

Recalculation of Activity and Osmotic Coefficients of Hydrohalic Acids and Some Alkali Metal Halides in Dilute Aqueous Solutions at 298.15 K

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Activity and osmotic coefficients are presented for dilute aqueous solutions of the following electrolytes at 298.15 K: HCl, HBr, HI, LiCl, NaCl, KCl and KBr. The values tabulated in this paper have been calculated from the Hückel equation with the parameter values determined by the author. These parameter values have been tested thoroughly, and most of the existing experimental activity coefficients can be predicted within experimental error using the Hückel equation and these values. Therefore, the activity and osmotic coefficients presented in this paper are probably the most reliable values available.

In 1948 Stokes and Robinson¹ published their well known paper in which a two-parameter equation was presented for activity coefficients of single electrolytes in aqueous solutions at 298 K. According to these workers, the equation applies for most electrolytes up to molalities greater than 1.0 mol kg⁻¹. From the theoretical point of view, the equation of Stokes and Robinson was based on the Debye–Hückel theory supplemented with a hydration correction. In the derivation of this correction, it was assumed that each molecule of the electrolyte in the solutions binds h molecules of water, and the true molality (moles of hydrated solute per 1000 g of free water) was used instead of the analytical molality (for details see Ref. 1).

The exact use of the two-parameter Robinson and Stokes equation¹ is not easy. Therefore, the equation was later simplified by Guggenheim and Stokes² and by Pan.^{3,4} The approximations made by Pan lead to a simple equation which is suitable for dilute electrolyte solutions. Based on this equation, in 1981 Pan presented new tables of activity and osmotic coefficients for several uni-univalent electrolytes in dilute aqueous solutions at 298 K. The coefficients were calculated with the original parameter values given by Stokes and Robinson.¹

Pan's simplified form⁴ of the equation of Robinson and Stokes¹ is functionally very similar to the equation presented by Hückel⁵ in 1925. In a recent paper⁶ the two parameters of Hückel's equation were recalculated for hydrohalic acids and some alkali metal halides under the conditions of Pan's tables.⁴ For most electrolytes, the activity coefficients calculated from Hückel's equation with these new parameter values differ significantly from the values obtained by Pan.⁴ Since only a few papers in the recent literature contain systematic information on the

thermodynamics of dilute electrolyte solutions, this discrepancy suggests that the activity coefficients presented by Pan have to be revised.

In the present paper, the predictive ability of Pan's equation is tested with good experimental data available in the literature. As a comparison, the same tests are carried out with Hückel's equation containing the recalculated parameter values mentioned above. In the previous study,⁶ the parameter values of Hückel's equation were thoroughly tested with the existing electrochemical, cryoscopic and isopiestic data. It was further shown then that the activity coefficients of several uni-univalent electrolytes can also be quite accurately calculated in dilute solutions from the general equations of Hamer and Wu⁷ and Pitzer.⁸

New tables for the activity and osmotic coefficients of HCl, HBr, HI, LiCl, NaCl, KCl and KBr, based on Hückel's equation with the recalculated parameter values mentioned above, will be presented below.

Equations

Stokes and Robinson¹ presented the two-parameter equation shown in eqn. (1) for the mean molal activity coefficient (γ_{\pm}) of an electrolyte of the type $M_{\nu_+}X_{\nu_-}$ at a molality m . In eqn. (1) $\nu = \nu_+ + \nu_-$, z_+ and z_- are the

$$\ln \gamma_{\pm} = - \frac{\alpha_c z_+ |z_-| (I_c)^{\frac{1}{2}}}{1 + \beta_c a^*(I_c)^{\frac{1}{2}}} - \frac{h}{\nu} \ln a_w - \ln [1 - M_w(h-\nu)m] \quad (1)$$

charge numbers of cation and anion, respectively, α_c and β_c are the Debye–Hückel constants and I_c is the ionic strength of the solution on the concentration scale; a_w is the activity and M_w ($= 0.018\ 015$ mol⁻¹) the molar mass of water, a^*

is (according to Debye–Hückel theory) the distance of the closest approach of ions (i.e. the ion size parameter) and h is the abovementioned hydration number of the electrolyte. The parameters a^* and h depend on the electrolyte.

