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Thermodynamic and Transport Properties of *o*-Chlorophenol with Aniline and *N*-Alkylanilines

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Densities and viscosities at five temperatures were determined for the systems *o*-chlorophenol with aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, *N*-ethylaniline, and *N*,*N*-diethylaniline. From the experimental data, the excess volumes, excess viscosities, partial molar excess volumes, and partial molar volumes were calculated. Various thermodynamic parameters of activation of viscous flow were calculated from the dependency of viscosity on temperature. The results are discussed in terms of theories of nonelectrolyte solutions and also the type and strength of interaction between the two components in solution.

This present paper continues our investigations of the thermodynamic and transport properties of binary acid–base mixtures (*1–3*). The systems *o*-chlorophenol (CP) with aniline (A), *N*-methylaniline (MA), *N*,*N*-dimethylaniline (DMA), *N*-ethylaniline (EA), and *N*,*N*-diethylaniline (DEA) were chosen to represent the acid–base interactions and were also chosen because of their polar characteristics, and the ability to form hydrogen bonding. Solutions of nonelectrolytes were classified by Barker and Smith (*4*) as (i) "nonpolar" solutions, (ii) "polar" solutions, and (iii) "associated" solutions. The above systems could be classified as ii and iii.

In the present paper, densities and viscosities of the five systems at different mole fractions were measured at 298, 303, 308, 313, and 318 K. From the experimental results the following thermodynamic functions have been calculated: V^E (excess volume), η^E (excess viscosity), G^{*E} (excess molar free energy of activation of flow), ΔH^{*E}, ΔS^{*E} (excess enthalpy and entropy of activation), and $\bar{V}_1$ partial molar quantities in solution. The results were discussed in terms of the type of interaction between CP with various substituted anilines. Viscosity and density measurements on *o*-chlorophenol with aniline and *N*,*N*-dimethylaniline at 25 °C were reported by Solimo et al. and our results agree well with published data (*5*).

Experimental Section

Densities of pure liquids and of mixtures were determined with an Anton-Paar DMA 45 densitometer with an accuracy in density measurements of ±0.0001 g/cm^3. A thermostatically controlled bath (SODEV), constant to ±0.001 °C, was used.

Viscosity measurements at various temperatures were done using modified Ostwald or Cannon–Fenske viscometers and a viscosity bath (Koehler Instrumentation). Viscometers were calibrated against pure liquids (acetone and benzene), and the accuracy was found to be ±0.005 cP. All chemicals used were either B.D.H. or Aldrich and were purified by the standard procedures described by Weissberger (*6*). Only colorless middle fractions were collected and used to prepare the mixtures, which were prepared by mixing weighed amounts of the pure liquids.

Results

The experimental values of density, ρ, and viscosity η for the five systems are listed in Tables I–V. The molar volume (V) of the solution was obtained from the expression

$$V = (X_1M_1 + X_2M_2)/\rho \tag{1}$$

where M_1, M_2 are molecular masses of the pure components 1 and 2 and X_1 and X_2 are their mole fractions.

Excess properties Y^E were calculated by the equation

$$Y^E = Y - [X_1Y_1 + X_2Y_2] \tag{2}$$

where Y, Y_1, and Y_2 are the specific properties of the mixture and of the pure components 1 and 2, respectively.

Excess molar free energy of activation of flow, G^{*E}, was calculated by using the equation

$$G^{*E} = RT\,[\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \tag{3}$$

where η and V are the viscosity and molar volume respectively of the mixtures, η_1, η_2 and V_1, V_2 are the viscosities and molar volumes of the pure components 1 and 2, respectively, R is the gas constant, and T is the absolute temperature (*7*). The excess functions were fitted with a Redlich–Kister (*8*) form of the type

$$X^E = X_1\,(1 - X_1)\sum_{j=1}^{n} a_j(1 - 2X_1)^{j-1} \tag{4}$$

where X^E represents the excess property under consideration. The least-squares method was used to determine the values of the coefficients a_j. In each case the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate (σ) with n

$$\sigma_x = [(X^E{}_{\text{obsd}} - X^E{}_{\text{calcd}})^2/(n_{\text{obsd}} - n)]^{1/2} \tag{5}$$

The values of these coefficients along with the standard error of estimate at five different temperatures have been given in Tables VI–VIII. Figures 1–3 show the values of η^E, V^E, and G^{*E} as a function of the mole fraction of *o*-chlorophenol. The continuous curves were generated by the computer aided plotter and the coefficients in Tables VI–VIII.

