

Phase Diagrams of the Ternary Gas Hydrate Forming Systems at High Pressures. Part II. Ethane–Methane–Water System

E.G. LARIONOV*, YU.A. DYADIN, F.V. ZHURKO and A.YU. MANAKOV

Siberian Branch, Institute of Inorganic Chemistry, Russian Academy of Science, 630090, Novosibirsk, Russia

(Received: 24 October 2005; in final form: 22 November 2005)

Key words: ethane, phase diagram, ternary system, methane, gas hydrates

Abstract

The sections of the phase diagram of a ternary system ethane–methane–water at pressures up to 1000 MPa were studied by means of the differential thermal analysis. The investigation was carried out under the conditions of excessive amount of the gas. It was established that two continuous rows of solid solutions belonging to the II type according to Rosenbom's classification (with a maximum) exist within the whole pressure range studied: one of them is based on the cubic structure I (CS-I) and another on the cubic structure II (CS-II). With an increase in pressure, the maxima at the decomposition curves of solutions based on CS-II shift towards the hydrates with higher ethane content. This was explained in terms of intrusion of ethane molecules into the small d-cavities of the CS-II which is caused by the pressure imposed.

Introduction

Methane and ethane are the main components of natural hydrocarbon gases existing in the regions of permafrost and in the bottom sediment of the great oceans in the form of gas hydrates. Enormous reserves of these hydrates make them a promising source of the raw material for the power engineering of the future. Intense investigations of physicochemical properties of gas hydrates are carried out in the research laboratories of the world; technological schemes and instrumentation for their production and transportation are being developed. In addition, investigation of gas hydrates is of significant academic interest from the viewpoint of the possibilities of the supramolecular arrangement of the simplest systems gas (a mixture of gases) – water.

It is known that the PVT regions of existence and the structure of gas hydrates depend on the composition of the hydrate-forming gas mixture. The primary information is usually obtained in the systematic investigation of gas hydrates from the phase P – T – x diagram (P is pressure, T is temperature, and x is composition), which allows one to know the hydrate decomposition temperature under the given P – x conditions and to be aware of the presence (and localization) of various phases in the system under investigation. Previous experimental works dealing with the investigation of the phase diagram of the CH_4 – C_2H_6 – H_2O system had been carried out as long ago as in the second half of the XX century

[1–3] (cited from [4]). However, the data were obtained only for separate, rather narrow concentration regions of the diagram related to the compositions reach in methane or in ethane; the data did not allow considering the diagram in general. In addition, investigations [1, 3] were carried out with pressure not higher than 5 MPa; in [2], the maximal pressure was 68.6 MPa (for two compositions containing methane 80.9 and 94.6%).

Under normal conditions, both gases form individual hydrates of the cubic structure I (CS-I). It might be expected that their mixtures should also form the hydrates of the same structure within the whole range of compositions. However, the possibility of the formation of the hydrate of cubic structure II (CS-II) for definite percentage of methane and ethane in the gas phase was predicted theoretically in [5]. Subramanian *et al.* [6, 7] showed experimentally using the Raman and NMR spectroscopy that at a temperature of 274.2 K and normal pressure, with the methane concentration in gas within the range 72–75 molar % in the presence of water in excess, the initial structure of the hydrate, CS-I, is transformed into CS-II. An inverse transition of CS-II into CS-I occurs if the concentration of methane in the mixture is increased up to 99.2–99.4 molar %.

Since the experimental data were insufficient to make up the phase P – T – x diagram within a broad range of the parameters of state, Ballard and Sloan [8] made an attempt to generate the diagram of the CH_4 – C_2H_6 – H_2O system using the procedure described in [9]. The model provided a good description of the experimental data under normal conditions; so, it was concluded that the

* Author for correspondence. E-mail: larionov@che.nsk.su

calculations for higher values of the parameters of state should be precise, too. The calculations were carried out for temperature within the range 274.2–303.1 K and pressure up to 120 MPa. A series of isothermal P – x sections of the phase diagram is presented in [8]; these sections provide evidence of the substantial transformation of the topology with temperature rise; the changes involve narrowing of the field of crystallization of the CS-II hydrate, which finally results in complete disappearance of CS-II from the diagram for the 303.1 K isotherm. The authors stress that additional experimental effects are necessary in order to confirm or deny predictions.

