ULTRASONIC STUDIES OF INTERMOLECULAR INTERACTIONS IN SYSTEM METHANOL-*N, N*-DIISOBUTYLFORMAMIDE

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*(Received May 28, 1996; revised version August 5, 1996;
in final form October 8, 1996)*

The ultrasonic velocity and density of methanol solutions of *N, N*-diisobutylformamide (DBFA) were measured at -5, 5 and 15°C over the entire concentration range. The compressibility, excess compressibility, partial molar compressibility, excess molar volume, partial molar volume were calculated. The concentration dependencies of the velocity and density are nonlinear. On taking account of the results for excess molar volume and excess molar compressibility, the minima of these functions are ascribed to the complex formation type $\text{CH}_3\text{OH}:\text{DBFA}$ and $\text{CH}_3\text{OH}:2\times\text{DBFA}$. These complexes are formed by hydrogen bond between methanol and *N, N*-diisobutylformamide molecules. The strong changes in the concentration dependencies of partial molar volume and partial molar compressibility (within range 0...0.1 mol. fraction amide) show that methanol and DBFA have strong interactions in the low-mole-fraction regions, too.

PACS numbers: 43.35.+d

1. Introduction

Much attention has been paid to acoustic studies of intermolecular interactions in aqueous solutions of non-electrolytes [1]. Obviously, it is connected to specific structure of water, whose molecules, due to extensive association, form certain three-dimensional structures. Upon mixing with another organic liquid, these structures undergo substantial transformations, and are converted into both quasi-clathrate structures and mixed molecular complexes, the latter produced by interactions occurring through the network of hydrogen bonds [2]. These phenomena are caused by the processes of hydrophilic and hydrophobic hydration.

So far, one-substituted amides have been used as the non-electrolyte in the studies of aqueous solutions of non-electrolytes [3-5]. As is generally known [3, 6],

amides in the liquid state form chain multimers owing to the occurrence of intermolecular hydrogen bonds. The topicality of investigations of liquid amides is also conditioned by the fact that similar hydrogen bonds of the type $N-H \cdots O$, play an important role in the stabilization of the structure of complex protein molecules.

There is a question what kind of interaction we can expect in non-aqueous solutions of amides. As a solvent methyl alcohol was chosen. The other component was *N,N*-diisobutylformamide, which is a disubstituted amide. Since this amide has alkyl with the saturated character the creation of hydrogen bond between its molecules is more difficult. Sometimes the group $\equiv C-H$ can constitute a proton-donor group yet. Together with oxygen atom it gives possibility to create a weak hydrogen bond between DBFA molecules. The present paper discusses the examination of methanol solutions of *N,N*-diisobutylformamide. Thus, the purpose of the study was to ascertain whether the self-association of both the alcohol and the amide will be more extensive, or the previous structure of components will be destroyed and mixed complexes will form.

A method of studying intermolecular interactions and the development of complexes in solutions is the determining of excessive and partial values of certain thermodynamic functions. The acoustic method focuses on determining the values of the adiabatic compressibility of the solutions by means of measuring the velocity of propagation of ultrasonic waves. Another necessary quantity to be established is the density of the solutions. This measurement, in turn, provides additional information on the ratio of volumes in the investigated solutions, and thereby generates data for volumetric studies.

2. The method of study

The concentration of the solutions to be studied was expressed as the mole fraction x_2 of *N,N*-diisobutylformamide.

The solutions were prepared using methyl alcohol (CH_3OH) marked "pure for analyses", made by the company Odczynniki, Poland (contents of $H_2O < 0.05\%$), and *N,N*-diisobutylformamide ($HCON[CH_2CH(CH_3)_2]_2$), marked "pure", made by Fluka AG, Switzerland (contents of $H_2O < 0.03\%$).

The ultrasonic velocity in the solutions under study was measured with MATEC (USA) equipment, using the method of *echo overlap* [7]. This method consists in measuring the time of the passage of each echo of the transmitted pulse; the time corresponds to the phase lag of an elastic wave over a given length of the specimen. The frequency of the ultrasonic transducers was 2.92 MHz. The relative error of the measurement of the velocity of ultrasound was no more than 0.01% throughout the range of concentration and temperature.

The density of the solutions was measured using the submersion diver method, which based on Archimedes' principle of buoyancy. In this case, the relative error was no more than 0.02%.

