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THERMODYNAMIC AND TRANSPORT PROPERTIES OF BINARY LIQUID ACID–BASE MIXTURES. PART 1

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ABSTRACT

Densities and viscosities were determined at five different temperatures for the systems quinoline (Q) with: phenol (P); *ortho*-chlorophenol (CP); and *meta*-cresol (MC). From the experimental results the excess volumes, excess viscosities, partial molar excess volumes and the partial molar volumes were calculated. From the dependency of viscosity on temperature, the thermodynamic parameters of activation of flow were also calculated and these results were discussed in terms of the type of interaction between the two components in solution.

INTRODUCTION

Viscosities of liquid mixtures need to be known for the solution of many problems concerning heat transport, mass transport and fluid flow. Recent interest in coal-derived liquid fuels resulted in many investigations on the strength of interaction between model acids and bases of asphaltenes and subfractions of asphaltenes by IR and NMR methods [1–5]. As part of program dealing with the investigation of phenol amine systems [6,7], this paper deals with the thermodynamic and transport properties of binary mixtures of quinoline with substituted phenols.

EXPERIMENTAL

Densities of pure liquids and their mixtures were determined with an Anton-Paar DMA 45 densitometer with an accuracy in density measurement of ±0.0001 g ml^{-1}. The density measurements at different temperatures were carried out using a Sodev temperatures controller with an accuracy of ±0.001°C.

Viscosity measurements at 25, 30, 35, 40 and 45°C were made using

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modified Ostwald or Cannon-Fenske viscometers and a viscosity bath (Koehler Instrumentation). Viscometers were calibrated against nanopure water and benzene, and the accuracy was found to be ±0.005 cP. All the chemicals used (B.D.H. or Aldrich) were purified by the standard procedures described by Weissberger et al. [8] and colourless middle fractions were collected. All mixtures were prepared by mixing weighed amounts of the pure liquids.

RESULTS AND DISCUSSION

The values of density and viscosity for all systems are presented in Tables 1–3. The density and viscosity values for pure compounds agree well with the literature values. The excess thermodynamic functions were calculated with the following equations

$$\eta^{E} = \eta - (X_1\eta_1 + X_2\eta_2) \tag{1}$$

$$V^{E} = V - (X_1V_1 + X_2V_2) \tag{2}$$

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

where η, η_1, η_2, V, V_1, V_2 are viscosities and molar volumes of the mixture and of the pure components, respectively. The molar volume of the mixture, V, is defined by

$$V = \frac{X_1M_1 + X_2M_2}{\rho} \tag{4}$$

where ρ is the density of the solution, and M_1 and M_2 are the molecular masses of the components. The excess functions were fitted with a Redlich–Kister [9] equation of the type

$$X^{E} = X_1(1 - X_1)\sum_{j=1}^{n} a_j(1 - 2X_1)^{j-1} \tag{5}$$

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

$$\sigma_x = \left[\Sigma\left(X^{E}_{\text{obs}} - X^{E}_{\text{cal}}\right)^2/(n_{\text{obs}} - n)\right]^{1/2} \tag{6}$$

The values adopted for the coefficients a_j were calculated with a Hewlett-Packard 3000 computer (using a program with a built-in F-test and various options) [10], and these, along with the standard error of the estimate, σ, are summarized in Tables 4–6.

Figures 1–3 show the experimental values of η^{E}, V^{E} and $G^{\ddagger E}$ as functions of the mole fraction of quinoline, respectively. The continuous curves were

