where the thermal expansion coefficients vs. composition of benzene have been plotted. The distribution of the experimental α values gives a curvature due to the departure from the "ideal" behavior of the mixture, where $\alpha^{id} = x_1\alpha_1 + x_2\alpha_2$. However, the sets of α values estimated through eq 3-5 are distributed along a straight lines. Figure 1 also shows that eq 4, derived from Lorentz-Lorenz, presents the smallest deviation with the experimental values but only about the central zone of concentration, increasing for the extreme mole fractions, being greater when approaching the composition richest in benzene. On the other hand, eq 3, derived from Gladstone-Dale, offers greater differences with regard to the experimental values and its utilization is not recommended to estimate the α values and its utilization is not recommended to estimate the α values of this binary mixture. Equation 5, derived from Eykman, gives results whose mean error, with regard to the experimental values, is 6.4%, while the mean errors of eq 3 and 4 are 13.3% and 2.2%, respectively.

Registry No. Benzene, 71-43-2; 1-heptanol, 111-70-6.

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Received for review June 27, 1984. Revised manuscript received April 8, 1985. Accepted April 23, 1985.

Excess Molar Volumes of Binary Mixtures of Butyl Formate with Normal Alcohols at 298.15 K

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Excess volumes at 298.15 K for binary mixtures of butyl formate with normal alcohols (C_1-C_{10}), determined from density measurements, are reported. The excess molar volumes were positive for *n*-alcohols with more carbon atoms than ethanol, sigmoidal for ethanol and negative for methanol. A suitable equation was used to fit the values of V_m^E.

Introduction

We have initiated an investigation to measure the thermodynamic properties of ester + alcohol binary mixtures. The present work reports the excess molar volumes of butyl formate + *n*-alcohols (from methanol to 1-decanol) at 298.15 K. As far as we know, there is no reference in the literature to previous experimental data of V_m^E for these mixtures and their behavior was found to be similar to that of other ester + alcohol systems. The excess molar volumes increase with the chain length of the alcohol except for methanol, the V_m^E values of which are negative, due to the arrangement of the small molecules of methanol with butyl formate. The values of V_m^E as a function of the molar fraction of the ester were fitted by applying a modified form of a smoothing equation already used by the author in previous papers (*1*, *2*).

Experimental Section

The butyl formate and all *n*-alcohols employed were supplied by Fluka. Their characteristics were as follows: methanol and ethanol (puriss >99.8 mol %), 1-propanol (puriss >99.5 mol %), 1-butanol (puriss >99.0 mol %), 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol (puriss >99.0 mol %), 1-nonanol (purum >98.0 mol %). All these products were dried by using an Union Carbide Type 4A molecular sieve by Fluka, and the densities and refractive indices determined for the alcohols were in quite good agreement with those found in the literature (*3*-*5*). Two attempts to purify the butyl formate resulted in a degree of purity of about 98%, as determined by gas chromatography. Its physical properties differ slightly from those found in the literature (ρ = 887.64 kg·m^{-3}; 886.3, extrapolated from ref 3, and n_D = 1.3869, 1.3874 (*3*)).

The densities of the binary liquid mixtures were measured by an Anton Paar DMA-55 vibrating-tube densimeter with a reproducibility of ±0.01 kg·m^{-3}. The apparatus was calibrated at atmospheric pressure with redistilled and degasified water [ρ(298.15 K) = 997.04 kg·$^{-3}$] (*3*) and benzene [ρ(298. 15 K) = 873.68 kg·m^{-3}] whose density was confirmed 5 times by a precision pycnometer. The former is the average value from the five runs.

The measuring cell of the apparatus was thermostated with a Heto-Birkerod ultrathermostat with an accuracy of ±0.01 K. The imprecision in the determination of the mole fractions of the ester was estimated at $\pm 6 \times 10^{-5}$, and the mean error in the determinations of the excess molar volumes, V_m^E, was ±0.001 cm^3·mol^{-1}.

Results and Discussion

The values of V_m^E calculated from the densities of the pure liquids and their mixtures, are listed in Table I. A graphical comparison of the results for the 10 systems studied is given in Figure 1, where the excess molar volumes are plotted against the mole fraction of butyl formate.

