Partial Molar Volumes and Viscosity *B* Coefficients of Benzyltriethylammonium Chloride in Dimethyl Sulfoxide + Water at Different Temperatures

Uday R. Kapadi*

School of Chemical Sciences North Maharashtra University, Jalgaon 425001, India

Sitaram K. Chavan

Department of Chemistry, Shivaji University, Centre for Post Graduate Studies, Solapur 413003, India

Omprakash S. Yemul

Polymer Section, Chemical Engineering Division, National Chemical Laboratory, Pune 411008, India

The viscosities of solutions of benzyltriethylammonium chloride have been measured in dimethyl sulfoxide (DMSO) + water mixtures at various temperatures (298, 303, 308, 313, and 318 K). The results have been analyzed using the Jones−Dole equation, and the viscosity *B* coefficients have been calculated. The density data have been analyzed using Masson's equation. The partial molar volume V_ϕ° at infinite dilution and the slopes V_s^* of Masson's equation at different compositions of DMSO have been interpreted in terms of solute−solvent and solute−solute interactions, respectively.

Introduction

The partial molar volume and viscosity measurements provide the information regarding ion−ion and ion−solvent interactions. Dimethyl sulfoxide + water mixtures remain popular solvent media for the study of ion solvation (*1*−*3*) and reaction kinetics and for electrochemical studies (*4*, *5*). Further, the DMSO + H_2O system has been extensively used in the study of organic reactions (*6*). The thermodynamics of ion−solvent interactions in this system is of considerable importance. In the work undertaken, we aimed to study quaternary ammonium salts in DMSO + water mixtures. These considerations led us to undertake the present study.

Experimental Procedure

Benzyltriethylammonium chloride was synthesized using the quaternarization reaction. Triethylamine and benzyl chloride (both AR grade, supplied by S. D. Chemical Co.) were refluxed in equimolar quantities for 3 h. The benzyltriethylammonium chloride obtained was recrystallized. The purity of the product was checked by procedures given in the literature (*7*). DMSO + H_2O mixtures of varying compositions as well as solutions of the electrolyte were made by mass with an accurancy of 0.0001 g. Viscosities were measured using a Cannon-Ubbelohde viscometer with an accuracy of ±0.1%.

The time of efflux through the capillary was measured with a precision of 0.1 s using a Rocar stopwatch.

Densities were measured using a pycnometer of about 7.4 cm^3 volume with an accuracy of 0.0001 $g{\cdot}cm^{-3}$. A precision thermostat (accuracy ±0.1 deg) was used throughout the work. The details of the experimental procedure are same as reported earlier (*8*).

Results and Discussion

The densities and viscosities of DMSO (A) + water (B) (0 to 1 mass fraction) at different temperatures were measured. These values are listed in Table 1. An overall increase in viscosity was observed up to $W_A = 0.7$; then further addition showed a decrease in viscosity. The

Table 1. Densities (d_0/g·cm^{-3}) and Viscosities (η_0/Pa·s) of DMSO (A) + Water (B) at Different Temperatures

DMSO W_A	d_0/g·cm^{-3}	η_0/Pa·s	DMSO W_A	d_0/g·cm^{-3}	η_0/Pa·s
		25 °C			
0.0	0.997 56	0.8893	0.60	1.082 84	3.4594
0.10	1.010 52	1.0973	0.70	1.092 95	3.7195
0.20	1.023 84	1.3496	0.80	1.098 42	3.4496
0.30	1.038 96	1.7189	0.90	1.098 68	2.2784
0.40	1.045 02	2.2379	1.00	1.096 02	2.0006
0.50	1.069 11	2.8294			
		30 °C			
0.0	0.996 07	0.7931	0.60	1.081 25	3.0647
0.10	1.009 84	0.9948	0.70	1.091 42	3.3057
0.20	1.022 83	1.2046	0.80	1.098 13	3.1510
0.30	1.037 72	1.5059	0.90	1.098 31	2.0662
0.40	1.053 41	1.9771	1.00	1.090 38	1.8102
0.50	1.067 86	2.5503			
		35 °C			
0.0	0.994 12	0.6922	0.60	1.077 96	2.6810
0.10	1.009 23	0.9157	0.70	1.090 23	2.9418
0.20	1.021 01	1.0928	0.80	1.094 82	2.7340
0.30	1.036 02	1.3418	0.90	1.095 91	1.8712
0.40	1.051 25	1.7346	1.00	1.085 24	1.6623
0.50	1.065 84	2.2908			
		40 °C			
0.0	0.992 83	0.6382	0.60	1.076 03	2.2503
0.10	1.008 16	0.7948	0.70	1.088 20	2.5503
0.20	1.008 16	0.9555	0.80	1.090 92	2.4777
0.30	1.034 94	1.1980	0.90	1.092 21	1.6706
0.40	1.049 95	1.5392	1.00	1.080 64	1.5152
0.50	1.063 61	1.9111			
		45 °C			
0.0	0.991 72	0.5862	0.60	1.074 92	2.1496
0.10	1.007 84	0.7098	0.70	1.086 99	2.3496
0.20	1.017 53	0.8496	0.80	1.088 38	2.0653
0.30	1.030 85	1.0594	0.90	1.091 16	1.5398
0.40	1.047 81	1.3196	1.00	1.076 83	1.3849
0.50	1.061 23	1.6496			

* To whom correspondence may be addressed.

