Effects of Temperature on Activity Coefficients in Aqueous Electrolyte Solutions

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In 1978, Kusik and Meissner (1978) presented an equation for the prediction of activity coefficients in aqueous electrolyte solutions, based on parameter q. In this work the temperature dependency of the Kusik-Meissner parameter, q, was studied.

Although the activity coefficients of electrolytes are readily available in binary and ternary solutions at 298.15K, little or no data are available at other temperatures. The calculation of properties such as activities, vapor pressures, solubilities, and those corresponding to strong electrolytes, currently found in leaching, precipitation, crystalization, evaporation processes and others, generally have been handicapped by this lack of data. There are several equations for predicting these activity coefficients (Kusik and Meissner, 1978; Bromley, 1973; and Pitzer, 1973) but unfortunately, little or no parameter values are available at temperatures other than 298.15K. In industrial practice it is common to find a wide range of temperature for which no correlation is available.

Kusik and Meissner presented the following equation:

$$\Gamma = [1 + B(1 + 0.1I)^q - B]\Gamma^* \tag{1}$$

with:

$$B = 0.75 - 0.065\,q$$
$$\text{Log}\,\Gamma^* = (-A\sqrt{I})/(1 + C\sqrt{I})$$
$$C = 1 + 0.055\,q\exp(-0.023\,I^3)$$
$$A = 0.5107$$

where Γ is the reduced activity coefficient, $\gamma_\pm^{1/z_+z_-}$, and I is the ionic strength. Values for q are given at 298.15K. The Eq. 1 may also be expressed as:

$$\text{Log}\,\gamma_\pm = (-A|Z_+Z_-|\sqrt{I})/(1 + C\sqrt{I}) + |Z_+Z_-|\,\text{Log}\,[1 + B(1 + 0.1\,I)^q - B] \tag{2}$$

Note that the first term of Eq. 2 has the form of Debye-Hückel's model.

Kusik and Meissner suggested the following equation for q at temperatures other than 298.15K (applicable for any ionic strength):

$$\frac{q_t - q_{25}}{t - 25} = a\,q_{25} + b^* \tag{3}$$

Table 1. Activity Coefficient Used in Regression Analysis

Electrolyte	N	NI	Temp. Range, K	Max. I
KCl*	108	9	273–313	4
KBr*	54	6	298–373	4
KOH*	117	9	273–353	17
LiCl**	80	5	273–373	18
NaOH*	88	8	273–308	4
NaBr*	108	9	273–313	4
NaCl*†	137	12	273–373	4
$BaCl_2^*$	45	5	273–318	4.5
$CdBr_2^*$	72	4	278–303	5.4
$CdCl_2^*$	24	3	273–313	0.3
$ZnCl_2^*$	48	4	283–313	3
ZnI_2^*	52	4	278–313	2.4

*From Harned & Owen (1943)
**From Gibbard & Scatchard (1973)
†From Robinson & Stoke (1965)

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Table 2. Values of Parameter q

Electrolyte	Temp. K	q	Avg. Dev.
KCl	273.15	0.4805	0.0039
	278.15	0.5880	0.0038
	283.15	0.7109	0.0042
	288.15	0.7963	0.0043
	293.15	0.8780	0.0046
	298.15	0.9468	0.0049
	303.15	1.0022	0.0052
	308.15	1.0484	0.0053
	313.15	1.0851	0.0055
KBr	298.15	1.1760	0.0060
	333.15	1.7542	0.0077
	343.15	1.8504	0.0090
	353.15	1.9469	0.0105
	363.15	2.0213	0.0116
	373.15	2.0883	0.0125
KOH	273.15	5.7065	0.5109
	283.15	5.5511	0.3509
	293.15	5.3856	0.2402
	303.15	5.2012	0.1259
	313.15	5.0305	0.1130
	323.15	4.8443	0.0816
	333.15	4.6498	0.0589
	343.15	4.4500	0.0463
	353.15	4.2175	0.1294
LiCl	273.15	6.4614	1.3172
	298.15	5.8548	0.8473
	323.15	5.3130	0.6593
	348.15	4.8014	0.5088
	373.15	4.3461	0.3765
NaOH	273.15	2.2948	0.0175
	278.15	2.4227	0.0150
	283.15	2.5308	0.0140
	288.15	2.6138	0.0119
	293.15	2.6721	0.0113
	298.15	2.7150	0.0106
	303.15	2.7624	0.0101
	308.15	2.7720	0.0097
NaBr	273.15	2.2770	0.0106
	278.15	2.4687	0.0097
	283.15	2.6639	0.0084
	288.15	2.7917	0.0092
	293.15	2.9457	0.0068
	298.15	3.0566	0.0066
	303.15	3.1613	0.0056
	308.15	3.2393	0.0049
	313.15	3.3019	0.0042
NaCl	273.15	1.6011	0.0092
	278.15	1.7786	0.0093
	283.15	1.9151	0.0091
	288.15	2.0400	0.0089
	293.15	2.1418	0.0083
	298.15	2.2237	0.0065
	303.15	2.3084	0.0068
	333.15	2.6934	0.0066
	342.15	2.6829	0.0073
	353.15	2.6832	0.0063
	363.15	2.6957	0.0062
	373.15	2.7003	0.0064
$BaCl_2$	273.15	1.1667	0.0036
	288.15	1.3639	0.0015
	298.15	1.4372	0.0013
	308.15	1.4938	0.0017
	318.15	1.5164	0.0015

