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THERMODYNAMIC PROPERTIES OF SOME BINARY MIXTURES CONTAINING CARBONYL COMPOUNDS

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ABSTRACT

The excess volumes of mixtures of benzaldehyde with cyclohexane, benzene, toluene and *p*-xylene, and of acetophenone and cyclohexanone with the same set of second components were measured at 298.15 and 308.15 K except for the cyclohexanone + cyclohexane mixture which was studied at 308.15 K only. Comments about the molecular interactions contributing to V^E are made on the basis of the results.

INTRODUCTION

The existence of dipole–induced-dipole interactions between the carbonyl group of cycloalkanone or aliphatic ketone and the benzene ring of an aromatic hydrocarbon has been indicated from excess enthalpy measurements of these systems [1,2]. As part of an investigation of the thermodynamic properties of such systems, we have measured the excess volumes, V^E, of benzaldehyde, acetophenone and cyclohexanone with aromatic hydrocarbons, so as to obtain additional information about the molecular interactions between carbonyl compounds and aromatic hydrocarbons.

EXPERIMENTAL

Cyclohexane, benzene, toluene and *p*-xylene were purified as described earlier [3,4]. Benzaldehyde (BDH, AR Grade) was treated with 10% sodium carbonate solution, until no carbon dioxide evolved. It was then washed with distilled water and dried over anhydrous calcium chloride. A small amount of hydroquinone was added during the drying operation. Finally, it was decanted and distilled. Acetophenone (Reanal, Budapest, Hungary) was dried over anhydrous potassium carbonate and distilled, retaining the middle fraction. Cyclohexanone (Baker Analyzed Reagent) was used as received after distillation. Purifications of the reagents were checked by comparing their densities with literature values [5]. Excess volumes were measured

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TABLE 1
Excess volumes of mixtures of carbonyl compounds with aromatic hydrocarbons

x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
$xC_6H_5CHO+(1-x)c-C_6H_{12}$ at 298.15 K			
0.1032	0.261	0.5467	0.442
0.2084	0.420	0.6017	0.401
0.2638	0.470	0.6862	0.329
0.3720	0.503	0.8172	0.194
0.4407	0.493	0.9240	0.078
At 308.15 K			
0.0912	0.253	0.5838	0.400
0.1433	0.354	0.6435	0.350
0.2051	0.435	0.6964	0.300
0.3068	0.503	0.7845	0.210
0.3652	0.509	0.8256	0.172
0.3966	0.505	0.8775	0.114
0.4403	0.491	0.9294	0.064
0.5414	0.437		
$xC_6H_5CHO+(1-x)C_6H_6$ at 298.15 K			
0.0754	−0.046	0.5494	−0.105
0.1734	−0.080	0.6451	−0.091
0.2458	−0.105	0.7701	−0.060
0.3488	−0.115	0.8421	−0.043
0.4480	−0.115	0.9274	−0.027
At 308.15 K			
0.0684	−0.056	0.5487	−0.140
0.1134	−0.089	0.6099	−0.128
0.1670	−0.108	0.6747	−0.113
0.2944	−0.138	0.7665	−0.089
0.3528	−0.146	0.8010	−0.072
0.4016	−0.143	0.8591	−0.051
0.4483	−0.147	0.9230	−0.036
0.4949	−0.143		
$xC_6H_5CHO+(1-x)C_6H_5CH_3$ at 298.15 K			
0.0820	−0.079	0.5461	−0.212
0.1608	−0.123	0.6535	−0.195
0.2684	−0.185	0.7595	−0.154
0.3595	−0.220	0.8693	−0.097
0.4228	−0.225	0.9361	−0.055
0.4730	−0.226		
At 308.15 K			
0.0770	−0.069	0.5342	−0.243
0.1411	−0.126	0.5933	−0.234
0.1960	−0.159	0.6622	−0.212
0.2727	−0.200	0.7615	−0.167
0.3586	−0.234	0.8216	−0.132
0.4290	−0.243	0.8699	−0.105
0.4890	−0.241	0.9323	−0.056

TABLE 1 (continued)