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Table I. Density and Viscosity Data for Aniline + *o*-Chlorophenol

x_1[a]	ρ, g·mL^{-1} 298 K	303 K	308 K	313 K	318 K	η, cP 298 K	303 K	308 K	313 K	318 K
0.0000	1.0174	1.0133	1.0089	1.0046	1.0002	3.695	3.097	2.663	2.329	2.057
0.1032	1.0479	1.0437	1.0391	1.0349	1.0303	4.945	4.142	3.556	3.110	2.671
0.2004	1.0760	1.0717	1.0669	1.0626	1.0578	6.157	5.008	4.265	3.638	3.036
0.3011	1.1043	1.0999	1.0949	1.0904	1.0854	7.228	5.792	4.728	3.900	3.241
0.4069	1.1326	1.1280	1.1227	1.1181	1.1129	8.070	6.329	4.979	4.024	3.322
0.5008	1.1566	1.1518	1.1464	1.1416	1.1361	8.810	6.859	5.417	4.382	3.611
0.6002	1.1799	1.175	1.1693	1.1644	1.1588	8.000	6.232	4.922	3.966	3.270
0.7016	1.2020	1.1969	1.1911	1.1861	1.1804	6.990	5.602	4.511	3.750	3.137
0.7852	1.2187	1.2135	1.2078	1.2026	1.1968	5.942	4.740	3.826	3.283	2.853
0.9025	1.2404	1.2352	1.2292	1.2240	1.2181	4.443	3.702	3.108	2.744	2.446
1.0000	1.2565	1.2511	1.2452	1.2398	1.2339	3.376	2.927	2.532	2.191	1.947

[a] Mole fraction of *o*-chlorophenol.

Table II. Density and Viscosity Data for *N*-Methylaniline + *o*-Chlorophenol

x_1[a]	ρ, g·mL^{-1} 298 K	303 K	308 K	313 K	318 K	η, cP 298 K	303 K	308 K	313 K	318 K
0.0000	0.9817	0.9777	0.9736	0.9696	0.9658	1.963	1.734	1.547	1.402	1.269
0.1013	1.0102	1.0062	1.0017	1.9976	0.9938	2.395	2.112	1.840	1.622	1.443
0.2024	1.0390	1.0347	1.0301	1.0257	1.0218	3.887	2.493	2.126	1.826	1.598
0.3005	1.0669	1.0624	1.0575	1.0530	1.0489	3.546	2.984	2.526	2.175	1.883
0.4032	1.0961	1.0914	1.0863	1.0815	1.0772	4.142	3.445	2.863	2.420	2.075
0.5007	1.1237	1.1190	1.1136	1.1087	1.1042	4.746	3.801	3.129	2.678	2.302
0.6027	1.1520	1.1471	1.1415	1.1363	1.1317	4.883	3.963	3.277	2.750	2.340
0.7000	1.1785	1.1734	1.1676	1.1623	1.1576	4.922	3.966	3.305	2.793	2.420
0.7936	1.2036	1.1983	1.1925	1.1871	1.1822	4.587	3.715	3.117	2.704	2.342
0.9042	1.2322	1.2269	1.2210	1.2155	1.2105	3.898	3.352	3.770	2.506	2.198
1.0000	1.2565	1.2511	1.2452	1.2398	1.2339	3.376	2.927	2.532	2.191	1.947

[a] Mole fraction of *o*-chlorophenol.

Table III. Density and Viscosity Data for *N*,*N*-Dimethylaniline + *o*-Chlorophenol

x_1[a]	ρ, g·mL^{-1} 298 K	303 K	308 K	313 K	318 K	η, cP 298 K	303 K	308 K	313 K	318 K
0.0000	0.9520	0.9480	0.9439	0.9398	0.9357	1.283	1.180	1.096	1.020	0.968
0.1002	0.9789	0.9748	0.9708	0.9664	0.9622	1.530	1.384	1.254	1.171	1.077
0.1990	1.0060	1.0017	0.9976	0.9930	0.9886	1.698	1.522	1.366	1.234	1.122
0.3025	1.0360	1.0315	1.0273	1.0225	1.0179	2.194	1.937	1.702	1.527	1.382
0.4016	1.0655	1.0608	1.0564	1.0514	1.0466	2.558	2.200	1.951	1.736	1.560
0.5020	1.0965	1.0915	1.0869	1.0817	1.0767	3.036	2.564	2.221	1.965	1.728
0.6009	1.1275	1.1223	1.1175	1.1121	1.1069	3.480	2.904	2.476	2.152	1.899
0.6991	1.1591	1.1537	1.1487	1.1431	1.1377	3.758	3.121	2.681	2.335	2.050
0.8000	1.1918	1.1863	1.1811	1.1754	1.1698	3.852	3.212	2.757	2.397	2.173
0.9019	1.2249	1.2193	1.2140	1.2082	1.2026	3.691	3.106	2.662	2.360	2.028
1.0000	1.2565	1.2511	1.2452	1.2398	1.2339	3.376	2.927	2.532	2.191	1.947

[a] Mole fraction of *o*-chlorophenol.

