Table XVI. Compound Constants for the Peng-Robinson Equation of State

compd	T_c, K	P_c, MPa	ω
dichloromethane	510.150	6.080	0.1990
benzene	562.160	4.898	0.2092
toluene	594.025	4.236	0.2607
nitromethane	588.000	6.313	0.3460
chlorobenzene	632.350	4.519	0.2490

+ nitromethane system. The points in the figures represent the evenly spaced Mixon et al. values while the curves represent the Barker method results.

The Peng-Robinson equation of state was used for all the results shown. Table XVI lists the compound constants used for the Peng-Robinson equation. The binary interaction constant was set to 0.0 for all four binaries.

Some peculiarities in the tables and figures for the calculated results are worthy of comment. For example, note in Tables VI and VII that the activity coefficient for benzene appears to go through a maximum near the $x_1 = 0$ end. The significant digits for the activity coefficients certainly do not extend to the fourth decimal digit but, nevertheless, it is reasonable to accept as valid a "flatness" in the benzene activity coefficient curve (if not an actual maximum) for this almost ideal system. Note in Tables VIII and IX, and in Figure 6, that toluene behaves in the same manner but without exhibiting a maximum.

The relative sensitivities of the infinite dilution activity coefficients obtained from the Mixon et al. and the Barker methods have been discussed in several preceding papers in this series. The Mixon et al. result is determined by the shape of the P vs. x_1 curve near the end point whereas the Barker result is obtained by the fit of the G^E equation over the entire binary composition range. Sometimes the results differ appreciably, as shown by the right end of the 298.05 K curve in Figure 7. Note in Figure 3 how small the deviation from Raoult's law is at 298.05 K at high x_1 values. The points in Figure 3 appear smooth enough but as discussed in previous papers—for example, (*5*)—errors in the 0.05 mmHg range can have a large effect when the deviation is small. Hence, one would tend to have more confidence in the Barker result in this instance.

A much more obvious example of the effect of scatter on the calculated results is illustrated in the 398.10 K isotherm in Figures 4 and 8. The $x_1 = 0.7891$ point (803.3 kPa) is obviously out of line, and other points on the isotherm show an unusual amount of scatter. As shown by the "smooth" values at 398.10 K in Table V, the cubic splined fit was allowed to fit most of the bad points quite closely. That "overfitted" splined fit has been reported here to illustrate the effect on the Mixon et al. activity coefficient curves when even slightly scattered data are fitted too closely.

The result of the overfitting is shown in Figure 8 where the activity coefficient curves at 398.10 K are obviously wrong for the Mixon et al. method. Anyone who needs the best possible activity coefficient curves for the dichloromethane + chlorobenzene system should first arbitrarily smooth the P vs. x_1 curve and use the smoothed values as input to the data reduction methods. Usually, the Barker method does an effective job of smoothing the P vs. x_1 data but, in this case, a relatively small amount of scatter affects it almost as much as the Mixon et al. method.

Registry No. Dichloromethane, 75-09-2; benzene, 71-43-2; toluene, 108-88-3; nitromethane, 75-52-5; chlorobenzene, 108-90-7.

Literature Cited

(1) Maher, P. J.; Smith, B. D. *J. Chem. Eng. Data* **1979**, *24*, 16.
(2) Mixon, F. O.; Gomowski, B.; Carpenter, B. H. *Ind. Eng. Chem. Fundam.* **1965**, *4*, 455.
(3) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(4) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(5) Khurma, J. R.; Muthu, O.; Munjal, S.; Smith, B. D. *J. Chem. Eng. Data* **1983**, *28*, 412.

