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Abstract

Full Text

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The Free Energy of KJ in Ethanol and Acetone

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The free energy of solvation of KJ (A_x) in ethyl alcohol can be calculated (ˆ1) from the value of the e.m.f. of a cell with transference. But this calculation method contains an error, since it is difficult to take into account the diffusion and interphase jumps of potential. Data on the magnitude of A_x for KJ in acetone, as well as for other salts, are not available.

In the present work, to determine the free energy of solvation of KJ in ethyl alcohol and acetone, we used a cell without transference

$$\text{(Hg)K} \mid \text{solution KJ} \mid \text{AgJ, Ag.}$$

Experimentally this cell was realized by us in the form of the cell shown in Fig. 1. The design of the cell provides for regulation, within known limits, of the hydrogen pressure in the vessel with the initial amalgam, reliable isolation of the amalgam consumed during the measurement, and replacement of the capillary. Potassium amalgam and silver iodide electrodes were prepared as described in works (2,3). The solvents used and KJ were prepared by purification of commercial chemically pure products and, in their physical properties, corresponded to literature data. Measurement of the e.m.f. was carried out with a potentiometer of type R-375 at 25°. During measurements, dry, thoroughly purified hydrogen was continuously bubbled through the KJ solution. The results of the measurements—

Fig. 1. Electrolytic cell for measuring e.m.f. 1 —capillary of the amalgam electrode; 2 —silver iodide electrode; 3 —inlet of hydrogen into the solution; 4 —outlet of hydrogen; 5 —vessel with the solution under investigation (solution volume 35 ml); 6 —vessel for collecting the spent amalgam; 7 —vessel with the initial amalgam

Table 1

E.m.f. of the cell (Hg)K|solution KJ|AgJ, Ag at various concentrations of KJ

Solvent	m, mol/kg	E.m.f., V	Solvent	m, mol/kg	E.m.f., V
Water	0.1000	1.8393	Acetone	0.02547	1.448
Water	0.0100	1.9497	Acetone	0.01274	1.465
Ethanol	0.02547	1.660	Acetone	0.00637	1.498
Ethanol	0.01274	1.688	Acetone	0.003185	1.526
Ethanol	0.00637	1.714	Acetone	0.001592	1.552
Ethanol	0.003185	1.736			

the emf of the cell (Hg)K|solution KJ|AgJ, Ag at various concentrations of KJ in water, ethanol, and acetone are given in Table 1.

By the commonly used graphical extrapolation method ([4]), we obtained values of the normal potentials (E_0) of the indicated cell in the specified solvents (in water, E_0 was obtained by calculation from the measured emf and the values of the activity coefficients ([5])). The values of E_0 are given in Table 2.

Table 2

Free energy of solvation of KJ in solvents

Solvent	E_0, V	A_x, kcal/mol
Water	1.709	137.4*
Ethanol	1.425	130.9
Acetone	1.208	125.85

* According to data from (1).

From the difference in the normal potentials of one and the same cell without transference in water and in a nonaqueous solvent, it is easy to calculate the difference in the free energies of solvation of KJ in H_2O and in this solvent. Taking the free energy of hydration of KJ to be 137.4 kcal/mol ([2]), from the differences determined by us in the solvation energies in water and ethanol, and in water and acetone, we calculated the free energies of solvation of KJ in these solvents. The corresponding values are given in Table 2.

The value A for KJ in ethanol, calculated from the emf of the cell with transference ([1]), is equal to 131.5 kcal/mol. It should be noted that the change in the free energy of solvation of KJ on going from H_2O to ethanol and acetone is parallel to the change in this quantity for HCl in the same solvents.

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Note: Figure translations are in progress. See original paper for figures.