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Some Physical Properties of Saturated, Supersaturated, and Undersaturated Aqueous Potassium Bichromate Solutions

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The solubility of potassium bichromate in water and the density, viscosity, and refractive index of saturated aqueous potassium bichromate solutions were determined between 20 and 60 °C. The apparent partial molal volume of the solute as a function of temperature and the dependence of the logarithm of solubility on reciprocal temperature show bends at about 40 °C. However, the temperature dependences of density, refractive index, and viscosity of saturated solutions do not show any unusual behavior at this temperature. Density and refractive index in undersaturated and supersaturated regions of the solutions saturated at particular temperatures are approximately linear functions of temperature around saturation points.

Introduction

It is usually observed that potassium bichromate (KBC) crystals grown from aqueous solutions at high and low temperatures have different morphologies. Kozlova et al. (*1*, *2*) reported that the change in morphology takes place at 52 °C and suggested that it is associated with phase changes in the KBC solutions. Since physical properties of solutions are determined by the nature of species present in them, the phase changes occurring at 52 °C should be evidenced by concomitant changes in physical properties. For example, changes in the properties of aqueous solutions of hydrated inorganic salts take place at transition temperatures above and below which different hydrates are stable (*3*, *4*). However, experimental data demonstrating changes in the physical properties of unhydrated salts are sparse.

Some workers (*3*, *4*) have reported bends and curvatures in curves of the temperature dependences of physical properties in the undersaturated and supersaturated regions of solutions saturated at particular temperatures. It has been suggested (*3*) that this behavior is associated with differences in the chemical species present in the solution. However, the experimental results obtained even for the same salts are often contradictory (*3*, *4*).

The purpose of this paper is to investigate the temperature dependence of the solubility of KBC and of the viscosity, density, and refractive index of its saturated aqueous solutions and to determine the temperature at which changes, if any, in these physical properties take place. To determine whether bends in the curves of physical properties vs. temperature take place at the saturation point for KBC solutions in undersaturated and supersaturated regions, these properties are also investigated in the neighborhood of the saturation point for some solutions saturated at different temperatures.

Experimental Section

All solutions investigated here were prepared with double-distilled water and recrystallized KBC. Saturation of a solution at a particular temperature was achieved by intensive stirring of the solution with an excess of crystalline KBC for more than 24 h. The solubility of KBC in water was estimated by weighing about 5-cm^3 samples of solution before and after evaporation at 60 °C for 48 h. There were two samples for each saturation temperature. The reproducibility was estimated to be about 0.1%. For the density measurements, a Westphal balance composed of about 10-cm^3 flow and an analytical balance was used. The experimental error was $\pm 10^{-4}$ g/cm^3. The viscosity and refractive index of the solutions were measured with an immersion viscometer (*5*) and an immersion refractometer (Carl Zeiss), respectively. The accuracies were $\pm 10^{-3}$ cP for viscosity and $\pm 2 \times 10^{-5}$ for refractive index. All measurements were made at particular temperatures between 20 and 60 °C and were obtained simultaneously in the same vessel placed in a thermostated water jacket. The temperature in the vessel was measured with a thermometer with an accuracy of ±0.05 K and the temperature control in the vessel was estimated to be better than ±0.01 K (*6*). All experimental data are listed in Tables I–III.

Results

The solubility of KBC in water as a function of temperature is expressed in the form of an Arrhenius-type equation

$$X = A \exp(-E/RT) \qquad (1)$$

and is illustrated in Figure 1. The mole fraction of KBC in the solution, X, is defined as $N_{\mathrm{KBC}}/(N_{\mathrm{KBC}} + N_{\mathrm{H_2O}})$, where N_{KBC} is the number of moles of KBC in the saturated solution at a particular temperature T and $N_{\mathrm{H_2O}}$ is the number of moles of pure water. R is the gas constant and A and E are experimental constants. It may be seen from Figure 1 that a change in the slope of the curve occurs at 42.0 °C. Below and above 42 °C, the values of A and E estimated from the experimental data by using a least-squares method are 681.292 and 6.649 kcal/mol and 138.409 and 5.652 kcal/mol, respectively. The mean standard deviation of experimental data from the approximation is 2.5×10^{-5}. As shown in Figure 1, our solubility data are in good agreement with the data obtained by Janse (*7*), but the data given in Gmelins handbook (*8*), and by Kearley (*9*) and Hartford (*10*), show poor agreement.

