ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 876–879. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.A. Fedorov, V.E. Tetenkova, P.V. Fabinskii, A.V. Fedorova, F.A. Buryukin, V.P. Tverdokhlebov, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 5, pp. 734–737.

Thermodynamics of Ferrocene Dissolution in Water–Methanol Solutions

V. A. Fedorov[a], V. E. Tetenkova[b], P. V. Fabinskii[b], A. V. Fedorova[b], F. A. Buryukin[b], and V. P. Tverdokhlebov[b]

[a] *Institute of Chemistry and Chemical Engineering, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia*

[b] *Siberian State Technological University, pr. Mira 82, Krasnoyarsk, 660049 Russia*
e-mail: chem@sibstu.kts.ru

Received October 23, 2007

Abstract—The polythermal solubility of ferrocene in water–methanol solutions in a wide range of their compositions was studied. Ferrocene solubility grows as temperature and methanol content increase. Thermodynamic functions of ferrocene transfer from water into water–methanol solutions were calculated. The results obtained were compared with the data on neon solubility in the same solvent.

DOI: 10.1134/S107036320805006X

Earlier, when studying properties of ferrocene (Fc) and its derivatives in various media, we have determined Fc solubility in a wide temperature range in various solvents and their mixtures with water [1–3] with various content (mole fraction N_2) of organic cosolvents (usually N_2 was varied from 0 up to 1.0, and 10–15 points were taken within this interval). At the same time data on Fc solubility in water-methanol solvents (including methanol) are scanty and are presented by a single publication [4] where Fc solubility was determined at 298 K for a limited number of mixed solvent compositions.

In this work we determined polythermal solubility of Fc in water–methanol mixtures of various compositions.

The experimental data (average of at least three parallel determinations) are presented in the table. The error of the solubility determination was 0.01–0.02 logarithm unit (log S). According to the table, the solubility (S, M) increases with increasing temperature and methanol mole fraction (N_2), starting from $N_2 > 0.1$. In the region of $N_2 < 0.1$ the first portion of added methanol (N_2 0.001) causes a rather sharp log S increase, further, approximately up to N_2 0.1–0.12, log S scarcely depends on N_2, and at N_2 greater than 0.12 log S monotonously increases.

The plots of $\Delta\log S$ vs. N_2 are presented in Fig. 1. For all temperatures under study they are practically parallel to each other, being straight lines almost parallel to the abscissa axis in the region of $N_2 < 0.1$.

$$\Delta\log S = \log S_{av} - \log S(H_2O) = \log [S_{av}/S(H_2O)]. \quad (1)$$

The parts of solubility curves at $N_2 < 0.03$ have been studied in more detail. These data in the form of $\Delta\log S$ as functions of N_2 in this region are presented in Fig. 2, which shows that the corresponding curves contain well pronounced maxima at N_2 0.001–0.002. The height of these maxima was the greatest at 288 K, decreasing with the growing temperature. As the temperature increased the maxima became better pronounced and slightly displaced to the region of lower methanol content.

The increase in Fc solubility with temperature at any methanol content points to the exothermic character of the dissolution. The log S–1/T dependences appeared linear with a correlation coefficient greater than 0.99. Therefore we were able to calculate enthalpy changes for the Fc dissolution (ΔH_d^0) by the slope of these dependences, i.e., taking ΔC_d^0 to be zero and ΔH_d^0 to be independent of temperature. The corresponding ΔH_d^0 values and also the entropy contributions ($T\Delta S_d^0$) calculated by ordinary thermo-

Logarithms of ferrocene (Fc) solubility, changes in enthalpy and entropy contributions to ΔG_d^0 for Fc dissolution in water-methanol solvents

