Solvophobic effects in binary nonaqueous mixtures

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In the framework of the McMillan—Mayer theory, the enthalpy, volume, and heat capacity coefficients of binary and ternary interactions of amides, alcohols, and acetonitrile in water and nonaqueous solvents were obtained at various temperatures. No pronounced regularities in changes in the coefficients of multiple interactions observed in aqueous solutions were found for nonaqueous solutions of the substances studied. None of the considered coefficients can be used as a criterion for solvophobicity.

Key words: aqueous and nonaqueous solutions, amides, alcohols, acetonitrile; McMillan—Mayer theory, coefficients of binary and ternary interactions; solvophobic effects; hydrophobic hydration, criteria for hydrophobicity.

At the present time, there is no unified approach to the description of solvophobic (solvophilic) effects. This is due to the inadequate theoretical basis as well as to the lack of experimental data and the unsystematic character of the data that exist. At the same time, the important role of solvophobic (and particularly hydrophobic) effects in wild life[1] calls for their systematic investigation. To promote further development of the theory of solvophobic effects, studies of diluted solutions are needed, since the principal types of interactions in solution at low concentrations of a solute can be described using theoretical methods.[2,3]

In the framework of the McMillan—Mayer theory,[2] experimental data are represented as polynomials of degrees in concentration; the coefficients of these polynomials correspond to the contributions to a certain thermodynamic property of the system from binary, ternary, and other multiple interactions of the solute molecules with one another in a certain solvent.

Expansions for certain molar thermodynamic functions can be described as follows:

— for the apparent molar volume[4]

$$\Phi_{v2} = \bar{v}^\circ + v_{22}m + v_{222}m^2 + \ldots; \tag{1}$$

— for the apparent molar heat capacity[4]

$$\Phi_{C_{p2}} = \bar{C}^\circ_{p2} + c_{22}m + c_{222}m^2 + \ldots; \tag{2}$$

— for the solution enthalpy[5]

$$\Delta_{\rm solv}H^m = \Delta_{\rm solv}H^\circ + h_{22}m + h_{222}m^2 + \ldots . \tag{3}$$

Here v, c, and h are the volume, heat capacity, and enthalpy coefficients for different (binary, ternary, *etc.*) interactions of the solute molecules, respectively.

As has been shown in several works,[4,6,7] the derivative of the second virial coefficient with respect to pressure $(\mathrm{d}B_{22}/\mathrm{d}p)_T$ is the most appropriate parameter for comparing hydrophobicities of compounds,[1] *i.e.*, hydrophobic effects are to a large extent related to the volume characteristics of the solution components. However, to calculate the $(\mathrm{d}B_{22}/\mathrm{d}p)_T$ values, numerous experimental data are needed which are not readily available. Therefore, easier accessible quantities, namely, the contributions from coefficients of binary, ternary, and other multiple intermolecular interactions to the studied thermodynamic properties and their derivatives are used by many authors.[8—16] In most cases they are the enthalpy (h),[10,11] heat capacity (c),[12,13] and volume (v)[14,15] coefficients. The commonly used practice is determination of coefficients h, v, and c from experimental data using equations of the type (1)—(3) and their comparative analysis without interpreting the values. Despite the fact that this procedure is easier, the obtained characteristics are less accurate and informative than the $(\mathrm{d}B_{22}/\mathrm{d}p)_T$ parameter. However, if the experimental data are reliable, then the h, v, and c values give adequate information on the hydrophobic properties of the substances. This is most clearly seen in the case of aqueous solutions of nonelectrolytes forming homologous series.