The dependence of the density of the saturated KBC solutions, d_s (g/cm^3), on temperature, t (°C) (Figure 2), can be approximated by a quadratic function of the form

$$d_s = 1.02247 + 2.0805 \times 10^{-3}t + 2.305 \times 10^{-5}t^2 \qquad (2)$$

The mean standard deviation of experimental data is 1.72×10^{-4} g/cm^3.

The apparent partial molal volume, ϕ, as defined by Millero (*11*)

$$\phi = (V - \bar{V}_{\mathrm{H_2O}}N_{\mathrm{H_2O}})/N_{\mathrm{KBC}} \qquad (3)$$

was calculated by using solubility and density data obtained from eq 1 and 2, respectively. In eq 3, V is the volume of the solution in cm^3 containing $N_{\mathrm{H_2O}}$ moles of pure water and N_{KBC} moles of KBC. $\bar{V}_{\mathrm{H_2O}}$ is the partial molal volume of water. A more practical equation for ϕ can be derived from eq 3 by using the relationships

$$N_{\mathrm{H_2O}} = M_{\mathrm{H_2O}}/\mu_{\mathrm{H_2O}}; \qquad N_{\mathrm{KBC}} = M_{\mathrm{KBC}}/\mu_{\mathrm{KBC}};$$

$$\bar{V}_{\mathrm{H_2O}} = \mu_{\mathrm{H_2O}}/d_{\mathrm{H_2O}}; \qquad V = M_s/d_s;$$

$$M_s = M_{\mathrm{H_2O}} + M_{\mathrm{KBC}} = \mu_{\mathrm{H_2O}}N_{\mathrm{H_2O}} + \mu_{\mathrm{KBC}}N_{\mathrm{KBC}} \qquad (4)$$

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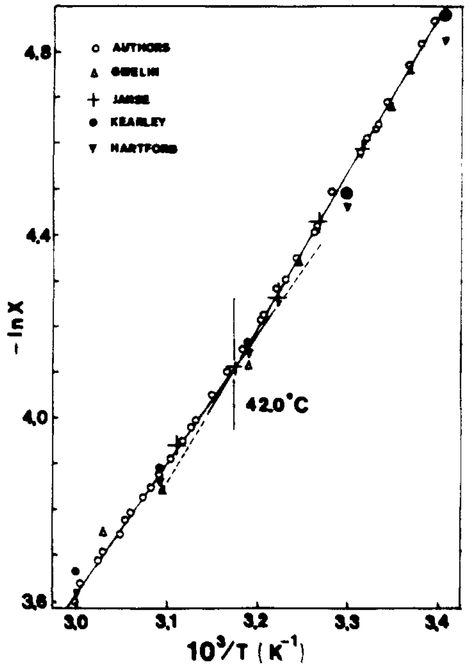

Figure 1. Logarithm of solubility as a function of reciprocal temperature: (○) present data, (+) Janse (*7*), (△) Gmelins Handbuch (*8*), (●) Kearley (*9*), (▼) Hartford (*10*).

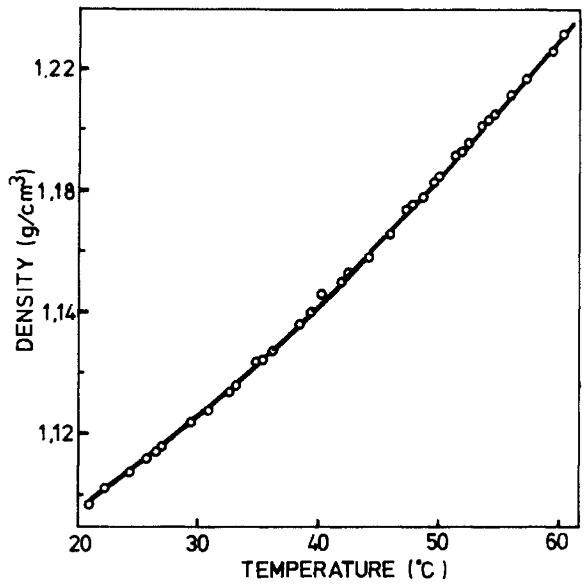

Figure 2. Dependence of the density, d_s, on the saturation temperature, t.

