[Communication No. 946 from the Kodak Research Laboratories]

Some Effects of Solvents upon the Absorption Spectra of Dyes. III. Temperature and Organic Solutions of Cyanine Dyes

By S. E. Sheppard and H. R. Brigham

Some reference to the influence of temperature on solutions of cyanine dyes was made in Part I.[1] The experiments reported there have been extended, particularly to include both polar and non-polar solvents, and both neutral (otherwise dipolar) and ionized cyanine dyes.

Apparatus and Experimental Procedure

Apparatus.—The cell used to measure the spectral absorption of these dyes is shown in Fig. 1. The cooling mixture was contained in a Dewar flask which had plane windows sealed in the bottom of each wall and parallel to each other. The cell in which the sample was placed was a cylindrical glass tube which had a plane window sealed onto one end, and this cell was set on the inside window of the Dewar flask. Then, in order to eliminate trouble caused by frost forming on the surface of the solution being measured, a cylindrical tube with windows sealed on each end parallel to each other was evacuated and placed inside the cell containing the solution. This tube was held in position by a holder so that the bottom was parallel to and at a known distance from the cell window. The distance between these two cell windows, *i. e.*, the thickness of the solution, was obtained by having the holder for the evacuated cell connected to a micrometer screw graduated to 0.1 mm. The plunger is long enough so that the lower end of the liquid to be examined is at the temperature of this liquid, while the upper end is free from external frost, because maintained at room temperature.

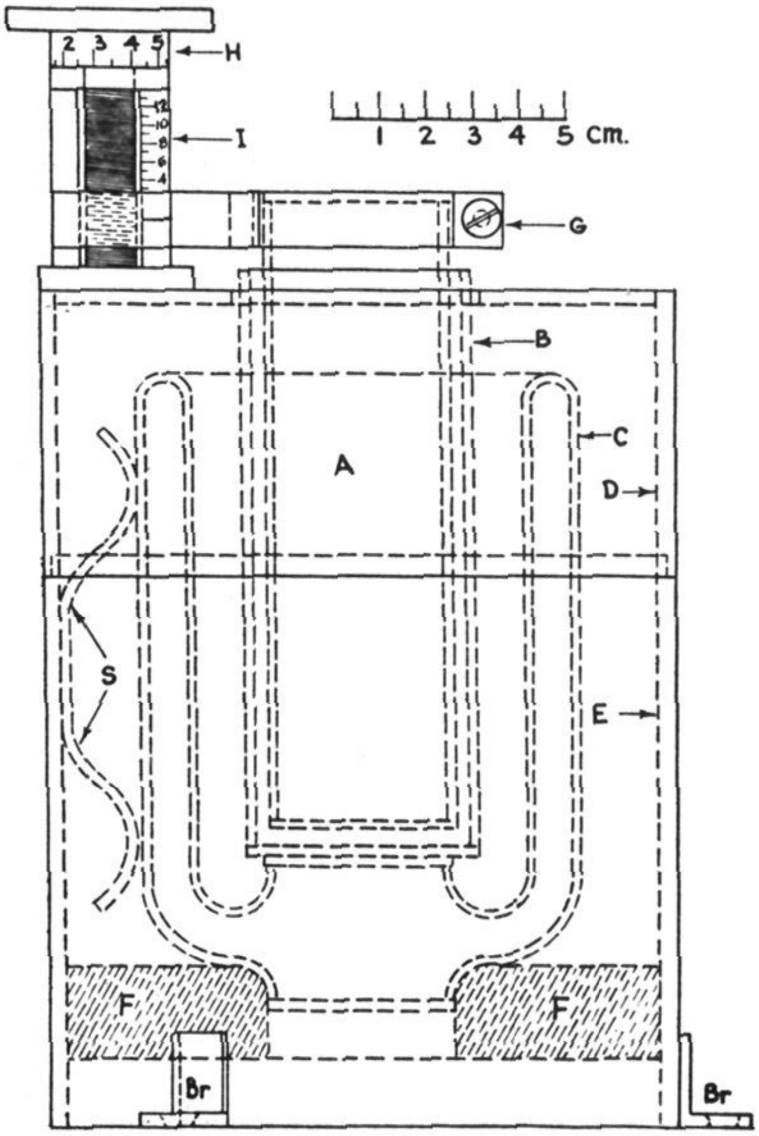
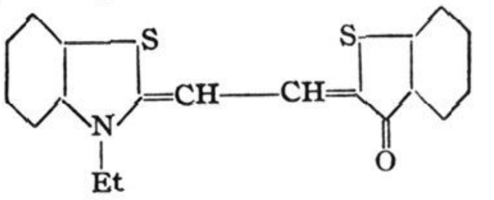


