of the hexane-hexene system, and for the hexane-2M-1 pentane system if more than about 0.85 mole fraction of DMF were used, but would be relatively ineffective in separating the C_6 isomeric olefins studied in this investigation. The similarity in the behavior of the three systems seems to indicate that the enhancement of the selectivity results almost entirely from the interactions of DMF with the olefin bond. The highest selectivity was found in the hexane–2M1P–DMF system; 2M1P has the smallest molar volume (124 cc. per mole) and has the methyl group located adjacent to the double bond. The selectivity for 4M1P (128 cc. per mole) is slightly larger than that for hexane-1 (126 cc. per mole) even though hexene-1 has a slightly smaller molar volume. Thus, the position of the methyl group must have a slight effect on the interaction and the related selectivity.

The selectivity and relative volatility are lower at the higher pressure for all systems studied, as would be expected, since the equilibrium temperature was increased about 15° C.

ACKNOWLEDGMENT

Assistance in the form of a traineeship by the National Aeronautics and Space Administration is gratefully acknowledged by the authors.

LITERATURE CITED

(1) Delzenne, A., *Chem. Eng. Sci.* **2**, 220 (1953).
(2) Dreisbach, R.R., *Advan. Chem. Ser.* **29**, 11-74 (1961).
(3) Houser, H.F., Van Winkle, M., IND. ENG. CHEM., CHEM. ENG. DATA SER. **2**, 12 (1957).
(4) Jones, C.A., Schoenborn, E.M., Colburn, A.P., *Ind. Eng Chem.* **35**, 666 (1943).
(5) Lyvers, H.J., Van Winkle, M., IND. ENG. CHEM., CHEM. ENG. DATA SER. **3**, 60 (1958).
(6) McMakin, L.E., Van Winkle, M., J. CHEM. ENG. DATA **7**, 9 (1962).
(7) Murti, P.S., Van Winkle, M., IND. CHEM., CHEM. ENG. DATA SER. **3**, 72 (1958).
(8) Prabhu, P.S., Van Winkle, M., J. CHEM. ENG. DATA **8**, 14 (1963).
(9) Qozati, A., Van Winkle, M., *Ibid.*, **5**, 269 (1960).
(10) Schuhmacher, J.P., Wibaut, J.P., *Rec. Trav. Chim.* **72**, 1037 (1958).
(11) Stephenson, R.W., Van Winkle, M., J. CHEM. ENG. DATA **7**, 510 (1962).
(12) Suryanarayana, Y.S., Van Winkle, M., *Ibid.*, 11, 7-12, (1966).
(13) Susarev, M.P., *J. App. Chem. USSR* **34**, 394 (1961).
(14) Van Ness, H.C., "Classical Thermodynamics of Non-Electrolyte Solutions," MacMillan, New York, 1964.
(15) Weimer, R.F., Prausnitz, J.M., *Hyd. Proc.* **44**, No. 9, 237 (1965).

RECEIVED for review January 24, 1966. Accepted April 21, 1966.

The System o-Nitroaniline–2,4-Dinitroaniline

LOHR A. BURKARDT
Chemistry Division, U. S. Naval Ordnance Test Station, China Lake, Calif.

No evidence of complex formation was found for the system o-nitroaniline–2,4-dinitroaniline. The eutectic contains 14.5 mole of 2,4-dinitroaniline and melts at 60.7° C.

IN THE COURSE of studies of the polymorphism of *o*-nitroaniline, knowledge of the phase diagram of the system *o*-nitroaniline–2,4-dinitroaniline became desirable. Since this system does not appear to have been previously investigated, a study was undertaken using an apparatus (*1*) which permits a stepwise approach to the liquidus point. Solid-liquid equilibrium was demonstrated at each thermal step by constancy of the light transmission of the sample.

The *o*-nitroaniline was recrystallized five times from a mixture of equal volumes of ethyl alcohol and water, and then vacuum-dried; the melting point was 70.6° C. The 2,4-dinitroaniline was recrystallized from hot ethyl alcohol and vacuum-dried; the melting point was 179.9° C.

Because of the rather deep color of melts of these materials, the apparatus was modified slightly. A stirrer was used, similar in general shape to that described (*1*), but having a solid glass plate with plane sides instead of a hole for the light to pass through. This arrangement reduced the amount of melt through which the light had to pass.

Six-gram samples of the required compositions were melted and stirred thoroughly. The temperature of the sample was allowed to fall until a small amount of solid was formed, then was raised stepwise; the sample was held at each temperature until the light transmission of the sample became constant. Unfortunately, the light transmission of the sample becomes very erratic just as the liquidus point is being reached, because of the small number of solid particles in the light beam. The liquidus was then approached by raising the bath temperature in 0.1° C. steps. The temperature was held constant for about 15 minutes at each step and the behavior of the solid particles, which were strongly illuminated, was followed visually. The temperature step at which solids were no longer visible at the end of the 15-minute period was taken as the liquidus temperature. Attempts at prolonging the time of holding the sample at the step immediately before complete solution of the solids led to some darkening of the sample, suggesting possible degradation of the sample. Such an effect could introduce a larger and more variable error than would be made by assuming the true liquidus temperature to be between the complete solution temperature step immediately preceding it. In this case the accuracy of the determination might be best expressed as the complete solution temperature, +0.0° to 0.1° C.