where M is the mass, d is the density, and μ is the molecular weight. The subscript s denotes the saturated solution. Substituting the values of V and $\bar{V}_{H_2O}$ from eq 4 into eq 3, one obtains

$$\phi = \frac{1}{d_s}\left(\mu_{KBC}N_{KBC} + \mu_{H_2O}N_{H_2O} - \mu_{H_2O}N_{H_2O}\frac{d_s}{d_{H_2O}}\right)\Big/ N_{KBC} \tag{5}$$

Now with the definition of mole fraction rewritten in the form

$$1/X - 1 = N_{H_2O}/N_{KBC} \tag{6}$$

the following form of eq 3 may be obtained:

$$\phi = (1/d_s)\left(\mu_{KBC} - \left(\frac{d_s}{d_{H_2O}} - 1\right)(1/X - 1)\mu_{H_2O}\right) \tag{7}$$

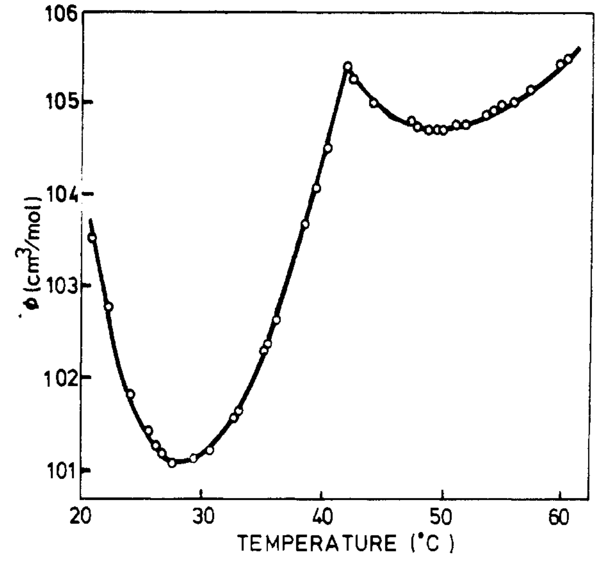

Figure 3. Graph showing the dependence of ϕ on t.

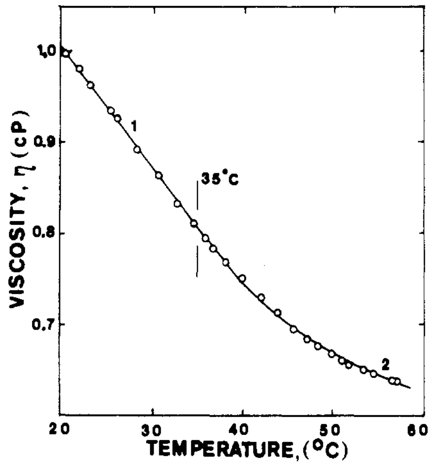

Figure 4. Dependence of viscosity of saturated aqueous KBC solutions, η, on temperature (curves 1 and 2 are drawn by using eq 8 and 9, respectively).

The calculated values of ϕ for different temperatures are listed in Table I and plotted in Figure 3.

The experimental viscosities, η (cP), of the saturated KBC solutions are plotted as a function of temperature in Figure 4. Below 35 °C the viscosity can be described as a linear function of temperature (Figure 4, curve 1)

$$\eta = 1.276 - 0.01328t \tag{8}$$

with correlation coefficient 0.9996. Above 35 °C, however, the experimental data are well fitted by a quadratic function (Figure 4, curve 2)

$$\eta = 1.522 - 0.02800t + 0.2189 \times 10^{-3}t^2 \tag{9}$$

The mean standard deviation of the experimental data from this approximation is 3×10^{-4} cP.