The above-described circumstances have attracted our attention to the investigation of the phase diagram of the ternary system methane–ethane–water within the region of existence of gas hydrates. Possible versions of the corresponding phase diagram and choice of the characteristic section depicting the main features of the system have been considered in detail in [10] and will not be given herein.

In the present study, we present for the first time the experimental data for building up a P – T – x phase diagram of the CH_4 – C_2H_6 – H_2O system within maximally broad range of compositions at pressure 50–1000 MPa.

Experimental

Measurements were carried out by means of differential thermal analysis with an excess amount of the gas (50–100%). Temperature of hydrate decomposition was measured with a chromel–alumel thermocouple calibrated over the standard reference substances (the values

Table 1. The numerical data on the curves of liquidus in the ethane–water system at a pressure up to 1000 MPa

P (MPa)	T (°C)	P (MPa)	T (°C)
5.0	15	380	47.1
7.5	15.5	400	48
10.8	16.2	430	49.9
20	17.8	450	50.8
30	19	482	52.3
45	20.8	505	53.5
50	21.4	530	54.5
60	22.7	545	55.3
70	23.9	580	57
101	27.1	615	58.3
109	27.5	637	58.8
135	29.7	660	59.9
165	32.4	695	60.7
180	33.3	723	61.5
195	34.9	755	62.4
210	35.9	783	63.2
225	37	802	64
245	38	848	65
257	39.4	900	66.5
306	42.6	919	66.6
330	44	957	67.2
357	45.6	1000	67.4

displayed by the thermocouple are practically independent of pressure up to 1000 MPa) with an error of $\pm 0.3^\circ\text{C}$. Pressure was measured with Burdon manometer (up to 250 MPa) and with a manganine manometer (up to 1000 MPa) calibrated at high pressure with respect

Table 2. The coefficients of equations T (°C) = $A + B*P + C*P^2 + D*P^3 + E*P^4$ (P , MPa) that approximate the lines of liquidus in the methane–ethane–water system within pressure range 50–1000 MPa with the gas in excess

$\text{C}_{\text{CH}_4}/\text{mol.}\%$	A	B	C	D	E	R	SD
0.0	18.94	0.0861	-3.23×10^{-5}	-1.1×10^{-8}	6×10^{-12}	0.9984	0.79
12.5	18.16	0.1630	-2.51×10^{-4}	2.4×10^{-7}	-10×10^{-11}	0.9997	0.34
25.0	20.33	0.1622	-2.39×10^{-4}	2.1×10^{-7}	-7×10^{-11}	0.9999	0.21
30.6	21.23	0.1468	-2.20×10^{-4}	2.1×10^{-7}	-8×10^{-11}	0.9994	0.49
37.5	20.37	0.1535	-2.44×10^{-4}	2.3×10^{-7}	-9×10^{-11}	0.9995	0.47
45.0	20.99	0.1531	-2.51×10^{-4}	2.5×10^{-7}	-10×10^{-11}	0.9996	0.44
50.0	20.69	0.1526	-2.34×10^{-4}	2.1×10^{-7}	-8×10^{-11}	0.9998	0.32
58.1	21.45	0.1445	-2.31×10^{-4}	2.3×10^{-7}	-9×10^{-11}	0.9993	0.52
66.7	21.32	0.1452	-2.41×10^{-4}	2.4×10^{-7}	-10×10^{-11}	0.9999	0.27
75.0	21.73	0.1392	-2.36×10^{-4}	2.3×10^{-7}	-9×10^{-11}	0.9996	0.38
83.3	21.72	0.1214	-1.68×10^{-4}	1.4×10^{-7}	-5×10^{-11}	0.9991	0.53
88.0	21.02	0.1315	-2.15×10^{-4}	1.7×10^{-7}	-5×10^{-11}	0.9990	0.52
95.2*	18.78	0.1677	-4.34×10^{-4}	6.2×10^{-7}	-4×10^{-11}	0.9991	0.46
95.2**	21.73	0.0595	-2.75×10^{-5}	–	–	0.9645	0.46
100.0***	17.70	0.1877	-4.91×10^{-4}	6.5×10^{-7}	-4×10^{-10}	0.9996	0.22
100.0****	–86.55	0.4956	-6.65×10^{-4}	4.0×10^{-7}	-9×10^{-11}	0.9970	0.22

Methane concentration is indicated for the initial gas mixture.

*Pressure range 50–700 MPa.