Fig. 1.—A, Cylindrical evacuated plunger; B, absorption tube holding sample; C, Dewar flask, note optical flats sealed in bottom; D and E, top and bottom of container; F, circular positioning block for Dewar flask; G, arm holding plunger; I and H, scale and vernier for plunger; S, positioning spring for Dewar flask; Br, mounting brackets.

A Hilger spectrometer, with a glass prism and calibrated for light in the visible part of the spectrum, was used for most of these measurements. The transmission was measured by the use of two barrier-layer photocells connected in a series-opposing circuit and with a potentiometer in each arm of the bridge. One of the photocells was held beneath the Dewar cell and was illuminated by part of the monochromatic light from a tungsten source after passing through the spectrometer. The second photocell was illuminated directly by the other portion of the same beam of light. The current was balanced out by means of the potentiometer so as to give a null reading instrument. The transmission is inversely proportional to the ratio of the resistance in the circuit when the solvent is in the light beam and when the dye solution is in the beam.

Other data were obtained on an instrument in which the spectrophotometer of the apparatus was replaced by a Bausch and Lomb monochromator. This was used with a photoelectric cell and amplifier. The transmission was measured by the ratio of the galvanometer deflection with the sample to that with the solvent in the beam.

Procedure.—The absorption spectra of dissolved ionized (cyanine) dyes are practically unaffected by the polarity of the solvent,[1] in respect of the position of absorption bands. We used as solvent for these a mixture of ethanol and diethyl ether, 50% each by volume. This solution became more viscous as the temperature was lowered and set to a clear glass at about −145°. This could be cooled somewhat below that temperature without losing transparency. However, at about −180°, the glass suddenly crystallized and shattered into opaque crystals, particularly if the sample was jarred. Most of the measurements were, therefore, made above −180°. As a neutral or non-ionized dye of cognate structure, a *merocyanine* having the structure



(Dye XXIII)

(I) was employed. Three solvents were used with this, of diminishing polarity, *viz.*, a 50:50 mixture of *ethanol* and *methanol*, *diethyl ether*, and *hexane*.

In the experiments in which a complete spectral absorption curve in the visible was measured at temperatures above −75°, the desired temperature was obtained by adding "dry-ice" to alcohol in the Dewar flask. For lower temperatures, liquid nitrogen was introduced into the Dewar flask in sufficient quantity to produce the desired temperature and still not have the dye solution immersed in the liquid nitrogen. The evaporation of the liquid nitrogen below the level of the inner window of the Dewar cell held the temperature of the solution constant for a time sufficient to make the measurements. The spectral ab-

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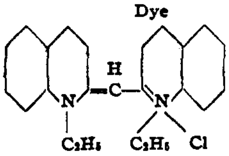
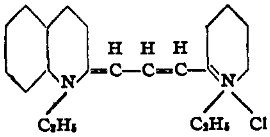
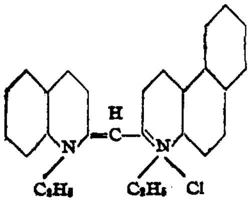
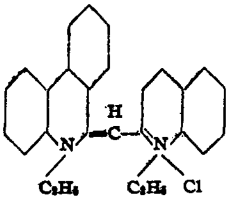
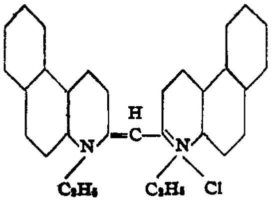
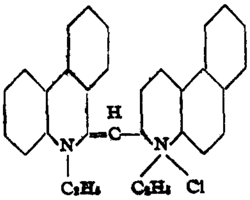
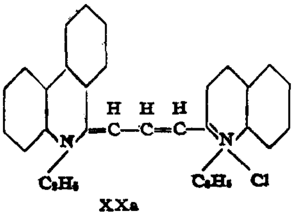
[1] S. E. Sheppard, P. T. Newsome and H. R. Brigham, This Journal, **64**, 2923 (1942).

