Thermochimica Acta, 65 (1983) 157–168
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC PROPERTIES OF AQUEOUS NON-ELECTROLYTE MIXTURES. ENTHALPY OF MIXING AND LIQUID–LIQUID EQUILIBRIUM OF WATER + ALIPHATIC ALDEHYDE MIXTURES

ITALO FERINO, BRUNO MARONGIU *, ROBERTO MONACI, VINCENZO SOLINAS and SERGIO TORRAZZA

Istituto di Chimica Fisica e Industriale, Università di Cagliari, 09100 Cagliari (Italy)

(Received 1 December 1982)

ABSTRACT

The liquid–liquid equilibrium, L–L, and the enthalpy of mixing, H_M, for water with ethanal, propanal and butanal mixtures were determined at 298.15 K.

For all the mixtures studied, H_M vs. x curves show exothermic mixing in the water-rich region which becomes endothermic at high aldehyde concentrations.

These curves have been interpreted in terms of intercomponent molecular interactions and hydrophobic stabilization of the water structure by molecules of aldehyde. The results obtained indicate that the number of alkyl groups in the aldehyde plays an important role in determining the magnitude of these effects and also influences the miscibility.

INTRODUCTION

Aliphatic aldehydes are known to give non-ideal mixtures with aliphatic hydrocarbons [1–4]. This behaviour may be ascribed to the influence of the dipole moment of the carbonyl group, CHO, which becomes manifest in the form of strong carbonyl–carbonyl interactions. The interactions are particularly strong when the aldehydes are mixed with substances having in their structure groups which are able to interact specifically with the carbonyl group, i.e. strongly polarizable groups (such as phenyl) or proton donors, as in chloroform [5], alcohols [5] and water [6,7].

Our results on aldehydes + *n*-alkanes mixtures [1,8] have demonstrated that the number of alkyl groups located near the carbonyl plays an important role in determining the extent of the molecular interactions involving the carbonyl group itself. With the aim of establishing the occurrence of such an effect when dealing with strongly polar solvents like water, we intend to

---

* To whom correspondence should be addressed.

carry out a systematic investigation on the thermodynamic properties of aqueous mixtures of aldehydes of general formula $CH_3(CH_2)_{m-2}CHO$ (with $m = 2,3,4$).

A search of the literature reveals that the thermodynamic studies on aldehydes + water mixtures are rather scarce and limited to ethanal ($m = 2$); moreover, the reported data are in considerable disagreement. The hydration equilibrium constants and the enthalpy of hydration, H_i, for ethanal have been determined by several authors [9–11]. The most extensive investigation in the hydration of aldehydes ($m = 2,3,4$) is due to Gruen and McTigue [9]. Ragaini and Cavenaghi [12] and Kurtz [10], by means of a combination of spectrophotometric and calorimetric data, determined for ethanal + water mixtures the enthalpy of mixing, H_M, as the difference between the total enthalpy change, H_T, and the enthalpy of hydration, $x'_i H_i$. Lombardi and Sogo [13] applied the high resolution NMR technique to study the hydration of ethanal and their results are in agreement with those obtained by other methods [9,11].

The liquid–vapor equilibrium (LVE) of ethanal + water mixtures has been investigated at pressures ranging from 1 atm [6,14] up to several atm [15] and the data have been correlated by means of Wilson and Van Laar equations; these correlations appear to be unsatisfactory because of the errors arising from these equations when the boiling points of the components are very different.

LVE data on butanal + water mixtures have also been reported [16], correlated by means of the Van Laar equation and the determined composition of the given azeotrope, while the only available investigation on liquid–vapor equilibria for the propanal–water system is the one published by Union Carbide Corp. [17].

All these measurements confirm the non-ideal behaviour of the aldehydes + water systems, as pointed out by the fact that the activity coefficients differ from unity [16] and show a precise trend in their values when changing the composition of the liquid phase.

Ethanal is completely miscible with water [18] while an extended miscibility gap is observed with propanal [19] and butanal [20] in water. Moreover, the behaviour of propanal with water is unusual since it exhibits a lower critical solution temperature (LCST).

As regards the system butanal + water, Smith and Bonner [7] have reported the liquid–liquid equilibrium (LLE) data at 298.15 K and incomplete data on a heterogeneous azeotrope while Pereligin and Smirnov [21] have recently determined some equilibrium data in the miscibility region.