**Pressure range 700–1000 MPa.

***Pressure range 50–620 MPa.

****Pressure range 620–1000 MPa.

to the melting point of mercury. An error of pressure measurements was not more than 1%. The procedure was described in detail in [11–13]. Methane and ethane contained not less than 99.95% of the main substance; they were not purified additionally. The gas mixtures were prepared by the volumetric procedure. The error of mixture preparation was about 1%. Twice distilled water, in which 0.01% non-ionogenic surfactant OP-10 was added, was used in the experiments. Though the addition of a surfactant decelerates hydrate formation at its first stage (nucleation), it accelerates substantially the process of crystal growth on the nuclei, which finally results in the acceleration of the reaction under consideration by a factor of several tens [14]. At the same time, the addition of such a small amount of the surfactant does not affect the gas hydrate decomposition point.

Results

The P – T curve of decomposition of the individual methane hydrate was plotted in [15], while the corresponding numerical experimental data were published in [10]. At a pressure up to 620 MPa, methane hydrate has CS-I; above this pressure it has H structure [16, 17]. The corresponding experimental data obtained in the present work for the hydrate of pure ethane are presented in Table 1. With an increase in pressure, the melting point of ethane hydrate increases monotonously, which is evidence of the fact that only one hydrate of the CS-I exists within the whole pressure range investigated.

For each experimental P – T curve obtained for the ternary system methane–ethane–water, the corresponding equations were adjusted by means of the least squares. The coefficients of polynomials approximating the decomposition curves for the whole investigated range of compositions of the ternary system are listed in Tables 2 and 3. A criterion for the choice of equation for the minimal mean square deviation of the experimental data from the adjusted values.

Monovariant equilibrium lines were not observed in the system under investigation for any composition investigated; a possible reason may be proximity of the corresponding thermal effects to the thermal effects of liquidus.

Table 3. The coefficients of equations T ($^{\circ}\text{C}$) = $A + B \cdot P + C \cdot P^2 + D \cdot P^3$ (P , MPa) that approximate the lines of liquidus in the methane–ethane–water system, within pressure range 50–200 MPa with the gas in excess

C_{CH_4} /mol. %	A	B	C	D	R	SD
10	14.08	0.2359	-7.03×10^{-4}	9.9×10^{-7}	0.9996	0.30
20	20.79	0.1618	-2.12×10^{-4}	–	0.9991	0.32
70	19.65	0.2104	-7.40×10^{-4}	1.2×10^{-6}	0.9990	0.29
80	21.02	0.1455	-2.18×10^{-4}	–	0.9979	0.35

Methane concentration is indicated for the initial gas mixture.

A comparison of the results obtained by us with the literature data available for the temperature and pressure range under investigation is presented in Figure 1. Some difference between our curves with those reported in [2] for gas mixtures can be explained by the difference in the compositions to be compared. The reasons of small deviations of our data for the hydrate of pure ethane from the results of [18] may be connected with the presence of a narrow region of solid solutions in the ethane–water system; this region is due to the variable filling of the cavities of hydrate framework with ethane

