Diffusion Coefficients, Kinematic Viscosities, and Refractive Indices for Heptane + Ethylbenzene, Sulfolane + 1-Methylnaphthalene, Water + *N*,*N*-Dimethylformamide, Water + Methanol, Water + *N*-Formylmorpholine, and Water + *N*-Methylpyrrolidone

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Diffusion coefficients (D_{12}), kinematic viscosities (ν), and refractive indices (n) are reported over the whole concentration range for the following binary systems: heptane + ethylbenzene and sulfolane + 1-methylnaphthalene at 313.15 and 333.15 K and water + *N*,*N*-dimethylformamide, water + methanol, water + *N*-formylmorpholine, and water + *N*-methylpyrrolidone at 283.15 and 313.15 K. The diffusion coefficients were measured by the dispersion method and compared with literature values. Each of the six system plots of the diffusion coefficients against mole fraction exhibits a minimum. For the aqueous systems, except water + *N*-formylmorpholine, the kinematic viscosities at a given temperature show a maximum and there is a corresponding minimum in D_{12}.

Introduction

Experimental liquid-phase diffusion coefficients and viscosities are the transport properties needed to evaluate mass-transfer phenomena and to design equipment for mass-transfer operations. However, relatively few experimental measurements have been made so far, largely because the experiments are tedious and expensive. The present molecular theories cannot be used to predict these properties accurately, especially for nonideal systems.

Diffusion coefficients can be measured by several methods such as laser light scattering, diaphragm cell, and interferometric and dispersion methods (Ghai et al., 1974; Johnson and Babb, 1956; Cussler, 1976; Gulari et al., 1973). The dispersion method offers several advantages: (a) Experiments can be carried out at small mole fraction differences (less than 0.001). The measured diffusion coefficient is therefore the differential coefficient as defined by Fick's law. (b) One experiment takes only 4–8 h. (c) Calibration of the apparatus is not required.

In this work, diffusion coefficients, kinematic viscosities, and refractive indices for heptane + ethylbenzene and sulfolane + 1-methylnaphthalene at 313.13 and 333.15 K and water + *N*,*N*-dimethylformamide, water + methanol, water + *N*-formylmorpholine, and water + *N*-methylpyrrolidone at 283.15 and 313.15 K were studied. Diffusion coefficients were measured by the dispersion method.

Experimental Method

In the dispersion method, a fluid of specified concentration flows through two long, thin capillaries at a constant speed in laminar flow. A sample (~20 μL) which has a slightly different concentration relative to the initial fluid is injected into one of the two capillaries. Due to diffusion, the concentration distribution of the sample plug broadens as it flows along the capillary tube. At the end of the capillary tube, this concentration distribution can be detected by a differential refractometer. The diffusion coefficient can then be calculated from the concentration distribution.

The apparatus has been described in detail by Baldauf et al. (1981, 1983). The experimental temperature was maintained within ±0.1 K. In previous studies (Baldauf, 1981; Melzer et al., 1989), the output signal of the differential refractometer was evaluated from a chart recording. In this work, the signal was recorded by a personal computer interfaced to the differential refractometer. The accuracy of measurement is improved.

The kinematic viscosities were measured with a KPG-Ubbelohde capillary viscometer with temperature controlled to within ±0.01 K. The accuracy of the measured kinematic viscosity is within 0.1%. The kinematic viscosities can be converted to the absolute viscosities by using density values from previous work (Chen and Knapp, 1995).

In order to estimate the refractive index difference Δn between the initial and injected mixtures (if Δn is too small, the concentration distribution could not be detected by the differential refractometer), the refractive indices for these systems were measured with an Abbe refractometer (Zeiss, type B) which was calibrated by using distilled and degassed water. The precision of the refractive index values is 0.01%.

The purity of the laboratory-distilled water was 99.99%, and the purities of other chemicals were over 99 mol %. All chemicals were degassed and used without further purification. Binary mixtures were prepared on a mass basis. The mole fraction error is estimated to be less than 0.0002.

Results and Discussion

Diffusion coefficients, kinematic viscosities, and refractive indices were measured over the whole concentration range for the following binary systems: heptane + ethylbenzene, and sulfolane + 1-methylnaphthalene at 313.15 and 333.15 K and water + *N*,*N*-dimethylformamide, water + methanol, water + *N*-formylmorpholine, and water + *N*-methylpyrrolidone at 283.15 and 313.15 K.

