than that for binary supercritical solubility data reported in the literature (*8*).

Glossary

a	energy parameter in Peng–Robinson equation of state (P–R EOS), (bar cm^3)/g-mol^2
A	dimensionless constant, $A = aP/R^2T^2$
b	covolume term in P–R EOS, cm^3/g-mol
B	dimensionless constant, $B = bP/RT$
b_0	Kirkwood–Buff (K–B) fitted parameter
b_1	K–B fitted parameter, K
E	enhancement factor, y_2P/p_2^{sat}
f	fugacity, bar
k_{ij}	binary interaction parameter between unlike molecules i and j
P	pressure, bar
p^{sat}	saturation pressure, bar
T	temperature, K
V	molar volume, cm^3/g-mol
V_{12}	K–B fitted parameter, cm^3/g-mol
v^s	solid-state molar volume, cm^3/g-mol
y	solubility (mole fraction)
Z	compressibility factor, $Z = PV/RT$
α	K–B scaling factor, $\alpha_{12} = (T_{c,1}/T_{c,2})^{1/2}(V_{c,1} + V_{c,2})/2$
ϕ^v	vapor-phase fugacity coefficient
ρ	molar density, (g-mol/dm^3)

Subscripts

i,j	components i and j
1	CF_4
2	CCl_4
c	critical

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Extension of the Falkenhagen–Leist–Kelbg Equation to the Electrical Conductance of Concentrated Aqueous Electrolytes

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The Falkenhagen–Leist–Kelbg (FLK) conductance equation, which is otherwise applicable only to dilute electrolyte solutions, has been modified by substituting into this equation the viscosity and dielectric constant of the solution in place of those of the solvent. This modified FLK equation with the ion-size parameter as the only adjustable parameter has been found to describe the reported equivalent conductance data of aqueous LiCl, NaCl, NaBr, NaI, and KF solutions satisfactorily up to 4 mol·dm^{-3}.

Introduction

Several arbitrary relations based on the Debye–Hückel model of an ionic atmosphere are available to deal with the concentration dependence of electrical conductance. The commonly used expressions for describing the electrical conductance behavior of electrolytic solutions at higher concentrations are obtained by modifying the Falkenhagen–Leist–Kelbg (FLK) equation (*1*) of the form

$$\Lambda_{FLK} = \left[\Lambda_0 - \frac{B_1c^{1/2}}{1 + Ba_0c^{1/2}}\right]\left[1 - \frac{B_2c^{1/2}F}{1 + Ba_0c^{1/2}}\right] \qquad (1)$$

where for 1:1 electrolytes $B = 50.29 \times 10^8/(\epsilon_0T)^{1/2}$, $B_1 = 82.5/[\eta_0(\epsilon_0T)^{1/2}]$, $B_2 = 8.204 \times 10^5/(\epsilon_0T)^{3/2}$, and $F = [\exp(0.2929Ba_0^{1/2}) - 1]/(0.2929Ba_0c^{1/2})$. η_0 and ϵ_0 are the viscosity and dielectric constant of water, respectively. c is the molar concentration, and T is the absolute temperature.

Wishaw and Stokes (*2*) empirically modified the FLK eq 1 by introducing into it a relative viscosity term. This modified equation may be written as

$$\Lambda_{WS} = \Lambda_{FLK}(\eta_0/\eta) \qquad (2)$$

where η is the viscosity of the solution. Equation 2 has been found to fit with moderate success the conductance data of electrolytic solutions up to fairly high concentrations. However, eq 2 fails to reproduce the conductance data when the viscosity ratio, η/η_0, becomes very high (*3–5*). Goldsack et al. (*6*) modified eq 1 by taking into consideration the effect of hydration on a_0, the ion-size parameter. Recently, Monica et al. (*3–5*) made another modification to eq 1 by taking into account the dependence of the electrophoretic term B_1 on the solution viscosity. From the expression for B_1 it is obvious that B_1 is inversely dependent on the viscosity of the solvent, η_0. They, however, incorporated this modification in eq 2 rather than in the FLK eq 1 and obtained an expression essentially of the same form as eq 2 with the B_1 term replaced by $B_{1\eta} = B_1\eta_0/\eta$. This new equation of Monica et al. was found (*3–5*) to describe the concentration dependence of Λ for several 1:1 electrolytes up to high concentrations.

