ground state, *i.e.*, (9) M + X → colorless products (II) + D. If k_9 (X) > k_8 > k_7 (D) then the rate of destruction of inhibitor is dependent on the rate of formation of the intermediate complex and is independent of the concentration of the inhibitor, as is observed. Furthermore, this postulation accounts for the fact that appreciable photoreduction of the bound dye cannot take place until most of the inhibitor is destroyed.

From considerations analogous to those used to calculate the Stern–Vollmer self-quenching relation[10] we obtain for the dependence of fluorescence intensity on dye concentration $(D)/[1 + k_4/k_2 (D)]$. Figure 2 shows that this relation is applicable up to a concentration of about 10^{-5} *M* ethyl violet bound to PMA, from which we calculate that $k_4/k_2 = 1.95 \times 10^5$ l./mole. If the dye molecules were free in solution k_4 would be proportional to the diffusion-controlled collision frequency but since these molecules are fixed to a polymer chain, energy transfer by other mechanisms occurs. There is evidence that energy transfer takes place in pigment systems present in photosynthetic cells and is much more efficient *in vivo* than *in vitro*.[13] Chlorophyll exists in *grana* of plants at concentrations as high as 0.1 *M*. If self-quenching of the metastable state, namely, D′ + D → 2D, were to occur in plants, as it does in solution,[5,14] one would not expect any photochemical processes involving this excited state in plants. On the other hand, our data show that step 4, namely, D* + D → D′ + D is of overwhelming importance for bound dye molecules and that the quantum yield actually increases with increasing dye concentration. In an analogous manner, since photochemical processes take place in photosynthezing systems where the bound pigments are in high concentration, there must be an intimate connection between this unusual behavior and the fact that chlorophyll exists in the bound state in living systems.

(13) L. N. M. Duysens, *Nature*, **168**, 548 (1951).

(14) H. Gaffron, *Biochem. Z.*, **264**, 251 (1933).

Brooklyn, N. Y.

[Contribution from the Department of Chemistry of the University of Kentucky]

Solvents Having High Dielectric Constants. III. Solutions of Sodium and Potassium Halides in N-Methylpropionamide and in N-Methylbutyramide from 30 to 60°[1a,b]

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Properties of solutions of sodium and potassium chlorides and iodides and potassium bromide in N-methylpropionamide and sodium and potassium chlorides in N-methylbutyramide have been measured at ten-degree intervals from 30 to 60° for concentrations ranging from 8×10^{-4} to 0.5 molar. Kohlrausch plots for all of the systems exhibit relatively good agreement with the Onsager limiting equation to 0.01 molar or more. Modifications of the Onsager equation, which include viscosity effects describe the conductances of the systems studied to concentrations of 0.2 to 0.3 molar. Both the bulk viscosity of the solvent and short-range viscosity effects around the ions appear to influence the conductance.

The properties of solutions of several alkali halides in N-methylacetamide were described in an earlier paper.[2] Good agreement with the limiting Onsager conductance equation to concentrations of 0.01 molar or more was exhibited by these systems. At higher concentrations deviations from the pattern usually observed with strong electrolytes in water were attributed primarily to viscosity effects. The present paper describes the behavior of some of these alkali halides as solutes in N-methylamides having higher molecular weights.

Experimental

The equipment, experimental procedures and purification of the salts have been described previously.[2]

Solvents.—N-Methylpropionamide was prepared by treating monomethylamine with propionic acid. Xylene was added and the mixture was heated to crack out the water and distil off the xylene–water mixture. By this means unreacted propionic acid is removed also as a xylene–acid azeotrope. After removing the xylene the product was redistilled several times at low pressure (5 mm.) through an efficient column. This process yielded N-methylpropionamide having a dielectric constant of 164 and a conductivity of 3×10^{-6} ohm^{-1} cm.$^{-1}$ at 30°.

N-Methylbutyramide was prepared by the same procedure as for N-methylpropionamide except that the distilling column was electrically heated to lower the temperature gradient. This was done to reduce the possibility of thermal decomposition. The conductivity of the product was 10^{-6} ohm^{-1} cm.$^{-1}$; its density and refractive index indicated a high degree of purity.