In the present work the mixtures of ethanal, propanal and butanal are investigated by experimentally determining the total enthalpy change, H_T, at 298.15 K, using the K_i and H_i values reported by Gruen and McTigue [9]. The enthalpy of mixing, H_M, for the systems ethanal + water (in the entire concentration range), propanal + water and butanal + water (in the homogeneous region only) is also calculated and the dependence of temperature on the liquid–liquid equilibrium (LLE) of the last two systems studied by means of gas–liquid chromatography in the 278.15–313.15 K range.

The experimental results are interpreted by referring to the "flickering cluster" model of liquid water proposed by Frank and Wen [22].

EXPERIMENTAL AND RESULTS

Materials

Aldehydes are easily oxidized and polymerized. Hence, the aliphatic aldehydes of pure reagent grade (Fluka AG, Switzerland) were first dried on a molecular sieve 3A and then distilled in a dry nitrogen atmosphere. Purity was higher than 99% as determined by GLC using a chromosorb W 80–100 mesh column. Water was prepared by passing through a mixed-bed ion-exchange resin column and then distilled twice.

TABLE 1

Total enthalpy change, H_T, enthalpy of hydrations, $x_1'H_1$, and enthalpy of mixing, H_M, at 298.15 K, of the ethanal(1)+water(2) mixtures

x_1	H_T (J mole^{-1})	$x_1'H_1$ (J mole^{-1})	H_M (J mole^{-1})
0.0101	−190	−136	−54
0.0509	−770	−527	−243
0.0593	−883	−603	−280
0.0715	−1022	−708	−314
0.0900	−1228	−856	−372
0.1015	−1341	−944	−397
0.1723	−1888	−1378	−510
0.2024	−2038	−1519	−519
0.2497	−2193	−1691	−502
0.3073	−2264	−1829	−435
0.3522	−2192	−1828	−364
0.4031	−2179	−1915	−264
0.4728	−1984	−1884	−100
0.5200	−1802	−1824	+22
0.6129	−1407	−1629	+222
0.6334	−1312	−1572	+260
0.6788	−1094	−1433	+339
0.7000	−996	−1362	+366
0.7499	−770	−1180	+410
0.8013	−554	−973	+419
0.9209	−143	−415	+272

In order to avoid oxidation, a dry-box with flowing nitrogen was always used for any kind of manipulation.

Calorimetric measurements

The total enthalpy change, H_T, has been measured using a Tian Calvet CRMT type calorimeter which was manually tilted. The principle of the apparatus and the experimental procedure are reported in the literature [23,24]. The mixing cell was suitably modified in order to guarantee a perfect seal of the lower and upper compartments containing the two liquids and it was equipped with a heating resistance to carry out calibration directly on each mixture.

The performance of the calorimeter was regularly checked by determining the excess enthalpies for some well-investigated test mixtures (tetrachloromethane + benzene and benzene + cyclohexane). The results obtained are in agreement within 1% with those of Stokes et al. [25].

All measurements were made at an average temperature of 298.15 ± 0.10 K. The experimental H_T values are listed in Tables 1, 2 and 3.

TABLE 2

Total enthalpy change, H_T, enthalpy of hydration, $x_1'H_1$, and enthalpy of mixing, H_M, at 298.15 K, of the propanal(1)+water(2) mixtures

x_1	H_T (J mole^{-1})	$x_1'H_1$ (J mole^{-1})	H_M (J mole^{-1})
0.0420	−557	−414	−143
0.0742	−871	−669	−202
0.0905	−1002	−781	−221
0.1204	−1188	−960	−228
0.1398	−1269	−1059	−210
0.1670	−1353	−1176	−177
0.2431[a]	−1312	−1268	−441
0.3647[a]	−1085	−1260	+175
0.5032[a]	−826	−1251	+425
0.6144[a]	−604	−1244	+640
0.6949	−274	−1025	+751
0.7235	−184	−946	+762
0.7779	−38	−784	+746
0.8257	+29	−630	+659
0.9112	+64	−333	+397

[a] Phase heterogeneity points.