Experimental

Using experimental and published data, we calculated the enthalpy, volume, and heat capacity coefficients of binary and ternary interactions for the solutions of acetonitrile (MeCN) in formamide (FA), *N*-methylformamide (MFA), *N,N*-dimethylformamide (DMF), and hexamethylphosphoric triamide (HMPA) and analogous coefficients for the solutions of these amides in

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Table 1. Coefficients of binary and ternary interactions of amides in water at different temperatures

Amide	T/K	h_{22}	h_{222}	T/K	v_{22}	v_{222}	T/K	c_{22}	c_{222}
FA	278.15	−155.1	−6.142	298.15	0.090	−0.004	283.15	2.310	−0.0293
	298.15	−108.0	3.466	308.15	0.072	0.004	293.15	1.657	−0.0203
	308.15	−86.80	1.980	318.15	0.054	−0.005	303.15	1.197	−0.0145
	318.15	−85.76	2.479				313.15	0.871	−0.0101
MFA	298.15	274.1	−9.24	278.15	−0.240	—	283.15	−2.33	0.1140
	308.15	271.1	−9.24	288.15	−0.160	—	293.15	−2.59	0.0896
	318.15	264.0	−15.0	298.15	−0.150	—	303.15	−2.92	0.0858
				308.15	−0.150	—	313.15	−3.40	0.0946
				318.15	−0.110	—			
DMF	298.15	523.6	3.50	293.15	−0.464	0.039	278.15	−2.280	0.035
	308.15	394.1	43.51	298.15	−0.337	0.021	298.15	−2.498	0.032
	318.15	217.9	109.5	303.15	−0.345	0.024	323.15	−3.796	0.049
				308.15	−0.162	0.010			
				313.15	−0.155	0.009			
				323.15	−0.039	0.002			
HMPA	298.15	5160.0	−242.2	283.15	−3.168	0.499	283.15	−41.83	10.990
	308.15	4846.0	−253.7	288.15	−7.471	1.798	288.15	−41.54	9.618
	318.15	4475.0	−266.0	293.15	−11.40	2.921	293.15	−43.85	8.830
				298.15	−11.80	3.058	298.15	−46.92	3.990

Note. Hereafter the coefficients h_{22} are given in J kg mol^{-2}; h_{222} in J kg^{2} mol^{-3}; v_{22} in cm^{3} kg mol^{-2}; v_{222} in cm^{3} kg^{2} mol^{-3}; c_{22} in J kg mol^{-2} K^{-1}; and c_{222} in J kg^{2} mol^{-3} K^{-1}.

Table 2. Coefficients of binary and ternary interactions of amides in acetonitrile (subscript 1) and those of binary and ternary interactions of acetonitrile in amides (subscript 2) at different temperatures

Amide	T/K	h_{22}	h_{222}	v_{22}	v_{222}	c_{22}	c_{222}	h_{11}	h_{111}	v_{11}	v_{111}	c_{11}	c_{111}
FA	283.15	−1398	50.97	0.781	−0.099	0.449	−0.020	−243	74	0.057	−0.010	0.967	−0.059
	298.15	−1284	56.56	0.973	−0.149	0.331	−0.015	−260	85	0.119	−0.015	0.807	0.013
	313.15	−1258	67.42	1.602	−0.217	0.290	−0.019	−273	96	0.136	−0.022	0.358	0.005
	328.15	−1223	79.18	2.128	−0.265	0.161	−0.012	−297	116	0.207	−0.023	0.310	−0.061
MFA	283.15	−811	−1.19	0.032	0.015	−0.021	−0.005	−51	20	0.014	0.002	0.000	−0.005
	298.15	−763	15.32	0.078	−0.003	−0.059	−0.007	−55	26	0.048	0.008	−0.008	−0.019
	313.15	−716	30.52	0.107	−0.004	−0.085	−0.012	−42	16	0.065	0.012	−0.010	−0.011
	328.15	−670	36.21	0.189	−0.021	−0.103	−0.017	−37	12	0.120	0.018	−0.020	−0.007
DMF	283.15	−127	−79.49	−0.174	0.048	−0.290	0.003	−760	35	−0.225	0.078	0.287	−0.132
	293.15	—	—	—	—	−2.566	0.392	—	—	—	—	−0.415	0.163
	298.15	−159	−61.23	−0.152	0.031	−2.921	0.465	−760	48	0.062	−0.010	−0.019	—
	303.15	—	—	—	—	−3.246	0.470	—	—	—	—	−0.329	0.103
	313.15	−175	−48.26	−0.128	0.021	−3.809	0.475	−757	50	1.141	−0.358	−0.463	0.215
	323.15	—		—	—	−4.075	0.647	—	—	—	—	0.284	−0.105
	328.15	−185	−42.50	−0.126	0.019	—	—	−755	48	−0.197	0.058	—	—
HMPA	283.15	−2589	−204	−5.061	0.578	9.477	−0.640	−119	52	−23.18	13.86	0.289	−0.117
	298.15	−2928	−462	−5.187	0.656	4.704	−0.248	−126	60	−17.45	7.12	−0.636	0.303
	313.15	−3848	−618	−6.004	1.125	3.448	−0.175	−126	61	−16.36	5.89	−0.123	0.066
	328.15	−5794	−974	−6.769	1.270	1.422	−0.014	−121	53	−15.78	5.28	1.153	−0.500

