Thermochimica Acta, 182 (1991) 123–131
Elsevier Science Publishers B.V., Amsterdam

Critical evaluation of solubility data in binary systems formed by methanol with *n*-hydrocarbons

Adam Skrzecz

Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa (Poland)

(Received 1 October 1990)

Abstract

The solubility data in binary methanol–*n*-hydrocarbon (from butane to hexadecane) systems are reviewed. A method for the critical evaluation of the experimental solubility data is proposed and discussed. The sets of equations describing as a function of the number of carbon atoms the critical solution temperature, the corresponding concentration, and the solubility in both liquid phases of a binary system formed by the series of normal hydrocarbons with methanol are proposed. The calculated and predicted data are compared with the experimental data available in the literature.

INTRODUCTION

Various types of solubility data are reported in the literature for the methanol–*n*-hydrocarbon systems. Amongst these, solubility, mutual solubility, and upper critical solution point (UCSP) data can be distinguished. Solubility data give the temperature and concentration corresponding to the disappearance or appearance of a single phase. The mutual solubility data report these values for two phases simultaneously. The UCSP data consist of the equilibrium temperature and the corresponding concentration.

Very often the experimental data reported by various authors for a given system differ from each other. As an example several sets of the experimental solubility data for the methanol–hexane system are shown in Fig. 1. These data show large discrepancies. Values reported for the upper critical solution temperature (UCST) are scattered in the range 301.3–317.0 K while corresponding concentrations vary in the range 0.4–0.6 mole fraction. The differences in solubility reported at normal temperature ($T = 298$ K) exceed 0.15 mole fraction. A similar large scattering of reported experimental data is observed in all other systems under consideration. This situation which is also common for the solubility data for other systems requires a special method suitable for the selection and critical evaluation of data.

0040-6031/91/$03.50

METHOD

There is no general method for the critical evaluation of solubility data. The problem is known and the selection of data is usually carried out using non-uniform methods. The type of method applied depends on the evaluator, the system discussed and the data themselves. Very important is the description of data, which should consist of the estimated errors reported by authors or compilers, apparatus and method used for measurements, purity of substances (method of purification, concentration of organic impurities, concentration of water). Another important factor is the confidence in the author(s) and/or in the laboratory of origin.

In such a way the selected and recommended values could be obtained. Further critical evaluation could be made by the comparison of experimental data in the set of systems containing one component and the series of homologues. In this case, increments between the members of the series could indicate systematic changes of property in the series. Such changes can be further discussed with the knowledge of the dependence of properties on the molecular structure. This could allow comparison of different systems and inconsistencies of experimental values within the series to be found. Sometimes prediction by interpolation is also possible. The comparison and,

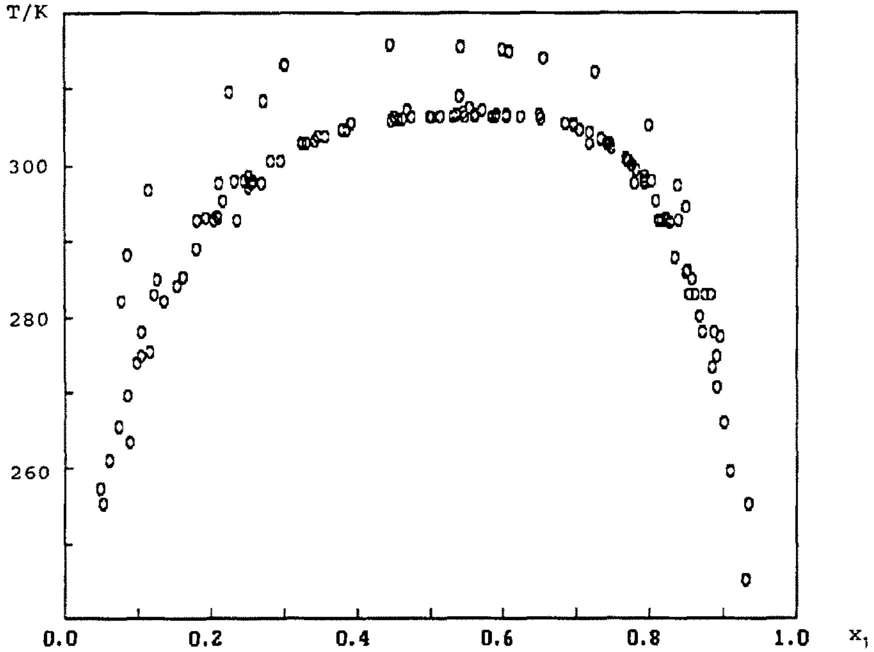

Fig. 1. Experimental solubility data for the methanol (1)–hexane (2) system reported in the literature.