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Excess Enthalpies of Some Ester + Alcohol Binary Mixtures

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The excess molar enthalpies of the binary liquid mixtures methyl butanoate + normal alcohol (C_4–C_{10}) and propyl ethanoate + normal alcohol (C_3–C_5) have been determined at atmospheric pressure and 298.15 K as a function of mole fraction. The apparatus used was a standard Calvet microcalorimeter equipped with a device allowing the exclusion of a vapor phase. The mixtures studied are all highly endothermic ($H^E > 0$), and the values of the excess molar enthalpies increase with length of the hydrocarbon chain of the alcohol. The H^E–x curves are practically symmetrical, with maxima at mole fractions of alcohol slightly below 0.5.

Introduction

Continuing with the work described in earlier articles (*1*, *2*), we have determined the excess molar enthalpies of the binary liquid mixtures formed by a linear ester (methyl butanoate or propyl ethanoate) and a normal alcohol (ranging from 1-butanol to 1-decanol in the case of methyl butanoate, and from 1-propanol to 1-pentanol in the case of propyl ethanoate), the measurements being made at 298.15 K and over the entire range of concentrations.

Experimental Section

The chemical products used were supplied by Fluka (Buchs, Switzerland). All were better than 99 mol % pure as supplied except the propyl acetate, which was purified before use by washing with saturated aqueous NaCl solution, drying with $MgSO_4$, and triple distillation in a rectifying column, the final purity being 99.6 mol %. Refractive indices and densities were measured with a Zeiss refractometer (Carl Zeiss, Jena, Germany) and a densimeter-vibratometer (Anton Paar, Graz, Austria). The values measured (Table I) agree well with pub-

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Table I. Densities (ρ) and Refractive Indices (n_D) of Pure Components at 298.15 K

	$\rho/(\mathrm{kg\ m^{-3}})$		n_D	
	this work	lit.	this work	lit.
methyl butanoate	892.49	885.22 (*5*)	1.387 53[a]	1.3878 (*3*)[a]
propyl acetate	882.76	883.03 (*4*)	1.384 28[a]	1.3842 (*3*)[a]
1-propanol	799.62	799.75 (*4*)	1.383 65	1.3837 (*4*)
1-butanol	805.95	806.0 (*4*)	1.397 18	1.3973 (*4*)
1-pentanol	811.27	811.5 (*4*)	1.407 60	1.4079 (*4*)
1-hexanol	815.93	815.9 (*4*)	1.415 99	1.4161 (*4*)
1-heptanol	818.25	818.7 (*6*)	1.422 20	1.4223 (*6*)
1-octanol	821.80	822.09 (*4*)	1.427 32	1.4275 (*4*)
1-nonanol	824.72	824.7 (*6*)	1.431 01	1.4319 (*6*)
1-decanol	826.65	826.3 (*6*)	1.435 17	1.4353 (*6*)

[a] Values at 293.15 K.

lished values (*3–6*). All chemicals were kept under molecular sieves (Union Carbide Type 4Å, 2.5–1.4 mm; beads from Fluka) and were partially degassed before use.

Excess molar enthalpies were determined by using a standard Calvet microcalorimeter (*7*) equipped with a device allowing the exclusion of a vapor phase (*8*). The volume of the calorimeter cell was approximately 10 cm^3. Temperature was kept constant to within $\pm 5 \times 10^{-3}$ K. The microcalorimeter was calibrated electrically before use and the calibration subsequently checked by using the standard hexane + cyclohexane mixture recommended by the IUPAC (*9*). The discrepancy between the H^E values measured and published values (*10*) was less than 1%.

Results and Discussion

The values of H^E found for the 10 binary mixtures studied are shown in Table II and Figures 1 and 2. Following Redlich and Kister (*11*), variable-degree polynomials of the form

$$H^E/(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{i=0}^{n-1} A_i(2x-1)^i \qquad (1)$$

were fitted to the data by the least-squares method with all points weighted equally. In this equation x is the mole fraction of alcohol and the number of coefficients A_i was determined for each mixture by using an F test (*12*) to the additional term at the same time as the existing parameters from zero. The values of the A_i and the standard deviations $\sigma(H^E)$ are shown in Table III. In Figures 1 and 2 the continuous curves have been calculated for each mixture by using eq 1 and the A_i of Table III.

