Yu. M. Povarov, A. I. Gorbanev, Yu. M. Kessler, and I. V. Safonova

1962

SovietRxiv

Abstract

Full Text

Physical Chemistry

Yu. M. Povarov, A. I. Gorbanev, Yu. M. Kessler, and I. V. Safonova

Activity Coefficients of Cesium Chloride in N-Methylformamide

(Presented by Academician A. N. Frumkin, October 16, 1961)

Earlier, concepts were developed explaining the discrepancies between electrostatic theory (^{1}) and experiment by the peculiarities of ion solvation and the interaction of their solvate shells (^{2}). According to these concepts, the magnitude of the discrepancies between theory (^{1}) and experiment for solvents having a dielectric constant (DC) close to that of water may differ substantially from the magnitude of the discrepancies for aqueous solutions because of the structural features of nonaqueous solutions. This proposition was confirmed experimentally (^{2}). In addition, it was suggested that, as the DC increases, the discrepancies should, in the general case, increase because of the increase in the desolvation energy of ions upon strengthening of the short-range ion-dipole interaction. In this connection, the activity coefficients of CsCl in N-methylformamide at 25° (DC = 182.4) were determined by measuring the emf of the galvanic cell without transference

$$\mathrm{Ag—AgCl} \mid \mathrm{CsCl}\ (m) \mid \mathrm{Cs}_x\mathrm{Hg} \mid \mathrm{CsCl}\ (m_0) \mid \mathrm{AgCl—Ag}.$$

The commercial solvent was carefully purified by distillation on a dephlegmator under vacuum, treatment with CaO followed by distillation under vacuum, and distillation under vacuum on a rectification column. Its electrical conductivity before measurement did not exceed $4 \cdot 10^{-7}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ (the best literature data are $8 \cdot 10^{-7}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ (^{3})). CsCl was purified by repeated recrystallization, the last two times from tridistillate. AgCl electrodes were prepared by the thermoelectrolytic method, chlorinated in an aqueous solution of 0.1 N HCl, dried after washing in a desiccator over P_2O_5 for several days, and before use were kept for several days in the pure solvent in an inert atmosphere. A cesium amalgam of concentration 0.5 wt.% was prepared by electrolysis of a CsCl solution, filtered under vacuum through a capillary of diameter $\sim 100\,\mu$, and stored in an inert atmosphere. Fluctuations of the cell temperature during measurements did not exceed 0.01°. The emf was measured with a high-resistance potentiometer R-375.

The measurement results were treated by the method of least squares. The dependence found for the logarithm of the activity coefficient $\gamma_\pm$ on the square

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

root of the molality is shown in Fig. 1 in comparison with literature data for formamide (^{4}) at 2° (DC = 126) and water at 25° (^{5}). As is seen from Fig. 1, in N-methylformamide there is indeed a sharp discrepancy between experiment and theory (^{1}), not previously observed for this salt in any of the solvents with DC values closer to that of water. This effect is so strongly expressed that the curve obtained is not described at all by any of the known equations that have proved satisfactory for aqueous solutions. In the interval 0—0.06 m, a linear dependence is observed (Fig. 2)

$$\lg \gamma_{\pm} = A\sqrt{m} \tag{1}$$

with a value of A differing from the theoretical one (^{1}) by 9.5%. In the interval 0—0.04 m, the second approximation (^{1}) is applicable with the parameter $a =$ 3.46 Å (the sum of the crystallographic radii):

$$\lg \gamma_{\mathrm{DII}} = -\frac{A\sqrt{m}}{1 + A_1 a\sqrt{m}}. \tag{2}$$

Within the limits 0—0.1 m, the equation with the linear term is applicable $^{(2)}$

$$\lg \gamma_{\pm} = \lg \gamma_{DII} + Bm. \tag{3}$$

A considerably better result is given by the equation

$$\lg \gamma_{\pm} = \lg \gamma_{DII} + Bm + Cm^2, \tag{4}$$

but it too conveys the course of the experimental curve only qualitatively. In order to determine the form of a polynomial suitable for describing the results obtained,

Fig. 1. Dependence of the activity coefficients of CsCl on concentration in different solvents: I—N-methylformamide, 25°; II—formamide, 2°, according to data $^{(4)}$; III—water, 25°, according to data $^{(5)}$. Dashed lines are the corresponding limiting slopes.

Fig. 2. Comparison of the experimental dependence of the activity coefficients of CsCl on concentration in N-methylformamide at 25° with theoretical curves. I —limiting law; II—second approximation of the Debye—Hückel theory, according to equation (2). a—experimental curve; b—calculated from equation (5); v—calculated from equation (6).

two more purely empirical expressions were also tested (in contrast to equations (1)–(4), which follow from the corresponding theories), namely,

$$\lg \gamma_{\pm} = \lg \gamma_{DII} + Bm + Cm^{3/2} \tag{5}$$

and

$$\lg \gamma_{\pm} = \lg \gamma_{DII} + Bm + Cm^{3/2} + Dm^2. \tag{6}$$

It turned out that (5) gives a result identical with (4), while (6) reproduces the course of the experimental curve quite satisfactorily. Since terms containing the concentration to powers greater than 1/2 arise from supplementing the theory (1) by taking various effects into account, it is quite evident that the nearly linear course of the curve in the region of low concentrations is connected with the accidental compensation of various effects. At the same time, the general course of the curve shows that the relative weight of these effects may depend strongly on concentration, as is the case, for example, also in hydrogen peroxide in the case of heats of dilution (2). One possible explanation of this is a change in the structure of the solution with concentration.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
16 X 1961

CITED LITERATURE

1. P. Debye, E. Hückel, Phys. Zs., **24**, 185, 305 (1923).
2. Yu. M. Kessler, A. I. Gorbanenav, DAN, **117**, 437 (1957); Izv. Vost. fil. AN SSSR, No. 4–5, 75 (1957); No. 6, 50 (1957).
3. C. M. French, K. H. Glover, Trans. Farad. Soc., **51**, 1418 (1955).
4. E. N. Vasenko, ZhFKh, **22**, 999 (1948).
5. H. S. Harned, Proc. Natl. Acad. Sci. U. S., **40**, 551 (1954); H. S. Harned, O. E. Schupp, J. Am. Chem. Soc., **52**, 3886 (1930).
6. G. Harned, B. Owen, *Physical Chemistry of Electrolyte Solutions*, IL, 1952.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.