TABLE 1

References for the experimental solubility data for methanol–n-hydrocarbon systems

System	References
Methanol–butane	13, 26
Methanol–pentane	7, 9, 10, 13, 22
Methanol–hexane	1, 2, 3, 4, 7, 8, 11, 12, 15, 16, 17, 20, 21,22, 23, 29, 30, 32, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44
Methanol–heptane	5, 6, 7, 9, 10, 11, 14, 18, 22, 23, 24, 25, 27, 31, 36, 40, 41, 45, 46
Methanol–octane	5, 9, 14, 19, 22, 23, 25, 27, 40, 41
Methanol–nonane	9,14, 15, 22, 23, 47
Methanol–decane	3, 9, 14, 15, 22, 47, 48
Methanol–undecane	9, 47, 48
Methanol–tetradecane	28
Methanol–hexadecane	33

even more, the prediction should be made with great care, as in some cases the change of property in a homologous series is not monotonic for various reasons unknown to the evaluator.

This paper considers all experimental solubility, mutual solubility and UCSP data reported in the literature for methanol–n-hydrocarbon systems, excluding high pressure data. The reference for the data under consideration are listed in Table 1.

The data sets for each system were fitted by means of the equation based on the suggestion by Malesinski in the form used by Franzosini [49]:

$$T = a_0 + \sum_{i=1}^{k} \left(a_i b^{2i}\right) \tag{1}$$

where T is the temperature in kelvin, $k \leq 4$ in most cases, $b = (x_1/x_1^c - x_2/x_2^c)/(x_1/x_1^c + x_2/x_2^c)$ while $x_1 + x_2 = 1.0$, a_0 is the upper critical solution temperature (UCST), a_i are adjustable parameters obtained from experimental data, x_1, x_2 are the compositions (in mole fraction) of components 1 and 2 respectively, and x_1^c, x_2^c are the compositions at UCST.

Equation (1) describes well the mutual solubility in the systems exhibiting UCST and characterized by a monotonic change in concentration with temperature. Franzosini [49] had used one set of parameters to describe simultaneously both branches of the solubility curve: a_0 is either an experimental value of UCST obtained in measurements or an adjustable parameter. Sometimes on the basis of extended information available a recommended value of a_0 can be found. In this paper the methanol-rich and hydrocarbon-rich phases are treated separately, which enables a more precise description.

RESULTS

The correlated solubility and UCSP data for the systems formed by methanol with the series of *n*-hydrocarbons containing from 4 to 16 carbon atoms were compared for each system. The comparison was made to enable the rejection of data sets differing drastically from the average or to obtain high accuracy data for each binary system. In this case the UCST data of Fischer and Neupauer [9] reported for C_5–C_{11} hydrocarbons are much higher (for the methanol–heptane system by 14.6 K) than several other data sets [10,11,18,22,41,47] determined in well-established laboratories. On the same basis, all UCST data reported by Fischer and Neupauer [9] for other systems also ought to be treated as erroneous. Another example of rejected data are those for the mutual solubility in methanol–octane and methanol–nonane systems, reported by Kogan et al. [23], which are not in agreement with other literature data and show significant deviations, when described with other systems of the series.

The weighted average of the experimental data are selected as most probable values of UCSP and the mutual solubility. These values are taken as recommended. The experimental data were described by the following equations representing the UCST and the corresponding concentration as

TABLE 2

Comparison of selected values of experimental UCSP and mutual solubility (x_1' and x_2'') at 300 K with values computed from eqns. (2–4) for methanol (1)–*n*-hydrocarbon (2) systems