TABLE 1

Density and viscosity data for the phenol + quinoline system

X_Q	$\rho(\mathrm{g\ cm^{-3}})$					$\eta(\mathrm{cP})$				
	298 K	303 K	308 K	313 K	318 K	289 K	303 K	308 K	313 K	318 K
0.0000	1.0720	1.0676	1.0633	1.0589	1.0545	9.410	7.553	6.106	4.971	4.056
0.1054	1.0778	1.0736	1.0694	1.0651	1.0630	12.704	10.204	8.195	6.728	5.655
0.1999	1.0846	1.0805	1.0763	1.0721	1.0702	17.286	13.094	10.472	8.655	7.159
0.3001	1.0902	1.0862	1.0821	1.0778	1.0761	20.986	15.718	12.403	10.083	8.328
0.4004	1.0936	1.0896	1.0856	1.0814	1.0796	19.771	14.984	11.866	9.694	8.054
0.4996	1.0955	1.0915	1.0875	1.0833	1.0816	14.311	11.026	8.920	7.310	5.886
0.5998	1.0952	1.0913	1.0874	1.0832	1.0815	10.235	8.240	6.902	5.796	4.902
0.6997	1.0935	1.0897	1.0859	1.0817	1.0801	7.295	6.110	5.266	4.553	3.996
0.7997	1.0915	1.0877	1.0838	1.0797	1.0779	5.580	4.797	4.143	3.608	3.172
0.9023	1.0898	1.0858	1.0821	1.0780	1.0763	4.054	3.537	3.095	2.718	2.416
1.0000	1.0891	1.0853	1.0815	1.0773	1.0737	3.475	3.092	2.777	2.489	2.243

TABLE 2

Density and viscosity data for the *meta*-cresol + quinoline system

X_Q	$\rho(\mathrm{g\ cm^{-3}})$					$\eta(\mathrm{cP})$				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	1.0299	1.0260	1.0221	1.0181	1.0141	13.194	9.877	7.599	6.146	4.968
0.0998	1.0402	1.0365	1.0325	1.0286	1.0247	15.259	11.507	8.895	6.912	5.586
0.1980	1.0501	1.0464	1.0424	1.0386	1.0348	19.928	15.034	11.457	8.917	7.128
0.3012	1.0594	1.0556	1.0516	1.0479	1.0441	25.297	19.236	15.095	11.940	9.595
0.3984	1.0670	1.0632	1.0593	1.0554	1.0517	22.873	17.850	14.046	11.421	9.188
0.4984	1.0728	1.0690	1.0650	1.0613	1.0574	15.794	12.711	9.986	8.111	6.608
0.5985	1.0770	1.0733	1.0694	1.0656	1.0618	11.025	8.925	7.269	6.172	5.184
0.6965	1.0803	1.0765	1.0726	1.0688	1.0651	7.376	6.266	5.301	4.512	3.835
0.7980	1.0831	1.0794	1.0755	1.0717	1.0679	5.594	4.872	4.223	3.686	3.204
0.8948	1.0857	1.0819	1.0780	1.0742	1.0704	4.358	3.761	3.291	2.959	2.620
1.0000	1.0891	1.0853	1.0815	1.0773	1.0737	3.475	3.092	2.777	2.489	2.242

TABLE 3

Density and viscosity data for the chlorophenol + quinoline system

X_Q	ρ (g cm^{-3})					η(cP)				
	298 K	303 K	308 K	313 K	318 K	298 K	303 K	308 K	313 K	318 K
0.0000	1.2575	1.2511	1.2452	1.2398	1.2339	3.376	2.927	2.532	2.191	1.947
0.0761	1.2490	1.2440	1.2382	1.2330	1.2275	4.871	4.063	3.469	2.998	2.614
0.1549	1.2414	1.2361	1.2310	1.2258	1.2204	7.882	6.073	5.006	4.205	3.590
0.2343	1.2327	1.2277	1.2225	1.2176	1.2124	11.682	9.042	7.403	6.048	4.979
0.3348	1.2203	1.2156	1.2106	1.2061	1.2006	19.635	14.392	11.490	9.267	7.306
0.4286	1.2064	1.2025	1.1968	1.1920	1.1880	26.303	18.197	14.089	11.034	8.786
0.5274	1.1888	1.1849	1.1804	1.1762	1.1706	21.744	16.116	12.365	9.852	7.927
0.6364	1.1645	1.1601	1.1556	1.1517	1.1466	12.935	10.285	8.401	7.017	5.922
0.7447	1.1400	1.1359	1.1319	1.1273	1.1238	8.205	6.433	5.506	4.762	4.170
0.8898	1.1112	1.1070	1.1031	1.0988	1.0953	4.628	4.058	3.581	3.171	2.824
1.0000	1.0891	1.0853	1.0815	1.0773	1.0737	3.475	3.092	2.777	2.489	2.243

TABLE 4

Coefficients for least-squares fit results by eqn. (5) for excess molar volumes ($cm^3\ mol^{-1}$)

