J. Chem. Eng. Data **2008,** *53,* 265–270

Excess Volumes of Binary Solutions of Methyl Formate, Ethyl Formate, Propyl Formate, and Benzyl Acetate with Bromo-, Chloro-, and Nitrobenzenes at (303.15, 308.15, and 313.15) K

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Excess volumes, V^E, of the binary liquid systems of methyl formate, ethyl formate, propyl formate, and benzyl acetate each with bromo-, chloro-, and nitrobenzenes have been derived from experimental density measurements at (303.15, 308.15, and 313.15) K and atmospheric pressure over the entire composition range. These excess volumes were fitted to the Redlich–Kister polynomial equation to derive the coefficients and standard errors. The excess volumes for all of the systems were found to be negative across the mole compositions.

Introduction

Among the various thermodynamic properties, the excess volume, V^E, has been of much interest for the practical purpose of determining composition from the density measurement. Excess volume could also provide information on the possible interactions between components of a binary mixture, such as molecular associations and dipole–dipole and dipole-induced-–dipole interactions. The volume of mixing data of binary mixtures consisting of esters and hydrocarbons is useful in the petrochemical and pharmaceutical industries. Alkyl formates are a group of esters whose behavior requires specific analysis because they form intermolecular associations by means of hydrogen bonds and may even exist as stable dimers. A survey of the literature reveals that the excess volumes for the binary mixtures of alcohol or *n*-alkanol with halogenated and nitroaromatic compounds[1–3] have been studied. In recent years, a few attempts[4] have been made to study the various thermodynamic and transport properties for the binary mixtures of esters with halogenated hydrocarbons. In our earlier paper,[5] we have reported the excess volumes, V^E, for methyl butyrate with bromo-, chloro-, and nitrobenzenes. In view of the importance of the alkyl formates, it is of interest to continue this work with an investigation of the excess volumes for the binary mixtures of alkyl esters with halogenated and nitroaromatic compounds. In this study, we report the excess volumes for the 12 binary systems of methyl formate, ethyl formate, propyl formate, or benzyl acetate with bromo-, chloro-, and nitrobenzenes at (303.15, 308.15, and 313.15) K. The study is expected to give some information about the interactions between unlike molecules.

Experimental Section

Materials. Benzyl acetate (Fluka, AG), methyl formate, ethyl formate, and propyl formate, all of high purity $x > 99$ % on a mole basis, were procured from Loba Chemie. These chemicals were used as received. Bromo-, chloro-, and nitrobenzenes all of analytical grade (AR) were freed from thiophene by shaking with sulphuric acid. The samples thus obtained were washed with sodium hydroxide and distilled water, dried thoroughly over anhydrous calcium chloride, and fractionally distilled 3 times. The purity of these liquids was verified by measuring their density and refractive index. Table 1 lists the densities and refractive indices measured for the pure components together with the literature values at 303.15 K.

Table 1. Comparison of Experimental Densities, ρ, and Refractive Indices, n_D, of Pure Liquids with Literature Values at 303.15 K

		ρ (g·cm^{-3})		n_D	
liquid	T (K)	experimental	literature	experimental	literature
methyl formate	303.15	0.9588	0.9586[6]	1.3393	1.3394[a]
	308.15	0.9506			
	313.15	0.9431	0.9429[b]		
ethyl formate	303.15	0.9083	0.9086[a]	1.3552	1.3553[a]
	308.15	0.9015			
	313.15	0.8948	0.8949[b]		
propyl formate	303.15	0.8942	0.8941[a]	1.3726	1.3728[a]
	308.15	0.8885			
	313.15	0.8828	0.8819[b]		
benzyl acetate	303.15	1.0484	1.0482[6]	1.4997[c]	1.4998[c]
	308.15	1.0450			
	313.15	1.0417			
chlorobenzene	303.15	1.0956	1.0955[6]	1.5191	1.5190[a]
	308.15	1.0907	1.0904[b]		
	313.15	1.0852	1.0850[b]		
bromobenzene	303.15	1.4814	1.4815[6]	1.5546	1.5546[a]
	308.15	1.4748			
	313.15	1.4680			
nitrobenzene	303.15	1.1934	1.1934[6]	1.5476	1.5477[a]
	308.15	1.1885	1.1887[6]		
	313.15	1.1835	1.1838[b]		

[a] Extrapolated values from ref 6. [b] From ref 7. [c] Measured and compared at 298 K from ref 8.

