TABLE I

REFRACTIVE INDICES (n^{t}D) OF NORMAL ALIPHATIC NITRILES (UNCOR.)

Nitrile	20.0°	25.0°	30.0°	35.0°	40.0°	45.0°	50.0°	55.0°	65.0°	75.0°
Butyro-	1.3842	1.3820	1.3798	1.3773	1.3754	1.3729	1.3706	1.3862	1.3636	1.3590
Valero-	1.3972	1.3950	1.3929	1.3908	1.3887	1.3864	1.3843	1.3820	1.3774	1.3727
Capro-	1.4069	1.4049	1.4028	1.4008	1.3986	1.3966	1.3944	1.3921	1.3878	1.3834
Enantho-	1.4144	1.4124	1.4104	1.4083	1.4064	1.4044	1.4022	1.4000	1.3960	1.3917
Caprylo-	1.4204	1.4183	1.4164	1.4145	1.4124	1.4104	1.4085	1.4063	1.4021	1.3980
Pelargono-	1.4254	1.4235	1.4216	1.4197	1.4176	1.4157	1.4137	1.4115	1.4075	1.4035
Capri-	1.4296	1.4276	1.4256	1.4237	1.4218	1.4199	1.4180	1.4159	1.4119	1.4080
Undecylo-	1.4330	1.4312	1.4293	1.4273	1.4254	1.4236	1.4217	1.4197	1.4156	1.4118
Lauro-	1.4360	1.4341	1.4322	1.4304	1.4286	1.4267	1.4248	1.4227	1.4188	1.4149
Tridecylo-	1.4387	1.4368	1.4349	1.4330	1.4312	1.4294	1.4275	1.4254	1.4216	1.4177
Myristo-	1.4410	1.4392	1.4373	1.4354	1.4335	1.4317	1.4298	1.4279	1.4240	1.4202
Pentadecylo-		1.4413	1.4395	1.4376	1.4356	1.4338	1.4320	1.4300	1.4261	1.4224
Palmito-				1.4396	1.4377	1.4358	1.4340	1.4319	1.4281	1.4244
Margaro-					1.4392	1.4373	1.4355	1.4336	1.4298	1.4260
Stearo-						1.4389	1.4370	1.4351	1.4313	1.4276

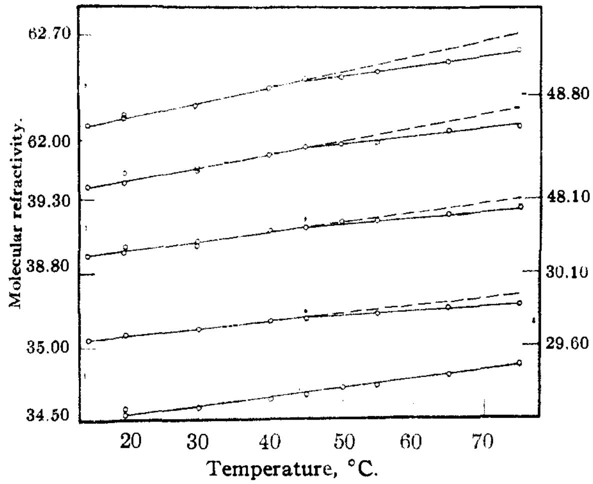

Fig. 2.—The variation of molecular refractivity with temperature: heptane (1); capronitrile (2); caprylonitrile (3); caprinitrile (4); tridecylonitrile (5).

tion of the graphs of the densities and of the refractive indices showed a distinct convergence of these curves at lower temperatures.

Highly purified specimens of *n*-heptane and *n*-octane were run as control substances. The refractive indices and the molecular refractivities of these compounds were found to be straight-line functions of temperature.

Summary

1. The refractive indices of the normal aliphatic nitriles from butyronitrile to stearonitrile inclusive were determined at a number of temperatures between 20 and 75°.

2. For each nitrile an abrupt change of slope in the refractive index *vs.* temperature curve occurs at 40–45°.

3. Corresponding graphs of the molecular refractivities also show a change of slope.

CHICAGO, ILL. RECEIVED NOVEMBER 19, 1943

[CONTRIBUTION NO. 508 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution of Sodium Chloride in Ethylene Glycol at 25°[1]

BY W. E. WALLACE, L. S. MASON AND A. L. ROBINSON

The heats of dilution of electrolytes of nearly all the common valence types have been extensively studied in aqueous solution. These heats of dilution, when extrapolated to infinite dilution, have provided ample opportunity for comparison with the Debye–Hückel limiting law. Further comparison of experiment with theory could be provided by a comparable body of data in non-aqueous media. Theory requires that, in the limit, ΦL_2, the relative apparent molal heat content of the solute, be linear with respect to the square root of the concentration, regardless of the solvent medium, but that for a salt of a given valence type ΦL_2 be dependent on certain characteristics of the solvent, namely, the dielectric constant, the temperature derivative of the dielectric constant, and the volume–temperature relationships for the particular solvent.

