Excess Volumes of Substituted Benzenes with *N,N*-Dimethylformamide†

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Excess volumes of binary liquid mixtures of *N,N*-dimethylformamide with toluene, ethylbenzene, chlorobenzene, bromobenzene, nitrobenzene, and aniline at 303.15 and 313.15 K have been measured with a dilatometer. Excess volumes are negative for the systems of *N,N*-dimethylformamide with toluene, ethylbenzene, chlorobenzene, bromobenzene, and aniline. The excess volumes are positive for the system *N,N*-dimethylformamide with nitrobenzene at 303.15 K and show a change in sign at 313.15 K.

Introduction

We report in this paper molar excess volume V^E for *N,N*-dimethylformamide with toluene, ethylbenzene, chlorobenzene, bromobenzene, nitrobenzene, and aniline at 303.15 and 313.15 K.

Experimental Section

Apparatus and Procedure. Excess volumes were measured by a batch dilatometer similar to that of Rao and Naidu (*1*). The dilatometer included a detachable capillary arrangement. The dilatometer consisted of two bulbs of different capacities connected through a U-tube with mercury at the bottom to separate the two components. One end of the first bulb was fitted with a capillary outlet, and the opposite end of the second bulb was closed with a ground-glass stopper. Five dilatometers of the type described above were used to cover the entire range of composition. The composition of each mixture was determined directly by mass, and the mole fraction was accurate to the fourth decimal place. The full dilatometer was placed in a thermostat that could be maintained to ±0.01 K. The measured V^E values were accurate to ±0.003 $cm^3 \cdot mol^{-1}$.

Materials. All the chemicals were purified by the standard methods described in the literature (*2*, *3*). *N,N*-Dimethylformamide was kept overnight over freshly ignited quick lime and distilled under reduced pressure. The middle fraction of the distillate was collected and kept over solid potassium hydroxide pellets for 24 h. It was then distilled under reduced pressure. Toluene was washed with concentrated sulfuric acid several times, until the acid developed no more color. It was then treated with sodium hydroxide solution, and the alkali was removed by washing with water. This was kept over anhydrous calcium chloride overnight, and the dried sample was refluxed with metallic sodium for 8 h and finally distilled over sodium. Ethylbenzene was purified by shaking with 6-mL portions of concentrated sulfuric acid until the layer was colorless and then with sodium carbonate solution. The sample was then shaken with water and finally dried twice with magnesium sulfate. After two distillations over sodium, the middle fraction of the second distillate was taken. Chlorobenzene was dried with calcium chloride and fractionally distilled. Bromobenzene and nitrobenzene were dried with calcium chloride and fractionally distilled under reduced pressure. Aniline was dried over caustic potash for about two days and distilled twice. The purities of the chemicals were checked by comparing the densities measured at 303.15 K with a bicapillary pycnometer and the refractive indices determined at 293.15 K with those reported in the literature (*2*, *4*–*6*). The accuracy of the refractive index measured was ±0.0002. The densities of the pure liquids are accurate to 2 parts in 10^5 parts. The purity of the liquids was further confirmed by GLC single sharp peaks. The measured densities and refractive index and those reported in the literature are given in Table 1.

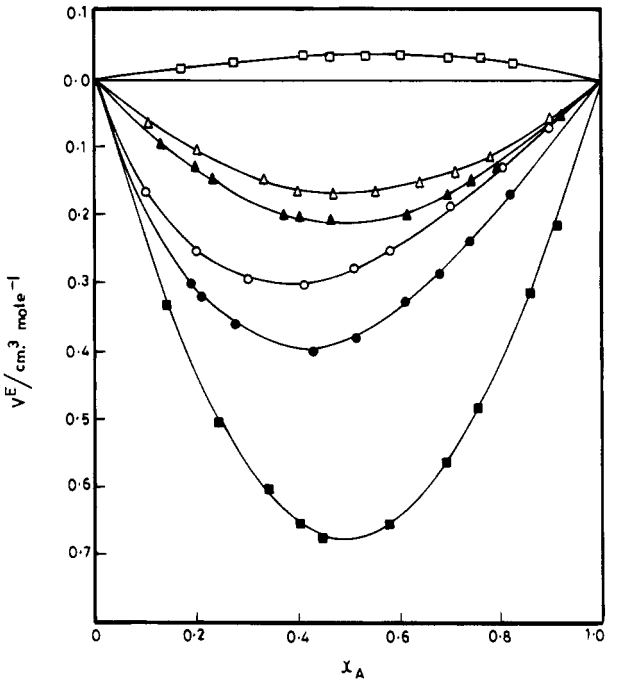

Figure 1. Excess volumes (V^E) for *N,N*-dimethylformamide (A) + toluene (B) (●), + ethylbenzene (B) (○), + chlorobenzene (B) (▲), + bromobenzene (B) (△), + nitrobenzene (B) (□), and + aniline (B) (■) at 303.15 K.

Results and Discussion

Excess volumes for binary mixtures of *N,N*-dimethylformamide with toluene, ethylbenzene, chlorobenzene, bromobenzene, nitrobenzene, and aniline at 303.15 and 313.15

† A part of the Ph.D. Thesis of R.S.R. (1992).