sorption was measured as quickly as possible, beginning at the point of maximum absorption and making readings on each side of the maximum. Thus, errors due to any change in the temperature would least affect the maximum position in the absorption spectrum. The temperature was measured by a calibrated thermocouple immersed in the dye solution.

TABLE I

Dye	Temp., °C.	$\epsilon \times 10^{-4}$	Half width in mμ	Relative band strength (area sq. cm.)
 Va	298	7.85	22.0	128.5
	203	7.90	16.0	106.5
	123	7.45	16.0	111.5
 VIIa	298	17.5	18.0	111.6
	202	15.1	16.5	99.3
	108	11.9	15.5	83.3
 XVIa	298	7.65	21.0	116.9
	229	9.0	18.0	127.0
	181	8.90	16.0	124.3
	153	8.4	19.0	124.0
 XVIIa	295	4.9	27.0	82.0
	215	5.4	24.0	84.6
	137	5.90	20.0	98.5
	95	6.7	19.0	101.2
 XVIIIa	298	9.0	20.0	144.0
	266	8.75	19.0	135.5
	222	9.20	16.0	146.0
	90	7.85	15.0	136.6
 XIXa	298	4.90	27.0	85.3
	229	5.10	28.0	84.5
	92	5.55	22.5	95.5
 XXa	298	7.10	21.0	99.5
	214	8.00	16.0	94.6
	105	7.30	17.0	88.7

For temperatures above the lowest, equilibrium was obtained by first cooling the sample slightly below the desired temperature and then letting it warm up. In some cases, readings were made on either side of the point of maximum absorption at various temperatures by allowing the same sample to warm up gradually and taking a series of readings at definite temperatures.

The cyanine dyes studied, the molecular extinction coefficient of the main band, the half-width of this band, and the area under the total absorption curve in the visible which has been defined above as the band strength at the various temperatures, are given in Table I. The extinctions were calculated on a concentration of dye in solution corrected for thermal cubic expansions.

Experimental Data

To conserve space, only selected typical absorption curves are shown; *e. g.*, in Fig. 2 the full absorption curves of Dye VIIa (pinacyanol chloride) for 298°, 202° and 108°K. The fall in total absorption is discussed later. More important features are: (i) there is little or no displacement of the absorption peak, (ii) the structure of the (multiple) band becomes better defined, that is, the β and γ auxiliary bands[2] show up more clearly. There is some evidence in this example, but less in other cases examined, that with falling temperature the γ and β bands are actually strengthened relative to the α band. This may indicate some tendency to "dimerization" in the organic mixed solvent at low temperatures, a phenomenon otherwise observed with these dyes only in aqueous solution.[2] However, evidence has been presented recently[3] by G. N. Lewis, *et al.*, for spectral absorption of "dimerization" type of methylene blue in 95% ethanol at low temperature (170°K.). Dimerization and associated spectral changes will be discussed more fully in later papers.