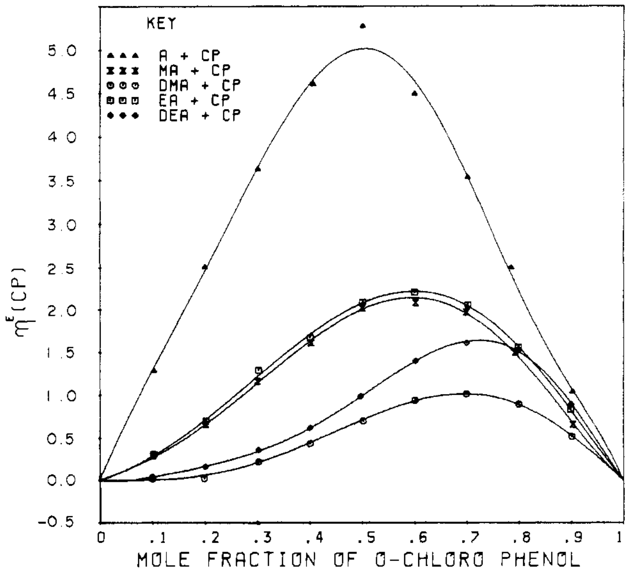

Figure 1. Plot of excess viscosity vs. mole fraction of *o*-chlorophenol at 298 K.

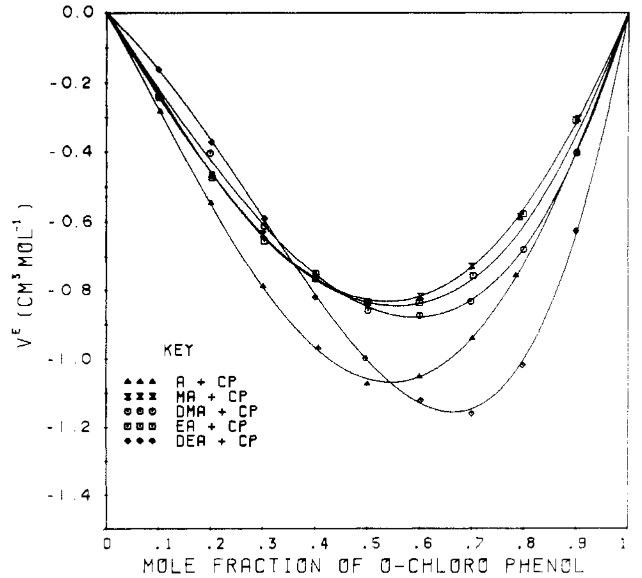

Figure 2. Plot of excess volume vs. mole fraction of *o*-chlorophenol at 298 K.

Table IV. Density and Viscosity Data for *N*-Ethylaniline + *o*-Chlorophenol

	ρ, g·mL^{-1}					η, cP				
x_1[a]	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	0.9565	0.9526	0.9484	0.9442	0.9396	1.947	1.741	1.549	1.392	1.263
0.1027	0.9838	0.9798	0.9754	0.9712	0.9669	2.403	2.117	1.852	1.673	1.491
0.2022	1.0114	1.0072	1.0026	0.9982	0.9936	2.916	2.487	2.161	1.885	1.670
0.3028	1.0401	1.0357	1.0309	1.0264	1.0216	3.666	3.051	2.557	2.206	1.925
0.4011	1.0688	1.0641	1.0593	1.0545	1.0495	4.186	3.372	2.828	2.407	2.166
0.5014	1.0990	1.0941	1.0892	1.0843	1.0792	4.763	3.807	3.160	2.662	2.287
0.6004	1.1294	1.1242	1.1193	1.1142	1.1090	5.010	4.028	3.314	2.771	2.372
0.7024	1.1613	1.1559	1.1508	1.1456	1.1402	5.008	3.972	3.299	2.782	2.392
0.7991	1.1917	1.1862	1.1809	1.1757	1.1702	4.647	3.751	3.134	2.670	2.317
0.8994	1.2236	1.2181	1.2125	1.2071	1.2014	4.064	3.335	2.844	2.452	2.137
1.0000	1.2565	1.2511	1.2452	1.2398	1.2339	3.376	2.927	2.532	2.191	1.947

[a] Mole fraction of *o*-chlorophenol.

