

$\epsilon\gamma_{\pm}$ = mean molal activity coefficient of HBr in the solvent referred to solvent standard state
 $\Delta G^{\circ}_t, \Delta H^{\circ}_t, \Delta S^{\circ}_t$ = free energies, enthalpies, and entropies of transfer on mole fraction scale, J
 $\Delta G^{\circ}_{t(\text{el})}$ = electrostatic Gibbs free energy of transfer, J
 $\Delta G^{\circ}_{t(\text{none})}$ = nonelectrostatic Gibbs free energy of transfer, J
 $\Delta G^{\circ}_{t(c)}$ = standard Gibbs free energy of transfer on molarity scale, J
 $\log_m \gamma_{\pm}$ = primary medium effect
 ϕ_w = volume fraction of water
 $K_s = 2R/F \ln(1000/M_{xy})$
 $K_w = 2R/F \ln(1000/18.0154)$

Literature Cited

- (1) Banerjee, S. K., Kundu, K. K., Das, M. N., *J. Chem. Soc.*, 161 (1967).
- (2) Bax, D., Deligny, C. L., Alfenaar, M., Mohr, W. J., *Recl. Trav. Chim. Pays-Bas*, **91**, 601 (1972).
- (3) Feakins, D., Watson, P., *J. Chem. Soc.*, 4686 (1963).
- (4) Feakins, D., Voice, P. J., *J. Chem. Soc., Faraday Trans.*, **68**, 1390 (1972).
- (5) Feakins, D., French, C. M., *J. Chem. Soc.*, 2581 (1957).
- (6) Franks, F., Ives, D. J. G., *Q. Rev., Chem. Soc.*, **20**, 1 (1966).
- (7) Hills, G. J., Ives, D. J. G., "Reference Electrodes", D. J. G. Ives and G. J. Janz, Ed., Academic Press, New York, N.Y., 1961, p 190.
- (8) Kalidas, C., Srinivas Rao, V., *J. Chem. Eng. Data*, **19**, 201 (1974).
- (9) Mussini, T., Formara, C. M., Andriago, P., *J. Electroanal. Chem.*, **33**, 189 (1971).
- (10) Popovych, O., *Crit. Rev. Anal. Chem.*, **1**, 1 (1970).
- (11) Srinivas Rao, V., Kalidas, C., *Indian J. Chem.*, in press.

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Solid + Liquid Phase Equilibria in Binary Mixtures of *N,N*-Dimethylformamide with Halobenzenes

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Solid-liquid phase diagrams have been obtained from time-temperature cooling and warming curves for the four binary systems formed from *N,N*-dimethylformamide with C_6H_5Cl , C_6H_5Br , $p-C_6H_4Cl_2$, and $p-C_6H_4Br_2$. All four are simple eutectic systems. The two solid-state phase transitions in $p-C_6H_4Cl_2$ were observed, and a solid phase transition at about 194 ± 3 K is reported for $p-C_6H_4F_2$.

During the course of a long-range investigation of molecular addition compound formation, the solid-liquid phase diagrams for four binary systems consisting of *N,N*-dimethylformamide (DMF) with C_6H_5Cl , C_6H_5Br , $p-C_6H_4Cl_2$, and $p-C_6H_4Br_2$ were obtained at 1 atm pressure and over the entire range of composition. These data are reported here. Efforts were made to measure the data with a degree of accuracy that would allow their use in thermodynamic calculations. Combined with other thermal data, they can, for example, be used to calculate activity coefficients (5).