The melting point of the eutectic was obtained by heating the completely solid sample through the eutectic melting point with temperature gradients of approximately 0.1° between the bath and sample. With such temperature gradients, a flat is obtained at the eutectic melting point.

No evidence of complex formation was found for this

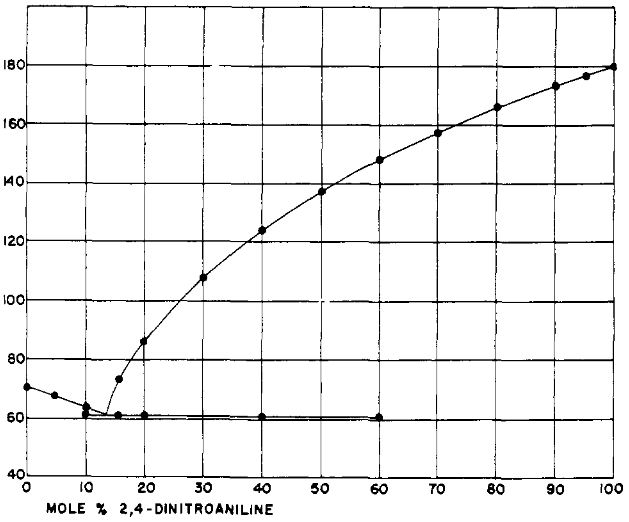


Figure 1. Phase diagram of system o-nitroaniline–2,4-dinitroaniline

Table I. Liquidus and Eutectic Temperature Data for Systemo-Nitroaniline–2,4-Dinitroaniline

Mole % 2,4-Dinitroaniline	Liquidus Temp., ° C.	Eutectic Temp., ° C.
0	70.6	...
5	67.0	...
10	64.0	60.7
16	73.1	60.7
20	86.0	60.7
30	108.1	...
40	123.3	60.7
50	136.6	...
60	147.8	60.7
70	157.3	...
80	165.6	...
90	172.9	...
95	176.5	...
100	179.9	...

system. A eutectic containing 14.5 mole % of 2,4-dinitroaniline and melting at 60.7° C. was found. In one instance, a melt having the composition 90 mole % *o*-nitroaniline, 10 mole % 2,4-dinitroaniline had a liquidus value of 62.3° C., instead of 64.0° C. which was obtained on other runs of the same composition. This point may represent a liquidus value for an unstable phase of *o*-nitroaniline with 2,4-dinitroaniline. Efforts to repeat this point failed.

Data for this system are shown graphically in Figure 1 and given in Table I.

LITERATURE CITED

(1) Burkardt, L.A., McEwan, W.S., Pitman, H.W., *Rev. Sci. Instr.* 27, 693 (1956).

RECEIVED for review January 26, 1965. Accepted March 24, 1966.

Extraction of Metals from Chloride Solutions with Amines

FOREST G. SEELEY and DAVID J. CROUSE
Oak Ridge National Laboratory, Oak Ridge, Tenn.

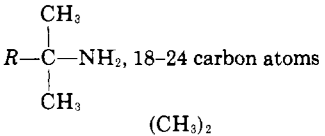
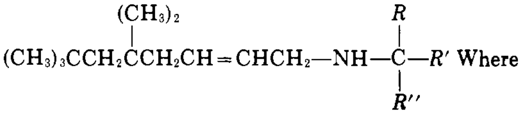
Extraction coefficients for 63 metal ions were determined from both hydrochloric acid and acidified lithium chloride solutions with representative primary, secondary, tertiary, and quaternary alkylammonium chlorides in diethylbenzene diluent. The aqueous chloride concentration was varied from 0.5 to 10M.

MUCH INTEREST in the liquid-liquid solvent extraction of metals with high molecular weight amines has developed since their ability to extract acid was reported in 1948 (*13*). Many investigators have examined the extraction characteristics of these reagents in both survey and process-oriented studies (*1–12*). With respect to the chloride system, many of the studies have been only with tertiary amines and, for the most part, have been limited to extractions from hydrochloric acid. In addition, different investigators have used a variety of diluents, making correlation of data from different sources difficult. In the work reported here, the extraction of 63 metal ions from both hydrochloric acid and acidified lithium chloride solutions was systematically surveyed with representative primary, secondary, tertiary, and quaternary alkylammonium chlorides in diethylbenzene diluent.

EXPERIMENTAL

Materials. A description of the amines chosen to represent the different amine types in the metal extraction tests is given in Table I. The amine concentration was 0.1*M*.

Table I. Description of Amines

Amine Type	Compound[a]	
Primary	Primene JM	 $R\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}NH_2$, 18-24 carbon atoms
Secondary	Amberlite LA-1	 $(CH_3)_3CCH_2\overset{(CH_3)_2}{C}CH_2CH{=}CHCH_2\text{—}NH\text{—}\overset{R}{\underset{R''}{C}}\text{—}R'$ Where $R + R' + R'' =$ 12-14 carbons
Tertiary	Alamine 336	R_3N, where the *R*'s are mixed *n*-octyl and *n*-decyl
Quaternary	Aliquat 336	$[R_3N\text{—}CH_3]^+Cl^-$, where the *R*'s are mixed *n*-octyl and *n*-decyl

[a] Primene JM and Amberlite LA-1 are supplied by Rohm and Haas Co.; Alamine 336 and Aliquat 336 are supplied by General Mills, Inc.