System	Temp. (K)	a_1	a_2	a_3	a_4	a_5	a_6	σ
Phenol +	298	−5.125	−1.424	3.634	1.441			0.018
quinoline	303	−5.212	−1.400	3.667	1.189			0.020
	308	−5.268	−1.389	3.658	1.243			0.017
	313	−5.333	−1.414	3.563	1.329			0.017
	318	−6.169	−1.417	1.842	1.487			0.025
m-Cresol +	298	−4.800	−1.616	2.345	0.8803			0.011
quinoline	303	−4.881	−1.582	2.610	0.6319	−0.7534		0.012
	308	−4.863	−1.572	2.331	0.6189			0.014
	313	−5.032	−1.583	2.115	0.8798			0.0092
	318	−5.075	−1.674	2.168	0.7605			0.0099
o-Chlorophenol +	298	−10.09	−2.873	10.50	−3.514	−10.50	9.436	0.023
quinoline	303	−10.36	−3.228	11.87	−1.636	−12.02	6.647	0.040
	308	−10.34	−2.781	10.91	−4.170	−10.87	9.635	0.061
	313	−10.61	−2.403	11.77	−6.903	−11.77	12.89	0.060
	318	−10.48	−3.665	10.06	−1.498	−10.11	2.979	0.052

TABLE 5

Coefficients for least-squares fit of results by eqn. (5) for excess viscosity (cP)

System	Temp. (K)	a_1	a_2	a_3	a_4	a_5	a_6	σ
Phenol +	298	33.65	94.51	25.25	−189.8	−75.41	126.5	0.40
quinoline	303	24.69	66.59	15.08	−142.5	−46.43	108.9	0.42
	308	19.37	48.55	12.54	−98.74	−37.78	74.12	0.32
	313	15.56	37.73	12.97	−73.22	−34.14	54.28	0.27
	318	12.47	30.62	14.49	−61.69	−31.96	50.06	0.32
m-Cresol +	298	32.98	118.3	32.92	−263.1	−101.2	176.4	0.40
quinoline	303	26.98	89.78	18.25	−213.3	−69.83	154.9	0.35
	308	21.22	70.25	15.27	−178.7	−57.45	138.5	0.31
	313	17.24	54.83	8.039	−146.5	−43.02	113.4	0.53
	318	13.76	42.62	5.886	−114.9	−33.51	89.47	0.45
Chlorophenol +	298	79.41	92.82	−216.3	−308.3	190.3	271.7	0.21
quinoline	303	55.52	54.16	−147.8	−156.8	130.9	122.1	0.16
	308	41.62	41.78	−100.5	−126.8	83.20	103.7	0.14
	313	32.11	30.61	−72.37	−93.92	57.78	78.39	0.13
	318	24.87	20.63	−53.74	−62.36	42.71	152.10	0.10

TABLE 6

Coefficients for least-squares fit of result by eqn. (5) for excess molar free energy of activation of flow (J mol^{-1})

System	Temp. (K)	a_1	a_2	a_3	a_4	a_5	a_6	σ
Phenol + quinoline	298	9227.0	1311.0	1218.0	−25240	−9626.0	21230	42
	303	8503	12500	1621.0	−28170	−9066.0	27850	59
	308	8130	11560	2437	−25020	−10380	25430	61
	313	7865	11290	3697	−23760	−11860	24840	67
	318	7519	11780	6177	−28500	−14780	32880	63
m-Cresol + quinoline	298	8444	14440	404.9	−32820	−11090	25760	62
	303	8387	14300	162.4	−34110	−10660	27910	76
	308	8010	14940	2196	−40120	−14050	36210	80
	313	7799	14730	1649	−41140	−13860	35560	46
	318	7479	14490	1938	−40550	−14090	34920	74
Chlorophenol + quinoline	298	19020	13040	−26800	−33560	24150	32050	43
	303	17360	10070	−24090	−16940	19790	9834	51
	308	16240	10180	−19720	−20680	13920	15050	46
	313	15380	9571	−16900	−20680	10700	16410	26
	318	14460	8312	−15620	−18990	10180	16400	43

obtained with the aid of a Watanabe (Miplot), PET computer and the coefficients in Tables 4–6. The variation of the viscosity of the liquids with temperature can be represented by the equation [11]

$$\eta = \frac{hN}{V} \exp(\Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R) \tag{7}$$