Experimental Section

Chemicals. Starting materials were all Aldrich reagent grade. The DMF, C_6H_5Cl , and C_6H_5Br were further purified by distillation in a 100-cm vacuum-jacketed distillation column packed with glass helices and operated at a reflux ratio of 50:1. The center third cut was retained for the experimental measurements. The $p-C_6H_4Cl_2$ and $p-C_6H_4Br_2$ were purified by melting and recrystallization. The first and last 20% of the sample to crystallize were discarded. Calculations of the change in melting point as a function of the fraction melted showed the following mole percent liquid soluble, but solid insoluble, impurities present: C_6H_5Cl , 0.13; C_6H_5Br , 0.01; $p-C_6H_4Cl_2$, 0.06; and $p-C_6H_4Br_2$, 0.04. All of the systems except DMF + C_6H_5Br were studied immediately after purification of the DMF with the impurity level in the DMF at 0.04 mol %. The DMF + C_6H_5Br system was studied almost a year later. The C_6H_5Br showed no increase in impurity. However, the impurities in the DMF had increased to 0.22 mol %.

Apparatus, Temperature Scale, and Accuracy of Measurements. The freezing point apparatus has been described previously (4). Temperatures were measured with a platinum resistance thermometer which had been calibrated by Leeds and Northrup Co. at the normal boiling temperature of oxygen, the triple point temperature of water, and at the normal melting temperatures of tin and zinc. We checked the calibrations at the beginning and end of the measurements, at the ice point (273.150 K), the mercury freezing point (234.29 K), and the sodium sulfate decahydrate transition temperature (305.534 K). Agreement within 0.01 K between these data and the Leeds and Northrup calibration leads us to believe that our temperature scale is accurate to within ± 0.03 K over the temperature range covered.

Melting temperatures were generally obtained from time-temperature warming curves. When supercooling was not excessive, cooling curves were also used. Freezing and melting temperatures generally agreed to within ± 0.03 K. The freezing points of the solutions are estimated to be well within 0.1 K.

Samples were prepared by weighing the components to ± 0.1 mg. Transfer of chemicals was made with hypodermic syringes to reduce evaporation or contamination of the sample.

Results and Discussion

Table I summarizes the freezing point data for the four systems, and Figures 1-4 are the phase diagrams. The eutectic points are as follows: C_6H_5Cl + DMF, 0.611 mol fraction of DMF and 192.59 K; C_6H_5Br + DMF, 0.690 mol fraction of DMF and 197.82 K; $p-C_6H_4Cl_2$ + DMF, 0.966 mol fraction of DMF and 211.28 K; $p-C_6H_4Br_2$ + DMF, 0.985 mol fraction of DMF and 212.15 K.

The dotted lines in Figures 1 and 2 are the predicted freezing points assuming ideal solution behavior. The freezing curves for chlorobenzene and bromobenzene were calculated assuming that ΔC_p of fusion is constant with temperature, and, hence, ΔH of fusion varies linearly with temperature. The procedure for making the calculations is described in more detail in an earlier paper (6). For DMF, the freezing curves were calculated as-

Table I. Freezing Points^a

Mole fraction of DMF	Freezing point, K	Mole fraction of DMF	Freezing point, K	Mole fraction of DMF	Freezing point, K
Chlorobenzene + <i>N,N</i> -Dimethylformamide					
0.0000	227.83 ^b	0.3858	210.21	0.7810	202.77
0.1092	223.41	0.5197	201.16	0.8919	208.04
0.2172	218.78	0.5953	194.31	1.0000	212.71 ^b
0.3128	214.17	0.6792	197.07		
Bromobenzene + <i>N,N</i> -Dimethylformamide					
0.0000	242.42 ^b	0.4010	223.46	0.7863	202.93
0.1161	237.54	0.5094	216.01	0.8894	207.75
0.2206	232.86	0.6152	206.98	1.0000	212.71 ^b
0.2932	229.35	0.7112	198.98		
<i>p</i> -Dichlorobenzene + <i>N,N</i> -Dimethylformamide					
0.0000	326.25 ^b	0.3368	310.21	0.9476	226.05
0.1343	320.14	0.4405	303.79	0.9627	216.37
0.2279	315.84	0.5009	299.65	0.9730	211.57
0.2547	314.50	0.6136	290.11	0.9870	212.12
0.2872	312.84	0.7326	276.89	1.0000	212.71 ^b
0.3018	312.05	0.7987	267.02		
0.3315	310.45	0.9011	244.61		
<i>p</i> -Dibromobenzene + <i>N,N</i> -Dimethylformamide					
0.0000	360.60 ^b	0.5188	333.36	0.9754	236.52
0.0971	355.90	0.5933	327.94	0.9897	212.29
0.2168	350.35	0.6852	319.43	1.0000	212.71 ^b
0.3292	344.62	0.8157	301.61		
0.3883	341.46	0.9009	281.08		

