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$$(D_{N_2O}\mu_L^{0.8})_{\text{amine soln}} = \text{constant} = (D_{N_2O}\mu_L^{0.8})_{\text{water}} \qquad (13)$$

for the diffusivities of N_2O in various aqueous alkanolamine solutions. The viscosities of these solutions ranged from 0.001 to 0.007 N s/m^2. It is assumed that this modified Stokes–Einstein relation can also be applied for the estimation of liquid-phase diffusivities at the higher viscosities up to 0.040 N s/m^2 for the solutions in the present study. If this assumption is justified, the diffusivities of CO_2 in solutions of DEA in aqueous ETG can be estimated from the correlation of eq 11 with the aid of the modified Stokes–Einstein relation

$$(D_{CO_2}\mu_L^{0.8})_{\text{amine soln}} = \text{constant} = (D_{CO_2}\mu_L^{0.8})_{\text{pure solvent}} \qquad (14)$$

Without knowledge about the exact value of the constant in eq 14 the diffusivity of CO_2 in a solution of DEA in aqueous ETG can be estimated from the viscosity of this DEA solution and the viscosity and diffusivity of CO_2 in the pure ETG solvent with the same ETG mass percentage. The relevant data can be calculated from eq 5–7 and 12.

4. Conclusions

The results of the experimental work from the present study lead to the following conclusions:

1. The ratio of the solubilities of CO_2 and N_2O in aqueous ETG at 298 K remains practically constant over the whole composition range of mixtures of water and ETG.
2. The N_2O analogy can be applied for the estimation of the solubilities of CO_2 in solutions of alkanolamines in aqueous ETG at 298 K.
3. Empirical and semiempirical correlations, based on new experimental data and literature data, are derived for the physicochemical properties for solutions of aqueous ETG at 298 K and can be used for the estimation of these properties in mass-transfer experiments with this viscous reaction system.

Glossary

c	concentration, mol/m^3
C_1	constant, eq 2
D	diffusivity, m^2/s
He	Henry coefficient, mol/(m^3 Pa)
m	dimensionless solubility, $c_L = mc_G$, mol/mol
P	pressure, Pa
r	correlation coefficient
R	gas constant, 8.3144 J/(mol K)
T	temperature, K
V	volume, m^3
x	DEA concentration, mol/kg
y	ETG mass percentage
z	water concentration, mol/kg

Greek Symbols

μ	dynamic viscosity, N s/m^2
ρ	density, kg/m^3

Subscripts

amine	amine
eq	equilibrium
G	gas
init	initial
L	liquid
solvent	solvent

Abbreviations

DEA	diethanolamine
ETG	ethylene glycol
ETG%	ethylene glycol mass percentage
MEA	monoethanolamine

Registry No. ETG, 107-21-1; DEA, 111-42-2; CO_2, 124-38-9; N_2O, 10024-97-2.

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Acidic Dissociation of Aqueous 4-Nitrocatechol

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Both primary and secondary acidic dissociation constants of aqueous 4-nitrocatechol (4-nitro-1,2-dihydroxybenzene) have been measured between 15 and 55 °C by pH potentiometry. The standard enthalpies and entropies of both dissociations are calculated from the temperature variations of the dissociation constants.

4-Nitro-1,2-dihydroxybenzene (4-nitrocatechol) is a weak diprotic acid. Several estimates of the acidic dissociation constant (*1*–*5*) have been reported, all in aqueous 0.1 M ionic strength media. Also, the enthalpy and entropy changes for the primary dissociation have been reported in aqueous 0.1 M ionic strength solution (*1*, *2*). However, we are unaware of measurements of the ΔH and ΔS parameters of the secondary dissociation. In the course of experiments to study acid–base tautomerism in 4-nitrocatechol, we required thermodynamic values (zero ionic strength aqueous media) of the two dissociation constants and the corresponding ΔH° and ΔS° parameters. Thus we made pH potentiometric measurements of dilute solutions of 4-nitrocatechol at several temperatures using pH potentiometry and report the results here.