Table V. Density and Viscosity Data for *N*,*N*-Diethylaniline + *o*-Chlorophenol

	ρ, g·mL^{-1}					η, cP				
x_1[a]	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	0.9299	0.9259	0.9219	0.9180	0.9139	1.919	1.709	1.534	1.402	1.279
0.1000	0.9525	0.9486	0.9444	0.9401	0.9361	2.116	1.858	1.668	1.507	1.370
0.2015	0.9776	0.9735	0.9690	0.9645	0.9604	2.366	2.053	1.818	1.626	1.470
0.3033	1.0050	1.0007	0.9960	0.9912	0.9868	2.722	2.310	2.013	1.775	1.641
0.4011	1.0338	1.0291	1.0240	1.0191	1.0144	3.122	2.589	2.192	1.940	1.701
0.4970	1.0642	1.0592	1.0537	1.0484	1.0436	3.629	2.933	2.432	2.120	1.841
0.6026	1.1001	1.0949	1.0891	1.0834	1.0781	4.195	3.337	2.741	2.318	1.998
0.7000	1.1363	1.1304	1.1243	1.1184	1.1128	4.548	3.533	2.890	2.420	2.086
0.7988	1.1745	1.1684	1.1620	1.1559	1.1502	4.623	3.605	2.938	2.463	2.129
0.9003	1.2152	1.2091	1.2030	1.1968	1.1913	4.120	3.320	2.769	2.361	2.135
1.0000	1.2565	1.2511	1.2452	1.2398	1.2339	3.376	2.927	2.532	2.191	1.947

[a] Mole fraction of *o*-chlorophenol.

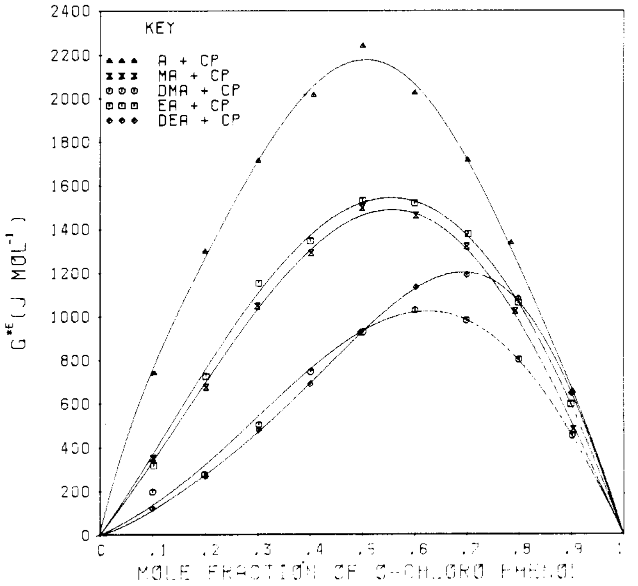

Figure 3. Plot of excess free energy of activation vs. mole fraction of *o*-chlorophenol at 298 K.

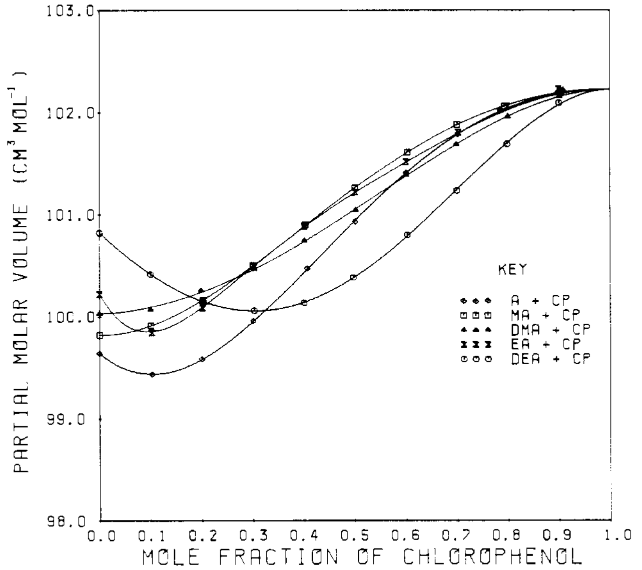

Figure 4. Plot of partial molar volume vs. mole fraction of *o*-chlorophenol at 298 K.