In order to fit the experimental data of V_m^E as a function of the mole fraction, when they are distributed in a uniform manner and have the same sign, we have used the following equation in previous papers (*1*, *2*)

$$V_m^E = C[Z(1 - Z)]^b \tag{1}$$

where

$$Z = \frac{x}{x + R(1 - x)} \tag{2}$$

However, eq 1 cannot be used when the experimental points are distributed in a sigmoidal form. The form of eq 1 must

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Table I. Values of Excess Molar Volumes, V_m^E, at 298.15 K for Butyl Formate (1) + *n*-Alcohols (2) Mixtures

x_1	V_m^E, $cm^3 \cdot mol^{-1}$
Butyl Formate + Methanol	
0.032 38	−0.0871
0.045 60	−0.0996
0.074 64	−0.1340
0.118 13	−0.1716
0.144 75	−0.1964
0.204 13	−0.2274
0.238 08	−0.2507
0.318 02	−0.2758
0.368 00	−0.2907
0.415 25	−0.2974
0.494 86	−0.2936
0.522 43	−0.2902
0.565 05	−0.2764
0.618 28	−0.2626
0.762 03	−0.1961
0.779 43	−0.1804
0.845 18	−0.1257
0.919 11	−0.0767
Butyl Formate + Ethanol	
0.007 73	−0.0080
0.016 26	−0.0146
0.024 20	−0.0158
0.071 60	−0.0217
0.104 34	0.0066
0.142 56	0.0184
0.207 59	0.0301
0.272 37	0.0394
0.355 45	0.0522
0.474 00	0.0627
0.521 29	0.0651
0.553 61	0.0663
0.619 55	0.0689
0.696 49	0.0657
0.761 50	0.0634
0.816 37	0.0589
0.828 44	0.0571
0.893 06	0.0452
0.943 08	0.0249
0.973 36	0.0048
Butyl Formate + 1-Propanol	
0.010 43	0.0002
0.020 86	0.0055
0.053 38	0.0157
0.091 26	0.0444
0.139 36	0.0600
0.256 41	0.1003
0.307 54	0.1113
0.390 59	0.1316
0.436 94	0.1379
0.464 86	0.1388
0.527 56	0.1379
0.573 75	0.1329
0.633 28	0.1294
0.729 84	0.1035
0.792 66	0.0873
0.842 03	0.0623
0.882 50	0.0446
0.949 54	0.0247
Butyl Formate + 1-Butanol	
0.023 61	0.0053
0.044 39	0.0169
0.091 97	0.0530
0.138 41	0.0735
0.191 19	0.1026
0.241 68	0.1271
0.297 00	0.1470
0.368 97	0.1628
0.405 07	0.1718
0.464 33	0.1771
0.516 43	0.1773
0.563 02	0.1715
0.597 93	0.1651
0.713 38	0.1388
0.812 32	0.1034
0.856 05	0.0833
0.920 77	0.0572
0.959 21	0.0337
Butyl Formate + 1-Pentanol	
0.043 29	0.0374
0.069 00	0.0651
0.099 68	0.0888
0.165 29	0.1358
0.246 83	0.1717
0.293 01	0.1934
0.334 54	0.2044
0.393 10	0.2109
0.434 29	0.2148
0.504 76	0.2150
0.554 23	0.2051
0.632 72	0.1017
0.719 40	0.1633
0.804 65	0.1326
0.839 30	0.1141
0.874 98	0.0910
0.937 64	0.0450
0.967 55	0.0241
Butyl Formate + 1-Hexanol	
0.034 99	0.0401
0.112 78	0.1078
0.177 82	0.1648
0.207 84	0.1820
0.289 55	0.2141
0.322 57	0.2259
0.405 32	0.2469
0.457 78	0.2520
0.503 36	0.2470
0.548 14	0.2473
0.599 44	0.2378
0.652 34	0.2271
0.731 71	0.1955
0.806 39	0.1563
0.860 04	0.1253
0.896 71	0.0936
0.945 50	0.0542
0.972 68	0.0301
Butyl Formate + 1-Heptanol	
0.057 49	0.0738
0.110 43	0.1336
0.161 90	0.1811
0.226 52	0.2240
0.285 54	0.2548
0.326 18	0.2772
0.368 92	0.2872
0.412 12	0.2980
0.467 33	0.3012
0.546 58	0.2979
0.609 89	0.2871
0.685 30	0.2616
0.278 55	0.2389
0.777 43	0.2078
0.847 15	0.1560
0.915 92	0.0962
0.944 95	0.0634
0.973 03	0.0342
Butyl Formate + 1-Octanol	
0.043 06	0.0582
0.099 66	0.1271
0.145 43	0.1848
0.224 60	0.2469
0.261 33	0.2752
0.309 81	0.3066
0.372 74	0.3263
0.433 40	0.3441
0.483 41	0.3498
0.529 04	0.3452
0.577 29	0.3358
0.640 42	0.3183
0.699 82	0.2859
0.763 24	0.2499
0.825 13	0.2086
0.887 49	0.1424
0.950 77	0.0683
0.976 83	0.0374
Butyl Formate + 1-Nonanol	
0.051 23	0.0786
0.106 10	0.1621
0.162 39	0.2320
0.216 81	0.2785
0.292 31	0.3281
0.319 16	0.3402
0.347 31	0.3552
0.396 70	0.3714
0.484 84	0.3754
0.464 64	0.3735
0.542 15	0.3620
0.639 40	0.3264
0.738 99	0.2766
0.814 24	0.2259
0.876 69	0.1645
0.925 85	0.1006
0.957 44	0.0609
0.977 07	0.0358
Butyl Formate + 1-Decanol	
0.025 36	0.0312
0.050 97	0.0773
0.106 20	0.1575
0.204 19	0.2794
0.245 45	0.3194
0.293 44	0.3507
0.352 93	0.4002
0.431 21	0.4256
0.477 73	0.4320
0.518 86	0.4321
0.605 68	0.4168
0.697 04	0.3681
0.754 36	0.3301
0.841 70	0.2417
0.870 68	0.2130
0.925 71	0.1272
0.965 34	0.0669
0.977 21	0.0460