As may be seen in Table II, all the excess enthalpies are positive, with maxima at values of x slightly above 0.5 in the case of the alcohol + propyl ethanoate mixtures and slightly below 0.5 in the case of alcohol + methyl butanoate mixtures. For a given ester, H^E increases with the chain length of the normal alcohol. That alcohol + propyl ethanoate mixtures are

Table II. Excess Molar Enthalpy H^E for Ester + Alcohol at 298.15 K

x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})
$x\mathrm{C_3H_7OH} + (1-x)\mathrm{CH_3COOC_3H_7}$					
0.1992	874	0.5210	1229	0.7125	1026
0.2537	1011	0.5224	1240	0.7518	941
0.3240	1134	0.5993	1175	0.7956	819
0.3835	1199	0.6401	1146	0.8280	718
0.4316	1223	0.6703	1101		
0.4778	1244	0.6970	1054		
$x\mathrm{C_4H_9OH} + (1-x)\mathrm{CH_3COOC_3H_7}$					
0.1741	846	0.4891	1318	0.6640	1183
0.2192	972	0.4993	1309	0.7175	1079
0.2783	1116	0.5650	1290	0.7622	952
0.3469	1214	0.5975	1273	0.8091	826
0.3854	1268	0.6234	1236	0.8278	751
0.4481	1311	0.6501	1214		
$x\mathrm{C_5H_{11}OH} + (1-x)\mathrm{CH_3COOC_3H_7}$					
0.1963	847	0.4550	1406	0.6368	1305
0.2637	1074	0.4734	1415	0.6816	1223
0.3167	1234	0.5303	1411	0.7301	1109
0.3516	1305	0.5505	1407	0.7775	967
0.3951	1358	0.5951	1360	0.8594	656
0.4356	1392	0.6095	1335		
$x\mathrm{C_4H_9OH} + (1-x)\mathrm{C_3H_7COOCH_3}$					
0.1197	865	0.4430	1565	0.6071	1468
0.1721	1089	0.4511	1558	0.6332	1435
0.2308	1245	0.4895	1570	0.6597	1366
0.2857	1388	0.5095	1560	0.6949	1281
0.3294	1453	0.5148	1557	0.7446	1147
0.3616	1503	0.5835	1506	0.7861	1021
0.3903	1533	0.6013	1495	0.8383	821
$x\mathrm{C_5H_{11}OH} + (1-x)\mathrm{C_3H_7COOCH_3}$					
0.1348	942	0.4703	1590	0.5651	1546
0.1884	1159	0.4739	1598	0.5751	1540
0.2459	1312	0.4920	1598	0.6231	1461
0.2918	1418	0.4982	1596	0.6772	1349
0.3428	1499	0.5305	1582	0.7301	1203
0.3972	1552	0.5339	1581	0.7764	1057
0.4450	1588	0.5475	1567	0.8290	842
0.4587	1591	0.5554	1551		