According to Eyring (*9*), the variation of viscosity of the liquids with temperatures can be represented by the equation

$$\eta = \frac{hN}{V} e^{\left(\frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R}\right)} \tag{6}$$

A plot of ln ($\eta V/hN$) against $1/T$ should be a straight line with the slope equal to $\Delta H^{\ddagger}/R$ and intercept equal to $-\Delta S^{\ddagger}/R$. The free energy of activation of viscous flow ($\Delta G^{\ddagger}$) is calculated at 298 K by using the equation

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{7}$$

Various parameters were obtained by the least-squares method. Activation parameters for the pure components and the excess activation parameters, Y^{*E}, calculated according to eq 3 are presented in Tables IX and X, respectively. Partial molar excess volumes and partial molar volumes were respectively calculated from the following equations

$$(V_1^{E})_{1,2} = (V^{E})_{1,2} + (1 - X_1)\left[\frac{\partial (V^{E})_{12}}{\partial X_1}\right]_{P,T} \tag{8}$$

$$\bar{V}_1 = V_1 + (V_1^{E})_{1,2} \tag{9}$$

where V_1^{E} is the partial molar excess volume, and $\bar{V}_1$ is the partial molar volume of component 1 in solution. Figure 4

Table VI. Coefficients for Least-Squares Fit of Results by Eq 4 for Excess Viscosity (cP)

system	temp, K	a_1	a_2	a_3	a_4	a_5	a_6	σ
aniline + *o*-chlorophenol	298	20.07	−0.6634	−20.75	7.738	15.15	−7.264	0.20
	303	14.62	0.3639	−13.83	2.587	10.88		0.14
	308	10.38	0.7258	−4.311	2.935			0.14
	313	7.814	0.4160	−3.609	2.403	4.977		0.13
	318	5.719	0.3248	0.1472	0.9384			0.10
N-methylaniline + *o*-chlorophenol	298	8.010	−5.484	−4.073	0.3836			0.05
	303	5.806	−3.209	−2.452	1.659			0.03
	308	4.389	−2.688	−2.122	2.249			0.02
	313	3.379	−1.888	−0.9567	−0.1339			0.03
	318	2.614	−1.579	−0.6649	−0.1350			0.03
N,*N*-dimethylaniline + *o*-chlorophenol	298	2.850	−5.134	0.4455	2.308	−0.3102		0.05
	303	2.060	−3.115	0.4924	−1.845	−0.8609	4.758	0.05
	308	1.646	−2.135	0.3948	−3.999	−0.9082	6.938	0.03
	313	1.448	−1.622	−0.3955	−4.288	1.224	6.280	0.03
	318	1.154	−0.805	0.9444	−8.341	−1.277	12.41	0.02
N-ethylaniline + *o*-chlorophenol	298	8.303	−5.400	−3.298	2.618	−0.1008		0.04
	303	5.839	−3.669	−2.216	2.646	−0.5207		0.05
	308	4.411	−2.673	−1.659	1.913	−0.0339		0.03
	313	3.426	−1.997	−1.174	1.435	0.6281		0.02
	318	2.775	−1.228	−1.082	0.4884	0.4395		0.02
N,*N*-diethylaniline + *o*-chlorophenol	298	3.966	−8.205	5.429	3.425	−5.312		0.02
	303	2.524	−5.036	2.845	2.454	−3.176		0.02
	308	1.671	−3.371	2.353	1.970	−2.747		0.02
	313	1.326	−2.227	0.8330	1.014	−0.7871		0.01
	318	0.9558	−1.173	0.9069	−0.5602	−0.1350		0.03

Table VII. Coefficients for Least-Squares Fit of Results by Eq 4 for Excess Volume ($cm^3\ mol^{-1}$)

system	temp, K	a_1	a_2	a_3	a_4	a_5	a_6	σ
aniline + *o*-chlorophenol	298	−4.239	0.9260	0.7234				0.008
	303	−4.273	0.8841	0.6706				0.010
	308	−4.216	0.8295	0.6474				0.009
	313	−4.284	0.7560	0.5120				0.009
	318	−4.252	0.6830	0.8104	0.08787	−0.6218		0.005
N-methylaniline + *o*-chlorophenol	298	−3.311	0.5669	0.3352				0.006
	303	−3.289	0.6359	0.2977	−0.3564			0.009
	308	−3.154	0.5223	0.3368	−0.1048			0.009
	313	−3.069	0.3839	0.3614				0.010
	318	−3.194	0.5216	−0.0959				0.010
N,*N*-dimethylaniline + *o*-chlorophenol	298	−3.390	1.335	−0.1463				0.013
	303	−3.274	1.159	−0.1183				0.014
	308	−3.409	1.110	−0.4301				0.015
	313	−3.223	1.045	−0.1892	−0.1485			0.015
	318	5.532	9.881	2.493	1.071	31.38	33.87	0.071
N-ethylaniline + *o*-chlorophenol	298	−3.342	0.7297	−0.2012	−0.4098	1.130		0.004
	303	−3.214	0.5312	−0.1723	−0.3859	1.007		0.006
	308	−3.273	0.8029	−0.0023	−0.6513	0.8148		0.004
	313	−3.216	0.7474	−0.2853	−0.7727	1.060		0.008
	318	−3.310	0.7909	−0.0418	−1.318			0.008
N,*N*-diethylaniline + *o*-chlorophenol	298	−4.009	3.340	−0.7387				0.018
	303	−3.822	2.971	−0.6244	−0.7304			0.009
	308	−3.478	2.587	−0.6068	−0.4532			0.008
	313	−3.107	2.350	−0.1067	−0.5168			0.014
	318	−3.033	1.884	−0.4904				0.009

shows the values of $\bar{V}_1$ as a function of the mole fraction of *o*-chlorophenol.