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

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{8}$$

Various parameters were obtained using the least-squares method and are

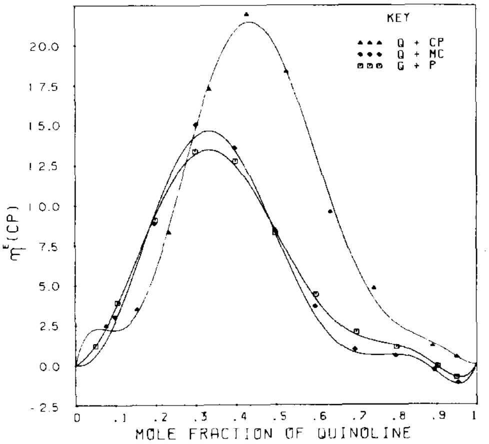

Fig. 1. Plot of excess viscosity vs. mole fraction of quinoline.

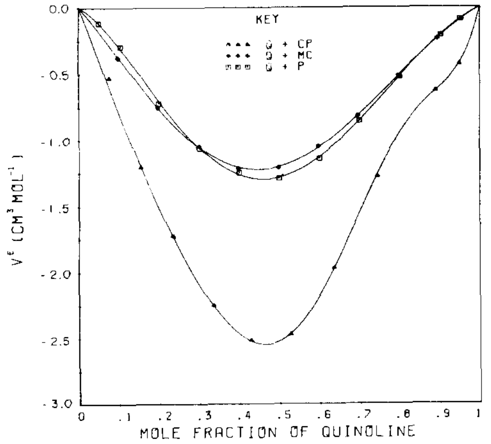

Fig. 2. Plot of excess volume vs. mole fraction of quinoline.

TABLE 7

Activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$ of viscous flow for the phenol + quinoline system

X_Q	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
0.0000	32.47 ± 0.07	45.74 ± 0.22	18.84 ± 0.09
0.1054	31.53 ± 0.54	39.88 ± 1.74	19.65 ± 0.74
0.1999	33.81 ± 1.30	44.90 ± 4.23	20.43 ± 1.81
0.3001	35.64 ± 1.35	49.20 ± 4.40	20.98 ± 1.88
0.4004	34.68 ± 1.27	46.23 ± 4.11	20.91 ± 1.76
0.4996	33.97 ± 0.72	46.18 ± 2.34	20.21 ± 1.00
0.5998	28.25 ± 0.55	29.48 ± 1.79	19.46 ± 0.77
0.6997	23.12 ± 0.50	14.81 ± 1.61	18.71 ± 0.69
0.7997	21.78 ± 0.14	12.24 ± 0.47	18.14 ± 0.20
0.9023	19.96 ± 0.10	8.50 ± 0.31	17.43 ± 0.13
1.0000	16.65 ± 0.07	− 1.55 ± 0.23	17.11 ± 0.10

presented in Tables 7–9. The values of the excess function, $Y^{\ddagger E}$, were calculated by the equation

$$Y^{\ddagger E} = Y^{\ddagger} - \left[X_1 Y_1^{\ddagger} + X_2 Y_2^{\ddagger} \right] \tag{9}$$

where $Y^{\ddagger}$, $Y_1^{\ddagger}$ and $Y_2^{\ddagger}$ are the activation parameters of the mixture and of the pure components, respectively. These are presented in Tables 10–12 and $\Delta G^{\ddagger E}$ is plotted as a function of the mole fraction of quinoline in Fig. 3. A plot of η^E vs. composition (Fig. 1) shows well-marked maxima for all systems. According to Fialkov [12], and Fort and Moore [13], the composition of the intermolecular complexes formed can be fixed at least to a first approximation from the molar relation indicated by the maxima. These complexes are more stable when the positive values of the maxima of η^E are large. The stochiometric relations of the complex formed can be obtained from Fig. 2. They are 2P · Q, 2MC · Q, 3CP · 2Q.

