

Mean Activity Coefficients in Aqueous Electrolyte Mixtures. 1. EMF Studies at 25 °C on the KCl–KF System

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Based on emf measurements at 25 °C, the mean molar activity coefficients for KCl and KF in aqueous solutions of the pure salts as well as the mixed salts have been calculated in the range of ionic strengths from 0.001 to 2–4 mol dm⁻³. The emf measurements were made using ion-selective electrodes for each of the three ions concerned. The precision obtained with each of the electrode pairs was better than ±0.1 mV. The results are compared with previous results for the pure salts and for trace activity coefficients of one salt in the presence of a large excess of the other. The mean activity coefficients for KCl and KF in mixed solutions with equal amounts of KCl and KF were found to be equal, within experimental error, to the corresponding mean activity coefficients in solutions of the pure salts at the same ionic strengths. The extrapolated value of the slope of the logarithm of the experimental mean ionic activity coefficients vs. the square root of the ionic strength is very close to the value given by the limiting law of Debye and Hückel in the case of KCl, but the experimental slope for KF is about 10 % lower.

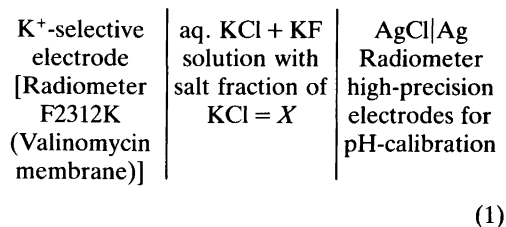
Mean activity coefficients for electrolytes in aqueous solutions at room temperature are determined mainly by means of (1) vapour-pressure measurements, (2) analysis of isopiestic equilibria and (3) emf measurements on appropriate cells. The three methods complement each other in the sense that the first two are used mostly at concentrations greater than 0.1 mol dm⁻³, due to limitations in experimental accuracy, whereas the emf-method may be used for high as well as low concentrations. The emf-method often involves a reference electrode with a salt bridge and an indicator electrode. Besides checking the reliability of the electrodes, one then has to “correct” for an – in principle – unmeasurable liquid–liquid junction potential. Such a correction is dubious and adds to the uncertainty of the measurements.

Many values of the mean activity coefficients for pure uni-univalent electrolytes in water at 25 °C have been reported in the literature (Ref. 1 contains data for 79 different compounds and

refers to further experimental work for 51 additional uni-univalent electrolytes). However, only few data are found for mixed KCl–KF solutions.^{2,3,4} The present paper presents data on the mean activity coefficients at 25 °C for pure and mixed aqueous solutions of KCl and KF at ionic strengths ranging from 0.001 to 4 mol dm⁻³. In our investigation, only cells *without* undeterminable salt bridge potentials were used.

Experimental

Emf was measured for the following two cells:



and

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K ⁺ -selective electrode as in (1)	Same solutions as in (1)	F ⁻ -selective electrode [Radiometer F1052F (LaF ₃ membrane)]
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(2)

The cells were built up in a water-jacketed Pyrex glass cell with lid. Through holes in the lid, the electrodes were immersed in about 100 cm³ of the solution. The temperature was held at 25±0.05 °C by means of circulating water from a thermostat. The K⁺ and F⁻ electrodes are based on highly ion-selective membranes. The Ag/AgCl electrodes were of the thermal-electrolytic type with asymmetry potentials not exceeding ±0.05 mV. These electrodes were prepared and kindly supplied by the pH-calibration department of Radiometer A/S, Copenhagen, Denmark. A more detailed description of the performance of these electrodes has been given earlier.^{5,6} Among ion-selective electrodes, the K⁺ and the F⁻ electrodes of the types used here are regarded as being the most selective and reliable.^{2,3,12,13}

Measurements were made on 15 different series of solutions with the following values of the salt fraction $X = c_{\text{KCl}} / (c_{\text{KCl}} + c_{\text{KF}})$: 0, 0.1, 0.2, 0.5, 0.8, 0.9 and 1.0. Each series consisted of solutions with the ionic strength (I) varying in steps from 0.001 to 0.1 mol dm⁻³, and additional measurements were carried out in more concentrated solutions. For $X = 0$ and 1, measurements were made on solutions with $I = 0.2, 0.5, 1.0, 2.0, 3.0$ and 4.0 mol dm⁻³. For $X = 0.5$, solutions with $I = 0.2, 0.4, 0.6, 1.0, 1.2, 1.6$ and 2.0 mol dm⁻³ were employed. Each series was prepared and selected at random, and measurements were made independently. The emf-values were registered on a pH-meter (PHM64, Radiometer, Copenhagen, Denmark) with an accuracy of ±0.1 mV. The stabilisation of the potentials with time was followed on a recorder (Radiometer).

