Enthalpy characteristics of dilute solutions of acetonitrile

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The enthalpies of mixing of acetonitrile with formamide, *N*-methylformamide, *N,N*-dimethylformamide, and hexamethylphosphoric triamide were measured in the temperature interval from 283.15 to 328.15 K. The enthalpy coefficients of binary and ternary interactions were calculated by the methods of the McMillan—Mayer theory. The contributions to the enthalpy of solution due to the formation of a cavity in the solvent, $\Delta_{cav}H^\circ$, and those due to the interaction of the solute with the solvent, $\Delta_{int}H^\circ$, were determined. The enthalpies of the specific and non-specific solvation of acetonitrile in the corresponding amides were calculated. Specific interactions were found to contribute the most to the solvation enthalpy of acetonitrile. The obtained values were compared with analogous values for solutions of acetonitrile in water and alcohols.

Key words: enthalpy of mixing, enthalpy of solution; coefficients of binary interaction; acetonitrile; formamide; *N*-methylformamide; *N,N*-dimethylformamide; hexamethylphosphoric triamide.

Amides and nitriles are widely used in various fields of science and technology as aprotic solvents with good donor-acceptor properties and high dielectric constants. The study of their dilute solutions is of theoretical interest since the principal types of their interactions in the range of low concentrations can be described by invoking several models based on different theoretical approaches.

Experimental

The heats of mixing ($\Delta_m H$) of acetonitrile (AN) with formamide (FA), *N*-methylformamide (MFA), *N,N*-dimethylformamide (DMFA) and hexamethylphosphoric triamide (HMPA) were measured in the composition range $0.00 \le X \le 0.15$ (X is the mole fraction of AN) in the temperature interval from 283.15 to 328.15 K. The measurements were carried out using a hermetically sealed isoperibolic calorimeter with an instrumental error of ±0.5%. The substances used were purified following the known procedures (see Ref. 1 for AN and DMFA, and Ref. 2 for FA, MFA, and HMPA).

Results and Discussion

The obtained values of $\Delta_m H$ of acetonitrile with amides at different temperatures are listed in Table 1. It can be seen that acetonitrile dissolves in FA and MFA with heat consumption, while it dissolves in DMFA and HMPA with heat evolution. The exothermicity of dissolution in HMPA increases while that in DMFA decreases, and the endothermicity of dissolution in FA and MFA decreases as the concentration of acetonitrile in the mixtures increases. This is indicated by the corresponding changes in the enthalpy of solution $\Delta_{sol}H$ ($\Delta_{sol}H = \Delta_m H/X_2$). The exothermicity of dissolution of AN in HMPA increases while that in DMFA decreases, and the endothermicity of dissolution in MFA increases while that in FA decreases as temperature increases.

The experimental data were processed by the methods of the McMillan—Mayer theory.[3] The enthalpy characteristics can be described by equations for the apparent molar enthalpy (Φ_{obs}), and for the relative partial molar enthalpies of the mixture components (L_i) we obtain:

$$\Phi_{obs} = \Delta_{sol}H^\circ - RT^2[1/2(\partial A_{22}/\partial T)_p m^* + \\ + 1/3(\partial A_{222}/\partial T)_p (m^*)^2 + \ldots], \qquad (1)$$

$$L_2 = -RT^2[(\partial A_{22}/\partial T)_p m^* + (\partial A_{222}/\partial T)_p (m^*)^2 + \ldots], \qquad (2)$$

$$L_1 = RT^2[1/2(\partial A_{22}/\partial T)_p (m^*)^2 + \\ + 2/3(\partial A_{222}/\partial T)_p (m^*)^3 + \ldots], \qquad (3)$$

where m^* is N_2/N_1; N_2 and N_1 are the numbers of the solute and solvent molecules, respectively. In addition to the partial molar enthalpy of the solute at infinite dilution ($\Delta_{sol}H^\circ$), Eqs. (1)—(3) also contain the derivatives with respect to temperature of A_{22}, A_{222}, *etc.*, which reflect the contributions from the binary, ternary, *etc.* interactions of the solute molecules with each other in a given solvent to a certain property. These values are given in Table 2. The $\Delta_{sol}H^\circ$ values were obtained by linear extrapolation of the dependence $\Delta_{sol}H = f(X)$ to infinite dilution, and the values of $(\partial A_{22}/\partial T)_p$ and

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 289—293, February, 1997.

