boiling point, it is the one whose results appear herein. (The second measurement gave $T_{bp} = 444.230$ K, and $(\Delta p/P)_{av} = 2.2 \times 10^{-4}$ for the Cox equation fitted to the comparative data only.)

The cohesive energy plot in Figure 1 displays all of the qualitative features which might have been predicted from the previous series studied (*6*, *8*, *9*): the acetate values lie on a curved line whose asymptote is parallel to the line defined by the *n*-alkane values. The displacement upward of the asymptote (postulated to be the induction energy for the longer members of a series) is expected to depend primarily on the dipole moment and is smaller (0.35 kcal/mol) for this series than for any studied to date. The series and their dipole moments (in Debye units) are nitriles (4.1), ketones (2.5), chlorides (2.1), and acetates (1.7). As in previous series, the orientation energy drops off rapidly with the length of the alkyl chain and is apparently negligible for members above pentyl acetate.

The contributions of dispersion, induction, and orientation to total cohesion in the *n*-alkyl acetates are presented in Table VII, as are the temperatures required to put them into corresponding states with *n*-hexane at 0 °C (*9*). An unexpected result is the relatively large orientation energy contribution in methyl acetate: 0.7 kcal/mol; compared to 0.6 for butyronitrile, 0.4 for 2-butanone, and 0.3 for 1-chloropropane. It is not clear how the compound with the smallest dipole moment and the smallest induction energy can exhibit the largest orientation energy, but, if the result is valid, the explanation must be associated with the much smaller size of the ester oxygen atom relative to the CH_2 group it replaces in the other series. The van der Waals volumes of Bondi (*2*) are respectively 3.7 and 10.23 for these two groups. When the volumes of the 2-ketone molecules (acetone: 39.0; 2-butanone: 49.3) are compared with that of methyl acetate (42.5) it turns out that the latter is considerably closer to acetone than to 2-butanone in size. As discussed in some detail in the first paper of this series, orientation energy depends very heavily on the size of the molecule in which the dipole finds itself, as well as on its moment. Thus

Table IV. Correlation of Density with Temperature[a]

acetate	temp range, °C	a	$-b \times 10^3$	$-c \times 10^6$	$-d \times 10^8$	ρ_{25}°C	10^3 |av diff|
methyl	0–55	0.959 96	1.2444	1.500		0.9279	0.32
ethyl	0–75	0.924 72	1.1735	0.9180		0.8948	0.40
propyl	24–100	0.910 04	1.0624	0.8448		0.8830	0.11
butyl	0–125	0.901 58	0.9976	0.5735		0.8763	0.21
pentyl	0–140	0.895 67	0.9350	0.5355		0.8720	0.16
hexyl	0–158	0.891 76	0.92043	−0.11206	0.262 88	0.8688	0.08
heptyl	0–155	0.888 44	0.88429	−0.10056	0.212 55	0.8664	0.10
octyl	25–160	0.886 29	0.8182	0.3598		0.8656	0.13
decyl	0–155	0.882 66	0.7892	0.2210		0.8628	0.21

[a] $\rho = a + bt + ct^2 + dt^3$; t in °C; ρ in g/cm^3.

Table V. Density Data

propyl acetate		hexyl acetate		heptyl acetate	
t	ρ	t	ρ	t	ρ
23.7	0.8845	0.12	0.8916	0.12	0.8883
25.0	0.8829	10.38	0.8823	8.17	0.8813
30.0	0.8773	20.83	0.8726	20.35	0.8705
35.0	0.8719	24.99	0.8688	24.99	0.8664
40.0	0.8661	37.93	0.8568	36.29	0.8565
50.0	0.8548	47.60	0.8479	45.09	0.8486
60.0	0.8433	56.06	0.8400	55.67	0.8392
70.0	0.8314	65.54	0.8312	65.31	0.8306
80.0	0.8198	75.95	0.8214	75.14	0.8217
100.0	0.7953	85.40	0.8124	85.11	0.8126
		95.11	0.8030	95.12	0.8036
		100.00	0.7983	105.05	0.7943
		110.00	0.7881	different sample of heptyl acetate	
		119.56	0.7787		
		129.91	0.7684	25.59	0.8656
		139.77	0.7583	36.89	0.8558
		150.02	0.7475	85.00	0.8124
		157.92	0.7387	104.80	0.7941
				125.0	0.7754
				135.0	0.7658
				155.0	0.7458

Table VI. Comparison of Boiling Points and Densities with Literature Values

	bp, K		ρ^{25}/g ml^{-3}	
acetate	this work	lit.	this work	lit.
methyl (1)	330.016	329.46[a,b]	0.9279	0.9278[a]
methyl (2)	330.028			
ethyl			0.8948	0.8946[a]
propyl	374.666	374.70[a]	0.8830	0.8830[a]
butyl	399.211	399.254[a]	0.8763	0.8764[c]
pentyl			0.8768[e]	0.8756[d]
hexyl	444.089	444.66, 444.7[c]	0.8690	0.8688[c]
heptyl	465.484	465.64[c]	0.8665	0.8663[c]
octyl			0.8698[e]	0.8705[d]
decyl	521.705	517[d]	0.8668[e]	0.8671[d]

[a] Reference 13. [b] See text. [c] Reference 11. [d] Reference 5. [e] At 20 °C.