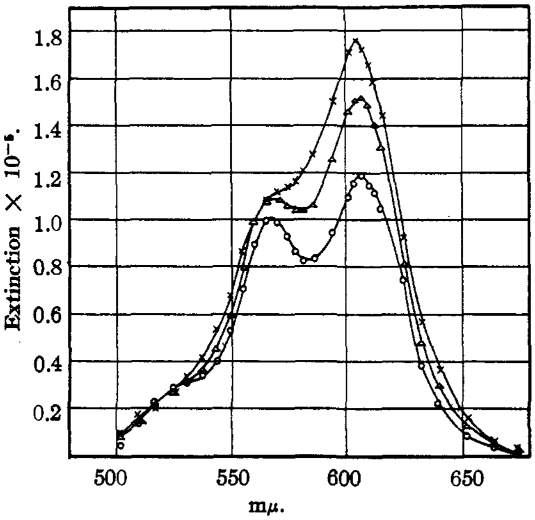


Fig. 2.—Absorption of dye VIIa solution: ×, at 298°K.; Δ, at 202°K.; O, at 108°K.

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(2) S. E. Sheppard, *Rev. Modern Physics*, **14**, 303 (1942).

(3) G. N. Lewis, O. Goldschmid, T. T. Magel and J. Bigeleisen, THIS JOURNAL, **65**, 1150 (1943).

If a phenyl group be attached to the quinoline nuclei, producing the isomeric dyes XVIa and XVIIa, the resultant molecules are more soluble in solvents of low or zero polarity. At the same time, the isomers differ in that XVI has a planar, and XVII a non-planar, configuration. These structural differences are reflected in the absorption spectra, and in the influence of temperature on the absorption spectra. The planar dye XVI indicates below 25° (298°K.) no change in band strength (*cf.* Fig. 3), but the band structure becomes sharper. With the corresponding non-planar dye XVIIa (*cf.* Fig. 4), the intensity of absorption, as shown both by the extinction at the maximum and by the band strength, actually increases as the temperature is lowered. Similar behavior, but in less marked degree, is shown by the planar and non-planar isomers XVIIIa and XIXa (*cf.* Table I).

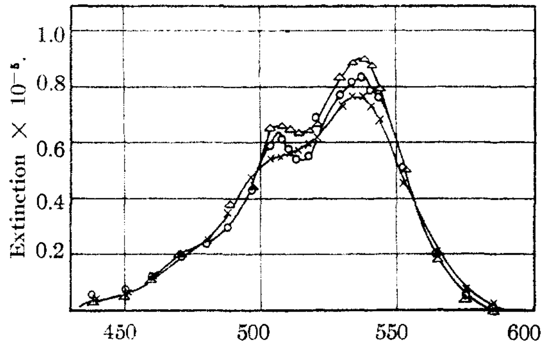


Fig. 3.—Absorption of dye XVIa solution: ×, at 298°K.; △, at 229°K.; ○, at 153°K.

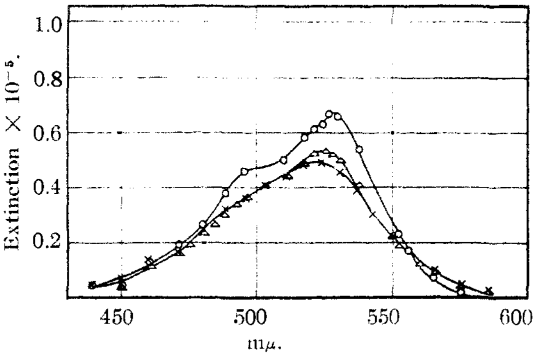


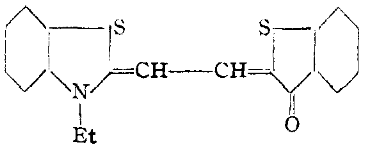
Fig. 4.—Absorption of dye XVIIa solution: ×, at 298°K.; △, at 215°K.; ○, at 95°K.

The behavior of a neutral cyanine dye (merocyanine, dye XXIII) on change of temperature in three different solvents—different in respect of molecular polar moment—is shown in Table II.