Methanol concentration		–log S at temperatures, K								$\Delta H_d^0 \pm \delta$, kJ mol^{-1}	$T\Delta S_d^0 \pm \delta$, kJ mol^{-1} K^{-1}
mol fraction	wt %	288	293	298	303	308	313	318	323		
0.001	0.178	3.96	3.90	3.85	3.78	3.72	3.65	3.61	3.56	20.84±0.27	–1.08±0.33
0.003	0.532	3.91	3.85	3.82	3.78	3.75	3.69	3.65	3.61	14.78±0.46	–6.96±0.52
0.005	0.885	3.95	3.90	3.86	3.80	3.75	3.71	3.64	3.60	18.10±0.52	–3.88±0.58
0.010	1.76	3.91	3.84	3.79	3.69	3.66	3.54	3.52	3.46	23.56±0.79	1.97±0.85
0.015	2.64	3.89	3.82	3.77	3.71	3.63	3.56	3.49	3.46	22.75±0.55	21.49±0.61
0.020	3.50	3.93	3.86	3.82	3.74	3.70	3.62	3.58	3.49	21.90±0.09	0.16±0.15
0.025	4.36	3.89	3.84	3.77	3.72	3.68	3.59	3.54	3.45	21.67±0.10	0.18±0.16
0.059	10	3.89	3.83	3.77	3.68	3.64	3.57	3.51	3.43	23.27±0.10	1.79±0.16
0.123	20	3.89	3.82	3.75	3.68	3.62	3.49	3.47	3.34	27.59±1.27	6.17±1.43
0.194	30	3.72	3.62	3.55	3.45	3.38	3.30	3.20	3.10	30.55±0.80	10.33±0.86
0.273	40	3.46	3.39	3.31	3.20	3.11	3.01	2.94	2.85	31.85±0.67	12.97±0.73
0.360	50	3.15	3.06	2.98	2.88	2.79	2.71	2.61	2.56	30.91±0.50	13.91±0.56
0.458	60	2.83	2.73	2.66	2.57	2.49	2.38	2.32	2.24	29.65±0.45	14.49±0.51
0.568	70	2.42	2.36	2.25	2.20	2.14	2.07	2.01	1.93	24.31±0.83	11.49±0.89
0.692	80	2.09	2.02	1.93	1.87	1.80	1.72	1.69	1.63	23.80±0.74	12.81±0.80
0.835	90	1.79	1.72	1.67	1.58	1.53	1.47	1.42	1.36	21.86±0.36	12.33±0.42
1	100	1.63	1.57	1.50	1.45	1.39	1.33	1.26	1.23	20.79±0.46	12.25±0.52

dynamic relations are presented in the table. The changes in ΔH_d^0 and $T\Delta S_d^0$ are rather complicated functions of N_2 and involve several extrema. We consider the analysis of the data obtained [$\Delta\log S = \log (S/S^0) = \log \Phi$; $\Delta_{tr}H^0$, $T\Delta_{tr}S^0$, and $\Delta_{tr}G^0$] as functions of $\log c_{MeOH}$ to be more informative (Fig. 3). The $\log \Phi$–$\log c_{MeOH}$ dependence consists of two linear parts: a straight line parallel to the abscissa axis (up to $\log c_{MeOH}$ ~0.7–0.8), and then a sharp increase in the form of a linear $\log \Phi$–$\log c_{MeOH}$ dependence at $\log c_{MeOH}$

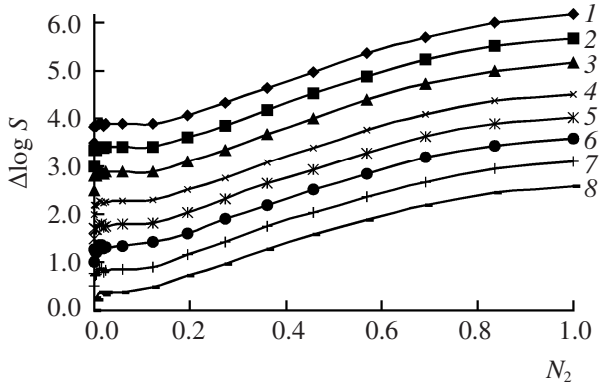

Fig. 1. Dependence of $\Delta\log S$ on methanol mole fraction for Fc dissolution at temperatures: (*1*) 288, (*2*) 293, (*3*) 298, (*4*) 303, (*5*) 308, (*6*) 313, (*7*) 318, (*8*) 323 K (each subsequent plot is displaced by 0.5 log unit relative to T 323 K).

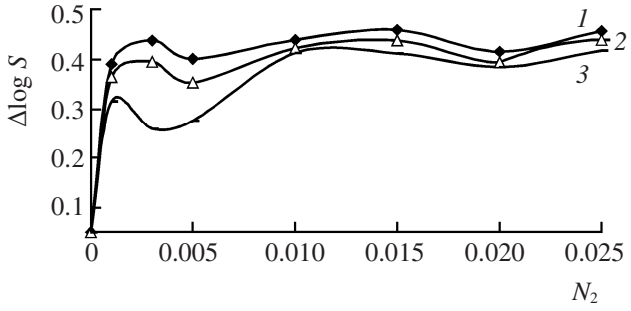

Fig. 2. Dependence of $\Delta\log S$ on methanol mole fraction for Fc dissolution in a solvent with a low alcohol content at temperatures: (*1*) 288, (*2*) 298, (*3*) 323 K.

