THE $Na^+,K^+/CN^-,I^-$ TERNARY RECIPROCAL SYSTEM

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The DTA method was used to obtain the phase diagram of the $Na^+,K^+/CN^-,I^-$ ternary reciprocal system. This system forms completely miscible solid solutions with two ternary minima with the parameters $x_{Na^+} = 0{\cdot}50$, $x_{I^-} = 0{\cdot}57$, $\Theta = 412°C$, and $x_{Na^+} = 0{\cdot}75$, $x_{I^-} = 0{\cdot}20$, $\Theta = 428°C$. The NaI–KCN diagonal is the stable diagonal.

This paper is a continuation of our previous paper[1] concerned with the four binary systems of the Na^+, K^+/CN^-, I^- ternary system, in which the phase diagrams of the binary systems obtained experimentally and calculated based on two different physical models were published. The present paper gives the experimental phase diagram of the ternary reciprocal system; its calculation correlation from the binary systems in terms of physical models, which is very extensive, will be published in a forthcoming paper.

EXPERIMENTAL

The chemicals and purification procedures, apparatus, and methods of measurement and analysis were as in the previous work[1].

RESULTS AND DISCUSSION

The samples of the ternary system were measured by the DTA method from the heating curves in view of the fact that at temperatures above the melting temperatures, appreciable evaporation of the samples takes place. Since all samples correspond to solid solutions with complete mutual miscibility and with minima in the liquidus and solidus curves, the DTA traces differed according to whether the sample composition was close to or far from these minima. In the former case the record exhibited one sharp peak, in the latter case two broader and less deep peaks were present. The temperature reading was accordingly more precise in the former case. For each

TABLE I

Average phase transition temperatures of samples of the ternary reciprocal system; labelling as in Fig. 1

Sample	x_{Na+}	x_{I-}	Θ_{sol} °C	Θ_{liq} °C	Sample	x_{Na+}	x_{I-}	Θ_{sol} °C	Θ_{liq} °C
U1	0·90	0·90	—	581	V1	0·10	0·90	635	643
U2	0·80	0·80	498	557	V2	0·20	0·80	541	—
U3	0·70	0·70	478	529	V3	0·30	0·70	482	537
U4	0·60	0·60	—	443	V4	0·40	0·60	—	480
UE	0·55	0·55	—	438	VF	0·45	0·55	—	420
U5	0·50	0·50	—	436	V5	0·50	0·50	—	436
U6	0·40	0·40	—	448	V6	0·60	0·40	—	428
U7	0·30	0·30	447	480	V7	0·70	0·30	—	469
U8	0·20	0·20	—	500	VC	0·75	0·25	433	461
U9	0·10	0·10	526	—	V8	0·80	0·20	—	474
					V9	0·90	0·10	—	511
A1	0·95	0·90	—	641	B1	0·85	0·90	—	595
A2	0·95	0·80	520	589	B2	0·85	0·80	522	571
A3	0·95	0·70	—	577	B3	0·85	0·70	511	—
A4	0·95	0·60	489	534	B4	0·85	0·60	428	479
A5	0·95	0·50	454	493	B5	0·85	0·50	428	503
A6	0·95	0·40	441	482	B6	0·85	0·40	432	486
A7	0·95	0·30	453	482	B7	0·85	0·30	429	464
A8	0·95	0·20	457	498	B8	0·85	0·20	432	474
A9	0·95	0·10	486	—	B9	0·85	0·10	480	530
C1	0·75	0·90	—	563	D1	0·65	0·90	—	557
C2	0·75	0·80	500	—	D2	0·65	0·80	485	532
C3	0·75	0·70	494	538	D3	0·65	0·70	426	474
C4	0·75	0·60	454	—	D4	0·65	0·60	416	—
C5	0·75	0·50	446	452	D5	0·65	0·50	—	416
C6	0·75	0·40	438	458	D6	0·65	0·40	419	436
C7	0·75	0·30	434	—	D7	0·65	0·30	421	439
C8	0·75	0·20	—	428	D8	0·65	0·20	431	446
C9	0·75	0·10	432	438	D9	0·65	0·10	427	453
E1	0·55	0·90	—	553	F1	0·45	0·90	—	557
E2	0·55	0·80	497	546	F2	0·45	0·80	498	511
E3	0·55	0·70	—	464	F3	0·45	0·70	—	481
E4	0·55	0·60	—	422	F4	0·45	0·60	—	489
E5	0·55	0·50	—	430	F5	0·45	0·50	—	431
E6	0·55	0·40	—	424	F6	0·45	0·40	428	461
E7	0·55	0·30	436	445	F7	0·45	0·30	439	465
E8	0·55	0·20	444	468	F8	0·45	0·20	458	—
E9	0·55	0·10	438	461	F9	0·45	0·10	448	—