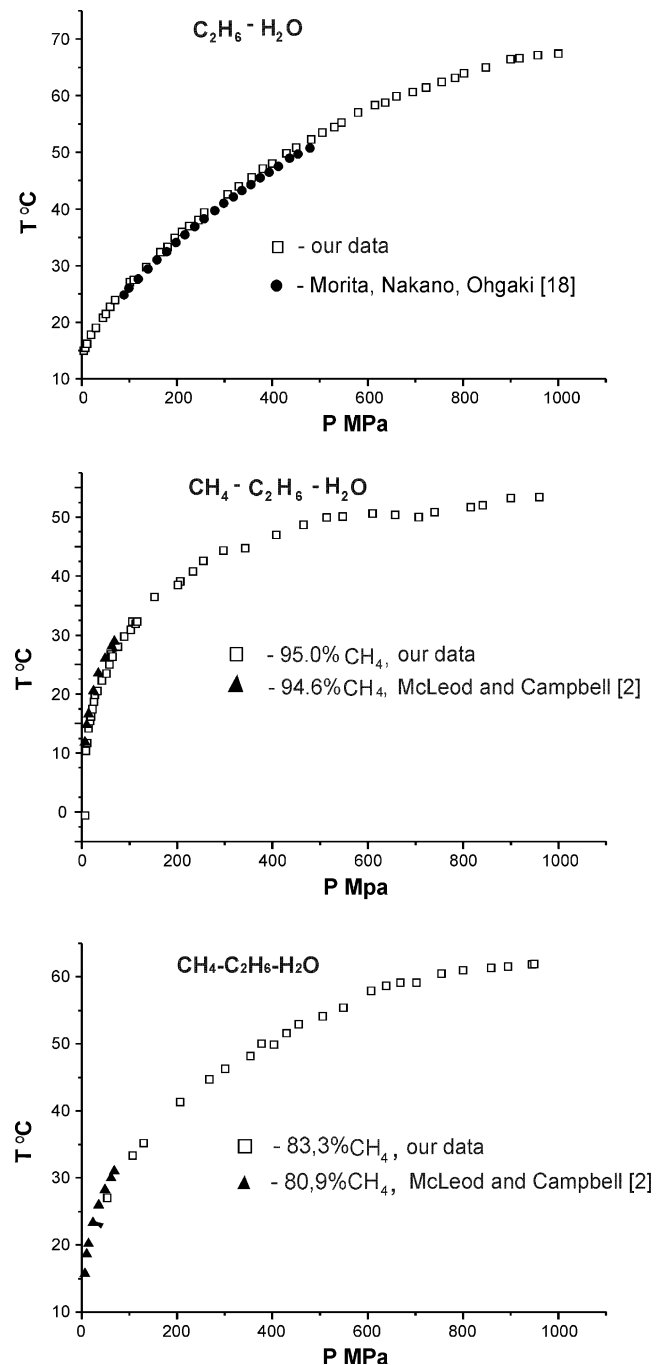


Figure 1. Comparison between the data obtained by us and those available from literature on the curves of hydrate decomposition in the ethane–water and methane–ethane–water systems. Methane concentration in the initial gas mixture is indicated.

molecules (see below). Our results were obtained with the gas present in excess, while the data of [18] were obtained in the case when water was present in excess, which causes a small discrepancy in the equilibrium hydrate decomposition temperature points. The isobaric and isothermal sections of the system under investigation, re-calculated from the experimental data, are shown in Figures 2 and 3, respectively. Here and below, the following designations are used: α is the solid solution based on the CS-I hydrate from the side of ethane, α' is the solid solution based on the CS-I hydrate form the side of methane, β is the solid solution based on the CS-II hydrate, γ is the solid solution based on the hydrate of H structure, l_1 is the liquid phase rich with water, l_2 is the liquid phase rich with ethane, g is the gas phase.

Discussion

One can see in Figures 2 and 3 that two clear maxima are observed at the liquidus curves. The first one is located within the region of low methane content at about 25–30 molar %, which approximately corresponds to filling of the large cavities of CS-I with ethane molecules and small

cavities of CS-I with methane molecules (in this case, the stoichiometry of the hydrate corresponds to $6C_2H_6 \cdot 2CH_4 \cdot 46H_2O$). According to [6, 7], at low pressure, a wide range of solid solutions of methane in ethane hydrate exists in the system from the side of ethane. Comparing this fact with the data obtained by us, we may surely speak of the formation of a continuous row of the solid solutions of II type according to Rosenbom's classification (with a maximum) on the basis of CS-I (the α phase) at a pressure up to 1000 MPa. It may be assumed that ethane mainly fills large cavities in the indicated structure, while methane, depending on its concentration, is likely to fill both small and large cavities.

The second maximum is most clearly exhibited at a medium pressure for the gas mixture ratio $2CH_4:C_2H_6$, which corresponds to the ratio of small to large cavities in the framework of CS-II (the β phase, Figure 2a and 3a). At about 50 MPa, the decomposition temperature of the β phase even exceeds the temperature of decomposition of α phase. Comparison of our data with those reported in [6, 7], where the existence of the double hydrate of methane and ethane possessing CS-II was discovered at low pressure, allows us to conclude that the hydrate of this structure exists at least at a pressure up to 50 MPa.