x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})	x	H^E/ (J mol^{-1})
$x\mathrm{C_6H_{13}OH} + (1-x)\mathrm{C_3H_7COOCH_3}$					
0.1480	1040	0.4265	1677	0.6085	1557
0.2224	1359	0.4301	1676	0.6449	1477
0.2592	1442	0.4712	1694	0.6685	1433
0.3191	1578	0.5022	1683	0.7480	1239
0.3495	1616	0.5297	1654	0.8353	912
0.3685	1636	0.5539	1643	0.8521	833
0.4156	1688	0.5789	1597	0.8958	644
$x\mathrm{C_7H_{15}OH} + (1-x)\mathrm{C_3H_7COOCH_3}$					
0.1497	1039	0.4427	1750	0.5208	1724
0.1978	1261	0.4586	1746	0.5575	1696
0.2401	1376	0.4638	1757	0.6156	1597
0.2904	1512	0.4774	1755	0.6684	1486
0.3354	1628	0.4863	1755	0.7204	1345
0.3618	1657	0.5000	1757	0.7821	1128
0.4351	1738	0.5164	1729		
$x\mathrm{C_8H_{17}OH} + (1-x)\mathrm{C_3H_7COOCH_3}$					
0.1283	1033	0.3639	1763	0.6502	1602
0.2055	1385	0.3988	1781	0.6894	1503
0.2331	1483	0.4194	1805	0.7226	1398
0.2614	1563	0.4581	1813	0.7227	1403
0.2824	1618	0.4679	1823	0.7836	1186
0.3057	1670	0.4991	1801	0.8755	745
0.3174	1693	0.5205	1790		
0.3549	1749	0.5819	1739		
$x\mathrm{C_9H_{19}OH} + (1-x)\mathrm{C_3H_7COOCH_3}$					
0.1264	1034	0.3915	1896	0.4640	1918
0.1658	1254	0.3988	1897	0.5111	1888
0.2023	1429	0.4127	1905	0.5338	1879
0.2467	1573	0.4177	1909	0.5605	1837
0.2889	1700	0.4350	1912	0.6244	1687
0.3578	1832	0.4417	1912	0.6857	1542
0.3849	1877	0.4554	1918	0.7447	1376
$x\mathrm{C_{10}H_{21}OH} + (1-x)\mathrm{C_3H_7COOCH_3}$					
0.0875	808	0.3726	1920	0.5307	1934
0.1568	1246	0.4241	1968	0.5563	1890
0.1986	1458	0.4260	1970	0.5829	1852
0.2289	1588	0.4261	1966	0.6369	1737
0.2709	1701	0.4617	1964	0.6951	1567
0.3168	1823	0.4863	1956	0.8040	1094
0.3185	1844	0.5101	1942	0.8790	726

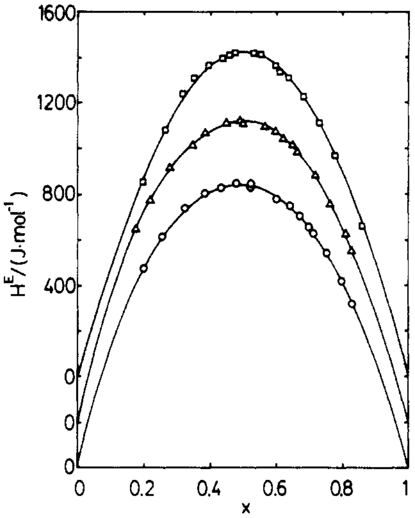

Figure 1. Excess enthalpy H^E plotted against mole fraction of normal alcohol at 298.15 K for the mixtures propyl ethanoate with normal alcohols: (O) 1-propanol, (△) 1-butanol, (□) 1-pentanol.

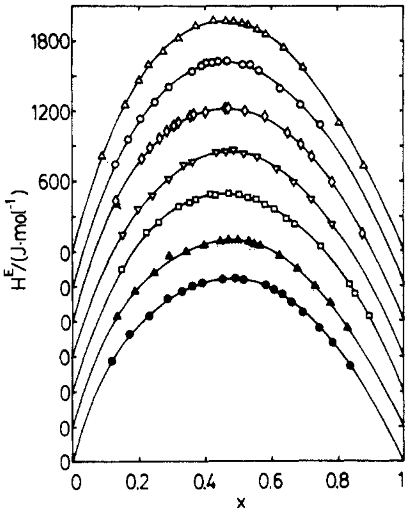

Figure 2. Excess enthalpy H^E plotted against mole fraction of normal alcohol at 298.15 K for the mixtures methyl butanoate with normal alcohols: (●) 1-butanol, (▲) 1-pentanol, (□) 1-hexanol, (▽) 1-heptanol, (◇) 1-octanol, (O) 1-nonanol, (△) 1-decanol.