Table VII. Contributions to Cohesion in the *n*-Alkyl Acetates

acetate	t, °C	E_{disp}[a]	E_{ind}	E_{orient}
methyl	20	6.1	0.45	0.7
ethyl	24	7.1	0.42	0.4
propyl	37	8.0	0.40	0.3
butyl	50	8.9	0.38	0.2
pentyl	61	9.8	0.37	0.1
hexyl	72	10.7	0.37	
heptyl	81	11.6	0.36	
octyl	91	12.4	0.36	
nonyl		13.3	0.35	
decyl	104	14.1	0.35	

[a] kcal mol^{-1}.

Table VIII. Second Virial Coefficients for Methyl and Propyl Acetates

		$-B$, L mol^{-1}		
acetate	T, K	ΔH_{vap} from ref *8*	ΔH_{vap} from ref *7*	lit. values
methyl	304.0	0.772		
	311.9		1.363,[a] 1.232[b]	1.319[c]
	313.5	0.950		
	327.7	1.064		1.215[d]
	329.9		1.142,[a] 1.169[b]	1.139,[c] 1.200[d]
propyl	335.4		2.113	2.098[c]
	336.1	1.850		
	343.7	1.756		
	350.9	1.666		
	353.7		1.755	1.756[c]
	363.4	1.602		
	374.9		1.477	1.478[c]

[a] Methyl acetate (2) vapor pressure data. [b] Methyl acetate (1) vapor pressure data. [c] From ref (*3*) using unpublished vapor pressure data of ref *1*. [d] Reference 4.

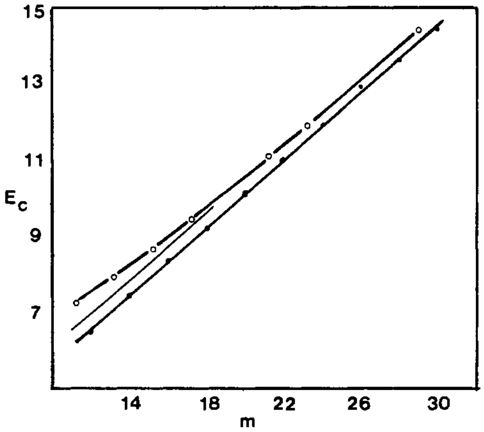

Figure 1. Cohesive energy plot for *n*-alkyl acetates. Open circles are the *n*-alkyl acetates; closed circles, the *n*-alkanes. Energies are in kcal mol^{-1}; the value for ethyl acetate was taken from ref *3*. *m* is the "equivalent" number of C–H bonds in the molecule (see ref *9*).

we should expect the orientation energy of the methyl acetate to be higher than a comparison with 2-butanone might indicate. On the other hand, more than simply dipole moment and molecular volume is involved, since even the smallest alkyl chlorides exhibit smaller orientation energies (*2*) than methyl acetate, in spite of their larger dipole moments (CH_3Cl, 1.87 D; C_2H_5Cl, 2.05 D). It appears that orientation energy is favored by a "hard" dipole (i.e., less polarizable) like the carbonyl group as opposed to a "soft" one (more polarizable) like the carbon–chlorine group.

No attempt will be made to provide a quantitative expression for the dependence of orientation energy on molar volume, dipole moment, and dipole polarizability, but it appears that all three of these quantities must be considered in such a correlation.

Second Virial Coefficients. We have combined our vapor pressure data with calorimetrically measured enthalpies of vaporization and the Clapeyron equation to estimate the second virial coefficient, B, in the equation

$$P\bar{V} = RT + BP$$

for methyl and propyl acetates. Two recent publications provide vaporization enthalpies for both compounds (*3*, *10*), and corresponding values for *B* are presented in Table VIII. Those based on ref *10* are more posistive in all cases than those interpolated from the data of ref *3*. The former for methyl acetate are suspect, since *B* does not vary in the expected sense with temperature.