Methods. Binary mixtures were prepared by mass in specially designed airtight glass-stoppered bottles. To prevent the samples from preferential evaporation, the mixtures were prepared by

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10.1021/je700150e CCC: $40.75

Table 2. Experimental Density, ρ, and Excess Volumes, V^E, of Binary Mixtures at Different Temperatures

x_1	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})
			Methyl Formate (1) + Chlorobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0724	1.0898	−0.038	1.0848	−0.046	1.0793	−0.056
0.1523	1.0828	−0.062	1.0776	−0.070	1.0721	−0.092
0.2990	1.0683	−0.079	1.0627	−0.086	1.0569	−0.103
0.4093	1.0561	−0.092	1.0501	−0.093	1.0441	−0.110
0.5185	1.0426	−0.095	1.0363	−0.100	1.0301	−0.117
0.5906	1.0328	−0.093	1.0264	−0.109	1.0199	−0.113
0.7079	1.0152	−0.086	1.0083	−0.095	1.0017	−0.111
0.7933	1.0008	−0.074	0.9936	−0.085	0.9869	−0.107
0.8669	0.9871	−0.054	0.9797	−0.071	0.9727	−0.084
0.9356	0.9732	−0.036	0.9654	−0.044	0.9583	−0.061
0.9646	0.9669	−0.022	0.9589	−0.025	0.9516	−0.033
			Methyl Formate (1) + Bromobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0853	1.4549	−0.056	1.4484	−0.077	1.4418	−0.101
0.1581	1.4304	−0.083	1.4238	−0.109	1.4173	−0.147
0.2880	1.3822	−0.109	1.3753	−0.134	1.3683	−0.149
0.4200	1.3265	−0.114	1.3193	−0.138	1.3122	−0.158
0.5298	1.2743	−0.117	1.2669	−0.142	1.2597	−0.163
0.6305	1.2209	−0.120	1.2135	−0.157	1.2061	−0.171
0.7170	1.1698	−0.112	1.1622	−0.145	1.1549	−0.169
0.8026	1.1140	−0.101	1.1062	−0.127	1.0990	−0.159
0.8711	1.0648	−0.087	1.0568	−0.103	1.0497	−0.139
0.9384	1.0119	−0.055	1.0039	−0.071	0.9965	−0.085
0.9681	0.9868	−0.027	0.9787	−0.0.35	0.9713	−0.046
			Methyl Formate (1) + Nitrobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0825	1.1818	−0.045	1.1771	−0.081	1.1720	−0.088
0.1554	1.1709	−0.087	1.1659	−0.115	1.1608	−0.136
0.2947	1.1472	−0.098	1.1420	−0.142	1.1366	−0.164
0.4138	1.1244	−0.102	1.1188	−0.143	1.1132	−0.171
0.5234	1.1010	−0.104	1.0951	−0.148	1.0892	−0.174
0.6166	1.0791	−0.112	1.0728	−0.150	1.0667	−0.178
0.7119	1.0541	−0.100	1.0476	−0.147	1.0412	−0.172