Hydrocarbon	Critical point				Mutual solubility			
	UCST (K)		x_1^c		x_1''		x_2'	
	Selec.	Calc.	Selec.	Calc.	Selec.	Calc.	Selec.	Calc.
Butane	265.8	265.6	0.403	0.401		[a]		[a]
Pentane	287.4	287.8		0.484		[a]		[a]
Hexane	306.8	306.9	0.546	0.551	0.2764	0.271	0.2248	0.227
Heptane	324.1	323.8	0.610	0.606	0.1738	0.180	0.1072	0.116
Octane	338.9	338.7		0.653	0.132	0.133	0.065	0.065
Nonane [b]	351.2	352.1		0.694	0.108	0.106	0.041	0.039
Decane	364.1	364.1		0.729	0.089	0.089	0.027	0.025
Undecane	375.2	374.9		0.760		0.078		0.016
Dodecane		384.6		0.789		0.071		0.011
Tridecane		393.2		0.814		0.066		0.008
Tetradecane		400.8		0.837		0.063		0.006
Pentadecane		407.5		0.857		0.060		0.004
Hexadecane	413.3	413.3	0.876	0.876	0.059	0.059	0.003	0.003

[a] System completely miscible at 300 K.

[b] Only one experimental UCST is available.

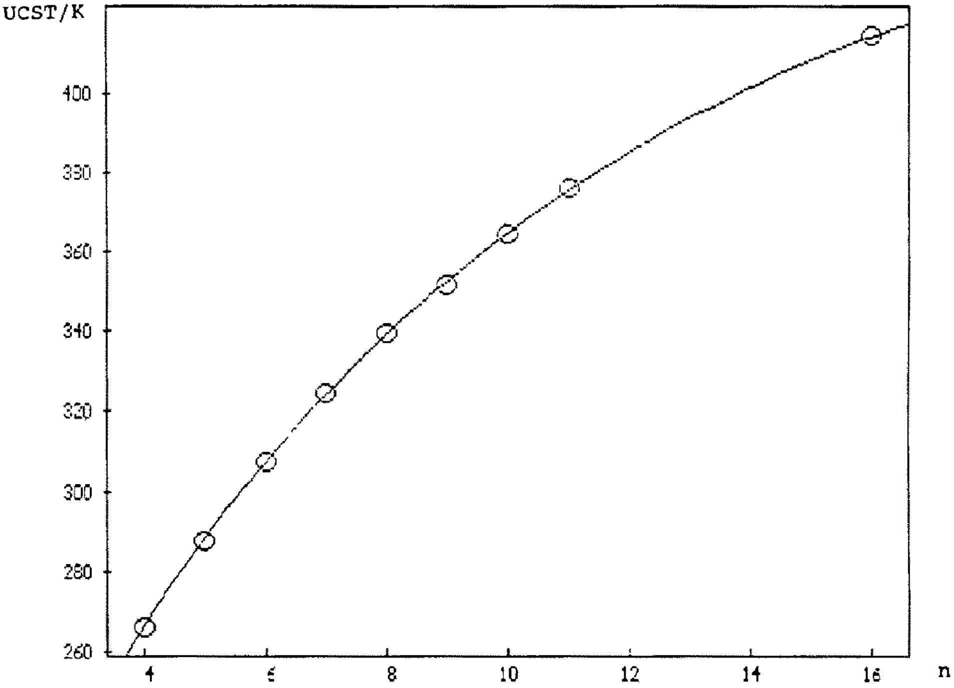

Fig. 2. UCST in the series methanol–n-hydrocarbons (C_4–C_{16}) as a function of carbon atoms and the curve obtained from eqn. (2).

function of the number of carbon atoms (n) in the hydrocarbon molecule

$$\mathrm{UCST} = a_0 = 140.47 + 60.45 \ln n + 11.564n - 0.3116n^2 \qquad (2)$$

$$x_1^c = -0.132 + 0.405 \ln n - 0.0072n \qquad (3)$$

The values of UCSP calculated from eqns. (2) and (3) are the most probable and can be treated as recommended values. The weighting factors ($\omega = 5$) were assigned for data [2,10,11,17,18,21,22,36,41] for the systems with hexane and heptane. These systems were accurately measured. The results obtained in various laboratories do not differ within experimental error and hence can be treated as reference. For all other data a weighting factor of unity was used.

The data selected according to the proposed procedure are reported in Table 2 and shown in Figs. 2 and 3 together with curves obtained by means of eqns. (2) and (3).