Table II. Parameters and Standard Deviations Obtained for the Mixtures of Butyl Formate (1) + *n*-Alcohols (2) by Using Eq 3 and Standard Deviation by Redlich–Kister

							$\sigma(V_m^E)$, $cm^3 \cdot mol^{-1}$	
	R	A_0	A_1	A_2	A_3	A_4	eq 3	Redlich–Kister[a]
methanol	0.1084	−4.6818	11.1134	−13.4978	6.0902		0.0039	0.0116 (4)
ethanol	0.1460	−1.1711	2.6035	3.3911	−10.0786	5.6591	0.0053	0.0116 (4)
1-propanol	0.2960	−0.0739	4.5087	−12.0758	14.0070	−5.9225	0.0034	0.0082 (4)
1-butanol	0.0120	3.6815	−15.1597	20.4779	−8.2719		0.0049	0.0054 (3)
1-pentanol	0.1898	0.6785	1.7992	−3.0162	1.3390		0.0029	0.0030 (4)
1-hexanol	0.8280	1.1789	−0.3253	−0.3349	0.5856		0.0028	0.0029 (3)
1-heptanol	2.6200	1.4142	−1.7157	5.1765	−6.7967	3.2918	0.0018	0.0021 (3)
1-octanol	1.4140	1.4113	0.3788	−1.6463	1.4875		0.0034	0.0035 (3)
1-nonanol	0.6193	1.5749	1.1501	−3.6705	2.5178		0.0038	0.0040 (4)
1-decanol	0.7821	1.3101	2.8914	−5.9793	3.8402		0.0052	0.0054 (3)

[a] The number in brackets indicates the degree produced by the smallest standard deviation.

therefore be modified to afford the possibility of cutting the axis of abscissas (mole fraction) at other points than zero and one. If eq 2 is substituted in (1), the product $x(1 - x)$ appears in the numerator of the resulting expression; therefore it is convenient to add the other function that permits the cut with the x axis, in exchange for removing the parameters b and C.