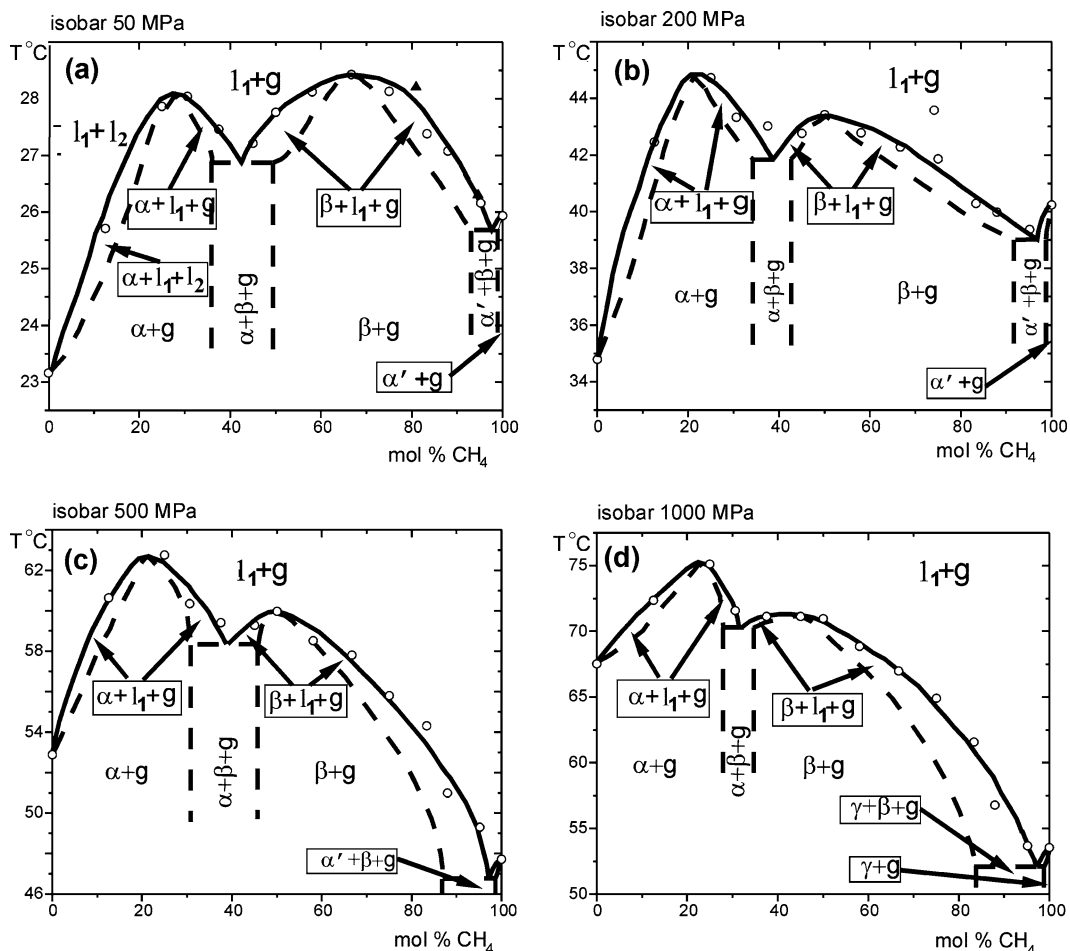


Figure 2. Isobaric sections of the phase diagram of methane-ethane-water at a pressure of 50, 200, 500 and 1000 MPa. For designations, see the text.

