amines at 1.00 mM concentration. Our results are quite comparable with the diffusion coefficients determined by Sharma and Kalia (*12*) for molecules of similar size in 0.1 M sulfuric acid. Typical results of Sharma and Kalia are 2,6-dimethoxyphenol ($D = 0.727 \times 10^{-5}$ cm^2 s^{-1}), *o*-ethoxyphenol ($D = 0.718 \times 10^{-5}$ cm^2 s^{-1}), and *p*-phenetidine ($D = 0.661 \times 10^{-5}$ cm^2 s^{-1}).

It should be noted that all the measurements in this work were made at 20 °C. Therefore the results should be slightly lower than the results presented by other workers in the field who have used 25 °C. Note, the 2% per degree correction mentioned by Gerhardt and Adams (*11*) which was originally from a work by Meites (*13*) is actually for the polarographic diffusion current. This diffusion current correction has a number of temperature-dependent terms in addition to the diffusion coefficient such as changes in the properties of mercury with temperatures. Meites indicates that the variation in a diffusion coefficient due to temperature is 0.4% per degree, which is in agreement with the diffusion coefficient correction commonly used for biomolecules (*14*). This would indicate that our results are approximately 2% lower than values obtained at 25 °C.

The precision of the repetitive results had an average coefficient of variation of ±6%. This is consistent with the precision limits of Gerhardt and Adams (*11*) and with Sharma and Kalia (*12*).

Glossary

i	current, A
t	time, s
n	electron number of the half-reaction
F	the Faraday constant, 96 485 C/equiv
A	electrode area, cm^2
D	diffusion coefficient, cm^2 s^{-1}
C_0	bulk solution concentration, mol/cm^3

Registry No. L-DOPA, 59-92-7; dopamine hydrochloride, 62-31-7; (±)-norepinephrine, 138-65-8; (−)-3,4-dihydroxynorepinephrine, 829-74-3; (±)-isoproterenol hydrochloride, 949-36-0; L-*β*-3,4-dihydroxyphenylalanine methyl ester, 7101-51-1; (−)-3-(3,4-dihydroxyphenol)-2-methyl-L-alanine, 555-30-6; 3,4-dihydroxyhydrocinnamic acid, 1078-61-1; (*R*)-(−)-epinephrine, 51-43-4.

Literature Cited

(1) Conference proceedings of Neurochemical Analysis of the Conscious Brain: Voltammetry and Push Pull Perfusion, New York, NY, April 17–19, 1985. Published in *Ann. N.Y. Acad. Sci.* **1986**, *473*.
(2) Kissinger, P. T.; Heineman, W. R. *Laboratory Techniques in Electroanalytical Chemistry*; Marcel Dekker: New York, 1984; p 611.
(3) Reilley, C. N. *Treatise on Analytical Chemistry*, *Part 1*; Kolthoff, I. M., Elving, P. J., Eds.; Wiley: New York, 1963; Vol. IV, p 2132.
(4) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley-Interscience: New York, 1974; p 75.
(5) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*; Wiley: New York, 1960; Chapter 5.
(6) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969 (author's note: this book is still in print).
(7) Soos, G. Z.; Lingane, P. J. *J. Phys. Chem.* **1964**, *68*, 3821–3826.
(8) Stackelberg, Von M. v.; Pilgram, M.; Toome, V. *Z. Elektrochem.* **1953**, *51*, 342–350.
(9) Lane, R. F.; Hubbard, A. T. *Anal. Chem.* **1976**, *48*, 1267–1293.
(10) Fike, R. R.; Curran, D. J. *Anal. Chem.* **1977**, *49*, 1205–1210.
(11) Gerhardt, G.; Adams, R. N. *Anal. Chem.* **1982**, *54*, 2618–2620.
(12) Sharma, L. R.; Kalia, R. K. *J. Chem. Eng. Data* **1977**, *22*, 39–41.
(13) Meites, L. *Polarographic Techniques*, 2nd ed.; Interscience: New York, 1965; p 140.
(14) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry*; W. H. Freeman: San Francisco, 1980; p 584.

Received for review June 6, 1988. Revised January 3, 1969. Accepted March 14, 1989. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Acknowledgment is also made to the Office of University Research, California State University, Long Beach, for partial support of this research.