One of the important factors ignored in the theoretical conductance equations is the variation in the dielectric constant of water caused by the addition of electrolyte. Although this point was highlighted by Goldsack et al. (*6*), no serious effort was

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Table I. Fitting of Equivalent Conductance Data of Aqueous LiCl Solutions at 25 °C with Λ_0 = 115.0 S•cm²•equiv⁻¹ to Equation 3

c/(mol·dm^{-3})	$10^2\eta$/(g·cm^{-1} s^{-1})	ϵ_{exp}	Λ_{exp}/(S·cm^2·equiv^{-1})	$\Lambda_{cal}{}^a$/(S·cm^2·equiv^{-1})
0.0001	0.8904	78.60	114.16	114.14
0.0005	0.8905	78.59	113.11	113.11
0.001	0.8905	78.59	112.37	112.35
0.005	0.8910	78.53	109.34	109.32
0.01	0.8916	78.46	107.32	107.21
0.05	0.8964	77.9	100.11	99.52
0.1	0.9025	77.2	96.53	94.78
0.5	0.9572	71.2	81.86	80.52
1.0	1.0257	64.9	73.00	73.13
2.0	1.1816	54.0	61.74	63.55
3.0	1.3596	46.0	52.51	53.61
4.0	1.5707	39.0	44.53	42.74

[a] a_0 = 3.16 Å, and the standard deviation in Λ is 1.0395.

Table II. Fitting of Equivalent Conductance Data of Aqueous NaCl Solutions at 25 °C with Λ_0 = 126.5 S•cm²•equiv⁻¹ to Equation 3

c/(mol·dm^{-3})	$10^2\eta$/(g·cm^{-1}·s^{-1})	ϵ_{exp}	Λ_{exp}/(S·cm^2·equiv^{-1})	$\Lambda_{cal}{}^a$/(S·cm^2·equiv^{-1})
0.0001	0.8904	78.60	125.59	125.62
0.0005	0.8904	78.59	124.50	124.56
0.001	0.8905	78.58	123.70	123.78
0.002	0.8908	78.57	122.67	122.72
0.005	0.8911	78.52	120.65	120.72
0.01	0.8917	78.43	118.53	118.60
0.02	0.8927	78.26	115.65	115.84
0.05	0.8952	77.76	111.06	111.02
0.1	0.8993	76.92	106.74	106.40
0.5	0.9305	70.2	93.62	92.19
1.0	0.9759	66.6	85.76	85.58
2.0	1.0854	57.0	74.71	76.23
3.0	1.2279	48.1	65.57	66.40
4.0	1.4068	42.0	57.23	55.84

[a] a_0 = 3.79 Å, and the standard deviation in Λ is 0.7171.

Table III. Fitting of Equivalent Conductance Data of Aqueous NaBr Solutions at 25 °C with Λ_0 = 128.3 S•cm²•equiv⁻¹ to Equation 3

c/(mol·dm^{-3})	$10^2\eta$/(g·cm^{-1}·s^{-1})	ϵ_{exp}	Λ_{exp}/(S·cm^2·equiv^{-1})	$\Lambda_{cal}{}^a$/(S·cm^2·equiv^{-1})
0.1	0.8949	77.1	110.60	109.33
0.5	0.9153	72.1	97.96	97.21
1.0	0.9438	65.0	90.60	90.02
2.0	1.0217	54.5	80.50	79.85
3.0	1.1308	50.0	72.39	72.98
4.0	1.3000	47.0	64.85	66.89

[a] a_0 = 4.79 Å, and the standard deviation in Λ is 1.1157.

