furnace legs, and finally using an off-center null point on the analytical balance to record the reversals. These radical departures from "normal" balance equilibration tube loadings did not appear to change the slope significantly, but as in the two previously reported pure cadmium loadings, a shift in the absolute bias was observed. The total bias shift, for equal amounts of cadmium in both legs, was 1.3 μv between extremes.

DISCUSSION OF RESULTS

The possible implications of the abrupt changes in cadmium activity with composition in the gold and copper alloys, without further investigations, are not entirely clear. The data suggest that over the more dilute concentration range, for any given system, one type of solution behavior is predominant, while in the more concentrated regions a rather different type of behavior results, with a very abrupt region of transition connecting the two. One possible explanation might involve two types of liquid structure which are incompatible, thus requiring a narrow composition range for transition.

An explanation for the observed behavior of pure cadmium is not available at this time. Work with pure mercury (*1*) and our many investigations presented above indicate that the observed phenomenon does not originate as an experimental artifact from the isopiestic balance. It would seem that any explanation must be derived from the physical chemistry of the system isolated within the balance tube. Although this matter has been pondered at great length in this laboratory, our thoughts are speculative and no definitive statement is warranted.

It is obvious from the data involving very dilute gold in cadmium that in the concentration range investigated it is impossible to differentiate between the behavior of the alloy and pure cadmium. Because of the uncertainties in the measurement of the slope of the thermocouple electromotive force bias, it is not possible to determine accurately the slope of the plot of activity *vs.* mole fraction for the most dilute gold-cadmium measurements (run 6).

The sloping thermocouple bias found in the pure cadmium investigations is significant only when large amounts of cadmium are transferred—i.e., very dilute alloy measurements. The measurements tabulated in Table I and illustrated in Figures 1, 2, and 3 are not significantly altered by this effect, although a correction has been applied.

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Binary Freezing Point Diagrams for Some Methyl Ketones and Their Complete Solubilities in Acetone, Methanol, Benzene, and Carbon Tetrachloride

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In the course of our investigations into the development of correlation procedures for the solubilities of long chain homologous and analogous compounds, the following highly pure methyl ketones were prepared: 2-tridecanone, 2-heptadecanone, and 2-nonadecanone. Since the methyl ketones are important in many chemical reactions and since mutual solubilization is very pronounced in most long-chain homologous compounds, an investigation into the mutual solubilization effects of the methyl ketones was undertaken. The investigation was extended to include the solubility behavior of the methyl ketones in two polar solvents—acetone and methanol—and two nonpolar solvents—benzene and carbon tetrachloride.

EXPERIMENTAL

The pure methyl ketones were recrystallized samples of fractionally distilled materials. The pure stearic acid was a recrystallized material prepared from the fractionally distilled methyl ester. The acetone, methanol, and carbon tetrachloride were reagent grade solvents freshly distilled. The benzene used was a reagent grade material dried over sodium wire and distilled through a packed column.

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Binary freezing point data have been obtained for 2-tridecanone, 2-heptadeconone, and 2-nonadecanone with each other and 2-nonadecanone with stearic acid. Solubility data were obtained for 2-tridecanone, 2-heptadecanone, and 2-nonadecanone in acetone, methanol, benzene, and carbon tetrachloride. Solubility data were calculated for the C_{11}, C_{12}, C_{14}, C_{15}, C_{16}, C_{18}, C_{20}, and C_{21} methyl ketones by the isopleth correlation method. X-ray diffraction data are reported for the C_{13}, C_{15}, C_{17}, and C_{19} methyl ketones along with the refractive indices for the C_{13}, C_{17}, and C_{19} methyl ketones.

Freezing point and solubility determinations were made by the thermostatic sealed tube method (*1*, *3*, *6*) which gives the true equilibrium temperature between the solid and the liquid of a given composition to within ±0.2° C after correction for thermometer calibration and emergent stem.