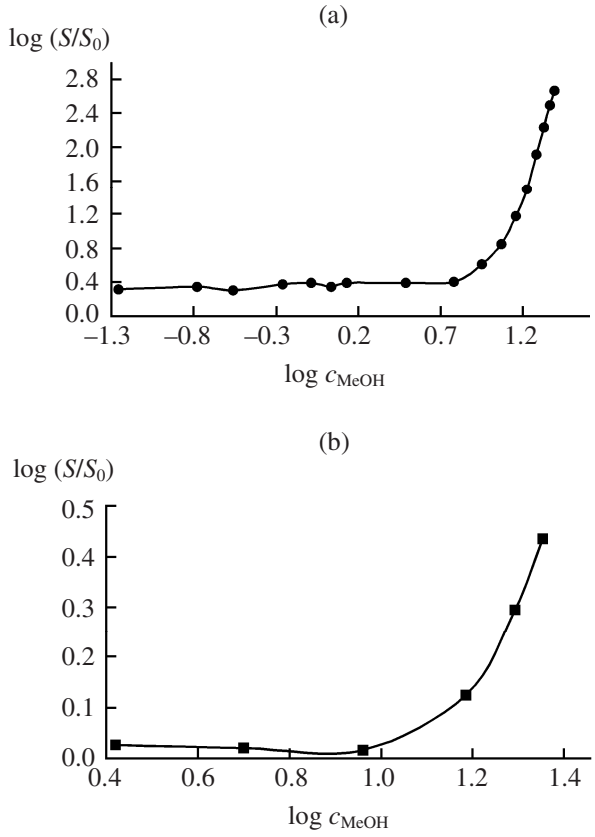

Fig. 3. Dependences of log (S/S^0) for (*1*) Fc and (*2*) Ne on the logarithm of methanol molar concentration.

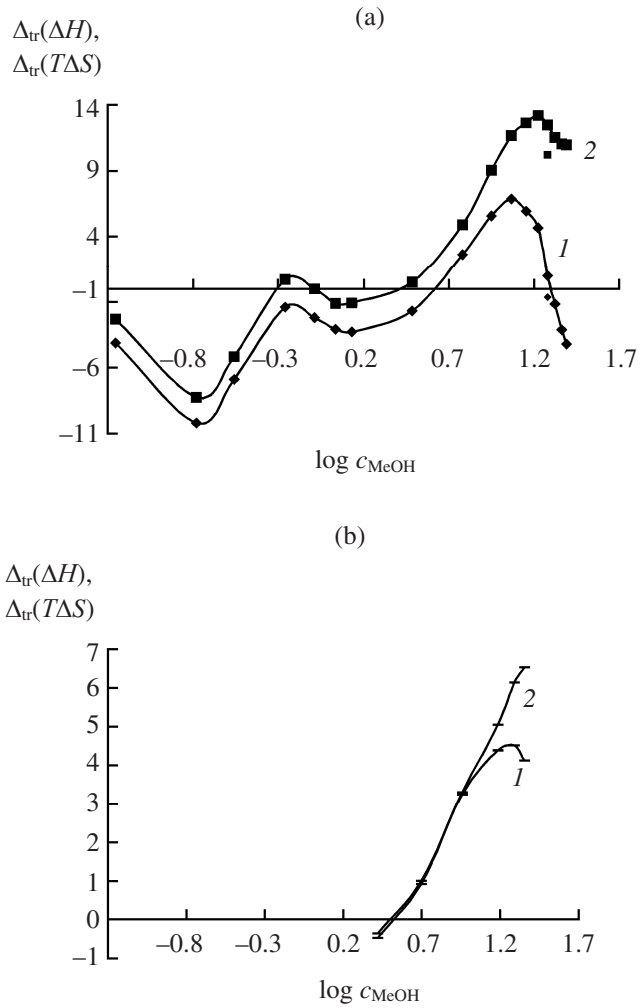

Fig. 4. Dependences of changes in (*1*) enthalpy and (*2*) entropy for transfer of (a) Fc and (b) Ne from alcohol into H_2O.

greater than 1.0. The cross point of these two straight lines corresponds to log c_{MeOH} ~ 1.0, i.e. c_{MeOH} ~ 10 M, and practically is independent of temperature. The concentration of water in this point is ~35 M.

The above-stated data were used to calculate changes in enthalpies, entropies, and Gibbs free energy for Fc transfer from alcohol into water. These data in the coordinates $\Delta_{tr}(\Delta H^0)$ and $\Delta_{tr}(T\Delta S^0)$ vs. log c_{MeOH} are given in Fig. 4.

The data obtained fit well into the concept of voids and solvation interactions in the studied system [5]. The straight line parallel to the abscissa axis in the coordinates log (S/S^0)–log $c(H_2O)$ corresponds to the hydrophobic hydration, which is accompanied by strengthening water structure (i.e. the hydrogen-bond network) due to the arrangement of CH_3 groups of methanol molecules in the voids of water structure. In this case the Fc solubility weakly depends on the methanol content. The presence of two minima in the $\Delta_{tr}(\Delta H^0)$ and $\Delta_{tr}(T\Delta S^0)$ dependences seems to be caused by filling the voids of different size in water structure. The first minimum in $\Delta_{tr}(\Delta H^0)$ is connected with filling voids of greater volume, and the second, of smaller volume. Negative changes of the enthalpy of Fc transfer from alcohol in H_2O are compensated by negative changes of $\Delta_{tr}(T\Delta S^0)$, i.e. by strengthening the hydrophobic hydration.

