Viscosities of Binary Liquid Mixtures of Nonelectrolytes

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Viscosities of the melts of binary mixtures of 1,2-dihydroxybenzene–1,3-dihydroxybenzene, 1,4-dibromobenzene–4-chloroaniline, 1,4-dibromobenzene–3-chloronitrobenzene, 4-chlorobromobenzene–3-chloronitrobenzene, 1,4-dibromobenzene–4-chlorobromobenzene, 4-chlorobromobenzene–4-chloroiodobenzene, and 1,2-dihydroxybenzene–1,2-diaminobenzene have been reported as a function of temperature and composition. The nature of interactions operating in these binary melts has been studied.

Solid-liquid equilibrium diagrams of binary mixtures showing congruent behavior, proves beyond doubt the formation of molecular compounds in them in their solid phase. Such molecular compounds have also been investigated in solutions by Rastogi and Nigam (*3*). Nigam and Singh (*6*) and Rastogi et al. (*7*) have reported the existence of associated complexes in their mixtures in the liquid phase but in the solid phase (in their solid-liquid equilibrium diagram), no such complex was observed. Such a result tempted us to study viscosities of binary mixtures for which phase diagrams were obtained earlier (*2*, 4) to have a deeper insight into the nature of interactions operating in these mixtures. We report here only the experimental data for viscosities of the melts of binary mixtures.

Experimental and Results

1,2-dihydroxybenzene, 1,3-dihydroxybenzene, 1,4-dibromobenzene, 4-chloroaniline, 4-chlorobromobenzene, 3-chloronitrobenzene, 4-chloroiodobenzene and 1,2-diaminobenzene (all BDH grade) were purified. Their purity was checked in the same manner as discussed earlier (*2*, *4*).

A modified Ubbelhode kinematic viscometer (*10*) was used for determining the viscosities of the melts of the following mixtures and their pure components at 110°, 115°, and 120°C.

Mixtures	Nature of phase diagram (*2*, *4*)
1. 1,2-Dihydroxybenzene + 1,3-dihydroxybenzene	Eutectic type
2. 1,4-Dibromobenzene + 4-chloroaniline	
3. 1,4-Dibromobenzene + 3-chloronitrobenzene	
4. 4-Chlorobromobenzene + 8-chloronitrobenzene	
5. 1,4-Dibromobenzene + 4-chlorobromobenzene	Complete miscibility in solid and liquid phases
6. 4-Chlorobromobenzene + 4-chloroiodobenzene	Complete miscibility having a minimum melting point at 0.3 mole fraction of 4-chlorobromobenzene
7. 1,2-Dihydroxybenzene + 1,2-diaminobenzene	Congruent type

The temperature of the bath containing paraffin oil was set correctly to ±0.1°C. The viscometer was calibrated against known viscosities (*9*) of pure melts of 1,2-dihydroxybenzene and 3-chloronitrobenzene at 110°, 115°, and 120°C. The constants of the viscometer were determined from the following relationships (*1*):

$$\text{Kinematic viscosity} = \nu = \eta/\rho = at - b/t \qquad (1)$$

where a and b are constants dependent on temperature; ν, η, ρ, and t are kinematic viscosity, coefficient of viscosity, density of flow, and time of flow for the melts of the compound under test. The values of a and b, determined by the least-squares method, are recorded below:

Temp, °C	a	b
110	0.0016852	2.2145
115	0.0017186	3.0650
120	0.0017478	7.3824

The absolute viscosities of 3-chloronitrobenzene were fitted in the following equation at different temperatures:

$$\eta(T) = A + Bt \qquad (2)$$

where A and B are the constants and t is the time of flow for the melt. The constants A and B, determined by the least-squares method, were $A = 0.1125$ and $B = 0.001875$. The kinematic viscosities for the melts of the above-mentioned binary mixtures at 110°, 115°, and 120°C were determined from Equation 1, and the absolute viscosities for the systems 1–5 and 7 were determined from Equation 1 using the measured values of densities (*5*). The densities for the system 4-chlorobromobenzene–4-chloroiodobenzene were not measured, so the absolute viscosities for this system were determined from using Equation 2. Newtonian flow for the melts of pure components and their binary mixtures were tested prior to the experimental determinations (Table I).

