Subscripts

A	denotes pure gas A (CH_4)
B	denotes pure gas B (CO_2)
C	denotes pure gas C (H_2S)
A–C	denotes gas mixture A–C ($CH_4 + H_2S$)
A–B–C	denotes gas mixture A–B–C ($CH_4 + CO_2 + H_2S$)
i	denotes component *i*
m	denotes mixture
n	denotes a nominal outlet condition
1	denotes inlet conditions (P_1, T_1) for gas mixture A–C ($CH_4 + H_2S$)
2	denotes inlet conditions (P_2, T_2) for gas B (CO_2)
0	denotes outlet conditions (P_0, T_0) for the ternary mixture ($CH_4 + H_2S + CO_2$)

Greek Letters

α	constant in BWR equation of state, dm^9/mol^3
γ	constant in BWR equation of state, dm^6/mol^2
α, β, γ, δ	constants in RK2 equation of state, eq 20 and 21; values and units are presented in ref *1*
ΔE_k	change of kinetic energy for gaseous system across calorimeter, J/mol
ΔH	change of molar enthalpy, J/mol
ΔH_m	heat of mixing, J/mol
ρ	gas density, mol/cm^3
ϕ	isothermal Joule–Thomson coefficient, J/(mol MPa)
Ω_a, Ω_b	constants in RK1 equation of state, dimensionless
ω_1, ω_2, ω_3	accentric factors for pure components CH_2, CO_2, and H_2S, respectively, dimensionless

Registry No. CH_4, 74-82-8; CO_2, 124-38-9; H_2S, 7783-06-4.

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Densities and Viscosities of Binary Solvent Mixtures of *N*-Methylacetamide with Aliphatic Alcohols

Liisa Pikkarainen

Department of Chemistry, University of Oulu, SF-90570 Oulu 57, Finland

Densities and viscosities of binary liquid mixtures of *N*-methylacetamide (NMA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol have been determined at 303.15 K. The excess volume, the excess viscosity, and the excess Gibbs energy of activation of flow have been calculated from the experimental data. The role of intermolecular interactions in the mixtures is discussed, and a comparison made with the corresponding binary mixtures of *N*,*N*-dimethylacetamide (DMA).

Introduction

Comparison of the dielectric properties of N-mono- and N,N-disubstituted amides of carboxylic acids on one hand and those of the amides of sulfonic acids on the other has revealed some interesting features. The dielectric permittivities of N-monosubstituted carboxamides are high and are significantly higher than those of the N,N-disubstituted analogues (*1–3*). At the same time, both N-mono- and N,N-disubstituted sulfonamides are characterized by high dielectric permittivities, with somewhat greater values for the N-monosubstituted amides (*1*). The high permittivities of N-monosubstituted carboxamides have been ascribed to formation of long N—H···O═C hydrogen-bonded chains (*3*, *4*), whose existence is supported by spectroscopic studies (*5*, *6*). N-Monosubstituted sulfonamides, for their part, appear to self-associate to cyclic polymers (*7*, *8*), and the high permittivities have been related mainly to the large dipole moments (*1*).

Our recent studies have dealt with the properties of binary mixtures of aliphatic alcohols with *N*-methyl- and *N*,*N*-dimethylmethanesulfonamide (*9*, *10*) and with *N*,*N*-dimethylacetamide (DMA) (*11*). To explore more fully the findings outlined above we continue now with studies on the mixtures of *N*-methylacetamide. Here we report the densities and viscosities of binary mixtures of *N*-methylacetamide (NMA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 303.15 K.

Experimental Section

Materials. Alcohols were the same as in the previous studies (*9–11*). *N*-Methylacetamide (a purum product of Fluka AG, Switzerland) was purified by distillation under reduced pressure followed by fractional crystallizations (*12*).