0.7915	1.0311	−0.087	1.0244	−0.138	1.0177	−0.157
0.8682	1.0069	−0.078	0.9997	−0.114	0.9928	−0.132
0.9369	0.9828	−0.038	0.9754	−0.077	0.9682	−0.087
0.9691	0.9709	−0.026	0.9630	−0.039	0.9556	−0.041
			Ethyl Formate (1) + Chlorobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0611	1.0868	−0.037	1.0820	−0.058	1.0765	−0.056
0.1230	1.0775	−0.062	1.0727	−0.094	1.0672	−0.111
0.2382	1.0594	−0.096	1.0544	−0.131	1.0487	−0.143
0.3486	1.0411	−0.123	1.0357	−0.142	1.0299	−0.158
0.4543	1.0225	−0.130	1.0169	−0.149	1.0110	−0.168
0.5535	1.0042	−0.137	0.9984	−0.155	0.9924	−0.177
0.6524	0.9849	−0.124	0.9789	−0.142	0.9728	−0.165
0.7443	0.9661	−0.111	0.9600	−0.135	0.9838	−0.159
0.8332	0.9469	−0.079	0.9408	−0.117	0.9344	−0.131
0.9183	0.9278	−0.056	0.9214	−0.080	0.9148	−0.084
0.9600	0.9179	−0.023	0.9113	−0.035	0.9047	−0.041
			Ethyl Formate (1) + Bromobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0616	1.4542	−0.025	1.4477	−0.039	1.4409	−0.045
0.1253	1.4253	−0.056	1.4187	−0.070	1.4119	−0.080
0.2469	1.3676	−0.120	1.3610	−0.145	1.3541	−0.157
0.3564	1.3124	−0.166	1.3056	−0.187	1.2986	−0.197
0.4626	1.2556	−0.195	1.2486	−0.205	1.2415	−0.211
0.5639	1.1980	−0.189	1.1909	−0.195	1.1838	−0.201
0.6593	1.1407	−0.168	1.1336	−0.173	1.1266	−0.186
0.7486	1.0840	−0.130	1.0770	−0.141	1.0701	−0.157
0.8373	1.0248	−0.081	1.0176	−0.086	1.0110	−0.103
0.9205	0.9665	−0.034	0.9597	−0.046	0.9530	−0.061
0.9606	0.9374	−0.009	0.9306	−0.016	0.9239	−0.024
			Ethyl Formate (1) + Nitrobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0631	1.1795	−0.044	1.1747	−0.066	1.1700	−0.104
0.1261	1.1651	−0.076	1.1603	−0.110	1.1558	−0.178
0.2363	1.1389	−0.132	1.1341	−0.188	1.1297	−0.284
0.3530	1.1095	−0.174	1.1047	−0.252	1.0999	−0.334
0.4591	1.0811	−0.189	1.0761	−0.269	1.0712	−0.360
0.5495	1.0558	−0.204	1.0505	−0.274	1.0454	−0.363
0.6563	1.0239	−0.174	1.0184	−0.244	1.0132	−0.340
0.7459	0.9958	−0.145	0.9900	−0.203	0.9846	−0.294
0.8359	0.9662	−0.103	0.9602	−0.156	0.9545	−0.232
0.9197	0.9374	−0.067	0.9308	−0.077	0.9248	−0.134
0.9600	0.9229	−0.029	0.9163	−0.043	0.9099	−0.068

