

# Solvation and Ion Pairing of Alkali-Metal Alkoxides in Dimethyl Sulfoxide. Conductometric Studies<sup>1</sup>

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**Abstract:** The effects of cation and alcohol concentration on the conductivity of 0.01 *M* lithium, sodium, potassium, and cesium salts of dimethyl sulfoxide (DMSO), methanol, and 2-methyl-2-propanol in DMSO have been determined. Dimethyl potassium and cesium behave as strong 1:1 electrolytes with limiting equivalent conductivities ( $\Lambda^\circ$ ) of 37.3 and 38.1, respectively. Dimethyl lithium and sodium exist partially as ion pairs, the ion-pairing constants being 370 and 127  $M^{-1}$  with limiting equivalent conductivities of 33.7 and 36.5, respectively. Cesium bromide in DMSO has a  $\Lambda^\circ$  of 39.9. The ionic conductivities of anions are greater than those of cations of comparable size, indicating that DMSO solvates cations more strongly than anions. Very large differences are observed in the equivalent conductivities of the various alkali-metal alkoxides. These differences are interpreted in terms of relative degrees of ion-pair formation. The ion-pairing constants for lithium, sodium, potassium, and cesium *tert*-butoxides are 10<sup>8</sup>, 10<sup>6</sup>, 270, and 200  $M^{-1}$ , respectively. Metal methoxides tend to associate more strongly than the corresponding salts of *tert*-butyl alcohol. Addition of alcohol to alkoxide solutions causes an increase in the conductance, an increase which is most pronounced for those alkoxides existing primarily as ion pairs. This conductivity change is interpreted in terms of ion-pair dissociation due to specific alkoxide solvation by alcohol. The effects of added alcohol on the degree of ion pairing of alkoxides are paralleled by changes in the apparent basicity of the alkoxides and by large rate variations in base-catalyzed reactions.

The nature of anions in dipolar aprotic solvents, such as dimethyl sulfoxide (DMSO), has aroused interest because of the tremendous increases in the rates of reactions of anions in these solvents.<sup>3</sup> Alkali-metal alkoxides, in particular, show this behavior. For example, Cram and coworkers observed racemization-rate increases of 10<sup>7</sup> with changes in the alcohol content of DMSO.<sup>4</sup> The variation in alkoxide reactivity with changes in protic solvent concentration is paralleled by corresponding changes in the base strength of alkoxides.<sup>5</sup> For example, methanol and *tert*-butyl alcohol have  $pK_A$ 's of 16 and 19, respectively, in alcohol solution. In pure DMSO, however, their respective acidity constants are 27.0 and 29.2, increases of over 10  $pK$  units. Particularly great changes in the apparent acidity of alcohols occur at alcohol concentrations of less than 10%. At low alcohol concentrations, the apparent acidity is also markedly dependent on the cation, with basicity of alkali-metal alkoxides increasing in the order  $Li < Na < K < Cs$ . This dependence of the base strength of the alkoxides on alcohol concentration and on counterion has been attributed to solvation of alkoxide ions by free alcohol and to ion pairing between alkoxide and metal cation.<sup>5</sup> Knowledge of the degrees of alkoxide solvation and of ion pairing in DMSO can contribute to an understanding of the relative importance of ground-state and

transition-state solvation in reactions in these systems.<sup>6</sup> Also, the application of highly basic media as a means of determining transition-state structure through studies of rate dependence on  $H^-$  of the medium must take into account the problem of ion pairing and specific solvation.<sup>7</sup> The study of such ionic interactions by conductivity measurements is particularly valuable because data can be obtained in dilute solutions. Consequently, the present conductometric study was initiated to ascertain the nature of the ionic species in DMSO solutions containing 0–10% alcohol.

## Experimental Section

**Dimethyl Sulfoxide.** DMSO (*ca.* 1 l., McKesson and Robbins) which contained about 1000 ppm water was placed into a dry, nitrogen-flushed, 2-l. round-bottom flask. About 6 g (at least 3 mol/mol of water present in the DMSO) of commercial sodium amide was added to the DMSO. The flask was immediately connected to a dry, nitrogen-flushed "Swissco" rotary evaporator; the evolving ammonia was removed under vacuum, and the DMSO was distilled at 0.1–0.2 mm. A forerun of *ca.* 100 ml was discarded before the major fraction was collected. The distillation required about 5 hr, during which time the pot temperature was maintained below 50°. The colorless liquid was collected in dry, 1-l. flasks fitted with three-way stopcocks at the top and a syringe-needle adapter connected to a stopcock on the bottom of the flask. Generally, two 1-l. portions of the DMSO were distilled consecutively. DMSO thus purified usually contained about 3 ppm (*ca.*  $2 \times 10^{-4} M$ ) water and essentially no other acidic impurities. The specific conductivity of the solvent was less than  $15 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  in all cases. The DMSO was stored under oxygen- and water-free nitrogen, which was used throughout this work to protect solutions from the atmosphere. In some of the later work, DMSO was distilled from sodium amide directly into the additional funnels. Avoidance of DMSO transfer from a storage vessel to the addition funnels lowered the water content to such a degree that water was no longer detectable either by Karl Fischer titration or by

(1) E. C. Steiner, R. O. Trucks, J. D. Starkey, and J. H. Exner, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, POLY 018.