TABLE II

EFFECT OF TEMPERATURE CHANGE ON MEROCYANINE DYE SOLUTIONS

Dye XXIII



Solvent	n_D	$\mu \times 10^{18}$	E	$\nu_{max} \times 10^{-12}$ at °K. 298°	195°	123°	log ϵ_{max} at °K. 298°	195°	123°
50:50 Ethanol: Methanol	1.343	1.69	29.8	537	532	530	4.94	5.03	5.11
Ethyl ether	1.351	1.12	4.33	577	558		4.76	4.83	
Hexane	1.375	0	1.87	587	577		4.89	4.72	

n_D = Refractive index for D line at 25°. μ = Polar moment at 25°. E = Dielectric constant at 25°. ν = Frequency in fresnels. log ϵ = Logarithm of extinction coefficient.

Discussion

The first feature apparent in the effect of temperature on cyanine dye solutions is the sharpening of the band structure with fall of temperature. This is to be attributed to the progressive elimination of rotational and vibrational energies—the latter, however, corresponding only to low energy values, of the order of rotational quanta. Larger vibrational energies, say from 600 to 2000 cm.$^{-1}$, the coupling of which with fundamental electronic transitions determines the main band structure of aromatic and heterocyclic molecules, of the polyenes,[4] and also of the cyanine dyes,[5] are not extinguished until very low temperatures are reached.

A secondary result of such sharpening of the band structure is liable to be an increase in the extinction at the position of maximum absorption. While this is generally observed for the early stages of lowering of temperature, it was generally found to be followed by a fall both of the extinction at λ_m and of band strength (Fig. 5). We were inclined to attribute this fall to desolution of the dye, in consequence of reduced solubility at lower temperatures; another possibility will be noted later. In the case of dye XVIIa—the non-planar isomer of XVIa—no decrease of the extinction was observed (Fig. 6) and again with XIXa, the non-planar isomer of XVIIIa, a maximum value of log ϵ (at 4.75)

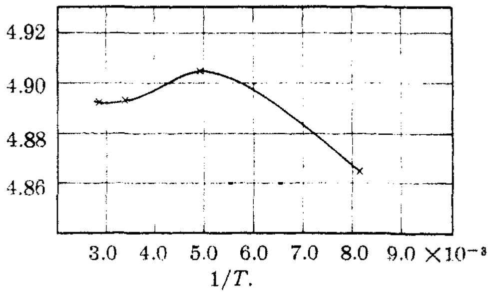


Fig. 5.—Temperature and extinction of dye Va.

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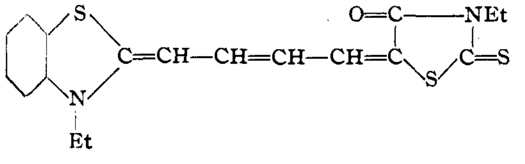
[4] K. W. Hausser, *Z. techn. Physik*, **15**, 10 (1934).

[5] S. E. Sheppard, R. H. Lambert and R. D. Walker, *J. Chem. Phys.*, **9**, 96 (1941).

was not reached until a very considerable lowering of temperature had been effected. As noticed elsewhere,[4] these non-planar dyes have a much more diffuse band and lower extinction than their planar isomers. The observations suggest that as lower temperatures are approached, the deviation from planarity tends to become less—possibly because of the lowering of thermal energy and increased capacity of the molecule to remain in a strained configuration. It is also possible that the solubility is less affected by temperature fall, which may be connected with a diminished ease of crystallization of non-planar dyes. It has been indicated elsewhere,[2] that such non-planar cyanines have less tendency to dimerize and do not form spectrally distinguishable mesophases.

Whereas the ionized cyanines dissolved in the diethyl ether–ethanol mixture showed little or no displacement of the absorption maxima in respect of wave length on change of temperature, the behavior of the non-ionized merocyanine (Dye XXIII) in various solvents is very different. In each solvent used, the absorption maxima are shifted toward the longer wave length; the shift or "red displacement" is least in the case of the mixed alcohols solvent of highest polarity, and greatest for the solvent (ethyl ether) of moderate polarity, while hexane, of zero polar moment, shows an intermediate value. These results, though less extensive than is desirable, appear to be in reasonable accord with the observations on solvents of differing polarity discussed in Part I.[1] In that, the alcohols were shown to behave as "superpolar" solvents, in which the "red displacement" approached a saturation value. In the case of solvents of zero polar moment, it may be presumed that lowering the temperature could increase the refractive index, and thereby have some, but not a large, displacement effect. There remains to be explained, therefore, the relatively large effect of lowered temperature with solvents of moderate polarity, such as *ether*.