TABLE 3

Total enthalpy change, H_T, enthalpy of hydration, $x_i'H_i$, and enthalpy of mixing, H_M, at 298.15 K, of the butanal(1)+water(2) mixtures

x_1	H_T (J mole^{-1})	$x_i'H_i$ (J mole^{-1})	H_M (J mole^{-1})
0.0107	−117	−99	−18
0.0204	−212	−182	−30
0.1407 [a]	−94	−220	126
0.2511 [a]	35	−238	273
0.4213 [a]	231	−267	498
0.5628 [a]	391	−294	685
0.6651 [a]	509	−312	821
0.7240 [a]	578	−321	899
0.8015 [a]	666	−336	1002
0.8559 [a]	698	−344	1042
0.8755	684	−316	1000
0.9399	547	−156	703
0.9779	267	−53	320

[a] Phase heterogeneity points.

Gas-chromatographic measurements

The liquid–liquid equilibria for the mixtures propanal + water and butanal + water have been investigated in the temperature range 278.15–313.15 K using a glass reactor (100 cm^3 volume) equipped with a thermostatic jacket and helicoidal stirring.

The stirring speed was measured by means of a stroboscope; the contact between the two fluids was started in nitrogen and only at a stirring speed of

TABLE 4

Data of liquid–liquid equilibrium at various temperatures for the propanal + water mixture X_A^A = Molar fraction of aldehyde in the aldehyde-rich phase; X_A^W = molar fraction of aldehyde in the water-rich phase.

T (K)	X_A^A	X_A^W
288.15	0.5621	0.3278
293.15	0.6277	0.2214
298.15	0.6715	0.1739
303.15	0.7000	0.1570
308.15	0.7231	0.1337
313.15	0.7354	0.1169

TABLE 5

Data of liquid–liquid equilibrium at various temperatures for the butanal + water mixtures X_A^A = Molar fraction of aldehyde in the aldehyde-rich phase; X_A^w = molar fraction of aldehyde in the water-rich phase.

T (K)	X_A^A	X_A^w
278.15	0.8986	0.0293
283.15	0.8929	0.0275
288.15	0.8870	0.0256
293.15	0.8813	0.0240
298.15	0.8754	0.0223
303.15	0.8695	0.0207
308.15	0.8634	0.0190
313.15	0.8576	0.0174

1600 r.p.m. was a fine dispersion of the two fluids reached.

After a contact time of about 10 min the mixture was allowed to decant so that the two phases could form; drawing off an aliquot of each one, homogenization with known quantities of 1,4-dioxane and gas-chromatographic analysis then followed.

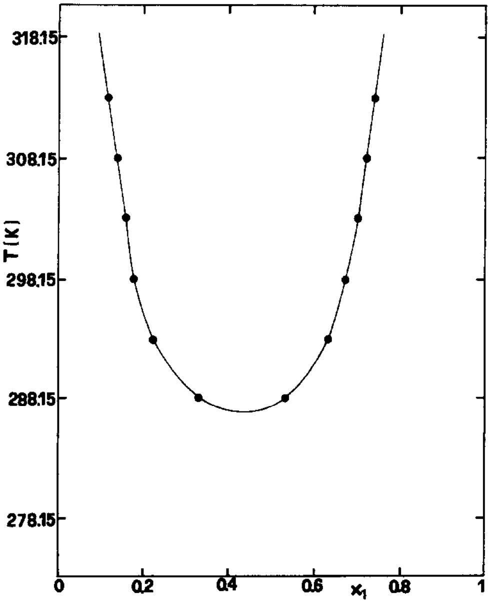

Fig. 1. Liquid–liquid equilibrium curve for the propanal(1)+water(2) system.

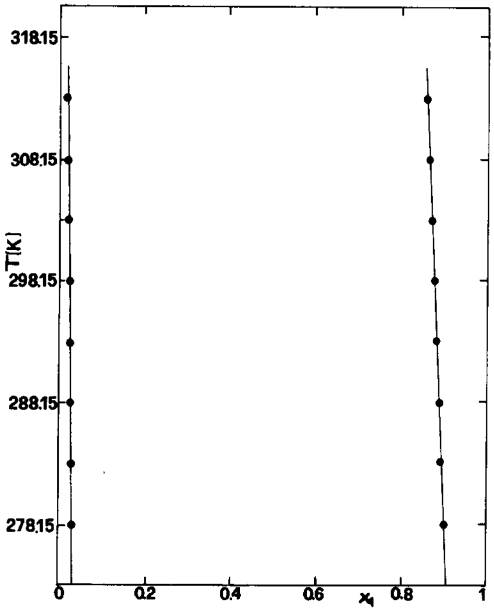

Fig. 2. Liquid–liquid equilibrium curve for the butanal(1)+water(2) system.

