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The Conductance of Alkali-Metal Sulfonates in Polar Organic Solvents

R. C. Little and C. R. Singleterry

Surface Chemistry Branch
Chemistry Division

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U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

ABSTRACT

The conductance of lithium and cesium dinonylnaphthalene sulfonates has been measured in a variety of solvents at 35°C. Linear Shedlovsky plots indicating a simple ion/ion-pair equilibrium were obtained for the following systems: LiDNNS-methanol, LiDNNS-ethanol, LiDNNS-n-butanol, and CsDNNS-acetone. Comparisons of dissociation constants from these plots with published data for the corresponding halides show an increased tendency toward association for the sulfonates, the dissociation constants being smaller by an order of magnitude than for the halide salts. Association beyond ion-pairs was indicated by the nonlinear Shedlovsky plots observed for the following systems: CsDNNS-ethanol, CsDNNS-n-butanol, CsDNNS-methylisobutyl ketone, CsDNNS-nitromethane, CsDNNS-1-nitropropane, LiDNNS-nitroethane, LiDNNS-1-nitropropane, LiDNNS-acetone, and LiDNNS-methylisobutyl ketone.

PROBLEM STATUS

This is an interim report. Work on other phases of the problem is continuing.

AUTHORIZATION

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INTRODUCTION

This laboratory has been engaged for some time in a research program aimed toward the production, purification, and study of high-molecular-weight organic salts in important oil systems with a view toward elucidating their specific function in these systems. A previous report (1) dealt with the solubility character of an important family of such salts, the dinonylnaphthalene sulfonates, in various types of solvents and emphasized the micellar character of the soaps.

Although there exists a significant amount of data in the literature on symmetrical salts in nonaqueous solvents, there appears to be little information available on the behavior of large asymmetric organic salts in polar nonaqueous solvents. It was therefore decided to initiate an exploratory study of the effect of polar solvents upon the conductance behavior of the sulfonates, particularly as regards specific effects such as cation size, dielectric constant, hydrogen bonding or oxygen coordination, and solubility parameter.

EXPERIMENTAL

Apparatus and Measurements

The conductance apparatus included an Industrial Instruments, Inc., Model RC 16B1 conductivity bridge and Fischer Scientific Co., low-conductance cell No. 9-366. The cell was placed in an oil bath at a temperature of 35.00° ± 0.04°C. The measurements were made at 35°C because information was already available at this temperature on the association of the DNNS salts in the solvents studied. The cell electrodes were very lightly platinized, since serious polarization effects were noted with the bright electrodes. The cell constant was determined with standard aqueous potassium chloride solution and was found to have a value of 0.208 cm^{-1}. All measurements were made at a conductance frequency of 1000 cycles per second. All critical sections of the apparatus were placed in a dry box to exclude moisture. An air pump (Cole-Palmer Model 7064) with a capacity of 600 cu in. per min circulated the dry-box air through a column of Linde 13X molecular sieve pellets. A fritted glass disk in series with the column prevented dust entrainment. The relative humidity within the dry box was monitored with an electronic hygrometer (Hygrodynamics, Inc.) and recorded during all operations. The relative humidity was less than 1.5 percent during the measurements.

Osmotic measurements were made with a commercial thermoelectric device, the Mechrolab Model 301A Osmometer. Molecular sieve materials were placed in the apparatus to maintain a water-free solvent atmosphere. Two Fenwal matched 10-K glass rod thermistors were soldered on the stainless steel leads of the commercial probe supplied with the unit. This minimized the erratic performance of the device observed when ion-conducting solutions were placed on the bare glass thermistor beads originally supplied with the device.

Materials

The lithium and cesium salts of a special grade of dinonylnaphthalene sulfonic acid (HDNNS, here abbreviated to LiDNNS and CsDNNS, respectively) are prepared by neutralization of an aqueous alcoholic solution of the acid by the appropriate base. The soaps were then lyophilized and stored in a desiccator over P_2O_5 until use. This acid and its salts have been described previously (2). All of the solvents used were ACS grade or better, except for the nitroparaffins. The latter were prepared by fractional distillation of Eastman practical grade chemicals. The solvents used and their properties at 35°C are listed in Table 1. The conductances listed in Table 1 are somewhat greater than the lowest values reported, at 25°C. The differences are usually more than would be expected from the higher temperature of the measurements. Conductance measurements were not extended to dilutions where uncertainty in the solvent correction would have been serious.