Effect of Acetamide on the Viscosities of Several Aqueous Electrolyte Solutions at Different Temperatures

Marian Woldan

Research and Development Centre for Standard Reference Materials, WZORMAT—Branch in Lodz, 90-132 Lodz, Poland

The relative viscosities of NaCl, NaI, KCl, KBr, and CsI solutions in water–acetamide mixtures have been measured at 298.15, 313.15, 333.15, 348.15 and 358.15 K. From these data the values of *A* and *B* coefficients of the Jones–Dole equation have been estimated. The values of ionic *B* coefficient for alkali-metal and halide ions were calculated. Ionic viscosity *B* coefficient values have been analyzed on the basis of structural contributions.

The variation of viscosity with temperature and solvent composition has been employed by many workers (*1*) to study the ion–solvent interaction in both aqueous and nonaqueous solutions. The *B* coefficient in water shows strong temperature dependence (*2–5*) which can be attributed to ion–solvent interactions, which should decrease at higher temperature where the water structure itself is diminished (*6*). Such interactions also should decrease with increasing ionic size. In the present paper an attempt has been made to deal with the ion–solvent interaction of alkali-metal and halide ions in water–acetamide mixtures of varying compositions to see the effect of size and nature of ion, temperature, and water–acetamide hydrogen bonding on the *B* coefficient of the viscosity.

Experimental Section

The methods of purification of acetamide and salts were described previously (*7*). The mixed solvents and all solutions used for investigations were made by weighing. The viscosity measurements were made in an Ubbelohde-type suspended level viscometer and carried out in a constant-temperature bath controlled to within 0.01 K. The procedure of viscosity measurements was the same as described earlier (*8*). The total uncertainty of viscosity was (3–6) $\times 10^{-4}$ mPa·s. The density of solutions were determined by the magnetic float densimeter with the precision 1×10^{-5} g cm^{-3}. All measurements were made at a series of concentration covering the range 0.005–0.2 mol dm^{-3} in water and three mixtures containing 5.10, 11.55, and 23.36 mol % acetamide in water at 298.15, 313.15, 333.15, 348.15, and 358.15 K.

Results

The relative viscosity of a solution containing electrolyte was obtained from the flow times of the electrolyte solution and

Table I. Ionic B Coefficients for Alkali-Metal and Halide Ions in Water–Acetamide Mixtures at Different Temperatures

ion	water	5.10 mol % $AcNH_2$	11.55 mol % $AcNH_2$	23.36 mol % $AcNH_2$
		298.15 K		
Na^+	0.085	0.114	0.126	0.134
K^+/Cl^-	−0.007	0.025	0.046	0.066
Cs^+	−0.035	0.000	0.024	0.051
Br^-	−0.040	−0.010	0.008	0.022
I^-	−0.083	−0.058	−0.049	−0.043
		313.15 K		
Na^+	0.082	0.112	0.125	0.134
K^+/Cl^-	0.008	0.041	0.063	0.085
Cs^+	−0.017	0.019	0.044	0.073
Br^-	−0.020	0.012	0.030	0.045
I^-	−0.060	−0.035	−0.025	−0.019
		333.15 K		
Na^+	0.082	0.113	0.126	0.135
K^+/Cl^-	0.022	0.056	0.079	0.101
Cs^+	0.000	0.037	0.063	0.091
Br^-	0.000	0.034	0.051	0.066
I^-	−0.042	−0.017	−0.006	0.000
		348.15 K		
Na^+	0.085	0.117	0.130	0.139
K^+/Cl^-	0.030	0.065	0.088	0.110
Cs^+	0.010	0.047	0.074	0.101
Br^-	0.010	0.044	0.061	0.076
I^-	−0.028	−0.003	0.008	0.015
		358.15 K		
Na^+	0.085	0.118	0.132	0.140
K^+/Cl^-	0.035	0.070	0.093	0.115
Cs^+	0.016	0.053	0.080	0.107
Br^-	0.014	0.048	0.065	0.080
I^-	−0.022	0.003	0.014	0.021

solvent mixture and their respective densities. The experimental data at 298.15, 313.15, and 333.15 K were reported earlier (*7*, *9*, *10*). Because the data of the relative viscosity are too extensive to report here, we have calculated instead the viscosity A and B coefficients using the Jones–Dole equation (*11*). The Jones–Dole coefficient A values fall in the range of 0.003–0.007. They gradually decrease with increasing ionic radii as well as for cations and anions. The effect of acetamide addition to water on A values is detected but it is small. The utility of the B coefficient of electrolyte to study ion–solvent interaction lies in the additivity principle. Since it is impossible to determine the B value for a single ion, we use the known convention $B_{(K^+)} = B_{(Cl^-)}$ (*6*). The values of ionic B coefficient for alkali-metal and halide ions calculated by this method are listed in Table I.