Table 2. (Continued)

Electrolyte	Temp. K	q	Avg. Dev.
$CdBr_2$	278.15	−2.7830	0.1321
	288.15	−2.6936	0.1257
	303.15	−2.6175	0.1199
	313.15	−2.6008	0.1194
$CdCl_2$	273.15	−5.4676	0.0086
	298.15	−7.6292	0.0072
	313.15	−8.2051	0.0079
$ZnCl_2$	283.15	1.6479	0.0294
	293.15	1.4758	0.0321
	303.15	1.2676	0.0330
	313.15	1.0301	0.0320
ZnI_2	278.15	4.2011	0.0353
	288.15	4.1713	0.0339
	303.15	4.0696	0.0328
	313.15	4.0000	0.0327

where

t = temperature in degrees celsius

a = −0.0079 for sulfates
−0.050 for other electrolytes

b^* = −0.0029 for sulfates
0.0085 for nonsulfates

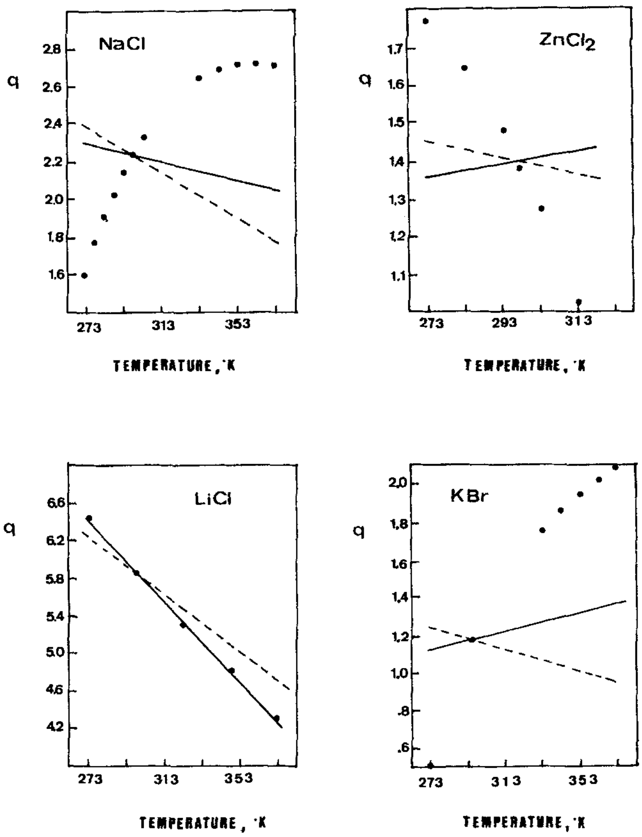

Figure 1. Evaluated q parameters (●) vs. values calculated using Eqs. 3 (—) and 4 (--).

Later, Meissner (1980) suggested the following equation:

$$q_t = q_{25}\left[1 - \frac{0.0027\,(t - 25)}{|Z_+ Z_-|}\right] \tag{4}$$

Using the above relations in this work, different electrolyte solutions were studied, so as to predict activity coefficients of strong electrolytes as a temperature function.