Before dealing with this problem, and in view of the sparsity of data, it is desirable to note that another type of merocyanine dye synthesized by Dr. L. G. S. Brooker, having the structure



as well as certain related compounds, have been found by Dr. C. West[6] to exhibit qualitatively very similar properties on change of temperature of their solutions. "In non-polar solvents, *e. g.*, hexane, and in strongly polar solvents, the position of the absorption band is not very dependent on temperature. In solvents of intermediate polarity, the position of the band is strongly temperature dependent." A restatement of the effect is to say that these solvents behave as if their polar moment were raised as the temperature falls. It has been pointed out, however, in previous papers of this series[1] that the polar moments ascertainable are either for the gas state, or less certainly for solutions, and are practically unknown for the liquid state. The fact that, relative to the absorption spectra of dyes, certain strongly associated liquids behave *as if* they had much higher moments than those measured in the gas state or in dilute solutions, suggests that increasing association at lower temperatures does effectively increase the polar moments of the liquids in question.

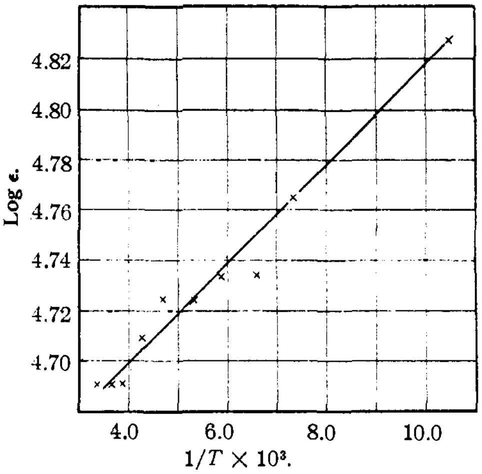


Fig. 6.—Temperature and extinction of dye XVIIa.

The total shift of the absorption band of (neutral) dyes with change of polar moment of solvent (in the present case, because of change of temperature) indicates that the coupling of *solvent* and *dye* molecules must be very sharp—practically an "all or none" affair. Otherwise, there would be no sharp or total displacement of the spectrum, but displacement associated with diffusion. This would happen if, for example, there were varying orientation of the same polar solvent molecule to the dye molecule, producing some sort of variable polarization of the latter. Actually, nothing of the sort seems to happen.

A change of capacity factor, *e. g.*, of the number of molecules effective, is observed, however, in the aforementioned changes of band strength and ϵ_{max} (extinction at peak of absorption band). In the case of fall of absorption with drop in temperature, two possibilities suggest themselves. One, already mentioned, is separation of the dye as crystals owing to decreased solubility. Another is reduction of number of (planar) dye molecules per unit time, *e. g.*, 10^{-8} sec.—suitably oriented to the electric vector of the light beam. As the temperature falls, the viscosity of the solvent increases; in fact, the mixed alcohol-ether solvent forms a clear glass at about 128°K. The importance of the orientation of planar dye molecules for the degree of absorption (extinction coefficient)

(6) Private communication.

has been shown by stretching elastic gels in which the dye was dissolved.[2] It is feasible that with increased viscosity reducing rotational and other brownian movement, effective reduction of the total absorption might occur. Alterations of *relative* intensity distribution in the full band can bring about, because of band-overlap, apparent changes of infraband intervals. Such alterations may be interpreted in terms of the relative "weights" of a principal electronic transition itself, and of higher[7] frequency members of a band spectrum produced by coupling thereof with vibrational quanta, such as that proper to a —C═C— bond.[4] How an enhancement of certain of these may be produced by difference in solvent, or by change of temperature of the same solvent, is not yet clear, and should be profitable to study.