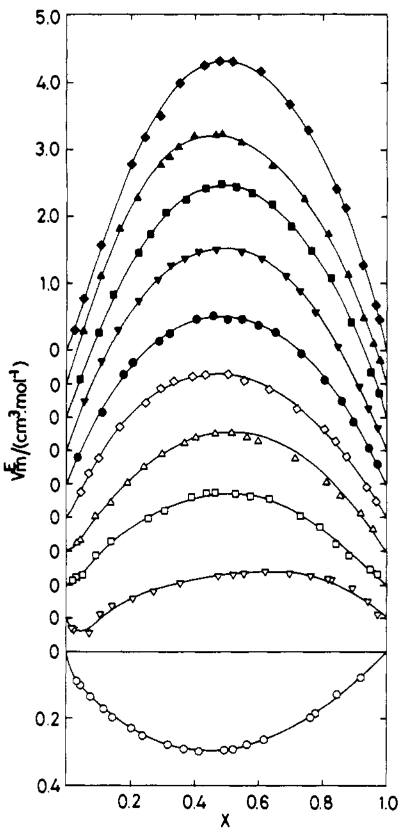

Figure 1. Excess molar volumes, V_m^E, for $x$butyl formate + $(1 - x)n$-alcohol at 298.15 K; experimental results: (○) methanol; (▽) ethanol; (□) 1-propanol; (△) 1-butanol; (◇) 1-entanol; (●) 1-hexanol; (▼) 1-heptanol; (■) 1-octanol; (▲) 1-nonanol; (◆) 1-decanol.

Several expressions were used, such as $Z(1 - Z)\sum_{i=0}^{m} A_i Z^i$ or $Z(1 - Z)\sum_{i=0}^{m} A_i x^i$, but the best results were obtained from

$$V_m^E = x(1 - x)\sum_{i=0}^{m} A_i Z^i \qquad (3)$$

with Z defined in the relationship 2. The values of the coefficients A_i were found by using a least-squares method and are given in Table II for each of the systems. The values of R—also shown in Table II—were found by an optimization technique in which R was varied, while keeping the number of coefficients, A_i, in the series constant until the minimum value of the standard deviation, $\sigma(V_m^E)$, was determined. In order to verify the applicability of eq 3, a comparison was made with another equation which is widely used at the present time, the Redlich-Kister eq 6, the coefficients of which were also determined by the least-squares method. The degree that produces the smallest deviation—between three and four—was used for both equations. The best results of $\sigma(V_m^E)$ are given in Table II, and it was found that the equation proposed gives a better adjustment than the Redlich-Kister equation, particularly when the values of V_m^E are very close to the axis of abscissas.

V_m^E is negative for the entire range of composition in the butyl formate + methanol system, and is positive from 1-propanol to 1-decanol. The butyl formate + ethanol system is a sigmoid with a small negative zone for high concentrations of ethanol. The negative values of V_m^E for the butyl formate + methanol system can be attributed to the fact that the small molecules of the alcohol are perfectly arranged among those of the ester, and it is observed that the effect of interaction among the components produces a greater steric impediment as the chain length of the normal alcohol increases.

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; 1-nonanol, 143-08-8; 1-decanol, 112-30-1; butyl formate, 592-84-7.

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Received for review February 11, 1985. Accepted April 23, 1985.

Excess Volumes of *n*-Butyric Acid + Various Polar and Nonpolar Solvents

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Excess volumes for the binary mixtures of cyclohexane, benzene, toluene, carbon tetrachloride, *n*-octane, methanol, and acetone with *n*-butyric acid at 298.15 K are reported over the complete mole fraction range. The results have been compared with the corresponding results for isobutyric acid and other lower acids reported earlier.

Introduction

Carboxylic acids, the self-associated liquids through hydrogen bonds, possess interesting mixing properties. Acetic acid with nonpolar solvents like cyclohexane, benzene, and carbon tetrachloride shows large positive excess volume (*1*, *2*) and larger positive free energy than enthalpy (*3*, *4*) yielding negative excess entropy. Kohler et al. have assigned this behavior to the breaking up of strongly interacting acetic acid dimer-monomer complexes in the presence of these solvents to undergo the following equilibria

$$\text{D-M} \rightleftharpoons \text{D} + \text{M} \qquad (1)$$

$$\text{M} + \text{M} \rightleftharpoons \text{D} \qquad (2)$$

The first step is associated with a large volume increase and the second step is isochoric with the volume of the dimer considered twice that of the monomer. Consequently the increasing addition of nonpolar solvent is associated with increase