Discussion

In the present study, *o*-chlorophenol was chosen as one of the components because it can function as a weak acid and also because of its limited polymerization through intermolecular hydrogen bonding in the pure state. The addition of amines causes the rupture of intramolecular and intermolecular hydrogen bonding in *o*-chlorophenol and this will be followed by association of unlike molecules through intermolecular hydrogen bonding or acid–base interaction.

In most theories of the behavior of nonelectrolyte solutions the major contribution to the deviation from ideal mixing is attributed to the dispersion forces (*10*). In such theories the deviations are expected to be positive. Negative deviations from ideal behavior in mixtures of molecules different in size can be accounted for by geometric consideration (*11*).

The behavior of various liquid mixtures were discussed on the basis of sign and magnitude of the values of V^E, η^E, and G^{*E}.

Figure 1 shows positive excess viscosities with well-marked maxima for all the systems. This behavior is evidence of the formation of a complex. The symmetric curve of η^E and G^{*E} vs. mole fraction for A + CP indicates that the energy necessary to break the hydrogen bonds in the mixing process for the pure liquids is similar for both components. In *o*-chlorophenol a small percentage of molecules are associated through intermolecular hydrogen bonds, while a majority of molecules are engaged by intramolecular hydrogen bonds, as established by infrared spectroscopic studies (*12*). Further, it has been shown that the shift in stretching frequency of free OH^- groups due to intramolecular hydrogen bonding is smaller than the corresponding shift due to intermolecular hydrogen bonding (*13*). This means that the intramolecular hydrogen bonds are weaker than the intermolecular hydrogen bonds. For the other systems the excess viscosity becomes less positive and the maxima shifts toward the higher mole fraction of *o*-chlorophenol. This

Table VIII. Coefficients for Least-Squares Fit of Results by Eq 4 for Excess Molar Free Energy of Activation Flow ($J \bullet mol^{-1}$)

system	temp, K	a_1	a_2	a_3	a_4	a_5	σ
aniline + *o*-chlorophenol	298	8713	−314.7	−4132	1267	4559	52
	303	7945	−101.7	−3523	1862	4066	52
	308	7055	37.42	−735.6	2938		68
	313	6425	51.66	−1130	2404	4312	79
	318	5747	55.16	−1122	1188	5378	78
N-methylaniline + *o*-chlorophenol	298	5849	−1787	−1744	751.8		31
	303	5188	−1142	−1783	303.5	1153	19
	308	4648	−1350	−1373	1244		26
	313	4218	−1020	−813.8	1193		39
	318	3823	−1158	−1446	918.7	1397	47
N,*N*-dimethylaniline + *o*-chlorophenol	298	3726	−2779	−643.3	816.6		60
	303	3252	−2333	−628.4	860.0		60
	308	2925	−2112	48.45	197.8	−1668	64
	313	2799	−1978	−341.7	−370.2		71
	318	2837	−1681	164.5			86
N-ethylaniline + *o*-chlorophenol	298	6080	−1631	−1173	43.50		28
	303	5215	−1435	−818.6	926.7	−743.5	40
	308	4734	−1030	−1069			26
	313	4301	−1182	−397.9	949.8		29
	318	4023	−655.2	−653.5	−20.17		32
N,*N*-diethylaniline + *o*-chlorophenol	298	3707	−4581	1965	1280	−1755	13
	303	2963	−3569	1199	1446	−1456	16
	308	2423	−2949	1511	1731	−1804	19
	313	2219	−2300	420.3	966.4	−384.8	8.7
	318	1905	−1324	904.8	−831.1		38

Table IX. Activation Parameters of Viscous Flow for Pure Compounds

compd	ΔH^*, $kJ \cdot mol^{-1}$	ΔS^*, $J \cdot mol^{-1}$	ΔG^*, $kJ \cdot mol^{-1}$
aniline	22.30	19.17	16.59
N-methylaniline	16.47	3.32	15.48
N,*N*-dimethylaniline	10.53	−14.36	14.81
N-ethylaniline	16.49	2.16	15.84
N,*N*-diethylaniline	15.24	−3.80	16.38
o-chlorophenol	21.29	15.21	16.68

indicates that the breaking energy of hydrogen bonding in *o*-chlorophenol, when mixing with *N*-methyl and *N*-ethylanilines, is not compensated by the weak N---H bonding of the base (*14*). It is not compensated at all when it is mixed with *N*,*N*-dimethyl and *N*,*N*-diethylanilines because of absence of hydrogen bonding. According to Fialkov (*15*), in systems whose excess viscosity shows well-marked maxima, the composition of the compound formed can be fixed, at least to a first approximation from the mole ratio at the maxima. One can conclude from the analysis of Figure 1 that, for the system A + CP, there is evidence of a complex formation in the molar relation A:CP (1:1). For the other systems we cannot find a molar relation because the maxima do not coincide.

