J. Chem. Eng. Data 1988, 33, 299–301

μ	Joule–Thomson coefficient

Subscripts

c	critical property
i, j	component identification

Registry No. H_2, 1333-74-0; CH_4, 74-82-8.

Literature Cited

(1) Hoxton, L. G. *Phys. Rev., Ser. 2* **1919**, *13*, 938.
(2) Roebuck, J. R. *Proc. Am. Acad. Arts Sci.* **1925**, *60*, 527.
(3) Johnston, H. L. *J. Am. Chem. Soc.* **1949**, *108*, 23102.
(4) Alhert, R. C.; Wenzel, L. A. *AIChE J.* **1969**, *15*, 256.
(5) Redlich, O.; Kwong, J.W.S. *Chem. Rev.* **1949**, *44*, 233.
(6) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
(7) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(8) Chueh, P. H.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1967**, *6*, 492.
(9) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd. ed.; McGraw-Hill: New York, 1977; p 629.
(10) Gunn, R. D.; Chueh, P. L.; Prausnitz, J. M. *AIChE J.* **1966**, *12*, 937.
(11) Muller, W. H.; Leland, T. W.; Kobayashi, R. *AIChE J.* **1961**, *17*, 267.
(12) Kim, A. G.; Douglas, L. J. U.S. Bureau of Mines: Report of Investigation RI7903; U.S. Department of Interior: Washington, DC, 1974.
(13) Eakin, B. E.; Devaney, W. E.; Bailey, N. L. *Proc. 54th Gas Processors Conv.—Enthalpy Measurements of Synthetic Gas Mixtures* **1976**, *52*.

Received for review June 17, 1986. Revised March 9, 1987. Accepted January 22, 1988.

Viscosities of Binary Solvent Mixtures of *N*,*N*-Diethylmethanesulfonamide with Aliphatic Alcohols

Liisa Pikkarainen

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

Viscosities were measured for binary solvent mixtures of *N*,*N*-diethylmethanesulfonamide (DEMSA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 303.15 K and used to calculate the excess viscosities and excess Gibbs energies of activation of flow. Both excess quantities were negative over the whole composition range for all mixtures studied, except the excess Gibbs energies for mixtures containing methanol, which were positive. The values decreased with the length of the alkyl chain of the alcohol and were smaller for the secondary and tertiary alcohols than for the primary analogues.

Introduction

As part of our studies on the thermodynamic properties of binary solvent mixtures of carboxamides and sulfonamides with aliphatic alcohols we recently reported the excess enthalpies (*1*) and the excess volumes (*2*) for binary mixtures of *N*,*N*-diethylmethanesulfonamide, $CH_3SO_2N(C_2H_5)_2$, with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol. The results were interpreted in terms of intermolecular interactions and geometrical effects in the mixtures. In continuation of this work we have now measured the viscosities of these binary mixtures at 303.15 K. The viscosities, together with the excess volumes from the earlier study (*2*), were used to calculate the excess viscosities and the excess Gibbs energies of activation of flow.

Experimental Section

Materials. The alcohols were the same as in the previous studies (*1*, *2*). *N*,*N*-Diethylmethanesulfonamide was prepared and purified as described earlier (*1*).

Measurements. Viscosities were measured with Cannon-Ubbelohde viscometers (*3*) (manufactured by Cannon Instrument Co., USA) equipped with an optoelectronic device for measuring the efflux time. Densities were available from the previous study (*2*). Viscosities are expressed in units of centipoise equal to 10^{-3} N s m^{-2}. The reproducibility in the viscosity measurements was within ±0.005 cP. The temperature of the water baths remained constant within ±0.02 K.

Table I. Viscosities η of Binary Mixtures of DEMSA with Aliphatic Alcohols at 303.15 K[a]