(2) (a) Halogens Research Laboratory; (b) Edgar C. Britton Research Laboratory.

(3) (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; (b) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969); *Quart. Rev., Chem. Soc.*, **16**, 163 (1962).

(4) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfeld, *J. Amer. Chem. Soc.*, **83**, 3678 (1961).

(5) (a) E. C. Steiner, J. D. Starkey, J. M. Tralmer, and R. O. Trucks, 153rd Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p Q33; *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **12**, C-11 (1967); (b) E. C. Steiner and J. D. Starkey, *J. Amer. Chem. Soc.*, **89**, 2751 (1967); (c) E. C. Steiner and J. M. Gilbert, *ibid.*, **87**, 382 (1965); (d) *ibid.*, **85**, 3051 (1963).

(6) See for example (a) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968); (b) P. Haberfeld, J. Friedman, and M. F. Pinkerton, *ibid.*, **94**, 71 (1972), and references therein.

(7) (a) A. Albagli, R. Stewart, and J. R. Jones, *J. Chem. Soc.*, 1509 (1970); (b) J. R. Jones, *Chem. Commun.*, 513 (1968); (c) A. F. Cockerill and R. T. Hargreaves, *ibid.*, 915 (1969).

conductometric titration with dimsyl salt solutions (see Results). The specific conductivity of solvent purified in this manner was generally about  $3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

**Alkali-Metal Amides.** Commercial sodium amide dispersion in mineral oil, obtained from Amend Drug and Chemical Co., was washed *ca.* six times with hexane under nitrogen. The amide was then dried under vacuum before use in the drying of DMSO. The lithium, sodium, potassium, and cesium amides used in the preparation of dimsyl salt solutions were prepared by addition of the metals to liquid ammonia and were stored in sealed tubes.

**Methanol.** Methanol had been purified by the method of Evers and Knox<sup>8</sup> and contained 7 ppm water ( $1.2 \times 10^{-5}$  mol fraction).

**2-Methyl-2-propanol.** *tert*-Butyl alcohol, which was distilled at  $81^\circ$ , contained 2700 ppm water. A 2-l. portion of this alcohol was distilled through a 3 ft.  $\times$  1 in. column packed with stainless steel saddles. About 800 ml of forerun was discarded. The colorless liquid remaining in the pot contained 23 ppm water ( $9.5 \times 10^{-5}$  mol fraction) and was used without further treatment in the conductance experiments.

DMSO solutions of alcohols were prepared by adding weighed amounts of degassed alcohol to a weighed sample of degassed DMSO in an addition funnel.

**Preparation of Dimsyl Salt Solutions.** To an addition funnel which had been evacuated and purged with nitrogen three times was added *ca.* 70 ml of DMSO from the storage vessel *via* a syringe needle. In all this work, transfers of liquids were made using gas-tight Hamilton syringes through three-way stopcocks. A stream of nitrogen through the side opening of the stopcocks allowed a constant blanket of protective nitrogen to be maintained over the liquids at all times. The DMSO was degassed ( $10^{-3}$  mm) and purged with nitrogen three times. About 2 g of the corresponding alkali-metal amide, stored in a sealed ampule fitted with a nitrogen inlet arm, was added to the DMSO under nitrogen. The resultant ammonia was removed under vacuum. The solution was degassed and nitrogen purged as usual. This method gave clear colorless solutions of dimsyl salts. No residual ammonia was detectable on titration of large samples of these solutions. The concentration of dimsyl ion was determined by titrating weighed samples of pure formanilide under nitrogen to a triphenylmethane end point that was stable for 1 min. In the titration of dimsyl sodium, 9-phenylxanthene was used as the indicator. The titrations were conveniently effected by adding the weighed amounts of dimsyl solution from a gas tight syringe to the formanilide, which had previously been weighed into a vial equipped with a magnetic stirrer and a three-way stopcock. The dimsyl solutions were generally about 0.1 *M*.

**Conductance Measurements.** Conductance measurements on the sodium and part of the potassium series were made with an Industrial Instruments conductivity bridge, Model RC-BD. The remainder of the work employed a Barnstead Still and Sterilizer Co. conductivity bridge, Model PM-70CB. Both instruments had been calibrated against standard resistances and gave identical results. The conductance cell contained two 1 cm<sup>2</sup> platinum electrodes 1 cm apart. The cell had a maximum volume of 200 ml, 67 ml being required to cover the electrodes and the magnetic stirring bar. To this cell were fitted four equilibrated burets surmounted by four equilibrated reservoirs containing deoxygenated DMSO, dimsyl salt solution, and two alcohol solutions. The side arms of the reservoirs were equipped with stopcocks so the reservoirs could be isolated from the rest of the system. The volumes of the buret tips had been calibrated. The whole assembly was evacuated to  $6 \times 10^{-4}$  mm and filled with pure nitrogen four times. The cell was lowered into a water bath that was thermostated at  $25.0^\circ$  and contained an air driven magnetic stirrer used to stir the solution in the cell, and the desired volumes of solutions were added at will. With this system, stirring, solution addition, and conductometric measurements could be carried out without difficulties due to oxygen or water contamination. Readings were stable for a minimum of 2 days.