1066-5285/97/4602-0274 $18.00 © 1997 Plenum Publishing Corporation

Table 1. Heats of mixing ($\Delta_m H$/J mol^{-1}) of acetonitrile in amides at different temperatures

Solvent	283.15 K		298.15 K		313.15 K		328.15 K	
	X_2	$\Delta_{mix}H$	X_2	$\Delta_{mix}H$	X_2	$\Delta_{mix}H$	X_2	$\Delta_{mix}H$
FA	0.0049	9.09	0.0054	10.02	0.0061	11.17	0.0051	9.49
	0.0090	16.51	0.0102	18.71	0.0119	21.50	0.0108	19.56
	0.0146	26.60	0.0152	27.40	0.0170	30.32	0.0173	30.81
	0.0204	36.65	0.0218	38.83	0.0209	36.94	0.0224	39.28
	0.0266	47.13	0.0271	47.63	0.0270	47.17	0.0269	46.70
	0.0337	58.88	0.0329	57.18	0.0321	55.59	0.0320	55.04
MFA	0.0089	13.08	0.0096	14.19	0.0094	13.81	0.0103	15.18
	0.0162	23.74	0.0179	26.16	0.0171	25.12	0.0180	26.50
	0.0229	33.37	0.0246	35.89	0.0242	35.40	0.0250	36.62
	0.0316	46.02	0.0329	47.80	0.0320	46.76	0.0330	48.29
	0.0394	57.15	0.0395	57.42	0.0388	56.56	0.0404	59.01
	0.0522	75.45	0.0458	66.43	0.0479	69.65	0.0489	71.23
DMFA	0.0062	−4.67	0.0076	−5.71	0.0049	−3.66	0.0041	−3.10
	0.0139	−10.47	0.0148	−11.12	0.0101	−7.55	0.0095	−7.11
	0.0220	−16.48	0.0229	-17.04	0.0150	−11.23	0.0147	−10.97
	0.0280	−20.81	0.0277	−20.56	0.0220	−16.33	0.0206	−15.21
	0.0331	−24.52	0.0322	−23.79	0.0273	−20.13	0.0256	−18.86
	0.0380	−28.01	0.0369	−27.09	0.0343	−25.11	0.0322	−23.52
HMPA	0.0221	−69.53	0.0217	−68.36	0.0234	−73.85	0.0263	−83.19
	0.0402	−126.95	0.0436	−137.99	0.0446	−141.38	0.0475	−150.86
	0.0559	−176.98	0.0558	−177.00	0.0719	−228.86	0.0658	−209.64
	0.0761	−241.69	0.0773	−245.89	0.0890	−284.09	0.0851	−271.89
	0.1035	−329.85	0.1018	−324.84	0.1138	−364.05	0.1049	−335.89
	0.1419	−453.80	0.1328	−424.96	0.1307	−418.76	0.1311	−420.96

Note. X_2 is the mole fraction of acetonitrile.

$(\partial A_{222}/\partial T)_p$ were calculated from Eq. (2). The values of $(\partial A_{22}/\partial T)_p$ and $(\partial A_{222}/\partial T)_p$ in Eqs. (1)—(3) are evidence of solvophobic effects in the mixtures.[3] At the present time, there is no unified approach to the description of solvophobic (solvophilic) effects, which is due to the inadequate theoretical basis as well as to the lack of experimental data and the unsystematic character of the data that exists.[4,5] To draw conclusions concerning the intermolecular interactions, one should compare $(\partial A_{22}/\partial T)_p$ and $(\partial A_{222}/\partial T)_p$ from Table 2 with the analogous values for aqueous and alcoholic solutions of acetonitrile, *i.e.*, for solvents with hydrophobic or possible solvophobic effects. Such values obtained by processing the literature data[6,7] using equations of the type (1)—(3) are listed in Table 3.