Discussion

As can be seen from Table I, the B coefficients for alkali-metal and halide ions in water–acetamide mixtures increase with increasing temperature. As acetamide is added to water, the values of B relative to pure water for all ions studied increase and even become positive for I^- ion at higher temperature. This is the same effect found for structure-breaking ions in pure water (*5*) and is attributed to the reduction in the structure of the solvent at the higher temperature. Thus, it also appears that the effect of the addition of acetamide to water is to reduce its structure. The values of coefficient dB/dT are given in Table II. They show a gradual decrease with increasing temperature. The effect of acetamide on dB/dT is very little. Moreover, the coefficient dB/dT for Na^+ ion is close to zero.

Table II. Temperature Coefficient dB/dT for Alkali-Metal and Halide Ions in Water–Acetamide Mixtures

ion	298–313 K	313–333 K	333–348 K	348–358 K
		Water		
Na^+	−0.0002	0.0000	0.0002	0.0000
K^+/Cl^-	0.0010	0.0007	0.0005	0.0005
Cs^+	0.0035	0.0008	0.0007	0.0005
Br^-	0.0013	0.0010	0.0007	0.0004
I^-	0.0015	0.0009	0.0009	0.0006
		5.10 mol % $AcNH_2$		
Na^+	−0.0001	0.0000 (5)	0.0003	0.0001
K^+/Cl^-	0.0011	0.0007 (5)	0.0006	0.0005
Cs^+	0.0013	0.0009	0.0007	0.0006
Br^-	0.0015	0.0011	0.0007	0.0004
I^-	0.0015	0.0009	0.0009	0.0006
		11.55 mol % $AcNH_2$		
Na^+	−0.0000 (7)	0.0000 (7)	0.0003	0.0002
K^+/Cl^-	0.0011	0.0008	0.0007	0.0005
Cs^+	0.0013	0.0009 (5)	0.0007	0.0006
Br^-	0.0015	0.0010 (5)	0.0007	0.0004
I^-	0.0016	0.0009 (5)	0.0009	0.0006
		23.36 mol % $AcNH_2$		
Na^+	0.0000	0.0000 (5)	0.0003	0.0001
K^+/Cl^-	0.0013	0.0008	0.0006	0.0005
Cs^+	0.0015	0.0009	0.0007	0.0006
Br^-	0.0015	0.0010 (5)	0.0007	0.0004
I^-	0.0016	0.0009 (5)	0.0010	0.0006

It is generally acknowledged (*6*) that the B coefficient is a measure of ion–solvent interaction arising from the size, shape, and structural effects (*12*, *13*). In this paper we assume that the B coefficient of an inorganic ion can be split into two terms

$$B_{\text{ion}} = B_{\text{i,v}} + B_{\text{i,s}} \tag{1}$$

where $B_{\text{i,v}}$ is the positive contribution due to size and shape of solvated ion and the dimension of electrostriction region around the ion and $B_{\text{i,s}}$ is the contribution related to the destruction of solvent structure in the region of collapsed solvent structure. We assume $B_{\text{i,v}}$ to be independent of temperature, which implies that the thickness of the fixed hydrophilic water shell, i.e., the innermost layer in the model of Frank and Wen (*14*), is also temperature independent. Because of the apparent asymptotic behavior of the functions $B = f(T)$ (excepting Na^+ ion) toward higher temperatures, we tried a fit with the relationship

$$B_{\text{i}(T)} = B_{\text{i,v}} + B_{\text{i,s(0)}} \exp[-a(T - 273.15)] \tag{2}$$