**Determination of Cell Constant.** Three 0.0746-g samples of reagent grade potassium chloride (Matheson Coleman and Bell), dried at  $110^\circ$  overnight, were weighed out and diluted to 1.00 l. with deionized water. The specific conductance,  $\kappa$ , of a  $1.00 \times 10^{-3}$  *N* solution of potassium chloride at  $25^\circ$  is  $1.47 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ .<sup>9</sup> The resistance of the solutions, *R*, was  $2.20 \times 10^3$ ,  $2.22 \times$

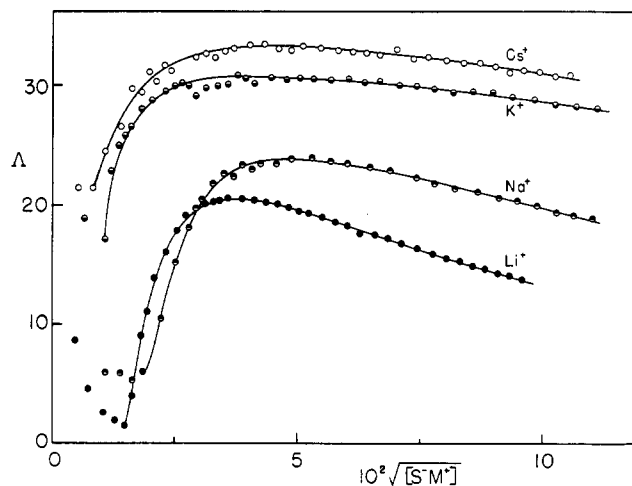


Figure 1. Apparent equivalent conductivity of dimsyl salts ( $\text{S}^- \text{M}^+$ ) in DMSO.

$10^3$ , and  $2.23 \times 10^3$  ohm. After correcting for the conductance contribution due to water, the cell constant, *d*, was determined to be  $0.329 \pm 0.001 \text{ cm}^{-1}$  from the relationship  $d = \kappa R$ . Because of the design of the cell, the cell constant varied both with resistance and with volume of solution. This variation was a maximum of 3% over the range of conditions used. Calibration curves were constructed and all readings corrected accordingly.

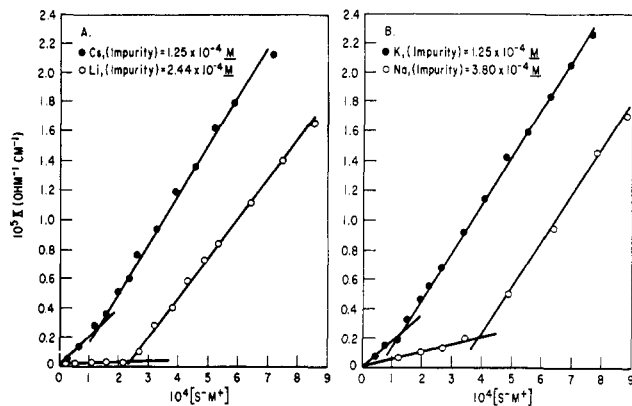
## Results

In attempting the conductometric measurements of DMSO solutions, it was necessary to work in the absence of atmospheric moisture and oxygen. The described apparatus served this purpose admirably and allowed convenient measurements over a wide range of solute concentrations. In achieving convenience of measurement over wide concentration ranges, however, the method sacrifices some of the precision usually inherent in conductivity studies. Generally, 70 ml of DMSO was added to the conductance cell, and then small amounts of the dimsyl salt solution were added to obtain the desired concentration. Alcohol was introduced from two burets, one containing a *ca.* 1 *M* solution and the other pure alcohol. By this method, it was possible to obtain data on the dimsyl salts over a range of concentration, as well as the desired data on the alkoxides. Since the dimsyl salt must be taken into account in evaluating the alkoxide conductances, the limiting conductances and ion-pairing constants of Li, Na, K, and Cs dimsyl were determined in alcohol-free solutions.