Each measurement took about 3–4 h in order to obtain emf-values stable to within ±0.1 mV. The precision of the voltage measurements need not be greater than ±0.1 mV, since the reproducibility of the two membrane electrodes in individual measurements is often not better than several millivolts. This does *not* mean that we cannot determine the cell potentials and the standard potentials to a precision better than ±0.1 mV. We shall see that by proper statistical treatment

of the data, we can attain an accuracy somewhat better than ±0.1 mV. The performance of the Ag/AgCl electrodes was tested with a digital voltmeter (DATA 3400, Instrutek, Horsens, Denmark) having an accuracy of ±0.01 mV.

The measurements were carried out using one K⁺ electrode, one F⁻ electrode and 3–4 Ag/AgCl electrodes. If one of the latter electrodes gave rise to an emf differing by more than 0.01 mV from the mean of the others, this electrode was replaced by a freshly prepared one.

Chemicals. KF and KCl (both *p.a.* Merck) were dried at 110 °C for at least 24 h and then used without further purification. Before weighing, both KF and KCl were cooled in desiccators with silica gel. This treatment is important, since especially KF is hygroscopic. Solutions with $I \geq 0.1$ mol dm⁻³ were made independently of each other by dissolving the correct amounts of chemicals (weighted with an accuracy of ±0.1 mg) in the appropriate volume of distilled and deionized water. The test of the water purity was that the conductivity was below 1.0 μS. Solutions with $I < 0.1$ mol dm⁻³ were made by careful dilution from stock solutions with higher concentrations. The densities of the solutions, required for conversion from molar concentration to molality and from mean molar to mean molal activity in order to compare with literature data, were determined pycnometrically.

Results

Emf (E_1 and E_2) of the two cells (1) and (2) obey the following reactions:

$$E_1 + (RT/F)\ln[(c_{\text{KF}} + c_{\text{KCl}})c_{\text{KCl}}(c^\ominus)^{-2}] = E_1^\ominus - (2RT/F)\ln y_{\pm}(\text{KCl}) \quad (3)$$

$$E_2 + (RT/F)\ln[(c_{\text{KF}} + c_{\text{KCl}})c_{\text{KF}}(c^\ominus)^{-2}] = E_2^\ominus - (2RT/F)\ln y_{\pm}(\text{KF}) \quad (4)$$

E_1^\ominus and E_2^\ominus are the standard potentials of the two cells and $y_{\pm}(\text{KCl})$ and $y_{\pm}(\text{KF})$ are the mean molar activity coefficients for KCl and KF, respectively, in a (mixed) solution with ionic strength $I_c = c_{\text{KCl}} + c_{\text{KF}}$. The symbols R , T and F have their usual meanings, and $c^\ominus = 1$ mol dm⁻³.

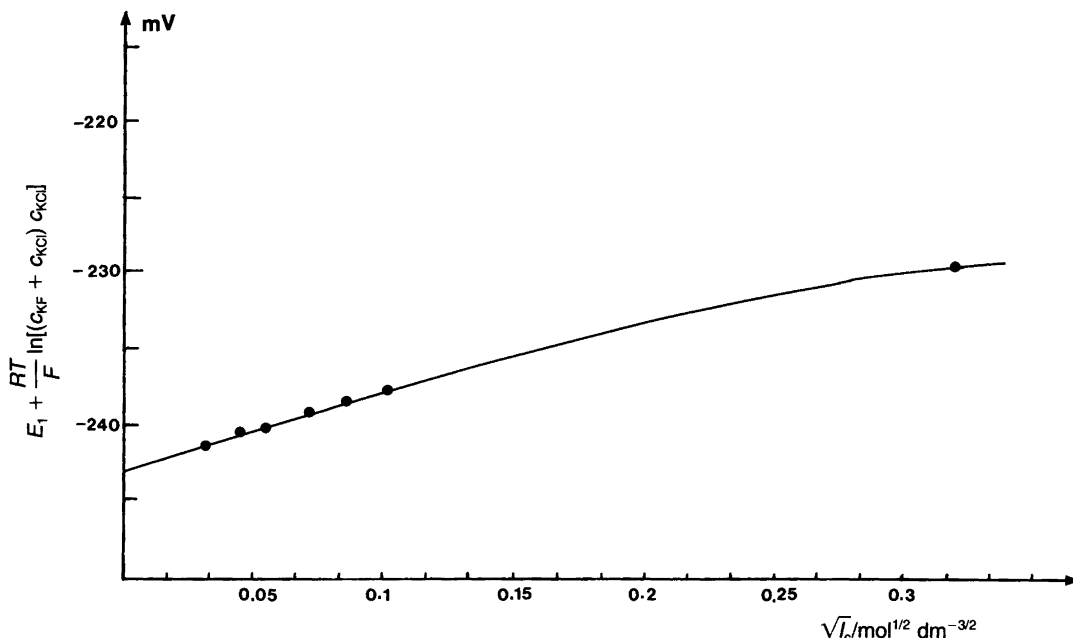


Fig. 1. Plot of left-hand side of eqn. (3) vs. $\sqrt{I_c}$ for a KCl-KF mixtures with the salt fraction of KCl = $X = 0.9$. The best fit to the experimental points at the 95 % significance level was obtained with a polynomial of 2nd degree.