Note. For the dimensionality of the coefficients, see note to Table 1.

water and MeCN. We also calculated the derivatives of coefficients A_{22} and A_{222} with respect to temperature and pressure for solutions of the above amides in MeCN in the temperature interval from 283.15 to 328.15 K. All the calculations were performed using Eqs. (1)—(3). The enthalpy coefficients of binary and ternary interactions for solutions of FA, MFA, DMF, and HMPA in MeOH, EtOH, and PrOH and those for solutions of these alcohols in the above amides at 313.15 K were also calculated. The results obtained are presented in Tables 1—5. The ratios between the values of the coefficients of binary and ternary interactions and the corresponding A_{22} and A_{222} derivatives have been reported previously.[1,4]

Table 3. Characteristics of binary and ternary interactions of amides in acetonitrile at different temperatures

Amide	T/K	$(\partial A_{22}/\partial T)\cdot 10^2$ /K^{-1}	$(\partial^2 A_{22}/\partial T^2)\cdot 10^4$ /K^{-2}	$(\partial A_{22}/\partial p)\cdot 10^2$ /cm^3 g J^{-1} mol^{-1}	$(\partial A_{222}/\partial T)\cdot 10^2$ /K^{-1}	$(\partial^2 A_{222}/\partial T^2)\cdot 10^4$ /K^{-2}	$(\partial A_{222}/\partial p)\cdot 10^2$ /cm^3 g J^{-1} mol^{-2}
FA	283.15	10.21	−7.75	0.83	−12.57	9.70	−1.29
	298.15	8.94	−6.34	0.62	−13.06	9.36	−1.14
	313.15	7.82	−5.19	0.62	−14.70	9.81	−1.28
	328.15	6.65	−4.15	0.49	−15.80	9.93	−1.04
MFA	283.15	5.90	−4.16	3.12	−1.24	0.93	−10.01
	298.15	5.56	−3.70	2.26	−3.57	2.44	−6.66
	313.15	5.14	−3.27	0.79	−7.50	4.95	−1.97
	328.15	4.57	−2.77	0.70	−6.70	4.42	−1.73
DMF	283.15	1.34	−0.73	0.77	8.19	−5.87	−2.35
	298.15	1.29	1.06	0.66	−1.04	−10.51	−2.15
	313.15	1.28	1.62	0.38	0.97	−14.74	−1.19
	328.15	1.29	1.94	0.24	−2.88	−13.90	−0.50
HMPA	283.15	−4.34	−2.35	1.57	−123.13	96.67	−4.86
	298.15	−0.73	−2.42	0.34	−141.51	99.74	−0.50
	313.15	22.95	−16.36	0,40	−148.18	97.05	−1.01
	328.15	31.66	−20.14	0.54	−154.27	94.74	−1.61

Table 4. Values of $\partial A_{22}/\partial T$ and $\partial A_{222}/\partial T$ for solutions of FA, MFA, and DMF in various solvents at 313.15 K

Solvent	$(\partial A_{22}/\partial T)\cdot 10^2$/K^{-1}			$(\partial A_{222}/\partial T)\cdot 10^2$/K^{-1}		
	FA	MFA	DMF	FA	MFA	DMF
H_2O	1.30	−0.07	−0.10	−2.61	0.01	−0.01
MeCN	7.82	5.14	1.28	−14.70	−7.50	0.97
MeOH	0.97	0.48	0.02	−1.15	−0.42	0.00
EtOH	1.31	0.95	0.91	−1.16	−1.02	−0.74
PrOH	1.96	0.78	1.29	−1.91	−0.58	−1.05