The solubility data at constant temperature can be treated in an analogous way. For example, the data at 300 K for $n \geq 6$ can be well described by the equations

$$\ln x_1'' = 8.148 - 7.682 \ln n + 1.343(\ln n)^2 \qquad (4)$$

$$\ln x_2' = 6.314 - 4.351 \ln n \qquad (5)$$

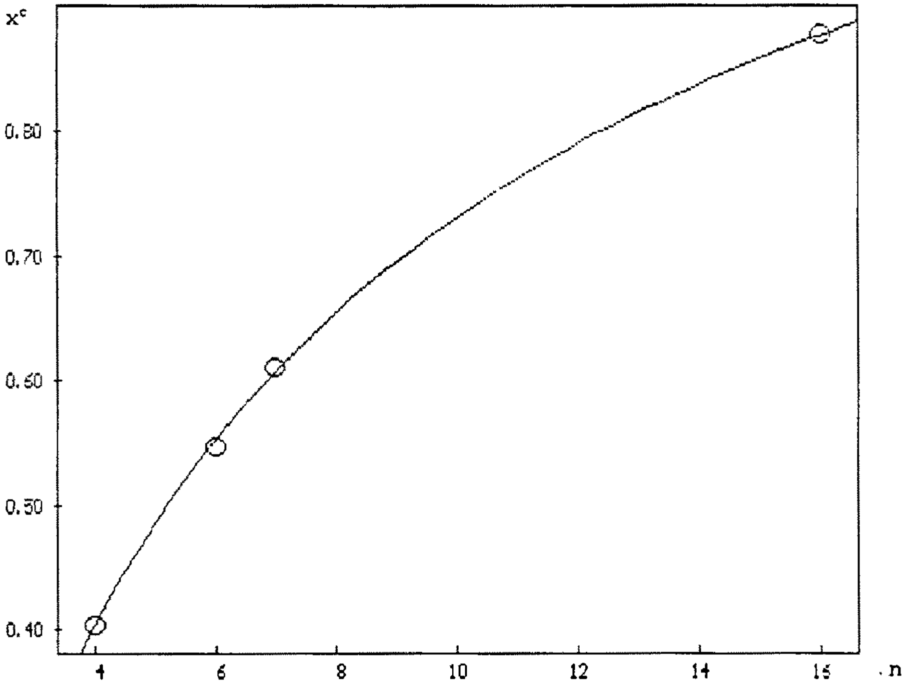

Fig. 3. Methanol concentration at UCST in the series methanol–*n*-hydrocarbons (C_4–C_{16}) as a function of carbon atoms and the curve obtained from eqn. (3).

TABLE 3

Parameters of eqn. (1) obtained by fitting of selected data for methanol–*n*-hydrocarbon systems

System	Range	a_0	x_1^c	a_1	a_2	a_3	Est. error [a]
Butane [b]	250–UCST	265.8	0.403	−23.51	92.08	−307.00	0.0010 A
				−16.32	6.10	−310.17	0.0010 B
Hexane	255–UCST	306.8	0.546	−21.24	0.19	−53.74	0.0004 A
				−9.57	−73.63	−40.75	0.0004 B
Heptane	270–UCST	324.1	0.610	−22.33	2.54	−60.46	0.0004 A
				−14.68	−32.11	−99.41	0.0004 B
Octane	285–UCST	338.7	0.653	−10.80	−72.32	24.30	0.0010 A
				−15.80	−48.44	−60.58	0.0010 B
Nonane	300–335	352.1	0.694	−81.30	166.15	−178.77	0.0010 A
				−69.80	134.21	−207.36	0.0010 B
Decane	300–336	364.1	0.729	−81.50	165.01	−180.74	0.0010 A
				−109.20	190.88	−216.79	0.0010 B
Hexadecane [b]	298–UCST	413.3	0.876	23.04	−138.17	0.0	0.0100 A
				21.30	−151.18	0.0	0.0100 B

[a] A, hydrocarbon-rich phase; B, methanol-rich phase.

[b] Description of experimental data (only one data set exists).