0021-9568/95/1740-0065$09.00/0

Table 1. Densities at 303.15 K and Refractive Indices at 293.15 K of Pure Components

compound	ϱ/(g·cm^{-3})		refractive index	
	present work	lit. (2, 4–6)	present work	lit. (2, 4–6)
N-*N*-dimethylformamide	0.941 19	0.941 20	1.3202	1.4305
toluene	0.857 64	0.857 70	1.4970	1.4969
chlorobenzene	1.095 47	1.095 50	1.5250	1.5248
bromobenzene	1.481 47	1.481 50	1.5600	1.5604
nitrobenzene	1.193 37	1.193 41	1.5525	1.5524
ethylbenzene	0.858 14	0.858 20	1.4957	1.4959
aniline	1.013 14	1.013 17	1.5865	1.5863

Table 2. Experimental Excess Molar Volumes V^E as a Function of x_A, Coefficients a_i for Eq 1, and Standard Deviations $\sigma(V^E)$ (cm^3·mol^{-1})

303.15 K		313.15 K	
x_A	V^E/(cm^3·mol^{-1})	x_A	V^E/(cm^3·mol^{-1})
N,*N*-Dimethylformamide (A) + Toluene (B)			
0.1933	−0.302	0.1494	−0.255
0.2099	−0.316	0.2518	−0.353
0.2781	−0.359	0.3538	−0.407
0.4269	−0.396	0.4565	−0.431
0.5070	−0.384	0.5993	−0.400
0.6125	−0.333	0.6573	−0.367
0.6820	−0.285	0.6851	−0.348
0.7369	−0.242	0.8362	−0.219
0.8230	−0.166	0.9181	−0.123
$a_0 = -1.5345$		$a_0 = -1.6941$	
$a_1 = 0.6180$		$a_1 = 0.2724$	
$a_2 = -0.0240$		$a_2 = -0.2268$	
$\sigma(V^E) = 0.003$ cm^3·mol^{-1}		$\sigma(V^E) = 0.003$ cm^3·mol^{-1}	
N,*N*-Dimethylformamide (A) + Ethylbenzene (B)			
0.0997	−0.162	0.0997	−0.125
0.1997	−0.255	0.1996	−0.235
0.2999	−0.295	0.2997	−0.316
0.4154	−0.297	0.4154	−0.356
0.5109	−0.278	0.5109	−0.354
0.5840	−0.247	0.5840	−0.325
0.6991	−0.185	0.6991	−0.249
0.8014	−0.130	0.8015	−0.160
0.8872	−0.075	0.8872	−0.088
$a_0 = -1.1122$		$a_0 = -1.4177$	
$a_1 = 0.6546$		$a_1 = 0.3640$	
$a_2 = -0.2502$		$a_2 = 0.4712$	
$\sigma(V^E) = 0.002$ cm^3·mol^{-1}		$\sigma(V^E) = 0.003$ cm^3·mol^{-1}	
N,*N*-Dimethylformamide (A) + Chlorobenzene (B)			
0.1280	−0.086	0.1280	−0.110
0.2043	−0.125	0.2043	−0.155
0.2298	−0.145	0.2432	−0.178
0.3667	−0.201	0.3683	−0.220
0.3976	−0.200	0.4808	−0.235
0.4598	−0.210	0.5928	−0.230
0.6079	−0.203	0.6421	−0.218
0.6942	−0.173	0.6909	−0.206
0.7388	−0.150	0.7345	−0.185
0.7947	−0.125	0.7947	−0.155
0.9202	−0.051	0.9202	−0.069
$a_0 = -0.8518$		$a_0 = -0.9512$	
$a_1 = 0.0268$		$a_1 = 0.0159$	
$a_2 = 0.2001$		$a_2 = -0.0116$	
$\sigma(V^E) = 0.003$ cm^3·mol^{-1}		$\sigma(V^E) = 0.002$ cm^3·mol^{-1}	