The experimental results are listed in Table 1. Each of the reported values for the diffusion coefficients is the

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Table 1. Diffusion Coefficients D_{12}, Kinematic Viscosities ν and Refractive Indices n of Six Binary Systems

T/K	x_1	$10^9 D_{12}$ ($m^2 s^{-1}$)	$10^6 \nu$ ($m^2 s^{-1}$)	n	T/K	x_1	$10^9 D_{12}$ ($m^2 s^{-1}$)	$10^6 \nu$ ($m^2 s^{-1}$)	n
			Heptane (1) + Ethylbenzene (2)						
313.15	0.0000		0.620	1.4863	333.15	0.0000		0.515	1.4770
	0.0007	2.45 ± 0.08				0.0011	3.01 ± 0.09		
	0.1965			1.4610		0.1986	2.91 ± 0.08		
	0.1997		0.567			0.1997		0.477	
	0.2039	2.38 ± 0.03				0.2026			1.4506
	0.3976		0.534			0.3947			1.4282
	0.3994	2.46 ± 0.09				0.3976		0.451	
	0.4155			1.4361		0.4021	3.02 ± 0.11		
	0.5909	2.58 ± 0.10				0.6025		0.436	
	0.6025		0.512			0.6026			1.4069
	0.6194			1.4143		0.6061	3.43 ± 0.12		
	0.7934			1.3971		0.7952			1.3871
	0.8005		0.500			0.8005		0.424	
	0.8050	3.10 ± 0.11				0.8063	3.91 ± 0.15		
	0.9991	3.70 ± 0.06				0.9990	4.32 ± 0.17		
	1.0000		0.495	1.3782		1.0000		0.419	1.3688
			Sulfolane (1) + 1-Methylnaphthalene (2)						
313.15	0.0000		2.117	1.6051	333.15	0.0000		1.488	1.5968
	0.0009	0.640 ± 0.013				0.0010	0.863 ± 0.019		
	0.1993	0.376 ± 0.010				0.2017		1.863	
	0.2017		2.756			0.2044	0.504 ± 0.012		
	0.2057			1.5881		0.2057			1.5805
	0.4017		3.444			0.4017		2.245	
	0.4034			1.5674		0.4030	0.378 ± 0.001		
	0.4094	0.277 ± 0.003				0.4034			1.5593
	0.5967			1.5434		0.5967			1.5360
	0.5979	0.205 ± 0.001				0.6019	0.317 ± 0.006		
	0.6074		4.237			0.6074		2.739	
	0.7920		5.009			0.7920		3.234	
	0.7967			1.5143		0.7967			1.5072
	0.7993	0.197 ± 0.006				0.8013	0.290 ± 0.012		
	0.9515	0.219 ± 0.007				0.9512	0.297 ± 0.007		
	1.0000		6.271	1.4780		1.0000		4.068	1.4720
			Water (1) + *N*,*N*-Dimethylformamide (2)						
283.15	0.0000		1.040	1.4350	313.15	0.0000		0.738	1.4220
	0.0030	1.50 ± 0.02				0.0044	2.73 ± 0.04		
	0.1040			1.4342		0.0465		0.767	
	0.1875			1.4332		0.1040			1.4210
	0.1988	1.09 ± 0.01				0.1875			1.4203
	0.2348		1.499			0.2029		0.912	
	0.3069			1.4310		0.2030	1.90 ± 0.04		
	0.4066		2.217			0.3069			1.4186
	0.4102			1.4286		0.4087	1.42 ± 0.01		
	0.4140	0.868 ± 0.005				0.4088		1.205	
	0.5072			1.4251		0.4102			1.4162
	0.6003	0.723 ± 0.002				0.5072			1.4130
	0.6066		3.633			0.6043		1.597	
	0.6099			1.4194		0.6052	1.38 ± 0.04		
	0.6860			1.4127		0.6099			1.4075
	0.7993		3.960			0.6860			1.4018
	0.8107	0.580 ± 0.001				0.8011	1.39 ± 0.02		
	0.8169			1.3935		0.8097		1.568	
	0.9200			1.3662		0.8169			1.3845
	0.9994	0.867 ± 0.016				0.9200			1.3604
	1.0000		1.323	1.3335		0.9687		0.856	
	-					0.9992	1.63 ± 0.02		
	-					1.0000		0.677	1.3335
			Water (1) + Methanol (2)						
283.15	0.0000		0.839	1.3340	313.15	0.0000		0.570	1.3210
	0.0020	1.46 ± 0.01				0.0017	2.75 ± 0.05		
	0.1028			1.3350		0.1028			1.3245
	0.1994		1.335			0.1977	2.24 ± 0.03		
	0.2015	1.08 ± 0.02				0.2193			1.3281
	0.2997			1.3410		0.2247		0.833	
	0.4033			1.3430		0.2997			1.3305
	0.4066	0.782 ± 0.010				0.3926		1.008	
	0.4174		1.962			0.3990	1.71 ± 0.03		
	0.5011			1.3465		0.4033			1.3332
	0.5976	0.643 ± 0.014				0.5011			1.3355
	0.5984		2.502			0.6017	1.43 ± 0.03		
	0.6077			1.3450		0.6077			1.3365
	0.6981			1.3448		0.6093		1.178	
	0.7909			1.3425		0.6981			1.3370
	0.7945		2.673			0.7909			1.3362
	0.7984	0.750 ± 0.006				0.7993	1.58 ± 0.04		
	0.8975			1.3370		0.8011		1.135	
	0.9986	0.967 ± 0.009				0.8975			1.3340
	1.0000		1.324	1.3335		0.9976	2.23 ± 0.01		
	-					1.0000		0.667	1.3335

