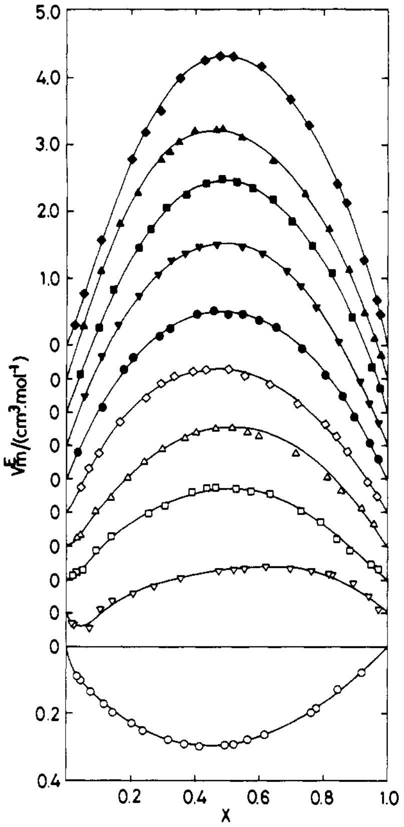

Figure 1. Excess molar volumes, V_m^E, for $x$butyl formate + $(1 - x)n$-alcohol at 298.15 K; experimental results: (O) methanol; (∇) ethanol; (□) 1-propanol; (△) 1-butanol; (◇) 1-entanol; (●) 1-hexanol; (▼) 1-heptanol; (■) 1-octanol; (▲) 1-nonanol; (♦) 1-decanol.

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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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

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Table I. Excess Volume of Mixtures Containing *n*-Butyric Acid at 298.15 K

x	V^E/cm^3 mol^{-1}	$10^4\delta V^E$/ cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}	$10^4\delta V^E$/ cm^3 mol^{-1}	x	V^E/cm^3 mol^{-1}	$10^4\delta V^E$/ cm^3 mol^{-1}
$x(n\text{-}C_3H_7CO_2H) + (1 - x)(c\text{-}C_6H_{12})$								
0.0702	0.2147	0	0.3813	0.7804	-9	0.7343	0.6084	3
0.1416	0.4022	-2	0.4717	0.8175	-9	0.8015	0.4864	6
0.2089	0.5516	26	0.5410	0.8090	13	0.8950	0.2780	7
0.2738	0.6592	-18	0.6267	0.7486	-3	0.9380	0.1679	-6
0.3209	0.7209	-9	0.6917	0.6726	3			
$x(n\text{-}C_3H_7CO_2H) + (1 - x)(C_6H_6)$								
0.0991	0.1063	7	0.4331	0.3253	-11	0.7159	0.2552	7
0.1741	0.1766	-15	0.4674	0.3306	-4	0.7907	0.1994	8
0.2375	0.2301	-8	0.5088	0.3303	-12	0.9056	0.0936	-1
0.3341	0.2950	29	0.6092	0.3102	1	0.9504	0.0492	-1
$x(n\text{-}C_3H_7CO_2H) + (1 - x)(C_6H_6)$								
0.0778	0.0290	4	0.3620	0.1178	26	0.5740	0.1320	-2
0.1102	0.0401	-4	0.3832	0.1190	-2	0.6556	0.1256	16
0.1540	0.0562	1	0.4023	0.1225	1	0.7652	0.0957	-25
0.2344	0.0810	17	0.4747	0.1319	11	0.8132	0.0822	-19
0.2806	0.0945	-17	0.5020	0.1335	11	0.9189	0.0418	10
$x(n\text{-}C_3H_7CO_2H) + (1 - x)(CCl_4)$								
0.0495	0.0397	3	0.3821	0.1526	13	0.7030	0.0848	-13
0.0892	0.0662	-1	0.4526	0.1461	-10	0.7114	0.0842	8
0.1980	0.1185	-13	0.5446	0.1315	1	0.8071	0.0520	5
0.2441	0.1351	9	0.6686	0.0989	16	0.9240	0.0162	-3
0.3144	0.1460	-14						
$x(n\text{-}C_3H_7CO_2H) + (1 - x)(n\text{-}C_8H_{18})$								
0.0913	0.1427	2	0.4060	0.4623	7	0.6866	0.4175	16
0.1551	0.2320	-2	0.4487	0.4481	15	0.7841	0.3221	-4
0.1853	0.2703	-9	0.4816	0.4839	11	0.8252	0.2709	-14
0.2775	0.3720	-2	0.5400	0.4829	6	0.9151	0.1436	7
0.3202	0.4094	4	0.5877	0.4695	-13			
0.3544	0.4332	-3	0.6496	0.4392	-21			
$x(n\text{-}C_3H_7CO_2H) + (1 - x)(CH_3OH)$								
0.0750	-0.1501	-2	0.4081	-0.7300	0	0.7073	-0.5826	-12
0.1309	-0.2700	14	0.4574	-0.7550	22	0.8294	-0.3488	-19
0.1400	-0.2925	-12	0.4975	-0.7653	-12	0.8613	-0.2778	9
0.2529	-0.5242	-18	0.5820	-0.7320	6	0.9214	-0.1502	5
0.2810	-0.5707	13	0.6414	-0.6752	0			
0.3602	-0.6830	13	0.6910	-0.6078	-6			
$x(n\text{-}C_3H_7CO_2H) + (1 - x)(CH_3)_2CO$								
0.0813	-0.2971	0	0.4912	-0.7745	7	0.7820	-0.4603	-1
0.1259	-0.4259	-6	0.5422	-0.7489	0	0.8568	-0.3227	-5
0.2194	-0.6224	13	0.6198	-0.6843	-7	0.8963	-0.2403	6
0.3508	-0.7647	5	0.6631	-0.6351	-3	0.9412	-0.1416	-1
0.4459	-0.7865	-8						