Table I. Viscosity Data for Binary Melts of Nonelectrolytes

Mole fraction of A	ν_{mix}, cSt			η_{mix}, cP		
	110°C	115°C	120°C	110°C	115°C	120°C
1,2-Dihydroxybenzene (A)–1,3-dihydroxybenzene (B)						
0.0000	7.25	6.42	5.45	8.59	7.58	6.42
0.1379	6.00	5.36	4.59	7.11	6.30	5.33
0.3071	4.86	4.35	3.79	5.71	5.09	4.43
0.4194	4.23	3.66	3.35	4.96	4.27	3.89
0.5307	3.70	3.34	2.96	4.33	3.89	3.44
0.6012	3.43	3.09	2.76	4.00	3.60	3.20
0.7345	2.94	2.72	2.41	3.42	3.16	2.79
0.8290	2.66	2.42	2.21	3.09	2.80	2.54
1.0000	2.23	2.04	1.89	2.58	2.36	2.18
1,4-Dibromobenzene (A)–4-chloroaniline (B)						
0.0000	0.742	0.757	0.715	0.896	0.844	0.805
0.0843	0.733	0.699	0.668	0.861	0.818	0.779
0.1874	0.676	0.642	0.612	0.842	0.796	0.757
0.3002	0.628	0.595	0.565	0.830	0.782	0.741

(*Continued on next page*)

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Table I. (Continued)

1,4-Dibromobenzene (A)–4-chloroaniline (B) (*Contd.*)

Mole fraction of A	ν_{mix}, cSt			η_{mix}, cP		
	110°C	115°C	120°C	110°C	115°C	120°C
0.3849	0.594	0.560	0.534	0.816	0.766	0.729
0.5068	0.557	0.523	0.495	0.811	0.759	0.716
0.6081	0.534	0.500	0.473	0.815	0.761	0.717
0.8506	0.500	0.463	0.440	0.848	0.782	0.741
1.0000	0.480	0.446	0.422	0.872	0.807	0.761
1,4-Dibromobenzene (A)–3-chloronitrobenzene (B)						
0.0000	0.690	0.659	0.633	0.880	0.837	0.801
0.1917	0.627	0.597	0.573	0.863	0.818	0.735
0.3062	0.594	0.564	0.541	0.852	0.807	0.771
0.3819	0.571	0.544	0.521	0.842	0.800	0.764
0.4527	0.549	0.521	0.500	0.830	0.785	0.751
0.5680	0.529	0.501	0.579	0.835	0.787	0.750
0.7321	0.510	0.479	0.456	0.849	0.796	0.755
0.9318	0.489	0.456	0.431	0.870	0.808	0.763
1.0000	0.480	0.446	0.422	0.872	0.808	0.761
3-Chloronitrobenzene (A)–4-chlorobromobenzene (B)						
0.0000	0.382	0.388	0.387	0.589	0.583	0.578
0.2982	0.447	0.441	0.435	0.639	0.628	0.619
0.3702	0.462	0.453	0.447	0.657	0.643	0.632
0.4566	0.482	0.471	0.461	0.666	0.659	0.646
0.5532	0.510	0.497	0.486	0.704	0.684	0.667
0.6594	0.546	0.529	0.517	0.739	0.715	0.696
0.7715	0.586	0.567	0.550	0.778	0.750	0.726
0.8713	0.628	0.605	0.584	0.819	0.786	0.757
1.0000	0.690	0.659	0.633	0.880	0.837	0.801
1,4-Dibromobenzene (A)–4-chlorobromobenzene (B)						
0.0000	0.390	0.388	0.387	0.589	0.583	0.578
0.2600	0.405	0.397	0.390	0.645	0.628	0.614
0.3331	0.411	0.401	0.392	0.663	0.643	0.625
0.4131	0.418	0.405	0.395	0.684	0.649	0.639
0.5880	0.432	0.413	0.399	0.730	0.694	0.668
0.6496	0.439	0.418	0.402	0.749	0.711	0.681
0.7561	0.452	0.428	0.410	0.787	0.741	0.706
1.0000	0.480	0.447	0.422	0.872	0.808	0.761
4-Chlorobromobenzene (A)–4-chloroiodobenzene (B)						
0.0000	0.447	0.446	0.443	0.640	0.616	0.591
0.1520	0.440	0.439	0.437	0.632	0.610	0.575
0.3131	0.433	0.432	0.430	0.625	0.602	0.567
0.4235	0.423	0.421	0.419	0.613	0.591	0.555
0.5026	0.413	0.412	0.411	0.605	0.583	0.547
0.5781	0.403	0.403	0.402	0.596	0.573	0.537
0.6317	0.398	0.398	0.397	0.591	0.568	0.532
0.7086	0.392	0.391	0.390	0.584	0.561	0.525
0.8510	0.388	0.387	0.386	0.581	0.558	0.521
1.0000	0.390	0.388	0.387	0.582	0.559	0.522
1,2-Dihydroxybenzene (A)–1,2-diaminobenzene						
0.0000	2.06	1.93	1.78	2.17	2.03	1.87
0.1150	2.44	2.27	2.06	2.61	2.42	2.19
0.3204	3.21	2.92	2.63	3.51	3.18	2.85
0.4232	3.53	3.16	2.82	3.90	3.48	3.10
0.4875	3.78	3.36	3.01	4.21	3.73	3.32
0.6054	3.57	3.18	2.84	3.98	3.57	3.18
0.6708	3.29	3.00	2.72	3.73	3.39	3.06
0.8286	2.88	2.60	2.37	3.30	2.96	2.69
1.0000	2.23	2.04	1.89	2.58	2.36	2.18

