Nonaqueous Electrolytes Handbook

VOLUME I

G. J. JANZ AND
R. P. T. TOMKINS

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Rensselaer Polytechnic Institute
Troy, New York

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PREFACE

In view of the growing importance and versatility of nonaqueous ionic solutions in a wide range of disciplines, it is important to present an authoritative and updated information source for such electrolyte systems.

Nonaqueous solvent systems provide a broad range of dielectric constants, from values of about 2 in nonpolar solvents (e.g., benzene, dioxane, and carbon tetrachloride) to as great as about 182 (e.g., *N*-methyl formamide). Further features are the wide liquid-state range and the fact that viscosities, dipole moments, and molecular structure may be varied almost at will. The three-dimensional hydrogen-bonded tetrahedral network solvent structure of water changes for alcohols (methanol, ethanol, propanol, and butanol) to chains of hydrogen-bonded molecules as a two dimensional network, and for *N*-substituted amides to a simple linear hydrogen-bonded one dimensional array. Even solvents with similar dielectric constants may have quite different structures and polar properties (e.g., ethylene chloride and ethylidene chloride) and hence may show different ion-solvent interactions.

The information in this handbook covers the literature to 1972 and includes data for some 210 solvents. No attempt has been made to repeat all the information supplied in 1924 by P. Walden ("Elektrochemie nichtwässriger Lösungen"), and much useful information will be found in that work. Our handbook focuses particularly on the more recent contributions, but nevertheless does draw on the earlier studies, where relevant, for the sake of completeness.

The book has been organized into eight well-defined areas: Physical Properties of Solvents, Solvent Purification, Electrical Conductance, Diffusion, Density, Viscosity, Transference Numbers, and Additional References and Data Sources. The latter section covers additional data sources and reviews not adequately described in the preceding sections; very recent data and references will also be found in this section. The method of presentation of material is briefly described in the introduction to each section to facilitate the use of the tabulated information. Bibliographies are given at the end of each section. A Compound Index is included.

Electrical conductance is unquestionably the property most widely investigated. In view of the wealth of data, this section has therefore been organized by solutes as follows: acids and alkali metal compounds, including ammonium compounds; quaternary ammonium salts and amines;

and, finally, all other solutes. For each, the data are reported not only for single component nonaqueous solvents, but also for mixed solvents. A more detailed classification occurs within those broad categories. For each solvent there is a list of all the solutes together with references for which data are reported elsewhere in the handbook.

Information on solubilities, EMF, vapor pressure, cryoscopy, heats of solution, polarography, and electrical double layer is in preparation and will be published at a later date.

We are indebted to our research co-workers for assistance in all phases of the preparation of "Nonaqueous Electrolytes Handbook."

G. J. Janz
R. P. T. Tomkins

② ACKNOWLEDGMENTS

We are pleased to acknowledge several colleagues for authoritative contributions and for encouragement and constructive criticisms throughout this work.

Dr. John Ambrose, during the period of his tenure of a postdoctoral appointment at Rensselaer, contributed significantly to the completion of the section on electrical conductance. Dr. H. V. Venkatasetty prepared the tables relating to the electrical conductance of quaternary ammonium salts and contributed to the solvent purification and physical properties sections. Professor J. N. Butler and Dr. R. J. Jasinski opened to us their extensive records, particularly their Government Technical Reports file. Professor D. N. Bennion and Dr. N. P. Yao compiled the tabulations on dimethyl sulfoxide and dimethyl sulfite. Professor R. J. Gillespie contributed to the compilations relevant to sulfuric and fluorosulfuric acids and related superacid media.

At Rensselaer the source material for this handbook is a cumulative file to which predoctoral and postdoctoral researchers in nonaqueous electrolytes have contributed on a continuing basis over a number of years. We wish to take this opportunity to thank the following members of this "team" for their very material assistance in this respect: E. J. Andalaft, Sarada Balasubrahmanyam, B. D. Briggs, F. W. Dampier, S. S. Danyluk, F. J. Kelly, Myrna P. Klotzkin, G. R. Lakshminarayanan, A. E. Marcinkowsky, G. E. Mayer, J. Meier, Sarah Singer, M. J. Tait, W. A. Tracinski, and P. J. Turner.

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I. PHYSICAL PROPERTIES OF SOLVENTS

(a) Single Solvents

INTRODUCTION

The physical properties which are most frequently used in treating electrochemical data are dielectric constant, viscosity, density, and specific conductance. In addition the liquid state range is of interest from the practical viewpoint, and this is indicated by the melting point and boiling point temperatures. This section includes values for these properties, where available.

No attempt for a critical selection has been made, but rather the properties are reported as given in the research publications (electrical conductance, diffusion, density, viscosity, and transference number studies). Properties from additional sources are included for comparison and reference. Cryoscopic and ebullioscopic constants, dipole moments, specific heats and refractive indices of the solvents are not reported.

The listing of the solvents is alphabetical by the names most commonly used in practice.