The X-ray long and short spacings measurements were made by the powder method of O'Connor *et al.* (*5*). A Phillips Electronics diffractometer was used also to obtain X-ray diffractions by the direct measurement technique with a strip chart recorder. The instrument was equipped with a copper target X-ray tube, and a 0.0007-inch thick nickel filter. Divergence and antiscattering slits used were one-fourth degree. The X-rays were generated at 30 kVp and 15 ma from 0 to 12.5°, 2θ and at 36 kVp and 16 ma from 12.5 to 25°, 2θ.

Refractive indices were determined at 30 and 60° C with a Bausch and Lomb refractometer.

RESULTS AND DISCUSSION

Experimental freezing point data for the binary mixtures are given in Table I and are represented graphically in Figure 1. In the stearic acid–2-nonadecanone system, curve A, a simple eutectic of 25.4% stearic acid melting at 52.7° C was observed. An incongruently melting 1:1 molecular compound (38.0%, 43.6° C) was observed, between 2-nonadecanone and 2-heptadecanone, which formed a eutectic mixture with 2-heptadecanone (30.0%, 43.0° C), curve B.

Two freezing points were obtainable for 2-heptadecanone at three compositions between 13 and 28% in the

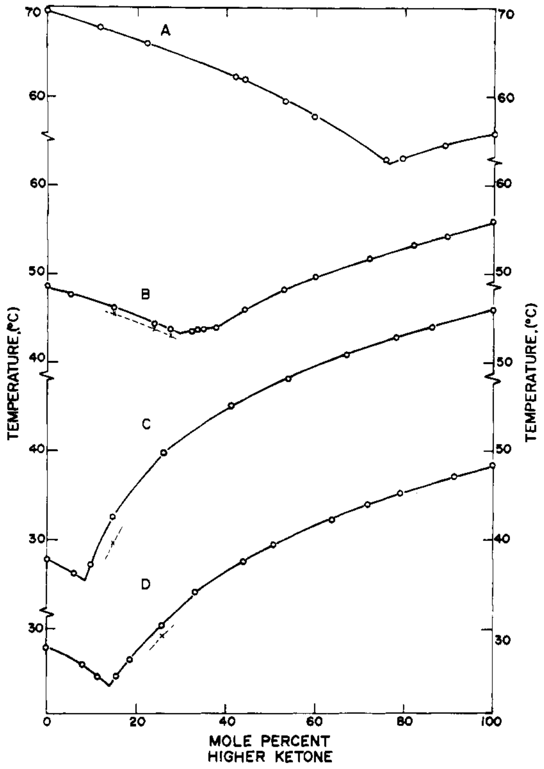

Figure 1. Binary freezing point diagrams for 2-nonadecanone with: *A*, stearic acid; *B*, 2-heptadecanone; *C*, 2-tridecanone; and *D*, 2-heptadecanone with 2-tridecanone

Table I. Binary Solubilities of Some Methyl Ketones with Each Other and 2-Nonadecanone with Stearic Acid

2-Tridecanone in 2-Nonadecanone		2-Heptadecanone in 2-Nonadecanone		2-Tridecanone in 2-Heptadecanone		2-Nonadecanone in Stearic Acid	
Mole %, C_{19}	*T*, ° C	Mole %, C_{19}	*T*, ° C	Mole %, C_{17}	*T*, ° C	Mole %, acid	*T*, ° C
100.00	55.6	100.00	55.6	100.00	48.2	100.00	69.5
86.38	53.9	89.70	54.0	91.20	46.9	91.20	67.6
78.16	52.6	82.20	53.0	79.47	45.0	77.81	65.9
67.00	50.6	72.19	51.6	72.09	43.7	65.91	63.8
53.86	47.8	60.24	49.4	63.87	41.9	58.01	62.2
41.24	44.8	52.98	48.0	50.74	39.2	56.15	61.9
34.98	42.8	44.23	45.7	44.12	37.2	46.42	59.5
25.96	39.5	38.0[a]	43.6[a]	33.33	33.8	39.76	58.0
14.75	32.2	37.76	43.6	25.56	30.0	39.64	57.7
	29.2[b]	35.14	43.4		28.7[b]	30.08	54.7
9.80	26.8	33.61	43.4	18.66	26.1	25.4[c]	52.7[c]
8.6[c]	25.0[c]	32.70	43.2		25.4[b]	24.10	52.9
6.12	25.8	30.0[c]	43.0[c]	15.72	24.2	20.96	53.5
0.00	27.6	27.63	43.4	14.0[c]	23.0[c]	20.54	53.5
			42.7[b]	11.32	24.2	10.96	54.6
		23.93	44.0	7.97	25.5	0.00	55.6
			43.4[b]	0.00	27.6		
		14.85	45.8				
			45.2[b]				
		5.30	47.3				
		0.00	48.2				

