Thermochimica Acta, 30 (1979) 384–390

Note

Solid – liquid phase diagrams and X-ray diffraction studies on mixtures. I.

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(Received 29 June 1978)

Present emphasis on energy research has led to increased interest in the nature of coal-derived asphaltenes which are constituents of coal liquefaction products[1]. Asphaltenes essentially possess an acid–base structure[2] and recent spectroscopic[3] and calorimetric[4] studies involving model compounds have shown that the separate acid and base components can interact with each other through the formation of hydrogen bonded complexes. As part of a program dealing with solid–liquid equilibria studies involving model compounds of asphaltenes, we report here the preliminary investigations dealing with the phase diagrams of simple phenols (acid) with wide variety of basic compounds.

EXPERIMENTAL

Materials

All chemicals used were supplied by either Aldrich or B.D.H. and were purified by fractional crystallization from ether–petroleum ether mixtures and dried under vacuum. The purity of the samples was checked by determining the melting temperatures and by thin layer chromatography[5, 6].

Procedure

Physical mixtures of different systems were prepared by careful weighing and then fused. The fused mixtures were ground to a very fine powder in an agate mortar.

All the heating–cooling curves were obtained with a Perkin-Elmer DSC-1 differential scanning calorimeter. Measurements were made with sealed aluminum sample pans supplied by Perkin-Elmer in order to prevent any volatile materials escaping and thereby changing the composition of the mixtures during the course of a run. Each run was repeated at least three times and it was found that the observed melting temperatures were highly reproducible. Samples of lead, indium and tin, supplied by Perkin-Elmer were used to calibrate the DSC unit which was further

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checked by using Thermetric Standards T-421 supplied by Fisher Scientific Company. Measurements were made with the heating rate ranging from 2.5 to 5.0°C min^{-1} and the range selection on the DSC varied from 8 to 4. All measurements were carried out with grade L nitrogen flushing through the DSC unit at a rate of 30 ml min^{-1}.

The heats of fusion of these complexes were determined as described in the DSC instructional manual using tin and indium as standards. The standards used were Calorimetric Standards (C-630) supplied by Fisher Scientific Company and were 99.999% pure. The areas of the curves were measured with a planimeter supplied