Table 1 (Continued)

T/K	x_1	$10^9 D_{12}$ ($m^2 s^{-1}$)	$10^6 \nu$ ($m^2 s^{-1}$)	n	T/K	x_1	$10^9 D_{12}$ ($m^2 s^{-1}$)	$10^6 \nu$ ($m^2 s^{-1}$)	n
			Water (1) + *N*-Formylmorpholine (2)						
283.15	0.0000		11.637	1.4898	313.15	0.0000		4.584	1.4791
	0.0854			1.4878		0.0029	0.731 ± 0.020		
	0.1933			1.4850		0.0854			1.4768
	0.2090	0.260 ± 0.006				0.1933			1.4745
	0.2195		10.954			0.1993	0.652 ± 0.016		
	0.2942			1.4812		0.2533		4.122	
	0.3969	0.236 ± 0.007				0.2942			1.4709
	0.4031		10.726			0.3945		3.921	
	0.4229			1.4750		0.4068	0.620 ± 0.009		
	0.5029			1.4700		0.4229			1.4649
	0.6056		9.363			0.5029			1.4600
	0.6190	0.325 ± 0.012				0.5999		3.412	
	0.6349			1.4580		0.6030	0.670 ± 0.002		
	0.7103			1.4480		0.6349			1.4488
	0.7906			1.4326		0.7103			1.4387
	0.7940		5.717			0.7906			1.4240
	0.8018	0.404 ± 0.011				0.8017		2.224	
	0.9030			1.3962		0.8031	0.748 ± 0.014		
	0.9996	0.605 ± 0.013				0.9030			1.3895
	1.0000		1.323	1.3335		0.9994	1.12 ± 0.02		
						1.0000		0.677	1.3335
			Water (1) + *N*-Methylpyrrolidone (2)						
283.15	0.0000		2.112	1.4741	313.15	0.0000		1.321	1.4627
	0.0026	0.810 ± 0.004				0.0037	1.38 ± 0.01		
	0.1226			1.4715		0.1226			1.4606
	0.2118		2.913			0.2019		1.679	
	0.2155	0.642 ± 0.002				0.2026	1.24 ± 0.01		
	0.2166			1.4698		0.2166			1.4590
	0.3149			1.4678		0.3149			1.4566
	0.3967		4.488			0.4003	1.04 ± 0.01		
	0.3987	0.448 ± 0.010				0.4033		2.071	
	0.4222			1.4640		0.4222			1.4530
	0.5105			1.4597		0.5105			1.4488
	0.5873			1.4548		0.5873			1.4442
	0.5969		7.896			0.5943		2.715	
	0.6004	0.356 ± 0.011				0.6014	0.925 ± 0.007		
	0.7034			1.4430		0.7034			1.4322
	0.7958		8.804			0.7926		2.674	
	0.7992	0.352 ± 0.010				0.8004			1.4157
	0.8004			1.4247		0.8007	0.864 ± 0.004		
	0.9507			1.3804		0.9257			1.3742
	0.9994	0.682 ± 0.020				0.9991	1.53 ± 0.01		
	1.0000		1.323	1.3335		1.0000		0.677	1.3335