Table 2 Continued

x_1	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})	ρ (g·cm^{-3})	V^E (cm^3·mol^{-1})
			Propyl Formate (1) + Chlorobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0499	1.0862	−0.025	1.0813	−0.031	1.0758	−0.033
0.1037	1.0760	−0.050	1.0711	−0.061	1.0656	−0.066
0.2072	1.0560	−0.074	1.0510	−0.086	1.0455	−0.095
0.3197	1.0339	−0.085	1.0288	−0.099	1.0232	−0.102
0.4114	1.0157	−0.091	1.0105	−0.104	1.0049	−0.110
0.5111	1.9957	−0.093	0.9905	−0.114	0.9848	−0.113
0.6096	0.9757	−0.089	0.9703	−0.097	0.9647	−0.108
0.7075	0.9556	−0.076	0.9502	−0.092	0.9446	−0.103
0.8070	0.9350	−0.064	0.9296	−0.086	0.9240	−0.099
0.9035	0.9148	−0.045	0.9093	−0.063	0.9036	−0.064
0.9513	0.9046	−0.022	0.8990	−0.031	0.8934	−0.043
			Propyl Formate (1) + Bromobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0535	1.4524	−0.022	1.4459	−0.030	1.4393	−0.045
0.1075	1.4229	−0.046	1.4164	−0.055	1.4099	−0.077
0.2154	1.3634	−0.106	1.3569	−0.115	1.3503	−0.128
0.3187	1.3052	−0.142	1.2988	−0.156	1.2921	−0.157
0.4198	1.2472	−0.162	1.2407.	−0.165	1.2342	−0.176
0.5206	1.1884	−0.170	1.1820	−0.175	1.1755	−0.178
0.6195	1.1295	−0.154	1.1232	−0.158	1.1169	−0.168
0.7169	1.0706	−0.128	1.0644	−0.130	1.0583	−0.146
0.8128	1.0116	−0.080	1.0057	−0.096	0.9997	−0.106
0.9071	0.9529	−0.048	0.9471	−0.058	0.9413	−0.069
0.9510	0.9252	−0.018	0.9195	−0.029	0.9137	−0.031
			Propyl Formate (1) + Nitrobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0536	1.1786	−0.049	1.1738	−0.064	1.1688	−0.071
0.1082	1.1633	−0.085	1.1585	−0.104	1.1535	−0.121
0.2064	1.1354	−0.139	1.1305	−0.165	1.1255	−0.189
0.3143	1.1042	−0.175	1.0991	−0.195	1.0939	−0.211
0.4165	1.0742	−0.198	1.0689	−0.209	1.0635	−0.215
0.5062	1.0475	−0.205	1.0421	−0.214	1.0367	−0.227
0.6162	1.0143	−0.198	1.0088	−0.205	1.0033	−0.215
0.7117	0.9849	−0.163	0.9795	−0.186	1.9740	−0.202
0.8107	0.9542	−0.127	0.9488	−0.155	0.9433	−0.175
0.9059	0.9242	−0.072	0.9187	−0.092	0.9132	−0.114
0.9528	0.9094	−0.048	0.9038	−0.059	0.8982	−0.070
			Benzyl Acetate (1) + Chlorobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0380	1.0932	−0.006	1.0884	−0.008	1.0831	−0.016
0.0730	1.0911	−0.016	1.0864	−0.021	1.0812	−0.029
0.1509	1.0865	−0.027	1.0820	−0.037	1.0771	−0.053
0.2370	1.0817	−0.038	1.0773	−0.042	1.0726	−0.055
0.3217	1.0772	−0.042	1.0730	−0.052	1.0685	−0.064
0.4161	1.0725	−0.044	1.0688	−0.054	1.0641	−0.062
0.5161	1.0677	−0.039	1.0684	−0.048	1.0597	−0.056
0.6232	1.0630	−0.037	1.0592	−0.044	1.0553	−0.050
0.7399	1.0581	−0.025	1.0545	−0.037	1.0508	−0.041
0.8651	1.0533	−0.020	1.0498	−0.026	1.0464	−0.039
0.9213	1.0512	−0.010	1.0478	−0.021	1.0445	−0.030
			Benzyl Acetate (1) + Bromobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0359	1.4608	−0.010	1.4545	−0.019	1.4480	−0.027
0.0904	1.4304	−0.021	1.4243	−0.026	1.4181	−0.036
0.1697	1.3882	−0.042	1.3824	−0.044	1.3765	−0.047
0.2397	1.3526	−0.050	1.3471	−0.054	1.3415	−0.056
0.3289	1.3095	−0.058	1.3044	−0.067	1.2991	−0.064
0.4231	1.2665	−0.063	1.2617	−0.071	1.2568	−0.072
0.5226	1.2236	−0.056	1.2191	−0.063	1.2146	−0.070
0.6203	1.1838	−0.047	1.1796	−0.056	1.1754	−0.063
0.7462	1.1358	−0.042	1.1319	−0.050	1.1281	−0.060
0.8688	1.0922	−0.034	1.0886	−0.043	1.0851	−0.056
0.9318	1.0708	−0.021	1.0673	−0.026	1.0639	−0.033
			Benzyl Acetate (1) + Nitrobenzene (2)			
	T (K) = 303.15		T (K) = 308.15		T (K) = 313.15	
0.0363	1.1863	−0.009	1.1816	−0.020	1.1768	−0.030
0.0735	1.1793	−0.027	1.1747	−0.039	1.1700	−0.051
0.1516	1.1651	−0.049	1.1606	−0.057	1.1562	−0.080
0.2365	1.1505	−0.069	1.1461	−0.072	1.1418	−0.088
0.3226	1.1364	−0.074	1.1322	−0.082	1.1280	−0.092
0.4162	1.1220	−0.079	1.1180	−0.093	1.1140	−0.106
0.5173	1.1074	−0.081	1.1 036	−0.101	1.0997	−0.107
0.6251	1.0928	−0.078	1.0891	−0.093	1.0854	−0.104
0.7408	1.0781	−0.064	1.0746	−0.087	1.0710	−0.090
0.8654	1.0633	−0.039	1.0599	−0.057	1.0566	−0.078
0.9323	1.0558	−0.027	1.0524	−0.036	1.0491	−0.047

Table 3. Parameters of Equation *2* for the Representation of V^E of the Binary Mixtures at Different Temperatures