x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
$x C_6H_5CHO + (1-x) p-C_6H_4(CH_3)_2$ at 298.15 K			
0.1075	−0.089	0.6035	−0.185
0.2174	−0.147	0.6666	−0.178
0.3223	−0.181	0.7289	−0.153
0.4109	−0.192	0.8489	−0.103
0.4890	−0.195	0.8947	−0.075
0.5207	−0.196	0.9364	−0.049
At 308.15 K			
0.0889	−0.079	0.4620	−0.209
0.1047	−0.089	0.5752	−0.202
0.1632	−0.125	0.6254	−0.191
0.2145	−0.144	0.7011	−0.174
0.3070	−0.185	0.8366	−0.126
0.3840	−0.201	0.9310	−0.064
$x C_6H_5COCH_3 + (1-x) c\text{-}C_6H_{12}$ at 298.15 K			
0.0870	0.313	0.5089	0.501
0.1889	0.508	0.5791	0.448
0.2906	0.578	0.6731	0.366
0.3523	0.582	0.7987	0.246
0.4065	0.565	0.8631	0.182
At 308.15 K			
0.0544	0.213	0.4654	0.535
0.1013	0.353	0.5135	0.498
0.1481	0.451	0.6077	0.407
0.1782	0.501	0.7400	0.276
0.2310	0.557	0.8310	0.182
0.3510	0.588	0.8993	0.110
0.4123	0.566		
$x C_6H_5COCH_3 + (1-x) C_6H_6$ at 298.15 K			
0.0650	−0.043	0.5527	−0.105
0.1428	−0.069	0.6615	−0.083
0.2474	−0.108	0.7674	−0.066
0.3579	−0.118	0.8660	−0.036
0.4058	−0.116	0.9103	−0.012
0.4627	−0.118		
At 308.15 K			
0.1076	−0.095	0.5452	−0.141
0.1650	−0.113	0.6072	−0.134
0.2450	−0.136	0.7072	−0.109
0.3051	−0.149	0.7457	−0.090
0.3771	−0.150	0.8243	−0.069
0.4331	−0.152	0.9258	−0.037
0.4828	−0.155		
$x C_6H_5COCH_3 + (1-x) C_6H_5CH_3$ at 298.15 K			
0.0769	−0.087	0.6353	−0.213
0.1436	−0.141	0.6918	−0.184
0.2824	−0.218	0.7624	−0.153

TABLE 1 (continued)

x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
0.3678	−0.238	0.8660	−0.090
0.4500	−0.250	0.9370	−0.042
0.5676	−0.230		
At 308.15 K			
0.0651	−0.078	0.5044	−0.260
0.1288	−0.132	0.5657	−0.247
0.1757	−0.176	0.6370	−0.233
0.2386	−0.212	0.7370	−0.187
0.3236	−0.246	0.8048	−0.147
0.3954	−0.264	0.8524	−0.116
0.4540	−0.270	0.9154	−0.075
$xC_6H_5COCH_3+(1-x)p\text{-}C_6H_4(CH_3)_2$ at 298.15 K			
0.0845	−0.083	0.6281	−0.224
0.1948	−0.167	0.7020	−0.199
0.2967	−0.215	0.7631	−0.164
0.3746	−0.246	0.8291	−0.124
0.4511	−0.251	0.8807	−0.097
0.4826	−0.254	0.9263	−0.066
At 308.15 K			
0.0716	−0.079	0.5460	−0.263
0.0952	−0.091	0.5888	−0.263
0.1986	−0.178	0.6679	−0.236
0.2785	−0.226	0.7725	−0.187
0.3611	−0.246	0.8301	−0.146
0.4290	−0.266	0.9295	−0.072
0.4803	−0.272		
$xc\text{-}C_6H_{10}O+(1-x)c\text{-}C_6H_{12}$ at 308.15 K			
0.1052	0.146	0.5642	0.157
0.1823	0.190	0.6350	0.136
0.3064	0.211	0.6954	0.117
0.3796	0.203	0.8339	0.070
0.4943	0.179	0.8753	0.055
$xc\text{-}C_6H_{10}O+(1-x)C_6H_6$ at 298.15 K			
0.1577	−0.142	0.5383	−0.215
0.2255	−0.175	0.6553	−0.175
0.2835	−0.195	0.7305	−0.147
0.4141	−0.220	0.8415	−0.099
At 308.15 K			
0.0881	−0.083	0.6056	−0.215
0.1573	−0.145	0.6636	−0.197
0.2540	−0.206	0.7363	−0.166
0.3302	−0.232	0.8168	−0.120
0.4149	−0.246	0.8927	−0.076
0.5113	−0.241		
$xc\text{-}C_6H_{10}O+(1-x)C_6H_5CH_3$ at 298.15 K			
0.1791	−0.125	0.5832	−0.186

TABLE 1 (continued)

x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
0.2693	−0.173	0.7789	−0.118
0.4557	−0.204	0.9055	−0.053
At 308.15 K			
0.0848	−0.074	0.5520	−0.216
0.1933	−0.150	0.6322	−0.191
0.2912	−0.193	0.7156	−0.159
0.3793	−0.220	0.8421	−0.094
0.4642	−0.230	0.8979	−0.069
xc-$C_6H_{10}O + (1-x)p$-$C_6H_4(CH_3)_2$ at 298.15 K			
0.1468	−0.028	0.7195	0.029
0.2872	−0.037	0.7962	0.034
0.3594	−0.031	0.9055	0.028
0.5024	−0.007		
0.6274	0.017		
At 308.15 K			
0.0883	−0.023	0.5932	0.003
0.2135	−0.040	0.7125	0.021
0.3220	−0.041	0.8317	0.025
0.4124	−0.032	0.9240	0.014
0.4970	−0.018		

dilatometrically [4] as a function of composition at 298.15 and 308.15 K with temperature control to ±0.01 K by a mercury/toluene regulator.