The refractive index, n, of saturated KBC solutions is a quadratic function of temperature and can be expressed by the relation

$$n = 1.34095 + 4.969 \times 10^{-4}t + 6.075 \times 10^{-6}t^2 \tag{10}$$

The mean standard deviation for this approximation is 3.6×10^{-5}. A plot of refractive index vs. temperature is presented in Figure 5.

Typical examples of the temperature dependence of density and refractive index of solutions saturated at particular temperatures in undersaturated and supersaturated regions are

Table I. Solubility (X), Density (d_s), Viscosity (η), Refractive Index (n), and Apparent Partial Molal Volume (ϕ) of Aqueous KBC Solutions at Saturation Point as a Function of Temperature[a]

t, °C	10^3X	d_s, g/cm^3	η, cP	n	ϕ, cm^3/mol
21.15	7.69 (7.73)	1.0765 (1.0768)	0.9958 (0.9951)	1.35440 (1.35418)	103.56
22.40	8.05 (8.12)	1.0819 (1.0806)	0.9780 (0.9785)	1.35508 (1.35513)	102.74
23.65	8.45 (8.51)		0.9632 (0.9619)	1.35606 (1.35610)	
24.40		1.0868 (1.0870)			101.78
25.70	9.17 (9.20)	1.0920 (1.0912)	0.9337 (0.9347)	1.35776 (1.35776)	101.39
26.60	9.66 (9.51)	1.0945 (1.0944)	0.9259 (0.9228)	1.35849 (1.35849)	101.22
26.95	9.72 (9.64)	1.0953 (1.0953)			101.17
27.75	9.93 (9.93)	1.0983 (1.0980)		1.35942 (1.35942)	101.05
28.45	10.22 (10.19)				
28.75			0.8931 (0.8942)	1.36012 (1.36026)	
29.40		1.1038 (1.1036)			101.10
30.90	11.16 (11.14)	1.1074 (1.1088)	0.8638 (0.8656)	1.36205 (1.36211)	101.19
32.80	12.06 (11.93)	1.1142 (1.1155)			101.54
33.15		1.1158 (1.1168)	0.8313 (0.8358)	1.36400 (1.36410)	101.62
33.80	12.13 (12.36)				
35.10	12.90 (12.95)	1.1236 (1.1239)	0.8101 (0.8089)	1.36579 (1.36588)	102.24
35.40		1.1244 (1.1250)			102.34
36.25	13.48 (13.48)	1.1272 (1.1282)	0.7935 (0.7946)	1.36679 (1.36695)	102.63
37.05	13.76 (13.87)		0.7835 (0.7851)		
38.50	14.68 (14.58)	1.1362 (1.1367)	0.7692 (0.7685)	1.36919 (1.36909)	103.64
39.40		1.1400 (1.1402)			104.04
39.95	14.78 (15.32)				
40.45	15.50 (15.53)	1.1462 (1.1439)	0.7508 (0.7486)	1.37094 (1.37089)	104.51
40.80	15.74 (15.78)				
42.00		1.1504 (1.1505)			105.39
42.50	16.62 (16.67)	1.1527 (1.1525)	0.7296 (0.7274)	1.37319 (1.37304)	105.26
44.20	17.46 (17.49)	1.1581 (1.1595)	0.7122 (0.7121)	1.37480 (1.37478)	105.00
46.00	18.40 (18.40)	1.1663 (1.1669)	0.6939 (0.6972)	1.37660 (1.37666)	105.22
46.60	18.70 (18.71)	1.1743 (1.1695)			
47.60	19.28 (19.24)	1.1743 (1.1737)	0.6858 (0.6852)	1.37836 (1.37837)	104.74
47.85		1.1754 (1.1748)			104.73
48.80	19.96 (19.89)	1.1789 (1.1789)	0.6767 (0.6769)	1.37958 (1.37967)	104.69
49.60		1.1835 (1.1824)			104.70
50.10	20.70 (20.61)	1.1847 (1.1846)	0.6682 (0.6686)	1.38117 (1.38109)	104.72
51.30	21.39 (21.29)	1.1920 (1.1899)	0.6604 (0.6617)	1.38223 (1.38243)	104.75
52.10	21.71 (21.76)	1.1934 (1.1934)	0.6564 (0.6574)	1.38291 (1.38333)	104.75
52.50		1.1957 (1.1952)			
53.70	22.50 (22.71)	1.2014 (1.2007)	0.6499 (0.6496)	1.38462 (1.38462)	104.86
54.20	22.98 (23.01)	1.2035 (1.2034)			104.89
54.80	23.58 (23.38)	1.2064 (1.2057)	0.6454 (0.6450)	1.38600 (1.38643)	104.96
55.95		1.2117 (1.2110)			105.01
56.80	24.47 (24.47)		0.6392 (0.6378)		
57.30	25.02 (24.97)	1.2169 (1.2174)	0.6376 (0.6363)		105.13
59.65	26.30 (26.54)	1.2257 (1.2286)			105.41
60.20	27.15 (26.91)	1.2318 (1.2313)	0.6294 (0.6297)		105.46