Table 1
Properties of Solvents Used for Conductance Study

Solvent	Dielectric Constant	Viscosity (poises)	Solubility Parameter (1)	Conductance at 25° (3) ($ohms^{-1}$ cm^{-1})	Conductance found, 35°C ($ohms^{-1}$ cm^{-1})
Methanol	30.7	0.0048	14.4	1.5×10^{-9}	8.7×10^{-7}
Ethanol	22.8	0.0091	12.9	1.35×10^{-9}	$<5.2 \times 10^{-8}$
Butanol	15.8	0.020	9.8	9.12×10^{-9}	$<5.2 \times 10^{-8}$
Acetone	19.7	0.0029	9.9	5.8×10^{-8}	1.2×10^{-7}
Methylisobutyl ketone	<13	–	9.5	–	$<5.2 \times 10^{-8}$
Nitromethane	35.1	0.0056	12.6	6.56×10^{-7}	1.04×10^{-6}
Nitroethane	27.4	0.0063	11.1	5×10^{-7} (30°C)	1.1×10^{-6}
1-nitropropane	22.7	0.0070	10.2	–	3.3×10^{-7}
ψ' amylalcohol	16.9 (20°C)	0.075	8.3	–	$<5.2 \times 10^{-8}$

Note – Dashes indicate that no data were available.

All solvents were freshly distilled from molecular-sieve materials under dry nitrogen before use. Solutions were made up in the dry box under a relative humidity of 3.5 percent or less.

RESULTS AND DISCUSSION

The properties of the eight solvents in which detailed conductance measurements were made are listed in Table 1. The conductance data for all 16 systems studied are presented in Fig. 1. Log conductance is plotted against the square root of the concentration. Shedlovsky (4) and Kohlrausch plots were constructed for all systems (Figs. 2-4), but only five gave linear Shedlovsky plots. Two others were found to give Kohlrausch plots, from which limiting conductances could be estimated. The curvature in the other plots made extrapolation unjustifiable. The constants derivable from these seven systems are reported in Table 2.

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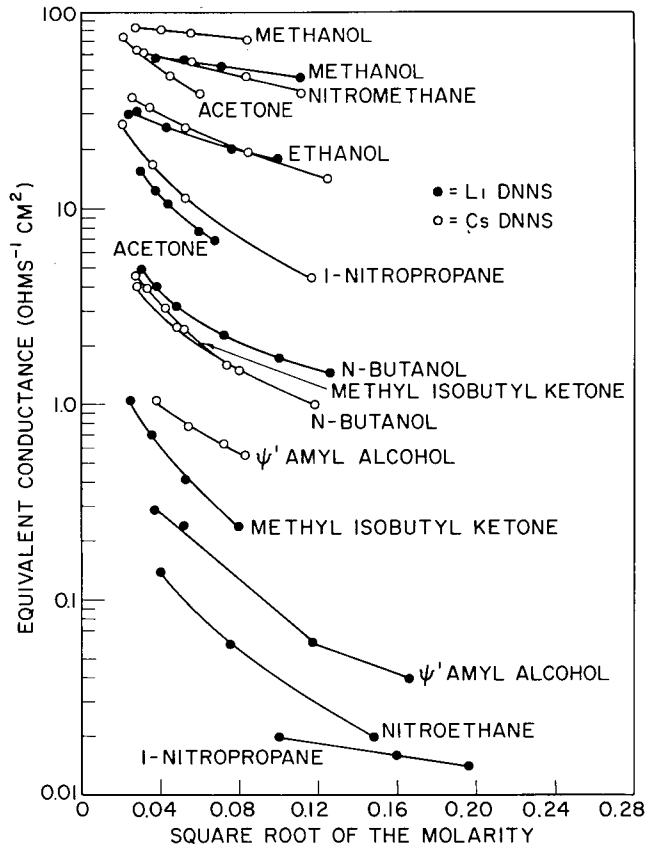