Probably the only significant study of heats of dilution of electrolytes in strictly non-aqueous solvents is the work of Jackson, Smith, Gatty and Wolfenden[2] who determined these properties for

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(1) This investigation was supported by a grant from the Buhl Foundation. This paper was presented to the Division of Physical and Inorganic Chemistry at the Pittsburgh meeting of the American Chemical Society, September, 1943.

(2) N. S. Jackson, A. E. C. Smith, O. Gatty and J. H. Wolfenden, *J. Chem. Soc.*, 1376–1379 (1934).

a number of electrolytes in several solvents, including methanol, nitrobenzene, nitromethane and water.

Chord-area plots[3] of their data for sodium chloride, sodium iodide, sodium perchlorate and tetraethylammonium bromide in methyl alcohol indicate extrapolated slopes of the order of 5000 to 7000, as compared to their theoretically calculated limiting slope of 2610. A single measurement for the lowest concentration of sodium perchlorate studied suggests a reversal in the direction of the theoretical slope, although here as in the other cases insufficient data are available at low concentration to permit a significant comparison with theory.[4,5]

Ethylene glycol was selected as the solvent in the present work because the Debye–Hückel theoretical limiting slope for electrolytes in this liquid is appreciably different from the value in water. The glycol is of relatively low volatility and exhibits satisfactory solubility behavior toward electrolytes.

Experimental

Heats of dilution were measured with a Lange-type differential adiabatic calorimeter, the design and operation of which have been completely described elsewhere.[6a,b,c,d]

The sodium chloride used was a c. p. product, which was dried thoroughly and used without further purification.

The ethylene glycol was obtained by fractionation of the best grade material supplied by the Carbide and Carbon Chemicals Corporation and the Coleman and Bell Company. Using a 12-plate column, the fraction whose boiling range was 197.7 to 197.8° at 760 mm. pressure was selected. After a set of dilution experiments the solvent was recovered from the salt by distillation using a Yoe still. The physical properties of the material agreed well with published values. The material had a freezing point of −12.8°, a boiling point of 197.7–197.8°, and a refractive index, n_D 1.4336 at 15°. Values from the literature are: −12.6°[7] and −13.2°[8] for the freezing point; 197.85° at 760 mm.[7] for the boiling point; and 1.43312 at 15°[7] and 1.4314 at 20°[8] for refractive index.

The purified product exhibited a strong tendency to take on atmospheric moisture. This was prevented by handling the glycol in a closed container under a carefully dried atmosphere. In spite of these precautions, a slight increase in water content was noted during the course of the investigation. Titration of the solvent using Karl Fischer reagent[9] showed a water content of about 0.1% at the beginning of the study and about 0.4% at the conclusion.

One of the chief experimental difficulties appeared to lie in the relatively high viscosity of the glycol. The time of mixing of the solutions was materially longer than in the case of aqueous solutions, stirring heats were greater, and attainment of thermal equilibrium conditions was slower. Greater opportunity for heat exchanges between the two halves of the calorimeter undoubtedly reduced the precision of the measurements as compared with studies of aqueous solutions.

Experimental Results and Treatment of Data

The treatment of data was essentially the same as used previously.[10]

In Table I, dilutions between the concentrations m_1 and m_2 will be referred to as the "long chord" dilutions, and dilutions between the concentrations m_3 and m_2 as the "short chord" dilutions.[10] The corresponding heats of dilution in calories are shown in columns 4 and 6 of Table I. It was assumed that the short chords could be represented by a three constant equation. Using established methods[3,11a,b] of analytical treatment, an equation for the slope, $S = \mathrm{d}(\Phi L_2)/\mathrm{d}m^{1/2}$, was derived. The equation

$$S = 1580 + 63{,}720m^{1/2} - 1{,}193{,}000m \qquad (1)$$

may be integrated to give

$$\Phi L_2 = 1580m^{1/2} + 31{,}860m - 397{,}700m^{3/2} \qquad (2)$$

A two constant equation

$$S = 3170 - 29{,}050m^{1/2} \qquad (3)$$

was also derived, but was found to give much larger deviations of calculated from observed heat effects. A plot of the short chords together with the curves obtained from equations (1) and (3) is shown in Fig. 1. A three constant equation using the theoretically calculated limiting slope was also derived.

$$S = 1970 + 43{,}750m^{1/2} - 889{,}900m \qquad (4)$$

It was found that this equation fitted the experimental values almost as well as equation (1).