Systematic experimental data on many physicochemical properties of aqueous nonelectrolyte solutions have been accumulated. However, attempts at finding an adequate measure of hydrophobicity to unambiguously interpret hydrophobic effects in solution have failed up to now.[4] Even fewer attempts have been made for nonaqueous solutions. Only one thing is clear, that for the manifestation of solvophobic effects in a solution solvophobic groups must be present in the molecule of the dissolved substance and the solvent must be structured. The question of how and to what extent a non-

Table 2. Characteristics of binary and ternary interactions of acetonitrile in amides at different temperatures

T/K	$\Delta_{sol}H°$ /kJ mol^{-1}	$(\partial A_{22}/\partial T)_p \cdot 10^2$	$(\partial A_{222}/\partial T)_p \cdot 10^2$
		K^{-1}	
	Formamide		
283.15	1.890±0.002	1.62	−16.50
298.15	1.885±0.002	1.73	−18.98
313.15	1.877±0.002	1.82	−21.43
328.15	1.874±0.002	1.98	−25.88
	N-Methylformamide		
283.15	1.475±0.001	0.26	−2.58
298.15	1.478±0.001	0.28	−3.38
313.15	1.479±0.001	0.22	−2.05
328.15	1.480±0.001	0.19	−1.53
	N,*N*-Dimethylformamide		
283.15	−0.760±0.001	−0.14	−1.26
298.15	−0.759±0.001	−0.20	−0.03
313.15	−0.757±0.001	−0.20	−0.21
328.15	−0.755±0.001	−0.20	−0.82
	Hexamethylphosphoric triamide		
283.15	−3.132±0.002	0.20	−0.73
298.15	−3.136±0.001	0.21	−0.84
313.15	−3.141±0.002	0.21	−0.85
328.15	−3.146±0.002	0.20	−0.74

Table 3. Characteristics of binary and ternary interactions of acetonitrile in amides, alcohols, and water at 298.15 K

Solvent	$(\partial A_{22}/\partial T)_p \cdot 10^2$	$(\partial A_{222}/\partial T)_p \cdot 10^2$
	K^{-1}	
FA	1.73	−18.98
MFA	0.28	−3.38
DMFA	−0.20	0.03
HMPA	0.21	−0.84
MeOH	0.74	0.68
EtOH	2.28	−2.79
Bu^{n}OH	2.05	−1.65
H_2O	−12.52	42.42

aqueous solvent must be structured so that the properties of its solutions are similar to those of aqueous solutions is left open. Therefore, in a few cases described in the literature, the problem of the presence or absence of solvophobic effects in nonaqueous solvents was solved on the basis of criteria defined for aqueous solutions. Using this approach, one can notice that the $(\partial A_{22}/\partial T)_p$ values (see Table 2 and 3) for solutions of acetonitrile in amides and alcohols are by an order of magnitude smaller than the corresponding values for aqueous solutions of AN, and of opposite sign. This confirms the data reported in Refs. 4, 8—10. The $(\partial A_{22}/\partial T)_p$ values for DMFA solutions were found to be small and positive.[8] As a result, a conclusion on the presence of solvophobic interaction in DMFA has been made. In contrast to aqueous solutions, the driving force of this interaction is enthalpy rather than entropy. No solvophobic effects were observed for DMFA solutions in aliphatic alcohols.[9] The solvophobic effects in methylacetamide have been described in the literature.[10]

Many analogous conclusions have been based on the interpretation of a particular property of the solution. However, it is incorrect, in general, to draw conclusions on the presence (absence) of solvophobic (solvophilic) effects relying on only the thermodynamic property, even though it might be evidence for solvophobicity (solvophilicity).[5]