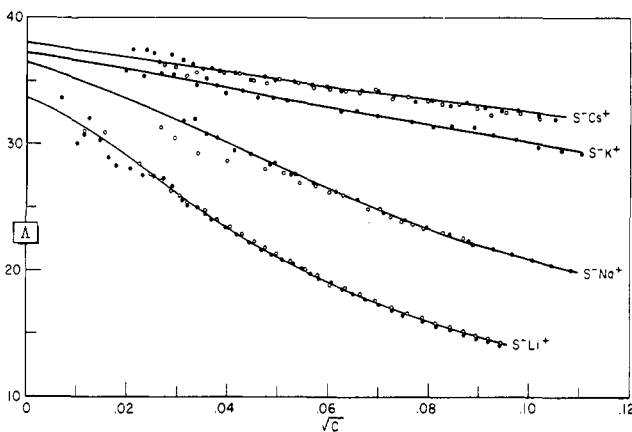
Plots of the apparent equivalent conductivity,  $\Lambda$ , *vs.* the square root of concentration of the dimsyl salts are shown for Li, Na, K, and Cs in Figure 1, where  $\Lambda = 1000\kappa/C$ ,  $\kappa$  is the specific conductivity, and *C* is the molar concentration of salt. The equivalent conductivity of the dimsyl salts appeared to be very low at low concentrations. As the concentration increased, however, the conductivity rose rapidly to a maximum and finally decreased in a normal manner at concentrations greater than  $1 \times 10^{-3}$  *M*. The anomalous results below  $10^{-3}$  *M* are attributed to the presence of about 3 ppm water, *ca.*  $2 \times 10^{-4}$  *M*. This amount of water could be estimated in each run by treating the initial points as a conductometric titration. Examples are shown in

(8) E. C. Evers and A. G. Knox, *J. Amer. Chem. Soc.*, **73**, 1739 (1951).

(9) H. M. Daggett, Jr., E. J. Bair, and C. A. Kraus, *J. Amer. Chem. Soc.*, **73**, 800 (1951).



**Figure 2.** Plot of specific conductivity vs. concentration of dimsyl salt added to DMSO. A: (●) Cs, impurity =  $1.25 \times 10^{-4} M$ , (○) Li, impurity =  $2.44 \times 10^{-4} M$ . B: (●) K, impurity =  $1.25 \times 10^{-4} M$ , (○) Na, impurity =  $3.80 \times 10^{-4} M$ .



**Figure 3.** Conductivity of dimsyl salts in DMSO. Open and closed circles represent data from two independent experiments. Values are corrected for impurity in the solvent. Lines are calculated curves,  $a = 4$ ,  $K$  as in Table I.

Figure 2. The correct concentration of dimsyl salt was obtained by subtracting the concentration of water from the formal concentration of dimsyl ion.

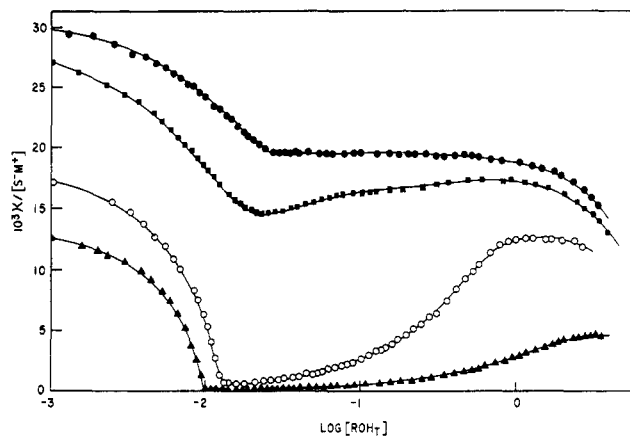
Plots of equivalent conductivity vs. the square root of the corrected concentrations gave normal curves for strong electrolytes in the case of dimsyl cesium and potassium and for partially associated electrolytes in the case of dimsyl sodium and lithium (Figure 3). The limiting equivalent conductivities and dissociation constants for the four salts were determined by the method of Fuoss and coworkers.<sup>10</sup> The results are listed in Table I.

**Table I.** Limiting Equivalent Conductivities, Ionic Conductivities, and Ion-Pairing Constants for Dimsyl Salts

Ion	$\Lambda^\circ$	$K^a$	$\lambda_{\pm}^b$
Li <sup>+</sup>	33.72	370	11.01
Na <sup>+</sup>	36.51	127	13.80
K <sup>+</sup>	37.30	15	14.59
Cs <sup>+</sup>	38.10	5	15.39
CH <sub>3</sub> SOCH <sub>2</sub> <sup>-</sup> (S <sup>-</sup> )			22.71

<sup>a</sup>  $K = [SM]/[S^-][M^+]/f_{\pm}^2$ . <sup>b</sup>  $\lambda_{Na^+}$  assumed to be 13.8: P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

(10) R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, **69**, 2581 (1965).