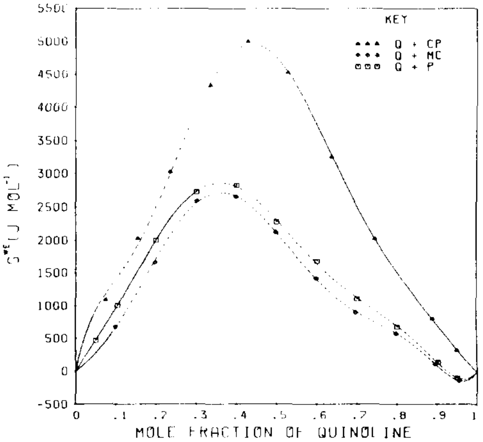

Fig. 3. Plot of excess free energy of activation vs. mole fraction of quinoline.

TABLE 8

Activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$ of viscous flow for the *m*-cresol + quinoline

X_Q	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
0.0000	37.71 ± 1.21	59.21 ± 3.93	20.06 ± 1.68
0.0998	39.14 ± 0.71	62.63 ± 2.30	20.47 ± 0.99
0.1980	40.08 ± 0.63	63.47 ± 2.04	21.16 ± 0.88
0.3012	37.52 ± 0.52	52.82 ± 1.70	21.78 ± 0.73
0.3984	35.23 ± 0.44	45.86 ± 1.42	21.56 ± 0.61
0.4984	33.98 ± 0.40	44.55 ± 1.29	20.70 ± 0.55
0.5985	29.05 ± 0.66	31.01 ± 2.15	19.81 ± 0.92
0.6965	25.22 ± 0.23	21.27 ± 0.76	18.88 ± 0.33
0.7980	21.40 ± 0.22	10.60 ± 0.73	18.24 ± 0.31
0.8984	19.27 ± 0.51	5.54 ± 1.66	17.62 ± 0.71
1.0000	16.65 ± 0.07	− 1.55 ± 0.23	17.11 ± 0.10

TABLE 9

Activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$, of viscous flow for the *o*-chlorophenol + quinoline system

X_Q	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
0.0000	21.20 ± 0.32	15.19 ± 1.03	16.68 ± 0.44
0.0761	23.74 ± 0.55	20.69 ± 1.73	17.57 ± 0.74
0.1549	29.96 ± 0.44	37.66 ± 1.4	18.73 ± 0.61
0.2343	32.58 ± 0.76	43.03 ± 2.46	19.76 ± 1.05
0.3348	37.49 ± 1.26	55.16 ± 4.10	21.05 ± 1.76
0.4286	41.88 ± 0.76	67.52 ± 2.46	21.76 ± 1.05
0.5274	39.00 ± 1.17	59.12 ± 3.79	21.38 ± 1.62
0.6364	30.07 ± 0.77	33.26 ± 2.51	20.16 ± 1.08
0.7447	25.55 ± 0.67	21.86 ± 2.50	19.04 ± 1.00
0.8898	18.89 ± 0.05	3.75 ± 0.17	17.77 ± 0.072
1.0000	16.65 ± 0.07	− 1.55 ± 0.23	17.11 ± 0.090

TABLE 10

Excess activation parameters for viscous flow for the phenol + quinoline system

X_Q	$\Delta H^{\ddagger E}$ (kJ mol^{-1})	$\Delta S^{\ddagger E}$ (J mol^{-1})	$\Delta G^{\ddagger E}$ (kJ mol^{-1})
0.1054	0.73	− 0.88	0.99
0.1991	4.48	8.58	1.92
0.3001	7.92	17.60	2.66
0.4004	8.55	19.40	2.76
0.4996	9.40	24.00	2.23
0.5998	5.27	12.10	1.66
0.6997	1.72	2.14	1.07
0.7997	1.97	4.31	0.68
0.9023	1.76	5.43	0.14

TABLE 11

Excess activation parameters of viscous flow for the *m*-cresol + quinoline system

X_Q	$\Delta H^{\neq E}$ (kJ mol^{-1})	$\Delta S^{\neq E}$ (J mol^{-1})	$\Delta G^{\neq E}$ (kJ mol^{-1})
0.0998	3.53	9.49	0.70
0.1980	6.54	16.30	1.68
0.3012	6.15	11.90	2.60
0.3984	5.91	10.90	2.67
0.4984	6.76	15.60	2.11
0.5985	3.94	8.17	1.51
0.6965	2.18	4.38	0.88
0.7980	0.49	−0.12	0.53
0.8948	0.40	0.69	0.19

