raise, not lower, the relaxation time.[22] There is some evidence of the occurrence of such an inversion in tribenzylamine,[22] where the relaxation time is 14 times that of benzophenone. The lowering of the value for diphenyl ether, then, cannot be explained by an "inversion" mechanism.

Another mechanism has been proposed by Fischer,[23] who concludes that the small relaxation time must be at least an order of magnitude smaller than the relaxation time for molecular rotation. He considers that the "atomic dipole moment" due to the lone-pair electrons on the oxygen atom is modified bv resonance with the phenyl rings. As the phenyl rings rotate around their bonds to the oxygen atom, they move into orientations which permit more or less resonance and thus change both the direction and the size of the "atomic moment." A small rotation of the ring can produce a large orientational effect and might be responsible for small relaxation time. This mechanism cannot be reconciled with the small reduced relaxation time found for diphenylmethane and bibenzyl in this study, for these molecules have no lone-pair electrons. Some mechanism in which orientation occurs through varying degrees of resonance contributions, not necessarily involving lone pair electrons, is still not impossible, since a charge shift might occur in diphenylmethane and bibenzyl through hyperconjugation of the methylene groups. The intramolecular orientation process does not usually occur to the complete exclusion of the molecular orientation process. Rather, it gives rise to a second absorption region which mav overlap and may obscure the absorption due to the slower molecular orientation. A future paper from this Laboratory[24] will examine these mechanisms in greater detail.

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[22] A. H. Price, *J. Phys. Chem.*, **62**, 773 (1958).

[23] E. Fischer, *Naturwissenschaften*, **43**, 153 (1956).

[24] K. Higasi and C. P. Smyth, to be published.

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Solvent Effects on the Polarographic Reduction of Metal Ions. II. Nitrile Solvents

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The ease of polarographic reduction of metal ions is greatest in benzonitrile, followed by phenylacetonitrile, acrylonitrile, propionitrile and acetonitrile, in that order. Comparison of polarographic half-wave potentials for the reduction of metal ions in the nitriles with infrared and chemical information on the interaction of nitriles with cations suggests a bridge mechanism for the reduction of metal ions in these solvents. The ease of reduction of metal ions in benzonitrile and acrylonitrile appears to be in a large measure due to the presence of a conjugated double bond system which facilitates electron transfer; ease of reduction in phenylacetonitrile appears to be due to the low dielectric constant (18.7) of this solvent.

In a previous communication,[1] the more positive (less reducing) $E_{1/2}$ values for the reduction of metal ions in benzonitrile as compared to those in acetonitrile were explained as being due to the delocalized electrons on the phenyl ring of benzonitrile facilitating electron transfer in the bridge mechanism for the reduction process. Three additional solvents, propionitrile, acrylonitrile and phenylacetonitrile, have been studied to elucidate more clearly the factors that influence polarographic $E_{1/2}$ values for metal ions in nitrile solvents.

Experimental

The polarographic technique, cells, instrumentation, supporting electrolyte and metal perchlorates have been described previously.[1]

Solvents.—Eastman practical grade solvents were purified as described. Propionitrile was fractionally distilled from phosphorus pentoxide with a three-foot column packed with glass helices. The middle fraction, b.p. 95–96° (735 mm.), was collected. Acrylonitrile was shaken intermittently with Molecular Sieve for two days and also fractionally distilled through the three-foot column, b.p. 78 ± 0.5° (735 mm.). Phenylacetonitrile was purified by fractional distillation at reduced pressure following passage through a column of highly activated alumina, b.p. 100° (*ca.* 8 mm.).

The water content of the polarographic solutions (containing supporting electrolyte and metal perchlorate) was determined by Karl Fischer titration to be *ca.* 0.01 *M*, which was essentially that found for the solvents.

Peak-type polarograms were obtained in several cases. Maximum suppressors, such as methyl red, sodium form of methyl red and Surfactol-100, were used to eliminate the peaks; they did not alter the shape or position of the polarographic waves.

Results

$E_{1/2}$ values for the polarographic reduction of metal ions are tabulated in Table I.

Discussion

The collection of $E_{1/2}$ values in Table I shows that the ease of polarographic reduction of metal ions is greatest in benzonitrile, followed by phenylacetonitrile, acrylonitrile, propionitrile and acetonitrile, in that order. Comparison of this order and the magnitudes of the differences in $E_{1/2}$ values with dielectric constants of the solvents: phenylacetonitrile (18.7), benzonitrile (25.2), propionitrile (27.2), acetonitrile (37.5) and acrylonitrile (38), indicates only partial correlation between dielectric constants of the solvents and the $E_{1/2}$ values for the metal ions in these solvents. The shift of half-wave potentials to less negative values going from acetonitrile to benzonitrile does not appear to be due to liquid junction effect, as such an effect would give constant shifts between solvents, which is not the case. Furthermore, the small difference (0.05 v.) in $E_{1/2}$ values for the weakly solvated barium ion between acetonitrile and benzonitrile suggests that liquid junction effect is small.

The ability of a nitrile to solvate an ion lies in the presence of the C≡N group. Participation of

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[1] R. C. Larson and R. T. Iwamoto, THIS JOURNAL, **82**, 3239 (1960).