Table 2. Values of the Constants A_i in Eq 1 and the Standard Deviations $\sigma(D_{12})$ for Six Binary Systems

T/K	A_0	A_1	A_2	A_3	A_4	$10^9 \sigma(D_{12})/(m^2 s^{-1})$
			Heptane + Ethylbenzene			
313.15	2.44018	−0.97712	2.25089	−0.03599		0.016
333.15	3.02119	−1.66025	5.21207	−2.24451		0.006
			Sulfolane + 1-Methylnaphthalene			
313.15	0.64070	−1.90605	3.72752	−3.85188	1.61425	0.039
333.15	0.86540	−2.68100	5.58300	−5.77211	2.31912	0.006
			Water + *N*,*N*-Dimethylformamide			
283.15	1.48742	−1.83158	0.25050	0.94093		0.071
313.15	2.75395	−5.45261	6.37565	−2.05367		0.019
			Water + Methanol			
283.15	1.47077	−2.30499	1.31848	0.49374		0.024
313.15	2.76048	−2.55526	−1.56142	3.60469		0.008
			Water + *N*-Formylmopholine			
283.15	0.32854	−0.49067	0.69088	0.07351		0.036
313.15	0.72337	−0.17613	−0.72069	1.28424		0.030
			Water + *N*-Methylpyrrolidone			
283.15	0.81063	−0.51090	−1.76579	2.14500		0.037
313.15	1.36300	0.28157	−4.50577	4.37246		0.051

average of three to six repeat measurements. The maximum error ΔD_{12} in three to six repeat measurements for each D_{12} is also summarized in Table 1. The accuracy of D_{12} measurements is estimated to be within ±3% except for the heptane + ethylbenzene system for which maximum error reaches ±4%. Diffusion coefficients and kinematic viscosities for the six binary systems are plotted against mole fraction in Figures 1−6. The results are fitted by means of a smoothing equation which is a polynomial in mole fraction as shown for D_{12} in the following:

$$10^9 D_{12}/(m^2 s^{-1}) = \sum_{i=0}^{4} A_i x_1^i \quad (1)$$

Values of the constants A_i in eq 1 and the standard deviations $\sigma(D_{12})$ for each system at each temperature are listed in Table 2.

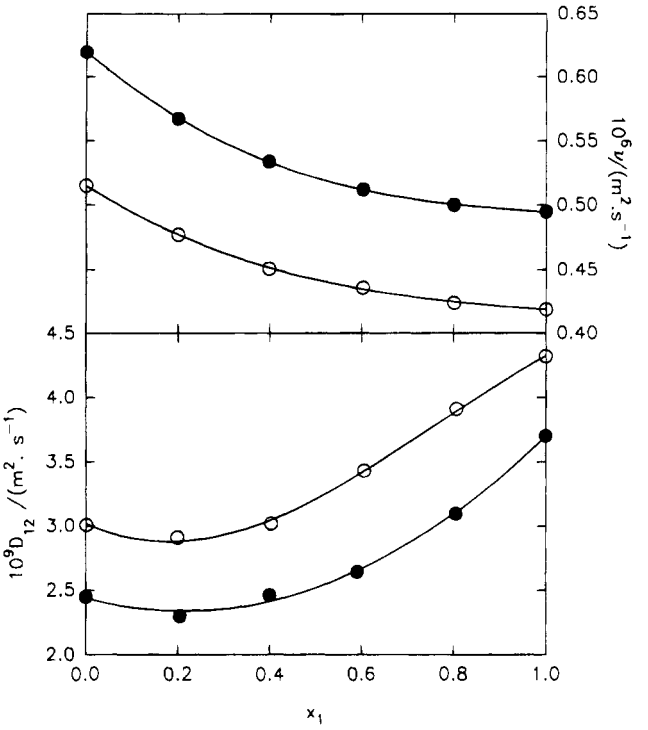

Figure 1. Diffusion coefficients D_{12} and kinematic viscosities ν for heptane (1) + ethylbenzene (2): ●, 313.15 K; ○, 333.15 K.