TABLE 12

Excess activation parameters for viscous flow for the *o*-chlorophenol + quinoline system

X_Q	$\Delta H^{\neq E}$ (kJ mol^{-1})	$\Delta S^{\neq E}$ (J mol^{-1})	$\Delta G^{\neq E}$ (kJ mol^{-1})
0.0761	2.88	6.77	0.86
0.1549	9.46	25.10	1.99
0.2343	12.45	31.80	2.98
0.3348	17.81	45.50	4.23
0.4286	22.63	59.50	4.90
0.5274	20.20	52.80	4.47
0.6364	11.77	28.70	3.21
0.7546	7.84	19.40	2.06
0.8898	1.73	3.45	0.71

The negative values of V^E in Fig. 2 for all three systems are explained by Prigogine [14] in terms of the different sizes of the molecules, or the dipole–dipole interactions between them. The intermolecular association complex also contributes to these negative values. Since all the chemical species are cyclic in the present investigation the differences in the size of the molecules are not important in the excess molar volume. From the minimum values of V^E for these systems, one can conclude that the acid–base interactions are stronger in CP + Q than in the other two systems.

According to Hildebrand's [15] free volume approach, those systems showing large positive viscosity deviations calculated from expression (1), also tend to show large negative deviations from volume additivity. If the free volume is actually necessary for flow, then shrinkage on mixing, which would appear to reduce the free volume, should be associated with an increase in viscosity. If one defines $H = \eta/\eta_i$ where η is the experimental viscosity and η_i is the calculated value according to the equation

$$\ln \eta_i = X_1 \ln \eta_1 + X_2 \ln \eta_2$$

then this quantity should be related to excess volumes according to Stairs [16]

$$H = V_i/(V_i + V^{\mathrm{E}}) \tag{10}$$

where V_i is the ideal free volume that would have existed had there been no shrinkage. From eqn. (10) one would expect a linear relationship between H^{-1} and V^{E}, however, when H^{-1} is plotted against V^{E}, the plot is nonlinear. Stairs [16] obtained a linear plot for several liquid pairs, when ln H was plotted against Y_1Y_2, where $Y_1 = [1 + (V_2/V_1)^K. (X_1^{-1} - 1)]^{-1}$, $Y_2 = 1 - Y_1$ and K is an adjustable parameter. Instead of using the above approach, in the present study when ln H is plotted against $G^{\ddagger\mathrm{E}}$, a linear plot passing through the origin is obtained for all three systems (Fig. 4). Since $G^{\ddagger\mathrm{E}}$ takes into account both the variation of the molar volume with the composition of the solution, and explains the viscosity of solutions derived from components differing in size, the observed behaviour is not unexpected. A single straight line is obtained for all three systems when $G^{\ddagger\mathrm{E}}$ is plotted against ln H. This is not surprising since in all these systems positive excess viscosities and negative excess volumes have been observed. Analysis of the published viscosity data further substantiates this point [17]. $G^{\ddagger\mathrm{E}}$ values are positive for all three systems (Fig. 3). Following the conclusion of Reed and Taylor [18] and Meyer et al. [19] the $G^{\ddagger\mathrm{E}}$ parameter may be considered a reliable criterion to detect, or to exclude the presence of interactions between unlike molecules. According to these authors, positive values of $G^{\ddagger\mathrm{E}}$ can be seen in binary systems where specific interactions between unlike molecules take place. The magnitudes of these values are excellent indicators of the strengths of specific interactions. $G^{\ddagger\mathrm{E}}$ values for the three systems increase in the order CP + Q > P + Q > MC + Q. The $G^{\ddagger\mathrm{E}}$ values for P + Q are found to be higher than those of the MC + Q system. This situation is the reverse of that

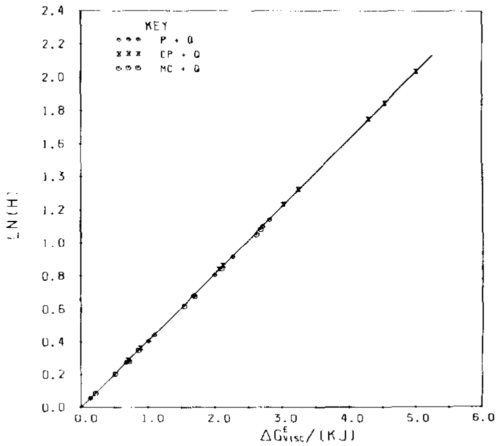

Fig. 4. Plot of ln H vs. $G^{*\mathrm{E}}_{\mathrm{visc}}$.

observed in Fig. 1 for η^E values. This could be explained considering that $G^{\ddagger E}$ represents the influence of η and V simultaneously [18]. The greater contraction for the P + Q system is compensated by its lesser excess viscosity when compared with the MC + Q system.