Solutions.—All solutions were prepared on a weight basis with transfers made in a dry-box. Sufficient quantities of solutions were prepared so that separate portions of each could be used for conductance, density and viscosity measurements.

Dielectric Constants.—Dielectric constants of N-methylbutyramide were measured with a General Radio Type 821-A Twin-T Impedance Measuring Circuit,[3] using a General Radio Type 1001-A Standard Signal Generator as a signal source and a Hallicrafters Model S-40A multiband receiver as a null detector. All measurements were made at 10 megacycles. The cell used was a modification of the type devised by Connor, Clark and Smyth[4] which has been described by Leader.[5]

Results

Properties of the solvents are listed in Tables I and II. A plot of dielectric constant against temperature at six points between 25 and 40° for N-methylbutyramide yielded a straight line from which the values at 50 and 60° were obtained by linear extrapolation.

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(1) (a) Presented at the 130th Meeting of the American Chemical Society in Atlantic City, September, 1956; (b) based in part on research performed under a contract with the U. S. Army Signal Corps.

(2) L. R. Dawson, P. G. Sears and R. H. Graves, This Journal, **77**, 1986 (1955).

(3) D. B. Sinclair, *Proc. Inst. Radio Eng.*, **28**, 310 (1940).

(4) W. P. Connor, R. P. Clark and C. P. Smyth, This Journal, **64**, 1379 (1942).

(5) G. R. Leader, *ibid.*, **73**, 856 (1951).

TABLE I

PROPERTIES OF N-METHYLPROPIONAMIDE[6]

Temp., °C.	30	40	50	60
Density (g./ml.)	0.9269	0.9188	0.9108	0.9029
Viscosity (poise)	0.04568	0.03541	0.02825	0.02278
Dielectric constant	164.3	148.9	(133.4)	(117.9)

TABLE II

PROPERTIES OF N-METHYLBUTYRAMIDE

Temp., °C.	Density, g./ml.	Viscosity, poise	Dielectric constant	Refractive index
25	0.9109 .9108[7]		128.4	1.4365 1.4365[7]
27.5			126.6	
30	.9068	0.07472	124.7	
32.5			122.8	
35			120.9	
40	.8992	.05542	117.2	
50	.8915	.04210	(109.7)	
60	.8840	.03313	(102.3)	

Results derived from the conductance data for the various systems are summarized in Table III. The conductance of each solution was corrected by subtracting the conductance of the solvent, and the data represent averages of duplicate or triplicate determinations. The precision throughout a series of measurements was of the order of 0.2 to 0.4%.

TABLE III

RESULTS DERIVED FROM CONDUCTANCE DATA FOR SOLUTIONS

Salt	Temp., °C.	Λ_0	$\Lambda_0\eta_0$	Exptl. negative slope	Onsager negative slope	Dev., %
			N-Methylpropionamide			
NaCl	30	11.3	0.515	9.1	8.9	2
	40	14.4	.510	12.6	11.9	5
	50	18.0	.509	16.4	15.7	5
	60	22.0	.502	20.9	20.6	2
KCl	30	11.6	0.530	9.8	8.9	2
	40	14.9	.527	12.3	12.0	3
	50	18.7	.527	16.5	15.6	5
	60	22.9	.521	19.9	20.7	−4
KBr	30	12.4	0.567	10.1	9.0	13
	40	15.9	.562	13.4	12.0	12
	50	19.8	.560	16.7	15.7	6
	60	24.4	.555	21.0	20.8	1
KI	30	13.7	0.624	10.3	9.0	11
	40	17.4	.615	12.9	12.1	7
	50	21.6	.610	16.3	16.0	2
	60	26.6	.604	20.4	21.0	1
NaI	30	13.4	0.610	10.0	9.0	10
	40	16.9	.599	11.5	12.1	−5
	50	21.0	.591	15.5	15.9	−3
	60	25.7	.583	19.6	20.9	−6
			N-Methylbutyramide			
NaCl	30	6.3	0.471	7.0	6.4	9
	40	8.4	.466	9.4	8.7	7
	50	11.0	.463	12.3	11.7	5
	60	13.9	.460	16.5	15.3	8
KCl	30	6.5	0.485	6.1	6.4	−5
	40	8.7	.482	8.2	8.8	−6
	50	11.4	.480	11.2	11.8	−5
	60	14.5	.480	14.7	15.4	−6