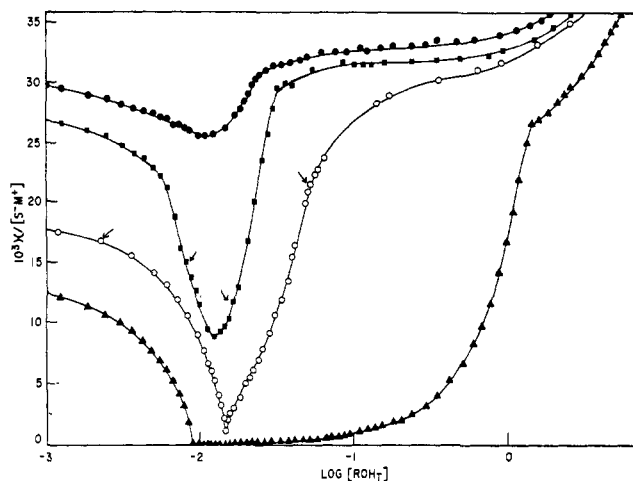
**Figure 4.** Plot of apparent equivalent conductance vs. log of added alcohol for the titration of dimsyl salts with 2-methyl-2-propanol: (●) [S<sup>-</sup>Cs<sup>+</sup>] = 0.0112 M, (■) [S<sup>-</sup>K<sup>+</sup>] = 0.0121 M, (○) [S<sup>-</sup>Na<sup>+</sup>] = 0.0121 M, (▲) [S<sup>-</sup>Li<sup>+</sup>] = 0.0092 M.

The variation of the conductance of dimsyl salt solutions upon addition of 2-methyl-2-propanol is shown in Figure 4. For comparison purposes, the data are plotted as the specific conductance divided by the base concentration vs. log [ROH] added. The curves show remarkable differences between the four alkali metals. The equivalent conductivity of the cesium system decreases from about 30 to 19 during the addition of 2.3 equivalents of *tert*-butyl alcohol. It remains constant as the alcohol concentration increases to about 0.6 M and then decreases rapidly as the alcohol concentration increases further. The curve for the potassium salt solution is very similar except for a slight minimum at about 2 equiv of alcohol. The curves for sodium or lithium salts are drastically different. There is a sharp decrease in conductivity during the addition of 1 equiv of alcohol. At the equivalence point, the equivalent conductivity is less than 1. Past this point there is a slow increase in conductance toward high alcohol concentrations. In this region, the conductance increases much faster in the sodium system than in the lithium system.

The effect of cation and of alcohol concentrations is even more pronounced in the methanol system, as may be seen in Figure 5. Decreases in conductance are observed for all four cations. Precipitates appear in the potassium and sodium cases at the left arrows and disappear as more alcohol is added, as designated by the right arrows in the figure. However, in all cases except the lithium one, the conductance increases very rapidly after the equivalence point and reaches a plateau at a conductance higher than the original value after the addition of about 10 equiv of alcohol. The conductivity increases abruptly at high methanol concentration, in contrast to the *tert*-butyl alcohol system, where a decrease occurs.

A brief study of CsBr was made in order to estimate the effect of added alcohol on the conductivity of a neutral salt and, incidentally, to check the utility of the titration method. A plot of equivalent conductivities vs. the square root of CsBr concentration in pure DMSO is shown in Figure 6 along with literature data for KBr<sup>11</sup> and CsI.<sup>12</sup> At the concentrations studied,

(11) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

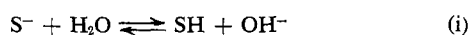


**Figure 5.** Plot of apparent equivalent conductivity vs. log of added alcohol for the titration of dimethyl salts with methanol: (●)  $[S^-Cs^+] = 0.0120 M$ , (■)  $[S^-K^+] = 0.0123 M$ , (○)  $[S^-Na^+] = 0.0125 M$ , (▲)  $[S^-Li^+] = 0.0092 M$ .

CsBr behaves as a strong electrolyte with a limiting equivalent conductivity of 39.9. Addition of *tert*-butyl alcohol to a 0.007 *M* CsBr solution caused a gradual, very small, increase in conductivity. At 0.05 *M* alcohol the conductivity had increased only 0.6% in strong contrast to the effect produced in the dimethyl solutions.

### Discussion

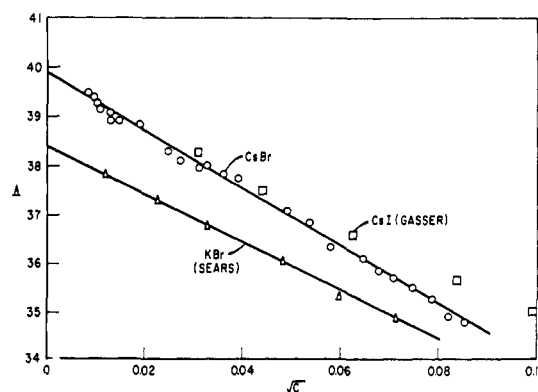
The determination of the conductivity behavior of the lyate ion of DMSO is inherently difficult due to its extreme basicity and to the difficulty in removing traces of weakly acidic materials, particularly water, from DMSO. Although a method was developed in the final stages of this work to reduce water concentrations below the detectable limit of a few tenths parts per million, most of the studies of the dimethyl ion,  $S^-$ , required a correction for about 3 ppm of water. A finite equilibrium exists for the reaction i, so that at



low concentrations a large fraction of the dimethyl ion may be converted to hydroxide ion. The mobility of unsolvated hydroxide ion should be very high, yet the conductivity at low concentrations is unexpectedly low. This implies that strong ion pairing exists between metal ion and hydroxide ion. At dimethyl salt concentrations of  $10^{-3}$  *M* or higher, the common ion effect should cause essentially complete ion pairing of any metal hydroxide. It was, therefore, assumed that any water present would merely eliminate an equivalent amount of conducting solute. The amount of water was estimated for each run as described above, and the true concentration of dimethyl salt was computed by subtraction. Data wherein the correction for water was greater than 20% were not used. The validity of this procedure was confirmed later in the work when more highly purified DMSO was available.