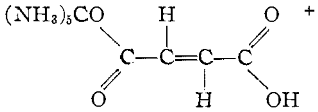
TABLE I

POLAROGRAPHIC DATA[a]

Compound	Benzonitrile[c]		Phenylacetonitrile		Acrylonitrile[d]		Propionitrile		Acetonitrile[e]	
	$E_{1/2}$	Slope	$E_{1/2}$	Slope	$E_{1/2}$	Slope	$E_{1/2}$	Slope	$E_{1/2}$	Slope
$LiClO_4$	−1.82	0.058	−1.83	0.056			−1.93	0.063	−1.95	0.068
$NaClO_4$	−1.73	.065	−1.73	.065			−1.82	.065	−1.85	.059
$Mg(ClO_4)_2$	−1.62	.082	−1.63				−1.72		−1.84	
$Ca(ClO_4)_2$	−1.73	.058	−1.79	.040			−1.83	.045	−1.82	.045
$Sr(ClO_4)_2$	−1.72	.074	−1.73				−1.78	.031	−1.76	.072
$Ba(ClO_4)_2$	−1.58	.032	−1.58	.033			−1.63	.037	−1.63	.044
$Cr(ClO_4)_3$										
Cr(II)/Cr(O)	−0.97	.034	−0.98	.044	−1.05		−1.07	.035	-1.12^{b}	.052
$Mn(ClO_4)_2$	− .98	.032	−1.02	.040	−1.05	0.034	−1.10	.036	-1.12^{b}	.028
$Fe(ClO_4)_3$										
Fe(II)/Fe(O)	− .79	.038					−0.94		-1.00^{b}	.055
$Co(ClO_4)_2$	− .49		−0.52	.037	−0.48		− .64	.033	-0.65^{b}	.037
$Ni(ClO_4)_2$	− .29	.059			− .33	.085	− .36		$- .33^{b}$	.031
$Cu(ClO_4)_2$										
Cu(I)/Cu(O)	− .20	.058	− .23	.072	− .27	.067	− .31	.063	$- .36^{b}$	.060
$Zn(ClO_4)_2$	− .53	.030	− .51	.034	− .56	.030	− .59	.035	$- .66^{b}$	.038
$Cd(ClO_4)_2$	− .17	.032	− .18	.033	− .19	.028	− .25	.033	$- .27^{b}$	.053
$AgClO_4$	+ .54	.053	+ .52	.061	+ .49	.059	+ .45	062	+ .42	.060

[a] 1 mmolar solutions with 0.1 *M* Et_4NClO_4 supporting electrolyte, except those in acetonitrile with superscript b. Where slopes are not reported, irregular polarograms were obtained. [b] 0.1 *M* $NaClO_4$ supporting electrolyte. [c] Previous paper. [d] Reduction of acrylonitrile occurs at −1.5 volt *vs.* S.C.E. [e] With thee xception of $Zn(ClO_4)_2$ and $AgClO_4$, data are those of Kolthoff and Coetzee, THIS JOURNAL, **79,** 870, 1852 (1957).

the C≡N group in solvation of metal ions should result in a change in the character of the C≡N groups. Current investigations in this Laboratory[2] show that when cations are added to these solvents new C≡N peaks appear in the 2240–2275 cm.$^{-1}$ infrared region. The $\Delta\nu$ value of the new C≡N peak from that for the pure nitrile may then be regarded as a measure of the extent of solvent-metal ion interaction. The magnitude of the $\Delta\nu$ values and hence basicity of the nitriles decreases in the order: benzonitrile, phenylacetonitrile, acrylonitrile, acetonitrile and propionitrile, with acetonitrile and propionitrile being closely alike in basicity. The study of French and Roe[3] on the ionization of picric acid in acetonitrile and benzonitrile also indicates a greater availability of electrons (basicity) in benzonitrile. The more positive $E_{1/2}$ values for the reduction of metal ions going from acetonitrile to benzonitrile cannot, therefore, be explained on the basis of lower solvation energies (basicity). The principal difference between benzonitrile and acrylonitrile on the one hand and propionitrile and acetonitrile on the other being the presence of a conjugated system of double bonds in the former solvents, it appears that the ease of reduction of metal ions in benzonitrile and acrylonitrile is in a large measure due to the conjugated system of double bonds facilitating electron transfer in the bridge mechanism involving nitrile molecules in the coördination sphere of the metal ions, much in the same manner as suggested by Taube[4] for the reaction between Cr^{++} and



Furthermore, benzonitrile with more delocalized electrons appears to be a better electron mediator than acrylonitrile.

Phenylacetonitrile, unlike benzonitrile, does not offer a conjugated system of double bonds to facilitate electron transfer. The more positive $E_{1/2}$ values in phenylacetonitrile as compared to those in acetonitrile and propionitrile must therefore be due to some other factor.

Solvation of metal ions involves both acid-base (basicity) and ion-dipole interactions. The dielectric constant of a medium, of course, governs the magnitude of the ion–dipole interaction. The dielectric constant for phenylacetonitrile, 18.7, being smaller than those for propionitrile, 27.2, and acetonitrile, 37.5, it appears that the more positive $E_{1/2}$ values in phenylacetonitrile probably are the result of smaller contributions of ion-dipole interaction to the solvation energies.

For the same reason, it appears that the more positive $E_{1/2}$ values in benzonitrile as compared to those in acrylonitrile may in part be the result of smaller ion-dipole interactions in benzonitrile due to the smaller dielectric constant of benzonitrile.

The results of this investigation strengthen our previous supposition that reduction of metal ions in nitrile solvents takes place *via* a bridge mechanism involving nitrile molecules in the coördination sphere of the metal ions.

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(2) Unpublished results.

(3) C. M. French and I. G. Roe, *Trans. Faraday Soc.*, **49,** 314, 791 1953).

(4) H. Taube, *Can. J. Chem.*, **37,** 129 (1959).