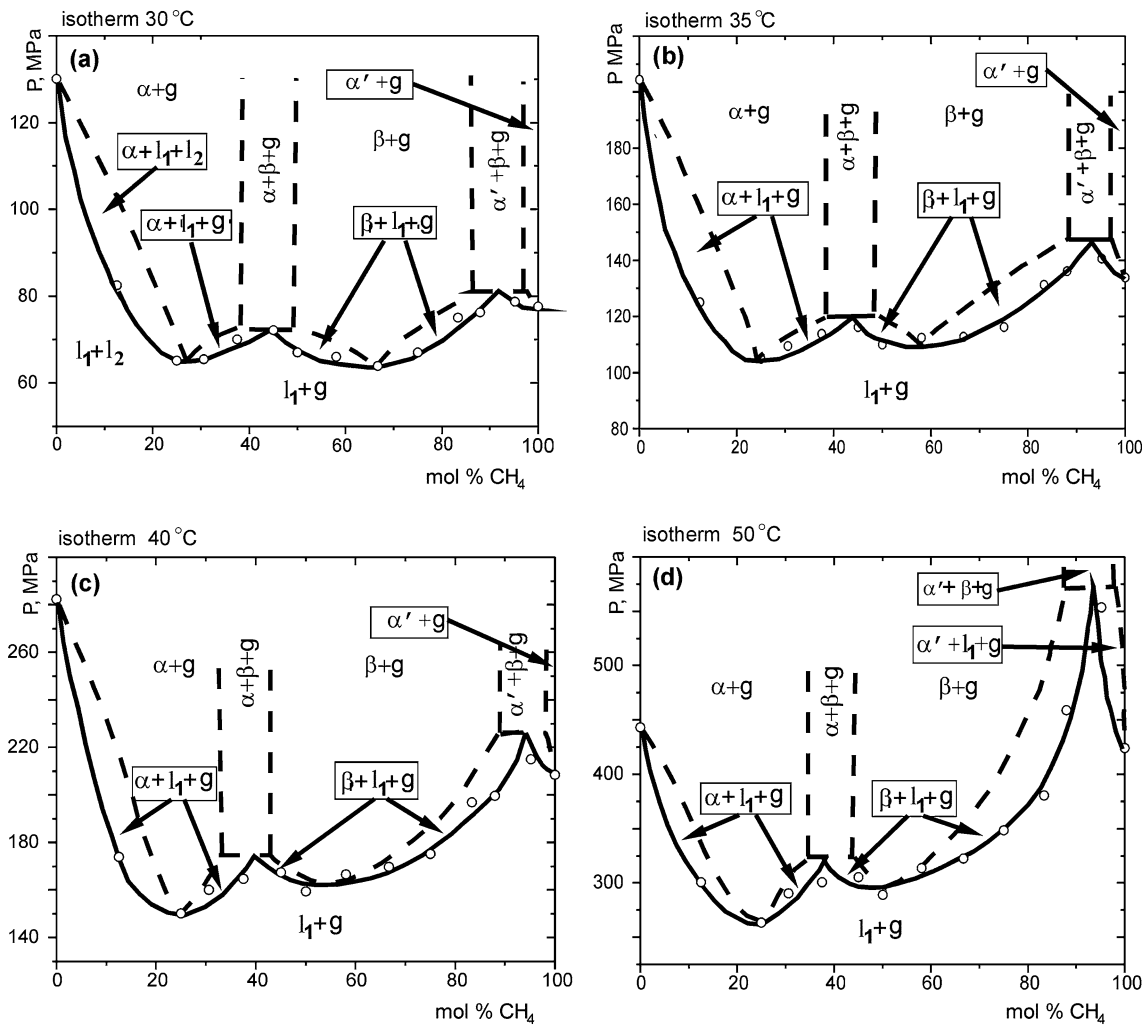


Figure 3. Isothermal sections of the phase diagram of methane–ethane–water at a temperature of 30, 35, 40 and 50°C. For designations, see the text.

However, with an increase in pressure (and the corresponding temperature rise) the picture changes substantially. The maxima at the curves of β phase decomposition get shifted towards the composition $\text{CH}_4:\text{C}_2\text{H}_6$ (see Figures 2 b–d and 3b–d), that is, to the side of an increase in ethane content of the β phase. The absence of sharp bends at the curves in P – T projection makes the appearance of a new phase in the system improbable. With an increase in pressure from 50 to 200 MPa, the shift is about 16–17 molar % and remains unchanged when pressure is further increased. This may be explained as follows. It was shown in [18, 19] that at low pressure the C_2H_6 molecules occupy mainly large T cavities in the individual ethane hydrate (CS-I); only an insignificant part of them fills small d cavities (according to [20], the extent of filling the small cavities with ethane under normal pressure is 5.8%). However, with an increase in pressure, the extent of filling d cavities with ethane increases rapidly [18]. Therefore, a substantial shift of the maxima at the decomposition curves of the β phase can be explained by the fact that an increase in pressure initiates an increase in the filling extent of small cavities with ethane in the CS-II structure of the double

hydrate. Ethane enters a competition with methane for d cavities.

For the same reason, the maxima on the curves of decomposition of the α phase should exhibit a small shift to the left with an increase in pressure. Since the number of small d cavities in CS-I is six times smaller than that for CS-II, this shift should be substantially smaller and equal to approximately 3 molar %. However, due to the insufficient amount of our experimental data, we cannot either confirm or deny this assumption.

One can see in Figures 2 and 3 that the monovariant curve that corresponds to the decomposition of methane hydrate in a ternary system (the equilibria $\alpha'\beta l_1 g$ and $\gamma\beta l_1 g$) is not observed in the experiments; this may be connected with the low solubility of ethane in methane hydrates of CS-I and H structures (α' and γ phases, respectively).