The instrument was a Carlo Erba Fractovap 1400 equipped with a flame-ionisation detector and a 2 m long column packed with 8% Carbowax 1500 on Chromosorb W (80–100 mesh). Nitrogen (14 cm^3 min^{-1}) was used as the carrier and the column temperature was 363.15 K. Table 4 and 5 list LLE data for propanal + water and butanal + water systems, respectively (see also Figs. 1 and 2).

DATA REDUCTION

As briefly outlined in the Introduction, the total thermal effect observed when mixing an aldehyde with water is the sum of two terms: the one due to the mixing of the aldehyde, H_M, and the other arising from the hydration reaction, $x_i'H_i$, where x_i' is the ratio between the number of moles of the hydrated aldehyde and the number of moles of the initial mixture and H_i represents the heat of reaction [4] at 298.15 K.

It must be noticed however, that the statement in the previous paragraph is strictly true only when the reaction

$$CH_3(CH_2)_{m-2}CHO + H_2O \rightleftarrows CH_3(CH_2)_{m-2}CH(OH)_2 \qquad (1)$$

is completely set up. Keeping in mind that the half-time for such reactions at 298.15 K is of the order of one minute (Bell and Clunie [11]) while the process of mixing occurs instantaneously, the total thermal effect can be

TABLE 6

Values of the hydration equilibrium constant, $K_i(T)$, at $T = 298.15$ K, and the hydration enthalpy, H_i, at $T = 298.15$ K, for the reaction: $CH_3(CH_2)_{m-2}CHO + H_2O \rightleftharpoons CH_3(CH_2)_{m-2}CH(OH)_2$ with $m = 2, 3, 4$, as determined by Gruen and McTigue [9]

m	K_i	$-H_i$ (K J mole^{-1})
2	0.98	23.849
3	0.69	27.196
4	0.48	29.706

written as

$$H_T = H_M + x_i' H_i \tag{2}$$

H_M has been calculated for the systems investigated in the present work by means of eqn. (2), using for H_T, the experimentally determined values, for H_i, the values reported by Gruen and McTigue [9] [listed in Table 6 together with the equilibrium constants, K_i, for the reaction given in eqn. (1)] and attributing to x_i' the values calculated from the equation

$$x_i' = \frac{K_H x_1 x_2}{V_m + K_H} \tag{3}$$

where $K_H = K_i/[H_2O]$ (with $[H_2O] = 55.5$ mole l^{-1}); x_1 and x_2 are the mole fractions of aldehyde and water, respectively, and V_m (l mole^{-1}) is the volume of the fluid mixtures. The last parameter is calculated as the sum of aldehyde and water volumes neglecting the volume variations due to mixing.

$$V_m = \frac{x_1 PM_1 + \rho_1 x_2 PM_2}{1000\rho_1} \tag{4}$$

where PM_1 and PM_2 are the molecular weights of aldehyde and water, respectively, while ρ_1 is the aldehyde density (g cm^{-3}).

These calculations have not been applied, of course, in the heterogeneity region of the mixtures propanal + water and butanal + water. In such situations the mole fraction of hydrated aldehyde is obtained from

$$\sum x_i' = [x_i']_w F_w + [x_i']_A F_A \tag{5}$$

where $F_A = (X_A - X_A^w)/(X_A^A - X_A^W)$ and $F_w = 1 - F_A$. F_A and F_w denote the molar fractions of organic and aqueous phase, respectively, while X_A^w and X_A^A represent the mole fractions of the aldehyde in the water-rich and aldehyde-rich regions; $[x_i']_w$ and $[x_i']_A$ are the mole fractions of the hydrated aldehyde in the original mixtures respectively in the aqueous and organic phases as