Evaluation of Parameters

As the Kusik-Meissner equation is an empirical expression, we can not make use of the dilution enthalpy data. Therefore, in order to estimate the Kusik-Meissner parameters, q, data of activity coefficients at different temperature are needed. The data used in this work are shown in Table 1, where N is the number of experimental points, and NI is the number of isotherms. Twelve single electrolyte solutions were used (66 isotherms and 933 experimental points). From these data, the value of q has been obtained using regressions analysis and by considering the constant, A, in Eq. 2 as a temperature function equal to the Debye-Hückel parameter. The results are shown in Table 2. The corresponding average deviations were evaluated from the following equation:

$$\text{average deviation} = \frac{1}{N}\Sigma[(\gamma_{\pm_{exp}} - \gamma_{\pm_{cal}})^2]^{1/2}$$

The maximum deviation in predicting the activity coefficients, using q values from Table 2 and Eq. 2, is generally less that 0.1.

Table 3. Parameters of Eq. 5

Electrolyte	a	b	$c \times 10^4$	$d \times 10^7$
KCl	−19.4072	0.1060	−0.6697	−2.0011
KBr	−41.8506	0.3329	−8.5483	7.4581
KOH	15.6147	−0.0780	2.3207	−2.0969
LiCl	17.2944	−0.0569	0.7297	−0.3613
NaOH	−48.5528	0.3973	−9.6112	6.8941
NaBr	−51.8890	0.4047	−9.3423	6.5420
NaCl	−47.1504	0.3890	−10.0578	8.6058
$BaCl_2$	−48.5876	0.4450	−13.1766	13.0144
$CdBr_2$	−1.8135	−0.0579	3.4471	−5.3621
$CdCl_2$	115.9530	−0.7726	12.0101	0.0
$ZnCl_2$	−11.1642	0.1071	−2.2609	0.2677
ZnI_2	−1.0627	0.0410	−0.7933	0.0

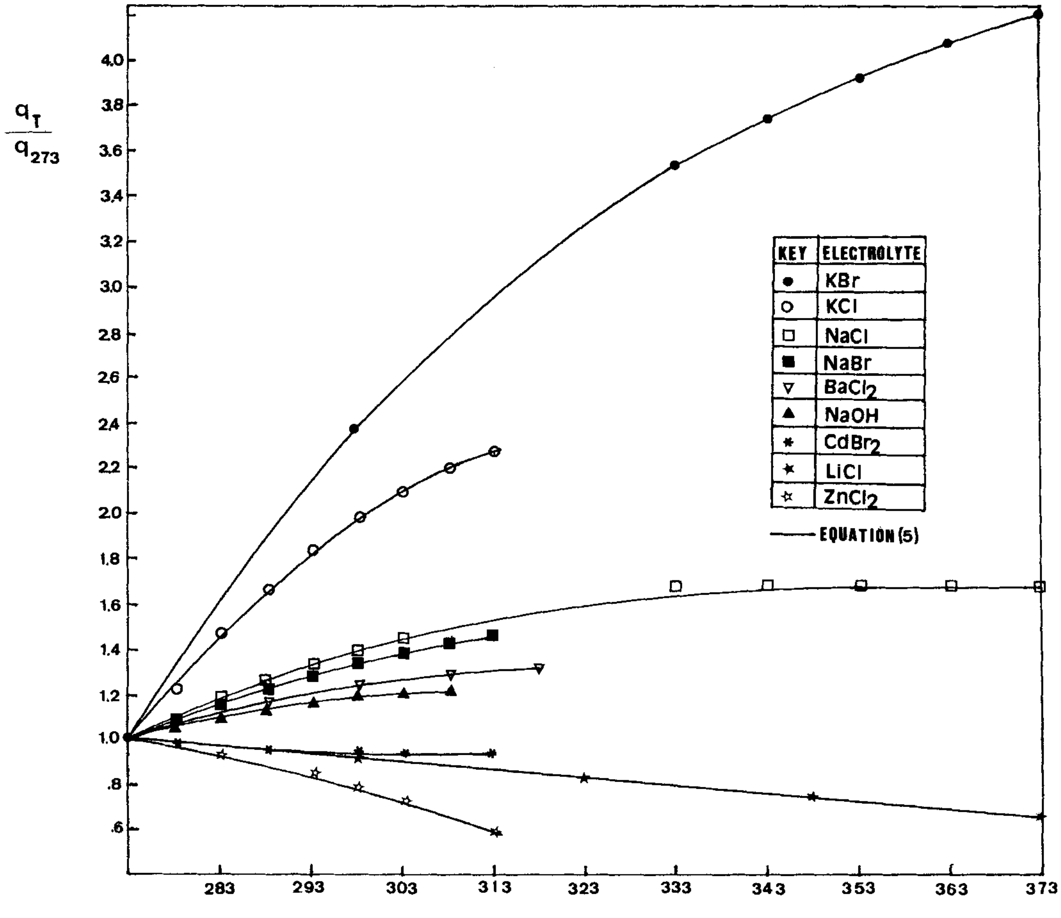

Figure 2. Evaluated q parameters vs. values calculated using Eq. 5.