T (K)	a_0	a_1	a_2	σV^E (cm^3· mol^{-1})
		Methyl Formate (1) + Chlorobenzene (2)		
303.15	−0.387	−0.027	−0.395	0.008
308.15	−0.361	−0.009	−0.283	0.002
313.15	−0.432	−0.039	−0.609	0.011
		Methyl Formate (1) + Bromobenzene (2)		
303.15	−0.461	−0.064	−0.459	0.018
308.15	−0.564	−0.055	−0.663	0.015
313.15	−0.633	−0.036	−0.996	0.010
		Methyl Formate (1) + Nitrobenzene (2)		
303.15	−0.421	0.029	−0.379	0.008
308.15	−0.567	−0.059	−0.790	0.017
313.15	−0.686	−0.064	−0.790	0.018
		Ethyl Formate (1) + Chlorobenzene (2)		
303.15	−0.530	−0.023	−0.135	0.007
308.15	−0.598	−0.001	−0.506	0.000
313.15	−0.678	−0.011	−0.569	0.003
		Ethyl Formate (1) + Bromobenzene (2)		
303.15	−0.796	0.014	0.521	0.004
308.15	−0.823	0.058	0.313	0.017
313.15	−0.854	0.014	0.153	0.004
		Ethyl Formate (1) + Nitrobenzene (2)		
303.15	−0.769	−0.052	0.008	0.016
308.15	−1.084	−0.025	0.009	0.007
313.15	−1.456	−0.033	−0.010	0.010
		Propyl Formate (1) + Chlorobenzene (2)		
303.15	−0.364	−0.028	−0.201	0.008
308.15	−0.418	−0.033	−0.342	0.004
313.15	−0.431	−0.058	−0.466	0.018
		Propyl Formate (1) + Bromobenzene (2)		
303.15	−0.685	0.004	0.309	0.001
308.15	−0.690	0.017	0.098	0.005
313.15	−0.710	0.059	−0.105	0.018
		Propyl Formate (1) + Nitrobenzene (2)		
303.15	−0.790	−0.008	−0.203	0.002
308.15	−0.831	−0.009	−0.508	0.003
313.15	−0.875	−0.036	−0.718	0.011
		Benzyl Acetate (1) + Chlorobenzene (2)		
303.15	−0.174	0.042	−0.003	0.014
308.15	−0.201	0.012	−0.089	0.004
313.15	−0.218	−0.004	−0.312	0.001
		Benzyl Acetate (1) + Bromobenzene (2)		
303.15	−0.233	−0.006	−0.089	0.002
308.15	−0.240	−0.010	−0.243	0.004
313.15	−0.255	−0.031	−0.340	0.010
		Benzyl Acetate (1) + Nitrobenzene (2)		
303.15	−0.338	−0.014	−0.031	0.005
308.15	−0.371	−0.065	−0.245	0.005
313.15	−0.392	−0.004	−0.488	0.001

transferring aliquots via a syringe into stoppered bottles. The solutions of each composition were prepared fresh, and all of the properties were measured the same day. The mass measurements, accurate to ± 0.01 mg, were taken on a Mettler's digital electronic single-pan balance (AE 240, Switzerland). For each binary mixture, a set of 11 compositions was prepared and their densities were measured at the respective compositions. The estimated uncertainty in the mole fraction was less than ± 0.0002.

Densities of the pure liquids and their mixtures were measured with a high-precision densitometer of the type DMA 38 (Anton Paar, Gmbtt) supplied by Karntner Strabe 322, Europe. The instrument has a built-in thermostat for maintaining the desired temperature and a display setting for showing three or four places of densities after the decimal point. The method and calibration of the instrument has already been reported elsewhere.[5] The repeatability in the densities for pure liquids and prepared binary mixtures have been found to be better than ± $3 \cdot 10^{-4}$ g·cm^{-3}. We have estimated the uncertainty in densities of the pure liquids used in the study by comparing our data at 303.15 K with literature values.[6–8] The uncertainty in the density measurements was found to be within ± $1 \cdot 10^{-4}$ g·cm^{-3}. The V^E values thus estimated from the density data were reported with an accuracy about 10^{-2} cm^{-3}·mol^{-1}. The refractive indices for the pure liquids, except for benzyl acetate, were measured at 303.15 K using a thermostatically controlled Abbe refractometer (Atago, 3T, Japan). An average of three to four readings was taken for each pure liquid. The uncertainty of the refractive indices were estimated to be less than ± $2 \cdot 10^{-4}$. The uncertainty in the temperature of ± 0.01 K during the refractive index measurements was maintained using an INSREF India circulator (model 020 A).