When we consider a uni-univalent electrolyte, Pan's three approximations^{3,4} are the following. In the Debye–Hückel term eqn. (2) holds, where c is the concentration of

$$I_c = c \approx \rho_w m \quad (2)$$

the electrolyte and ρ_w the density of water. The second is eqn. (3), where φ is the osmotic coefficient of water in the

$$\ln a_w = -vm\varphi M_w \approx -vmM_w = -2mM_w \quad (3)$$

solution studied and in dilute solutions it is near to one. The third is eqn. (4).

$$\ln [1 - M_w(h-v)m] \approx -M_w(h-v)m = -M_w(h-2)m \quad (4)$$

With these approximations, eqn. (1) can be presented for a uni-univalent electrolyte in the form of eqn. (5), where at

$$\ln \gamma_{\pm} = -\alpha m^{1/2} / (1 + \beta a^* m^3) + 2M_w(h-1)m \quad (5)$$

298 K, $\alpha = \alpha_c \rho_w^{1/2} = 1.1762 \text{ (kg mol}^{-1}\text{)}^{1/2}$ and $\beta = \beta_c \rho_w^{3/2} = 3.287 \text{ (kg mol}^{-1}\text{)}^{3/2} \text{ nm}^{-1}$. By means of the Gibbs–Duhem equation, eqn. (6) can be derived from eqn. (5) for the

$$\varphi = 1 - \frac{\alpha}{(\beta a^*)^{3/2} m} [(1 + \beta a^* m^3) - 2 \ln (1 + \beta a^* m^3) - (1 + \beta a^* m^3)^{-1}] + M_w(h-1)m \quad (6)$$

osmotic coefficient. The Hückel equation used in the previous paper⁶ from our laboratory has the form of eqn. (7),

$$\ln \gamma_{\pm} = -\alpha m^{1/2} / (1 + \beta a^* m^3) - \ln (1 + 2M_w m) + b_1 m / m^\circ \quad (7)$$

where $m^\circ = 1 \text{ mol kg}^{-1}$. In this equation the approximation given by eqn. (8) can be made in dilute electrolyte

$$\ln (1 + 2M_w m) = +2M_w m \quad (8)$$

solutions, and so eqns. (5) and (7) are equivalent if eqn. (9)

$$h = b_1 / (2M_w m^\circ) \quad (9)$$

holds. By means of eqn. (9) the values of h can be calculated from the values of b_1 presented in the previous paper⁶ for the various uni-univalent electrolytes.

Calculations and results

The parameters of the Robinson–Stokes equation for different electrolytes have primarily been estimated from the measured results of isopiestic determinations.¹ It is well

known that this method is not very accurate at molalities $< 0.1 \text{ mol kg}^{-1}$. Using accurate experimental data measured in dilute solutions, it is not possible to check the activity coefficients of all electrolytes included in Pan's tables.⁴ Reliable electrochemical measurements are available only for the following electrolytes: HCl, HBr, HI, LiCl, NaCl, KCl and KBr.⁶ In Pan's paper⁴ the subsequent values are presented for parameters a^* and h of these electrolytes: HCl ($a^* = 0.447 \text{ nm}$, $h = 8.0$), HBr (0.518 nm, 8.6), HI (0.569 nm, 10.6), LiCl (0.432 nm, 7.1), NaCl (0.397 nm, 3.5), KCl (0.363 nm, 1.9) and KBr (0.385 nm, 2.1). The following values of these parameters are given in Ref. 6 [the values of h have been calculated from eqn. (9) as mentioned above]: HCl ($a^* = 0.38 \text{ nm}$, $h = 11.57$), HBr (0.50 nm, 10.2), HI (0.53 nm, 9.46), LiCl (0.48 nm, 3.80), NaCl (0.42 nm, 3.16), KCl (0.37 nm, 2.69) and KBr (0.41 nm, 0.833).