Comparison of a plot of equation (2) with a "point-to-point"[4,12] plot indicates that the error of extrapolation to infinite dilution was not greater than ± 5 calories. By combination of

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(3) T. F. Young and O. G. Vogel, THIS JOURNAL, **54**, 3030 (1932).

(4) E. Lange and A. L. Robinson, *ibid.*, **52**, 4218 (1930), reported heats of dilution of potassium chloride in 15% sucrose solutions and in 5% urea solutions as solvents. Measurements were made to sufficiently low concentrations so that extrapolations to infinite dilution could be made. A linear relationship between ΦL_2 and $\sqrt{c}$ at the lower concentrations was observed. The values of the limiting slopes were about the same as for pure water, although the theoretical limiting slope (using the dielectric constant data of Kockel, *Ann. Physik*, **77**, 417 (1926)) had a sign opposite to the experimental slope in the case of the urea solutions. This discrepancy suggested a redetermination of the dielectric constants of the urea solutions. Calculations using later measurements of the dielectric constants (J. Wyman, Jr., THIS JOURNAL, **55**, 4116 (1933)) of the urea solutions provided reasonably good agreement between the experimental and theoretical limiting slopes.

(5) H. S. Harned, J. O. Morrison, F. Walker, J. G. Donelson and C. Calmon, *ibid.*, **61**, 49 (1939), have made a comprehensive study of the thermodynamic properties of HCl as a function of its concentration, the temperature and dielectric constant, by means of electromotive force measurements of the cell: H_2/HCl (m) dioxane (X), H_2O (Y)/AgCl − Ag in dioxane-water solutions having a dielectric constant range from 80 to 10 from 0 to 50°. It was found that observed values of $\bar{L}_2$ in dilute solutions at 25° displayed an increasing tendency to be higher than the limiting values as the dielectric constant decreased.

(6) (a) E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1930); (b) E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934); (c) T. H. Dunkelberger and A. L. Robinson, *ibid.*, **60**, 1301 (1938); (d) W. E. Wallace and A. L. Robinson, *ibid.*, **63**, 958 (1941).

(7) Timmermans and Hennaut-Roland, *J. chim. phys.*, **32**, 589 (1935).

(8) A. F. Gallaugher and H. Hibbert, THIS JOURNAL, **58**, 813 (1936).

(9) D. M. Smith, W. M. D. Bryant and J. Mitchell, Jr., *ibid.*, **61**, 2407 (1939).

(10) A. L. Robinson and W. E. Wallace, *Chem. Rev.*, **30**, 195 (1942).

(11) (a) T. F. Young and W. L. Groenier, THIS JOURNAL, **58**, 187 (1936); (b) T. F. Young and P. Seligman, *ibid.*, **60**, 2379 (1938).

(12) E. Lange, J. Monheim, and A. L. Robinson, *ibid.*, **55**, 4733 (1933).

TABLE I

INTERMEDIATE HEATS OF DILUTION OF SODIUM CHLORIDE IN ETHYLENE GLYCOL

Moles/1000 g. of glycol $10^5 m_1$	$10^5 m_2$	$10^5 m_3$	Calories $-q_{1\rightarrow 2}$	$\Delta q_{1\rightarrow 2}$	$-q_{3\rightarrow 2}$	Eqn. (5) $\Delta q_{3\rightarrow 2}$	Eqn. (2) $\Delta q_{3\rightarrow 2}$	Cal./mole salt $-\Delta H_{1\rightarrow 2}$	$-\Delta H_{3\rightarrow 2}$
17,400	187.0	372.2	0.951	+0.031	0.134	−0.019	+0.015		
17,400	187.0	372.2	.899	− .021	.101	− .052	− .017	451 ± 4	29 ± 2
17,400	187.0	372.2	.928	+ .008	.127	− .026	+ .009		
8,967	93.95	187.0	.391	− .013	.052	− .006	− .007		
8,967	93.95	187.0	.407	+ .003	.077	+ .019	+ .018	396 ± 7	38 ± 3
8,967	93.95	187.0	.439	+ .035	.076	+ .018	+ .017		
8,967	93.95	187.0	.401	− .003	.032	− .026	− .027		
4,536	47.21	93.95	.1714	+ .0020	.0385	+ .0173	+ .0161		
4,536	47.21	93.95	.1547	− .0147	.0113	− .0099	− .0111	318 ± 7	26 ± 5
4,536	47.21	93.95	.1769	+ .0075	.0401	+ .0189	+ .0177		
4,536	47.21	93.95	.1592	− .0102	.0185	− .0027	− .0039		
2,277	23.71	47.21	.0774	+ .0101	.0117	+ .0040	+ .0040		
2,277	23.71	47.21	.0768	+ .0095	.0009	− .0068	− .0068	289 ± 4	13 ± 4
2,277	23.71	47.21	.0712	+ .0039	.0085	+ .0008	+ .0008		
2,277	23.71	47.21	.0770	+ .0097					
1,144	10.92	23.71	.0332	+ .0071	.0038	+ .0007	+ .0009		
1,144	10.92	23.71	.0202	− .0059	.0006	− .0025	− .0023	181 ± 23	11 ± 3
1,144	10.92	23.71	.0187	− .0074	.0042	+ .0011	+ .0013		