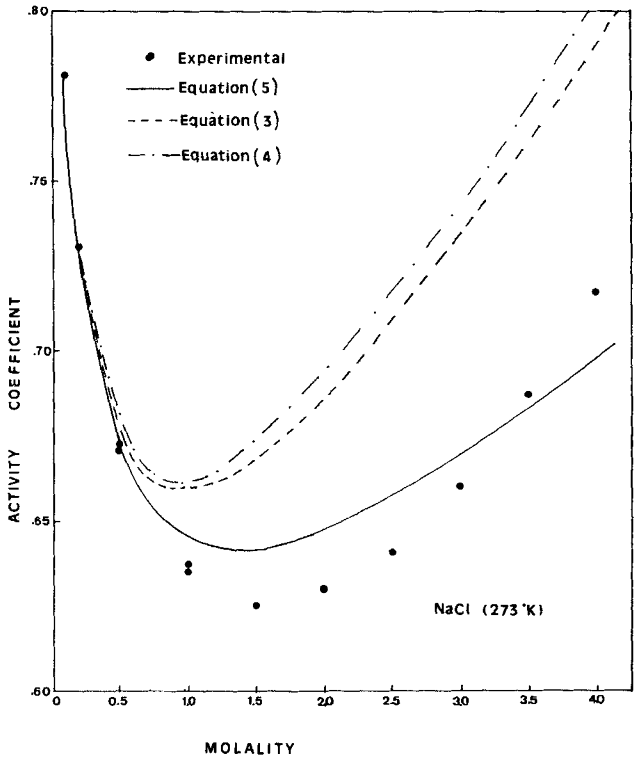

Figure 3. Deviation in predicting activity coefficients using Eqs. 3, 4, 5 for predicting q parameters.

Discussion

The comparison of the evaluated q parameters with the values calculated using Eqs. 3 and 4, are shown in Figure 1. As we see it, Eqs. 3 and 4 do not represent the evaluated parameters, q (except LiCl). Furthermore, the q temperature dependence proved to be nonlinear, opposite to the dependence indicated by Eqs. 3 and 4.

In order to predict q parameters, the following equation is proposed:

$$q = a + b\,T + cT^2 + dT^3 \tag{5}$$

where T is in Kelvin degrees and parameters a, b, c, d are as presented in Table 3.

Comparison of evaluated q/q_{273} parameters at different temperatures with calculated values, by using Eq. 5, are shown in Figure 2.

Here, q_{273} values were calculated at 273.15K. The degree of deviation from experimental data in predicting activity coefficient values by using Eqs. 3, 4, and 5, are shown in Figure 3 for an NaCl system at 273K. From the above data it is concluded that the dependence of the Kusik-Meissner parameter follows Eq. 5.

Literature Cited

Bromley, L. A., "The Thermodynamic Properties of Strong Electrolytes in Aqueous Solution," *AIChE J.*, **19**, 313 (March 1973).

Gibbard, H. F., G. Scatchard, "Liquid Vapor Equilibrium of Aqueous Lithium Chloride from 25 to 100C, from 1.0 to 18.5 Molal, and Related Properties," *J. Chem. Eng. Data*, **18**, 293 (March, 1973).

Harned, H. S., B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Book Corp., New York, (1943).

Kusik, C. L., H. P. Meissner, "Electrolyte Activity Coefficients in Inorganic Processing," *AIChE Symp. Ser.*, **173**, 14 (1978).

Meissner, H. P., "Prediction of Activity Coefficients of Strong Electrolytes in Aqueous System. Thermodynamics of Aqueous System with Industrial Applications," *ACS Symp. Ser.*, **133**, 496 (1980).

Pitzer, K., "Thermodynamics of Electrolytes: I. Theoretical Bases and General Equations," *J. Phys. Chem.*, **77**, 268 (1973).

Robinson, R. A., R. M. Stokes, "Electrolytes Solutions, 2nd ed., revised, Butterworths, London (1965).

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