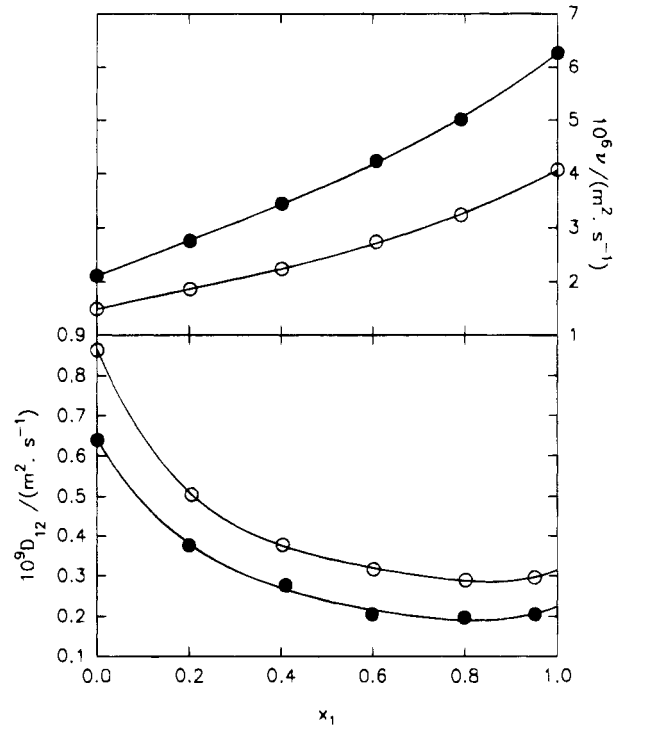

Figure 2. Diffusion coefficients D_{12} and kinematic viscosities ν for sulfolane (1) + 1-methylnaphthalene (2): ●, 313.15 K; ○, 333.15 K.

As expected, the diffusion coefficients decrease with increasing viscosities. The system heptane + ethylbenzene has the lowest viscosity values and largest diffusion coefficients. From Table 1 and Figures 1–6, the following characteristics were found: (1) The diffusion coefficients of the six systems at each temperature exhibit a minimum. The shift of the minimum is not obvious by changing the temperature. (2) For the aqueous systems, except water + *N*-formylmorpholine, the formation of complexes of water and organic molecules leads to a maximum in the viscosity

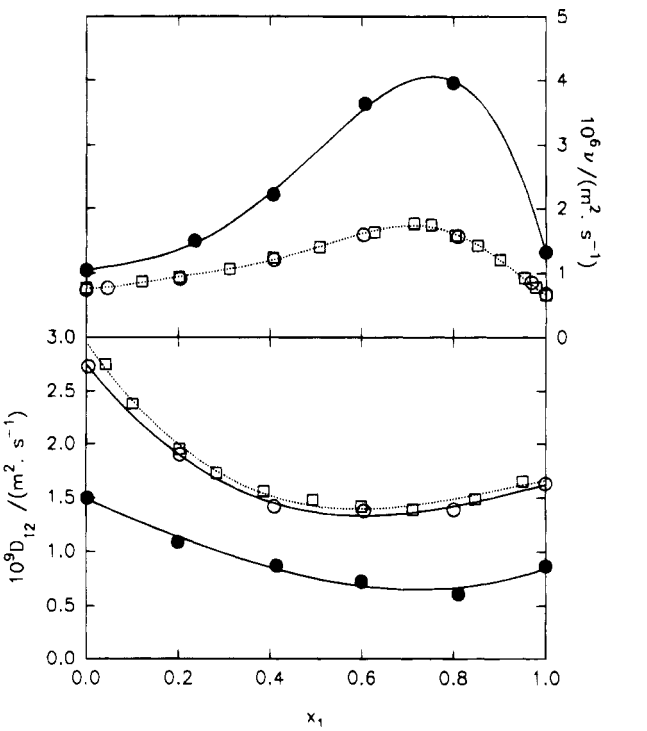

Figure 3. Diffusion coefficients D_{12} and kinematic viscosities ν for water (1) + *N*,*N*-dimethyformamide (2): ●, 283.15 K; ○, 313.15 K; □, literature data (Della Volpe et al., 1986) at 313.15 K.