All measurements were taken at three temperatures: -5 , $+5$ and $+15^\circ C$, the medium being thermostatic with an accuracy of $0.05^\circ C$; temperature was measured by means of a platinum thermistor operating in a Wheatstone bridge circuit, with an accuracy of $0.025^\circ C$.

3. The results of the experiments

Experimental results of the measurements of ultrasonic velocity c and of the density ρ of the medium in the system methanol-DBFA are presented for concentration and temperature in Table I. Figures 1 and 2 present the same results graphically. The curves representing both quantities are eminently nonlinear regarding the composition, which obviously testifies to intermolecular interactions between the components of the solution. However, sound velocity and density are not molar quantities, therefore the determination of the composition of the complexes is made more difficult.

TABLE I

The ultrasonic velocity and density in the system of CH₃OH-DBFA.

x_2 mol.frac.	Temperature [°C]					
	-5		5		15	
	c [m/s]	ρ [10 ³ kg/m ³]	c [m/s]	ρ [10 ³ kg/m ³]	c [m/s]	ρ [10 ³ kg/m ³]
0	1209.29	0.81525	1172.19	0.80595	1136.87	0.79665
0.0499	1245.79	0.83205	1212.45	0.82133	1178.31	0.81395
0.1001	1279.04	0.84302	1245.39	0.83420	1211.39	0.82511
0.1999	1328.97	0.85948	1294.23	0.84976	1259.48	0.84225
0.3001	1362.19	0.86950	1327.99	0.86044	1292.60	0.85248
0.3997	1386.10	0.87620	1351.28	0.86716	1316.11	0.86008
0.5001	1403.99	0.88093	1373.68	0.87155	1333.93	0.86523
0.6000	1417.69	0.88444	1387.83	0.87542	1347.66	0.86889
0.7002	1428.21	0.88686	1398.32	0.87789	1358.39	0.87184
0.8006	1436.33	0.88899	1405.17	0.87981	1366.50	0.87358
0.9005	1442.56	0.89041	1411.26	0.8814	1373.19	0.87558
1	1452.50	0.89183	1416.58	0.88265	1378.08	0.87674

TABLE II

The values of the coefficients of the exponential function describing dependences $c = f(x_2)$, $\rho = f(x_2)$ and $\beta_s = f(x_2)$.

	Temperature [°C]								
	-5	5	15	-5	5	15	-5	5	15
	values for c			values for ρ			values for β_s		
c_1	1480	1436	1404	0.8955	0.8874	0.8799	4.9122	5.5307	5.8469
c_2	-112	-80	-100	-0.053	-0.045	-0.066	2.0466	0.8986	1.3008
c_3	-0.185	-0.176	-0.165	-0.381	-0.446	-0.333	0.1558	0.0893	0.0969
c_4	-160	-183	-0.167	-0.027	-0.036	-0.017	1.4300	2.6029	2.5625
c_5	-0.59	-0.44	-0.53	-0.113	-0.139	-0.088	-0.800	0.3235	0.3700
	δc [m/s]			$\delta \rho$ [10 ³ kg/m ³]			$\delta \beta_s$ [10 ⁻¹⁰ m ² /N]		
$\pm$	1.52	1.37	0.340	0.0003	0.0003	0.0003	0.0079	0.0096	0.0044

Attention: δ — a standard deviation for the fitting of the curves.

Fig. 1. The dependence of ultrasonic velocity on concentration in the system of methanol-DBFA (x_2 — mole fraction of DBFA).

Fig. 2. The dependence of density on concentration in the system of methanol-DBFA (x_2 — mole fraction of DBFA).

The coefficient of adiabatic compressibility β_s was given by Laplace's formula ($\beta_s = 1/\rho c^2$).

It appeared that the dependence of the velocity of ultrasound, the density of the solutions and the coefficient of adiabatic compressibility, on the concentration

could be expressed by an exponential function of the type

$$y = c_1 + c_2 \exp(x/c_3) + c_4 \exp(x/c_5), \quad (1)$$

where y is c , ρ or β_s ; $x = x_2$; Table II presents the values of the coefficients $c_1 \dots c_5$.

4. The analysis of the results

4.1. The excessive functions of molar volume and adiabatic compressibility

One of the methods of determining the composition of the molecular complexes developing in a solution is the investigation of the dependence of the excessive functions of certain thermodynamic quantities on the composition of the solution. The measurements described above made it possible to determine the values of excessive molar volume ΔV_m and excessive molar adiabatic compressibility $\Delta(V_m\beta_s)$. As these values are molar quantities, they afford a comparison of the properties of the solutions and a study of selected systems of liquids [5].