Measurements were carried out with a digital density meter DMA 40 (Anton Paar K.G., Austria) and Cannon-Ubbelohde viscometers (Cannon Instrument Co, USA) (*13*) as before (*9–11*). The viscosities are expressed in units of centipoise equal to 10^{-3} N s m^{-2}. The experimental values of the density and viscosity of *N*-methylacetamide were 0.950 28 g cm^{-3} and 3.829 cP at 303.15 K (literature values 0.9503 g cm^{-3} (*14*) and 3.836 cP (*15*) (an interpolated value), respectively).

Table I. Densities ρ and Viscosities η of the Binary Mixtures at 303.15 K[a]

x	$\rho/(\mathrm{g\ cm^{-3}})$	η/cP	x	$\rho/(\mathrm{g\ cm^{-3}})$	η/cP
NMA + Methanol					
0.0999	0.814 66	0.644	0.6050	0.912 29	1.778
0.2019	0.841 92	0.798	0.6998	0.923 34	2.134
0.3029	0.864 23	0.980	0.7934	0.932 86	2.561
0.3939	0.881 21	1.175	0.8995	0.942 34	3.140
0.5040	0.898 62	1.457			
NMA + Ethanol					
0.1049	0.804 52	1.108	0.6023	0.895 88	2.084
0.2021	0.824 90	1.237	0.6979	0.910 29	2.402
0.3699	0.857 06	1.520	0.7994	0.924 57	2.792
0.4024	0.862 83	1.584	0.8950	0.937 21	3.236
0.5109	0.881 32	1.833			
NMA + 1-Propanol					
0.1069	0.812 80	1.816	0.5976	0.889 60	2.537
0.1939	0.826 61	1.891	0.6966	0.904 75	2.785
0.3142	0.845 59	2.033	0.7922	0.919 22	3.066
0.3918	0.857 86	2.142	0.9015	0.935 76	3.443
0.4791	0.871 35	2.289			
NMA + 2-Propanol					
0.1100	0.795 74	1.922	0.5547	0.873 12	2.490
0.2078	0.812 76	2.005	0.6962	0.897 81	2.824
0.3061	0.829 80	2.099	0.8005	0.915 95	3.115
0.3988	0.845 94	2.217	0.8927	0.931 91	3.418
0.4962	0.862 91	2.377			
NMA + 1-Butanol					
0.0988	0.814 46	2.320	0.5957	0.883 80	2.820
0.2013	0.827 91	2.369	0.6947	0.899 22	3.015
0.2993	0.841 13	2.428	0.8011	0.916 32	3.259
0.3951	0.854 46	2.527	0.8918	0.931 45	3.503
0.4945	0.868 75	2.651			
NMA + 2-Methyl-2-propanol					
0.0809	0.789 54	4.253	0.5002	0.854 10	3.864
0.1017	0.792 82	4.365	0.6021	0.872 04	3.776
0.2071	0.808 47	4.448	0.7095	0.891 92	3.752
0.3102	0.823 76	4.220	0.8039	0.909 90	3.747
0.4103	0.839 39	4.026	0.9007	0.929 45	3.778

[a] x is the mole fraction of NMA.

Results and Discussion

The experimental results of measurements of densities and viscosities of the binary mixtures are shown in Table I. The excess volume V^E, the excess viscosity η^E, and the excess Gibbs energy of activation of flow ΔG^{*E} were calculated from the experimental data with the following equations:

$$V = [(1 - x)M_1 + xM_2]/\rho \tag{1}$$

$$V^E = V - [(1 - x)V_1^* + xV_2^*] \tag{2}$$

$$\eta^E = \eta - [(1 - x)\eta_1^* + x\eta_2^*] \tag{3}$$

$$\Delta G^{*E} = RT\{\ln \eta V - [(1 - x) \ln \eta_1^* V_1^* + x \ln \eta_2^* V_2^*]\} \tag{4}$$

where ρ, η, and V are the density, viscosity, and molar volume of the mixture, M_1 and M_2 are the molar masses, η_1^* and η_2^* are the viscosities, V_1^* and V_2^* are the molar volumes of the alcohol and NMA, respectively, and x is the mole fraction of NMA.