Literature Cited

(1) Ambrose, D., National Physical Laboratory, private communication, Oct 1978.
(2) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(3) Connett, J. E.; Counsell, J. F.; Lee, D. A. *J. Chem. Thermodyn.* **1976**, *8*, 1199.
(4) Dymond, J. H.; Smith, E. B. "The Virial Coefficients of Gases"; Clarendon Press: Oxford, 1969.
(5) "Handbook of Chemistry and Physics", 55th ed.; CRC Press: Cleveland, OH, 1974.
(6) Meyer, E. F.; Hotz, C. A. *J. Chem. Eng. Data* **1976**, *21*, 274.
(7) Meyer, E. F.; Hotz, R. D. *J. Chem. Eng. Data* **1973**, *18*, 359.
(8) Meyer, E. F.; Renner, T. A.; Stec, K. S. *J. Phys. Chem.* **1971**, *75*, 642.
(9) Meyer, E. F.; Wagner, R. E. *J. Phys. Chem.* **1966**, *70*, 3162.
(10) Svoboda, V.; Vesely, F.; Holub, R.; Pick, J. *Collect Czech. Chem. Commun.* **1977**, *42*, 943.
(11) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950.
(12) Wagner, R. E.; Meyer, E. F. *J. Chem. Educ.* **1968**, *45*, 349.
(13) Wojciechowski, M.; Smith, E. *J. Res. Natl. Bur. Stand.* (U.S.) **1937**, *18*, 499.

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Volumetric Behavior of Ethylene and Ethylene–Hydrogen Mixtures

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A Burnett apparatus designed and fabricated was used to collect volumetric data for ethylene and ethylene–hydrogen mixtures. Measurements were made in the temperature range 298.15–423.15 K at intervals of 25 K and in the pressure range 0.3–7.0 MPa. Virial coefficients derived from the compressibility data are tabulated. The data are fitted to different equations of state.

Introduction

The recent IUPAC (*1*) tabulation of *PVT* data for ethylene revealed that data are available above 1.5 MPa in the temperature range 298.15–423.15 K. The recent measurements of Douslin and Harrison (*2*) also do not extend below 1.5 MPa. The data of Charnley et al. (*3*) and Daniel and Stoltzenberg (*4*) do extend in the pressure range 0–20 MPa, but the temperatures are limited to 318.15 K. However, below 0.1 MPa, data are available (*5*–*7*) up to 473.15 K. In order to extract information about intermolecular forces, it is necessary to have information on *PVT* properties at reasonably low pressures over a sufficient temperature range. Further, as ethylene is a very important industrial chemical, it is better to have as much experimental data in all ranges of pressure and temperature as possible. For these reasons the work described in this paper was undertaken.

A detailed literature survey revealed that there are practically no *PVT* data on ethylene–hydrogen mixtures except for two points (*8*). Therefore, the *PVT* behavior of ethylene–hydrogen mixtures was studied in the range 298.15–423.15 K up to 7.0 MPa.

Experimental Apparatus and Procedure

Table I. Properties of Chemicals Used ($T = 303.15$ K)

	refractive index		density	
	present work	lit.	present work	lit.
water	1.331 80	1.331 92 (*10*)	0.995 65	0.995 504 (*11*)
benzene	1.494 74	1.494 68 (*12*)	0.868 25	0.868 25 (*13*)
toluene	1.491 45	1.491 26 (*13*)	0.857 25	0.857 60 (*13*)

Table II. Analyses of Ethylene and Hydrogen

ethylene: ethylene, 99.5; carbon dioxide, 0.2; propane, nitrogen, and hydrogen, 0.1 each

hydrogen: hydrogen, 99.932; carbon dioxide, 0.029; oxygen, 0.029; nitrogen, 0.008

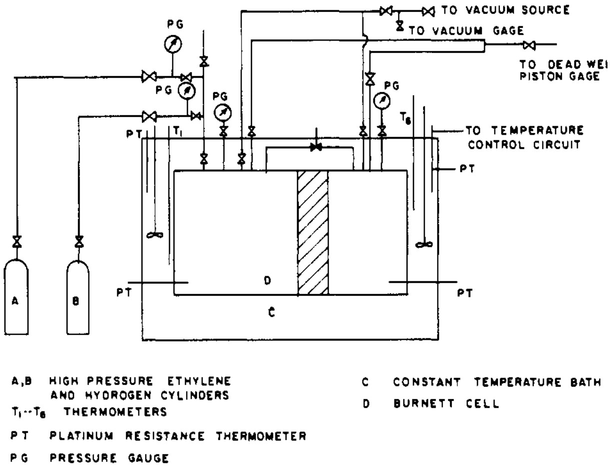

Figure 1. Schematic diagram of Burnett cell assembly.

The details of the experimental setup and procedure have been discussed by Prasad (*9*). A schematic diagram of the general arrangement is shown in Figure 1. The Burnett cell was fabricated from a 9-cm diameter AISI 304 stainless steel rod. The compartment dimensions were 13.0 and 6.5 cm in length and 5 cm in diameter. The compartments of the cell were