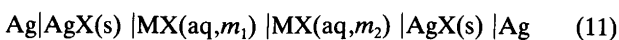
If Pan's activity coefficients are correct, they predict the best measured results in dilute solutions, so that the prediction errors should be small and random. To test the validity of Pan's activity coefficients, therefore, the equation used by him is applied to predict the results of reliable electrochemical measurements. For these tests a set of measured data is chosen for each electrolyte under consideration. It has been confirmed that the chosen sets contain very reliable and precise experimental values.⁶ As mentioned above, the results obtained by means of the new parameter values of Hückel's equation⁶ are also included in the tests presented here.

Reliable data for dilute hydrobromic and hydriodic acid solutions have been measured by Hetzer *et al.*^{9,10} using hydrogen silver halide cells. Accurate measurements^{11–14} have also been made in dilute hydrochloric acid solutions, using cells of this kind. However, the experimental electromotive forces of the most extensive study, published by Bates and Bower,¹⁴ on hydrogen silver chloride cells have not been reported in the literature, and so this study had to be omitted from the present calculations. Of the remaining studies, the most accurate set is probably the one of Hills and Ives¹⁶ measured using a hydrogen calomel cell,^{6,15} and these results are included in the present calculations. The electromotive force of a hydrogen silver (or mercurous) halide cell depends on the molality according to eqn. (10),

$$E = E^\circ - (2RT/F) \ln (\gamma_{\pm} m / m^\circ) \quad (10)$$

where E° is the standard value of E , and the other symbols have their usual meaning.

For alkali metal halides, the most accurate experimental activity coefficients in dilute solutions can be obtained by means of concentration cells of type (11) with transference.



Here M is now Li^+ , Na^+ or K^+ and X is Cl^- or Br^- . The relationship between E and the molalities m_1 and m_2 can be expressed by⁶ eqn. (12), where t_+ is the transference

$$E = - (2RT/F) \left[t_+(1) \ln (m_2/m_1) + t_+(1) \ln [\gamma_{\pm}(2)/\gamma_{\pm}(1)] + \int_{m_1}^{m_2} \Delta t_+ (dm/m) + \int_{\gamma_{\pm}(1)}^{\gamma_{\pm}(2)} \Delta t_+ (d\gamma_{\pm}/\gamma_{\pm}) \right] \quad (12)$$

number of the cation and $t_+(1)$ is that in solution 1 of cell (11) and where $\Delta t_+ = t_+ - t_+(1)$. When the aim is to predict the experimental data measured in concentration cells of type (11) by means of the different activity coefficient equations, the transference numbers and their dependence on concentration are needed. In the present calculations the equations determined in the previous paper⁶ are used for the t_+ values of LiCl, NaCl, KCl and KBr. These equations apply at 298 K to molalities $<0.1 \text{ mol kg}^{-1}$ and have the general form of eqn. (13). In the previous paper,

$$t_+ = t_+^{\infty} - A (m/m^{\circ})^{\frac{1}{2}} + B (m/m^{\circ}) \quad (13)$$

the following values were determined for the parameters of eqn. (13) from the existing results of the measurements by the moving-boundary method: LiCl ($t_+^{\infty} = 0.336 46$, $A = 0.082 92$, $B = 0.065 77$), NaCl ($0.396 17$, $0.048 03$, $0.043 99$), KCl ($0.490 47$, $0.003 85$, $0.006 67$) and KBr ($0.484 76$, $0.015 07$, $0.051 53$).

The results of the tests and the most reliable sets are shown in the seven graphs of Figs. 1 and 2. In all graphs the errors of the anticipated EMF values are presented as a function of the molality. The errors have been calculated from eqn. (14). The predicted EMF values have been

$$e(E) = E(\text{observed}) - E(\text{predicted}) \quad (14)$$

calculated from eqn. (10) (HCl, HBr and HI) or from eqn. (12) (LiCl, NaCl, KCl and KBr) by means of the activity coefficient equation (5) with the two categories of the values of a^* and h presented above. E° in eqn. (10) has been determined for each set in such a way that the sum of the errors in that set is zero.