the long chord heats of dilution with those calculated from equation (2), a series of values of ΦL_2 for the entire concentration range studied was obtained. A least squares treatment of the values yielded the following equation for ΦL_2

$$\Phi L_2 = 2502m^{1/2} - 4036m + 2837m^{3/2} \qquad (5)$$

The plot of equation (5) is shown in Fig. 2. Circles represent the experimental values.

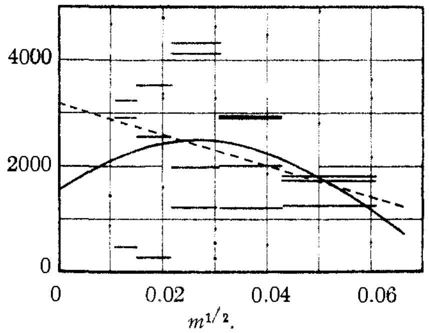

Fig. 1.—Plot of short chords ($\bar{P} = -\Delta H_{3\rightarrow 2}/\Delta m^{1/2}$) vs. $m^{1/2}$ and equations 1 and 3 for sodium chloride in ethylene glycol.

q-Values for the long chord dilutions were calculated from equation (5) and q-values for the short chord dilutions were calculated from equations (5) and (2). The deviations of calculated from observed values are shown in columns 5, 7 and 8, respectively, in Table I. Examination of these deviations shows that equation (2) is somewhat better than equation (5) for the short chord dilution range. This is perhaps to be expected considering that equation (2) was derived from the short chord range.

Relative Partial Molal Heat Contents.—Equations for $\overline{L}_1$ and $\overline{L}_2$ may be obtained directly from equation (5) by Rossini's method.[13]

$$\overline{L}_1 = -22.54m^{3/2} + 72.71m^2 - 76.68m^{5/2} \qquad (6)$$

$$\overline{L}_2 = 3753m^{1/2} - 8072m + 7093m^{3/2} \qquad (7)$$

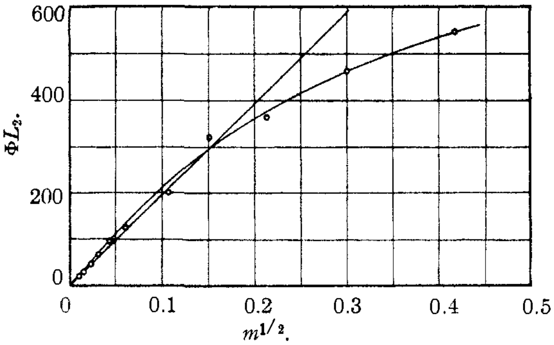

Fig. 2.—ΦL_2 (calories per mole of salt) vs. $m^{1/2}$. Curve is equation 5. The straight line is the theoretical limiting slope. Circles are experimental values.

Values of $\overline{L}_1$ and $\overline{L}_2$ at several rounded concentrations calculated from equations (6) and (7) are given in Table II.