Data for the viscosities of the melts at different temperatures for binary mixtures have been presented in Figures 1–7. The figures represent the best fit of experimental data.

The plot of η_{mix} against composition exhibiting a maximum or positive deviation from rectilinear dependence on volume or mole fraction should mean the presence of specific interactions

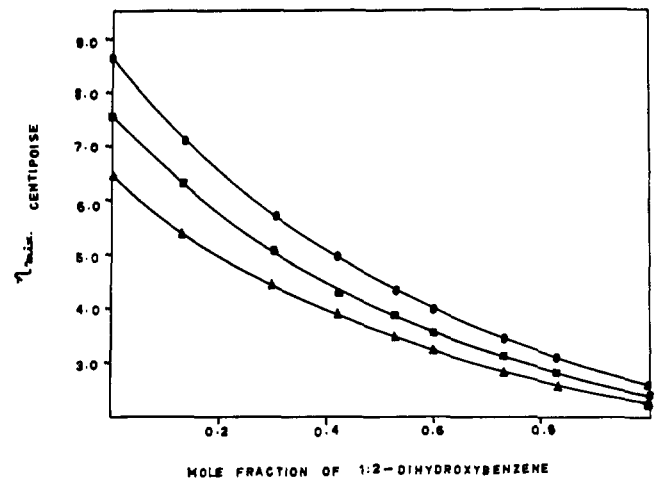

Figure 1. Temperature dependence of viscosity for 1,2-dihydroxybenzene–1,3-dihydroxybenzene

● 110°C. ■ 115°C. ▲ 120°C

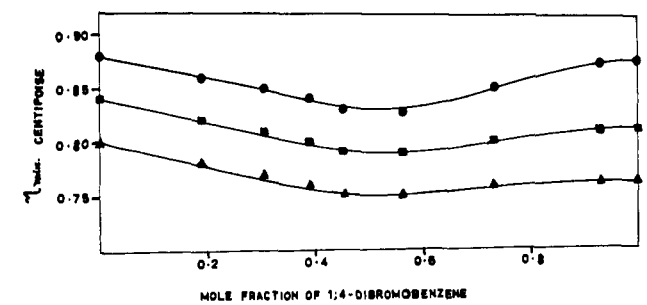

Figure 2. Temperature dependence of viscosity for 1,4-dibromobenzene–4-chloroaniline

● 110°C. ■ 115°C. ▲ 120°C

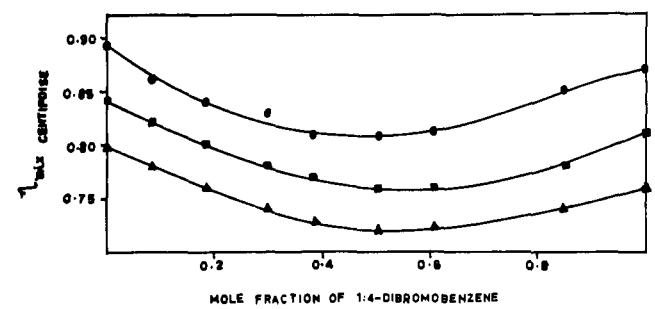

Figure 3. Temperature dependence of viscosity for 1,4-dibromobenzene–3-chloronitrobenzene