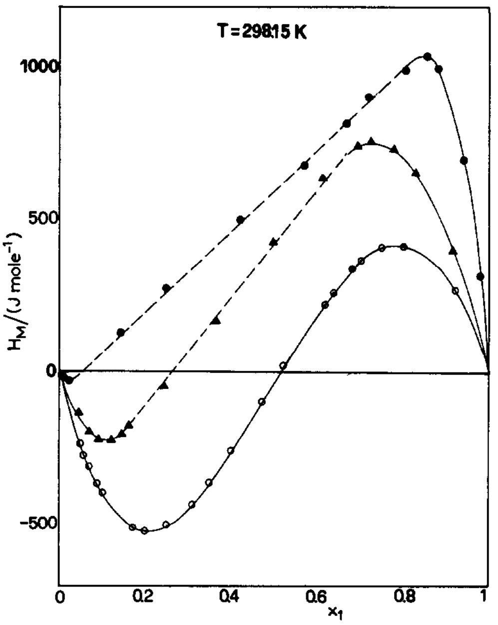

Fig. 3. Enthalpy of mixing, H_M, at 298.15 K, of aldehyde(1)+water(2) mixtures vs. x_1, the mole fraction of aliphatic aldehyde. Experimental H_M results: ○, A_2, ethanal; ▲, A_3, propanal; ●, A_4, butanal.

given by the equations

$$[x_i']_w = \frac{K_H[H_2O]_w}{1 + K_H[H_2O]_w}$$

$$[x_i']_A = \frac{K_H[H_2O]_A}{1 + K_H[H_2O]_A} \tag{6}$$

with $[H_2O]_w = X_w/[V_m]_w$ and $[H_2O] = X_w/[V_m]_A$. V_m values can be calculated from

$$[V_m]_w = \frac{X_A^w PM_A + X_w^w PM_w \rho_A}{1000\ \rho_A}$$

$$[V_m]_A = \frac{X_A^A PM_A + X_w^A PM_w \rho_A}{1000\ \rho_A} \tag{7}$$

The H_M values resulting from this calculation procedure are reported in Tables 1–3 (see also Fig. 3).

DISCUSSION

As can be seen from Fig. 3, the enthalpy of mixing, H_M, for mixtures of water with three aliphatic aldehydes shows the same evolution, i.e. exothermic in the water-rich region and endothermic when there is a greater concentration of aldehydes. The extension of these two regions, the magnitude and concentration of the maximum and minimum of the S-shaped curves of H_M depend on geometric and energetic factors characteristic of the various aldehydes.

This behaviour can be qualitatively interpreted by referring to the flickering cluster model of liquid water proposed by Frank and Wen [22]: the water molecules are bound by hydrogen bonds so as to form microscopic clusters of various sizes and shapes. The clusters are in dynamic equilibrium with other water molecules, bound more weakly, which occupy the cavity of the clusters and the interstitial spaces. Formation and break-down of the cluster is essentially determined through a cooperative phenomenon of forming and breaking of hydrogen bonds. By introducing a solute into liquid water, the formation of the cluster is helped or disturbed according to the geometric and energetic relations between water and the solute.

In the light of this model, the exothermic character observed at high mole fractions of water should derive essentially from an increase or rearrangement of the water structure by formation of intercomponent hydrogen bonds and hydrophobic hydration around the aliphatic chain of the aldehyde molecule. The authors think that for the mixtures studied, the hydrophobic stabilization process should involve, above all, water molecules of the cavities and the interstitial spaces of the flickering cluster model, which would gather round the molecules of aldehyde so as to form new clusters.

This enhancement of the water structure constributes exothermically to the process of the solution formation. Comparative analysis of the enthalpies of mixing of the mixtures of aldehydes shows that the exothermic effect increases with decrease of the hydrophobic/hydrophilic ratio. The authors observe $\Delta H_{M,max} \simeq -300$ J mole^{-1} when moving from propanal to butanal and $\Delta H_{M,max} \simeq 500$ J mole^{-1} from ethanal to butanal. When comparing these results, the endothermic contribution deriving from molecular interactions present in pure aldehydes is also to be taken into consideration.

The enthalpies of mixing for aliphatic aldehydes mixtures with an inert solvent like *n*-heptane [1,8] show that the molecular interactions between ethanal molecules are stronger and therefore determine a greater endothermic contribution to the excess enthalpy of the mixture. Consequently, the exothermic contribution of the intercomponent hydrogen bonds and the hydrophobic effect is even greater than $\Delta H_{M,max}$ which is seen as a global mixing effect. Moreover, the contribution of the hydrophobic chain, should be more important with butanal than with propanal and ethanal.