A negative value of V^E indicates strong interactions between the components of the mixture. When the strength of interaction between the components increases, V^E becomes increasingly negative. The minimum value of V^E for these systems can be explained by the strength of the base (*16*) and the stability of the association complex. Stability of the association complex accounts for the relative negative values. The basicity of the anilines decreases in the order: DEA > EA > DMA > MA > A. Examination of Figure 2 indicates that the V^E values at minima follow the order DEA < A < DMA < EA < MA. The observed order for V^E can be explained on the basis of strength of acid–base interaction and the ability to form hydrogen-bonded complexes.

According to Hildebrand (*17*) free volume is necessary for flow and then shrinkage on mixing (which would reduce free volume) should be associated with increase in viscosity. If H is defined as equal to η/η_i where η is the observed viscosity and η_i (ideal viscosity) is calculated according to the equation

$$\ln \eta_i = (X_1 \ln \eta_1 + X_2 \ln \eta_2) \qquad (10)$$

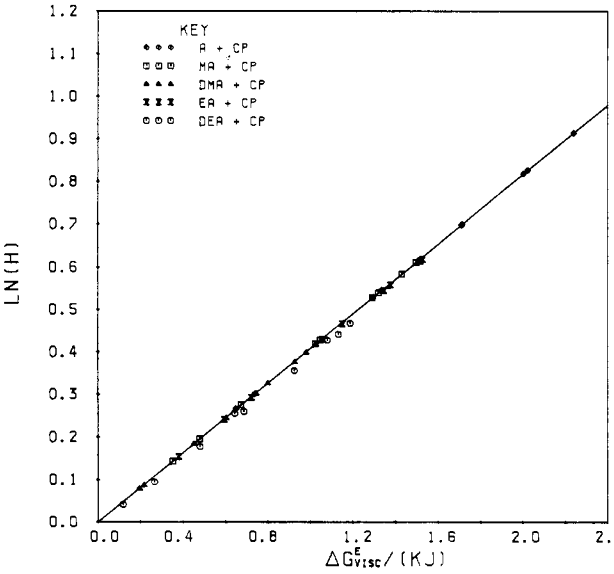

Figure 5. Plot of ln H vs. G^{*E} at 298 K.

then this quantity should be related to free volume according to Stairs (*18*) by the equation

$$H^{-1} = (V_i + V^E)/V_i \qquad (11)$$

where V_i is the ideal free volume that would have existed had there been no shrinkage. However, when H^{-1} is plotted against V^E the plot is nonlinear. In the present study when ln H is plotted against G^{*E} a single straight line is obtained for all the systems (Figure 5). Since G^{*E} takes into account both the variation of molar volume with composition of the solution and explains the viscosity of solutions derived from components of differing size, the observed behavior is not unexpected. Also in all these systems, positive η^E and negative V^E have been observed. The values of ΔH^* for pure compounds are positive, indicating that association and dipole interactions vary in the order A > CP > EA > MA > DEA > DMA. The negative values of ΔS^* for nonassociated liquids, viz., DMA and DEA, indicate that the formation of activated complexes introduces molecular order, while positive values for other components show that the formation of activated complexes in each case

Table X. Excess Activation Parameter for Viscous Flow[a]