Conclusions

According to Figs. 1 and 2, the experimental activity coefficients of dilute solutions of only HBr and KBr can be accurately predicted by means of Pan's equation. Only in these two cases is the pattern formed by the errors random. Therefore, the activity and osmotic coefficients presented in Pan's paper⁴ are not entirely reliable. This statement is probably also true for the values of the remaining electrolytes presented in Pan's work that are not tested in the present paper. Unfortunately, no reliable data measured at 298 K are presently available in the literature that can confirm this conclusion.

On the other hand, the activity and osmotic coefficients presented in Tables 1 and 2, respectively, can be recommended for the electrolytes. The values in these tables have

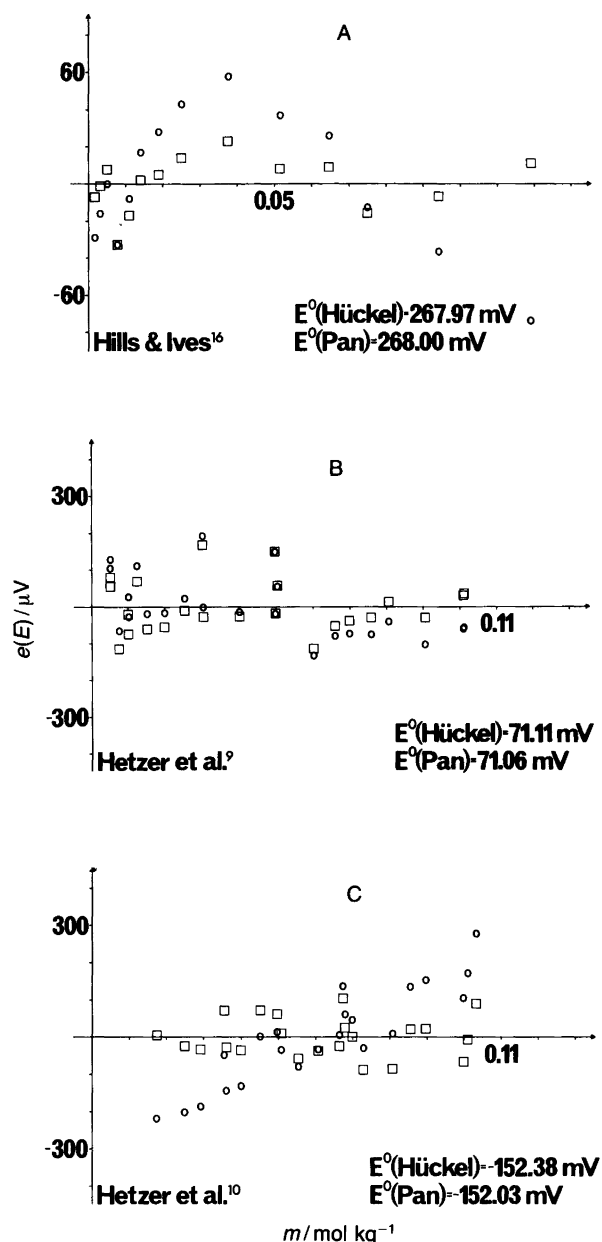


Fig. 1. Results of the sets measured in galvanic cells without a liquid junction. The difference between the measured and predicted EMF values is presented as a function of the molality of the solutions. □, Hückel; ○, Pan; (A) HCl, (B) HBr, (C) HI.

been calculated from eqns. (5) and (6) with the values of a^* and h determined in Ref. 6 and presented above. As mentioned earlier, these values have been thoroughly tested with the existing experimental data from various sources.⁶ In the same way as shown in Figs. 1 and 2, the experimental data can in most cases be reproduced excellently by applying Hückel's equation with these parameter values. Therefore, the activity and osmotic coefficients of Tables 1 and 2 are probably the most reliable values available and can be recommended as reference values, especially for further theoretical studies in this field.