x	η/cP	x	η/cP	x	η/cP
		Methanol			
0	0.514	0.3717	1.234	0.6922	2.289
0.0650	0.604	0.4509	1.451	0.7686	2.636
0.1394	0.730	0.5148	1.645	0.8304	2.956
0.2155	0.884	0.5856	1.878	0.9084	3.414
0.2885	1.034				
		Ethanol			
0	0.990	0.3659	1.424	0.6622	2.217
0.0656	1.000	0.4606	1.635	0.7430	2.533
0.1402	1.067	0.5135	1.765	0.8454	3.026
0.2228	1.175	0.5968	2.002	0.9395	3.597
0.2849	1.274				
		1-Propanol			
0	1.728	0.3821	1.793	0.6850	2.461
0.0661	1.610	0.4421	1.884	0.7587	2.716
0.1423	1.583	0.5219	2.039	0.8085	2.925
0.2148	1.612	0.5944	2.204	0.8907	3.334
0.3057	1.693				
		2-Propanol			
0	1.783	0.3391	1.686	0.6857	2.433
0.0680	1.593	0.4088	1.792	0.7556	2.684
0.1441	1.544	0.4524	1.863	0.8417	3.057
0.2157	1.565	0.5136	1.984	0.9259	3.518
0.2582	1.598	0.5952	2.183		
		1-Butanol			
0	2.272	0.3626	1.985	0.6908	2.550
0.0631	2.045	0.4515	2.078	0.7579	2.742
0.1404	1.942	0.5227	2.175	0.8437	3.089
0.2197	1.918	0.6053	2.340	0.9281	3.552
0.2937	1.942				
		2-Methyl-2-propanol			
0	3.376	0.3944	2.453	0.7621	3.010
0.0764	2.857	0.4712	2.501	0.8534	3.304
0.1463	2.630	0.5369	2.579	0.9381	3.657
0.2364	2.482	0.6062	2.664	1.0	4.059
0.3171	2.437	0.6888	2.796		

[a] x is the mole fraction of DEMSA.

Results and Discussion

Measured viscosities of the pure components and mixtures are reported in Table I. The viscosities of the pure components are in good agreement with the literature values: 0.510

0021-9568/88/1733-0299$01.50/0

Table II. Coefficients A_i of Eq 3 for η^E and the Standard Deviations $\sigma(\eta^E)$

	methanol	ethanol	1-propanol	2-propanol	1-butanol	2-methyl-2-propanol
A_0	−2.7586	−3.1784	−3.6030	−3.8605	−4.0837	−4.7761
A_1	0.9338	1.0216	0.7365	0.4876	0.6469	−0.5923
A_2	−0.4407	−0.7195	−1.0563	−1.2037	−1.3664	−1.7695
A_3	0.0229	−0.0660	−0.4206	−0.5682	−0.6550	−0.9441
A_1		−0.3783	−0.5821	−1.1845	−1.0705	−1.7078
$\sigma(\eta^E)/\mathrm{cP}$	0.003	0.002	0.002	0.004	0.006	0.010

Table III. Coefficients A_i of Eq 3 for ΔG^{*E} and the Standard Deviations $\sigma(\Delta G^{*E})$

	methanol	ethanol	1-propanol	2-propanol	1-butanol	2-methyl-2-propanol
A_0	2728.3	−608.8	−2399.3	−2794.7	−3293.7	−3665.6
A_1	1362.7	−59.43	−584.4	−996.0	−468.5	−1022.8
A_2	492.0	−654.3	−894.8	−1199.5	−937.7	−1223.3
A_3	−305.5	−1020.8	−924.6	−1358.4	−1131.4	−602.0
A_4	−704.7	−592.9	−666.9	−1320.5	−861.3	−806.2
$\sigma(\Delta G^{*E})/\mathrm{J\ mol^{-1}}$	8	4	2	5	6	10

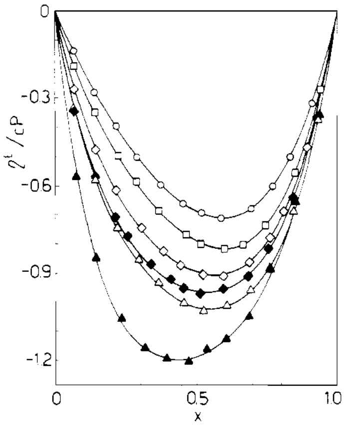

Figure 1. Excess viscosities η^E of the mixtures of DEMSA with aliphatic alcohols vs the mole fraction x of DEMSA: (○) methanol; (□) ethanol; (◇) 1-propanol; (◆) 2-propanol; (△) 1-butanol; (▲) 2-methyl-2-propanol. The solid lines are derived from eq. 3.