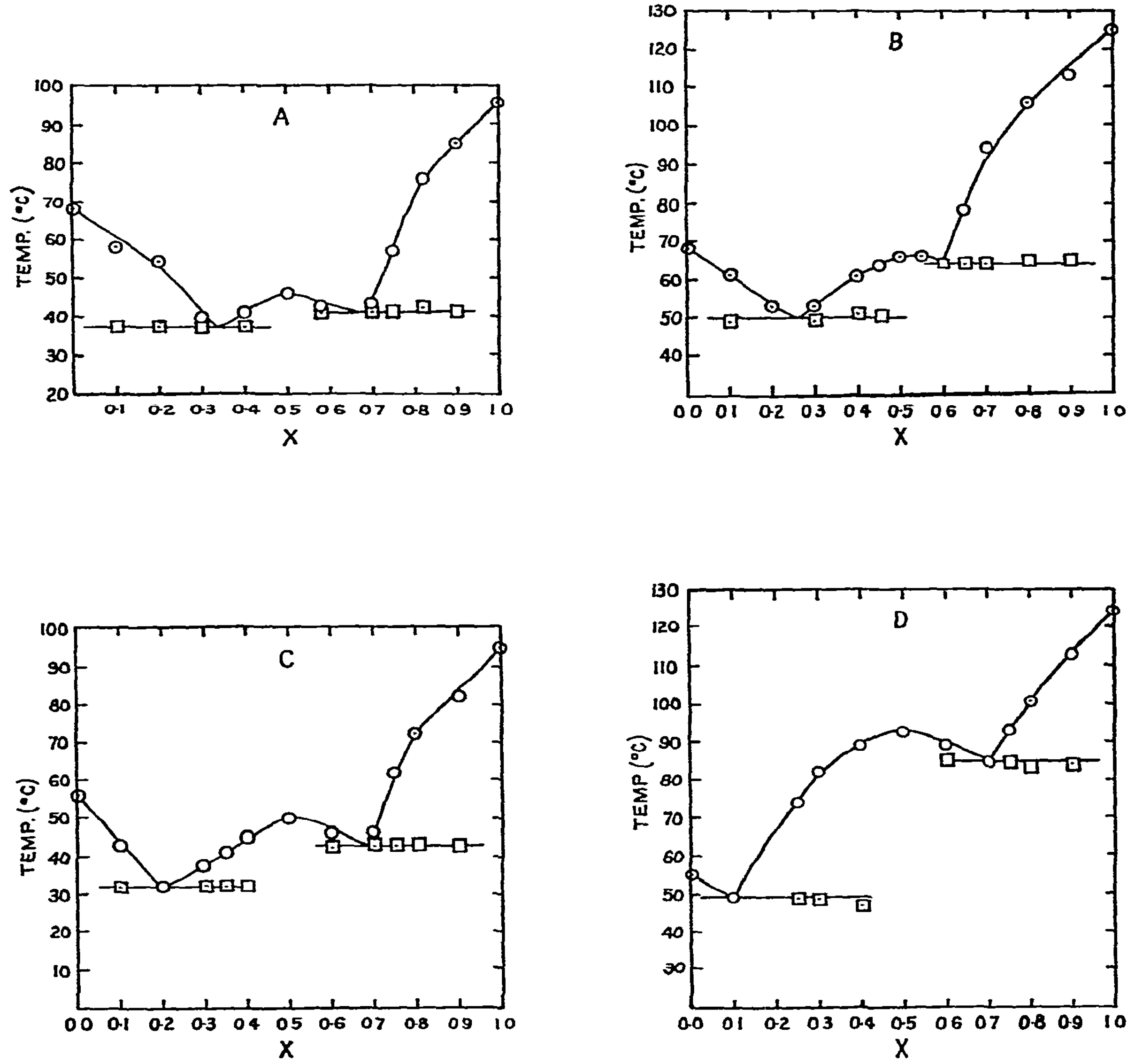

Fig. 1. Plots of melting temperatures against mole fraction x of A, x α-naphthol + $(1 - x)$ p-chloroaniline; B, x β-naphthol + $(1 - x)$ p-chloroaniline; C, x α-naphthol + $(1 - x)$ p-anisidine; D, x β-naphthol + $(1 - x)$ p-anisidine.