ACETALDEHYDE (ETHANAL), CH_3CHO

b.p. (°C)	*m.p.* (°C)	*Viscosity* (millipoise)	*Dielectric* constant	Density (g/ml)
20.8 [178]	−121 [178]	2.797 (0°) [279] 2.557 (10°) [279] 2.2 (20°) [279]	21.8 (10°) [314] 21.1 (21°) [314]	0.7834 (18°) [178]

ACETAMIDE, CH_3CONH_2

b.p. (°C)	m.p. (°C)	Viscosity (millipoise)	Dielectric constant	Specific conductance ($mho \cdot cm^{-1} \times 10^8$)	Density (g/ml)
221.5 [17]	81.5 [17]	16.3 (94°) [16] 13.2 (105°) [17] 10.6 (120°) [17]	59.2 (83°) [1] 60.6 (94°) [16]	260 (94°) [17]	0.980 (105°) [17] 0.967 (120°) [17]

ACETIC ACID, CH_3CO_2H

b.p. (°C)	m.p. (°C)	Viscosity (millipoise)	Dielectric constant	Specific conductance ($mho \cdot cm^{-1} \times 10^8$)	Density (g/ml)
118.10 [2]	16.63 [3]	12.32 (20°) [7]	6.13 (20°) [4]	1.12 [5]	1.04922 (20°) [6]

ACETIC ANHYDRIDE, $(CH_3CO)_2O$

b.p. (°C)	m.p. (°C)	Viscosity (millipoise)	Dielectric constant	Specific conductance ($mho \cdot cm^{-1} \times 10^8$)	Density (g/ml)
140.0 [6]	−73.1 [6]	11.0 (18°) [8]	20.7 (18.5°) [9]	40 [10]	1.0810 (20°) [6]

ACETONE, $(CH_3)_2CO$

b.p. (°C)	m.p. (°C)	Viscosity (millipoise)	Dielectric constant	Specific conductance (mho·cm^{-1} $\times 10^8$)	Density (g/ml)
56.2 [18]	−95.4 [18]	3.02 [19][27] [28][16][30]	20.7 [19][27] [28][16][30]	0.051–13 [19] [20][21][22] [23][23][25] [26][27][28] [29][16][30] [15][31]	0.7845 [19] [20][21][23] [28]
		3.04 [20] [21] [23][24]	20.14 [29]	12 (35°) [22]	0.78345 [31]
		2.954 [16][30]	20.47 [20][21] [23]		0.7840 [26]
		3.000 [31]	29.5 (−50°) [19]		0.868 (−50°) [19]
		7.77 (−50°) [19]	28.1 (−40°) [19]		0.857 (−40°) [19]
		6.57 (−40°) [19]	26.8 (−30°) [19]		0.846 (−30°) [19]
		5.67 (−30°) [19]	25.6 (−20°) [19]		0.836 (−20°) [19]
		4.96 (−20°) [19]	24.4 (−10°) [19]		0.825 (−10°) [19]
		4.37 (−10°) [19]	23.3 (0°) [19]		0.814 (0°) [19]
		3.91 (0°) [19]	22.2 (10°) [19]		0.802 (10°) [19]
		3.51 (10°) [19]	21.2 (20°) [19]		0.791 (20°) [19]
		3.18 (20°) [19]	20.7 (20°) [32]		
		2.9 (35°) [22]	19.7 (35°) [22]		

ACETONITRILE, CH_3CN

b.p. (°C)	m.p. (°C)	Viscosity (millipoise)	Dielectric constant	Specific conductance (mho·cm^{-1} $\times 10^8$)	Density (g/ml)
81.6 [18]	−45.7 [18]	3.39 [42]	35.95 [37] [46]	1–100 [33] [35][36][38] [28][39][40] [42][44][45] [46]	0.77663 [46]

ACETONITRILE CH_3CN *(Continued)*

b.p. (°C)	m.p. (°C)	Viscosity (millipoise)	Dielectric constant	Specific conductance (mho·cm⁻¹ × 10⁸)	Density (g/ml)
		3.409 [46]	35.99 [38] [40]		0.7767 [28] [37]
		3.412 [37]	36.0 [27]		0.7768 [33] [38][39][40] [45]
		3.437 [34]	36.01 [24] [28][41]		0.77682 [43]
		3.4392 [43]	36.77 [43]		0.77683 [34]
		3.44 [27]	37.5 [42][33] [16][45][30]		0.7769 [35]
		3.449 [24] [28][41]			0.778 [42]
		3.45 [16][30]			
		3.55 [39]			
		3.594 [38] [40]			
		8.01 (−40°) [42]	49.9 (−40°) [42]	8.0 (−40°) [42]	0.845 (−40°) [42]
		6.83 (−30°) [42]	47.8 (−30°) [42]	9.3 (−30°) [42]	0.835 (−30°) [42]
		5.87 (−20°) [42]	45.7 (−20°) [42]	10.6 (−20°) [42]	0.825 (−20°) [42]
		5.09 (−10°) [42]	43.5 (−10°) [42]	12 (−10°) [42]	0.815 (−10°) [42]
		4.421 (0°) [34]	41.7 (0°) [42]	13.4 (0°) [42]	0.8052 (0°) [34]
		4.53 (0°) [39]	39.8 (10°) [42]	15.2 (10°) [42]	0.804 (0°) [42]
		4.48 (0°) [42]	38.67 (15°) [43]	17.6 (20°) [42]	0.793 (10°) [42]
		3.97 (10°) [42]	38.2 (20°) [42]		0.782 (20°) [42]
		3.57 (20°) [42]	37.67 (20°) [43]		0.78050 (20°) [43]
		3.5891 (20°) [43]	37.31 (22°) [45]		0.77516 (27°) [45]
		3.3813 (27°) [45]	36.38 (27°) [45]		0.77342 (30°) [45]
		3.2905 (30°) [45]	35.82 (30°) [45]		0.74975 (50°) [34]
		3.22 (35°) [39]			
		2.7535 (50°) [34]			