The results for V^E, η^E, and ΔG^{*E} are plotted in Figures 1–3. They were fitted to the equation

$$Y^E = x(1 - x) \sum_{i=0}^{n} A_i(1 - 2x)^i \tag{5}$$

where Y^E is $V^E/(\mathrm{cm^3\ mol^{-1}})$ or η^E/cP or $\Delta G^{*E}/(\mathrm{J\ mol^{-1}})$. Coefficients A_i of the fitting equation together with the standard deviations $\sigma(Y^E)$ are summarized in Table II.

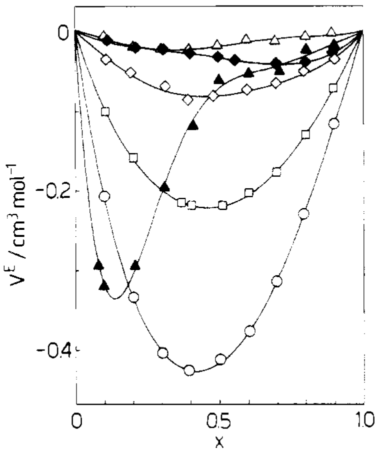

Figure 1. Excess volumes V^E of the mixtures of NMA with aliphatic alcohols against the mole fraction, x, of NMA: (○) methanol; (□) ethanol; (◇) 1-propanol; (◆) 2-propanol; (△) 1-butanol; (▲) 2-methyl-2-propanol.

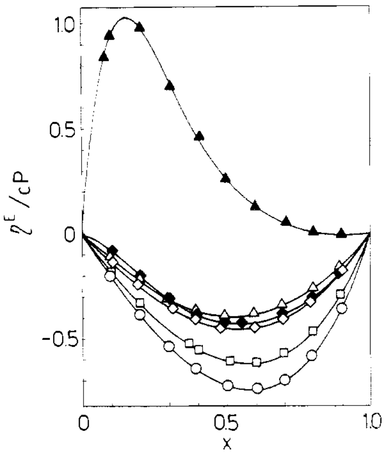

Figure 2. Excess viscosities η^E of the mixtures of NMA with aliphatic alcohols against the mole fraction, x, of NMA. The symbols are the same as in Figure 1.

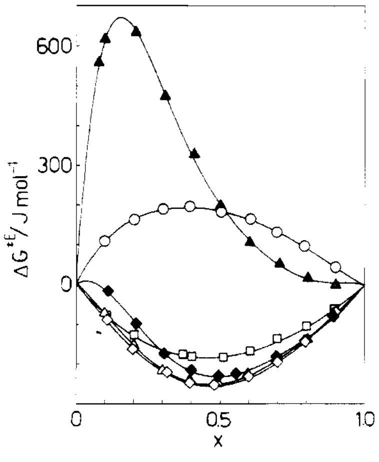

Figure 3. Excess Gibbs energies of activation of flow ΔG^{*E} of the mixtures of NMA with aliphatic alcohols against the mole fraction, x, of NMA. The symbols are the same as in Figure 1.

The excess volumes for the binary mixtures are negative over the whole composition ranges. The values for the primary alcohols decrease in the following sequence: 1-butanol > 1-propanol > ethanol > methanol (Figure 1). Since the carbonyl group of NMA has a considerable proton-accepting ability (*16*), appropriate negative contributions, especially in the mixtures of the lower primary alcohols (*17*), may be expected to originate in O—H···O═C hydrogen bonding between the amide

Table II. Coefficients A_i of Eq 5 and the Standard Deviations $\sigma(Y^E)$ at 303.15 K