[a] Incongruent melting point for 1:1 molecular compound. [b] Metastable form. [c] Eutectic point.

Table II. Solubilities of Methyl Ketones

2-Undecanone[a]		2-Dodecanone[a]		2-Tridecanone		2-Tetra-decanone[b]		2-Penta-decanone[b]		2-Hexa-decanone[b]		2-Hepta-decanone		2-Octa-decanone[b]		2-Nona-decanone		2-Eicosanone[a]		2-Henei-cosanone[a]	
Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C	Mole %	t, °C
Acetone																					
80	9.6	80	17.4	79.99	23.9	80	30.2	80	35.8	80	41.2	75.99	45.0	80	49.6	71.90	51.8	80	...	80	...
60	5.5	60	13.4	63.81	20.8	60	26.5	60	32.1	60	37.2	73.58	44.4	60	46.0	51.08	48.2	60	53.6	60	...
40	0.6	40	8.5	44.81	16.6	40	21.9	40	27.6	40	32.8	49.33	40.0	40	42.1	31.29	44.0	40	49.6	40	53.3
20	−6.6	20	1.6	31.31	13.0	20	15.5	20	26.7	20	27.0	30.59	35.4	20	36.6	15.30	39.4	20	44.6	20	48.6
10	−12.6	10	−4.1	23.34	10.3	10	10.4	10	16.7	10	22.4	21.01	32.6	10	32.7	8.01	36.0	10	41.1	10	45.0
				16.26	7.2							10.88	28.6			4.03	32.4				
				11.98	5.1							4.88	23.9			2.25	29.1				
				9.63	3.2							2.59	19.4			0.99	23.2				
												1.96	17.6			0.66	20.3				
												1.11	13.2			0.58	19.0				
												0.72	9.9			0.34	15.0				
Methanol																					
80	10.7	80	18.1	87.98	25.7	80	30.8	80	36.4	80	41.0	60.24	43.8	80	49.6	74.61	53.1	80	56.9	80	60.2
60	8.3	60	15.9	69.50	23.5	60	28.5	60	34.2	60	38.9	57.87	43.7	60	47.6	46.82	50.0	60	54.6	60	58.1
40	5.9	40	13.5	53.10	21.8	40	26.3	40	32.0	40	36.8	47.72	42.7	40	45.6	20.60	47.6	40	52.9	40	56.3
20	2.9	20	10.7	40.66	20.3	20	23.8	20	29.6	20	34.5	30.87	40.8	20	43.5	5.79	46.0	20	50.8	20	54.4
10	0.0	10	8.0	29.54	18.9	10	21.6	10	27.8	10	32.7	17.86	39.5	10	42.0	2.81	44.9	10	49.6	10	53.0
5	−6.7	5	3.6	19.39	17.4	5	19.5	5	26.1	5	31.4	10.26	38.4	5	41.0	1.89	44.0	5	48.7	5	52.3
				6.69	14.9							4.79	36.7			0.99	42.2				
				5.97	12.9							1.89	34.0			0.84	40.7				
				3.94	11.0							0.98	30.5			0.62	40.3				
												0.62	26.0			0.32	37.2				
																0.21	35.2				
																0.10	32.8				
Benzene																					
80	9.1	80	16.8	83.49	24.3	80	29.5	80	35.2	80	40.0	74.87	44.1	80	48.7	78.63	52.5	80	54.9	80	59.4
60	3.8	60	11.6	74.53	22.5	60	23.8	60	30.5	60	35.6	49.74	37.9	60	44.6	61.98	49.1	60	52.1	60	55.6
		40	4.4	50.71	15.7	40	18.0	40	24.0	40	29.1	32.47	30.9	40	38.7	41.04	43.2	40	46.2	40	49.9
				33.89	8.6	20	5.6	20	12.3	20	17.9	17.12	21.6	20	28.2	21.48	33.5	20	36.9	20	41.0
				24.40	2.4							13.58	18.5			10.59	24.4				
												11.14	16.1			5.69	17.6				
												5.78	8.7			3.99	14.1				
												3.98	5.0			2.33	9.3				
																1.24	4.5				
Carbon Tetrachloride																					
80	9.2	80	16.8	86.30	24.9	80	29.4	80	35.0	80	40.0	80.55	45.0	80	48.6	59.11	48.5	80	55.0	80	58.8
60	3.7	60	11.5	73.08	21.9	60	24.7	60	30.4	60	35.6	60.07	40.8	60	44.6	36.22	41.3	60	52.3	60	55.6
40	−3.8	40	4.3	57.95	17.9	40	16.9	40	23.7	40	29.0	49.10	37.8	40	38.6	20.95	33.5	40	46.3	40	50.2
20	−15.3	20	−7.0	50.81	15.5	20	6.7	20	12.8	20	18.2	36.39	32.7	20	28.1	14.21	27.8	20	36.6	20	40.5
				40.05	11.5							25.10	27.1			7.84	19.9				
				30.13	6.7							15.03	19.8			4.56	14.5				
				23.98	3.0							10.05	14.6			1.28	1.7				
												8.32	12.1								
												5.81	8.0								
												4.57	5.2								
												3.44	2.0								