The values of $(\partial A_{22}/\partial T)_p$ for solutions of AN in amides are of the same sign but are nearly an order of magnitude lower, while the values of $(\partial A_{222}/\partial T)_p$ are negative and coincide with the analogous values for solutions of amides in acetonitrile in their order of magnitude and sign.[11] Relying on these data, one can assume that the energetics of the interaction of acetonitrile molecules in amides is comparable to the energetics of the interaction of amide molecules in acetonitrile. Temperature has little effect on the $(\partial A_{22}/\partial T)_p$ and $(\partial A_{222}/\partial T)_p$ values, so we failed to find any regularities in the changes in the obtained values as the temperature changed.

Apart from the coefficients of binary, ternary, *etc.* interactions, the effect of the solute molecules on the structure of the solvent and the relation of this effect to the values of measured properties when it is not complicated by the interactions of solute molecules can be elucidated from the partial molar values of the solutes at infinite dilution, including $\Delta_{sol}H°$. Interpretation of the partial values is rather complicated and requires some concept. Previously,[12] the assumption was made that in the dissolution of a molecule a cavity is formed in the solvent, whose size corresponds to that of a solute molecule. In addition, the molecule is transferred from the gas phase to this cavity and interacts with the solvent molecules. Therefore, we can write:

$$\Delta_{sol}H° = \Delta_{ev}H° + \Delta_{cav}H° + \Delta_{int}H° - RT + \alpha_{ex}RT^2, \quad (4)$$

where $\Delta_{ev}H°$ is the enthalpy of vaporization of the solute, $\Delta_{cav}H°$ is the change in the partial molar enthalpy related to cavity formation in the solvent, $\Delta_{int}H°$ is the change in the partial molar enthalpy related to the interaction between the solute and the solvent, and α_{ex} is the coefficient of thermal expansion of the solvent.

Calculations of the contribution from the formation of the cavity in the solvent were carried out using the scale particles theory (SPT),[13] and temperature changes in the diameter of the hard sphere of the solvent molecule:[14]

$$\Delta_{cav}H° = RT^2 \frac{\alpha_{ex} - 3\lambda_1}{(1-J)^3} \times$$
$$\times \left\{(1-J)^2 + 3(1-J)\frac{\sigma_1}{\sigma_2} + 3(1+2J)\frac{\sigma_1^2}{\sigma_2^2}\right\} -$$
$$- RT^2 \frac{3J}{1-J} \cdot \frac{\sigma_2}{\sigma_1} \cdot \left(1 + \frac{2+J}{1-J} \cdot \frac{\sigma_2}{\sigma_1}\right)\lambda_1 + \frac{\pi}{6} pN_A\sigma_2^3, \quad (5)$$

where $J = \pi/6 \cdot \sigma_2{}^3 \cdot N_A/V_s$ is the packing coefficient of the solvent molecules; σ_1 and σ_2 are the diameters of hard spheres of the solvent and the solute, respectively; V_s is the molar volume of the pure solvent; $\lambda_1 = (\partial \ln\sigma_1/\partial T)_p$; p is the external pressure; N_A is the Avogadro constant.

Knowing $\Delta_{cav}H°$, one can determine $\Delta_{int}H°$ from Eq. (4). The values of $\Delta_{cav}H°$ and $\Delta_{int}H°$ obtained are given in Table 4.

Table 4. Values of $\Delta_{cav}H°$ and $\Delta_{int}H°$ of acetonitrile in amides at varied temperatures (T/K)

Solvent	$\Delta H°$ /kJ mol^{-1}	283.15	298.15	313.15	328.15
FA	$\Delta_{cav}H°$	11.65	12.72	13.83	14.95
	$\Delta_{int}H°$	−40.80	−41.81	−42.88	−43.96
MFA	$\Delta_{cav}H°$	14.03	15.16	16.37	17.61
	$\Delta_{int}H°$	−43.66	−44.75	−45.92	−47.13
DMFA	$\Delta_{cav}H°$	22.26	23.45	24.60	25.71
	$\Delta_{int}H°$	−54.20	−55.35	−56.46	−57.54
HMPA	$\Delta_{cav}H°$	14.14	14.83	15.49	16.14
	$\Delta_{int}H°$	−48.38	−49.01	−49.62	−50.23