● 110°C. ■ 115°C. ▲ 120°C

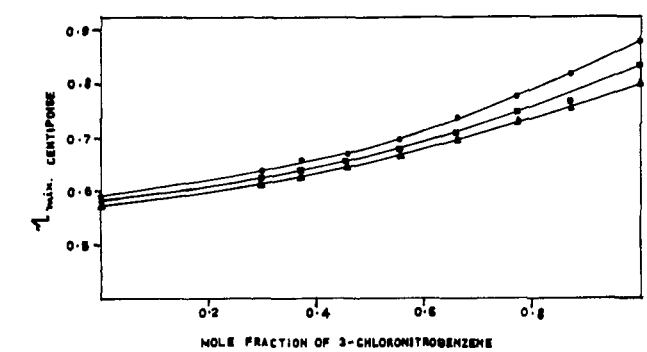

Figure 4. Temperature dependence of viscosity for 3-chloronitrobenzene–4-chlorobromobenzene

● 110°C. ■ 115°C. ▲ 120°C

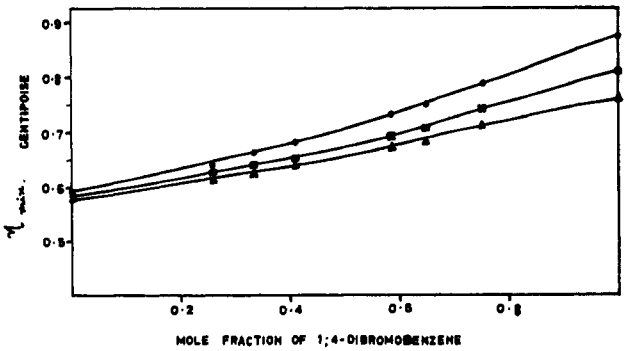

Figure 5. Temperature dependence of viscosity for 1,4-dibromobenzene–4-chlorobromobenzene

● 110°C. ■ 115°C. ▲ 120°C

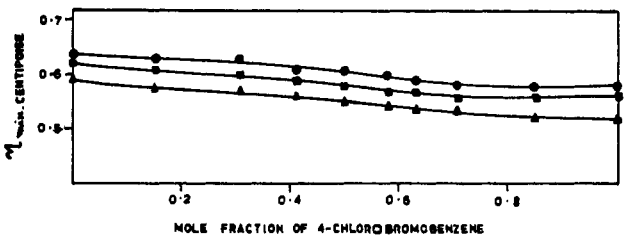

Figure 6. Temperature dependence of viscosity for 4-chlorobromobenzene–4-chloroiodobenzene

● 110°C. ■ 115°C. ▲ 120°C

resulting in the formation of complex between them (*3*). The negative deviations from rectilinear behavior should mean, on the other hand, the presence of dominant dispersive forces in the mixtures. Figures 1 through 6 showed negative deviations from the rectilinear dependence, and hence mainly dispersive forces are present in these mixtures. In Figure 7, a positive deviation is observed which would mean that specific interactions resulting in the formation of a complex compound should be present. Figures 1 to 7 thus supported the results obtained from their phase diagrams (*2*, *4*).

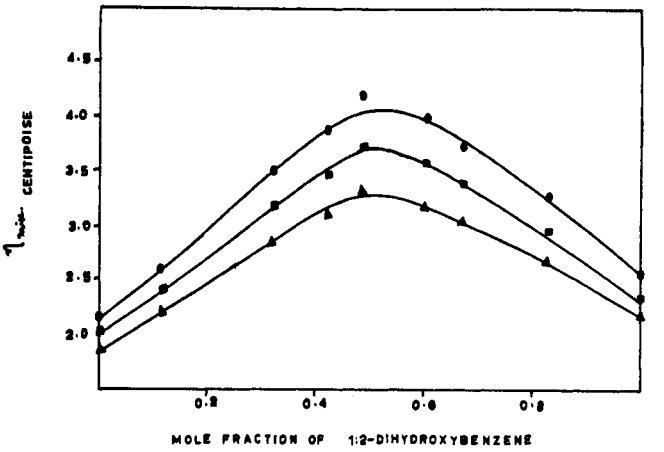

Figure 7. Temperature dependence of viscosity for 1,2-dihydroxybenzene–1,2-diaminobenzene

● 110°C. ■ 115°C. ▲ 120°C

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