Table 5. Coefficients h_{22} and h_{222} for solutions of amides in alcohols and those for solutions of alcohols in amides at 313.15 K

Solvent	Solute	h_{22}	h_{222}
FA	MeOH	43.4	−0.85
MFA	MeOH	40.6	−0.62
DMF	MeOH	37.2	2.07
FA	EtOH	93.9	−2.40
MFA	EtOH	114.0	−2.87
DMF	EtOH	76.6	−0.41
FA	PrOH	140.0	−3.89
MFA	PrOH	134.5	−3.04
DMF	PrOH	132.7	−1.72
MeOH	FA	−126.0	3.2
EtOH	FA	−245.0	6.7
PrOH	FA	−480.0	18.7
MeOH	MFA	−62.8	1.2
EtOH	MFA	−179.0	5.9
PrOH	MFA	−191.0	5.7
MeOH	DMF	25.3	−2.7
EtOH	DMF	−170.0	4.2
PrOH	DMF	−316.0	10.5

Note. For the dimensionality of the coefficients, see note to Table 1.

Results and Discussion

As can be seen from the data in Tables 1—5, most of the h_{22} coefficients are negative (except for h_{22} for solutions of alcohols in amides) and their absolute values decrease in the sequence FA > MFA > DMF for the amide solutions. The v_{22} values are positive for the solutions of FA and MFA in MeCN (or MeCN solutions in FA and MFA) and negative for the solutions of DMF and HMPA in MeCN (or MeCN solutions in DMF and HMPA). No pronounced regularities in changes in the signs and the values of the c_{22} coefficient for the solutions under study are observed. In the series of aqueous solutions of FA, MFA, and DMF (see Table 1) the h_{22} coefficients are negative for FA and positive for the other compounds. On the other hand, the c_{22} and v_{22} values are positive for FA and negative for MFA and DMF. For HMPA (a typical hydrophobic substance[1,4]) $h_{22} > 0$, $c_{22} < 0$, and $v_{22} < 0$, whereas for FA (a typical hydrophilic substance) $h_{22} < 0$, $c_{22} > 0$, and $v_{22} > 0$, *i.e.*, the corresponding coefficients of binary interactions for hydrophobic and hydrophilic compounds have opposite signs. As follows from data in Table 1, the coefficients of binary interactions change signs on going from FA to amides containing larger numbers of hydrophobic groups in their molecules. As a rule, the absolute values of coefficients of binary interactions in homologous series increase on going from one homologue to another.

However, such a pronounced regularity observed for aqueous solutions is always traced only for v_{22}, being in parallel with the principal criterion for hydrophobicity $(\mathrm{d}B_{22}/\mathrm{d}p)_T$: at 298.15 K, the $(\mathrm{d}B_{22}/\mathrm{d}p)_T$ values ($\times 10^2$ cm^3 mol^{-1} bar^{-1}) for the series FA, MFA, DMF, and HMPA are equal to +0.38, −1.08, −1.78, −31.00, respectively,[4] (see v_{22} in Table 1); the correlation coefficient (r) for the linear dependence $(dB_{22}/dp)_T = f(v_{22})$ is equal to 0.999. The calculations performed showed that a good correlation between the v_{22} values and the number of the methyl groups in the amide molecule (N_C) is observed for aqueous solutions of the above amides (r = 0.998). Thus, adding the Me groups in the series FA, MFA, and DMF makes a constant contribution to v_{22} equal to ~0.2 cm^3 kg mol^{-2}. The h_{22} and c_{22} values in this series change nonmonotonically. The correlation coefficient between the h_{22} and $(dB_{22}/dp)_T$ values is equal to 0.986, that between the h_{22} and N_C values is equal to 0.984; the correlation coefficient between the c_{22} and $(dB_{22}/dp)_T$ values is equal to 0.968, and that between the c_{22} and N_C values is equal to 0.962. In this connection, good correlation should also be observed between the $(dB_{22}/dp)_T$ and N_C values (r = 0.999). The above correlations confirm the conclusion that the hydrophobic effects in aqueous solutions are mostly due to changes in volume in the hydrate environment of the solute molecule.[4]