Table 5. Enthalpy characteristics (kJ mol^{-1}) of acetonitrile in amides, alcohols, and water at 298.15 K

Solvent	$\Delta_{sol}H^\circ$	$\Delta_s H^\circ$	$\Delta_{cav}H^\circ$	$\Delta_{int}H^\circ$
FA	1.89	−31.02	12.72	−41.81
MFA	1.48	−31.42	15.16	−44.75
DMFA	−0.76	−33.66	23.45	−55.35
HMPA	−3.14	−36.04	14.83	−49.01
MeOH	3.93	−28.97	13.03	−40.39
EtOH	6.40	−26.50	12.16	−37.00
Pr^{n}OH	8.17	−24.73	11.00	−34.00
Bu^{n}OH	9.13	−23.77	16.59	−38.56
H_2O	−1.56	−34.46	4.46	−36.63

Note. The enthalpy of vaporization of acetonitrile, $\Delta_{vap}H$, equals 32.90 kJ mol^{-1}.

Analogous values for acetonitrile solutions in several alcohols and water are listed in Table 5. As can be seen from the data of Tables 4 and 5, the $\Delta_{cav}H^\circ$ values are positive and nearly the same for all solvents mentioned, except water and DMFA. The insignificant difference between $\Delta_{cav}H^\circ$ for acetonitrile in various solvents can be explained by the fact that the decrease in the packing coefficient of the solvent molecules as the molar volume of the solvent increases is compensated for by the increase in the σ_1/σ_2 ratio in Eq. (5). A temperature increase results in an increase in the endothermicity of $\Delta_{cav}H^\circ$ values. On the other hand, the $\Delta_{int}H^\circ$ values are negative, and their exothermicity increases as temperature increases.

The enthalpy of solvation $\Delta_s H^\circ$ ($\Delta_s H^\circ = \Delta_{sol}H^\circ - \Delta_{vap}H^\circ$) can be divided into two components:

$$\Delta_s H^\circ = \Delta_s^{sp} H^\circ + \Delta_s^{nsp} H^\circ \quad , \tag{6}$$

the specific enthalpy of solvation, $\Delta_s^{sp}H^\circ$, and the nonspecific enthalpy of solvation, $\Delta_s^{nsp}H^\circ$.

The $\Delta_s^{sp}H^\circ$ value is due to the formation of bonds between the molecules according to a donor-acceptor mechanism and hence reflects the donor and acceptor ability of a substance. Other types of interactions are included in $\Delta_s^{nsp}H^\circ$. Previously,[15] empiric equations were suggested which allowed one to calculate $\Delta_s^{sp}H^\circ$ for nonelectrolytes in solvents not associated by H-bonds. To increase the accuracy of the calculation using the (σ/ξ) criterion for electron donors ($\sigma/\xi > 1.442$) and electron acceptors ($\sigma/\xi < 1.442$) (where $\sigma = 8.83 + 0.04337\ DN_{SbCl_6}$; $\xi = 6.125 + 0.029\ AN$ [16]), two equations were obtained.[15]

For electron-donor nonelectrolytes:

$$\Delta_s^{sp} H^\circ = (0.023 - 0.013\ AN_{sub})DN_{solv} + \\ + (0.66 - 0.054\ DN_{sub})AN_{solv}; \tag{7}$$

For electron-acceptor nonelectrolytes:

$$\Delta_s^{sp} H^\circ = (-0.03 - 0.02\ AN_{sub})DN_{solv} + \\ + (-0.34 - 0.021\ DN_{sub})AN_{solv}. \tag{8}$$

The indices "sub" and "solv" refer to the solute and the solvent, respectively.