Table IV. Fitting of Equivalent Conductance Data of Aqueous NaI Solutions at 25 °C with Λ_0 = 127.2 S•cm²•equiv⁻¹ to Equation 3

c/(mol·dm^{-3})	$10^2\eta$/(g·cm^{-1}·s^{-1})	ϵ_{exp}	Λ_{exp}/(S·cm^2·equiv^{-1})	$\Lambda_{cal}{}^a$/(S·cm^2·equiv^{-1})
0.01	0.8908	78.50	119.24	119.75
0.05	0.8913	77.90	112.79	113.33
0.1	0.8922	77.10	109.40	109.67
0.5	0.9011	71.10	98.83	98.98
1.0	0.9171	64.8	92.53	92.68
2.0	0.9705	55.5	83.66	83.30
3.0	1.0774	50.2	75.76	75.54

[a] a_0 = 6.10 Å, and the standard deviation in Λ is 0.3484.

Table V. Fitting of Equivalent Conductance Data of Aqueous KF Solutions at 25 °C with Λ_0 = 128.5 S•cm²•equiv⁻¹ to Equation 3

c/(mol·dm^{-3})	$10^2\eta$/(g·cm^{-1}·s^{-1})	ϵ_{exp}	Λ_{exp}/(S·cm^2·equiv^{-1})	$\Lambda_{cal}{}^a$/(S·cm^2·equiv^{-1})
0.0010	0.8905	78.59	126.04	125.74
0.0024	0.8906	78.57	124.48	124.30
0.0036	0.8908	78.55	123.72	123.41
0.0049	0.8909	78.54	122.95	122.62
0.0062	0.8910	78.52	122.30	121.94
0.0075	0.8912	78.50	121.71	121.33
0.0092	0.8913	78.48	121.05	120.63
0.3	0.9260	74.7	98.13	96.44
0.5	0.9456	72.8	91.73	90.84
1.0	1.0061	69.0	83.63	83.06
2.0	1.1397	61.4	73.45	74.20
3.0	1.2955	54.8	65.89	67.30
4.0	1.4825	48.1	59.12	58.74

[a] a_0 = 2.74 Å, and the standard deviation in Λ is 0.7443.

made to date to examine this aspect. The depression in the dielectric constant of aqueous electrolytic solutions with increasing concentration is well established, and theoretical models have been developed to explain such a dielectric constant depression (*7–14*). The dielectric constants of aqueous solutions are reported to decrease linearly up to concentrations of about 2 mol·dm^{-3} and nonlinearly if higher concentration ranges are covered. We have, therefore, made an attempt in this work to modify eq 1 by substituting in it the viscosity and dielectric constant of the electrolytic solution in the place of those of the solvent.

Results and Discussion

The modified form of eq 1 can be written as

$$\Lambda = \left[\Lambda_0 - \frac{B_1(c)c^{1/2}}{1 + B(c)a_0c^{1/2}}\right]\left[1 - \frac{B_2(c)c^{1/2}F(c)}{1 + B(c)a_0c^{1/2}}\right] \quad (3)$$

where $B(c) = 50.29 \times 10^8/(\epsilon T)^{1/2}$, $B_1(c) = 82.5/[\eta(\epsilon T)^{1/2}]$, $B_2(c) = 8.204 \times 10^5/(\epsilon T)^{3/2}$, and $F(c) = [\exp(0.2929B(c) \times c^{1/2}a_0) - 1]/(0.2929B(c)c^{1/2}a_0)$. ϵ is the dielectric constant of the solution. It may be noted that eq 3 is different from eq 1 in the sense that in eq 3 B, B_1, and B_2 are indirectly concentration-dependent, whereas in eq 1 they are not.

In the literature, reliable dielectric constant data up to high concentration are unfortunately not available for many electrolyte solutions. We could find (*7*, *12–15*) such data only for LiCl, NaCl, NaBr, NaI, and KF aqueous solutions. The reported (*4*, *5*, *16–22*) equivalent conductance data of these five aqueous solutions were therefore fitted to eq 3 at 25 °C with use of an iterative least-squares method. While fitting the conductance data to eq 3, the values of Λ_0 for these solutions were evaluated from the reported values of equivalent ionic conductances for each ion (*23*). This procedure has the advantage that eq 3 has essentially only one adjustable parameter, a_0. The best fit values of the a_0 parameter obtained in this fashion for the five solutions under consideration are tabulated in Tables I–V. From these tables it is apparent that eq 3 with only one adjustable parameter can reproduce reasonably well the equivalent conductance data of the aqueous solutions up to 4 mol·dm^{-3}. Beyond this concentration, the data fittings were however found to be not very good.