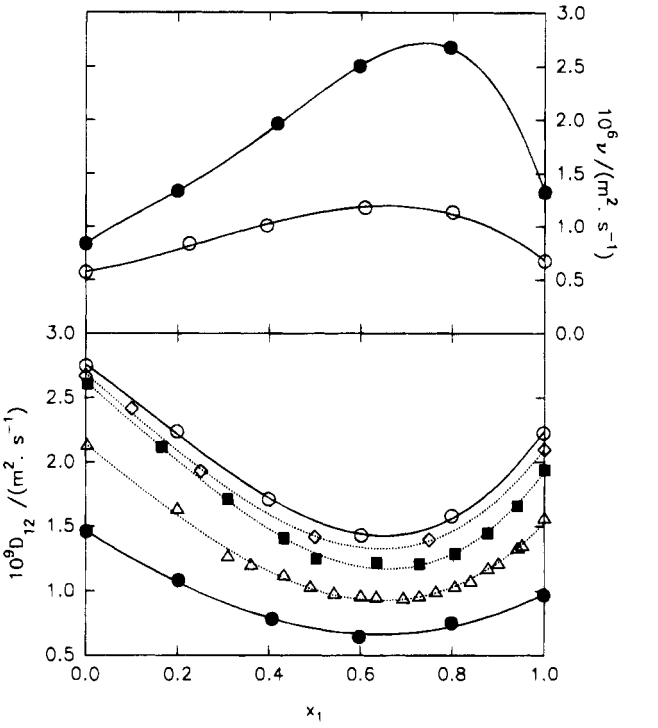

Figure 4. Diffusion coefficients D_{12} and kinematic viscosities ν for water (1) + methanol (2): ●, 283.15 K; ○, 313.15 K; ◇, literature data (Lee and Li, 1991) at 313.15 K; △, ■, literature data (Van de Ven-Lucassen et al., 1995) at 298.15 and 308.15 K, respectively.

at each temperature. The maximum in the viscosity becomes less pronounced as the temperature is raised. A corresponding minimum occurs for the diffusion coefficient. (3) For water + *N*-formylmorpholine, the kinematic viscosities show no maxima. The difference between two pure viscosities for this system is much larger than those for the other systems.

Table 3. Diffusion Coefficients of Water at Infinite Dilution in Methanol and *N*-Methylpyrrolidone (D_{12}^{∞}) and of Methanol and *N*-Methylpyrrolidone at Infinite Dilution in Water (D_{21}^{∞})

	$10^9 D_{12}^{\infty}/(m^2 s^{-1})$			$10^9 D_{21}^{\infty}/(m^2 s^{-1})$		
T/K	this work	lit.	ΔD_{12}^{∞}/%	this work	lit.	ΔD_{21}^{∞}/%
	Water in Methanol			Methanol in Water		
298.15	2.12	2.13[a]	0.5	1.59	1.56[a]	2
308.15	2.54	2.61[a]	2.7	2.02	1.94[a]	4
	Water in *N*-Methylpyrrolidone			*N*-Methylpyrrolidone in Water		
283.15	0.810	0.762[b]	6	0.682	0.663[b]	3
313.15	1.35	1.38[b]	2	1.53	1.37[b]	10

[a] Van de Ven-Lucassen (1995). [b] te Riele et al. (1995).