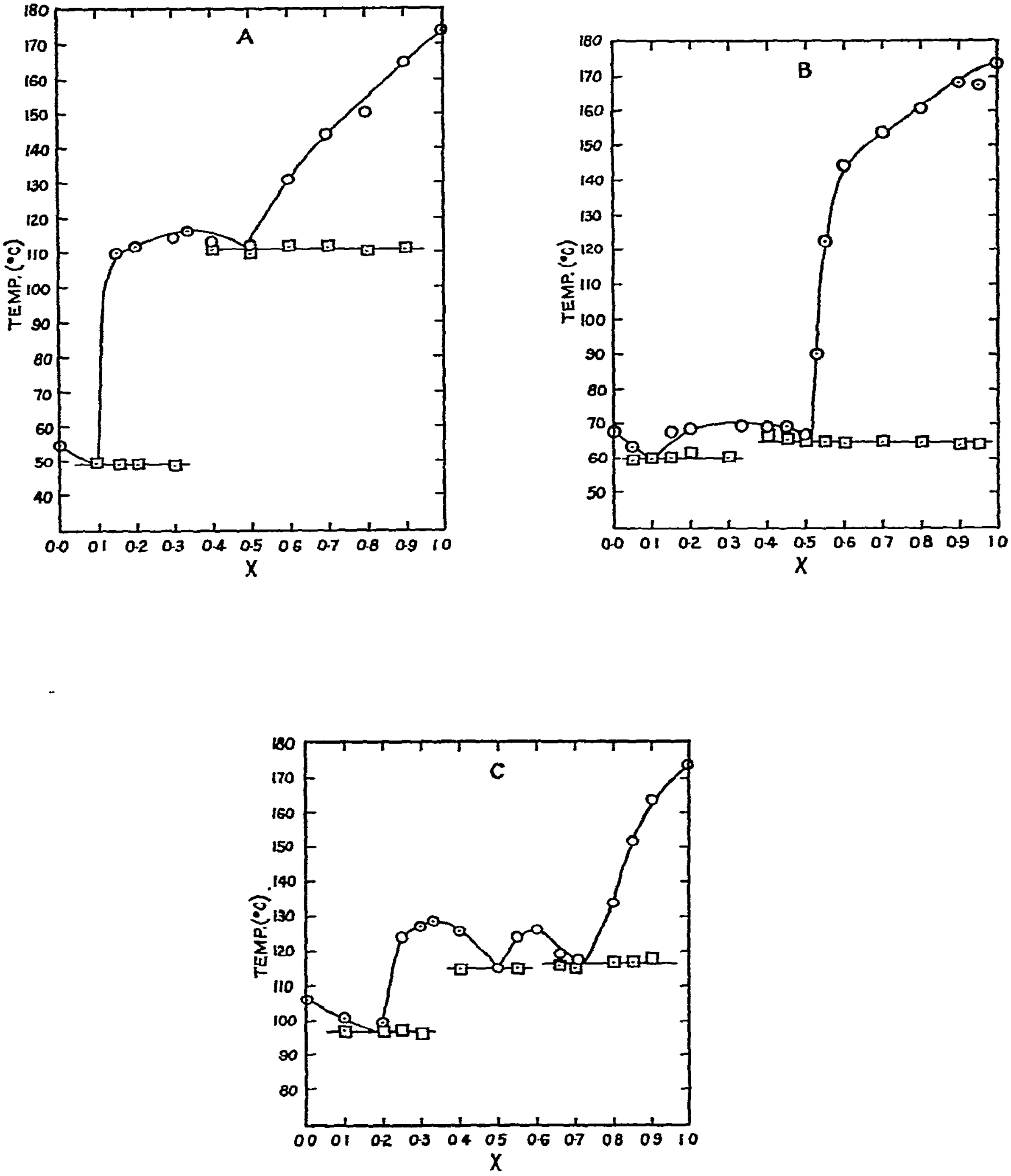

Fig. 2. Plots of melting temperatures against mole fraction x of A, x hydroquinone + $(1 - x)$ *p*-anisidine; B, x hydroquinone + $(1 - x)$ *p*-chloroaniline; C, x hydroquinone + $(1 - x)$ antipyrine.

by K. Hattori and Co. Ltd. Pan and sample weighings were made with a Cahn G-2 electrobalance.

X-Ray diffraction traces of the samples were recorded on a Norelco X-ray diffraction unit using CuK_α radiation[7].

RESULTS AND DISCUSSION

Solid and liquid equilibrium results for the various systems are plotted in Figs. 1–3.

It is evident from the analysis of Figs. 1–3 that mixtures of α- and β-naphthols and hydroquinone with *p*-chloroaniline and *p*-anisidine form congruent melting type phase diagrams indicating the formation of complexes in the solid phase in these mixtures. *p*-Nitroaniline forms a simple eutectic diagram with hydroquinone and *p*-nitrophenol. The phase diagram of the hydroquinone–antipyrine system indicates the formation of two compounds in the solid phase. The number, formula and melting temperature of the complexes determined from the phase diagrams are presented in Table 1 along with heats of fusion.

Compound formation in these systems was further confirmed by X-ray diffraction studies and the results are presented in Fig. 4 and Table 2.

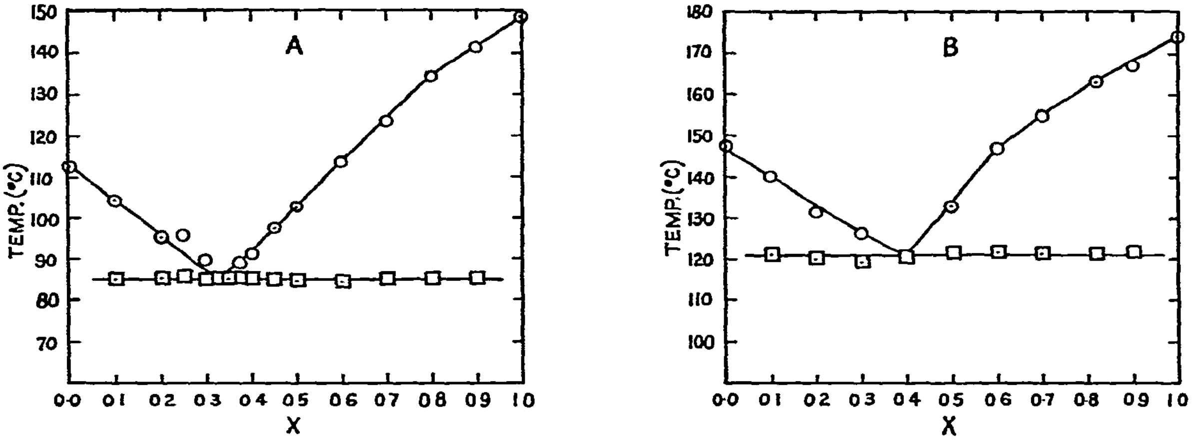

Fig. 3. Plots of melting temperatures against mole fraction x of A, x *p*-nitrophenol + $(1 - x)$ *p*-nitroaniline; B, x hydroquinone + $(1 - x)$ *p*-nitroaniline.