Results and Discussion

The experimental data on the density, ρ, and excess volume, V^E, for the 12 binary mixtures of methyl formate, ethyl formate, propyl formate, or benzyl acetate each with bromo-, chloro-, and nitrobenzenes at (303.15, 308.15, and 313.15) K are listed in Table 2. The values of V^E were calculated from the density data using the relation

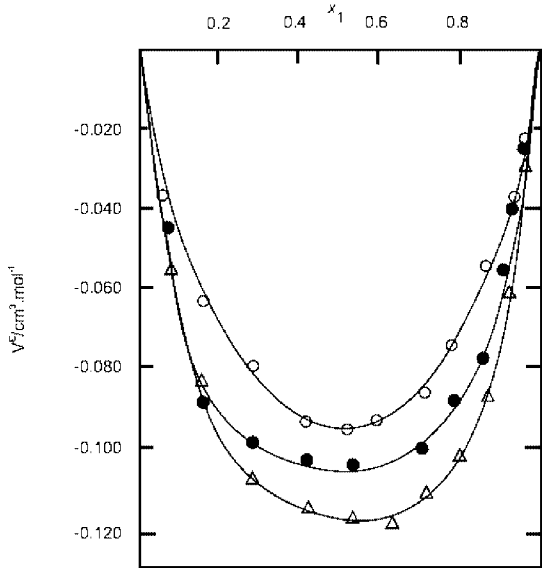

Figure 1. Excess volume as a mole fraction of methyl formate (1) + ○, chlorobenzene; △, bromobenzene; and ●, nitrobenzene at 303.15 K. Solid lines are fitted values calculated by using coefficients from Table 3 and eq 2.

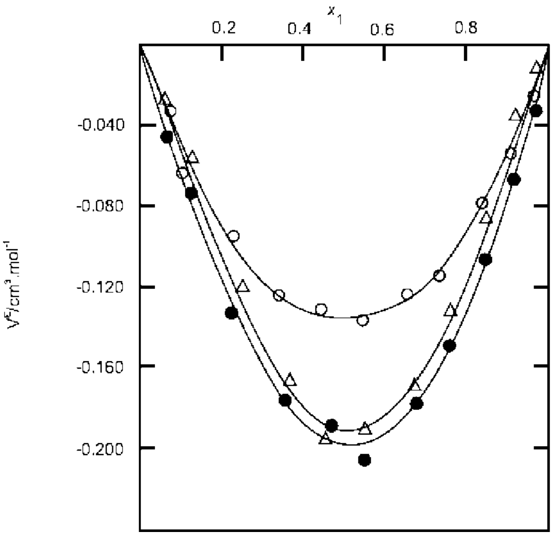

Figure 2. Excess volume as a mole fraction of ethyl formate (1) + ○, chlorobenzene; △, bromobenzene; and ●, nitrobenzene at 303.15 K. Solid lines are fitted values calculated by using coefficients from Table 3 and eq 2.

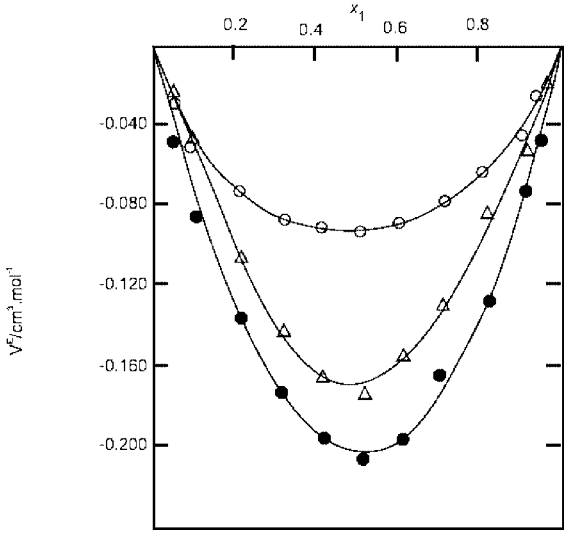

Figure 3. Excess volume as a mole fraction of propyl formate (1) + ○, chlorobenzene; △, bromobenzene; and ●, nitrobenzene at 303.15 K. Solid lines are fitted values calculated by using coefficients from Table 3 and eq 2.