[a] Determined by extrapolation using isopleth method. [b] Determined by interpolation using isopleth method.

2-nonadecanone–2-heptadecanone system. Simple eutectics were exhibited by both the 2-nonadecanone–2-tridecanone (8.6%, 25.0° C) and the 2-heptadecanone–2-tridecanone (14.0%, 23.0° C) systems, curves C and D. Two freezing points were observed in the latter systems for both 2-nonadecanone and 2-heptadecanone in the same 13 to 28% region but for only one composition of each.

When two freezing points were obtained, the higher temperature, representing equilibrium with the stable modification, was always the one observed upon initial heating of the sample. To obtain the corresponding equilibrium temperature for the metastable form it was necessary to heat the sample a few degrees above the initial melting point and rapidly chill the sample in an ice bath. The sample then melted at the lower temperature.

Complete experimental solubility data have been tabulated in Table II for 2-tridecanone, 2-heptadecanone, and 2-nonadecanone in acetone, methanol, benzene, and carbon tetrachloride. The methyl ketones would have to be characterized as being more soluble in nonpolar solvents than in the polar solvents. The solubilities of the methyl ketones reported herein are greater in benzene and less in acetone, methanol, and carbon tetrachloride than those reported by Hoerr *et al.* (*2*). Likewise solubilities previously reported (*9*), obtained using the isopleth method and the data of Hoerr *et al.*, are also similarly different since the accuracy and precision of the isopleth method are dependent upon those of the experimental data.

It was observed (*7*) that the X-ray crystal spacings of the long chain methyl ketones do not exhibit alternation. Shenton and Smith (*8*) more recently reported that the freezing points likewise do not alternate. Since there is no alternation in the series, the freezing points and the solubilities of both the odd and even carbon number adjacent and intermediate members of the homologous series can be estimated using the isopleth correlation method (*9*). The experimentally determined freezing points and those obtained by the isopleth method are listed in the first column in Table III which also includes the published data of Hoerr *et al.* (*2*) and that of Morgan and Holmes (*4*) for comparison.