TABLE 1

TYPE, MELTING TEMPERATURE (T_m), HEAT OF FUSION (L_f) OF THE COMPLEX

System	*Type of complex*	T_m *(K)*	L_f *(cal/g)**
α-Naphthol + *p*-chloroaniline	1/1	318.85	30.75 ± 0.47
α-Naphthol + *p*-anisidine	1/1	323.15	36.76 ± 0.57
β-Naphthol + *p*-chloroaniline	1/1	339.15	23.86 ± 0.35
β-Naphthol + *p*-anisidine	1/1	365.65	45.15 ± 0.42
Hydroquinone + *p*-chloroaniline	1/2	343.15	25.08 ± 0.62
Hydroquinone + *p*-anisidine	1/2	389.15	55.48 ± 0.32
Hydroquinone + antipyrine	1/2	401.65	32.30 ± 0.44
Hydroquinone + antipyrine	3/2	399.15	30.45 ± 0.59

* L_f values are given with their average deviation. Each run was made at least four times.

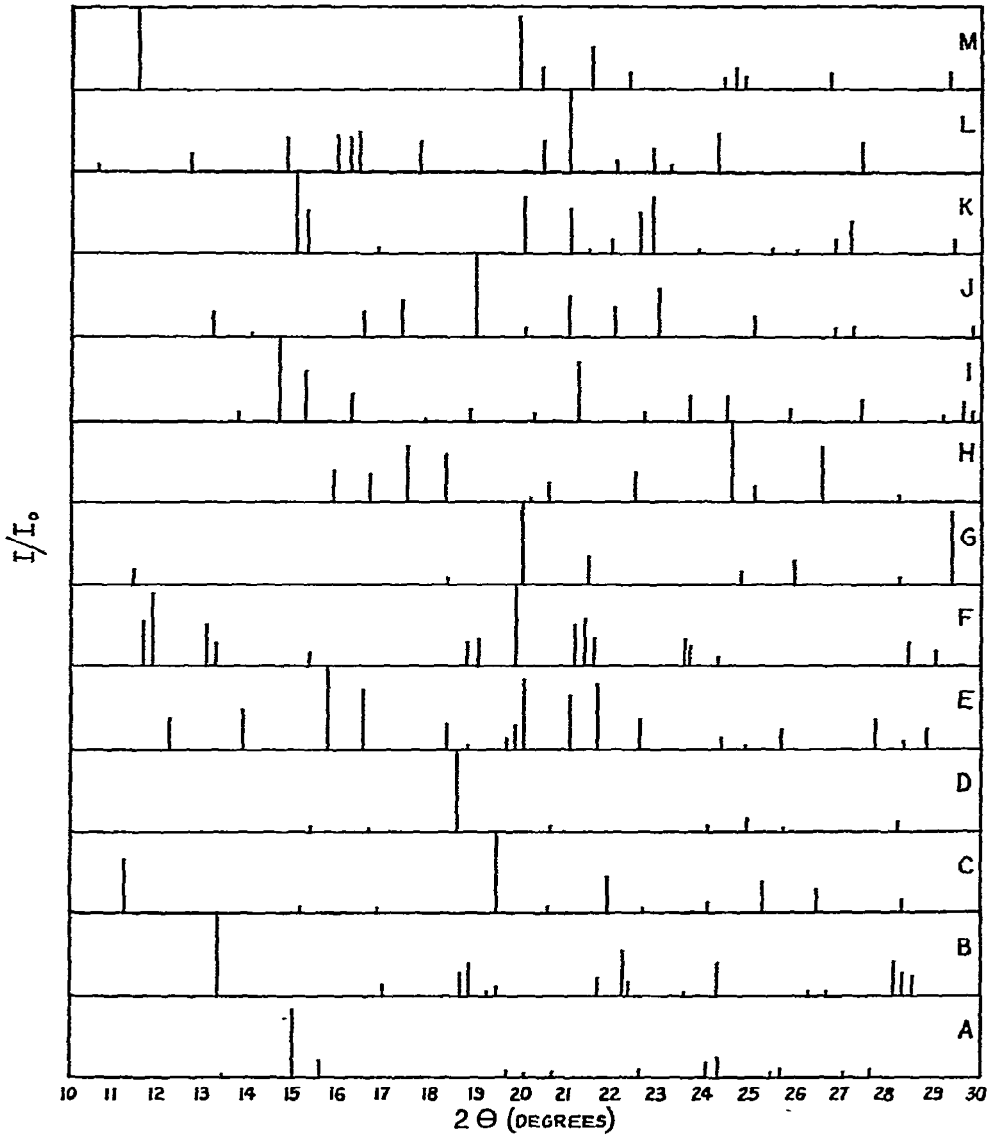

Fig. 4. X-Ray diffraction patterns of A, α-naphthol; B, *p*-anisidine; C, β-naphthol; D, *p*-chloroaniline; E, hydroquinone; F, antipyrine; G, β-naphthol-*p*-chloroaniline; H, hydroquinone-2 *p*-chloroaniline; I, α-naphthol-*p*-chloroaniline; J, 2 anipyrine-3 hydroquinone; K, α-naphthol-*p*-anisidine; L, hydroquinone-2 antipyrine; M, β-naphthol-*p*-anisidine.

The phase diagram of the antipyrine–hydroquinone system differs slightly from the previously reported one[8] in the melting and eutectic temperatures. However, the X-ray diffraction studies of the compounds formed in this system agree very well with the previous studies[8].

The heat of fusion of the addition compound A_xB_y formed between the species A and B can be estimated from the freezing curve between the two eutectic temperatures

$$\frac{1}{T} - \frac{1}{T_c} = -\frac{R}{L_f} \ln (X_A)^x (X_B)^y + \frac{R}{L_f} \ln (X_A)^x_c (X_B)^y_c$$

TABLE 2

X-RAY DIFFRACTION DATA OF THE COMPLEXES*

1		*2*		*3*		*4*		*5*		*6*	
2θ	I/I_0	2θ	I/I_0	2θ	I/I_0	2θ	I/I_0	2θ	I/I_0	2θ	I/I_0
11.50	100	15.05	100	13.70	11	11.40	26	12.20	100	15.80	39
19.90	90	15.24	55	14.62	100	18.30	11	20.00	92	16.60	35