^a 0 °C = 273.150 K. ^b Corrected to zero percent impurity.

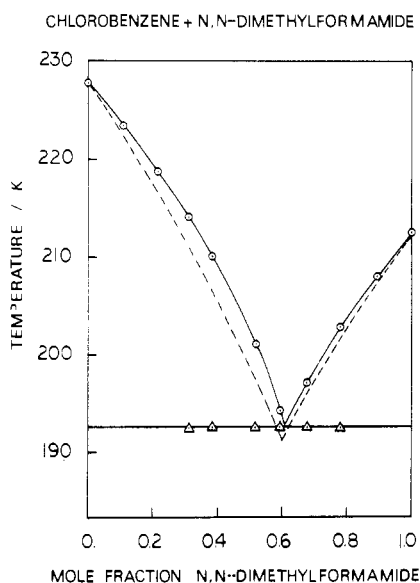


Figure 1. Solid + liquid phase equilibria for chlorobenzene + *N,N*-dimethylformamide: O, melting temperature; Δ, eutectic temperature. The dotted lines give the predicted freezing curves assuming ideal solution behavior.

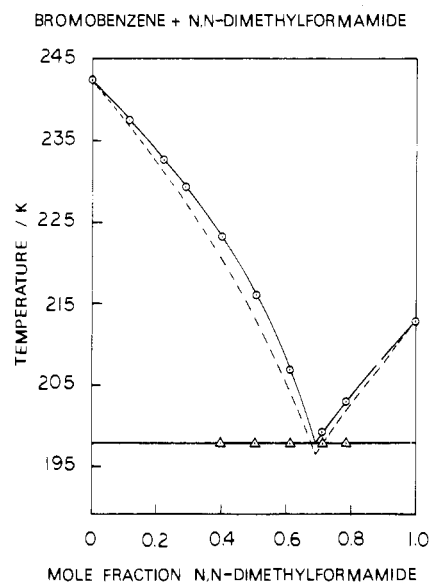


Figure 2. Solid + liquid phase equilibria for bromobenzene + *N,N*-dimethylformamide: O, melting temperature; Δ, eutectic temperature. The dotted lines give the predicted freezing curves assuming ideal solution behavior.

suming ΔH of fusion is constant with temperature since reliable heat capacity data are not available for DMF. Over the more narrow freezing range for DMF, the assumption of constant ΔH of fusion does not seem unreasonable.

A comparison of the experimental and calculated values indicates positive deviations from Raoult's law over the entire composition range for both systems, which suggests that strong intermolecular interactions such as charge transfer are not present.

The freezing point of pure *p*-C₆H₄Cl₂ obtained in this study

agrees exactly with the literature (2). Our value for C₆H₅Br is 0.11 K higher than ref 2 and 0.06 K lower than the earlier work of Stull (7). Our value for the freezing point of *p*-C₆H₄Br₂ is 0.15 K higher than the 1940 work of Deffet (1). The largest discrepancy occurs with C₆H₅Cl, the freezing point obtained in this study being 0.26 K higher than ref 2, and closer to (0.06 K lower) the earlier work of Stull (7).