Table III. Coefficients A_i and Standard Deviations $\sigma(H^E)$ for Representation of Excess Enthalpies H^E at 298.15 K by Eq 1

	A_0	A_1	A_2	A_3	A_4	$\sigma(H^E)$/ (J mol^{-1})
$(1 - x)CH_3COOC_3H_7$						
$+ xC_3H_7OH$	4958	-216	883	-432		6
$+ xC_4H_9OH$	5266	0	756	-1110		7
$+ xC_5H_{11}OH$	5688	0	-530	216		10
$(1 - x)C_3H_7COOCH_3$						
$+ xC_4H_9OH$	6269	-533	443	-1487	1941	8
$+ xC_5H_{11}OH$	6363	-541	651	-1817	977	5
$+ xC_6H_{13}OH$	6690	-1080	1528			10
$+ xC_7H_{15}OH$	6979	-797	-168	-494	2410	9
$+ xC_8H_{17}OH$	7222	-885	1451	-1263		5
$+ xC_9H_{19}OH$	7574	-1380	1135			13
$+ xC_{10}H_{21}OH$	7818	-1296	763	-1223		8

less endothermic than mixtures of methyl butanoate with the same alcohols may be explained by propyl ethanoate and methyl butanoate being positional isomers whose polarization values (1.88 (*13*) and 1.717 (*14*) D, respectively) show that there is greater charge displacement in the acetate. Thus, although more energy is required to destroy the molecular structure of the acetate than that of the butanoate, the energy released on forming hydrogen bonds with the alcohol present is also greater in the case of the acetate, and the final figure is lower for normal alcohol + methyl butanoate mixtures.

Registry No. $C_3H_7COOCH_3$, 623-42-7; $CH_3COOC_3H_7$, 109-60-4; C_3H_7OH, 71-23-8; C_4H_9OH, 71-36-3; $C_5H_{11}OH$, 71-41-0; $C_6H_{13}OH$, 111-27-3; $C_7H_{15}OH$, 111-70-6; $C_8H_{17}OH$, 111-87-5; $C_9H_{19}OH$, 143-08-8; $C_{10}H_{21}OH$, 112-30-1.

Literature Cited

(1) Fernández, J.; Paz Andrade, M. I.; Sarmiento, F.; Bravo, R. *J. Chem. Thermodyn.* **1983**, *15*, 1145–9.
(2) Bravo, R.; Paz Andrade, M. I.; Kehiaian, H. V. *Acta Cient. Compostelana* **1979**, *16*, 141.
(3) Weast, R., Ed. "Handbook of Chemistry and Physics", 61st ed.; CRC Press: Boca Raton, FL, 1980–81.
(4) Riddick, J. A.; Bunger, W. B. "Techniques of Chemistry", 3rd ed.; Wiley-Interscience: New York, 1950; Vol. 1.
(5) Dusart, O.; Piekarski, C.; Piekarski, S.; Viallard, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1976**, *73*, 837.
(6) Wilhoit, R. C.; Zwolinski, B. *J. Phys. Chem. Ref. Data* **1973**, *2*, Suppl. No. 1.
(7) Calvet, E.; Prat, H. "Microcalorimetrie, Applications Physico-Chimiques et Biologiques"; Masson: Paris, 1965.
(8) Paz Andrade, M. I. "Les Développments Recents de la Microcalorimetrie"; Ed. du CNRS: Paris, 1967; p 243.
(9) Westrum, E. F. Jr., Ed. *Bull. Thermodyn. Thermochem.* **1970**, *13*, 507.
(10) McGlashan, M. L.; Stoeckli, H. F. *J. Chem. Thermodyn.* **1969**, *1*, 589.
(11) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 341.
(12) Bevington, P. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969; p 200.
(13) Müller, H.; Sack, H. *Phys. Z.* **1930**, *31*, 815.
(14) Wolf, K. L.; Gross, W. J. *Z. Phys. Chem., Abt. B* **1931**, *14*, 305.

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