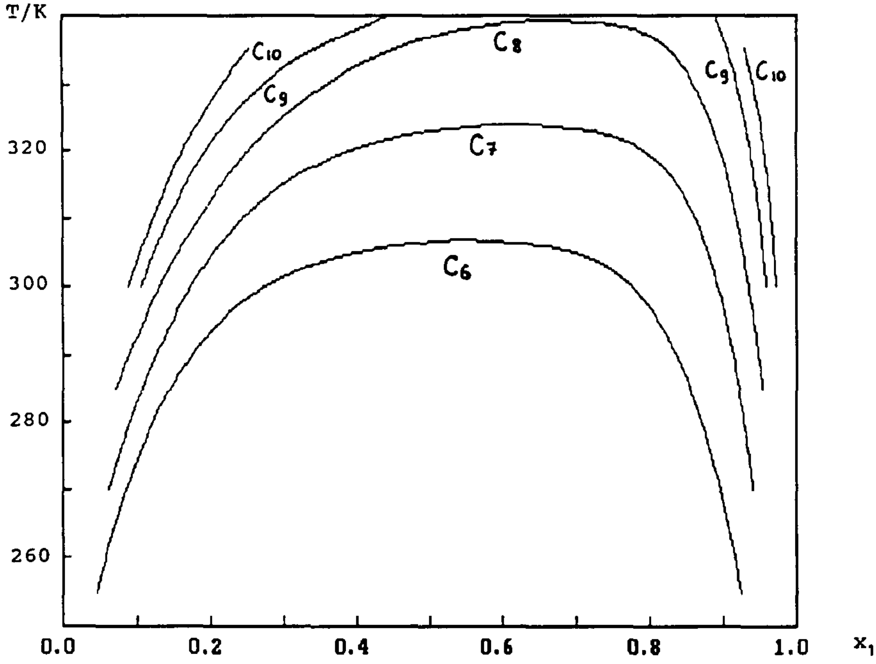

Fig. 4. Recommended mutual solubility in the series methanol–*n*-hydrocarbons (C_6–C_{10}).

where x_1' and x_2'' are the mole fractions of methanol and *n*-hydrocarbon in the hydrocarbon and methanol rich phases respectively.

In Table 2 the results of predictions from eqns. (2–5) are compared with the experimental values selected by the recommended procedure. As a final result the internally consistent set of selected data for the methanol–*n*-hydrocarbon systems is obtained. These data were fitted to eqn. (1). The parameters obtained, together with estimated errors, are reported in Table 3. An example of the recommended data is shown in Fig. 4. The data obtained can be recommended for future use.

CONCLUSIONS

For a critical evaluation of methanol–*n*-hydrocarbon systems the comparison of various available literature solubility data (upper critical solubility and mutual solubility) in the series was found to be very efficient. It allows one to find consistent numerical values for each particular system and for the set formed by one component with the homologous series. The method has a general character and can be recommended for testing of the experimental results from various measurements. The equations proposed in this paper have been found to describe the solubility data within the accuracy of a good experiment.

