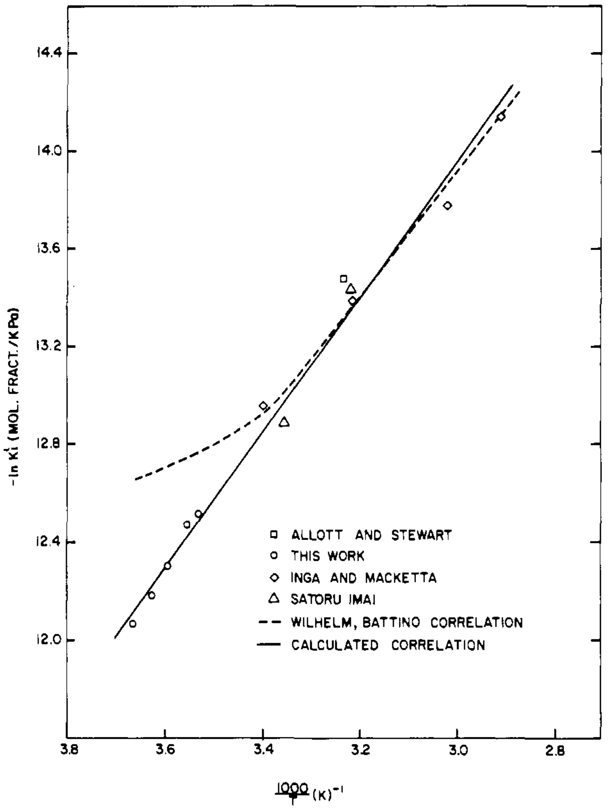

Figure 4. Comparison of experimental data and correlations at zero salt concentration.

1.6%, well within the accuracy stated by Miller (*10*). When the data of the present study were extrapolated to the temperature range of Inga and McKetta, the data were above those of Inga by 2.6%. A further extrapolation (over 30 K) to the temperature range of Allot and Stewart showed agreement to within 6%. A comparison with the data of Saturu shows agreement within 4%. As shown in Figure 4 the correlation of Wilhelm et al. (*5*) for cyclopropane solubility fit the data between 298 and 344 K acceptably; however, there is a significant deviation for the low-temperature data of this work.

Glossary

a, b, c, d	constants in eq 1 and Table II
C	KCl concentration in solution, g/L
K_i	reciprocal Henry's constant, kPa^{-1}
P	pressure, kPa
P_{final}	equilibrium pressure, kPa
P_i	partial pressure, kPa
x_i	mole fraction of component i in solution

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Activity Coefficient of Hydrochloric Acid in the System $HCl-NH_4Cl-KCl-H_2O$ at Constant Total Molality 0.5 mol kg^{-1} at 298.15 K

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The activity coefficients of hydrochloric acid in aqueous mixed solutions with ammonium and potassium chlorides at a constant total molality of 0.5 mol kg^{-1} have been determined at 298.15 K from electromotive force measurements of the cell, Pt,H_2(g, 1 atm)|HCl(m_1), NH_4Cl(m_2), KCl(m_3)|AgCl|Ag, with $m_1 + m_2 + m_3 = 0.5$ mol kg^{-1} and $m_3/(m_2 + m_3) = 0.25$, 0.50, and 0.75. A simple additive scheme based on Harned's rule for the composing binary electrolyte solutions of the acid permits an accurate prediction of the experimental activity coefficients of the acid.

There exist abundant data for activity and osmotic coefficients in binary salt mixtures in aqueous solutions but those concerning mixtures of three or more salts, such as are representative of natural brines, are scarce. For such mixtures, it should be feasible to predict their properties from experimental data for binary solutions of the component salts, using equations such as those of Wood and co-workers (*1–3*) or the more recent equations of Pitzer (*4*). However, it could be more convenient in many cases to resort to simpler empirical means of estimating them. Gieskes (*5*) has proposed a simple additive scheme for representing the activity coefficient of an electrolyte in a multicomponent electrolyte solution. He wrote, for the activity coefficient of component 1 in the presence of other salts, 2, 3, ..., N,

$$\log \gamma_1 = \log \gamma_1^0 - \sum_{i=2}^{N} \alpha_{1i} y_i I \qquad (1)$$

where I is the total ionic strength of the solution, y_i is the ionic strength fraction of component i, and γ_1^0 is the activity coefficient of component 1 in its own solution to which I refers. α_{1i} is the Harned coefficient for component 1 in binary solutions with component i; it is assumed to vary only with I and not with