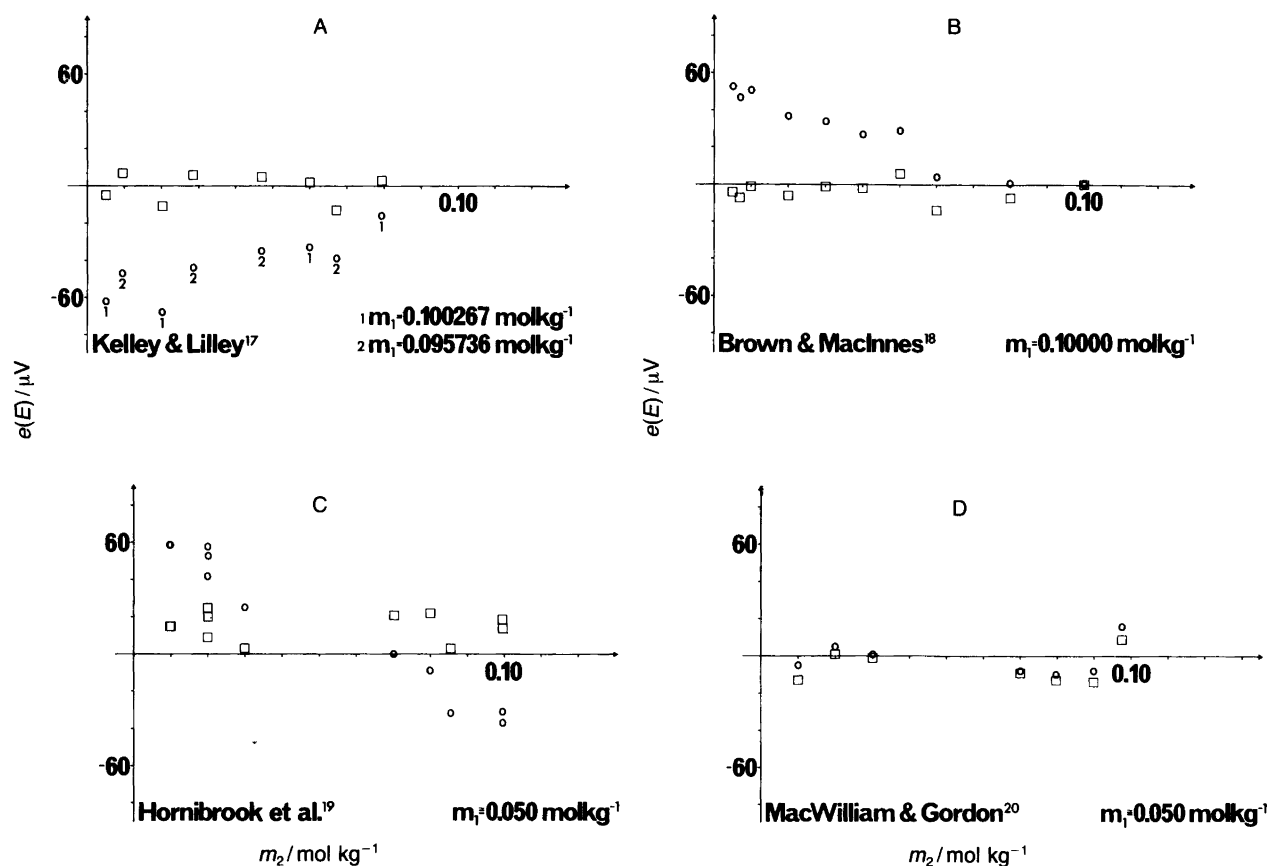


Fig. 2. Results for the sets measured in galvanic cells with a liquid junction. The difference between the measured and predicted EMF values is presented as a function of the molality of the solutions. \square , Hückel; \circ , Pan; (A) LiCl, (B) NaCl, (C) KCl, (D) KBr.

Table 1. Activity coefficients in dilute aqueous solutions of uni-univalent electrolytes at 298.15 K.