The increase in Fc solubility above log c_{MeOH} value of 0.9–1.0 is caused by destruction of water structure. In this case water concentration is 30–35 M and the ratio $c_{MeOH} : c(H_2O)$ is 1 : (3.5–4.0). We believe that it corresponds to embedding methanol molecules in the

tetrahedral water structure. Above this ratio free water molecules begin to appear, fill the voids in the solvent structure thus hampering ferrocene dissolution [$\Delta_{tr}(\Delta H^0)$ becomes more positive], and a maximum appears on the $\Delta_{tr}(\Delta H^0)$ dependence, but the negative effect of the enthalpy factor is completely compensated by the the entropy contribution that becomes positive due to destruction of the solvent structure (Fig. 4). Further the value of $\Delta_{tr}(\Delta H^0)$ decreases because of the formation of the alcohol structure with predominat chain associates resulting in a decrease in energy expenditures for the formation of voids for Fc arrangement.

Thus, the approach to the interpretation of equilibria [6] can be also used in the case under consideration, i.e. when a solid phase participates in the equilibrium. Linear parts of the log S–log c_{MeOH} dependences (Fig. 3) correspond to the operation of the dilution factor. The absence of specific interactions with solvent components is the factor that causes the log S independence of MeOH and also H_2O concentrations. The second linear part of the dependences under consideration is connected with the structural changes of the solvent. The cross point of these linear dependences where the $c_{MeOH} : c(H_2O)$ ratio is 1 : (3.5–4) corresponds to the beginning of the destruction of the hydrogen-bond network in the solvent and to the transformation of the water structure to the structure of water-alcohol solvent with the formation of the chain associates MeOH–H_2O and MeOH–MeOH.

The obtained data on the thermodynamics of Fc dissolution in water–methanol solutions well correlate with the data on neon (Ne) solubility under the same conditions [7]. The changes of thermodynamic parameters upon Ne dissolution as functions of a solvent composition are presented in Fig. 4 in the logarithmic coordinates. A sharp rise in the solubility is observed in exactly the same way, but at a slightly greater value of log $c_{MeOH} > 1.2$ (Fig. 3) as compared to the Fc solubility. At lower MeOH concentrations the Ne solubility depends on the solvent composition only slightly. The analogy is also observed in the changes in ΔH_d^0 and $T\Delta S_d^0$ for Ne dissolution in the studied solvent.

EXPERIMENTAL

Ferrocene (technical grade) was purified according to a known procedure, identified by the melting point (sublimation temperature) and absorption spectra. Methanol was subjected to double distillation. Water–methanol solutions of desired compositions were prepared from purified methanol and bidistilled water. Details of the technique of the determination of Fc solubility in mixed water–methanol solvents are given in [8].

ACKNOWLEDGMENTS

This work was financially supported by Krasnoyarsk Regional Scientific Fund (grant no. 16G253).

REFERENCES

1. Fabinskii, P.V., Tverdokhlebov, V.P., Dmitrenko, G.A., and Fedorov V.A., *Zh. Fiz. Khim.*, 1999, vol. 73, no. 9, p. 1577.
2. Tverdokhlebov, V.P., Fedorov, V.A., and Buryukin, F.A., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.,* 2004, vol. 47, no. 4, p. 24.
3. Tarasova, A.V., Tetenkova, E.V., Fabinskii, P.V., and Fedorov, V.A., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol*., 2005, vol. 8, no. 6, p. 12.
4. Pendin, A.A., Karabaev, S.O., and Susareva, O.M., *Zh. Fiz. Khim.*, 1987, vol. 61, no. 4, p. 972.
5. Zhleznyak, N.I., *Doctorate (Chem.) Dissertation,* Ivanovo, 2006.
6. Fedorov, V.A. and Belevantsev, V.I., *Zh. Neorg. Khim.*, 2003, vol. 48, no. 4, p. 680.
7. Krestov, G.A. and Patsatsiya, K.M., *Zh. Fiz. Khim.*, 1971, vol. 45, no. 7, p. 1768.
8. Fabinskii, P.V., Dem'yanenko, E.A., Sachivko, A.V., Skvortsova, V.S., Robov, A.M., Tverdokhlebov, V.P., and Fedorov V.A., *Koord. Khim*., 1997, vol. 23, no. 5, p. 366.