To determine the above-mentioned functions, the molar volume of the solutions V_m was calculated ($V_m = [(1 - x_2)M_1 + x_2M_2]/\rho - M_1$ and M_2 are the molecular weight of, respectively, methyl alcohol and DBFA).

The excessive function of molar volume was determined using the formula

$$\Delta V_m = V_m - [(1 - x_2)V_1 + x_2V_2], \quad (2)$$

where V_1 and V_2 are the molar volume of, respectively, methyl alcohol and DBFA.

Based on the calculated molar volume V_m and the coefficient of adiabatic compressibility β_s the values of molar adiabatic compressibility $V_m\beta_s$ were calculated ($V_m\beta_s = -(\partial V/\partial p)_s$). The following formula gave the value of the excessive function of adiabatic compressibility:

$$\Delta(V_m\beta_s) = V_m\beta_s - [(1 - x_2)(V_m\beta_s)_1 + x_2(V_m\beta_s)_2], \quad (3)$$

where $(V_m\beta_s)_1$ and $(V_m\beta_s)_2$ are the adiabatic compressibility of, respectively, methyl alcohol and DBFA.

Figure 3 presents the dependence of the excessive molar volume V_m , and Fig. 4, of the excessive adiabatic compressibility $\Delta(V_m\beta_s)$, on the mole fraction of DBFA. These relationships may be expressed using the Redlich-Kister polynomial (the solid lines in Figs. 3 and 4) [8]:

$$y = x(1 - x) \sum_{i=1}^n a_i(1 - 2x)^{i-1}, \quad (4)$$

where y is ΔV_m or $\Delta(V_m\beta_s)$; $x = x_2$; Table III presents the values of the coefficients of the polynomial a_i .

For the entire concentration range we can observe a decrease in the molar volume and compressibility of the solution. The decrease indicates an increase in the association degree of molecules and a stronger intermolecular interaction between components in the solution as compared with pure components. This indicates the "stiffening" of the solution structure and an increase in the energy of near-arrangement in the liquid, too.

As can be noticed, both quantities ΔV_m and $\Delta(V_m\beta_s)$ reach minimum in the interval concentration 0.33–0.5 mole fraction of amide. Hence, the most likely

Fig. 3. The dependence of the excess molar volume on concentration in the system of methanol-DBFA (x_2 — mole fraction of DBFA).

TABLE III

The values of the coefficients of the Reidlich-Kister polynomial for the functions $\Delta V_m = f(x_2)$ and $\Delta(V_m\beta_s) = f(x_2)$.

	Temperature [°C]					
	-5	5	15	-5	5	15
	values for ΔV_m			values for $\Delta(V_m\beta_s)$		
a_1	1.493	1.566	1.553	5.725	8.735	9.772
a_2	0.522	0.344	0.166	4.495	2.081	4.147
	$\delta(\Delta V_m)$ [10^{-6} m ³ /mol]			$\delta[(\Delta V_m\beta_s)]$ [10^{-15} m ⁵ /(N mol)]		
$\pm$	0.016	0.022	0.025	0.11	0.10	0.12

Fig. 4. The dependence of the excess molar compressibility on concentration in the system of methanol-DBFA (x_2 — mole fraction of DBFA).

molecular complexes being formed in the solutions will assume the form: DBFA: CH_3OH and DBFA: $2 \times \text{CH}_3\text{OH}$. Due to the break-up of self-associates of methanol and amide, mixed complexes were created; they were formed through the hydrogen bond. The above can be presented diagrammatically as follows:

The position of the minimum in the curves which represent both excessive functions, and the values of this minimum shift when temperature varies, because of the changes in the thermodynamic equilibrium and in the quantitative ratio of the various types of mixed complexes.

4.2. The partial molar volume and the partial molar compressibility

Partial molar volume and partial molar compressibility are quantities which characterise the behaviour of individual components in the solution.