Conclusions and Summary

Some effects of change of temperature on the absorption spectra of cyanine dyes in organic solvents have been measured over a temperature range from *ca.* 300 to 90°K. In this range the ionized cyanine dyes showed no appreciable displacement of the wave lengths of maximum absorption. The spectra became appreciably sharper as the temperature fell, which is attributed to suppression of rotational and low order vibrational energies. Temperatures were not reached sufficiently low to eliminate the vibrational quanta responsible (by coupling with the electronic transition) for the auxiliary absorption bands. The sharpening produced at first an increase in $\epsilon_{\max}$ (or log $\epsilon_{\max}$) but as the temperature was further lowered a reduction in band strength occurred—less or absent in the case of non-planar dyes. Non-ionized merocyanine dyes show a greater or less displacement of the spectrum with change of temperature, depending upon the polarity of the solvent. A notably sharp coupling of solvent and soluble (dye) molecules is indicated by this displacement.

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(7) Rarely lower; the lower values $\nu_0 - \Delta\nu$ seem to be generally prohibited in absorption. The "extra" band of merocyanines in the gas state or in non-polar solvents[3] may be an exception.

[CONTRIBUTION FROM THE EASTERN EXPERIMENT STATION, U. S. BUREAU OF MINES]

The System Potassium Carbonate–Sodium Carbonate–Water at 100 and 150°[1]

BY GUY ERVIN, JR., A. L. GIORGI AND C. E. MCCARTHY

Introduction

A study of the solubility relations in aqueous solutions of the carbonates of sodium and potassium was undertaken at this Laboratory in connection with a laboratory and pilot-plant investigation[1a] of a process for the production of potassium carbonate from wyomingite, a leucite-bearing rock found in Wyoming. The process involves a base-exchange step by which a solution containing a mixture of sodium and potassium carbonate is obtained. For the separation of the carbonates it is proposed to evaporate at 100°, producing the monohydrate, $Na_2CO_3{\cdot}H_2O$, followed by the anhydrous double salt, $K_2CO_3{\cdot}Na_2CO_3$. The resulting solution is cooled to 25°, crystallizing out potassium carbonate sesquihydrate, $K_2CO_3{\cdot}3/2H_2O$. The mother liquor from the crystallization step is recirculated to the double-salt step, and the double salt is recirculated to the original solution, thus effecting a continuous process with no material discarded. An accurate knowledge of solubility is essential to operation of the process.

Two previous studies of this system in the high-temperature range have been made in Russia[2] in connection with a similar technological problem on the treatment of solutions obtained by alkaline leaching of nepheline. At 50° and lower the system has been adequately studied by Hill and Miller.[3] The authors' results at 100° are in essential agreement with those of Makarow and Schulgina. However, those authors present data at 120, 140, and 145° which indicate that the double-salt field becomes smaller with increasing temperature and ceases to exist at 145°; upon the basis of this result they propose evaporation at 145°, thus simplifying the process by eliminating the need for recycling the double salt. In the present study at 150° conclusive evidence was obtained to prove that the double salt exists at this temperature and has actually a slightly larger field than at 100°, which is in accord with theory. Findlay (The Phase Rule, 8th Ed., p. 237) states: "... the general rule can be given, that if the water of crystallization of the two constituent salts together is greater than that of the double salt, the latter will be produced from the former on raising the temperature." This is a direct result of van't Hoff's law of mobile equilibrium, which is a particular case of the theorem of Le Chatelier.

Experimental Procedure

The sodium carbonate and potassium carbonate used were Baker c. p. reagents. Qualitative tests showed the absence of impurities. For the majority of the runs the

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(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

(1a) Unpublished work, Bureau of Mines, U. S. Department of the Interior, College Park, Md.

(2) Makarow and Schulgina, *Bull. Acad. Sci. U. S. S. R. Classe sci. chim.*, 511 (1940); Vasiliev, *Trans. State Inst. Applied Chem.*, **23**, 110 (1935).

(3) Hill and Miller, THIS JOURNAL, **49**, 669 (1927).