REFERENCES

1 A.D. Alekhin, M.G. Barkov and N.P. Kuleshova, Ukr. Fiz. Zh., 28 (1983) 68.
2 D. Balasubramanian and P. Mitra, J. Phys. Chem., 83 (1979) 2724.
3 E.C. Bingham, Am. Chem. J., 37 (1907) 549.
4 L.S. Budantseva, T.M. Lesteva and M.S. Nemtsov, Zh. Fiz. Khim., 50 (1976) 1343; Deposited Doc. VINITI, (1976) 438-76.
5 L.S. Budantseva, T.M. Lesteva and M.S. Nemtsov, Zh. Fiz. Khim., 50 (1976) 1344; Deposited Doc. VINITI, (1976) 437-76.
6 N.I. Chernova, Zh. Fiz. Khim., 39 (1965) 2388.
7 R.E. Cornish, R.C. Archibald, E.A. Murphy and H.M. Evans, Ind. Eng. Chem., 26 (1934) 397.
8 J.B. Ferguson, J. Phys. Chem., 36 (1932) 1123.
9 R. Fischer and E. Neupauer, Mikrochem. Ver. Mikrochim. Acta, 34 (1949) 319.
10 A.W. Francis, J. Am. Chem. Soc., 76 (1954) 393.
11 A.W. Francis, Ind. Eng. Chem., 36 (1944) 764.
12 I.G. Grekova, E.T. Shimanskaya and Yu. I. Shimanskii, Ukr. Fiz. Zh., 26 (1981) 283.
13 U. Haarhaus and G.M. Schneider, J. Chem. Thermodyn., 20 (1988) 1121.
14 H. Higashiuchi, Y. Sukuragi, Y. Iwai, Y. Arai and M. Nagatani, Fluid Phase Equilib., 36 (1987) 35.
15 I.F. Hoelscher, G.M. Schneider and J.B. Ott, Fluid Phase Equilib., 27 (1986) 153.
16 E.J. Howard and W.H. Patterson, J. Chem. Soc., 129 (1926) 2787.
17 G. Hradetzky and H.-J. Bittrich, Int. DATA Ser., Sel. Data Mixtures, Ser. A, (1986) 216.
18 G. Hradetzky and H.-J. Bittrich, Int. DATA Ser., Sel. Data Mixtures, Ser. A, (1986) 217.
19 Y. Iwai, Y. Nishimura, Y. Wanatabe and Y. Arai, Fluid Phase Equilib., 25 (1986) 107.
20 N.L. Kasapova, G.I. Pozharskaya, Yu.D. Kolpakov and V.P. Skripov, Zh. Fiz. Khim., 57 (1983) 2182.
21 J.R. Khurma and D.V. Fenby, Aust. J. Chem., 35 (1982) 1281.
22 R.W. Kiser, G.D. Johnson and M.D. Shetlar, J. Chem. Eng. Data, 6 (1961) 338.
23 V.B. Kogan, I.V. Deizenrot, T.A. Kul'byaeva and V.M. Fridman, Zh. Prikl. Khim., 29 (1956) 1387.
24 T.M. Letcher, S. Wootton, B. Shuttleworth and C. Heyward, J. Chem. Thermodyn., 18 (1986) 1037.
25 I. Nagata, Thermochim. Acta, 114 (1987) 227.
26 K. Noda, K. Sato, K. Nayatsuka and K. Ishida, J. Chem. Eng. Jpn., 8 (1975) 492.
27 J.B. Ott, I.F. Hoelscher and G.M. Schneider, J. Chem. Thermodyn., 18 (1986) 815.
28 I. Pliskin and R.E. Treybal, J. Chem. Eng. Data, 11 (1966) 49.
29 C. Quantie, Proc. R. Soc. London, Ser. A, 224 (1954) 90.
30 F.C. Radice and H.N. Knickle, J. Chem. Eng. Data, 20 (1975) 371.
31 M. Ranjan, V. Jayalaxmi, V. Vani and E.S.R. Gopal, Indian J. Phys. A 60, (1986) 98.
32 M.M. Rising and J.S. Hicks, J. Am. Chem. Soc., 48 (1928) 1929.
33 M. Rogalski and R. Stryjek, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 28 (1980) 139.
34 V. Rothmund, Z. Phys. Chem., 26 (1898) 433.
35 T.S. Rudakovskaya, L.I. Vinogradova, V.S. Timofeev and L.A. Serafimov, Sb. Nauchn. Tr. Ivanov. Energ. Inst., 14 (1972) 249.
36 L.G. Savini, D.R. Winterhalter and H.C. van Ness, J. Chem. Eng. Data, 10 (1965) 171.
37 R. Schmidt, G. Werner and H. Schuberth, Z. Phys. Chem., 242 (1969) 381.
38 A. Schuekarew, Z. Phys. Chem., 71 (1910) 90.
39 V. Sementschenko, S. Gratschewa and E. Davidoffskaja, Kolloid. Z., 68 (1934) 275.
40 V.F. Sergeeva and I.Z. Ustanova, Zh. Obshch. Khim., 43 (1973) 1878.
41 L. Sieg, Chem. Ing. Tech., 23 (1951) 112.
42 V.P. Skripov, V.S. Vitkalov and Yu.D. Kolpakov, Zh. Fiz. Khim., 54 (1980) 1754.

43 B.A. Smirnov and A.A. Predvoditelev, Zh. Fiz. Khim., 28 (1954) 906.
44 R. Suhrmann and R. Walter, Abh. Braunschweig. Wiss. Ges., 3 (1951) 135.
45 G. Tagliavini and G. Arich, Ric. Sci., 28 (1958) 1902.
46 B. Viswanathan, K. Govidarajan and E.S.R. Gopal, Indian J. Pure Appl. Phys., 11 (1973) 157.
47 K. Zieborak and Z. Maczynska, Rocz. Chem., 32 (1958) 295.
48 K. Zieborak, Z. Maczynska and A. Maczynski, Bull. Acad. Pol. Sci., Cl. 3, 4 (1956) 153.
49 P. Franzosini, Int. DATA Ser., Sel. Data Mixtures, Ser. A (1974) 172.