S0021-9568(96)00216-6 CCC: $14.00

Table 2. Viscosities and Densities of Benzyltriethylammonium Chloride Solution in DMSO (A) + Water (B) at Different Temperatures

0.04 M Solution

	t/°C						t/°C				
W_A	25	30	35	40	45	W_A	25	30	35	40	45
					η/Pa·s						
0.0	0.9391	0.8461	0.7412	0.6382	0.5908	0.60	3.4343	3.0764	2.7091	2.2633	1.9686
0.10	1.1267	1.0457	1.9294	0.8104	0.7222	0.70	3.7287	3.3300	2.9588	2.5627	2.1640
0.20	1.3718	1.2163	1.1176	0.9751	0.8679	0.80	3.4653	3.1679	2.7529	2.4915	2.0895
0.30	1.7428	1.5209	1.3653	1.2150	1.0816	0.90	2.2915	2.0928	1.8849	1.6816	1.5562
0.40	2.2633	2.0052	1.7529	1.5529	1.3333	1.00	2.0055	1.8148	1.6664	1.5211	1.3899
0.50	2.8668	2.5653	2.3091	1.9287	1.6663						
					ρ/g·cm^{-3}						
0.0	0.9994	0.9979	0.9966	0.9543	0.9372	0.60	1.0834	1.0826	1.0788	1.0775	1.0759
0.10	1.0118	1.0112	1.0101	1.0094	1.0089	0.70	1.0945	1.0927	1.0919	1.0897	1.0884
0.20	1.0253	1.0239	1.0224	1.0218	1.0198	0.80	1.0995	1.0901	1.0961	1.0925	1.0898
0.30	1.0401	1.0394	1.0380	1.0364	1.0317	0.90	1.1004	1.0995	1.0967	1.0937	1.0929
0.40	1.0552	1.0543	1.0527	1.0510	1.0489	1.00	1.0983	1.0931	1.0873	1.0826	1.0791
0.50	1.0701	1.0690	1.0670	1.0651	1.0629						

0.08 M Solution

	t/°C						t/°C				
W_A	25	30	35	40	45	W_A	25	30	35	40	45
					η/Pa·s						
0.0	0.9743	0.8881	0.7792	0.6412	0.5946	0.60	3.5117	3.0960	2.7254	2.2843	1.9960
0.10	1.1549	1.0732	0.9509	0.8339	0.7281	0.70	3.8039	3.3450	2.9856	2.5836	2.1777
0.20	1.3856	1.2339	1.1307	0.9856	0.8849	0.80	3.4745	3.1960	2.7699	2.5058	2.1019
0.30	1.7503	1.5424	1.3843	1.2888	1.1026	0.90	2.3117	2.1189	1.9104	1.7013	1.5679
0.40	2.2980	2.0261	1.7699	1.5745	1.3483	1.00	2.0094	1.8186	1.6694	1.5248	1.3932
0.50	2.8738	2.5836	2.3248	1.9522	1.6830						
					ρ/g·cm^{-3}						
0.0	1.0015	0.9916	0.9983	0.9973	0.9953	0.60	1.0840	1.0835	1.0822	1.0781	1.0770
0.10	1.0128	1.0118	1.0109	1.0101	1.0095	0.70	1.0954	1.0942	1.0933	1.0912	1.0905
0.20	1.0265	1.0257	1.0251	1.0237	1.0225	0.80	1.0998	1.0998	1.0979	1.0938	1.0929
0.30	1.0412	1.0402	1.0392	1.0381	1.0356	0.90	1.1012	1.1001	1.0980	1.0946	1.0931
0.40	1.0558	1.0551	1.0547	1.0530	1.0520	1.00	1.1002	1.0952	1.0892	1.0844	1.0809
0.50	1.0709	1.0699	1.0682	1.0670	1.0666						