The solid phase transitions that exist in *p*-C₆H₄Cl₂ are evident. They show up in the cooling curves as halts that become longer in length as the mole fraction of *p*-C₆H₄Cl₂ increases. These are

P-DICHLOROBENZENE + N,N-DIMETHYLFORMAMIDE

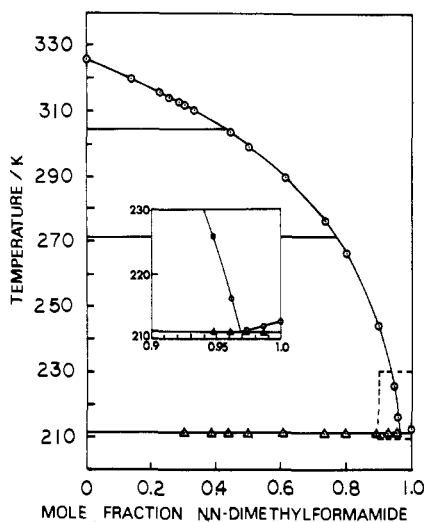


Figure 3. Solid + liquid phase equilibria for *p*-dichlorobenzene + *N,N*-dimethylformamide: O, melting temperature; Δ, eutectic temperature.

P-DIBROMOBENZENE + N,N-DIMETHYLFORMAMIDE

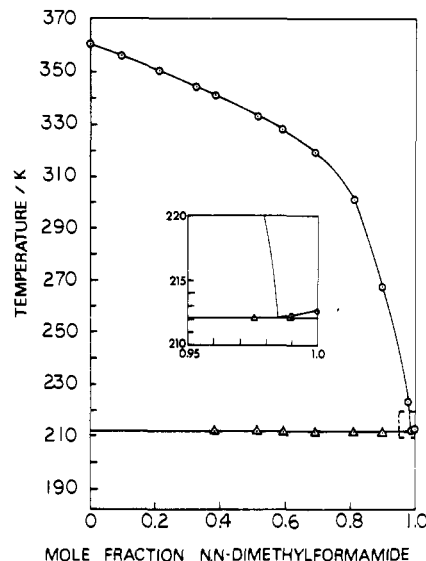


Figure 4. Solid + liquid phase equilibria for *p*-dibromobenzene + *N,N*-dimethylformamide: O, melting temperature; Δ, eutectic temperature.

sluggish, low energy transformations that are difficult to bring into equilibrium in our time-temperature apparatus, but they have been recently studied calorimetrically by Dworkin et al. (3), and it is their values of 271.77 and 304.35 K that are plotted in Figure 3.

Sufficient exploratory work was done on binary mixtures of DMF with C_6H_5F and $p-C_6H_4F_2$ to ascertain that these systems are also simple eutectic systems. Finding a single eutectic at the same temperature at mole fractions 0.30, 0.50, and 0.70 with no other invariant points present was considered evidence of the lack of compound formation in solutions of composition between 1:2 to 2:1.

In the course of making these measurements a phase transition in $p-C_6H_4F_2$ was observed, both in the pure material and in the mixtures. In our time-temperature apparatus, the low temperature form appears when the temperature is lowered to 191 K, and converts to the high temperature form when the

temperature is raised to 197 K. To establish the equilibrium transition temperature, which is somewhere between these two values, would require a calorimetric study.

Literature Cited

- (1) Deffet, L., *Bull. Soc. Chim. Belg.*, **49**, 223 (1940).
- (2) Dreisbach, R. R., *Adv. Chem. Ser.*, No. 15, 134-150 (1955).
- (3) Dworkin, A., Figuiere, P., Ghelfenstein, M., Szwarc, H. Quatrieme Conference Internationale de Thermodynamique Chimique, 1975.
- (4) Goates, J. R., Ott, J. B., Budge, A. H., *J. Phys. Chem.*, **65**, 2162 (1961).
- (5) Goates, J. R., Sullivan, R. J., *J. Phys. Chem.*, **62**, 188 (1958).
- (6) Shirts, R. B., Goates, J. R., Ott, J. B., *J. Chem. Thermodyn.*, **6**, 493 (1974).
- (7) Stull, D. R., *J. Am. Chem. Soc.*, **59**, 2726 (1937).

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