To conclude, it should be noted that the existence of solid solutions based on CS-II in the phase diagrams within the temperature and pressure ranges up to 75°C and 1000 MPa, respectively, denies the conclusions of theoretical investigation [8], predicting the disappearance of this phase at a temperature as low as 30°C.

Conclusions

It was established in the investigation of the phase diagram in the ethane–methane–water system:

- (1) Within the whole temperature and pressure range investigated for this system, two continuous rows of solid solutions of type II according to Rosenbom's classification (with a maximum) exist on the basis of CS-I and CS-II.
- (2) With an increase in pressure, C the maxima at the curves of decomposition of the solutions based on CS-I get shifted towards the hydrates with higher ethane content, which has been explained by the pressure-initiated insertion of methane molecules into the small d cavities of CS-II.

Acknowledgements

This work was supported by RFBR grant 00-03-32563a and by the grant of Presidium SD RAS No. 76 "Gas hydrates".

References

1. W.M. Deaton and E.M. Frost Jr.: *Gas Hydrates and Their Relationship to the Operation of Natural Gas Pipeline*, U.S. Bureau of Mines Monograph 8, New-York (1946).
2. H.O. McLeod and J.M. Campbell: *J. Petrol. Technol.* **222**, 590 (1961).
3. G.D. Holder and G.C. Grigoriou: *J. Chem. Thermodyn.* **12**, 1093 (1980).
4. E.D. Sloan: *Clathrate Hydrates of Natural Gases*, Marcel Dekker Inc, New-York, Basel (1990).
5. E.M. Hendriks, B. Edmonds, R.A.S. Moorwood, and R. Szczepanski: *Fluid Phase Equilib.* **117**, 193 (1996).
6. S. Subramanian, R. Kini, S.F. Dec, and E.D. Sloan: *Chem. Eng. Sci.* **55**, 1981 (2000).
7. S. Subramanian, A.L. Billard, R.A. Kini, S.F. Dec, and E.D. Sloan: *Chem. Eng. Sci.* **55**, 5763 (2000).
8. A.L. Billard and E.D. Sloan: *Chem. Eng. Sci.* **55**, 5773 (2000).
9. A.K. Gupta, P.R. Bishnoi, and N. Kalogerakis: *Fluid Phase Equilib.* **63**, 65 (1991).
10. E.Ya. Aladko, Yu.A. Dyadin, A.Yu. Manakov, F.V. Zhurko, and E.G. Larionov: *J. Supramol. Chem.* **2**, 369 (2002).
11. Yu.A. Dyadin, E.G. Larionov, T.V. Mikina, and L.I. Starostina: *Mendeleev Commun.* **44** (1996).
12. Yu.A. Dyadin, E.G. Larionov, T.V. Mikina, and L.I. Starostina: *Mendeleev Commun.* **74** (1997).
13. Yu.A. Dyadin, E.G. Larionov, D.S. Mirinskij, T.V. Mikina, E.Ya. Aladko, and L.I. Starostina: *J. Incl. Phenom.* **28**, 271 (1997).
14. O.B. Kutergin, V.P. Melnikov, and A.N. Nesterov: *Dokl. RAN* **323**, 549 (1992).
15. Yu.A. Dyadin, E.Ya. Aladko, and E.G. Larionov: *Mendeleev Commun.* **34** (1997).
16. I.-M. Chou, A. Sharma, R.C. Burruss, S. Jinfu, Mao Ho-kwang, R.J. Hemley, A.F. Goncharov, L.A. Stern, and S.H. Kirby: *PNAS* **97**(25), 13484 (2000).
17. J.S. Loveday, R.J. Nelmes, M. Guthrie, D.D. Klug, and J.S. Tse: *Phys. Rev. Lett* **87**(21), 215501 (2001).
18. K. Morita, S. Nakano, and K. Ohgaki: *Fluid Phase Equilib.* **169**, 167 (2000).
19. T. Sugahara, K. Sugahara, and K. Ohgaki, *Proceedings of the Fourth International Conference on Gas Hydrates*, Yokohama, May 19–23, p. 608 (2002).
20. K.A. Udachin, C.I. Ratcliffe, and J.A. Ripmeester, *Proceedings of the Fourth International Conference on Gas Hydrates*, Yokohama, May 19–23, p. 604 (2002).