Before being able to determine the mean activity coefficients from eqns. (3) and (4), we have to determine the standard potentials E_1 and E_2 without any circuitry in the arguments. Many authors have employed the extended Debye-Hückel equation (or the Güntelberg equation) in the dilute region in order to find the standard potentials. However, here, we do not wish to apply any external assumption to the data, and we therefore use an objective, statistical method described in the section below. The standard potentials should be determined to an uncertainty of ± 0.1 mV or less in order to be able to obtain a relative error of 0.002 in y_{\pm} . We should also be able to check that the values of the standard potentials found are independent of the salt fraction (X). If so, we have a nice indication that there are no disturbing interferences from the non-specific ions in the behaviour of the ion-selective electrodes.

Finally, for practical reasons we should check how reproducible the membrane electrodes themselves are, i.e. how much the standard potentials between a given electrode and a reference electrode, and between another electrode of

the same type and the same reference electrode differ.

Determination of E^{\ominus} . In eqns. (3) and (4), the left-hand sides are experimental quantities, whereas each of the right-hand sides involve two unknowns for each experiment. The fundamental postulate is that one unknown (E^{\ominus}) should be the same from experiment to experiment. We also know from basic electrolyte theory, that the limiting dependence of $\ln y_{\pm}$ on the ionic strength for small ionic strengths is a square-root dependence. Therefore, we fit the experimental left-hand sides of eqns. (3) and (4) by the most significant least-squares polynomial in the square-root of the ionic strength at the 95 % significance level for the 15 experimental series mentioned. An example of this procedure for a specific salt fraction is shown in Fig. 1. The value of the standard potential for the given salt fraction is found as the intercept. The standard error of the standard potential is found as the standard error of the smoothed polynomial values at zero ionic strength. Similarly, from the first polynomial coefficient the limiting slope $(2RT/F)\alpha$ and its

Table 1. Standard potentials (E^\ominus) and Debye-Hückel limiting slopes (α) for different salt fractions (X) of KCl determined as in Fig. 1. The standard deviations are denoted $\pm S$. Measurements on cell (1).

	X									
	1.0	1.0	0.9	0.8	0.5	0.5	0.2	0.2	0.1	
E_{KCl}^\ominus	-242.2	-244.6	-243.0	-243.0	-243.9	-243.5	-243.4	-241.2	-241.8	
$\pm S$	0.9	0.3	0.2	0.2	0.3	0.3	0.3	0.5	0.8	
α_{KCl}	0.999	1.048	1.187	1.138	1.193	1.133	1.327	1.065	0.994	
$\pm S$	0.158	0.027	0.021	0.029	0.037	0.047	0.039	0.11	0.155	

Table 2. Standard potentials (E^\ominus) and Debye-Hückel limiting slopes (α) for different salt fractions (X) of KCl determined as in Fig. 1. The standard deviations are denoted $\pm S$. Measurements on cell (2).

	X						
	0.0	0.1	0.2	0.5	0.8	0.9	
E_{KF}^\ominus	-441.1	-440.2	-441.4	-441.9	-440.0	-440.3	
$\pm S$	0.3	0.3	0.2	0.1	0.2	0.3	
α_{KF}	0.915	0.791	1.188	1.131	0.747	0.940	
$\pm S$	0.030	0.057	0.034	0.106	0.038	0.042	

standard error are easily calculated.

The results for the KCl measurements in 9 experimental series are shown in Table 1. The results for the KF measurements in 6 experimental series are shown in Table 2. The distribution of the standard potentials as well as the limiting slopes seems to be completely random, so there is no systematic dependence on the salt fraction. Interference of foreign ions in the performance of the three electrodes can therefore be ruled out, and separate statistical pooling of all the results in each of the tables is possible. For the standard potential we have, for example (S_i is the standard deviation estimate of the i 'th series):

$$E^\ominus(\text{pool}) = \frac{\sum_i E_i^\ominus / (S_i)^2}{\sum_i 1 / (S_i)^2} \pm \frac{1}{\left[\sum_i 1 / (S_i)^2 \right]^{1/2}} \quad (5)$$