Temperature is an important factor affecting the structure and state of the substances as well as the intermolecular interactions in solutions. A strong temperature dependence is known to be characteristic of hydrophobic effects.[4] However, temperature dependences of the coefficients of multiple interactions were not studied even in aqueous solutions of the substances in the bulk. Only a few attempts at performing such a type analysis for several systems were made.[17–22] Data listed in Table 1 as well as the published data[1,23] allow one to conclude that the absolute values of the enthalpy and volume coefficients of binary interactions of nonelectrolytes in water decrease as temperature increases, whereas the absolute values of the heat capacity coefficients increase as temperature increases. The temperature dependences of the coefficients of binary interactions for the amide solutions of the homologous series of FA in MeCN are the same as those for their aqueous solutions (see Tables 2 and 3). By analogy with aqueous solutions, where the energy of hydrophobic effects decreases as temperature increases, one may conclude that the energy of solvophobic effects in the acetonitrile solutions of amides also decreases as temperature increases.

The coefficients of ternary interactions for aqueous solutions are, as a rule, an order of magnitude lower than those for binary interactions and have opposite signs.[1] A tendency for their absolute values to increase is observed in the series FA, MFA, and DMF (see Table 1). No analogous regularities in changes in the coefficients of ternary interactions are observed for acetonitrile solutions of the above amides (see Tables 2 and 3). No pronounced tendencies in changes in these coefficients are also observed as temperature varies.

Hydrophobic effects are to a large extent due to the spatial network of hydrogen bonds in water and to their cooperative behavior. The structures with a developed network of hydrogen bonds also exist in other strongly associated solvents (alcohols, formamide, *etc.*); therefore, effects similar to hydrophobic effects should most likely be sought in analogous solvents. However, the authors of Ref. 23, who studied the volume and heat capacity characteristics of the solutions of DMF in several aliphatic alcohols, had not found solvophobic effects. On the contrary, similar effects were observed in solutions of a number of amides in DMF[24] and in those of several higher hydrocarbons in MFA.[25] It is not a certain structure of the solvent that is crucial for the manifestation of solvophobic effects, but correlations in the mutual positions of the solvent molecules and existence of a discrete spatial structure of a liquid.[6] Thus, the solvophobic effects can become apparent in various solvents irrespective of the type of their association. Hence, the study of a wide variety of the properties of various substances might allow one to establish the regularities in their changes and to relate them to the solvophobic effects.

Since the criterion for hydrophobicity $(dB_{22}/dp)_T$ correlates with the N_C values, the values of the coefficients of binary interactions that are also well correlated with N_C can be used to estimate the solvophobic effects in nonaqueous solutions (if there is no opportunity to calculate the $(dB_{22}/dp)_T$ parameter) provided that the nature of these effects in water and nonaqueous solvents remains unchanged. In fact, we found a good correlation between the N_C and h_{22} values (r = 0.998) for solutions of amides in acetonitrile. Correlations between the N_C and v_{22} values and those between the N_C and c_{22} are much worse (r = 0.896 and 0.838, respectively). Good correlation is also observed between the N_C and h_{22} values for the solutions of the same amides in MeOH (r = 0.997, calculated using the published data[26]). Hence it follows that the solvophobic effects are likely to occur in mixtures of amides with MeCN, MeOH, and DMF.[24] Unlike aqueous solutions, the enthalpy factor rather than the entropic factor is the driving force for these effects. At the same time, it was shown previously[27] that the h_{22} coefficients of several nonelectrolytes in DMF do not correlate linearly with the N_C values. Thus, one cannot draw a conclusion on the existence of solvophobic effects in the system based only on coincidence of the dependences for two to three "gross" coefficients. It follows from the above analysis of the dependences of coefficients h, v, and c that none of them can be used as a criterion for the solvophobic properties of the substances in nonaqueous solvents. Because of a lack of necessary data, we failed to calculate the $(dB_{22}/dp)_T$ derivative for the nonaqueous mixtures considered above. It seems likely that this quantity cannot be the same criterion for nonaqueous systems as it is for aqueous solutions.

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