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composition at a particular temperature. Equation 1 is a logical extension of Harned's rule (6, 7). It has been used by Lerman (8) to calculate activity coefficients in Dead Sea brines. Sometimes, a quadratic term is required,

$$\log \gamma_1 = \log \gamma_1{}^0 - \sum_{i=2}^{N} \alpha_{1i} y_i I - \sum_{i=2}^{N} \beta_{1i} y_i{}^2 I^2 \qquad (2)$$

where β_{1i} is the corresponding quadratic coefficient for binary solutions of 1 with i. The validity of these equations has been tested by Christenson (9) for some mixtures involving a univalent chloride and two divalent chlorides. Although these equations predict the experimental data for these systems reasonably well, they do not appear to be universally applicable, according to the investigations of Lietzke et al. (10) for the system $HCl-CsCl-BaCl_2-H_2O$. A further test of the validity of eq 1 is attempted in the present paper which reports activity coefficients for HCl in aqueous solutions of NH_4Cl and KCl at 298.15 K, derived from electromotive force measurements of the cell

$$Pt,H_2(g,\ 1\ atm)|HCl(m_1),NH_4Cl(m_2),KCl(m_3)|AgCl|Ag \qquad (A)$$

The total molality, $m_1 + m_2 + m_3$, was kept constant at 0.5 mol kg^{-1} and the salt molality ratios were fixed at $m_3/(m_2 + m_3)$ = 0.25, 0.50, and 0.75.

Experimental Section

Hopkins and Williams' AnalaR hydrochloric acid was diluted to the composition of the azeotropic mixture and distilled twice, with retention of the middle third. The distillate was assayed by gravimetric chloride analysis and used to prepare appropriate stock solutions of the acid. Merck "pro analysi" ammonium chloride was recrystallized and dried at 353 K while Hopkins and Williams' AnalaR potassium chloride was dried at 413 K after a single recrystallization. Stock solutions of the salts were prepared from the dried solids.

The experimental procedure and the cell used have been described in detail elsewhere (11). A batch of three silver–silver chloride electrodes was prepared and the bias emf's between themselves were <0.02 mV after aging for at least 2 days. One electrode was selected for use throughout the measurements and periodically returned to the storage vessel to check its potential against those of the unused electrodes to ensure that the bias emf did not exceed 0.05 mV. The experimental cell was maintained at 298.15 ± 0.01 K.

The emf readings were recorded with a Data Precision Model 3500-E digital multimeter which was checked for accuracy by measurement of the emf's of certified laboratory standards. Cell equilibrium was assumed to have been attained when the emf readings were constant within 0.01 mV for about an hour. Factors affecting the functioning of the cell and the preparation of the solutions should not cause the overall uncertainty in the experimental emf to exceed 0.1 mV.

Results and Discussion

The emf's of cell (A) are given in Table I for values of $m_3/(m_2 + m_3)$ = 0.25, 0.50, and 0.75. These have been corrected to a hydrogen pressure of 1 atm (101.325 kPa). The activity coefficient of the acid, γ_1, is derived from the equation

$$\log \gamma_1 = -\tfrac{1}{2}[(E - E^0)/k + \log m_1(m_1 + m_2 + m_3)] \qquad (3)$$

where $k = (RT \ln 10)/F$ and E^0 is the standard emf of the cell found equal to 0.222 50 V, following recommended measurement (12) with an 0.01 mol kg^{-1} solution of the acid.

From eq 1,

$$\log \gamma_1 = \log \gamma_1{}^0 - \alpha_{12} m_2 - \alpha_{13} m_3 \qquad (4)$$

Table I. Electromotive Force of Cell (A) and Activity Coefficients for HCl in the System $HCl-NH_4Cl-KCl-H_2O$ at Constant Total Molality 0.5 mol kg^{-1} at 298.15 K