function	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
			NMA + Methanol			
V^E/(cm^3 mol^{-1})	-1.6684	-0.4908	-0.2221	-0.2391		0.002
η^E/cP	-2.8916	0.9494	-0.2723	0.1703		0.002
$\Delta G^{\ddagger E}$/(J mol^{-1})	741.8	303.8	159.7	209.3		2
			NMA + Ethanol			
V^E/(cm^3 mol^{-1})	-0.8833	-0.1279	-0.0726	-0.0885		0.001
η^E/cP	-2.4195	0.6946	-0.1697	0.7550		0.002
$\Delta G^{\ddagger E}$/(J mol^{-1})	-720.3	-137.1	-10.10	48.88		2
			NMA + 1-Propanol			
V^E/(cm^3 mol^{-1})	-0.3242	-0.0685	-0.0567	0.1392		0.004
η^E/cP	-1.7984	0.3533	0.0952	0.0120		0.002
$\Delta G^{\ddagger E}$/(J mol^{-1})	-1011	-160.7	187.7	99.98		2
			NMA + 2-Propanol			
V^E/(cm^3 mol^{-1})	-0.1368	0.1092	-0.1368	-0.0201		0.001
η^E/cP	-1.6855	0.3779	0.4050	0.5900		0.002
$\Delta G^{\ddagger E}$/(J mol^{-1})	-926.4	-73.04	627.2	809.8		3
			NMA + 1-Butanol			
V^E/(cm^3 mol^{-1})	-0.0785	-0.0982	-0.0090	0.0966		0.002
η^E/cP	-1.5586	0.1335	0.2127	0.2474		0.002
$\Delta G^{\ddagger E}$/(J mol^{-1})	-1001	-195.0	268.1	295.7		3
			NMA + 2-Methyl-2-propanol			
V^E/(cm^3 mol^{-1})	-0.2902	-0.5788	-1.7242	-2.3796	-1.1298	0.006
η^E/cP	1.0669	3.3046	4.7951	4.9797	2.4426	0.009
$\Delta G^{\ddagger E}$/(J mol^{-1})	814.1	2111	2749	3271	2101	5

and alcohol molecules. In addition, geometrical effects allowing accommodation of the component molecules into each other's structures and thereby a more dense liquid structure seem possible in these mixtures (*18*, *19*). The values of V^E do not, however, fall below -0.5 cm^3 mol^{-1}, which suggests to us that effects due to heteroassociation are to a fair extent cancelled by breakup of the self-association aggregates of the alcohols as well as those of NMA.

Just as in dielectric permittivity, the chainlike self-association of NMA is reflected in its viscosity, which is considerably greater than that of DMA (0.871 cP at 303.15 K (*11*)). The viscosities of all the mixtures, except those of 2-methyl-2-propanol, increase smoothly from the value of the pure alcohol to that of NMA as the mole fraction of NMA increases, and yield negative excess viscosities (Figure 2). Moreover, of the alcohols other than 2-methyl-2-propanol only methanol has positive values of $\Delta G^{\ddagger E}$ (Figure 3). Consequently, like the excess volumes the viscosity behavior of the mixtures of the primary alcohols suggests that the association and dissociation processes are balanced in such a way that the degree of association does not change appreciably when the components are mixed (*19*-*22*).

In regard to the proton-donating ability of 2-methyl-2-propanol (*23*), its mixtures with NMA show unexpectedly negative values of V^E at low mole fraction of NMA. The viscosity vs. composition curve has a maximum, and positive excess viscosities are found. Furthermore, the excess Gibbs energy of activation of flow has a maximum at about the same composition of mixture as η^E has, and as V^E has a minimum. The observation that these results suggest considerable interactions between unlike molecules might seem surprising. However, the presence of the NH proton in the NMA molecule allows it to act as a proton donor as well as an electron donor, and the oxygen atom of 2-methyl-2-propanol has the best proton-accepting ability among the alcohols studied (*24*).

Further insight into the role of the NH proton of NMA may be obtained through comparison of the present results with those of the corresponding mixtures of DMA (*11*). Here again the most striking features are presented by the mixtures of 2-methyl-2-propanol. The values of V^E are significantly smaller and the values of η^E and $\Delta G^{\ddagger E}$ significantly greater for the mixtures of NMA than mixtures of DMA. Since, on the other hand, the proton-accepting ability of DMA is somewhat greater than that of NMA (*16*, *25*), the results together may be regarded as evidence for formation of N-H···O hydrogen bonds between NMA and 2-methyl-2-propanol.

Registry No. NMA, 79-16-3; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-methyl-2-propanol, 75-65-0.

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