Solubilities for each of the ketones in acetone, methanol, benzene, and carbon tetrachloride determined by the isopleth correlation method are listed in Table II. For those systems which tend to produce isopleths having slight curvature, the values obtained by extrapolation are less precise than the interpolated values. Figure 2 illustrates the isopleths obtained for the methyl ketones in acetone.

The refractive indices, n_D, of the pure ketones determined at 60° C are: 2-tridecanone, 1.41937; 2-heptadecanone, 1.42836; and 2-nonadecanone, 1.43247; and at 30° C 2-tridecanone, 1.43129.

Table III. Freezing Point Temperatures

	Our Data	Hoerr *et al.* (*2*)	Morgan and Holmes (*4*)
2-Nonanone		–7.46	
2-Decanone			14.0
2-Undecanone	(13.5)[a]		
2-Dodecanone	(21.0)		20
2-Tridecanone	27.6	27.46	27.5
2-Tetradecanone	(33.6)		33
2-Pentadecanone	(38.9)		39.0
2-Hexadecanone	(41.8)		43
2-Heptadecanone	48.2		48.0
2-Octadecanone	(52.0)		52.0
2-Nonadecanone	55.6	54.59	55.0
2-Eicosanone	(59.1)		
2-Heneicosanone	(62.2)		

[a] Values in parentheses calculated by isopleth correlation method.

The X-ray long spacings obtained for 2-tridecanone, 36.81; 2-pentadecanone, 42.60; 2-heptadecanone, 47.39; and 2-nonadecanone, 52.22 Å are in good agreement with those of Saville and Shearer (*7*). Only one short spacing at 4.10 Å was common to all four ketones. The relative intensities

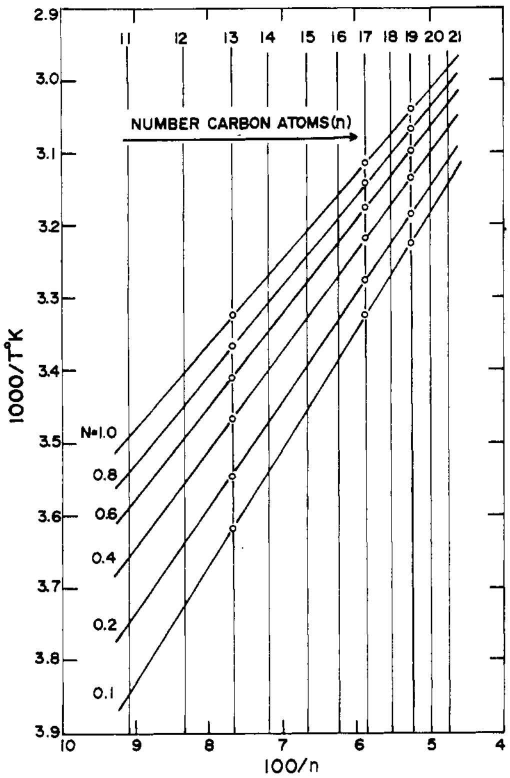

Figure 2. Isopleth plot for the methyl ketones in acetone (*N* = mole fraction)