It may be worthwhile to discuss why the introduction of the solution dielectric constant in eq 1 extends its applicability to higher concentrations. The depression in the dielectric constant with increasing concentration is due to the decrease in the deformation and orientation polarizabilities of the solution. Water molecules when present in the hydration spheres of ions contribute less toward the deformation and orientation polarizabilities of the solution (*24*). As a consequence, the dielectric constant of the aqueous solution becomes less than that of pure water. Therefore, when the dielectric constant of the solution is substituted in eq 1 in place of that of water, indirectly to some extent the effect of ion-solvent interactions or ionic hydration is accounted for. This, in turn, might result in the

J. Chem. Eng. Data 1991, 36, 104-111

extension of the concentration range of application of the FLK eq 1.

Registry No. LiCl, 7447-41-8; NaCl, 7647-14-5; NaBr, 7647-15-6; NaI, 7681-82-5; KF, 7789-23-3.

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High-Pressure Vapor–Liquid Equilibria for Binary Mixtures Containing a Light Paraffin and an Aromatic Compound or a Naphthene in the Range 313–473 K

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The experimental study summarized here represents a continuing effort to obtain phase equilibrium data on selected binary systems. The lighter components of the binaries are methane, ethane, and propane. The heavier components are toluene, *m*-xylene, mesitylene, *n*-propylbenzene, cyclohexane, methylcyclohexane, and *n*-propylcyclohexane. Three apparatuses based on a static method were used at three temperatures (ca. 313, 393, and 473 K) and pressures up to the critical one.

Introduction

This work is a contribution to the Gas Processors Association Project to establish a data bank of high-pressure vapor–liquid equilibria (VLE) between natural gas components and heavier hydrocarbons. Binary VLE were measured by using several experimental methods (*1*–*4*).

Consistency tests on our lowest pressure data have been presented for two binaries (*5*). Careful measurements at pressures close to atmospheric allow calculation of cross second and third virial coefficients, only if heavy-component vapor-phase composition is precise and exempt of systematic errors. The main interest of testing our data through the Prausnitz–Keeler (*6*) test was to find out that some of our previous data had systematic errors. New experimental measurements (*5*), coupled with data obtained with a specially developed new apparatus (dynamic type), made it possible to identify the unsatisfactory operating conditions of the capillary sampling system. When they were modified it became possible to obtain reliable new results. All the data presented in this paper satisfy the Prausnitz–Keeler test.

Experimental Section

Apparatus and Procedure. The three apparatuses used in this work are based on the static method with analysis of the equilibrium phases. They differ mainly by the sampling system. The first, apparatus 1, developed by Legret et al. (*7*), had detachable microcells to sample both phases between 1 and 100 MPa, at 233–433 K. This equipment is particularly suited for studies at temperatures that are low compared to the components' normal boiling temperatures. Sampling microcells are removed from the equilibrium cell and placed inside a special heated injection assembly to a gas–liquid chromatograph (GLC).

The second apparatus, apparatus 2, developed by Figuière et al. (*8*), uses two valves to perform microexpansion sampling between 0.5 and 40 MPa, at 333–673 K. The sampling valves are part of the equilibrium cell. The equilibrium temperature has to be higher than the bubble temperature of the heaviest component at GLC carrier gas pressure to ensure fast vaporization of liquid samples.

Apparatus 3, designed by Laugier and Richon (*9*) to combine the advantages of the two preceding apparatuses, uses sampling by capillaries. The capillaries limit the sample size by hydrodynamic slow flow and connect the sampling tip immersed in the temperature-controlled liquid bath where the equilibrium cell is immersed to the heated injector. In this way, the temperature of the on-line injection chamber has no effect on that of the equilibrium cell.

Since the volumes of the samples in each of the three apparatuses are sufficiently small (2×10^{-5}% to 2×10^{-4}%), compared to the cell volumes, sampling does not disturb the state of equilibrium.

Pressure *P* measurements were performed by using membrane pressure transducers calibrated with a dead-weight

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