RESULTS

The experimental results for V^E at 298.15 and 308.15 K are listed in Table 1. The results were fitted by the method of least squares to the equation

$$V^E\ (\mathrm{cm^3 mol^{-1}}) = x(1-x)\sum_{i=0}^{i=2} A_i(1-2x)^i \qquad (1)$$

where x is the mole fraction of the carbonyl compound. The coefficients A_i along with the standard deviations $\sigma(V^E)$ are given in Table 2.

DISCUSSION

Excess volumes are positive for the carbonyl compounds + cyclohexane mixtures over the entire mole fraction range, negative for all other mixtures, except cyclohexanone + p-xylene mixtures where a change of sign is observed from negative to positive in the ketone-rich region. The temperature coefficient of V^E is negative for all the mixtures.

TABLE 2

Parameters for eqn. (1) and the standard deviation, $\sigma(V^E)$, of the excess volumes

System	T (K)	A_0	A_1	A_2	$\sigma(V^E)$ ($cm^3 mol^{-1}$)
$x C_6H_5CHO + (1-x) c\text{-}C_6H_{12}$	298.15	1.882	1.040	0.168	0.001
	308.15	1.852	1.236	0.276	0.002
$x C_6H_5CHO + (1-x) C_6H_6$	298.15	−0.432	−0.240	−0.104	0.006
	308.15	−0.561	−0.190	−0.167	0.005
$x C_6H_5CHO + (1-x) C_6H_5CH_3$	298.15	−0.888	−0.079	−0.081	0.005
	308.15	−0.983	−0.067	0.054	0.003
$x C_6H_5CHO + (1-x) p\text{-}C_6H_4(CH_3)_2$	298.15	−0.786	−0.074	−0.128	0.002
	308.15	−0.820	0.001	−0.218	0.004
$x C_6H_5COCH_3 + (1-x) c\text{-}C_6H_{12}$	298.15	2.032	1.438	1.035	0.002
	308.15	2.026	1.648	0.811	0.002
$x C_6H_5COCH_3 + (1-x) C_6H_6$	298.15	−0.454	−0.252	0.028	0.006
	308.15	−0.578	−0.264	−0.229	0.005
$x C_6H_5COCH_3 + (1-x) C_6H_5CH_3$	298.15	−0.973	−0.273	0.008	0.003
	308.15	−1.046	−0.190	−0.063	0.003
$x C_6H_5COCH_3 + (1-x) p\text{-}C_6H_4(CH_3)_2$	298.15	−0.995	−0.106	−0.009	0.004
	308.15	−1.077	−0.037	−0.033	0.004
$x c\text{-}C_6H_{10}O + (1-x) c\text{-}C_6H_{12}$	308.15	0.700	0.625	0.512	0.004
$x c\text{-}C_6H_{10}O + (1-x) C_6H_6$	298.15	−0.872	−0.244	−0.030	0.004
	308.15	−0.957	−0.199	−0.017	0.005
$x c\text{-}C_6H_{10}O + (1-x) C_6H_5CH_3$	298.15	−0.806	−0.157	0.097	0.003
	308.15	−0.889	−0.189	0.082	0.004
$x c\text{-}C_6H_{10}O + (1-x) p\text{-}C_6H_4(CH_3)_2$	298.15	−0.036	−0.358	0.112	0.002
	308.15	−0.062	−0.316	0.029	0.004

The positive V^E of carbonyl compound + cyclohexane mixtures can be ascribed to the breaking of dipole–dipole interactions of > C=O groups of the pure carbonyl compounds. The negative values of V^E for the benzene mixtures may be due to the dipole–induced-dipole moment interactions between the carbonyl group and the benzene ring [2]. Introduction of a methyl group into the benzene ring makes V^E more negative for all three mixtures of carbonyl compounds indicating the increase in the contribution of dipole–induced-dipole interactions to V^E in going from benzene to toluene. However, introduction of the second methyl group does not have the same effect on V^E for the mixtures of different carbonyl compounds; V^E decreases for benzaldehyde + p-xylene, remains nearly the same for acetophenone mixtures, and exhibits a change in sign for the cyclohexanone mixtures.

It may be of interest to compare the excess volumes of three carbonyl compounds. Excess volumes for benzaldehyde and acetophenone with a particular aromatic hydrocarbon are nearly the same, whereas they are different for mixtures of cyclohexanone with the same aromatic hydrocarbon. Part of this difference in V^E may be due to the presence of π–π'

interactions between the π-electrons of the phenyl group of benzaldehyde and acetophenone with π'-electrons of the aromatic ring [6] which are absent in cyclohexanone mixtures.

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