of the proportion of dimers. In continuation of the work reported on the excess volumes of acetic, propionic, and isobutyric acids (*5-7*) in various polar and nonpolar solvents, the present paper summarizes such results for *n*-butyric acid with various solvents. The comparison of the results of the various acids presents a study of the effect of structural features of the alkyl chain of the acids and shows the presence of acid-solvent interactions.

Experimental Section

Materials. Distilled *n*-butyric acid (LR) was redistilled over potassium permanganate in a 1.2-m-long fractionating column and the middle fraction distilling at 435.7 K was collected. Other solvents used were of AR grade and were purified as described in literature (*8*). The purities of the samples were checked by measuring their densities and refractive indices which were found to agree very well with those in the literature (*8*). The samples were thoroughly degassed before use.

Excess Volume Measurements. Excess volumes (V^E's) were measured by using a batch dilatometer introduced by Lark and Palta. This dilatometer does not involve the use of greased stoppers. Its design and working are described elsewhere (*9*). The temperature of the 150-L water thermostat was maintained at 298.15 ± 0.01 K.

Table II. Values of Constants in Eq 1 and Standard Deviations at 298.15 K

$x(n\text{-}C_3H_7CO_2H)$	A	B	C	σV^E/cm^3 mol^{-1}
$+(1 - x)(c\text{-}C_6H_{12})$	3.2725	0.2220	-0.2350	0.0012
$+(1 - x)(C_6H_6)$	1.3276	0.0515	-0.2889	0.0013
$+(1 - x)(C_6H_5CH_3)$	0.5314	-0.0882	-0.0784	0.0014
$+(1 - x)(CCl_4)$	0.5611	0.3473	-0.0451	0.0011
$+(1 - x)(n\text{-}C_8H_{18})$	1.9369	-0.0770	-0.2341	0.0011
$+(1 - x)(CH_3OH)$	-3.0560	-0.0564	1.3062	0.0014
$+(1 - x)((CH_3)_2CO)$	-3.0860	-0.8378	-0.2707	0.0007

Results and Discussion

V^E values for *n*-butyric acid + $c\text{-}C_6H_{12}$, + C_6H_6, + $C_6H_5CH_3$, + CCl_4, + $n\text{-}C_8H_{18}$, + CH_3OH, + $(CH_3)_2CO$ as a function of composition at 298.15 K are summarized in Table I and illustrated in Figure 1. These values have been fitted by the method of least squares to the equation

$$V^E/\text{cm}^3\ \text{mol}^{-1} = x(1 - x)[A + B(1 - 2x) + C(1 - 2x)^2] \qquad (3)$$

where x stands for the mole fraction of the acid. Values of A, B, and C constants along with the standard deviation for each system are given in Table II. Deviation of each observed