TABLE II

m	$-\overline{L}_1$, cal./mole solvent	$\overline{L}_2$, cal./mole NaCl
0.0001	2.18×10^{-5}	37
.0005	2.34×10^{-4}	80
.001	6.42×10^{-4}	111
.01	1.60×10^{-2}	302
.05	1.13×10^{-1}	514
.1	2.28×10^{-1}	602
.2	4.79×10^{-1}	698

Comparison of Theory and Experiment

The volume-temperature relationships for

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[13] F. D. Rossini, *Bur. Standards J. Research*, **4**, 313 (1930); **6**, 791 (1931).

ethylene glycol as determined by Gibson and Loeffler[14] together with the dielectric constant data of Akerlof[15] were used for the computation of the theoretical limiting slope for a uni-univalent electrolyte in this solvent. The value is 1970 cal.-kg.solvent-moles.$^{-1/2}$ The presence of 0.4% of moisture reduces the limiting slope by about 1%. The experimental limiting slopes are 1580 from equation (1) and 2502 from equation (5). The former value is to be recommended since it was obtained by a method specifically developed for the evaluation of such quantities. The probable error of the limiting slope of equation (1) has been calculated to be ±1188.[16] This value, although relatively large, indicates that the experimentally determined limiting slope is essentially in agreement with the theoretical slope.

A comparison of ΦL_2 values for sodium chloride in glycol with those in water[11b] in the concentration range studied shows that the heat effects in general are greater in glycol than in water by a factor of 5 or 6. This might have been anticipated from the theoretical limiting slopes (477 for water). The ΦL_2 curve for water shows a maximum in the neighborhood of $m^{1/2} = 0.4$. A maximum was not realized in glycol in the concentration range studied, although the shape of the curve (Fig. 2) indicates that a maximum might occur at $m^{1/2} = 0.6$ to 0.7.

It may be noted also that the ΦL_2 curve for aqueous solutions is below the limiting law curve over the complete concentration range, but that the curve for glycol is slightly above the limiting law in the lower concentrations (Fig. 2). The same is true for $\bar{L}_2$ values in the two solvents. This behavior with decreasing dielectric constant is in qualitative agreement with the behavior of hydrochloric acid in dioxane–water mixtures.[5]

Summary

Heats of dilution of sodium chloride in ethylene glycol have been measured from 0.17*m* to 0.0001*m* at 25°. Equations for the relative apparent molal heat content of the solute and for the relative partial molal heat contents of the solute and solvent have been derived.

The experimental limiting slope is in agreement with the theoretically calculated limiting slope.

PITTSBURGH, PA. RECEIVED OCTOBER 6, 1943

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[14] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **63**, 898 (1941).

[15] G. Akerlof, *ibid.*, **54**, 4125 (1932).

[16] A. G. Worthing and Joseph Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Factors Determining the Course and Mechanisms of Grignard Reactions. XII. The Effect of Cobaltous Chloride on the Reaction of Methylmagnesium Bromide with Alicyclic Chlorides

BY M. S. KHARASCH, FRANCES ENGELMANN AND W. H. URRY

Introduction.—It was recently shown[1] that, in the presence of cobaltous chloride, phenylmagnesium bromide reacts with aliphatic halides (methyl, ethyl, propyl, *n*-butyl bromides and *t*-butyl chloride) to yield biphenyl and the saturated and unsaturated hydrocarbons derived from the alkyl halide used. A free radical mechanism was postulated to explain these results. In order to study the behavior of alicyclic free radicals in solution, the reactions of a number of alicyclic chlorides with methylmagnesium bromide in the presence and in the absence of cobaltous chloride have now been investigated.

Procedure.—The Grignard reactions were carried out according to the directions of Kharasch, Lewis and Reynolds,[1] with two modifications: a trap cooled in dry-ice was placed between the reaction flask and the gas collector, and a 10% excess of Grignard reagent was used. Twenty-gram samples were used in reactions with bornyl and isobornyl chlorides. With *cis*- and *trans*-2-methylcyclohexyl chlorides and cyclohexyl chloride, 50-g. samples were used in the cobaltous chloride catalyzed reactions, and 25-g. samples in the control experiments. In the reactions catalyzed by cobaltous chloride, the mixtures were refluxed for five hours and allowed to stand overnight. In the control experiments where no cobaltous chloride was used, refluxing was continued for twenty-eight hours.

The reaction products were analyzed by procedures described in detail in the experimental part.

Results.—The results of the reactions between the alicyclic halides and methylmagnesium bromide (shown in Table I) indicate that the normal condensations are extremely slow, and that, consequently, the secondary reaction (elimination of hydrogen chloride and formation of the unsaturated compounds) predominates.

The reaction of methylmagnesium bromide and the alicylic halides takes an entirely different course when about 5 mole per cent. of cobaltous chloride is first added to the Grignard reagent. The results are summarized in Table II.

The column headed "Unsaturated Compound" refers to camphene and bornylene in experiments

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[1] Kharasch, Lewis and Reynolds, THIS JOURNAL, **65**, 493 (1943).