0.12 M Solution

	t/°C						t/°C				
W_A	25	30	35	40	45	W_A	25	30	35	40	45
					η/Pa·s						
0.0	1.0023	0.9241	0.7822	0.6439	0.5976	0.60	3.5444	3.1267	2.7588	2.3117	2.0352
0.10	1.1960	1.1052	0.9836	0.8614	0.7699	0.70	3.8339	3.3830	3.0189	2.6163	2.2032
0.20	1.4169	1.2614	1.1673	1.0169	0.9109	0.80	3.5091	3.2326	2.7986	2.5411	2.1307
0.30	1.7797	1.5666	1.4150	1.3869	1.1052	0.90	2.4084	2.1516	1.9424	2.3882	1.5993
0.40	2.3274	2.0575	1.7934	1.6071	1.3810	1.00	2.0119	1.8223	1.6714	1.5273	1.3953
0.50	2.9084	2.6196	2.3607	1.9843	1.7241						
					ρ/g·cm^{-3}						
0.0	1.0029	1.0007	0.9994	0.9989	0.9965	0.60	1.0855	1.0846	1.0828	1.0802	1.0796
0.10	1.0134	1.0128	1.0119	1.0111	1.0104	0.70	1.0959	1.0946	1.0935	1.0917	1.0907
0.20	1.0269	1.0260	1.0247	1.0239	1.0228	0.80	1.1080	1.1050	1.0989	1.0943	1.0933
0.30	1.0415	1.0407	1.0402	1.0381	1.0370	0.90	1.1120	1.1090	1.0990	1.0950	1.0940
0.40	1.0572	1.0561	1.0549	1.0531	1.0524	1.00	1.1017	1.0968	1.0907	1.0858	1.0825
0.50	1.0715	1.0706	1.0693	1.0672	1.0668						

0.16 M Solution

	t/°C						t/°C				
W_A	25	30	35	40	45	W_A	25	30	35	40	45
					η/Pa·s						
0.0	1.0213	0.9501	0.7843	0.6445	0.5997	0.60	3.5803	3.1830	2.8189	2.3575	2.0607
0.10	1.2261	1.1385	1.0150	0.8947	0.8071	0.70	3.8535	3.4405	3.0633	2.6522	2.2692
0.20	1.4673	1.2993	1.2134	1.0588	0.9477	0.80	3.5705	3.2960	2.8516	2.6111	2.2006
0.30	1.8535	1.6176	1.4830	1.4869	1.1627	0.90	2.3888	2.1901	1.9790	2.4287	1.6594
0.40	2.3686	2.1084	1.8366	1.6424	1.4294	1.00	2.0133	1.8241	1.6732	1.5291	1.3971
0.50	2.9563	2.6529	2.4169	2.0228	1.7666						
					ρ/g·cm^{-3}						
0.0	1.0040	1.0019	1.0009	1.0002	0.9974	0.60	1.0858	1.0847	1.0830	1.0818	1.0799
0.10	1.0136	1.0130	1.0123	1.0112	1.0105	0.70	1.0964	1.0953	1.0937	1.0929	1.0908
0.20	1.0273	1.0264	1.0247	1.0240	1.0229	0.80	1.0111	1.1060	1.9910	1.0946	1.0935
0.30	1.0418	1.0408	1.0403	1.0384	1.0372	0.90	1.1250	1.1190	1.1099	1.0951	1.0941
0.40	1.0581	1.0564	1.0549	1.0532	1.0525	1.00	1.0960	1.9038	1.0852	1.0806	1.0768
0.50	1.0720	1.0708	1.0695	1.0674	1.0670						

Table 3. Least Squares Fit Parameter of Eq 1

	t/°C									
	25		30		35		40		45	
W_A	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
0.10	0.0352	0.5631	0.0303	0.5345	0.0987	0.6979	0.0988	0.7504	0.1296	0.4855
0.20	0.0922	0.5063	0.0914	0.5548	0.0939	0.4861	0.1400	0.7740	0.0937	0.5484
0.30	0.0725	0.2507	0.0743	0.4830	0.0644	0.4809	0.1220	0.5267	0.0463	0.5379
0.40	0.0442	0.4211	0.0490	0.3819	0.0628	0.4007	0.0794	0.5523	0.0992	0.5682
0.50	0.0659	0.3544	0.0595	0.3852	0.0543	0.3698	0.0500	0.4183	0.0744	0.4981
0.60	0.0259	0.3099	0.0630	0.3596	0.0467	0.2901	0.0534	0.3535	0.0610	0.4327
0.70	0.0557	0.2701	0.0487	0.3051	0.0512	0.2454	0.0473	0.3212	0.0498	0.2957
0.80	0.0449	0.2273	0.1740	0.2366	0.0420	0.2824	0.0503	0.3103	0.0465	0.2478
0.90	0.0554	0.3175	0.0252	0.2934	0.0268	0.3421	0.0477	0.3143	0.0606	0.3124