Fig. 1 - The equivalent conductance of cesium and lithium dinonylnaphthalene sulfonates in polar organic solvents

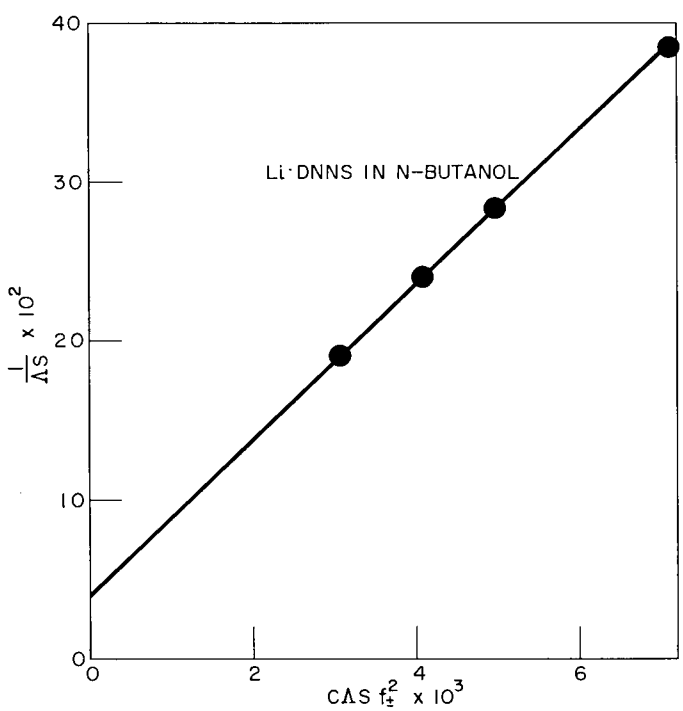

Fig. 2 - Shedlovsky plot for lithium dinonylnaphthalene sulfonate in n-butanol

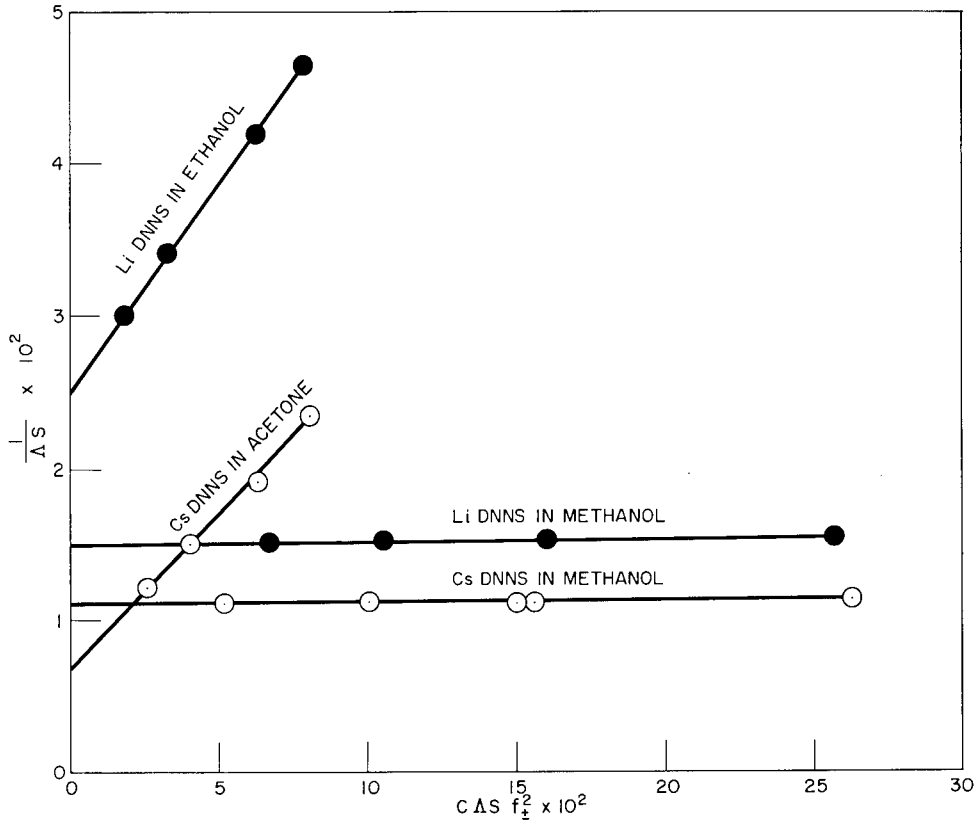

Fig. 3 - Shedlovsky plots for lithium dinonylnaphthalene sulfonate in ethanol and methanol; for cesium dinonylnaphthalene sulfonate in acetone and methanol

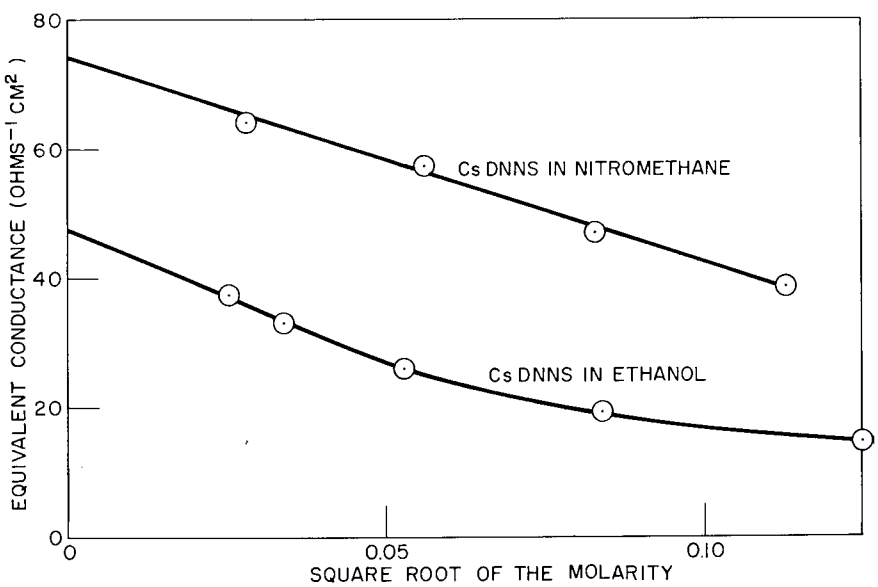

Fig. 4 - Kohlrausch plots for the cesium dinonylnaphthalene sulfonate in nitromethane and ethanol

Table 2
Conductance and Dissociation of Some Dinonylnaphthalene Sulfonates in Polar Organic Solvents

Salt	Shedlovsky Plots	Solvent	Limiting Equivalent Conductance <ohms^{-1} cm^2	Walden Product	Dissociation Constant	Bjerrum Parameter (Angstroms)
LiDNNS	Linear	methanol	67	0.31	1.2×10^{-1}	7.1
CsDNNS	Linear	methanol	91	0.44	1.7×10^{-1}	(7.3)
LiDNNS	Linear	ethanol	40	0.36	2.2×10^{-3}	3.5
LiDNNS	Linear	n-butanol	24	0.49	3.4×10^{-4}	3.0
CsDNNS	Linear	acetone	145	0.42	2.4×10^{-4}	2.1
CsDNNS	Nonlinear	ethanol	48-9	0.44	–	–
CsDNNS	Nonlinear	nitromethane	74	0.41	–	–

Single-point measurements of conductance of LiDNNS were also made in cyclohexane, dioxane, carbon tetrachloride, and benzene (not shown). The equivalent conductances of 0.01 molar solutions were less than 0.005 ohm^{-1} cm^{-2}. Sodium dinonylnaphthalene, 0.018 N, gave an equivalent conductance of 0.036 ohm^{-1} cm^{-2} in ethylacetate. Further measurements were not attempted in these solvents.