303.15 K		313.15 K	
x_A	V^E/(cm^3·mol^{-1})	x_A	V^E/(cm^3·mol^{-1})
N,*N*-Dimethylformamide (A) + Bromobenzene (B)			
0.1024	−0.060	0.1024	−0.050
0.1988	−0.105	0.1893	−0.093
0.3311	−0.145	0.3243	−0.142
0.4010	−0.156	0.4326	−0.165
0.4716	−0.165	0.5315	−0.171
0.5501	−0.165	0.6405	−0.160
0.6405	−0.151	0.7403	−0.126
0.7128	−0.135	0.8227	−0.090
0.7768	−0.116	0.9011	−0.051
0.9011	−0.064		
$a_0 = -0.6540$		$a_0 = -0.6879$	
$a_1 = -0.0269$		$a_1 = -0.0224$	
$a_2 = -0.0460$		$a_2 = -0.1983$	
$\sigma(V^E) = 0.002$ cm^3·mol^{-1}		$\sigma(V^E) = 0.002$ cm^3·mol^{-1}	
N,*N*-Dimethylformamide (A) + Nitrobenzene (B)			
0.1706	0.015	0.2038	−0.024
0.2656	0.022	0.3636	+0.016
0.4068	0.031	0.3832	+0.011
0.4592	0.034	0.4100	+0.004
0.5314	0.032	0.5178	−0.011
0.5982	0.033	0.5982	−0.009
0.6971	0.034	0.6619	−0.006
0.7608	0.032	0.7608	−0.002
0.8196	0.024	0.8547	+0.002
$a_0 = 0.1351$			
$a_1 = 0.0490$			
$a_2 = 0.0190$			
$\sigma(V^E) = 0.002$ cm^3·mol^{-1}			
N,*N*-Dimethylformamide (A) + Aniline (B)			
0.1428	−0.331	0.1228	−0.248
0.2460	−0.498	0.2053	−0.392
0.3378	−0.604	0.3522	−0.575
0.4034	−0.649	0.4382	−0.635
0.4382	−0.669	0.5545	−0.663
0.5844	−0.655	0.6398	−0.642
0.6904	−0.562	0.7089	−0.597
0.7565	−0.479	0.7666	−0.530
0.8604	−0.306	0.8604	−0.369
0.9071	−0.215	0.9104	−0.258
$a_0 = -2.6900$		$a_0 = -2.6434$	
$a_1 = 0.0910$		$a_1 = -0.5200$	
$a_2 = 0.1198$		$a_2 = -0.1198$	
$\sigma(V^E) = 0.004$ cm^3·mol^{-1}		$\sigma(V^E) = 0.003$ cm^3·mol^{-1}	

K are reported in Table 2 and graphically represented in Figures 1 and 2. The excess volume measurements were made to determine the relative effects of the substitutional group in the benzene ring. Variation of excess volume with mole fraction has been represented with an empirical equation in the form

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_A x_B[a_0 + a_1(x_A - x_B) + a_2(x_A - x_B)^2] \quad (1)$$

The values of the parameters a_0, a_1, and a_2 are obtained by the method of least squares, and the values are given in Table 2. The standard deviation has been calculated using the relation

$$\sigma(V^E) = [\sum(V^E_{obs} - V^E_{cal})^2/(n - p)]^{1/2} \quad (2)$$

where n is the number of results and p is the number of parameters.

The excess volumes are negative for the binary systems of *N*,*N*-dimethylformamide with toluene, ethylbenzene, chlorobenzene, bromobenzene, and aniline at 303.15 and 313.15 K. In general excess volumes can be ascribed to dipolar association between the unlike components which leads to a contraction in volume. The observed excess volumes for *N*,*N*-dimethylformamide with nitrobenzene are

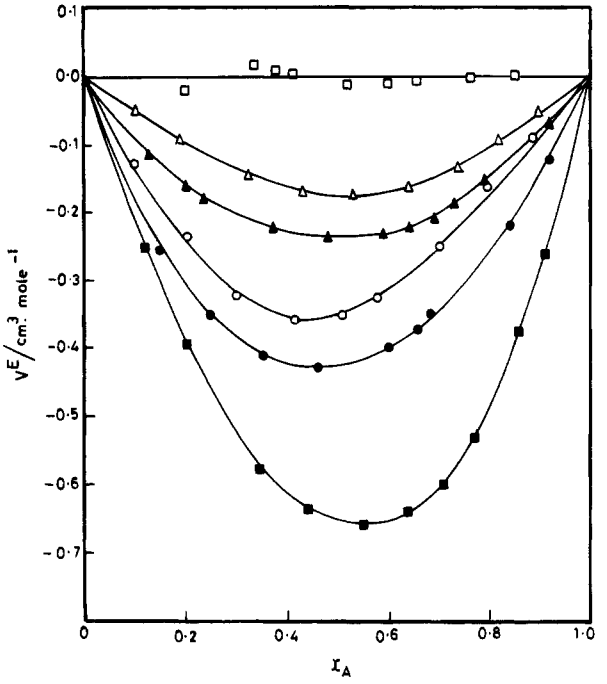

Figure 2. Excess volumes (V^E) for *N*,*N*-dimethylformamide (A) + toluene (B) (●), + ethylbenzene (B) (○), + chlorobenzene (B) (▲), + bromobenzene (B) (△), + nitrobenzene (B) (□), and + aniline (B) (■) at 313.15 K.

positive at 303.15 K and show a change in sign at 313.15 K. The dipolar dissociation and shape and size of the molecules contribute to an expansion in volume. The more negative values of V^E for *N*,*N*-dimethylformamide with aniline might be due to an additional dipole−dipole interaction between the components. The graphical representation shows that the curves are symmetric for all the systems except for *N*,*N*-dimethylformamide + nitrobenzene.

The algebraic values of V^E for the six binary systems fall in the order nitrobenzene > bromobenzene > chlorobenzene > ethylbenzene > toluene > aniline. V^E values lower than those indicated in the literature (*7*) are obtained for the systems of *N*,*N*-dimethylformamide with toluene, chlorobenzene, and nitrobenzene at 303.15 and 313.15 K.

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Received for review October 25, 1993. Revised April 22, 1994. Accepted May 7, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1994.