Table 4. Computed Parameters of Eq 2

	t/°C									
	25		30		35		40		45	
W_A	V°_ϕ/ $cm^3 \cdot mol^{-1}$	V^*_s/$cm^3 \cdot L^{1/2} \cdot mol^{-3/2}$	V°_ϕ/ $cm^3 \cdot mol^{-1}$	V^*_s/$cm^3 \cdot L^{1/2} \cdot mol^{-3/2}$	V°_ϕ/ $cm^3 \cdot mol^{-1}$	V^*_s/$cm^3 \cdot L^{1/2} \cdot mol^{-3/2}$	V°_ϕ/ $cm^3 \cdot mol^{-1}$	V^*_s/$cm^3 \cdot L^{1/2} \cdot mol^{-3/2}$	V°_ϕ/ $cm^3 \cdot mol^{-1}$	V^*_s/$cm^3 \cdot L^{1/2} \cdot mol^{-3/2}$
0.10	179.7	64.2	173.8	81.3	200.0	15.5	182.3	60.5	187.9	50.9
0.20	165.8	88.5	168.2	79.5	181.4	48.7	111.0	80.9	123.9	64.7
0.30	171.8	81.2	158.0	62.4	160.2	84.2	157.6	80.8	145.0	84.1
0.40	182.2	23.2	190.7	19.6	172.1	55.4	157.0	77.7	126.4	60.1
0.50	148.1	73.8	177.9	42.4	179.6	26.1	148.3	65.6	116.4	54.8
0.60	163.7	80.2	165.8	57.7	134.6	62.4	161.9	40.2	131.2	24.1
0.70	116.1	36.1	162.0	60.7	148.5	79.1	163.6	48.9	134.3	30.6
0.80	112.7	60.5	182.7	21.8	151.4	77.3	157.0	74.3	118.8	48.5
0.90	113.8	33.3	153.6	25.0	172.2	36.5	155.9	70.0	121.3	77.2

viscosities and densities at different concentrations of benzyltriethylammonium chloride in DMSO + water at different temperatures are given in Table 2.

The relative viscosities of the benzyltriethylammonium chloride in DMSO + H_2O mixtures were calculated using the Jones−Dole equation (*9*).

$$\eta/\eta_0 = \eta_\gamma = 1 + Ac^{1/2} + Bc \qquad (1)$$

where η and η_0 are the viscosities of the solution and the solvent, respectively. *c* is the concentration in molarity. *A* is the Falkenhagen coefficient (*10*) depending on the long-range Coulombic forces related to ion−ion interactions, and *B* is an adjustable parameter related to the size of the ions and ion−solvent interaction.

The values of *A* and *B* coefficients obtained at various temperatures using a least squares method are given in Table 3. The values of *A* were found to be positive in the entire range of DMSO + H_2O. The values of *B* are positive and large. The densities of benzyltriethylammonium chloride in solutions of dimethyl sulfoxide + water, at different temperatures, have been used to calculate the apparent molar volume V_ϕ of the solute using the procedure reported earlier (*11*).

The concentration dependence of limiting apparent molar volumes V_ϕ has been explained in terms of Masson's equation (*12*).

$$V_\phi = V^\circ_\phi + V^*_s \qquad (2)$$

where V°_ϕ is the partial molar volume at infinite dilution and V^*_s is the experimental slope. The values of V°_ϕ and V^*_s obtained in the entire range of composition at different temperatures are listed in Table 4.

Literature Cited

(1) Wells, C. F. *J. Chem. Soc., Faraday Trans 1* **1981**, *77*, 1515−1528.
(2) Cox, B. G.; Natarajan, R.; Waghore, W. E. *J. Chem. Soc., Faraday Trans 1* **1979**, *75*, 1780−1787.
(3) Janardhanan, S.; Kalidas, C. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2363−2370.
(4) Parker, A. *J. Q. Rev. Chem. Soc.* **1962**, *16*, 163−187.
(5) Jassinski, R. J. *High energy batteries*; Plenum: New York, 1967.
(6) Buncel, E.; Wilson, H. *Adv. Phys. Org. Chem.* **1977**, *14*, 133−140.
(7) Blokhra, R. L.; Parmer, M. L. *Aust. J. Chem.* **1974**, *27*, 1407−1411.
(8) Kapadi, U. R.; Chavan, S. K. *J. Indian Chem. Soc.* **1994**, *71*, 269−271.
(9) Jones, G.; Dole, M. *J. Am. Chem. Soc.* **1929**, *51*, 2950−2964.
(10) Falkenhagen, H.; Vernan, E. L. *Z. Phys.* **1932**, *33*, 140−147.
(11) Kapadi, U. R.; Chavan, S. K. *Indian J. Technol.* **1994**, *1*, 314−316.
(12) Masson, D. O. *Philos. Mag. B* **1929**, 218−225.

Received for review June 25, 1996. Accepted February 7, 1997.[⊗]

JE960216+

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.