system	x_1[a]	ΔH^{*E}	ΔS^{*E}	G^{*E}
aniline + *o*-chlorophenol	0.1032	1.08	1.12	0.75
	0.2004	4.57	1.10	1.30
	0.3011	8.94	24.00	1.72
	0.4069	12.59	35.51	2.00
	0.5008	12.74	35.27	2.23
	0.6002	12.98	36.81	2.01
	0.7016	9.33	25.61	1.70
	0.7852	6.81	18.55	1.28
	0.9025	1.54	3.15	0.60
N-methylaniline + *o*-chlorophenol	0.1013	2.53	7.25	0.37
	0.2024	5.46	15.99	0.69
	0.3005	6.38	17.89	1.05
	0.4032	8.29	23.50	1.29
	0.5007	8.82	24.74	1.45
	0.6027	8.93	25.23	1.41
	0.7000	7.44	20.65	1.28
	0.7936	5.29	14.48	0.97
	0.9042	1.21	2.53	0.46
N,*N*-dimethylaniline + *o*-chlorophenol	0.1002	1.44	4.18	0.19
	0.1990	3.02	9.36	0.23
	0.3025	3.87	10.97	0.60
	0.4016	3.83	10.42	0.73
	0.5020	5.37	14.99	0.90
	0.6009	6.16	17.33	1.00
	0.6991	4.97	13.51	0.95
	0.8000	2.89	7.17	0.75
	0.9019	2.32	6.34	0.43
N-ethylaniline + *o*-chlorophenol	0.1027	1.10	2.44	0.37
	0.2022	3.80	10.38	0.71
	0.3028	6.81	19.07	1.13
	0.4011	7.03	19.30	1.28
	0.5014	9.22	25.98	1.48
	0.6004	9.45	26.74	1.48
	0.7024	8.42	23.80	1.32
	0.7991	6.36	17.92	1.01
	0.8994	3.67	10.46	0.55
N,*N*-diethylaniline + *o*-chlorophenol	0.1000	0.48	1.25	0.11
	0.2015	2.96	4.31	0.25
	0.3033	2.35	6.41	0.44
	0.4011	5.34	15.73	0.65
	0.4970	7.55	22.40	0.88
	0.6026	9.51	28.27	1.08
	0.7000	10.34	30.93	1.12
	0.7988	9.67	29.03	1.02
	0.9003	4.74	13.99	0.58

[a] Mole fraction of *o*-chlorophenol; units: ΔH^{*E}, G^{*E}, kJ·mol^{-1}; ΔS^{*E}, J·mol^{-1}.

involves less order probably due to destruction of H bonds. The values of $\Delta G^{\ddagger}$ depend on the sign and magnitude of the corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and is positive for all systems.

The values of excess activation parameters for the mixtures are positive for each of the binary systems studied and increase with increase in *o*-chlorophenol concentration. Following the conclusion of Reed and Taylor (*19*) and Meyer et al. (*20*), the G^{*E} parameter may be considered as a reliable criterion to detect or exclude the presence of interaction between unlike molecules. According to the authors, positive values and the magnitude are excellent indicators of the strength of specific interactions. G^{*E} values for the system decrease in the order: A + CP > EA + CP > MA + CP > DEA + CP > DMA + CP.

According to Somsen and co-workers (21), better information can be obtained from the shape of partial molar volumes against composition curves. As may be seen in Figure 4, $\bar{V}_1$ show a pronounced decrease starting from the value in pure *o*-chlorophenol with well-defined broad minima for the systems of A + CP, DEA + CPf, and EA + CP at different compositions. These minima are indications of the strength of the interaction between the components. For the other two systems only a slight curvature is observed instead of a minimum. The values of partial molar volume of *o*-chlorophenol at infinite dilution are 99.64 cm^3/mol for A + CP system, 99.82 cm^3/mol for MA + CP system, 100.03 cm^3/mol for DMA + CP system, 100.22 cm^3/mol for EA + CP system, and 100.82 cm^3/mol for DEA + CP system. One can conclude that the addition of 1 mol of *o*-chlorophenol in a large quantity of the different anilines produce volume contraction (ΔV) in the order DEA < EA < DMA < MA < A.

From the analysis of the above thermodynamic quantities and the observed minima in the partial molar volume–composition curves, one can conclude that the strength of interaction in the systems studies follows the order A + CP > EA + CP > MA + CP > DEA + CP > DMA + CP, indicating that the main type of interactions are intermolecular hydrogen bonding and acid–base type.

Glossary

V^E	excess volume
η^E	excess viscosity
G^{*E}	excess molar free energy of activation of flow
ΔH^{*E}	excess molar enthalpy of activation of flow
ΔS^{*E}	excess molar entropy of activation of flow
ρ	density
V	molar volume of the solution
M	molecular mass
X	mole fraction
R	gas constant
σ_x	standard error of estimate
$\Delta H^{\ddagger}$	molar enthalpy of activation of flow
$\Delta S^{\ddagger}$	molar entropy of activation of flow
$\Delta G^{\ddagger}$	molar free energy of activation of flow
h	Planck's constant
N	Avogadro's number
$(V_1^E)_{12}$	partial molar excess volume of 1
$\bar{V}_1$	partial molar volume of 1

Subscripts

i	component in a mixture
E	excess
1, 2	component number in a mixture

Registry No. CP, 95-57-8; A, 62-53-3; MA, 100-61-8; DMA, 121-69-7; EA, 103-69-5; DEA, 91-66-7.

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