The summations are over each of the series for a given salt fraction in either Table 1 or Table 2. The same variance weighing procedure is applied

to the limiting slopes. We obtain the following pooled values:

$$E_{\text{KCl}}^\ominus(\text{pool}) = (-242.96 \pm 0.09) \text{ mV} \quad (6)$$

$$E_{\text{KF}}^\ominus(\text{pool}) = (-441.35 \pm 0.075) \text{ mV} \quad (7)$$

$$\alpha_{\text{KCl}}(\text{pool}) = (1.155 \pm 0.012) \text{ mol}^{-1/2} \text{ dm}^{3/2} \quad (8)$$

$$\alpha_{\text{KF}}(\text{pool}) = (1.077 \pm 0.009) \text{ mol}^{-1/2} \text{ dm}^{3/2}. \quad (9)$$

The value of α for KCl is statistically almost indistinguishable from the value obtained using the Debye-Hückel limiting law for 1:1 electrolytes at 25 °C ($\alpha = 1.1779 \text{ mol}^{-1/2} \text{ dm}^{3/2}$). However, the limiting slope for KF is clearly different and about 10 % lower.

Test of electrode individualities. When the K^+ electrode in cell (1) was replaced by a new one of the same type, and when the standard potential was determined by the same procedure as described above, the following value was obtained:

$$"E_{\text{KCl}}^\ominus" = (-240.65 \pm 0.10) \text{ mV}.$$

The difference between this value and that given

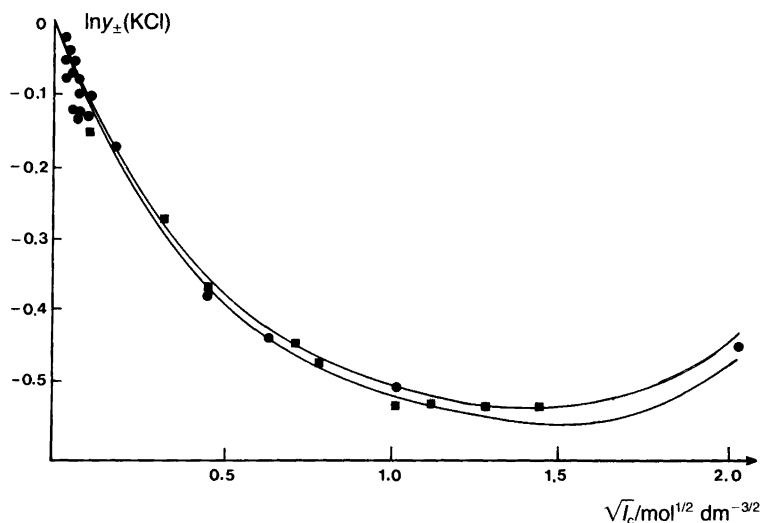


Fig. 2. Plot of $\ln\gamma_{\pm}(\text{KCl})$ vs. $\sqrt{I_c}$ as found from experiments with cell (1). For $I_c \geq 0.1 \text{ mol dm}^{-3}$ two different symbols have been used: Filled circles represent values for pure KCl solutions, and filled squares represent values for KCl-KF mixtures with the salt fraction $X = 0.5$. The space between the two fully drawn curves represents the standard error belt of the smoothed values as calculated by the best approximating least-squares polynomial at the 95 % significance level for the pooled results:

$$\ln\gamma_{\pm}(\text{KCl}) = -1.175 p + 1.101 p^2 - 0.547 p^3 + 0.117 p^4 \quad (p = \sqrt{I_c}).$$

in eqn. (6) is 2.3 mV, and is clearly significant. The difference can only be ascribed to individual differences between the two K^+ electrodes. Similarly, when the F^- electrode in cell (2) was replaced by a new one of the same type we found:

$$"E_{\text{KF}}^{\ominus}" = (-440.50 \pm 0.10) \text{ mV}.$$

This value differs 0.8 mV from the value given in eqn. (7). The difference between the two F^- electrodes is less than the difference between the two K^+ electrodes, but is still clearly significant. Consequently, in order to measure the cell potentials with an accuracy of ± 0.1 mV for the smoothed values and in order to be able to determine mean activity coefficients with any useful accuracy, all the experiments have to be carried out with the *same* K^+ electrode and with the *same* F^- electrode.

Calculation of mean activity coefficients. Knowing the standard potentials (E^{\ominus}) in eqns. (3) and (4) we may calculate $\ln\gamma_{\pm}(\text{KCl})$ for all the experimental emf measurements on cell (1) and $\ln\gamma_{\pm}(\text{KF})$ for all the emf measurements on cell (2). The measurements up to an ionic strength of 0.1

mol dm^{-3} have been described above. Further measurements were made at the following ionic strengths (all in mol dm^{-3}): (1) For $X = 1$, cell (1), $I_c = 0.2, 0.5, 1.0, 2.0$ and 4.0. (2) For $X = 0$, cell (2), $I_c = 0.2, 0.5, 1.0, 3.0$ and 4.0. (3) For $X = 0.5$, cells (1) and (2), $I_c = 0.2, 0.4, 0.6, 1.0, 1.2, 1.6$ and 2.0.