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Table I. Acidic Dissociation Constants of 4-Nitrocatechol at Various Temperatures

T, °C	I^a	pK_{a1}	pK_{a2}	ref
15.0	0	7.065 ± 0.008[b]	11.372 ± 0.010	this work
20.0	0	7.010 ± 0.010	11.252 ± 0.012	this work
20.0	0.1	6.76	11.0	*1*
25.0	0	6.930 ± 0.008	11.182 ± 0.009	this work
25.0	0.1	6.70	10.85	*2*
25.0	0.1	6.86	10.71	*3*
28.7	0.1	6.65	10.80	*5*
30.0	0	6.860 ± 0.008	11.006 ± 0.009	this work
30.0	0.1	6.59	10.75	*4*
35.0	0	6.776 ± 0.008	11.006 ± 0.009	this work
45.0	0	6.639 ± 0.010	10.886 ± 0.013	this work
55.0	0	6.558 ± 0.012	10.863 ± 0.005	this work

[a] Ionic strength of medium, M. [b] Uncertainties are standard error estimates calculated from nonlinear regression analysis and modified to include an estimated ±0.004 pH uncertainty due to pH meter calibration procedure.

Experimental Section

Weighed 0.5–1.0-mmol portions of purified 4-nitrocatechol were added to 40.00 mL of water in a thermostated (±0.05 °C) cell under continuous N_2 purge. After 0.5 h at each measurement temperature ranging from 15 to 55 °C, the solutions were titrated with 0.2 or 0.5 M standardized NaOH solution by use of an Orion Model 801 pH meter equipped with conventional glass and reference electrodes. The pH meter was calibrated with 0.05 *m* 1:1 K_2HPO_4:KH_2PO_4 buffer solution for which the temperature-dependent pH values are reported by Bates (*6*). The calibration procedure was repeated after each titration, and the drift was always less than ±0.005 pH. Titration end-point volumes calculated from the titration curves always yielded 4-nitrocatechol analyses within ±1% of the gravimetric values.

Data Analysis

For each titration we recorded approximately 20 pH vs titrant volume data and analyzed these by an elaborate nonlinear regression method reported previously (*7*). The method involves the numerical solution of a set of model equations describing the acid dissociation equilibria, mass and charge conservation equations, and the Debye–Hückel activity coefficient correlation. The digital computer program (*7*) provided weighted least-squares best fit values and standard error estimates for the two acidic dissociation constants and the equivalence point volume. We monitored the validity of the model equations by observing the residuals between observed and calculated data. Between 0 and 2.0 mol of NaOH/mol of 4-nitrocatechol, these residuals were always acceptably small and appeared to be randomly scattered along the titration curve. Furthermore, repeated titrations using diferent electrodes yielded pK values consistent to within 1–2 standard errors. Our results together with previously determined values are shown in Table I.

Table II. Enthalpy and Entropy Changes of Acidic Dissociations of 4-Nitrocatechol

I^a	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}	method
		Primary Dissociation	
0.1	5.73	−11	pH potentiometry (*2*)
0.1	5.7	−11.5	calorimetry (*1*)
0	5.7 [illegible] 0.2[b]	−12.5 ± 0.6[b]	pH potentiometry[c]
		Secondary Dissociation	
0	5.7 ± 0.5[b]	−32.4 ± 2.0[b]	pH potentiometry[c]

[a] Ionic strength of medium, M. [b] Standard error estimates calculated from van't Hoff linear regression. [c] This work.

$\Delta H°$ and $\Delta S°$ values for the acidic dissociations were found from the slopes of conventional van't Hoff plots in the forms pK vs T^{-1} and T(pK) vs T, respectively. All four plots were linear, and the slopes were extracted by weighted least-squares analysis. The calculated thermodynamic parameters are shown in Table II.

Discussion

Our thermodynamic values of pK_{a1} and pK_{a2} in Table I appear to be approximately consistent with the earlier reported estimates at 0.1 M ionic strength. For example, at 25 °C the previously reported (*2*) value of pK_{a1} is 6.70 while we obtained the corresponding value 6.930 ± 0.008 at zero ionic strength. The two values differ by an amount essentially equal to 2 log $\gamma_\pm$, where $\gamma_\pm$ represents the mean ionic activity coefficient for H^+ and 4-nitrocatechol monoanion. Thus a reasonable estimate of $\gamma_\pm = 0.80$ yields a value of 0.19 pK units for 2 log $\gamma_\pm$, which closely approximates the observed difference of 0.23 pK units. Similarly we observe that our pK_{a2} values and primary dissociation thermodynamic parameters are consistent with earlier values reported in 0.1 M ionic strength.

Registry No. 4-Nitrocatechol, 3316-09-4.

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