Discussion

Figure 1 shows Kohlrausch plots which are typical of the solutions studied in this investigation. The close resemblance of these to plots for the same salts in N-methylacetamide reported previously[2] is apparent. In Table III the agreement between the experimental and theoretical Onsager slopes may be seen. In fact, the experimental conductance curves for these solutions can be represented by the Onsager equation to within ten per cent. to a concentration of 0.01 *N*. Thus, the range of applicability for the theoretical equation is about four time as large on a volume concentration basis and sixteen times as large on a mole fraction basis as is found in aqueous solutions.

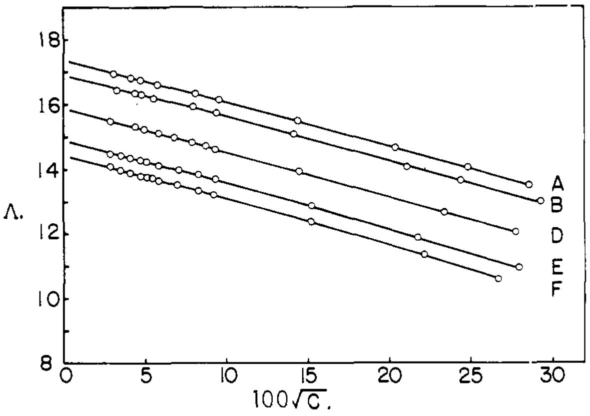

Fig. 1.—Kohlrausch plots for typical salts in N-methylpropionamide at 40°: A, KI; B, NaI; D, KBr; E, KCl; F, NaCl.

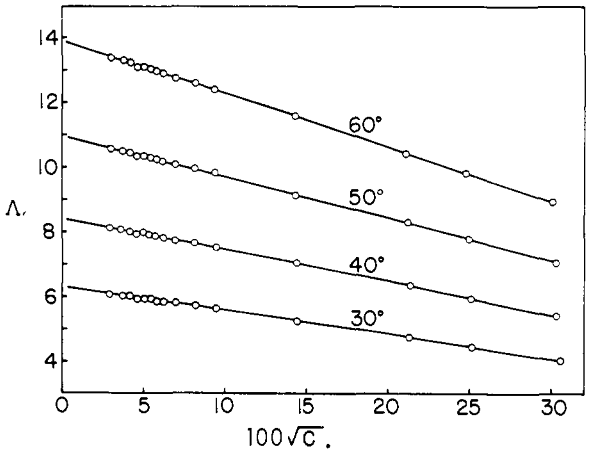

Fig. 2.—Equivalent conductance of solutions of NaCl in N-methylbutyramide.

Increased viscosity of the solvents having higher molecular weights lowers the conductance of the solutes. The alkali halides fall into the same series of decreasing mobilities in each of these solvents as in water, although the difference for the corresponding potassium and sodium salts is very small.

Although the Onsager equation is a limiting relation, it is noteworthy that this equation can be modified empirically so that in these solvents it de-

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[6] G. R. Leader and J. R. Gormley, THIS JOURNAL, **73**, 5731 (1951).

[7] G. F. D'Alelio and E. E. Reid, *ibid.*, **59**, 109 (1937).

scribes the conductance behavior to 0.2 N or more. These relationships may be expressed as

$$\Lambda\sqrt{\eta_r} = \Lambda_0 - (\alpha + \beta\Lambda_0)\sqrt{C} \tag{1}$$

$$\Lambda + (\alpha + \beta\Lambda_0)\sqrt{C} = \Lambda_0 + BC\theta_r \tag{2}$$

Data derived from plots of $\Lambda\sqrt{\eta_r}$ *versus* $\sqrt{C}$ and $\Lambda + (\alpha + \beta\Lambda_0)\sqrt{C}$ *versus* $C\theta_r$ for three salts are presented in Table IV.