The limiting conductivities and ion-pairing constants were obtained by an iterative process through relationship ii, the use of which has been described by Fuoss

(12) M. D. Archer and R. P. H. Gasser, *Trans. Faraday Soc.*, **62**, 3451 (1966).



**Figure 6.** Plot of equivalent conductivity vs.  $\sqrt{C}$  for 1:1 salts in DMSO.

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + E'c\gamma \ln(6E_1'c\gamma) + Lc\gamma - K_a c\gamma f^2 \Lambda \quad (ii)$$

and coworkers.<sup>10</sup> The dielectric constant of DMSO was taken as 46.6, the viscosity as 0.0196 P, and the temperature as 298.1°K. Because of difficulties with solvent purification and the relatively low precision of the titration method, full use of the equation was not achievable. In particular, it was not possible to obtain valid estimates of the ion size parameters, and a value of 4 Å was assumed throughout. Ion-pairing constants were obtained through the relationships  $\Lambda = (c_i/c)\Lambda_i$  and  $K_a = (c - c_i)/c_i^2 f_{\pm}^2$  where  $\Lambda$  is the observed formal equivalent conductivity,  $c$  the formal concentration of solute,  $K_a$  the ion pairing constant, and  $f_{\pm} = (\exp -0.7875c_i^{1/2})/(1 + 0.3017ac_i)$ . It was assumed that ion pairs have activity coefficients of unity. The assumption of constant ion size,  $a$ , causes a relatively high uncertainty in the values of  $K$  for the Cs and K salts.

Limiting ionic conductivities for the alkali-metal cations of the dimethyl salts agree well with those reported by other investigators. The conductivities are summarized in Table II. If the conductivity of  $Na^+$  in

**Table II.** Limiting Ionic Conductivities in DMSO<sup>a</sup>

Ref	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>
11		13.8	14.4			24.2	23.8
This work	11.0	13.8	14.6	15.4 <sup>b</sup>		24.2	
12, e	11.0, 11.8	13.8		16.1	23.9	24.2	23.8
f		14.2 <sup>d</sup>	15.0 <sup>d</sup>			23.8 <sup>d</sup>	23.4 <sup>d</sup>
g		13.8	15.2	16.5	22.7	23.6	23.3
h <sup>i</sup>					24.4	24.1	23.8

<sup>a</sup>  $\lambda_0$ 's based on  $\lambda_0^{Na^+} 13.8$  and on  $\lambda_0^{Br^-} 24.2$ .<sup>11</sup> <sup>b</sup> From dimethyl series. <sup>c</sup> From cesium bromide. <sup>d</sup> Based on  $\lambda_0^{Na^+} 14.2$ . <sup>e</sup> J. S. Dunnett and R. P. H. Gasser, *Trans. Faraday Soc.*, **66**, 2872 (1970). <sup>f</sup> M. Della Monica, D. Masciopinto, and G. Tessari, *ibid.*, **66**, 2872 (1970). <sup>g</sup> F. Calmes-Perraud and Y. Doucet, *C. R. Acad. Sci., Ser. C*, **271**, 780 (1970). <sup>h</sup> D. E. Arrington and E. Griswold, *J. Phys. Chem.*, **74**, 123 (1970). <sup>i</sup> Based on tetraalkylammonium salts.

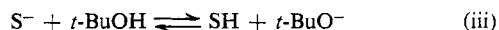
DMSO is taken as 13.8,<sup>11</sup> the internal consistency of the data is good. This agreement supports the general validity of our conductometric method.

In general, the limiting equivalent conductivity of ions increases as the ionic size decreases. In DMSO, the ionic conductivity of the metal ions increases from

about 11 for  $\text{Li}^+$  to 16 for  $\text{Cs}^+$ . Therefore, the mobility of the cations in DMSO increases with increasing ionic radius. Such a trend indicates that the small cations are solvated more strongly than the larger ions. Such specific cation-DMSO interaction has also been deduced by spectroscopic measurements.<sup>13</sup> With the anions, on the other hand, no correlation of limiting equivalent conductivity with ion size is apparent since  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  all have  $\lambda^0$ 's of about 24. In water and in alcohol, ionic conductivities of cations and anions of similar size, such as  $\text{K}^+$  and  $\text{Cl}^-$ , are approximately equal,<sup>14,15</sup> which is attributed to cation solvation and anion solvation *via* hydrogen bonding. In methanol, for example, the equivalent ionic conductivities range from 52.4 for  $\text{Cl}^-$  to 56.6 for  $\text{Br}^-$  to 62.8 for  $\text{I}^-$ , and for cations the conductivities are 39.8 for  $\text{Li}^+$ , 45.2 for  $\text{Na}^+$ , and 52.4 for  $\text{K}^+$ .<sup>16a</sup> In DMSO, the greater conductivity of anions over cations indicates that there is no significant contribution to anion solvation by hydrogen bonding. Rather, weak solvation may occur *via* ion-dipole interactions on which is superimposed an interaction due to the polarizability of the anion and the solvent.<sup>3b</sup> Conductometric and spectroscopic measurements in other aprotic solvents have shown the ability of hydrogen donors such as alcohol to interact specifically with anions.<sup>17</sup>