All the values of $\ln\gamma_{\pm}(\text{KCl})$ for $X = 0.5$ and 1 and all the values of $\ln\gamma_{\pm}(\text{KF})$ for $X = 0$ and 0.5 were fitted by the four most significant least-squares polynomials in the square-root of I_c at the 95 % level of significance. When the uncertainty belts of the smoothed polynomial values are plotted against $\sqrt{I_c}$ it is seen that the curves for $\ln\gamma_{\pm}(\text{KCl})$ for $X = 0.5$ and for $X = 1$ are statistically almost indistinguishable at the 95 % level (the two curves are within one or two standard errors from each other). Similarly, the curves for $\ln\gamma_{\pm}(\text{KF})$ for $X = 0$ and $X = 0.5$ are found to be almost indistinguishable. This means that within experimental error, the values of the mean activity coefficients for KCl as well as KF are *unaltered by the mixing with the other salt if only the total ionic strength is the same*. However, the KF curves are clearly different from the KCl curves (the values of γ_{\pm} are closer to unity for the former than for the latter).

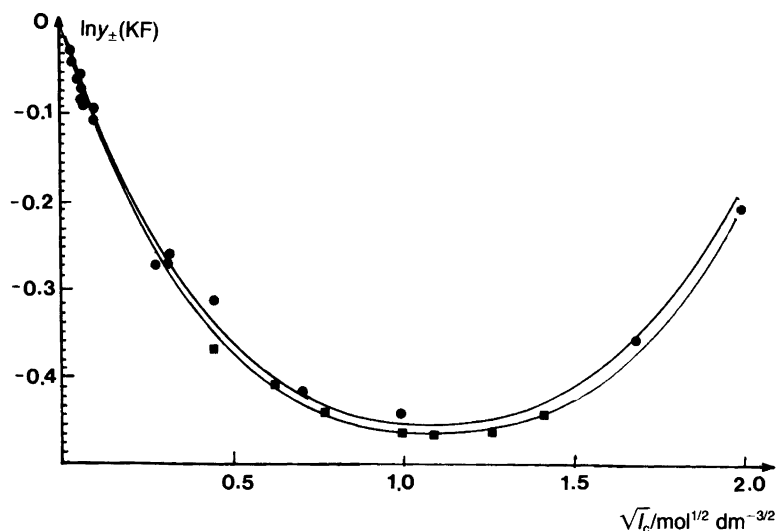


Fig. 3. Plot of $\ln\gamma_{\pm}(\text{KF})$ vs. $\sqrt{I_c}$ as found from experiments with cell (2). For $I_c \geq 0.1 \text{ mol dm}^{-3}$ two different symbols have been used: Filled circles for pure KF solutions and filled squares for KCl-KF mixtures with the salt fraction $X=0.5$. The space between the two fully drawn curves represents the standard error belt of the smoothed values as calculated by the best approximating least-squares polynomial at the 95% significance level for the pooled results:

$$\ln\gamma_{\pm}(\text{KF}) = -1.118 p + 1.011 p^2 - 0.446 p^3 + 0.098 p^4 \quad (p = \sqrt{I_c}).$$

Thus, all the KCl results may be pooled in one single polynomial. The standard error belt of the smoothed $\ln\gamma_{\pm}(\text{KCl})$ values is hereby further reduced. The result is shown in Fig. 2. The most significant polynomial (95%) is given in the figure legend. It is based on 56 different values of $\gamma_{\pm}(\text{KCl})$ calculated using eqn. (3) from individual emf measurements on cell (1). The standard error belt shown in Fig. 2 implies that the true values of $\ln\gamma_{\pm}(\text{KCl})$ lie within the belt with a probability of 66%. Simultaneously, the belt represents the standard error belt for the polynomial values (to avoid misunderstanding: The belt shown does *not* include 66% of the individual measurements. The standard error belt of the individual measurements around the polynomial would be considerably broader). A similar "super-curve" has been constructed for KF (Fig. 3). The standard error belt shown is based on polynomial smoothing of 40 individual measurements on cell (2) by means of eqn. (4).

For ionic strengths $\geq 0.1 \text{ mol dm}^{-3}$, the measurements on mixed solutions and on solutions of pure salts have been given different symbols in Figs. 2 and 3. By direct inspection, it is quite clear

that the points belong to the same curve and not to two different curves in each of the two figures. Nevertheless, the pooled KF curve is also clearly different from the pooled KCl curve. The mean activity coefficient for KF is closer to unity than that for KCl.