$m_1{}^a$	$m_2{}^a$	$m_3{}^a$	E^b	$-\log \gamma_1$ (exptl)	$-\log \gamma_1$ (calcd)^c
		$m_3/(m_2 + m_3) = 0.25$			
0.500 01	0	0	0.272 25	0.1195	0.1196
0.382 92	0.087 82	0.029 26	0.280 09	0.1278	0.1277
0.251 12	0.186 67	0.062 20	0.291 96	0.1365	0.1368
0.125 29	0.281 04	0.093 65	0.310 91	0.1457	0.1455
0.065 09	0.326 19	0.108 69	0.328 20	0.1496	0.1496
0.030 74	0.351 95	0.117 28	0.347 76	0.1520	0.1520
		$m_3/(m_2 + m_3) = 0.50$			
0.500 01	0	0	0.272 25	0.1195	0.1196
0.431 14	0.034 42	0.034 43	0.276 65	0.1245	0.1242
0.277 49	0.111 20	0.111 25	0.289 17	0.1346	0.1345
0.147 43	0.176 20	0.176 27	0.306 43	0.1431	0.1432
0.073 50	0.213 15	0.213 23	0.324 90	0.1481	0.1482
0.042 52	0.228 63	0.228 72	0.339 19	0.1500	0.1502
		$m_3/(m_2 + m_3) = 0.75$			
0.500 01	0	0	0.272 25	0.1195	0.1196
0.423 35	0.019 18	0.057 48	0.277 12	0.1245	0.1246
0.287 40	0.053 19	0.159 42	0.288 14	0.1335	0.1334
0.151 09	0.087 29	0.261 64	0.305 76	0.1428	0.1423
0.080 73	0.104 89	0.314 40	0.322 37	0.1471	0.1469
0.033 99	0.116 58	0.349 45	0.344 97	0.1503	0.1499

[a] In mol kg^{-1}. [b] In volts. [c] Calculated from eq 4, with α_{12} = 0.071, α_{13} = 0.063, and $\log \gamma_1{}^\circ = -0.1196$.

Table II. Parameters of Equation 5 with α_{12} Set Equal to 0.071

$m_3/(m_2 + m_3)$	$E^{\circ\prime}$	$-\log \gamma_1{}^0$	α_{13}
0.25	0.236 64 ± 0.000 02^a	0.1195	0.064 ± 0.002^a
0.50	0.236 66 ± 0.000 02	0.1197	0.0621 ± 0.0009
0.75	0.236 64 ± 0.000 02	0.1195	0.0647 ± 0.0005
1.00^b	0.236 68 ± 0.000 01	0.1197^c	0.0641 ± 0.0002

[a] Standard error from least-squares analysis. [b] Unpublished data (17) for the system $HCl-KCl-H_2O$. [c] Based on E° = 0.222 52 V determined in unpublished work (17).

Downes (13) and Robinson, Roy, and Bates (14) have recently made precise determinations of α_{12}. From their results one can define a mean value of α_{12} = 0.071 ± 0.002. As for α_{13}, Harned and Gancy (15) found it equal to 0.054 on the basis of four emf measurements while Harned and Hamer (16) determined it to be 0.062. There is compelling evidence that the results of Harned and Gancy are in error (4, 13). Measurements of the cell used by Harned and co-workers have been repeated in this laboratory (17), giving α_{13} = 0.0641 with a standard error of 0.0006. Further confirmation of the value of α_{13} is desirable and this can be obtained from the present experimental data as follows. Equations 1 and 3 give

$$E + k \log m_1(m_1 + m_2 + m_3) - 2k\alpha_{12}m_2 = E^{0\prime} + 2k\alpha_{13}m_3 \qquad (5)$$

where $E^{0\prime} = E^0 - 2k \log \gamma_1{}^0$ and α_{12} is assigned the value of 0.071 based on the combined values of Downes (13) and Robinson, Roy, and Bates (14). $E^{0\prime}$ (and hence $\log \gamma_1{}^0$) and α_{13} are evaluated from eq 5 by the method of least squares and reported in Table II. It is apparent that an average α_{13} = 0.063 ± 0.002 adequately describes all the experimental data here as well as data for the system $HCl-KCl-H_2O$ (17). Further, this value agrees well with that found by Harned and Hamer (16) despite the fact that these investigators determined it from two experimental points only. The experimental activity coefficients of the acid are presented in Table I together with those calculated from eq 4 using α_{12} = 0.071, α_{13} = 0.063, and $\log \gamma_1{}^0$ = −0.1196. The agreement between experimental and calculated values is excellent, thus demonstrating the applicability of eq 1 to the present system.