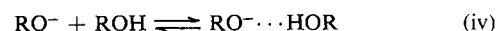
The addition of alcohol to solutions of dimsyl salts produces large changes in the conductance of the solutions. The addition of alcohol to a cesium bromide solution, on the other hand, has a negligible effect on the conductance. In a similar solvent, dimethylformamide, the addition of 1% water also does not affect the conductance of salt solutions.<sup>17d</sup> Consequently, medium effects cannot account for the large variations in conductance that are observed at low alcohol concentrations in Figures 4 and 5.

The change in the conductance of the dimsyl salt-*tert*-butyl alcohol system (Figure 4) indicates the existence of ion pairs of metal alkoxides and demonstrates specific alkoxide solvation by free alcohol in these systems. As alcohol is added to the dimsyl salt, *t*-BuO<sup>-</sup> is formed according to (iii). If both S<sup>-</sup> and



RO<sup>-</sup> exist as free ions, the decrease in conductivity should be linear. Actually, the convex nature of the conductivity curve requires the existence of both dimsyl- and alkoxide-metal ion pairs. In the cesium system, the conductance decreases during the addition of 2.3 equiv of alcohol relative to the dimsyl concentration; *i.e.*, the dimsyl salt is only converted to butoxide ions with an excess of alcohol, in accord with equilibrium iii. The conductance then remains constant over a large range of alcohol concentration. This constancy suggests that cesium *tert*-butoxide exists largely as free ions. The decrease in the con-

ductance at high alcohol concentration, where  $[\text{ROH}]/[\text{DMSO}] = 0.1$ , may be due to increasing ion-pair formation with decreasing solvent polarity since the dielectric constant of *tert*-butyl alcohol is approximately one-fourth that of DMSO ( $\sim 12$  vs. 46.6). Ion-pair formation is also consistent with the fact that sodium *tert*-butoxide has a very low conductance in *tert*-butyl alcohol.<sup>18</sup> The potassium, sodium, and lithium salt conductances decrease with varying degrees of sharpness upon the addition of alcohol to the dimsyl salts. The conductance of the sodium and lithium systems reaches a minimum at stoichiometric concentrations of added alcohol. This equivalence point implies that equilibrium iii lies completely to the right. The much larger decreases in conductance for sodium and lithium cations compared to cesium implicate the formation of greater amounts of ion pairs or aggregates. Past the equivalence point, further addition of alcohol to solutions containing ion pairs increases the conductances of the solutions. This conductance increase indicates that ion pairs or aggregates are dissociating to free ions. Since cations are solvated by DMSO, this dissociation must be due to solvation of the anion by excess alcohol. Thus, alcohol, a good anion solvator,<sup>17</sup> can stabilize the highly energetic alkoxide anion to such an extent that stabilization by cation interaction becomes less significant. The conductance behavior, therefore, supports the postulated specific solvation of alkoxides by alcohol *via* hydrogen bond formation as shown below.



The data presented in Figure 5 demonstrate that alkali-metal methoxides are less dissociated than *tert*-butoxides since even cesium methoxide shows the characteristic decrease in conductivity attributable to ion pairing. As in the *tert*-butyl alcohol system, the sodium and lithium alkoxides show strong ion pair or aggregate formation. However, methanol solvates its conjugate base more strongly than *tert*-butyl alcohol, as indicated by the sharp increase in the conductance past the equivalence point. At high alcohol concentration, *ca.* 1 M, there is another abrupt conductance increase which is probably related to a change in the polarity of the bulk solvent. At these high alcohol concentrations, the conductivities of the methoxides tend toward the limiting equivalent conductivities of 90–100 for completely dissociated methoxides in pure methanol.<sup>14</sup>

At concentrations of alcohol lower than 0.05 M, both the conductance and acidity data<sup>5</sup> require that a finite acid-base equilibrium exists between dimsyl ion and alcohol, that ion pairing occurs between cations and anions for dimsyl and alkoxide salts, and that alkoxides are specifically solvated by alcohol. The well-defined, significant changes in the conductances invited a more quantitative analysis by a computerized curve-fitting process. From Scheme I, the concentrations of all conducting species were calculated, and a solution conductance was calculated and compared to the observed conductance. The mathematical analysis showed that the chemical model in Scheme I gives satisfactory fits.<sup>19</sup> Briefly, equilibria  $K_0$ – $K_3$  were