Discussion

Bagg and Rechnitz,² and Leyendekkers³ have previously studied the activity coefficients in mixtures containing F^- ions. Leyendekkers used an F^- -sensitive electrode in combination with a liquid-membrane Cl^- electrode to determine the trace activity of F^- in NaF-NaCl and NaF-KCl mixed solutions. Bagg and Rechnitz investigated postulated single-ion activities of F^- in mixtures containing trace concentrations of NaF and KF in solutions with a large excess (up to 4 mol per kg water) of another salt (NaCl, KCl, KBr or KI). We do not agree on the concepts behind these so-called "single-ion activities", since they are based on cells with salt bridges (see the discussion in Ref. 9) and on the hydration theory of Robinson and Stokes which one of us (T.S.S.) has

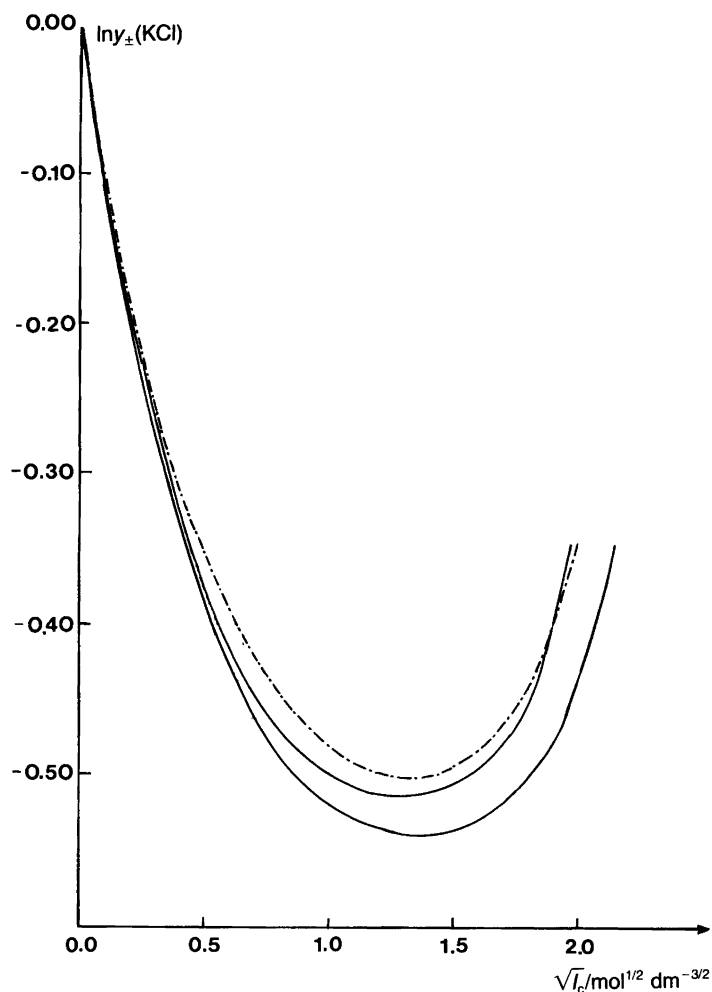


Fig. 4. Results from Hamer and Wu (Ref. 1, Tables 1 and 28) for $\ln \gamma_{\pm}(\text{KCl})$ in pure KCl solutions (dashed curve), together with our pooled results for $\ln \gamma_{\pm}(\text{KCl})$ in pure and mixed KCl-KF solutions (standard error belt of approximating polynomial between the two solid curves).

criticised elsewhere (Ref. 20, Appendix II).[§] Nevertheless, the above-mentioned work is interesting, since it is found that the single-ion activity coefficient for trace concentrations of F^- in NaF-NaCl mixtures up to 1 mol per kg water and in KF-KA mixtures up to 4 mol per kg water ($A = \text{Cl, Br, I}$) is, within experimental error, the same as the single-ion activity coefficient for F^- in the solutions of pure NaF and KF at the same ionic strength. This finding accords well with our

[§]A paper from our group describing the calculation of real single-ion activities by statistical mechanics using a specially designed Monte Carlo technique is in preparation.

results for the mean activity coefficient for KF in equimolar mixtures of KF and KCl.

Robinson and Stokes⁴ give numerous examples of mixed electrolyte solutions for which the measured mean activity coefficients are in agreement with Harned's rule. The KCl-KF system is not included in the list, but neither is it included among the very few exceptions to Harned's rule also mentioned by Robinson and Stokes. According to the results presented in this paper and elsewhere,^{2,3} the KCl-KF system represents a special case with respect to Harned's rule, with Harned coefficients equal to zero.