[a] The values of X, d_s, η, and n, calculated from eq 1, 2, 8 and 9 (below and above 35 °C) and 10, are given in parentheses.

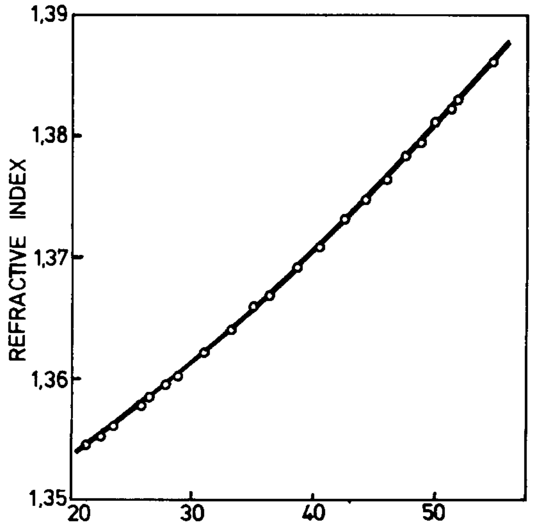

Figure 5. Dependence of refractive index, n, of saturated KBC solutions on temperature.

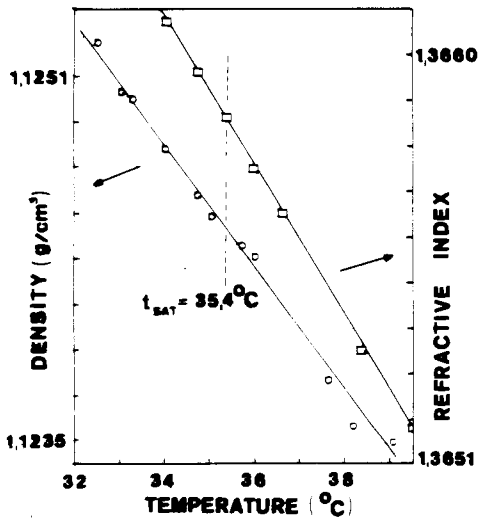

Figure 6. Temperature dependence of density (curve 1) and refractive index (curve 2) in undersaturated and supersaturated regions of KBC solution saturated at 35.4 °C.

shown in Figure 6. The correlation coefficients of d and n for various saturation temperatures were greater than 0.993 and 0.999, respectively. This implies that both d and n are linear functions of temperature around the saturation point.

Table II. Densities (d) of Aqueous KBC Solutions Saturated at Temperature t_s as a Function of Temperature t in Supersaturated and Undersaturated Regions