In the increase of the water structure, an important role is also played by the geometry and size of the molecules of aldehyde and the hydrophobic stabilization process, which should mainly concern the water molecules of the cavities and the interstitial spaces of the clusters, and be carried out without considerably affecting the pre-existing water structure. The authors think that this process can be more easily realised with the smaller aldehyde which, because of its small size, can more easily get into the cavities of clusters, substituting the water molecules which can then take part in the formation of new clusters or intercomponent hydrogen bonds.

According to this model, the maximum increase in water structure should coincide with H_M minimum. At this concentration almost all the water molecules should be engaged in the clusters and intercomponent hydrogen bonds and thus further addition of aldehyde should set off a competitive process of formation of hydrogen bonds with the consequent decrease of water–water bonds and increase of water–aldehydes bonds.

The endothermic character of aldehyde-rich mixtures is a consequence of the fact that intercomponent hydrogen bonds are weaker than those between water molecules. The magnitude of the endothermic effect for the mixtures of aldehydes decreases with increase in their electron-donor strength.

Several studies have been carried out which show the change in the phase behaviour of homologous series of solutes, for which the increasing chain length results in $|\Delta S_M|$ increasing faster than $|\Delta H_M|$. This is because ΔH_M is, to some extent at least, governed by the polar group (–CHO) whereas, ΔS_M is largely determined by the apolar group (CH_3– or –CH_2–). In suitable systems a gradation of phase behaviour is found, from solutes which are completely miscible (ethanal), through solutes which exhibit an LCST (propanal), and finally to solutes which exhibit a miscibility gap at all temperatures (butanal), (see Figs. 1 and 2).

ACKNOWLEDGEMENT

This work was supported by the Consiglio Nazionale delle Ricerche (C.N.R.) of Rome.

REFERENCES

1 B. Marongiu, H. Bros, M. Coten and H.V. Kehiaian, J. Chim. Phys., 72 (1975) 375.
2 B. Marongiu and H.V. Kehiaian, Int. Data Ser., Sel. Data Mixtures, Ser. A, 1 (1974) 58.
3 R.R. Tarakad and W.A. Scheller, J. Chem. Eng. Data, 24 (1979) 119.
4 I. Matsunaga and T. Katayama, J. Chem. Eng. Jpn., 6 (1973) 397.
5 R.P. Kirsanova and S.Sh. Byk, Zh. Prikl. Khim. (Leningrad), 31 (1958) 1610.
6 K.F. Coles and F.P. Popper, Ind. Eng. Chem., 42 (1950) 1434.
7 T.E. Smith and R.F. Bonner, Ind. Eng. Chem., 43 (1951) 1169.
8 I. Ferino, B. Marongiu, V. Solinas, S. Torrazza and H.V. Kehiaian, Fluid Phase Equilibria, in press.

9 L.C. Gruen and P.T. McTigue, J. Chem. Soc., (1963) 5224.
10 J.L. Kurtz, J. Am. Chem. Soc., 89 (1967) 3524.
11 R.P. Bell and J.C. Clunie, Trans. Faraday Soc., 48 (1952) 439.
12 V. Ragaini and C. Cavenaghi, Chim. Ind. (Milan), 51 (1969) 370.
13 E. Lombardi and P.B. Sogo, J. Chem. Phys., 32 (1960) 635.
14 S.G. D'Avila and R.S.F. Silva, J. Chem. Eng. Data, 15 (1970) 421.
15 V. Bareggi, S. Mori, P. Schwarz and P. Beltrame, Chim. Ind. (Milan), 50 (1968) 1224.
16 V. De Simone, P. Palumbo, R. Valentino and G. Volpicelli, Chim. Ind. (Milan), 56 (1974) 103.
17 Aldehydes, Union Carbide Corp., New York, 1960.
18 Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 1, Interscience, New York, (1963) p. 77.
19 Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 16, Interscience, New York, 1963, p. 548.
20 Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 3, Interscience, New York, 1963, p. 865.
21 V.M. Pereligin, V.S. Smirnov, Izv. Vyssh. Uchebn. Zaved Pishch. Tekhnol., 2 (1970) 211.
22 H.S. Frank and W.Y. Wen, Discuss. Faraday Soc., 24 (1957) 133.
23 M. Coten, F. Camia and M. Laffitte, Fr. Pat. 1527186.
24 D. Bares, M. Soulie and J. Metzger, J. Chim. Phys., 70 (1970) 1531.
25 R.H. Stokes, K.N. Marsh and R.P. Tomlins, J. Chem. Thermodyn., 1 (1969) 211.