Although direct comparisons of conductance curves in various solvents can have only qualitative significance, the fact that reliable dissociation constants could not be estimated for two thirds of the systems studied makes such comparisons interesting. If the conductances of the cesium and lithium sulfonates at 35°C are compared solvent by solvent, the following features appear.

1. The equivalent conductances of the cesium and lithium DNNS differ from each other by a factor of less than two in methanol, ethanol, and butanol, although the conductance for either varies by a factor of ten from methanol to butanol, even after account is taken of differences in viscosity.

2. The cesium solutions in acetone and methylisobutyl ketone have about five times the conductance of the lithium sulfonate in these solvents.

3. The cesium sulfonate in nitroethane and 1-nitropropane has 300 to 400 times the conductance of the lithium soap in the same solvents.

These spectacular differences in behavior are believed to be a result of differing degrees of solvation of the cations and of competition between solvent and sulfonate oxygen for coordination with the lithium ion. For the cesium salt, whose cation would be expected to be only weakly solvated in any solvent, the order of decreasing conductance is roughly that of the decreasing dielectric constants of the solvents, and also of their decreasing solubility parameters. (The conductance in each of the nitroparaffins is displaced one step downward from the dielectric-constant order.) The conductances observed correspond in order of magnitude to those to be expected from the sizes of the unsolvated ions and from the dielectric constant and viscosity of the solvents (5). For the lithium sulfonate, however,

the conductance in the nitroparaffins falls to the bottom of the list, while the conductance of the butanol solution is promoted to a place above the ketones.

In the alcohols, the solvation of the lithium ion appears to give it an effective diameter such that its behavior parallels approximately that of the cesium ion. In the two ketones, the lithium DNNS conductance falls significantly below that of the cesium salt, suggesting that the interaction of the lithium ion with the solvent is insufficient to prevent close approach to the sulfonate ion in the ion pair. Solubilization studies (6)* indicate the same order of interaction of sodium or magnesium sulfonates with an alcohol and with acetone. In the nitroparaffins the energy of interaction of the lithium ion with the solvent must be so slight that coordinative association with the sulfonate oxygen controls dissociation. This interpretation is confirmed by osmotic measurements on lithium DNNS solutions in nitroethane and 1-nitropropane. An aggregation number equivalent to five soap molecules was found in these solvents.

The specific solvation through hydrogen bonding or coordination which prevents close approach during ion-pair formation should be distinguished from the interaction between a free ion and neighboring dipoles which sometime results in solvent transport and reduced mobility of the ions in an electrical field. In the present instance there is a possibility of specific solvation by coordination of the cation with oxygen atoms, or of hydrogen bonding of the alcohols to sulfonate oxygen. The anion solvation is constant when the cesium and lithium sulfonates are compared in a given solvent, except as the cation may compete with the solvent for space adjacent to the sulfonate group.

It is seen from Table 2 that four of the five systems giving linear Shedlovsky plots were in alcohols and that one of the two systems giving useful Kohlrausch plots was cesium sulfonate in ethanol. The two remaining entries in this table are for cesium DNNS in acetone and nitromethane, respectively. It has been shown (1) that alcohols are the solvents in which the dinonylnaphthalene sulfonates show the least tendency to associate to dimeric or larger aggregates, and that while the tendency to association is greater in acetone, it decreases as the diameter of the cation increases. On the other hand, the systems for which neither alkali sulfonate gave regular behavior involve solvents in which dimer, trimer, or large aggregation units are known to predominate. It is concluded that such association is chiefly responsible for the failure of two thirds of the systems to give linear Shedlovsky plots. In addition to the disturbances introduced by association of neutral sulfonate molecules, it must be expected that the dissociated ions would frequently form part of an association complex such as $(LiDNNSLi)^+$, $(DNNS.Li.DNNS)^-$ or larger units for which the simple equilibrium, ion pair $\rightleftharpoons$ ions, could not be expected to hold.

Such association effects fall off with decreasing concentration. It is possible that more systems would have shown regular behavior if conductance measurements had been carried to solutions more dilute than 10^{-4} N. Since some sulfonate association must be expected even in the alcohols, it is possible that the linearities reported may have involved small compensating deviations. On this account the dissociation constants reported cannot be considered to have high precision, although they throw useful light on the ionic behavior of high-molecular-weight organic salts in polar organic media.