t_s = 26.65 °C		t_s = 32.70 °C		t_s = 35.40 °C	
t, °C	d, g/cm^3	t, °C	d, g/cm^3	t, °C	d, g/cm^3
28.10	1.0940	36.50	1.1135	38.20	1.1236
27.10	1.0943	35.90	1.1137	37.65	1.1238
26.75	1.0944	35.40	1.1138	36.05	1.1243
26.40	1.0944	34.40	1.1140	35.80	1.1244
26.20	1.0945	33.10	1.1142	35.10	1.1245
25.90	1.0946	32.20	1.1144	34.80	1.1246
25.20	1.0947	31.35	1.1146	34.10	1.1248
		29.90	1.1150	33.35	1.1250
				33.10	1.1250
				32.60	1.1252
t_s = 41.00 °C		t_s = 50.80 °C		t_s = 53.80 °C	
t, °C	d, g/cm^3	t, °C	d, g/cm^3	t, °C	d, g/cm^3
48.50	1.1442	54.30	1.1876	56.70	1.2012
47.00	1.1445	52.70	1.1880	56.00	1.2013
45.50	1.1450	51.80	1.1883	55.15	1.2014
44.25	1.1456	51.20	1.1884	54.85	1.2015
43.00	1.1457	50.70	1.1886	54.70	1.2015
41.80	1.1460	50.20	1.1887	54.15	1.2016
41.15	1.1462	49.50	1.1888	53.70	1.2018
40.65	1.1463			53.10	1.2019
39.80	1.1466			52.50	1.2020
39.50	1.1467			51.90	1.2023

Table III. Refractive Index (n) of Aqueous KBC Solutions Saturated at Temperature t_s as a Function of Temperature t in Supersaturated and Undersaturated Regions

t_s = 41.0 °C		t_s = 35.4 °C	
t, °C	n	t, °C	n
47.60	1.370 56	39.60	1.365 17
45.40	1.370 83	38.40	1.365 35
44.25	1.371 02	36.65	1.365 65
43.00	1.371 25	36.00	1.365 75
42.15	1.371 37	35.40	1.365 86
41.60	1.371 47	34.75	1.365 86
41.00	1.371 57	34.05	1.366 07
40.50	1.371 67		
39.75	1.371 77		
39.45	1.371 81		

Discussion and Conclusions

From the curves of the temperature dependence of solubility and ϕ it follows that a change in the physical properties of aqueous saturated KBC solutions takes place at a temperature of about 40 °C. The temperature dependence of viscosity of dilute and concentrated solutions also shows a change at this temperature (*12*). The fact that the change takes place at the same temperature (about 40 °C) for undersaturated and saturated solutions implies that it is associated with the properties of solvent water itself rather than the compound or its concentration. In fact Benson (*13*) has reported that the compressibility of water exhibits a minimum at 45 °C.

The dependences of the density and refractive index of the KBC solutions saturated at particular temperatures are linear functions of temperature in the supersaturated and undersaturated regions (Figure 6). This observation indicates that the natures of species present in the undersaturated and supersaturated solutions are essentially the same.

Finally, it should be remarked that Kozlova et al. (*1*, *2*) have reported a temperature of 52 °C where, according to them, phase transition in the structure of the KBC solution takes place. The results presented here, on the other hand, show that changes in some of the physical properties of saturated and undersaturated KBC solutions occur at approximately 40 °C, not 52 °C, and that this temperature is associated with the properties of solvent water. However, in order to prove or disprove the thesis proposed by Kozlova et al. (*1*, *2*) that a change in the morphology of KBC takes place at a temperature of 52 °C, it is necessary to have detailed data of a series of experiments on the growth morphology of KBC crystals under known conditions of supersaturation and temperature. The results of our growth experiments on KBC (*14*) show that a sudden change in the morphology does not occur at the above temperature.

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Glossary

A	preexponential factor in eq 1
d_s	density of saturated solution, g/cm^3
d_{H_2O}	density of water, g/cm^3
E	activation energy in eq 1, kcal/mol
M_s	mass of the solution, g
M_{KBC}	mass of KBC, g
M_{H_2O}	mass of H_2O, g
N_{KBC}	mole number of KBC
N_{H_2O}	mole number of H_2O
n	refractive index of the solution
R	gas constant
t	temperature, °C
T	temperature, K
V	volume of the solution, cm^3
$\bar{V}_{H_2O}$	molar volume of pure water, cm^3/mol
X	mole fraction of KBC in the solution
μ_{H_2O}	molecular weight of water
μ_{KBC}	molecular weight of KBC
ϕ	apparent partial molal volume, cm^3/mol
η	viscosity of the solution, cP

Registry No. KBC, 7778-50-9.

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