Partial molar excess volumes were calculated from the equation

$$(V_1^E)_{1,2} = (V^E)_{1,2} + (1 - X_1)\left[\frac{\partial (V^E)_{1,2}}{\partial X_1}\right]_{P,T} \tag{11}$$

Partial molar excess volumes thus obtained (Fig. 5) are used to calculate the partial molar volumes of the components (Figs. 6 and 7) by adding together the molar volumes, V_i^*, of the pure component and the partial molar excess volume, V_i^E. From the analysis of Fig. 6 we may conclude that the addition

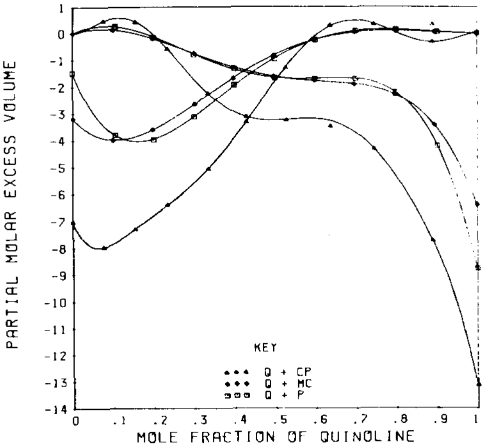

Fig. 5. Plot of partial molar excess volume vs. mole fraction of quinoline.

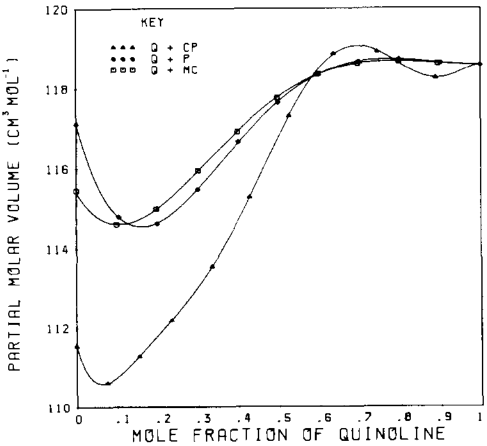

Fig. 6. Plot of partial molar volume of quinoline in solution vs. mole fraction of quinoline.

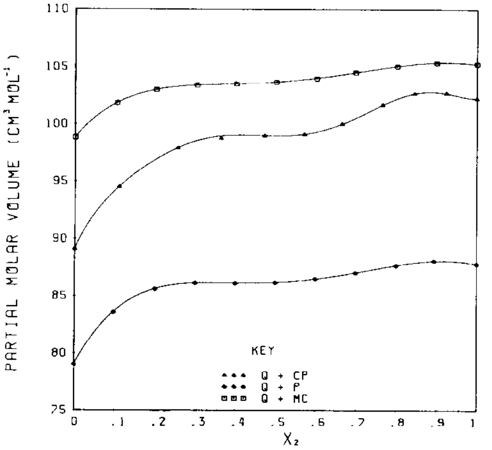

Fig. 7. Plot of partial molar volumes of phenols in solution vs. mole fraction of phenols.

of 1 mol of quinoline in a large volume of the different phenols produces a volume contraction in the order phenol < *meta*-cresol < *ortho*-chlorophenol.

From these observations one can infer that the strength of interactions increases in the following order: *ortho*-chlorophenol + quinoline > phenol + quinoline > *meta*-cresol + quinoline. Since the pK_a values of these phenols increase [20] in the order: *meta*-cresol > phenol > *ortho*-chlorophenol, one can expect the strength of acid–base interactions between quinoline (base) and phenols (acid) to increase in the order: *ortho*-chlorophenol + quinoline > phenol + quinoline > *meta*-cresol + quinoline.

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