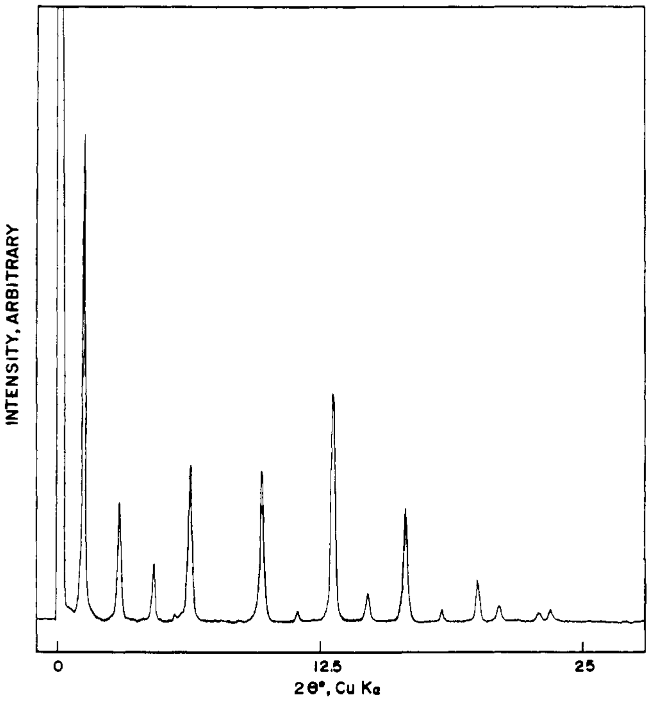

Figure 3. X-ray diffraction pattern for 2-nonadecanone illustrating relative intensities of successive orders

of the successive orders are illustrated in Figure 3. The fifth order was missing in the diffraction patterns of all but that of 2-tridecanone.

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Temperature Dependence of Diffusion and Viscosity in Aqueous Urea Solutions

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The temperature dependence of viscosity and the diffusion of zinc ion in aqueous urea solutions were measured over the range 298° to 319° K. The viscosities range from 0.593 cp (no urea, 319° K) to 1.378 cp (7*M* urea, 298° K). The diffusion coefficients, measured polarographically, range from 4.32 x 10^{-6} cm^2 sec^{-1} (7*M* urea, 298° K) to 10.63 x 10^{-6} cm^2 sec^{-1} (0*M* urea, 319° K). The viscosities and diffusion coefficients were fitted to Arrhenius equations; activation data for energy and entropy for seven solutions, 0*M* to 7*M* urea, are reported. These data suggest some transition in structure as urea concentration is increased, and that the transition affects differently the temperature dependence of these two transport properties.

The physical effects of urea added to aqueous solutions are of continuing interest in such areas as protein denaturation (*6*), diffusion (*2, 8*) and micelle formation (*7*). A review of these effects is available (*1*) and interpretations of these effects have recently been discussed (*4*).

The experimental data of the physical properties of aqueous solutions of urea, however, are as yet insufficiently complete to state definitively the mechanistic effect of urea in water. The temperature dependence of physical properties of aqueous urea solutions has not been extensively investigated and it has been recently suggested that such data should be revealing (*9*). Accordingly, we report here the concomitant effects of urea concentration and temperature upon the related transport properties of diffusion and viscosity. The diffusing species is zinc ion, 0.4*M* KNO_3, 0 to 7*M* in urea, over the temperature range 298° to 319° K. The viscosities range from 0.593 cp (no urea, 319° K) to 1.378 cp (7*M* urea, 298° K).

EXPERIMENTAL

All solutions were prepared in distilled water, using reagent-grade chemicals without further purification. The stock zinc nitrate solution was standardized chelometrically. The required concentrations of KNO_3 and urea were obtained by adding the required weights before dilution to volume.

Diffusion coefficients were measured using polarography at the dropping mercury electrode. A Leeds & Northrup electrochemograph was used: capillary and temperature characteristics were controlled using a Leeds & Northrup Polarotron.

Viscosity measurements were made with use of an Ostwald viscometer calibrated using distilled water. Density measurements were made using a Westphal balance calibrated using distilled water. By using a Sargent Thermonitor for temperature control (±0.01° C) and a Fisher thermometer having 0.1° C subdivisions for temperature measurements, the viscosity measurements (average of three determinations) were reproducible to ±0.5% and the density measurements were more precise, ±0.1%.

RESULTS

Diffusion. The experimental values of average current (i, μA), zinc ion concentration (C, mmole 1^{-1}), mercury drop time (t, sec), and mercury drop weight (m, mg sec^{-1}) were inserted into the expanded Ilkovic equation (*5*)

$$i = 607\ nD^{1/2}\ Cm^{2/3}t^{1/6}\cdot[1 + 34\ m^{-1/3}t^{1/6}D^{1/2}] \qquad (1)$$

where n is the number of electrons necessary for the electro-