where $B_{\text{i,s(0)}} = B_{\text{i,s}}$ for $T = 273.15$ K and a is a constant for a given ion. The unknown parameters $B_{\text{i,v}}$, $B_{\text{i,s(0)}}$, and a in eq 2 were found from the minimization condition of the function defined as

$$f_{(B_{\text{i,v}},B_{\text{i,s(0)}},a)} = \sum_{i=1}^{n} [B_{(T_i,B_{\text{i,v}},B_{\text{i,s(0)}},a)_{\text{theor}}} - B_{(T_i)_{\text{exptl}}}]^2$$

where n is the number of experimentally measured B values. The results of the fits of the ionic $B_{\text{i}(T)}$ data to this equation are collected in Table III. For Na^+ ion the calculation of a is too uncertain because of the nearly horizontal course of the B coefficient against temperature. From Table III it can be seen that the $B_{\text{i,v}}$ values increase gradually with the increase of the contents of acetamide in the mixed solvents. Probably the number of water molecules in the innermost layer around the ion increases because of the loosening of water structure by acetamide. It may be also that in mixtures containing larger amounts of acetamide the ions are too solvated by acetamide molecules. Moreover, one can note that the $B_{\text{i,v}}$ coefficient decreases with increasing ionic radii. The dependence of $B_{\text{i,v}}$ on the ionic radius is considerably larger for anions than for cations. The different behavior of cations and anions probably can be explained in terms of different dipole orientation of solvent molecules around cations and anions. The $B_{\text{i,s(0)}}$ values obtained for all ions (excepting Na^+) in all solutions under study

Table III. Parameters of Eq 2 for Ions in Water-Acetamide Mixtures

ion	$B_{i,v}$	$-B_{i,s(0)}$	a	$\Delta = \left[\frac{1}{n}\sum_{i=1}^{n}(B_i^{\text{calcd}} - B_i^{\text{exptl}})^2\right]^{1/2}$
		Water		
Na^+	0.0835			
K^+/Cl^-	0.0570	0.0984	0.01745	0.000 36
Cs^+	0.0474	0.1214	0.01577	0.000 31
Br^-	0.0340	0.1305	0.02239	0.000 43
I^-	0.0150	0.1448	0.01598	0.001 00
		5.10 mol % $AcNH_2$		
Na^+	0.1141			
K^+/Cl^-	0.0957	0.1078	0.0167	0.000 34
Cs^+	0.0848	0.1269	0.0162	0.000 31
Br^-	0.0706	0.1374	0.0215	0.000 63
I^-	0.0373	0.1442	0.0169	0.000 69
		11.55 mol % $AcNH_2$		
Na^+	0.1270			
K^+/Cl^-	0.1156	0.1114	0.0188	0.000 23
Cs^+	0.1127	0.1330	0.0164	0.000 30
Br^-	0.0864	0.1351	0.0220	0.000 56
I^-	0.0492	0.1485	0.0169	0.000 70
		23.36 mol % $AcNH_2$		
Na^+	0.1358			
K^+/Cl^-	0.1347	0.1133	0.0205	0.000 50
Cs^+	0.1333	0.1309	0.0188	0.000 55
Br^-	0.0998	0.1398	0.0233	0.000 46
I^-	0.0562	0.1503	0.0170	0.000 79

are negative. In the case of aqueous solutions the $B_{i,s(0)}$ values as absolute values are larger than $B_{i,v}$ values. From this it follows that the addition of acetamide to water reduces the difference between $B_{i,v}$ and $B_{i,s(0)}$; however, the $B_{i,s(0)}$ values increase only a little. Moreover, it is noticed that the coefficient $B_{i,s(0)}$ as absolute value increases with increasing ionic radii. The facts observed lead one to conclude that the I^- ion has the largest breaking effect on the structure of water-acetamide mixture. The effect of temperature on $B_{i,s}$ (parameter a) decreases with increasing ionic radii.

Glossary

A	viscosity coefficient, $(dm^3\ mol^{-1})^{1/2}$
B	viscosity coefficient, $dm^3\ mol^{-1}$
dB/dT	temperature coefficient of B, $dm^3\ mol^{-1}\ deg^{-1}$
$B_{i,v}$	positive contribution due to size and shape of solvated ion
$B_{i,s}$	negative contribution related to destruction of solvent structure by ion
a	parameter of eq 2

Registry No. NaCl, 7647-14-5; NaI, 7681-82-5; KCl, 7447-40-7; KBr, 7758-02-3; CsI, 7789-17-5; acetamide, 60-35-5.