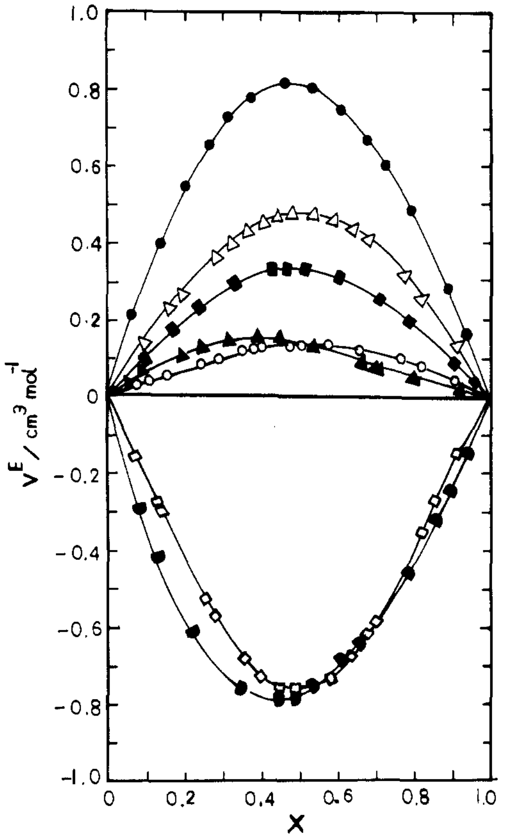

Figure 1. V^E vs. mole fraction plots at 298.15 K: $x(n\text{-}C_3H_7CO_2H) + (1 - x)(c\text{-}C_6H_{12})$, ●; $(1 - x)(n\text{-}C_8H_{18})$, △; $(1 - x)(C_6H_6)$, ■; $(1 - x)(CCl_4)$, ▲; $(1 - x)(C_6H_5CH_3)$, ○; $(1 - x)(CH_3OH)$, □; $(1 - x)((CH_3)_2CO)$, ◗.

value from the corresponding calculated value from eq 3 is also given in Table II. It may be seen that the results are quite precise and individual deviations seldom exceed the standard deviation which for any system is <0.0015 cm^3 mol^{-1}. This is also the order of estimated uncertainty arising from the uncertainty of various measurable quantities.

V^E values for the equimolar mixtures of the presently studied systems reported in this work have been compared with those of corresponding mixtures containing other carboxylic acids in Table III. It may be seen that obeying the general trend, V^E is maximum for mixtures with cyclohexane. The magnitude reduces to just half with n-octane and benzene mixtures and appreciably in the case of mixtures with toluene and carbon tetrachloride. The pK values of acetic, n-butyric, isobutyric, and propionic acids are 4.76, 4.82, 4.86, and 4.88. It is expected that the order of dimerization constant of various acids would increase in the same order. The increasing dimerization constant would lead to smaller number of available monomers and thus to smaller volume increase associated with eq 1. However, the observed order of V^E values, as seen for a given nonpolar solvent from Table III, decreases from acetic, propionic, n-butyric, and isobutyric acid. Also the decrease of V^E in the case of toluene and carbon tetrachloride mixtures is much sharper than in the case of all other acids except acetic acid. This shows that in addition to the contribution from eq 1 there are strong acid-solvent interactions which decide the magnitude of V^E and which increase as the electron releasing inductive effect of alkyl chain of acid increases.

Table III. Comparison of Excess Volume (cm^3 mol^{-1}) of Equimolar Mixtures at 298.15 K

	CH_3CO_2H	$CH_3CH_2CO_2H$	$CH_3(CH_2)_2CO_2H$	$(CH_3)_2CHCO_2H$
$c\text{-}C_6H_{12}$	1.564	1.070	0.818	0.741
C_6H_6	0.815	0.388	0.332	0.333
$C_6H_5CH_3$	0.725	0.241	0.132	0.142
CCl_4	0.725	0.267	0.141	0.155
CH_3OH	−0.715	−0.861	−0.764	−0.748
$n\text{-}C_8H_{18}$			0.484	
$(CH_3)_2CO$			−0.772	

The large negative V^E values in the case of methanol and acetone mixtures arise due to depolymerization of acids accompanied with strong hydrogen-bonded heterocomplex formation. In the experimental time of 20–25 min spent for the measurement of the total volume, after the components were mixed no esterification was observed in the case of mixtures with methanol.

Glossary

V^E	excess volume, cm^3 mol^{-1}
A, B, and C	constants for the eq 3
x	mole fraction of n-butyric acid
σ	standard deviation, cm^3 mol^{-1}
δ	individual deviation, cm^3 mol^{-1}

Registry No. n-Butyric acid, 107-92-6; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; carbon tetrachloride, 56-23-5; methanol, 67-56-1; acetone, 67-64-1.

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