Fig. 4 shows our results on $\gamma_{\pm}(\text{KCl})$ together with the results from the compilation of Hamer

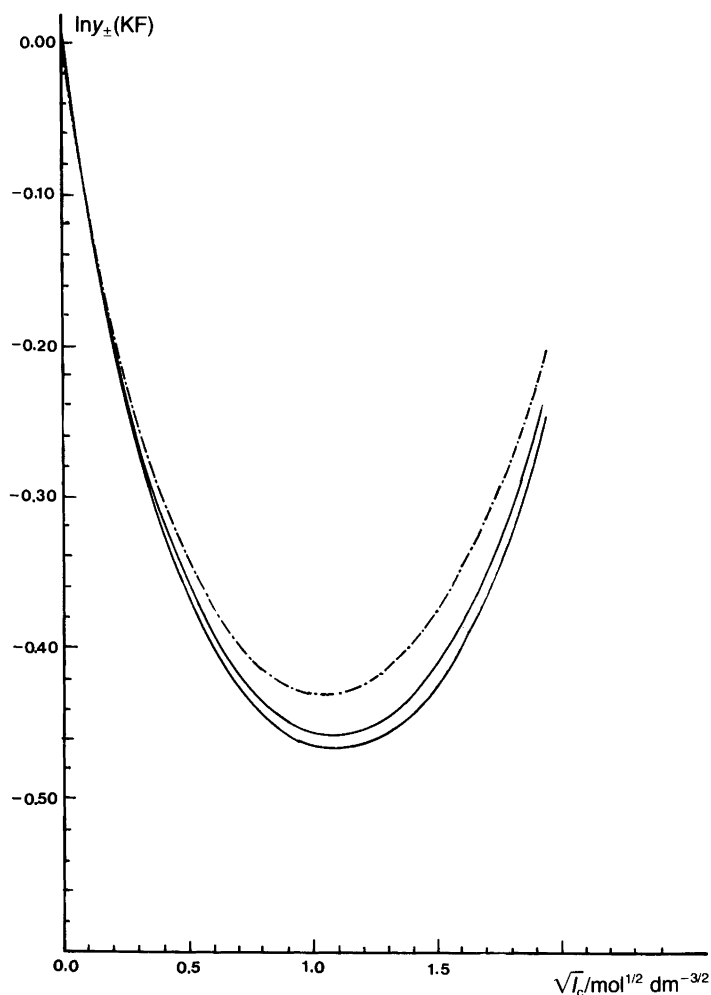


Fig. 5. Results from Hamer and Wu (Ref. 1, Table 27) for $\ln \gamma_{\pm}(\text{KF})$ in pure KF solutions (dashed curve), together with our pooled results for pure KF solutions and for mixed KF-KCl solutions (standard error belt of approximating polynomial between the two solid curves).

and Wu of all measurements on KCl solutions (Ref. 1, Tables 1 and 28). For the sake of comparison, the values of Hamer and Wu for the mean molal activity coefficients have been converted to the mean molar activity coefficients, as used in the present study, and molalities have been transformed to molarities. The transformations were made using data for the densities of aqueous KCl solutions at 25°C. The Hamer and Wu curve (dashed) lies slightly above the uncertainty belt of our measurements of $\ln \gamma_{\pm}(\text{KCl})$ in pure and in mixed solutions. The difference between the two sets of data seems significant only in an intermediate concentration range ($\sqrt{I_c}$ from about 0.3 to about 1.3 $\text{mol}^{1/2} \text{ dm}^{-3/2}$). We think that the differences are due to the circumstance that our mea-

surements are made with only one electrolyte, whereas the majority of the measurements in the compilation of Hamer and Wu were made with cells with two electrolytes (many having liquid junctions). Typically, two Ag/AgCl electrodes¹⁶ or two calomel electrodes^{17,18,19} are dipped into two solutions of KCl, i.e. a reference solution and the solution of interest. If the variation of the transference number for K^+ in KCl solutions with concentration and the mean activity in the reference solution are both known, the mean activity in the solution to be examined can be found by the method of Longworth (Ref. 7, p. 156). Thus, considerable uncertainty is introduced from two sources: (1) The independent measurements of the transference number by the Hittorf or by the

moving boundary method, and (2) the assumption of the validity of the extended Debye-Hückel equation (or the Güntelberg equation) for the mean activity in some dilute reference system. Concerning the second source of uncertainty, it should be emphasized that the extended Debye-Hückel equation has never been verified theoretically. On the contrary, recent high-precision Monte Carlo simulations by our group^{21,22} indicate that the extended Debye-Hückel equation is not even valid at extreme dilution. In the studies referred to, however, the reference solutions were mostly not more dilute than 0.1 mol per kg water. At this concentration the use of any form of Debye-Hückel theory is highly dubious. The first source of uncertainty is probably less important than the second, since there is only a single electrolyte present in the diffusion zone. Theoretical problems first arise when three or more ions are present in the diffusion zone,^{5,8,9} as is the case in the measurements of Bagg and Rechnitz² or of Leyendekkers.³ Nevertheless, the superfluous introduction of measurements of a transport property into a thermodynamic study should be avoided.