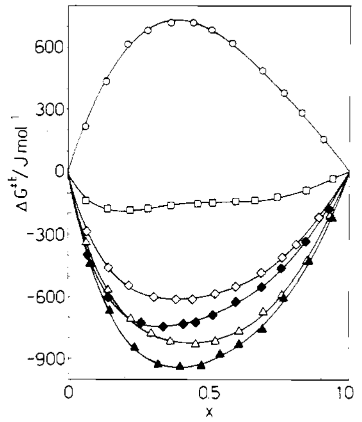

Figure 2. Excess Gibbs energies of activation of flow ΔG^{*E} of the mixtures of DEMSA with aliphatic alcohols vs the mole fraction x of DEMSA. The symbols are the same as in Figure 1.

cP for methanol (*4*), 0.991 cP for ethanol (*4*), 1.72 cP for 1-propanol (*4*), 1.77 cP for 2-propanol (*4*), 2.28 cP for 1-butanol (*4*), 3.383 cP (interpolated value) for 2-methyl-2-propanol (*5*), and 4.076 cP (interpolated value) for DEMSA (*6*). The excess viscosity η^E and the excess Gibbs energy of activation of flow ΔG^{*E} were calculated with the equations

$$\eta^E = \eta - [(1 - x)\eta_1 + x\eta_2] \quad (1)$$

$$\Delta G^{*E} = RT\{\ln \eta V - [(1 - x) \ln \eta_1 V_1 + x \ln \eta_2 V_2]\} \quad (2)$$

where η, η_1, and η_2 are the measured viscosities, V, V_1, and V_2 are the molar volumes (available from ref *2*) of the mixture, alcohol, and DEMSA, respectively, and x is the mole fraction of DEMSA.

Graphical representations of η^E and ΔG^{*E} as functions of x are given in Figures 1 and 2. To the excess quantities we fitted the equation

$$Y^E = x(1 - x)\sum_{i=0}^{n} A_i(1 - 2x)^i \quad (3)$$

where Y^E is η^E/cP or ΔG^{*E}/(J mol^{-1}). Coefficients A_i of these fitting equations together with the standard deviations $\sigma(Y^E)$ are collected in Tables II and III.

As the results in Table I indicate, the viscosities of the mixtures of DEMSA with methanol and ethanol increase with the mole fraction of DEMSA and, if presented graphically, appear as regularly rising concave curves. The curves of η for the mixtures of the other alcohols show minima, that of 2-methyl-2-propanol showing a particularly deep minimum. Accordingly, the excess viscosities are negative over the whole composition range for all mixtures studied. Further, the values of ΔG^{*E} are negative for all mixures except those containing methanol, which exhibit positive values. The values of η^E and ΔG^{*E} decrease with the length of the alkyl chain of the alcohol and are smaller for the secondary and tertiary alcohols than for the primary analogues.

The high viscosities of pure sulfonamides have been ascribed to the association of their molecules, mainly by dipole–dipole interactions (*6*, *7*). The sulfonyl group of sulfonamides can function as a proton acceptor, but its proton-accepting ability is relatively weak; it is considerably weaker than that of the carbonyl group of the corresponding carboxamides, for example (*8*–*11*). Alcohols, in turn, are known to be extensively self-associated through hydrogen bonding in the pure state (*12*). Mixing of DEMSA with an alcohol tends to occasion breakup of amide–amide and alcohol–alcohol interactions. In addition, the unlike molecules may interact with each other by hydrogen bonding or dipolar interactions.

The results, in the main, indicate that the balance between different effects in the present mixtures results in a liquid structure where the flow is easier than would be expected on the basis of the viscosities of the pure components. This suggests that the dissociation effects are predominating over the association effects, especially in the mixtures of the higher alcohols. At the same time, some contributions due to heteroassociation appear, but they seem to be small in the mixtures of methanol and still smaller in the mixtures of the other alcohols; mixtures where a strong specific interaction between unlike molecules is predominant are characterized by distinct maxima in the viscosity vs composition curves, by positive excess viscosities, and by positive values of ΔG^{*E} (*13*–*17*).

Finally a comment on the relationship between the present results and the excess enthalpies (*1*) and the excess volumes (*2*) of the mixtures is in order. The excess viscosity and the

J. Chem. Eng. Data **1988**, *33*, 301-306

excess enthalpy respond with a similar sensitivity to the different effects arising when the components are mixed: the excess viscosities are distinctly negative and the excess enthalpies distinctly positive, and the magnitude of both increases with the length of the alkyl chain of the alcohol. At the same time, the excess volumes are smaller, especially for the lower alcohols, than would be expected on the basis of the excess enthalpies and excess viscosities. This, we think, is evidence of the significance of geometrical effects, which affect the excess volumes more than they affect the excess enthalpies and excess viscosities.

Registry No. DEMSA, 2374-61-0; 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.