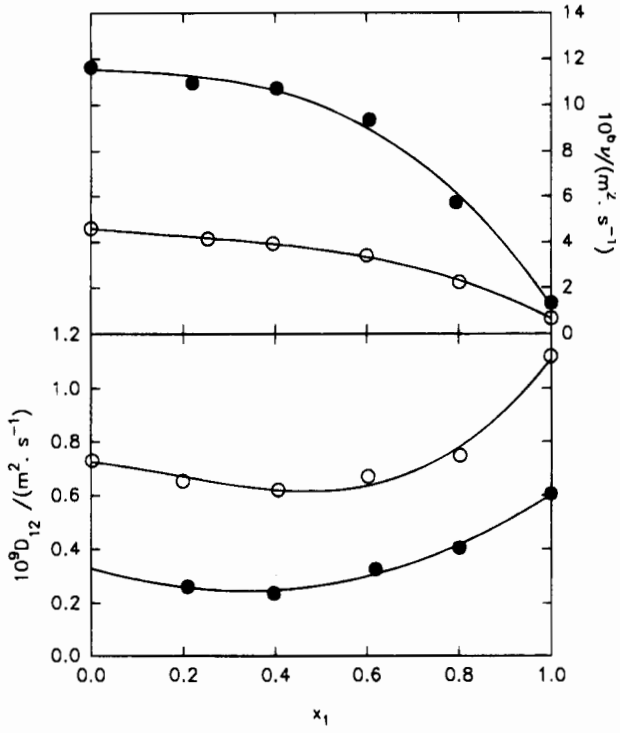

Figure 5. Diffusion coefficients D_{12} and kinematic viscosities ν for water (1) + *N*-formylmorpholine (2): ●, 283.15 K; ○, 313.15 K.

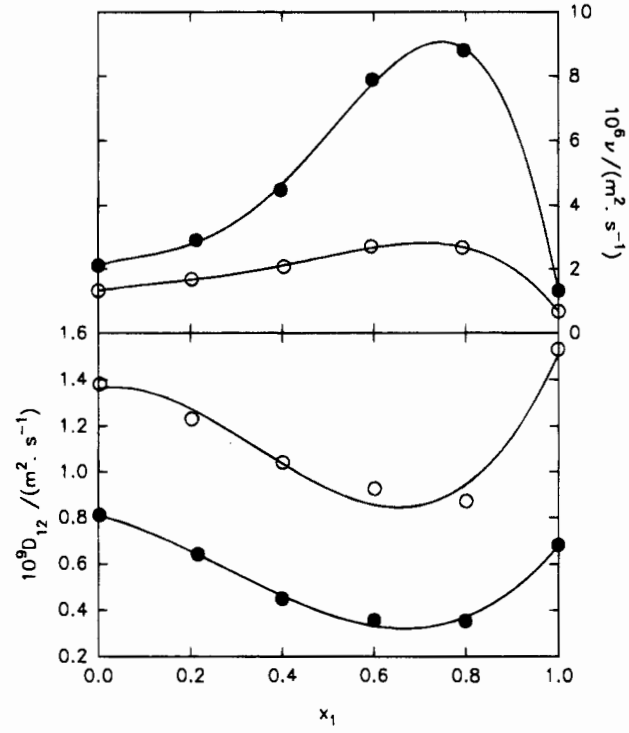

Figure 6. Diffusion coefficients D_{12} and kinematic viscosities ν for water (1) + *N*-methylpyrrolidone(2): ●, 283.15 K; ○, 313.15 K.

Comparisons of the present results with literature data are shown in Figures 3 and 4. For the water + *N*,*N*-dimethylformamide system at 313.15 K, the differences between the present and the literature kinematic viscosity values (Della Volpe et al., 1986) are less than 1%; the values of D_{12} are a little lower than the literature values with a deviation of 1–3%. For the water + methanol system, D_{12} data at 298.15, 308.15, and 313.15 K are available in the literature (Van de Ven-Lucassen et al., 1995; Lee and Li, 1991) and are shown in Figure 4. At 313.15 K, the present D_{12} data are a little higher than the literature data with deviations of 2–5%. The diffusion coefficients of water at infinite dilution in methanol D_{12}^{∞} and of methanol at infinite dilution in water D_{21}^{∞} at 298.15 and 308.15 K are interpolated from the present results and compared with the literature data as shown in Table 3. Table 3 shows that the deviations of the present data from the literature data for water + methanol change from 0.5% to 4%. The average deviation is only 2.3%. By this comparison, it can be concluded that the present and the literature D_{12} data for water + methanol are in agreement within the accuracy of the Taylor dispersion method. A similar comparison is made for water + *N*-methylpyrrolidone as listed in Table 3. The literature values D_{12}^{∞} and D_{21}^{∞} at 283.15 and 313.15 K are calculated from a correlation equation (te Riele et al., 1995). The differences between the present and the calculated values appear to be acceptable except for D_{21}^{∞} at 313.15 K.

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