Some other cells used in the studies included in the compilation of Hamer and Wu were without liquid junctions. Typically, a potassium amalgam electrode bridged the KCl solution to be measured and the KCl reference solution.^{14,15} In such cells, the need for independent measurements of the transference number is eliminated, but the objection concerning the use of the extended Debye-Hückel equation can still be made. Furthermore, there is always some doubt remaining about the stability of potassium amalgam electrodes in aqueous solution (hydrogen evolution). In summary, for the region where our data deviate from the compilation of Hamer and Wu we believe that our data are superior.

Fig. 5 shows our pooled results for KF, together with the data for pure KF solutions taken from the compilation of Hamer and Wu (Ref. 1, Table 27). The latter data have been transformed from mean molal to mean molar activity coefficients by means of density data. Contrary to what is the case in Fig. 4, Fig. 5 exhibits two separate curves in the entire concentration range above about 0.3 mol dm⁻³. At the same ionic strength, the values of $\gamma_{\pm}(\text{KF})$ of Hamer and Wu are closer to unity than ours.

The curve of Hamer and Wu is based on twelve

isopiestic measurements in the concentration range from 0.1 to 4.0 mol per kg water¹⁰ and thirty-two isopiestic measurements in the concentration range 2.0 to 17.5 mol per kg water.¹¹ The last study is mostly outside the concentration range studied in this paper. Thus, the twelve measurements in Ref. 10, together with a few measurements from Ref. 11 should be compared to our 40 experiments in the concentration range 0.001 to 4.0 mol dm⁻³ using the same electrodes throughout. Hamer and Wu reported that they sometimes had to adjust the values of activity coefficients obtained by different experimental methods in order to obtain internal consistency. Thus, the problems encountered when data for activity coefficients from different sources are compared are well known. Again, we believe that our results are superior in the concentration range studied here.

In a paper in preparation (part 2), we provide a semi-quantitative explanation of the peculiar behaviour of the KCl-KF system in terms of approximate statistical mechanical calculations. We shall see that the system is highly pathological due to the smallness of the ions involved and the small differences in size. It is much more common to encounter systems where the activity coefficients in mixtures at constant ionic strength are dependent on the salt fraction. Furthermore, the two families of $\ln \gamma_{\pm}$ vs. $\sqrt{I_c}$ curves tend to converge in between in an almost common curve for the two trace activities in many other systems (see Ref. 4). An explanation for this latter feature – which seems paradoxical in relation to what is found here – will also be given in part 2.

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References

1. Hamer, J. W. and Wu, Y.-C. *J. Phys. Chem. Ref. Data* 1 (1972) 1047.
2. Bagg, J. and Rechnitz, G. A. *Anal. Chem.* 45 (1973) 1069.
3. Leyendekkers, J. V. *Anal. Chem.* 43 (1971) 1835.
4. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Revised 2nd ed., Butterworths, London 1965.
5. Østerberg, N. O., Jensen, J. B., Sørensen, T. S. and Caspersen, L. D. *Acta Chem. Scand., Ser. A* 34 (1980) 523.
6. Sørensen, T. S. and Jensen, J. B. *J. Nonequilib. Thermodyn.* 9 (1984) 1.
7. Mac Innes, D. A. *The Principles of Electrochemistry*, Dover Publications, New York 1961.
8. Østerberg, N. O., Jensen, J. B. and Sørensen, T. S. *Acta Chem. Scand., Ser. A* 32 (1978) 721.
9. Østerberg, N. O., Sørensen, T. S. and Jensen, J. B. *J. Electroanal. Chem.* 119 (1981) 93.
10. Robinson, R. A. *J. Am. Chem. Soc.* 57 (1935) 1167.
11. Tamas, J. and Kosza, G. *Magy. Kem. Foly.* 70 (1964) 148.
12. Armstrong, R. D., Lockhart, J. C. and Todd, M. *Electrochim. Acta* 31 (1986) 591.
13. Armstrong, R. D. and Todd, M. *Electrochim. Acta* 31 (1986) 1413.
14. Parton, H. N. *Trans. Faraday Soc.* 33 (1937) 617.
15. Lebed, V. I. and Aleksandrov, V. V. *Russ. J. Phys. Chem.* 38 (1964) 1414.
16. Haas, K. and Jellinek, K. Z. *Phys. Chem.* 162 (1932) 153.
17. Harned, H. S. *J. Am. Chem. Soc.* 38 (1916) 1986.
18. Getman, F. H. *J. Am. Chem. Soc.* 42 (1920) 1556.
19. Bird, E. W. and Nixon, R. M. *J. Phys. Chem.* 34 (1930) 1412.
20. Sørensen, T. S. *Acta Chem. Scand., Ser. A* 32 (1978) 571.
21. Sloth, P., Sørensen, T. S. and Jensen, J. B. *J. Chem. Soc., Faraday Trans. 2*, 83 (1987) 881.
22. Sørensen, T. S., Sloth, P., Jensen, J. B. and Nielsen, H. B. *Acta Chem. Scand., Ser. A. Submitted for publication.*

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