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Solubility of Hexane, Phenanthrene, Chlorobenzene, and *p*-Dichlorobenzene in Aqueous Electrolyte Solutions

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The solubilities of hexane, phenanthrene, chlorobenzene, and *p*-dichlorobenzene were determined in water and in aqueous solutions of NaCl, Na_2SO_4, KCl, NaBr, and NH_4Cl at 25 °C. The salting-out effect is well represented by the Setschenow equation. A correlation based on the McDevit–Long theory is presented which gives the salting-out factor as a function of organic solute molar volume and an empirical constant characteristic of the electrolyte. The data for the chlorobenzenes suggest that the correlation may be applicable to halogenated hydrocarbons.

Introduction

A knowledge of the solubility of hydrocarbons and halogenated hydrocarbons in water and in aqueous electrolyte solutions is important in assessing the fate and effects of discharges of oil and other toxic compounds. Salt effects (salting-in and salting-out) of electrolytes have been investigated for several aromatic hydrocarbons (*1–7*) and theories have been proposed to explain these effects (*1*, *2*). The effect of electrolytes on the activity coefficients of naphthalene has also been studied (*8*, *9*). The solubilities of methane (*10*), butane (*11*), alkylbenzenes (*12*), medium molecular weight aromatic hydrocarbons (*13*), and higher molecular weight alkanes (*14*) in water and seawater have also been reported. Most of the experimental data fit the empirical Setschenow equation in which the logarithm of the ratio of solubility in salt solution and in water is expressed as a linear function of concentration of the electrolyte.

In this work, experimental solubilities are presented of a low molecular weight alkane (hexane), a polynuclear aromatic hydrocarbon (phenanthrene), and two halogenated aromatics (chlorobenzene and *p*-dichlorobenzene) in a number of electrolyte solutions together with a brief review of available experimental data for other hydrocarbons. The aim is to provide a fuller understanding of the extent to which electrolytes modify the properties of dilute aqueous solutions of hydrophobic compounds. These data also permit direct estimation of the effects of electrolytes on Henry's law constants, which are essential in vaporization rate calculations and on aqueous–organic partition coefficients which are frequently used as indicators of bioaccumulation.

Experimental Section

Saturated solutions were prepared by adding an excess amount of the solute in salt solutions of various concentrations for 24 h, followed by settling in a 25 °C temperature bath for at least 48 h before analysis.

The solubility of hexane in salt solutions was determined by vapor extraction followed by GC analysis using an established technique (*15*). The dissolved hexane was extracted by purified helium and subsequently trapped in a sample loop in liquid nitrogen. The hydrocarbon was then injected into the GC column by quick immersion of the sample loop in a hot oil bath.

The gas chromatograph was a Hewlett-Packard Model 5750 equipped with a flame ionization detector and a 10 ft. long, $^1/_8$ in. o.d. stainless steel column packed with 10% SE 30 ultraphase on high-performance Chromosorb P, 60/80 mesh.

The solubility of phenanthrene was determined by fluorescence, using an Aminco-Bowman spectrophotofluorometer (American Instrument Ltd.). Approximately 50 mL of aqueous salt solution saturated with phenanthrene was extracted with 5 mL of cyclohexane. No phenanthrene was detected in a second extract. Electrolyte solutions were filtered through glass wool prior to extraction. Standard calibration solutions were prepared by directly weighing 0.1 g of phenanthrene followed by serial dilution in cyclohexane to a concentration of 1 mg/L. The fluorescence intensity of the cyclohexane extract was then measured. It was often necessary to dilute the cyclohexane extract in order that the measured intensity was within the linear range of the calibration curve.

Originally, the fluorescence intensity was measured directly from the aqueous solution to determine the concentration of phenanthrene. However, it was later found that although salt solutions do not seem to interfere with the fluorescence spectra, they do have concentration quenching effects on the fluorescence intensity.

The solubilities of chlorobenzene and *p*-dichlorobenzene were determined by solvent extraction followed by GC analysis.

The *n*-hexane used was pure grade (99 mol %), chlorobenzene was of certified grade, obtained from Fisher Scientific, phenanthrene was of fluorescence grade from Eastman Kodak, and *p*-dichlorobenzene was obtained from BDH. Cyclohexane was of distilled-in-glass grade from Caledon Laboratories, Ontario. All the salts used were of reagent grade from Fisher and BDH.

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