TABLE IV

NEGATIVE SLOPES OF PLOTS DERIVED FROM MODIFIED EQUATIONS FOR N-METHYLPROPIONAMIDE SOLUTIONS

Salt	Temp., °C.	Eq. 1	Eq. 2
KBr	30	10.1	6.9
	40	13.4	7.0
	50	16.7	6.6
	60	21.0	4.7
KI	30	9.3	6.7
	40	11.7	5.6
	50	14.2	5.4
	60	17.7	2.7
NaI	30	9.2	5.5
	40	11.6	5.7
	50	14.5	3.2
	60	11.7	2.4

In all cases the Walden product, $\Lambda_0\eta_0$, decreases as the temperature rises, but only from one-third to one-half as rapidly as in water. The Walden product temperature coefficient is smaller for salts in N-methylbutyramide than in N-methylpropionamide; it is smaller for potassium salts than for the corresponding sodium salts in both solvents. The divergences from a strict proportionality between the viscosity temperature coefficient for the solvent and the mobility temperature coefficient for the ions leads to the conclusion that the conductance phenomenon is associated with a sort of short-range viscosity about each ion. The short-range viscosity may include distortion and other effects resulting from interaction between the solvodynamic unit and molecules or molecular groups about it, which may not change with temperature as much as the bulk viscosity of the solvent. Comparison of data for sodium and potassium salts reveals that, in the N-methylamides, thermal agitation has less effect on the short-range viscosity about the ion having the smaller crystallographic radius. The short-range viscosity around the sodium ion does not decrease with rising temperature as rapidly as the bulk viscosity; the mobility of the ion remains more nearly constant and the product decreases. In water the comparative behavior of the sodium and potassium salts is reversed with the product for the potassium salts decreasing more rapidly. It is evident that in the case of an unsolvated or slightly solvated ion (K^+ in N-methylamides) or an ion with a firmly bound sheath of solvent molecules (Na^+ or Li^+ in water) viscosity effects close to the solvodynamic unit respond to temperature changes much like the viscous forces in the body of the solvent. If the ion is partially solvated (K^+ in water) or its interaction with the solvent consists principally of distortion of the solvent structure (Na^+ in N-methylamides) the short-range viscosity exhibits less response to changes in temperature.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AT THE UNIVERSITY OF TEXAS]

The Thermodynamic Properties of Acetone

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The vapor heat capacity and heat of vaporization of acetone have been determined calorimetrically. These data were used in conjunction with molecular structure and spectroscopic information to evaluate the barriers to internal rotation in the acetone molecule and to compute tables of the thermodynamic functions. Correlation of the effects of gas imperfection in the experimental data provided an equation of state and the parameters of a Stockmayer potential function for the representation of the intermolecular forces acting in acetone vapor.

As part of a program for the study of thermodynamic properties of the industrially important oxygenated hydrocarbons, the vapor heat capacity of acetone has been determined over a range of temperatures and pressures (338 to 439°K. and $^1/_3$ to $^5/_3$ atm.). These data were used in conjunction with molecular structure and spectroscopic information from the literature to evaluate the barriers to internal rotation in the acetone molecule and to compute tables of the thermodynamic functions at selected temperatures from 0 to 1500°K. Also obtained in the experimental studies were heats of vaporization in the temperature range from 300 to 345°K. Information obtained upon evaluating the effects of gas imperfection in the experimental data has been employed to obtain an equation of state and to indicate something of the nature of the intermolecular forces acting in acetone vapor.

Physical Constants and Definitions.—All data reported here are based on the 1954 Atomic Weights,[1] the values of the fundamental physical constants reported by Rossini, *et al.*,[2] and the following definitions: 0°C. = 273.15°K. and 1 cal. = 4.1840 abs. joules. All measurements of temperature were made with platinum resistance thermometers, so that temperatures reported are on the defined International Temperature Scale.

The Material.—The sample studied was "Baker Analyzed Reagent" acetone with assay of 99.7% acetone; water was

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[1] E. Wichers, THIS JOURNAL, **76**, 2033 (1954).

[2] F. D. Rossini, F. T. Gucker, H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).