sample the trace was measured at least in duplicate, and averages of the obtained phase transition temperatures are given in Tables I and II. The precision of determination for the various samples was from ±1°C to ±10°C.

TABLE II

Average phase transition temperatures of samples of the ternary reciprocal system; labelling as in Fig. 1

Sample	x_{Na^+}	x_{I^-}	Θ_{segr} °C	Θ_{sol} °C	Θ_{liq} °C
G1	0·35	0·90	—	—	570
G2	0·35	0·80	—	500	576
G3	0·35	0·70	—	—	487
G4	0·35	0·60	405	463	—
G5	0·35	0·50	403	—	489
G6	0·35	0·40	—	—	441
G7	0·35	0·30	—	440	460
G8	0·35	0·20	—	444	489
G9	0·35	0·10	367	440	520
H1	0·25	0·90	—	529	604
H2	0·25	0·80	458	—	597
H3	0·25	0·70	437	—	544
H4	0·25	0·60	409	487	520
H5	0·25	0·50	396	480	—
H6	0·25	0·40	370	—	480
H7	0·25	0·30	—	—	476
H8	0·25	0·20	384	456	—
H9	0·25	0·10	365	—	491
I1	0·15	0·90	—	623	650
I2	0·15	0·80	422	561	633
I3	0·15	0·70	370	518	579
I4	0·15	0·60	383	515	569
I5	0·15	0·50	386	504	525
I6	0·15	0·40	388	478	512
I7	0·15	0·30	386	—	501
I8	0·15	0·20	384	—	500
I9	0·15	0·10	—	475	601
a	0·525	0·575	—	—	435
b	0·50	0·55	—	—	414
c	0·60	0·50	—	—	442
d	0·70	0·25	—	433	441
e	0·70	0·20	—	—	441
f	0·50	0·57	—	—	412

A total of 107 samples of the ternary reciprocal system were measured. Experimental points concerning the binary systems were taken from ref.[1]. The composition of 81 samples corresponded to the intersections of always two isoconcentration sections mutually perpendicular and having constant concentrations of the individual kinds of cations or anions. The composition of 20 samples corresponded to the points of intersection of the NaI–KCN or KI–NaCN diagonals with some isoconcentration section, and the composition of 6 samples was off these points of intersection and served to refine the positions of the ternary minima of the liquidus and solidus

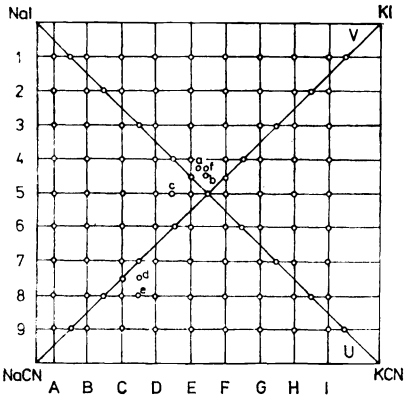

FIG. 1

Distribution of samples of the ternary reciprocal system with respect to their composition

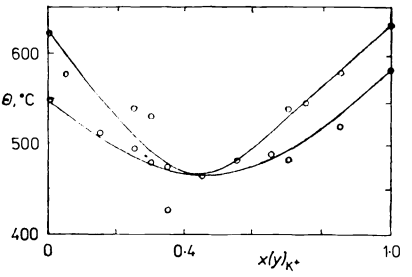

FIG. 2

Dependence of phase transition temperature on sample composition for isoconcentration section 3