Table 2 shows that both sulfonates are strongly dissociated in methanol, as are KCl and NaCl in this solvent (7). The Bjerrum parameters (a = 7.1 and 7.3 respectively) are close to the critical distance for ion-pair formation in methanol (8.9 A). Figure 1 shows that CsDNNS must also be strongly dissociated in nitromethane, although a linear Shedlovsky plot was not obtained.

*Further information on this subject is contained in unpublished work by S. Kaufman of the Naval Research Laboratory.

Table 2 also makes it possible to compare the behavior of lithium DNNS in three homologous alcohols. The progression in properties is qualitatively that to have been expected from the dielectric constants of the solvents. However, the dissociation constants and the Bjerrum parameters in ethanol and n-butanol are lower than those found for lithium chloride in ethanol (8) and for lithium iodide in n-butanol (9). In ethanol $K_{LiDNNS} = 2 \times 10^{-3}$ at 35°C, a = 3.5 A; $K_{LiCl} = 1.8 \times 10^{-2}$ at 25°C, a = 5.4 A. In n-butanol $K_{LiDNNS} = 3 \times 10^{-4}$, a = 3.0 A; $K_{LiI} = 1.4 \times 10^{-3}$, a = 3.7 A. These differences suggest that the sulfonate oxygens coordinate lithium ions more strongly than do the halide ions, thus repressing dissociation.

When the Walden products calculated from viscosities and the limiting conductances of Table 2 are compared, it is seen that for the cesium sulfonate systems the product is constant within the experimental error, as might be expected if the solvent-cesium ion interactions were slight and if solvation of the sulfonate ion altered its total surface by only a small percentage in any case. The Walden constant for lithium, on the other hand, varies by an amount greater than the experimental uncertainty, which might be expected if there were strong and specific interactions with some of the solvents.

By combining published data (10-12) with that given for CsDNNS in this report, estimates were made of the limiting conductance of the $DNNS^-$ ion in methanol, ethanol, and acetone at 35°C. The values obtained were methanol, $\Lambda o_{DNNS} = 26$; ethanol, $\Lambda o_{DNNS} = 20$; acetone, $\Lambda o_{DNNS} = 61$. The corresponding ion Walden products are 0.13, 0.18, and 0.18. In view of the uncertainties involved in adjustment of the published data to 35°C and the possibility of differences in solvent interaction, the agreement of the Walden products is as good as can be expected.

It thus appears, from the data reported here, that ion dissociation and conductance of high-molecular-weight organic salts in polar organic solvents cannot be predicted simply from experience with small anion ion pairs in the same solvents, but will depend strongly on the degree of interaction of the ionic moiety of the anion with the various cations. Conductance will also be altered by solute association. The data are not considered sufficient to show whether the ion-pair dissociation is also influenced by the presence in the anion of a low-dielectric-constant hydrocarbon radical whose dimensions are significant in comparison with the radius of strong electrostatic ion-ion interaction in solvents having a moderate dielectric constant.

SUMMARY

A study of the conductance of alkali dinonylnaphthalene sulfonates in alcohols, ketones, and nitroparaffins has led to the following generalizations about their conductance behavior.

1. Alkali-metal sulfonates do not necessarily conform to the behavior observed for smaller symmetrical salts.

2. The association tendency of the sulfonates in alcoholic solutions, as reflected in the ion-pair dissociation constants, is greater than for the corresponding halides.

3. The conductance of the sulfonates is drastically lowered when extensive association takes place.

4. If solvation of the cation is relatively weak, extensive association to large aggregates can take place, especially if the cation has a strong tendency to coordinate with anionic oxygen.

5. Much of the observed behavior for the sulfonates can be ascribed to differing degrees of solvation of the cations and to a competition between sulfonate anion and solvent molecules for the cation.

6. The low limiting ion conductances observed for the sulfonate anion in methanol, ethanol, and acetone are consistent with the bulky size of the anion.

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