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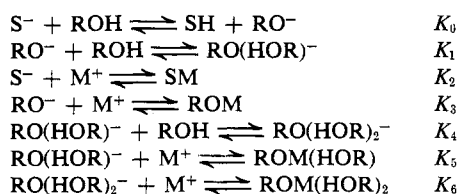
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## Scheme I



postulated to rationalize the experimental observations. However, preliminary model testing required the additional equilibria  $K_4$ – $K_6$  to account for the shapes of the curves.  $K_2$  for all cations and the limiting equivalent conductivities of the dimsyl salts were evaluated independently. Limiting equivalent conductivities of *tert*-butoxide and its solvates were estimated from the size and shape of these ions compared to ions of known conductivities. The effective ionic radius,  $a$ , has only a small effect on calculated conductivities and was arbitrarily set at 4 Å for all ions. The cesium–*tert*-butyl alcohol system was scrutinized first because of the small amounts of ion pairing which allow the solvation effects to be dominant and, therefore, easier to evaluate. For the region of low alcohol concentrations,  $K_0$ ,  $K_1$ , and  $K_3$  affect the shape of the curve in such a dramatic manner that they can be estimated very satisfactorily. Then, by extending the curve-fitting process to the higher concentrations of alcohol, values for  $K_4$ – $K_6$  can be determined by their effect on the shape of the curve. Since  $K_0$ ,  $K_1$ , and  $K_4$  are independent of cation, these values can then be used in the examination of the other cation systems. The chemical model in Scheme I represents the simplest model that is in accord with both conductivity and acidity measurements. The estimated values for the equilibria are presented in Table III. These values are reasonable

**Table III.** Relative Equilibrium Constants for Alkali-Metal *tert*-Butoxides in DMSO

M	$K_0$	$K_1$	$K_2$	$K_3$	$K_4$	$K_5$	$K_6$
Li	800	400	370	$10^8$	30	500	250
Na	800	400	127	$10^6$	30	200	100
K	800	400	15	270	30	150	60
Cs	800	400	5	200	30	75	50

and internally consistent. The numerical values for  $K_3$ , the equilibrium between *tert*-butoxide and metal ion, reinforce the great differences between lithium and sodium, with ion-pairing constants of  $10^8$  and  $10^6$ , and the much more dissociated potassium and cesium alkoxides ( $K_3 = 270$  and 200). Solvation of alkoxide by one alcohol, however, effectively diminishes this cation dependence as illustrated by the relatively small differences in equilibrium constants for  $K_5$ , ion pairing of the monosolvates.

The conductometric data, obtained by direct mea-

surements of the solution, agree very well with the acidity data,<sup>5</sup> obtained by chemical correlations, of these systems. The equilibria in Table III satisfactorily fit the acidity data; however,  $K_0$  must be 400 instead of 800 for a good fit. Differences in the basicity of the various metal *tert*-butoxides at very low alcohol concentrations result from the differences in the amount of ion pairing or aggregation. At higher alcohol concentrations, all metal alkoxides exist as dissociated, solvated alkoxides and there is no basicity variation with cation. The basicity of cesium, potassium, and sodium *tert*-butoxides in DMSO becomes equivalent at about 0.8 *M* alcohol, at a ratio of about 80 ROH/RO<sup>-</sup>. At this alcohol to alkoxide ratio, conductivity data indicate complete dissociation of solvated butoxides. Lithium *tert*-butoxide has the same base strength as the other metal alkoxides only at greater than 5 *M* alcohol, in agreement with the relatively low conductance of lithium *tert*-butoxide at 1–2 *M* alcohol. The difference in basicity between the metal methoxides is even more pronounced than in the *tert*-butyl alcohol system. Cesium and potassium methoxides have the base strength at 0.004 *M* alcohol (ROH/RO<sup>-</sup> ~0.4), sodium methoxide at ca. 0.1 *M* (ROH/RO<sup>-</sup> ~10). At these alcohol to alkoxide ratios, all three methoxides exist in the solvated, dissociated form according to conductance data. The basicity of lithium methoxide becomes equivalent to the other metal methoxides at 1 *M* methanol (ROH/RO<sup>-</sup> ~100), again in excellent agreement with conductance data.

The marked variation in the nature of the alkoxides in DMSO with alcohol concentration and cation is reflected in the basicity of these solutions. Correspondingly, base-catalyzed reactions involving alkali-metal alkoxides in aprotic solvents like DMSO should also be affected by cation and the concentration of hydroxylic solvents. Rates of reaction for the methoxide-catalyzed racemization of a nitrile decrease greatly as methanol is added to DMSO.<sup>4</sup> Similar dependencies on solvent and cation have been observed in base-catalyzed olefin isomerizations.<sup>20</sup> A systematic study of cation and alcohol concentration based on the model presented in this paper would be highly desirable since large increases in basicity can be achieved simply by variation of counterion and by alteration of the solvation shell of the alkoxide. Details of the *H*-studies, their correlation with this conductivity work, comparison with literature values for the dimsyl salt-alcohol equilibria,<sup>21,22</sup> and correlation of kinetic data with these equilibria will be described in a future publication.

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