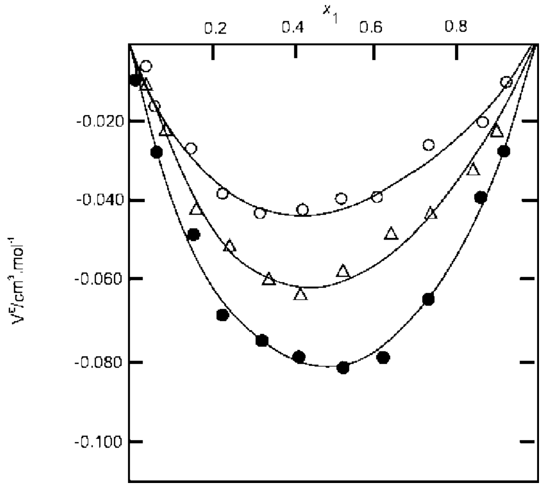

Figure 4. Excess volume as a mole fraction of benzyl acetate (1) + ○, chlorobenzene; △, bromobenzene; and ●, nitrobenzene at 303.15 K. Solid lines are fitted values calculated by using coefficients from Table 3 and eq 2.

$$V^E\ (\text{cm}^3\text{·mol}^{-1}) = (x_1M_1 + x_2M_2)/\rho_{12} - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \tag{1}$$

where x, M, and ρ are the mole fraction, molar mass, and density, respectively. ρ_{12} is the density of the liquid mixture. The dependence of V^E on composition may be expressed by an empirical equation proposed by Redlich–Kister[9] as follows:

$$V^E\ (\text{cm}^3\text{·mol}^{-1}) = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \tag{2}$$

where x_1 and x_2 denote the mole fractions of components 1 and 2, respectively, a_0, a_1, and a_2 are constants evaluated by the method of least squares. The summary of a_0, a_1, a_2 and the standard deviation σ (V^E) between experimental and fitted V^E values are given in Table 3.

The graphical variation of V^E as a function of the mole fraction of the ester for all of the studied binary systems at 303.15 K is shown in Figures 1 to 4. The V^E values at other temperatures follow the same trends but show different values; hence, these data are not graphically represented. In all of the graphs, the points represent the experimental V^E values of eq 1, while the solid lines are drawn from the values calculated using coefficients from Table 3 of eq 2. The V^E profiles of all binary systems studied are characterized by an initial increase in negative values following maxima at about $x_1 = 0.5$ and then a decrease. Further, the excess volumes for all of the systems, except benzyl acetate, were found to be highly negative across the mole composition. The rise in the temperature from (303.15 to 313.15) K has always increased the overall magnitude of V^E values. The large negative volume changes in a mixture rich in ester may be due to strong interactions between benzene-substituted hydrocarbons and ester molecules.

For the binary systems of methyl formate, the V^E values at 303.15 K decrease with an increase in the concentration of methyl formate and pass through a point at about $x_1 = 0.51$. A comparison of V^E values of these mixtures show that the magnitude of V^E values for nitrobenzene fall between the values of chloro- and bromobenzenes and lie in the order of

$$V^E\ (C_6H_5Cl) < V^E\ (C_6H_5NO_2) < V^E\ (C_6H_5Br)$$

However, at the higher temperatures [(308.15 and 313.15) K], the V^E values lie in the order of

$$V^E\ (C_6H_5Cl) < V^E\ (C_6H_5Br) < V^E\ (C_6H_5NO_2)$$

In the case of ethyl formate systems, the comparison of V^E values at about $x_1 = 0.5$ shows that the V^E values for bromo- and nitrobenzenes appear to be of almost the same magnitude at 303.15 K, However, at higher temperatures [(308.15 and 313.15) K], the V^E values for these systems fall in the order of

$$V^E\ (C_6H_5Cl) < V^E\ (C_6H_5Br) < V^E\ (C_6H_5NO_2)$$

While for propyl formate and benzyl acetate systems, the V^E values at $x_1 = 0.5$ at all of the studied temperatures follow the same order as above.

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Received for review March 24, 2007. Accepted September 5, 2007. Financial support to M.V.R. through UGC Project, Western Zone (MP/WRO/23-205/99), Pune, India, is gratefully acknowledged.

JE700150E