Literature Cited

(1) Stokes, R. H.; Mills, R. *International Encyclopedia of Physical Chemistry and Chemical Physics*; Pergamon: New York, 1965; Vol. 3.
(2) Kaminsky, M. *Z. Phys. Chem. (Munich)* **1955**, *5*, 154.
(3) Kaminsky, M. *Z. Phys. Chem. (Munich)* **1956**, *8*, 173.
(4) Kaminsky, M. *Z. Phys. Chem. (Munich)* **1957**, *12*, 206.
(5) Kaminsky, M. *Discuss. Faraday Soc.* **1957**, *24*, 171.
(6) Stokes, R. H.; Mills, R. *Viscosity of Electrolytes and Related Properties*; Pergamon: New York, 1965.
(7) Woldan, M. *Z. Phys. Chem. (Munich)* **1986**, *150*, 201.
(8) Woldan, M. *J. Chem. Eng. Data* **1985**, *30*, 479.
(9) Woldan, M. *Z. Phys. Chem. (Leipzig)* **1988**, *269*, 628.
(10) Woldan, M. *Rev. Roum. Chem.* **1988**, *33*, 125.
(11) Jones, G.; Dole, M. *J. Am. Chem. Soc.* **1929**, *51*, 2950.
(12) Kraeft, W. D.; Einfeldt, J. *Z. Phys. Chem. (Leipzig)* **1968**, *237*, 267; *Z. Phys. Chem. (Leipzig)* **1968**, *239*, 415.
(13) Krumgalz, B. S. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1275.
(14) Frank, M. S.; Wen, W. Y. *Discuss. Faraday Soc.* **1957**, *24*, 133.

Received for review June 4, 1987. Revised June 14, 1988. Accepted July 20, 1988.

Isobaric Vapor–Liquid Equilibrium for the Cumene–Phenol System

Emilio Cepeda,* Cristina González, and Jose M. Resa

Departamento de Química Técnica, Colegio Universitario de Alava, Apartado 450, Vitoria, Spain

Isobaric vapor–liquid equilibrium data for the cumene–phenol system were obtained at 13.33, 53.33, and 101.33 kPa pressures by using a vapor recirculating type of equilibrium still. The system forms a minimum-boiling azeotrope at atmospheric pressure. The activity coefficient data were tested for thermodynamic consistency by the methods of Herington, Black, and van Ness and correlated by the Norrish and Twigg, van Laar, and Wilson equations.

Introduction

Cumene can be converted to phenol and acetone via cumene hydroperoxide (*1*). In this process, the result is a mixture of cumene, phenol, and acetone. Cumene free of phenol is required for recycling to the cumene oxidation stage because the presence of phenol is detrimental for the oxidation. For the separation of this mixture, fractional distillation can be used, but the data in the literature for vapor–liquid equilibrium on this system are conflicting. Lecat (*2*) and Norrish and Twigg (*3*) did not find an azeotropic point at atmospheric pressure. In contrast, a patent (*4*) lists an azeotrope of 0.97 mole fraction cumene.

Table I. Physical Properties of the Pure Compounds: Density, Refractive Index, and Boiling Point

	ρ, g/cm³		n_D		T_B, K	
	obsd	ref *6*	obsd	ref *6*	obsd	ref *6*
cumene (T = 298.15 K)	0.8574	0.8575	1.4889	1.4889	425.54	425.54
phenol (T = 318.15 K)	1.0542	1.0545	1.5400	1.5402	454.96	454.98

In the present paper, the vapor–liquid equilibrium of the cumene–phenol system was measured in order to clarify the different results at 13.33, 53.33, and 101.33 kPa. Furthermore the composition of the azeotrope at 101.33 kPa was determined by using a packed column.

Experimental Section

Chemicals. Cumene was supplied by Merck, and phenol was supplied by PANREAC. They are analytical-grade reagents and were purified by distillation in a laboratory column. Physical properties of these components are listed in Table I along with their literature values.

Apparatus and Procedure. The still used to obtain vapor–liquid equilibrium data was an Othmer modified vapor–liquid