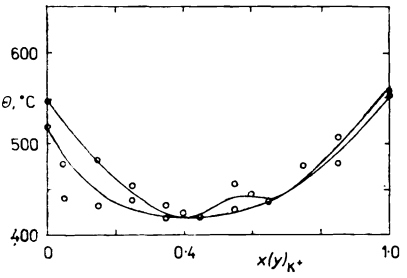

FIG. 3

Dependence of phase transition temperature on sample composition for isoconcentration section **6**

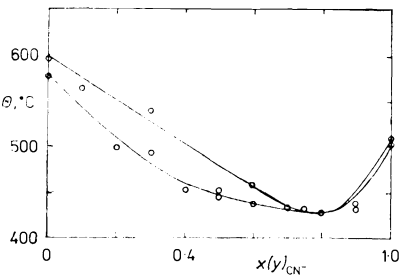

FIG. 4

Dependence of phase transition temperature on sample composition for isoconcentration section C

surfaces of the system. The distribution of the points with respect to the sample composition is shown in Fig. 1. The results of measurement for the 107 points are summarized in Tables I and II. For some samples with high potassium salt concentrations (sections G, H, I), in addition to the peaks corresponding to the solidus and liquidus curves, another peak appears in the DTA record at a temperature lower than the solidus temperature, presumably corresponding to the solid solutions segregation curve. As a matter of fact, a relatively high temperature of segregation of solid solutions has been observed in the DTA traces of the KI–KCN binary system[1]. For the isoconcentration sections shown in Fig. 1, the experimental points were fitted with liquidus and solidus curves by using the method of smoothing cubic splines[2], which were chosen so that they passed through the limiting points of the liquidus and solidus curves and approximated their common minima. The limiting points were derived from the data[1]. Examples of experimental point fitting are shown in Figs 2 through 5 as the isoconcentration sections 3, 6, C and G of the phase diagram of the ternary system.

The minima in the liquidus and solidus curves of all the isoconcentration sections were projected into the base (Fig. 6); in the projection, the experimental points corresponding to the minima are fitted with curves starting in the minima of the four binary systems and intersecting in two ternary minima. The experimental points were fitted with three regression polynomials of the fourth (curves $a-d$) and third (curve e) degrees. Based on a consecutively performed analysis of residuals, one point was eliminated from branches c and e. These points are shown as full circles in Fig. 6. One ternary minimum lies in the NaI–NaCN–KCN system and its parameters

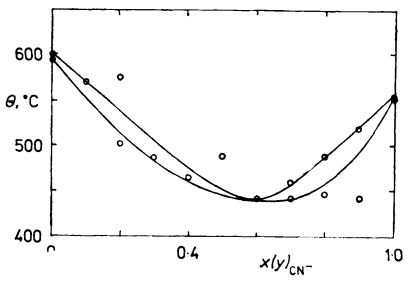

FIG. 5

Dependence of phase transition temperature on sample composition for isoconcentration section G

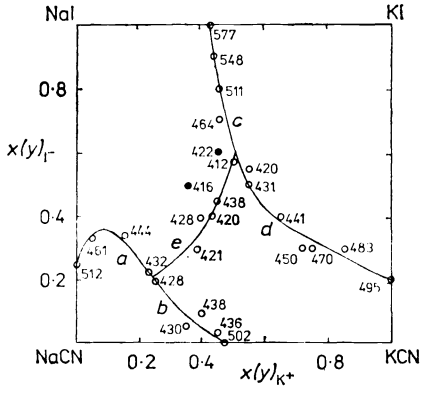

FIG. 6

Projection of the phase diagram of the $Na^+,K^+/CN^-,I^-$ ternary reciprocal system into the base

are $x_{Na^+} = 0{\cdot}75$, $x_{I^-} = 0{\cdot}20$, $\Theta = 428°C$; the other ternary minimum lies in the NaI–KI–KCN system and its parameters are $x_{Na^+} = 0{\cdot}50$, $x_{I^-} = 0{\cdot}57$, $\Theta = 412°C$. The NaI–KCN diagonal is the stable diagonal.

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