Equations (7) and (8) contain donor and acceptor numbers for the dissolved substance and for the solvent (DN_{sub}, DN_{solv}, and AN_{sub}, AN_{solv}, respectively), *i.e.*, not only the effect of the medium but also the effect of the solute is taken into account.

The following equation has been proposed[15] to calculate the enthalpy of non-specific solvation:

$$\Delta_s^{nsp} H^\circ = -7.5 - V_w[0.091 - 4.42 \cdot 10^{-4}\sigma^2_{solv} + \\ + 1.616(n^2_{sub} - 1)/(n^2_{sub} + 2)], \tag{9}$$

where V_w is the van der Waals molar volume of the solute (calculated from the contributions taken from Ref. 17), $\sigma^2{}_{solv}$ is the density of the cohesion energy, and n_{sub} is the refractive index of the solute.

Equations (8) and (9) were used in calculations in the case of acetonitrile since it has a σ/ξ ratio of 1.415 and is an electron acceptor (according to the classification given above). The results obtained are listed in Table 6.

The acetonitrile molecule is an electron donor in the formation of H-bonds with the molecules of FA, MFA, alcohols, and water (the nitrogen atom is the donor).[18] In compounds with DMFA and HMPA, which are stronger electron donors, AN exhibits acceptor properties.[18,19] This can be clearly seen from the data of Table 6, where the values of the first and second terms of Eq. (8) are given in the first and second columns, respectively. The first term reflects specific interactions in solutions, where the solute acts as an electron acceptor while the solvent acts as an electron donor. The second term, on the other hand, reflects the donor properties of the solute and the acceptor properties of the solvent. For FA, MFA, alcohols, and water, AN serves as an electron donor, and the major contribution to the enthalpy of specific solvation is from the second term. For mixtures of AN with DMFA and HMPA (which are stronger electron donors than AN), the first term of Eq. (8) is crucial. As was shown in Ref. 20, the

Table 6. Values of $\Delta_s^{sp}H^\circ$ and $\Delta_s^{nsp}H^\circ$ (kJ mol^{-1}) of acetonitrile in amides, alcohols, and water at 298.15 K

Solvent	$-\Delta_s^{sp}H^\circ$			$-\Delta_s^{nsp}H^\circ$	$-\Delta_s H^\circ$
	I	II	(I + II)		
FA	9.79	25.31	35.10	3.02	38.12
MFA	9.46	17.75	27.21	7.62	34.83
DMFA	10.85	10.18	21.03	13.56	34.59
HMPA	15.83	6.74	22.57	15.27	37.84
MeOH	7.79	26.27	34.06	8.96	43.02
EtOH	7.83	23.60	31.43	11.24	42.67
Pr^{n}OH	8.08	22.26	30.34	12.23	42.57
Bu^{n}OH	7.96	19.53	27.49	12.79	40.28
H_2O	7.34	34.86	42.20	9.08	33.12

Note. I and II are the values of the first and the second terms in Eq. (8), respectively.

methyl protons of DMFA and HMPA as well as the formyl proton of DMFA do not participate in the formation of molecular complexes and associates in mixtures of these amides with AN. The C=O and P=O groups are electron-donor centers in the DMFA and HMPA molecules, respectively. Dipole-dipole interactions play a determining role in the association processes for mixtures of DMFA and HMPA with AN.[20] The exothermicity of the $\Delta_s^{nsp}H^o$ values increases in the series of solvents FA < MFA < DMFA < HMPA, and a constant contribution to $\Delta_s^{nsp}H^o$ of about 5 kJ mol^{-1} can be noted in the homologous formamide series. The values of the enthalpy of solvation obtained by Eq. (6) are listed in Table 6 and coincide well with the expermental data (see Table 5) for solvents not associated due to H-bonds (DMFA and HMPA). Good agreement is also observed for water. The distinctions obtained from experimental data and by Eq. (6) between the enthalpy of solvation of AN in FA and particularly in alcohols associated *via* H-bonds apparently reflect their inner self-association.

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Received December 9, 1995;
in revised form July 25, 1996