A characteristic behaviour of partial molar volumes of components in the solution has been obtained from the dependence of the density of solutions on the concentration. Partial molar volume $\bar{V}_1$ of the alcohol and the amide $\bar{V}_2$ were calculated from the following relations:

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{n_2, p, T} = \frac{M_1 \rho + [M_1(1 - x_2) + M_2 x_2] x_2 \left(\frac{\partial \rho}{\partial x_2} \right)}{\rho^2}, \quad (5)$$

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2} \right)_{n_2, p, T} = \frac{M_2 \rho - [M_1(1 - x_2) + M_2 x_2](1 - x_2) \left(\frac{\partial \rho}{\partial x_2} \right)}{\rho^2}. \quad (6)$$

The partial derivative $\partial \rho / \partial x_2$ was determined by a differentiation of Eq. (2), applying the values of the coefficients presented in Table II.

Figure 5 presents the relationships of the values of the partial molar volume of the components of the solution, expressing them as relative changes regarding the concentration $(\bar{V}_i - \bar{V}_i^0) / \bar{V}_i^0 = f(x_2)$ ($\bar{V}_i^0$ is the molar volume of the pure component). This method of illustrating the results was chosen to determine which of components of the solution has a decisive influence on the total change of the molar volume of solution ΔV_m .

An analysis of the shape of the curves which represent the partial molar volume regarding the concentration (Fig. 5) yields the following conclusions.

Generally, the changes of partial molar volumes in solutions are rather small, especially for region with the low concentration of amide.

For the concentration about 0.3 mole fraction of amide each component accounts to a similar degree for the changes in the volume of the solution; in the interval of concentration of 0.3...0.1, it is mainly methyl alcohol which accounts for such changes. The self-associated molecules of alcohol were permanently destroyed.

The small extreme of the partial molar volume is observable at the temperatures of 5°C and -5°C, in the interval of concentration where the mole fraction of the amide amounts to 0...0.1. Because in this region of concentration we have only three experimental points the clear interpretation of these results is difficult. We must take into consideration the error of measurements, too.

The values of the partial molar adiabatic compressibility of the alcohol K_1 and the amide K_2 was calculated based on the dependence of the coefficient of the adiabatic compressibility of the solutions on the concentration. The partial derivative $\partial \beta_s / \partial x_2$ was determined by a differentiation of Eq. (2), applying the

Fig. 5. The dependence of the partial molar volumes on concentration in the system of methanol-DBFA (x_2 — mole fraction of DBFA).

values of the coefficients presented in Table II. The following relationships were used in the calculations:

$$K_1 = -\frac{\partial \bar{V}_1}{\partial p} = \beta_s \bar{V}_1 - V_m x_2 \frac{\partial \beta_s}{\partial x_2}, \quad (7)$$

$$K_2 = -\frac{\partial \bar{V}_2}{\partial p} = \beta_s \bar{V}_2 + V_m (1 - x_2) \frac{\partial \beta_s}{\partial x_2}. \quad (8)$$

Figure 6 presents the relationships of the values of the partial molar volume of the components of the solution, expressing them as relative changes in the partial molar compressibility regarding to the concentration $(K_i - K_i^0)/K_i^0$ (K_i^0 is the molar compressibility of the pure component).

The partial molar compressibility of the components of the solution follows similar patterns (Fig. 6) as the partial molar volume (Fig. 5). In the interval of concentration where the mole fraction of the amide amounts to 0.3 ... 1, it is mainly the alcohol which accounts for the changes in the elasticity of the medium, while

Fig. 6. The dependence of the partial molar compressibility on concentration in the system of methanol-DBFA (x_2 — mole fraction of DBFA).

in the interval of 0...0.3, the compressibility of the solutions is determined by the destruction of the structures of the amide aggregates.

The relations $K_1(x_2)$ and $K_2(x_2)$ point to a strong intermolecular interaction between component in the solutions and mixed complex formation, especially in the range of low concentrations.

5. Conclusions

Ultrasonic and volumetric studies of the alcoholic solutions of *N,N*-diisobutylformamide suggest that the following type of intermolecular interaction occurs there.

Within the concentration of 0.33...0.5 mole fraction of amide the influence of two substances which form self-associates, i.e., methanol and amide under investigation, leads to the formation of mixed complexes composed of DBFA:CH₃OH and DBFA:2×CH₃OH, while at the same time own associates are being broken up. The given molecular complexes originate due to the existence of a hydrogen bond

between the molecules of methanol and DBFA. The responsibility for the change of molar volume and adiabatic compressibility of the solution is mainly borne by methanol, which destroys its self-associated molecules.

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