Literature Cited

(1) Pikkarainen, L. *J. Chem. Eng. Data* **1987**, *32*, 427.
(2) Pikkarainen, L. *J. Chem. Eng. Data* **1987**, *32*, 429.
(3) Cannon, M. R.; Manning, R. E.; Bell, J. D. *Anal. Chem.* **1960**, *32*, 355.
(4) Raznjevic, K., Ed. *Thermodynamische Tabellen*; VDI Verlag GmbH: Düsseldorf, 1977.
(5) Washburn, E. W., Ed. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; McGraw-Hill: New York, 1930.
(6) Stoeckinger, T. M. Ph.D. Dissertation, University of Kentucky, 1968.
(7) Vaughn, J. W.; Sears, P. B. *J. Phys. Chem.* **1958**, *62*, 183.
(8) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974.
(9) Jarva, M.; Saastamoinen, M.; Virtanen, P. O. I. *Finn. Chem. Lett.* **1974**, 169.
(10) Pikkarainen, L. *Finn. Chem. Lett.* **1980**, 33.
(11) Hovius, K.; Zuidema, G.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 633.
(12) Huyskens, P. *J. Mol. Struct.* **1983**, *100*, 403.
(13) Assarsson, P.; Eirich, F. R. *J. Phys. Chem.* **1968**, *72*, 2710.
(14) Westmeier, S. *Z. Phys. Chem.* (*Leipzig*) **1976**, *257*, 950.
(15) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1966**, *62*, 1112.
(16) Solimo, H. N.; Riggio, R.; Davolio, F.; Katz, M. *Can. J. Chem.* **1975**, *53*, 1258.
(17) Jannelli, L.; Rakshit, O.; Sacco, A. *Z. Naturforsch. A* **1974**, *29*, 355.

Received for review June 16, 1987. Accepted January 22, 1988.

Heat Capacity of Aqueous FeCl$_2$ from 349 to 597 K

Robert H. Wood,* Dorothy E. White, and William E. Davis

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Peter T. Thompson

Department of Chemistry, Swarthmore College, Swarthmore, Pennsylvania 19081

A differential, flow, heat-capacity calorimeter has been used to measure the heat capacity of FeCl$_2$(aq) at molalities from 0.06 to 3.5 mol kg^{-1} and temperatures from 350 to 600 K at a pressure near 17.9 MPa. The results do not show the large negative values of $C_{p,\phi}$ characteristic of strong electrolytes at high temperatures and low molalities, indicating that FeCl$_2$(aq) like NiCl$_2$(aq) is mainly undissociated at high temperatures and molalities above 0.06 mol kg^{-1}. A sharp maximum in $C_{p,\phi}$ versus temperature may be due to the effects of association equilibria.

Introduction

This work is part of a continuing investigation of the heat capacities of aqueous electrolyte solutions at high temperatures using a flow calorimetric technique (*1-6*). Previous work has shown that alkali-metal halides and alkaline-earth halides have characteristically large, negative apparent molar heat capacities at 600 K and low molalities (*1*, *3-6*) and this has been attributed to large interactions between ions and water, together with the changes in the properties of water as its critical point is approached (*1*, *7-15*). Corresponding effects have been found for enthalpies of solution of salts in water (*7*, *8*). In contrast, the only transition-metal halide for which data are available, NiCl$_2$, does not show these characteristic large negative apparent molar heat capacities at temperatures up to 572 K, and this has been attributed to association of the Ni^{2+} with Cl$^-$ ions.

In this paper we report measurements on another transition-metal halide, FeCl$_2$. Because of experimental difficulties the results are not as accurate as the measurements on the previous systems, but they are the only direct experimental measurements on this system. A knowledge of the thermodynamic properties of aqueous FeCl$_2$ is important in understanding a number of problems in the corrosion of electric power boilers at high temperatures and in the geochemistry of iron-bearing minerals.

Experimental Section

Solutions. The FeCl$_2$ solutions were prepared by dilution of concentrated stock solutions which were prepared separately for each of the two heat capacity runs. In most respects the procedures for the preparation of the stock and run solutions were the same for both sets of data, which were taken about 1.5 years apart. The stock solution was prepared in a 2-L bottle equipped with valves and stainless steel entry ports which allowed storage and transfer to be accomplished under an N$_2$ atmosphere at all times. Solvent used to prepare all solutions was carefully degassed ion-exchange water containing known amounts of HCl ($\simeq$0.0007 M). Starting material was Baker "analyzed" FeCl$_2$·4H$_2$O containing 99.9% "Fe" by KMnO$_4$ titration (i.e., total iron) and no listed impurities present at more than 0.005%. The weighed salt was dissolved in known

0021-9568/88/1733-0301$01.50/0