$m/\text{mol kg}^{-1}$	HCl	HBr	HI	LiCl	NaCl	KCl	KBr
0.001	0.9652	0.9656	0.9657	0.9653	0.9651	0.9649	0.9649
0.002	0.9521	0.9528	0.9530	0.9522	0.9518	0.9515	0.9516
0.003	0.9426	0.9435	0.9437	0.9427	0.9421	0.9416	0.9418
0.004	0.9348	0.9361	0.9363	0.9350	0.9342	0.9335	0.9337
0.005	0.9282	0.9297	0.9300	0.9284	0.9274	0.9266	0.9268
0.006	0.9224	0.9242	0.9246	0.9226	0.9214	0.9204	0.9208
0.007	0.9172	0.9193	0.9197	0.9174	0.9161	0.9149	0.9153
0.008	0.9125	0.9148	0.9152	0.9127	0.9112	0.9099	0.9103
0.009	0.9082	0.9107	0.9112	0.9083	0.9067	0.9053	0.9058
0.01	0.9042	0.9069	0.9074	0.9043	0.9025	0.9010	0.9015
0.02	0.8748	0.8795	0.8804	0.8746	0.8714	0.8687	0.8695
0.03	0.8555	0.862	0.8630	0.8547	0.8504	0.8467	0.8476
0.04	0.8411	0.849	0.850	0.840	0.8342	0.8296	0.8307
0.05	0.8298	0.839	0.840	0.827	0.8211	0.8157	0.8168
0.06	0.8206	0.831	0.832	0.817	0.8101	0.8039	0.805
0.07	0.8128	0.824	0.826	0.809	0.8005	0.7936	0.795
0.08	0.8063	0.818	0.820	0.801	0.7921	0.7845	0.786
0.09	0.8006	0.813	0.815	0.794	0.7847	0.7764	0.777
0.1	0.7957	0.809	0.811	0.788	0.778	0.7691	0.770

Table 2. Osmotic coefficients in dilute aqueous solutions of uni-univalent electrolytes at 298.15 K.

$m/\text{mol kg}^{-1}$	HCl	HBr	HI	LiCl	NaCl	KCl	KBr
0.001	0.9884	0.9887	0.9886	0.9885	0.9884	0.9882	0.9883
0.002	0.9843	0.9846	0.9846	0.9843	0.9840	0.9838	0.9839
0.003	0.9811	0.9816	0.9817	0.9812	0.9809	0.9806	0.9807
0.004	0.9786	0.9793	0.9794	0.9787	0.9783	0.9779	0.9781
0.005	0.9765	0.9773	0.9775	0.9766	0.9761	0.9756	0.9758
0.006	0.9747	0.9756	0.9758	0.9748	0.9742	0.9736	0.9738
0.007	0.9731	0.9742	0.9744	0.9731	0.9724	0.9719	0.9720
0.008	0.9716	0.9728	0.9730	0.9717	0.9709	0.9702	0.9704
0.009	0.9703	0.9716	0.9719	0.9703	0.9694	0.9687	0.9689
0.01	0.9691	0.9705	0.9708	0.9691	0.9681	0.9673	0.9676
0.02	0.9604	0.9629	0.9633	0.9601	0.9584	0.9570	0.9574
0.03	0.9552	0.9585	0.9591	0.9545	0.9521	0.9501	0.9505
0.04	0.9517	0.9557	0.9564	0.9503	0.9474	0.9448	0.9453
0.05	0.9492	0.954	0.9545	0.9472	0.9437	0.9407	0.9411
0.06	0.9474	0.953	0.953	0.945	0.9407	0.9372	0.9376
0.07	0.9461	0.952	0.953	0.943	0.9382	0.9343	0.9346
0.08	0.9453	0.951	0.952	0.941	0.9360	0.9317	0.9320
0.09	0.9447	0.951	0.952	0.940	0.9342	0.9295	0.930
0.1	0.9444	0.951	0.952	0.938	0.9326	0.9275	0.928

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