20.40	29	16.80	8	15.19	61	19.95	100	20.41	13	17.40	68
21.48	51	20.00	70	16 22	34	21.40	40	21.16	39	18.25	58
22.30	20	21.00	55	17.80	3	24.75	21	21.83	53	20.10	6
24.35	15	21.41	5	18.80	15	25.95	29	22.61	21	20.50	26
24.60	25	21.90	20	20.20	7	28.20	14	24.06	45	22.38	36
24.80	14	22.55	50	21.18	71	29.35	89	26.50	13	24.50	100
26.68	20	22.80	70	22.60	9	30.90	14	27.60	34	25.00	19
29.30	21	23.80	5	23.60	31	31.80	14	27.95	13	26.50	68
33.70	4	25.40	7	24.40	30	34.00	21	29.40	26	28 20	7
33.90	4	25.95	5	25.80	11	36.80	31	31.60	13	30.40	36
		26.80	20	27.40	26			33.30	13	31.40	10
		27.14	40	29.16	5			37.40	8	32.42	25
		29.40	20	29.60	21			38.25	8	33.50	13
		30.36	30	29.80	13			41.95	21	36.56	7
		32.00	8	34.62	12						
		33.80	10								
		34.75	5								

* 1, *p*-Anisidine–β-naphthol; 2, *p*-anisidine–α-naphthol; 3, *p*-chloroaniline–α-naphthol; 4, *p*-chloroaniline–β-naphthol; 5, hydroquinone–2 *p*-anisidine; 6, hydroquinone–2 *p*-chloroaniline.

where L_f is the heat of fusion of the addition compound, T_c its melting temperature, X_A and $(X_A)_c$ are the mole fractions of the species at the temperatures T and T_c, and x and y are integers. The plots of $1/T - 1/T_c$ vs. $-\ln (X_A)^x (X_B)^y$ showed large scattering from linearity indicating that these mixtures are far from being ideal[9]. In all these systems, the complex formation is mainly due to hydrogen bonding and the nature of these complexes is being further investigated in solution by various spectroscopic methods[10].

ACKNOWLEDGEMENT

The authors wish to express their appreciation to Dr. D. F. Arseneau, Director of Bras d'Or Institute, Sydney, for providing DSC equipment and summer research stipend to L.M. They also wish to thank Dr. E. A. Secco of St. F.X. University, Antigonish for providing X-ray facilities and N.R.C. for the generous financial support.

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